Harbor Community Monitoring Study (HCMS)

Saturation Monitoring

Final Report

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ABSTRACT

The Harbor Community Monitoring Study (HCMS) was conducted to characterize the spatial variations in concentrations of toxic air contaminants (TACs) and their co-pollutants within the communities of Wilmington, West Long Beach, and San Pedro in California's South Coast Air Basin (SoCAB). Saturation monitoring consisting of 7-day time-integrated sampling at 23 locations was conducted as part of the HCMS by the Desert Research Institute. Samples were collected for four consecutive weeks in four seasons during 2007. Measurements at twenty sites included oxides of nitrogen (NOx) and sulfur dioxide (SO_2) using Ogawa passive samplers, and benzene, toluene, ethylbenzene, and xylenes (BTEX), formaldehyde and acetaldehyde using Radiello passive diffusive samplers. Additionally, 7-day integrated Teflon and quartz filters were collected with portable mini-volume samplers and analyzed for $PM_{2.5}$ mass and organic carbon (OC) and elemental carbon (EC). Nitrogen dioxide (NO_2) and hydrogen sulfide (H_2S) were also measured at three of the sites using Ogawa and Radiello passive samplers, respectively, and full sets of passive measurements (including NO_2 but not H_2S) were made at three additional near-roadway locations. Diesel particulate matter (DPM) concentrations were estimated at each site from the EC concentrations times the slope of the correlation between total carbon and EC at the near road sampling locations. The annual average DPM concentrations were higher near diesel truck traffic but were comparable to the MATES-III fixed monitoring sites at sampling locations 300m or more from traffic. Results are qualitatively consistent with the ARB's modeling estimates of DPM concentrations. Higher average SO_2 levels were measured at the east boundary of a refinery and in the port area, but corresponding increases in BTEX were not observed near the refinery. Results from the HCMS are compared to similar data for other areas of the South Coast Air Basin using data from the Third Multiple Air Toxics Evaluation Study (MATES-III). Average BTEX levels in the Harbor Communities were generally comparable or less than at other air monitoring locations in the basin. Formaldehyde and other carbonyl compounds that are formed in the atmosphere were lower in the Harbor Communities than inland areas of the basin. Week-to-week variations were higher than site-to-site variability in concentrations of most pollutants.

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EXECUTIVE SUMMARY

The Harbor Community Monitoring Study (HCMS) was conducted to characterize the spatial variations in concentrations of toxic air contaminants (TAC) and their co-pollutants within the communities of Wilmington, West Long Beach, and San Pedro in California's South Coast Air Basin (SoCAB). These communities were chosen for this study because of the high density of emission sources in the area and close proximity of residents to these emission sources. These sources include the Ports of Los Angeles and Long Beach, petroleum refineries, intermodal rail facilities and diesel trucks (high traffic volumes associated with the movement of goods from one of the busiest port complexes in the world). The HCMS consisted of three types of air pollution sampling: a high density ("saturation") air monitoring network of 23 sampling locations operated by the Desert Research Institute, mobile sampling by the University of California, Los Angeles and California Air Resources Board (CARB), and a network of particle counters operated by the University of Southern California. HCMS was conducted during 2007 concurrently with on-going monitoring programs in the study area by the South Coast Air Quality Management District (SCAQMD) and the Ports of Los Angeles and Long Beach. This report describes and evaluates the methods used by DRI and summarizes the results and findings of the HCMS saturation monitoring program.

Project Objectives and Hypotheses

The saturation monitoring program by Desert Research Institute was designed to characterize the spatial variations in concentrations of selected TAC and related pollutants within the study area. Data from the monitoring program were used to: characterize the spatial gradients in annual average concentrations of air toxics within the communities relative to the sources of emissions; evaluate the adequacy of existing routine air quality monitoring to characterize exposure concentrations within the community; correlate ambient concentrations of NOx, black carbon and $PM_{2.5}$ with proximity to truck traffic; and evaluate lower cost monitoring techniques and approaches for characterizing neighborhood-level exposures to toxic air contaminants. The spatial variations in annual concentrations of TACs measured during the HCMS were compared to data from the Multiple Air Toxics Exposure Study–III (MATES-III) (SCAQMD, 2008) and to relevant data from monitoring sites in the port area and elsewhere in the basin. These technical objectives can be rephrased into the following specific hypotheses.

1. Passive monitoring methods can be used to measure 1-week average ambient concentrations of selected pollutants with sensitivity and precision comparable to conventional monitoring methods (averaged over the same period).
2. Gradients in pollutant concentrations exist within the Harbor Communities (i.e., measurable variations in ambient concentrations) and can be related to a location's proximity to emissions from either stationary or mobile sources.
3. Ambient concentrations of black carbon are correlated to proximity to truck traffic and day-of-week variations in diesel truck traffic volume.
4. The existing air quality monitoring in the area is not adequate to characterize the spatial variations in cumulative exposure within the community.
5. Seasonal variations in meteorology affect the pattern and magnitude of ambient concentrations of toxic air contaminants.

Overview of the HCMS Saturation Monitoring

The term "saturation monitoring" refers to ambient air monitoring for the purpose of establishing detailed spatial variations in pollutant concentrations at the community scale. The HCMS saturation monitoring by DRI consisted of the 23 sites listed in Table ES-1. The sampling sites are listed in the tables approximately from west to east (left to right in the bar charts of data presented in this report). The first letter in the site identification corresponds to community (i.e., W for Wilmington, L for Long Beach, P for Port of Los Angeles and S for San Pedro). "Near Ref" and "Res" denote near refinery and residential, respectively.

Table ES-1. HCMS saturation monitoring site locations and descriptions.

Site ID	Near Road	Near Ref	Res	Near Port	Site Description	Community
PB47				x	Berth 47 near upwind boundary of Port of Los Angeles	POLA
SELB			x	x	Residential near west end of Port of Los Angeles	San Pedro
WEMD		x	x		Residential near east fenceline of a refinery	Wilmington
WE11	x	x			East edge of SR-110, 400 m east of refinery fenceline	Wilmington
WFST		x	x		Residential 800 m east of refinery fenceline	Wilmington
WGUL			x		Residential	Wilmington
WMCD			x		Residential	Wilmington
WMAR			x		Residential	Wilmington
WSWI	x			x	Open lot adjacent to W. Harry Bridges at north end of Port of Los Angeles	Wilmington
WLAK			x		Residential	Wilmington
WF49				x	Fire station at north end of Port of Los Angeles	Wilmington
WMCF			x		Residential	Wilmington
WPIO	x		x		Residential near Alameda St.	Wilmington
WCOL	x		x		Residential, 1/2 block north of Pacific Coast Highway	Wilmington
LOCN	x				Near road adjacent to ICTF	Long Beach
LHUD	x				School district maintenance facility near SR-47	Long Beach
LWIN			x		Residential	Long Beach
LWBC			x		Residential	Long Beach
LSUP	x			x	Business on Anaheim St.	Long Beach
LBER	x				Near road 18 m west of I-710	Long Beach
LW71	x				West edge of I-710 near Pacific Coast Highway	Long Beach
LE71	x				East edge of I-710 near Pacific Coast Highway	Long Beach
LBPW	x				Business 300 m from east edge of I-710	Long Beach

The core set of measurements at the 20 sites indicated in Figure ES-1 as yellow dots included oxides of nitrogen (NOx) and sulfur dioxide (SO_2) using Ogawa passive samplers and VOC (benzene, toluene, ethylbenzene and xylenes) and carbonyl compounds (formaldehyde and acetaldehyde) using Radiello passive samplers. Additionally, 7-day integrated Teflon and quartz filters were collected with portable Airmetrics MiniVol samplers and analyzed for $PM_{2.5}$ mass and organic carbon (OC) and elemental carbon (EC). Nitrogen dioxide (NO_2) and hydrogen sulfide (H_2S) were also measured at three core sampling sites using Ogawa and Radiello passive samplers, respectively, (indicated as vertical line within the site symbols). In addition to the 20 core sites, full sets of passive measurements (including NO_2 but not H_2S) were made at three additional near-roadway locations (indicated as horizontal line within the site symbols). Temperature and relative humidity were monitored continuously at four sampling sites. Due to consistency, averages of the four measurements were used to apply temperature and relative humidity corrections to the Ogawa and Radiello passive sampling data. The time-integrated sampling was supplemented with continuous measurements of VOC, $PM_{2.5}$ and black carbon at four sites during three of the four sampling seasons. Passive samples were also collected for NOx, SO_2, VOC and aldehydes at University of Southern California during the summer and fall seasons for comparisons with the data collected in the Harbor area.

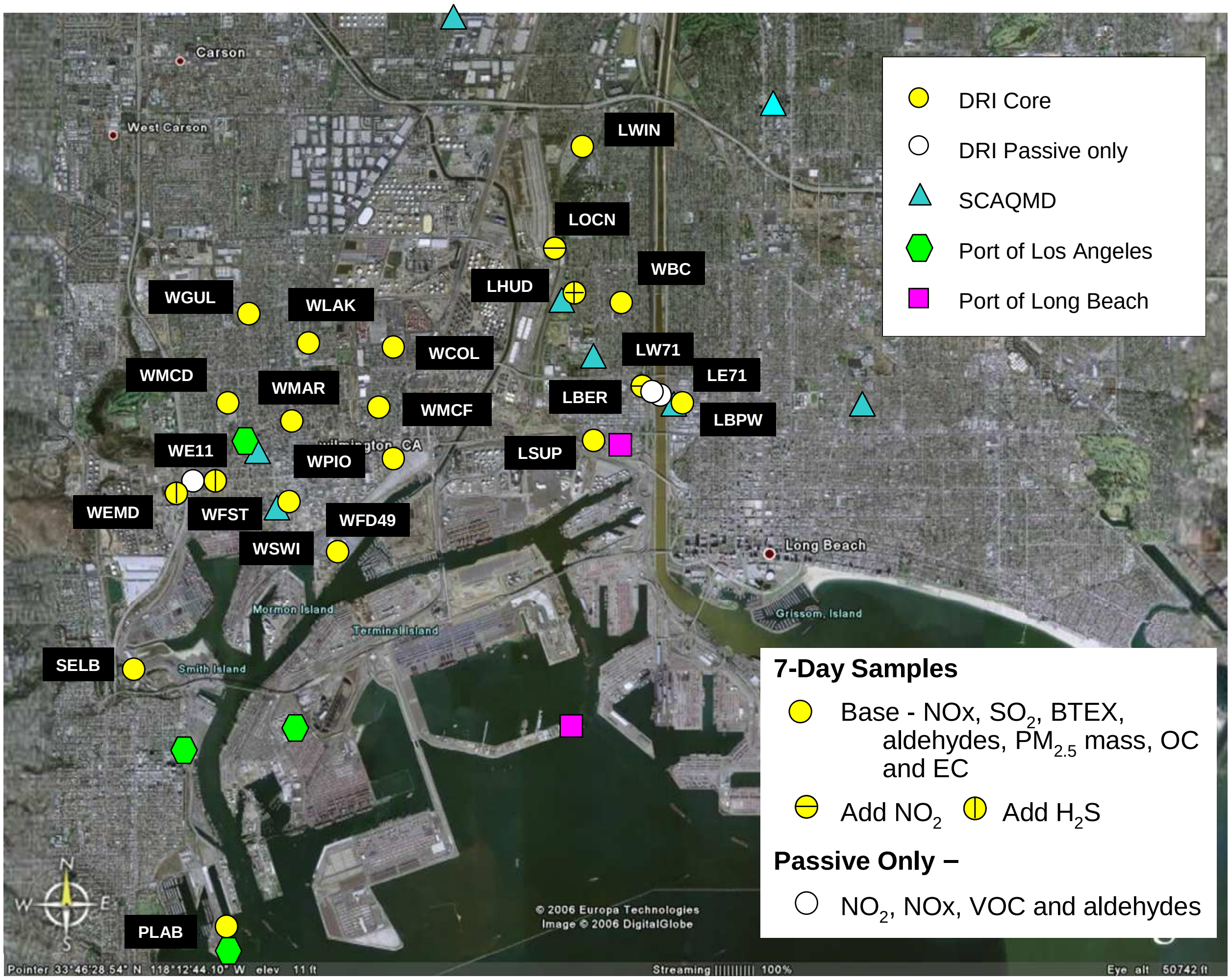

Figure ES-1. HCMS saturation monitoring sites relative to monitoring sites operated by the SCAQMD, Port of Los Angeles and Port of Long Beach.

AirMetric Minivol Aerosol Sampler
(20” long by 7” in diameter)

Ogawa passive samplers for NOx and SO2
(thumb size in protective cup shield)

Radiello passive samplers for VOC, aldehydes and H2S
(size of a roll of pennies)

Figure ES-2. Samplers used in the HCMS.

The saturation monitoring network consisted of sites that were intended to represent varying spatial scales relative to emission sources. Neighborhood-scale sampling sites represent an area of the community with relatively uniform land use within 0.5 to 4 kilometers. Microscale sampling sites characterize higher roadside exposures within several meters to 100 meters from I-710 and I-110. Middle scale (100 m to 0.5 km) sampling sites characterize near-road exposures and higher exposures that may be observed near major stationary sources. Urban-scale represents the upwind boundary that may contain a mix of aged urban emissions during periods of onshore flow following the morning offshore flow. The wind roses from data collected by the ARB in 2001-2 at the Wilmington Park Elementary School showed that winds in the study area are almost exclusively from 135 (southeast) to 315 degrees (northwest) throughout the year.[1] Winds were most frequently from the northwest during winter, southeast during summer and west during spring and fall. Winds were typically calm overnight and switch from northerly during the morning to southerly in the afternoon. This flow reversal was less pronounced during the winter. The westerly component of the wind peaks during mid-afternoons throughout the year. There were two main clusters of sampling sites in the HCMS saturation monitoring network, one in West Long Beach and the other throughout Wilmington.

The cluster in Long Beach was designed to characterize the impact of diesel emissions from truck traffic near the port along the I-710 Freeway and near the Intermodal Container Transfer Facility (ICTF) near the north end of the Terminal Island Freeway. DRI's continuous black carbon and $PM_{2.5}$ measurements were concentrated in this area and are aligned from the I-710 at Anaheim Street to near the ICTF along a northwest direction (LBPW-DRI, LBER, LHUD and LOCN). Three of the SCAQMD monitoring sites are located along a similar trajectory. Passive-only measurements were made at the east (LE71) and west (LW71) edges of I-710 between Pacific Coast Highway and Anaheim Street. A core sampling site was located adjacent to Pacific Coast Highway, which carries a high volume of truck traffic. Two additional core sites were located in residential areas of West Long Beach.

The cluster in Wilmington included six neighborhood sites spaced throughout the community (WGUL, WLAK, WMCD, WMAR, WMCF, and WCOL). Two additional sites were located near Harry Bridges Blvd. (WSWI) and Alameda Street (WPIO) to measure potential impact of diesel traffic. Another site was located at the north end of the Port of Los Angeles (WF49) to characterize the transport of emissions from the port area. A group of two core sites and one passive-only site were located downwind of a refinery. The passive only site was located on the east edge of the I-110 freeway (WE11). One core site was near the fence line of the refinery (WEMD) and the other was located about 1.2 km east on the other side of the I-110 freeway (WFST).

The wind roses indicated that the potential for transport of emissions from the port area to San Pedro is less than to the areas north and east of the port area. Accordingly, our coverage in this area is not as extensive as in the other two communities. The monitoring network included one site in the residential area of San Pedro (SELB) across the street from the Port of Los Angeles China Shipping Terminal and the Yang Ming Intermodal Facility and another site collocated with the Port of Los Angeles Boundary Site on Berth 47 (PB47).

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[1] Wilmington School is located about 800 m east of the HCMS sampling site labeled WMCF, which is located near the center of the study area.

Samples were collected during the HCMS for four consecutive weeks in four seasons in 2007: 2/13/07 to 3/13/07 (winter), 5/15/07 to 6/12/07 (spring), 7/31/07 to 8/28/07 (summer), and 11/13/07 to 12/11/07 (fall). This sampling schedule was used in order to maximize the number of sampling sites with the resources available while providing sufficient data to determine representative annual mean ambient concentrations of TACs. The saturation monitoring relied greatly on community volunteers that offered their residences or businesses for many of our sampling sites. The Air Resources Board held several meetings with the local community to publicize the objectives and scope of the proposed study and provided reports of progress during the study. Public meeting were held prior to (April 25, 2006), during (January 10, 2007 and August 1, 2007), and after (April 17, 2008) the field study. The meetings were held in the evening at the Wilmington Senior Citizen's Center and included presentations by ARB staff and HCMS researchers followed by open discussion. The ARB also established a web site for the HCMS at http://www.arb.ca.gov/research/mobile/hcm/hcm.htm to post relevant project information.

Finding and Conclusions

The Harbor Community Monitoring Study (HCMS) was conducted to characterize the spatial variations in concentrations of toxic air contaminants (TACs) and their co-pollutants within the communities of Wilmington, West Long Beach, and San Pedro in California's South Coast Air Basin (SoCAB). The saturation monitoring component of the HCMS had five hypotheses.

Hypothesis #1. *Passive monitoring methods can be used to measure 1-week average ambient concentrations of selected pollutants with sensitivity, accuracy and precision comparable to conventional monitoring methods.*

Precision, accuracy, and sampling rates of the passive sampling methods were evaluated under both laboratory and field conditions prior to the saturation monitoring program. They were first evaluated in the laboratory using a flow-through chamber with known pollutant concentrations. Then a pilot study was conducted at the SCAQMD monitoring station in North Long Beach to determine the replicate precision of passive measurements for NO_2, NOx, SO_2, H_2S, benzene, toluene, ethylbenzene, xylenes, 1,3-butadiene, formaldehyde, acetaldehyde, and acrolein under field conditions. The passive measurements were compared with the SCAQMD continuous NOx, NO_2 and SO_2 data and time-integrated samples collected and analyzed by DRI for organic air toxics using active sampling methods (i.e., canisters and chemically-impregnated cartridges). Concentrations of $PM_{2.5}$ mass, OC and EC measured on the 7-day integrated aerosol samples were also compared to the corresponding averages of daily 24-hour samples. One of the core HCMS sampling sites was collocated at a SCAQMD monitoring site during the main field study for quality assurance purposes. Passive samples were collected in triplicate at this site (LHUD) during the winter and summer seasons to determine measurement precision and were compared to the District's continuous monitors and parallel samples collected by DRI with active sampling methods.

This hypothesis is generally true with a few exceptions. The detection limits and precision specified by the manufacturer for compounds quantified in the HCMS are compared in Table ES-2 to the mean values measured during the study at the HCMS quality assurance site. Mean ambient concentrations were well above the detection limits during the study for all compounds with the exception of SO_2, H_2S, and acrolein. The replicate precisions for the HCMS were better than 10 percent for compounds with ambient concentrations greater than five times the limit of detection. The results for 1,3-butadiene from passive samplers with Carbograph 4 were not quantitative due to back diffusion and are not reported in the HCMS.

Table ES-2. Seven-day average mixing ratios (ppbv) of passive measurements at the Hudson monitoring station and measurement precision based on replicate samples.

	DQO [1]		**HCMS Winter**			**HCMS Summer**		
	MDL	Precision	Mean	Precision [2]		Mean	Precision [2]	
	ppbv	%	ppbv	ppbv	%	ppbv	ppbv	%
Nitrogen Oxides (NOx)	0.32		73.0	2.03	2.8%	29.4	0.65	2.2%
Nitorgen Dioxide (NO_2)	0.32		28.5	1.50	5.3%	19.5	0.96	4.9%
Sulfur Dioxide (SO_2)	0.54		1.1	0.107	9.8%	1.0	0.196	19.8%
Hydrogen Sulfide (H_2S)	0.20	8.7%	0.8	0.036	4.8%	0.9	0.117	12.5%
Benzene	0.015	8.3%	0.6	0.014	2.3%	0.3	0.026	7.5%
Toluene	0.002	8.3%	1.7	0.039	2.3%	1.0	0.044	4.2%
Ethylbenzene	0.002	9.1%	0.3	0.008	2.4%	0.2	0.014	6.7%
Xylenes	0.002	11.3%	1.4	0.031	2.2%	0.7	0.063	9.2%
Formaldehyde	0.07	13.8%	2.7	0.06	2.2%	1.8	0.12	6.7%
Acetaldehyde	0.05	15.9%	1.9	0.05	2.8%	0.7	0.03	4.7%
Acrolein	0.120	16.5%	0.028	0.015	52.0%	0.010	0.005	47.4%

[1] Data quality objectives (DQO) are based upon manufacturers' specifications for 7-day exposure period and one standard deviation precision.

[2] Mean of the absolute differences between average of triplicates and individual sample (12 values per season).

Note: Shaded values denote mean ambient values that are less than five times the minimum detection limit (MDL).

The accuracy of the passive measurements were evaluated in the laboratory using a flow-through chamber with known pollutant concentrations, and in the field during a pilot study and the summer and winter seasons of the main study. The field evaluations compared the 7-day integrated passive measurements with corresponding time averages of continuous NOx and SO_2 measurements or averages of seven consecutive 24-hour canisters and DNPH cartridge samples. The results summarized in Table ES-3 show that most passive measurements were in reasonable agreement with the measurements methods that are commonly used in state and local monitoring air programs. The accuracy of passive measurements of acrolein and H_2S could not be evaluated during this study as their ambient concentrations were often below the limits of detection.

Passive measurements of NOx were in good agreement (± 6%) with time-averaged continuous NO data during the laboratory evaluations. Passive NOx measurements were consistently lower than SCAQMD's NOx analyzer by about 15 to 20% during the pilot study, but these differences may be related to occasional concentration gradients from vehicles passing by the monitoring station because the inlet for District continuous monitors was located at the front of building and passive samplers were at the back. Passive SO_2 measurements were within

20% of the District continuous monitor, which is comparable to its precision during the summer HCMS. Passive measurements of NOx were generally in good agreement with SCAQMD's NOx analyzer during the main study when ambient levels were above the detection limit of the continuous analyzers.

Table ES-3. Assessments of accuracy of passive measurements using standards and comparisons with reference methods and commonly used active sampling methods.

	Lab Evaluation		Pilot Study		HCMS Winter	
Compounds	Reference Value (ppbv)	Passive-Ref % Δ	Reference Value (ppbv)	Passive-Ref % Δ	Reference Value (ppbv)	Passive-Ref % Δ
Nitrogen Oxides (NOx)	17.20	6.2%	10.8	-24.6%	80.1	-8.9%
Nitorgen Dioxide (NO_2)	21.80	-1.4%	17.2	-17.9%	42.2	-24.5%
Sulfur Dioxide (SO_2)			1.7	18.2%		
Hydrogen Sulfide (H_2S)	2.10	-5.2%				
Benzene	2.57	-18.3%	0.37	-21.6%	0.70	-13.8%
Toluene	2.37	-5.5%	1.09	20.2%	1.93	-11.1%
Ethylbenzene	1.28	41% or (-6%)[1]	0.13	31% or (-8%)[1]	0.37	0.1%
m,p-Xylenes	1.02	-12.7%	0.45	2.2%	1.26	-11.7%
o-Xylene	0.43	-12.2%	0.18	0.0%	0.51	-7.5%
Formaldehyde	5.20	-2.3%	1.10	11.8%	4.97	-38.9%
Acetaldehyde			1.04	-43.3%	1.91	31.0%
Acrolein			0.24	-79.2%		

[1] Using our experimentally determined sampling rate of 37.4 ml/min rather than 25.7 ml/min published by Radiello reduced values by factor of 0.69.

Verifying the sampling rates of the passive samplers was a major objective of the laboratory evaluations. The experimentally determined sampling rates for benzene, toluene xylenes were within 20% of those published by Radiello. A significantly higher sampling rate than that reported by Radiello was measured for ethylbenzene. The experimentally determined sampling rate for ethylbenzene was 37.4 ml/min versus 25.7 ml/min published by Radiello. The experimentally determine sampling rate was used to determine ethylbenzene concentrations for the main HCMS, which results in concentrations that are a factor of 0.69 lower than using the rate published by Radiello. The passive samples for all BTEX compounds were stable for storage times of up to 14 days at -18º C. Passive measurements of BTEX species were generally within ± 15% of corresponding samples collected by active sampling methods that are commonly used in state and local monitoring programs.

Passive measurements of formaldehyde and acetaldehyde were in good agreement with diluted standards for the laboratory evaluations. Passive sampler values were slightly higher during pilot study for formaldehyde compare to time-averaged DNPH samples. However, one out of the seven 24-hour DNPH samples was invalid. Acetaldehyde measured by the passive sampler was 43% lower than values obtained by active sampling on DNPH cartridges. Acetaldehyde had poor accuracy probably due to effects from ozonolysis and from low collection efficiencies, which may also apply to "reference" samples collected actively on DNPH cartridges.

Passive sampling methods for NOx, NO_2, SO_2, H_2S, BTEX and formaldehyde are viable alternatives to continuous instruments or active sampling methods and are especially applicable for saturation monitoring and assessment of personal exposures. The ability of passive methods to collect samples over long exposure times allows for monitoring of ambient concentrations with comparable or better limits of detection and precision than active sampling methods. Passive monitors have no pumps or other moving parts and are very compact and portable. No special training is required for their deployment and operation. The low associated labor means that passive monitoring is often cost-effective over other methods of measurement. Laboratory analysis costs are the main expense for this type of monitoring. We provide basic standard operating procedures for the Ogawa and Radiello passive samplers in Appendix B and C, respectively, which can be tailored to specific projects.

Hypothesis #2. *Gradients in pollutant concentrations exist within the Harbor Communities (i.e., measurable variations in ambient concentrations) and can be related to a location's proximity to emissions from either stationary or mobile sources.*

This hypothesis is true for NOx, SO_2, and elemental carbon, and is less so for $PM_{2.5}$. Annual average NOx and EC concentrations were 2 to 4 times higher at sampling sites located near diesel truck traffic than the mean concentrations at the sites in residential areas of the study area (Figure ES-3). The spatial variations of NOx and EC concentrations near the I-710 freeway are consistent with sharp decreases in pollutant concentrations with distance from the roadway. The EC concentrations at LBER and LBPW (about 18 m west and 300 m east of the I-710 freeway, respectively) were 2.26 ± 0.13 and 1.24 ± 0.08 times higher than the Wilmington Community mean, respectively. The sampling site 300 m downwind of I-710 (LBPW) had slightly higher EC concentrations to the two residential sites in west Long Beach (ratios of 1.09 ± 0.04 for LWIN and 1.08 ± 0.07 for LWBC). These results are qualitatively consistent with the ARB's modeling estimates of DPM concentrations in 2002 (CARB, 2006) shown in Figure ES-4. EC concentrations were also significantly higher at LOCN (near the ICTF), LSUP (adjacent to Pacific Coast Highway), LHUD (near east edge of the Terminal Island Freeway), WSWI (adjacent to W. Harry Bridges Blvd. at the north boundary of Port of Los Angeles) and with ratios to Wilmington Community mean of 2.62 ± 0.26, 1.76 ± 0.11, 1.64 ± 0.28, and 1.85 ± 0.11, respectively. EC levels were uniformly lower at the four Wilmington community sampling sites and at the residential sampling site in San Pedro.

The spatial variations of $PM_{2.5}$ concentrations between residential and near-source sampling locations are far less than for EC (Figure ES-5). Note that the average EC concentration was 1.3 $\mu g/m^3$ compared to 13.0 $\mu g/m^3$ for $PM_{2.5}$. The contributions of diesel exhaust are superimposed on the contributions of other sources of $PM_{2.5}$ from both within and outside the study area. In addition to direct emissions of particulate matter from motor vehicles (primary emissions), ambient $PM_{2.5}$ consists of nitrates, sulfates, and organic aerosols that are formed in the atmosphere (secondary pollutants) from NOx, SO_2, and volatile and semi-volatile organic compounds, respectively. Secondary pollutants are formed at varying rates that allow time for dispersion. Thus, atmospheric concentrations of secondary pollutants tend to be more uniform spatially than concentrations of primary pollutants, which can be significantly higher near sources of emissions (e.g., spatial variations for NOx and EC in Figure ES-3). Directly-emitted PM from outside the study area is generally well-mixed during transport into the study area and contributes to the community background concentrations. The results in Figure ES-4 show that the roadside gradients in $PM_{2.5}$ are relatively small and that contributions of $PM_{2.5}$ from outside the study area may be large relative to local contributions.

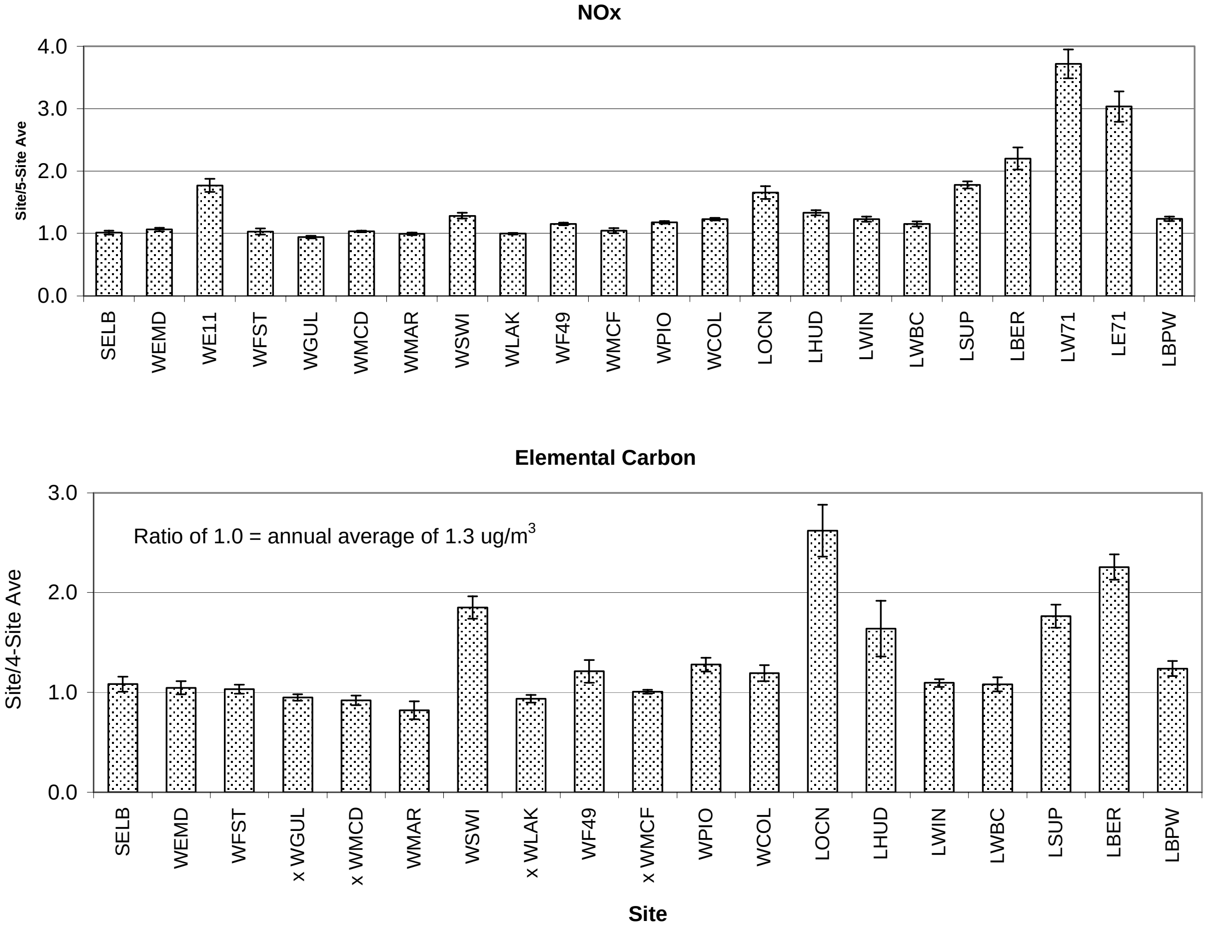

Figure ES-3**.** NOx and EC concentrations normalized to the mean of the residential sampling sites in Wilmington (identified with x). Uncertainties are standard errors of the mean ratios.

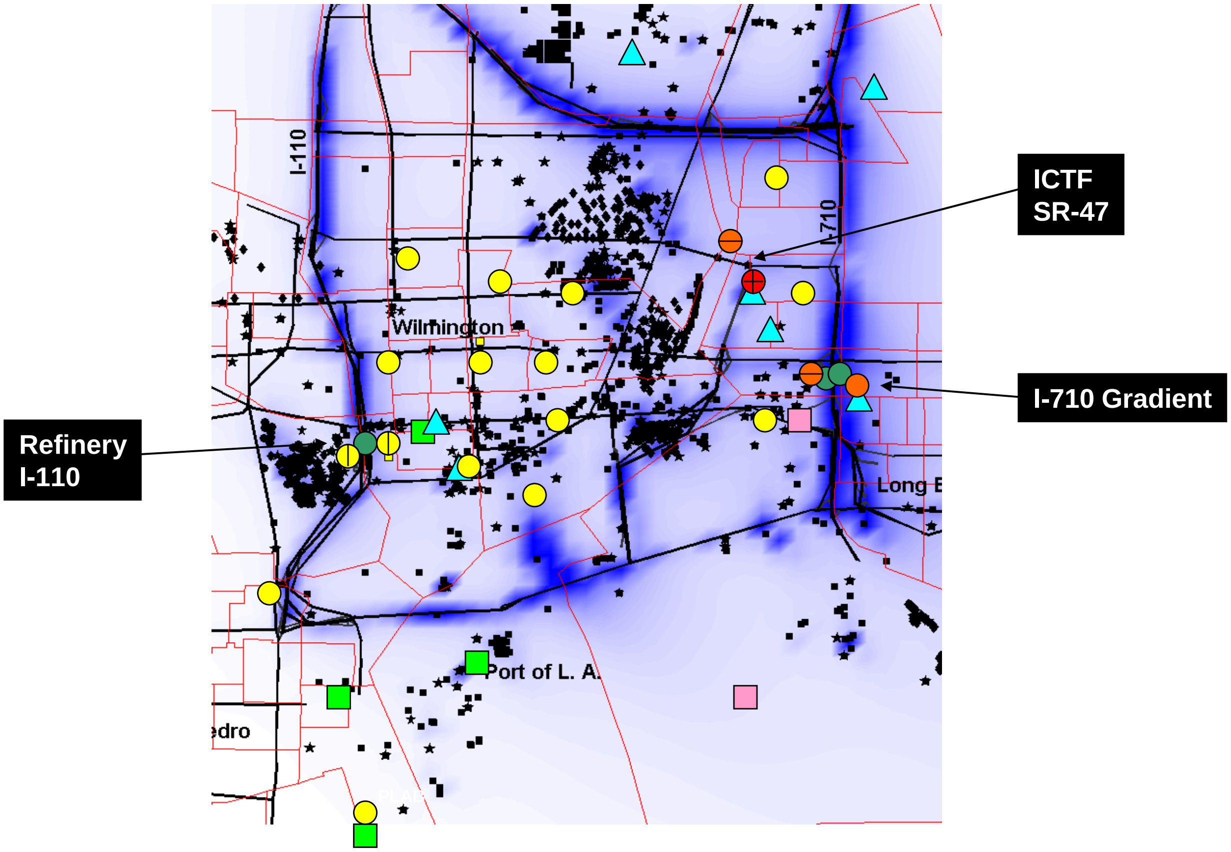

Figure ES-4. Locations of HCMS sites on spatial mapping of ARB's modeling estimate of annual average DPM concentrations. Black symbols indicate locations of stationary emission sources.

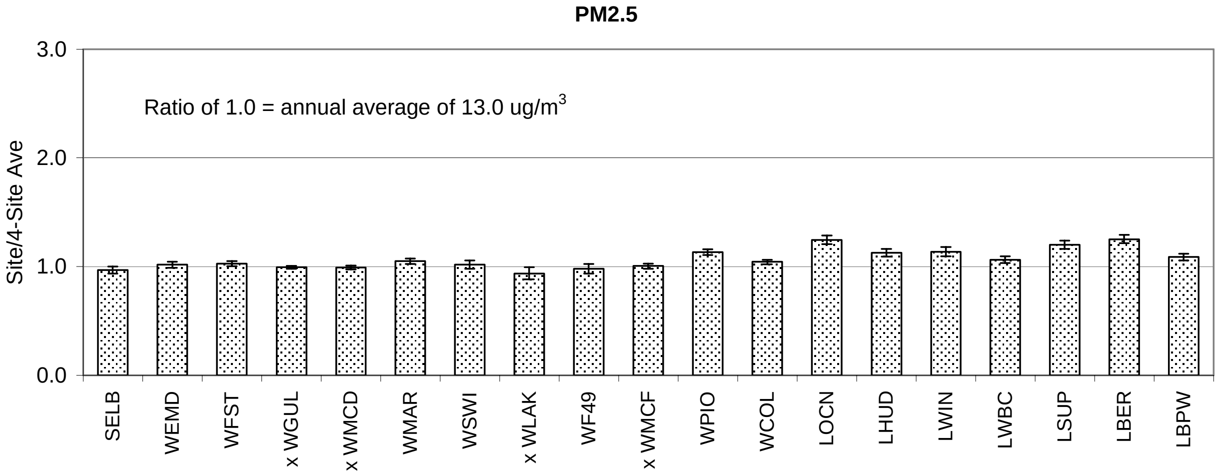

Figure ES-5**.** PM2.5 concentrations normalized to the mean of the residential sampling sites in Wilmington (identified with x). Uncertainties are standard errors of the mean ratios.

The spatial pattern of SO_2 concentrations (Figure ES-6) is consistent with higher levels occurring near a refinery (WEMD) and the port (e.g., WSWI, WF49, LSUP). Annual mean mixing ratios of SO_2 were highest at the site adjacent to the east boundary of a refinery (2.02 ± 0.33 higher than the Wilmington Community mean) and dropped to 1.48 ± 0.13 about 400 m east of refinery. SO_2 levels were comparable to the Wilmington Community at the site about 800 m east of refinery (1.05 ± 0.13). However corresponding increases in BTEX were not observed near the refinery.

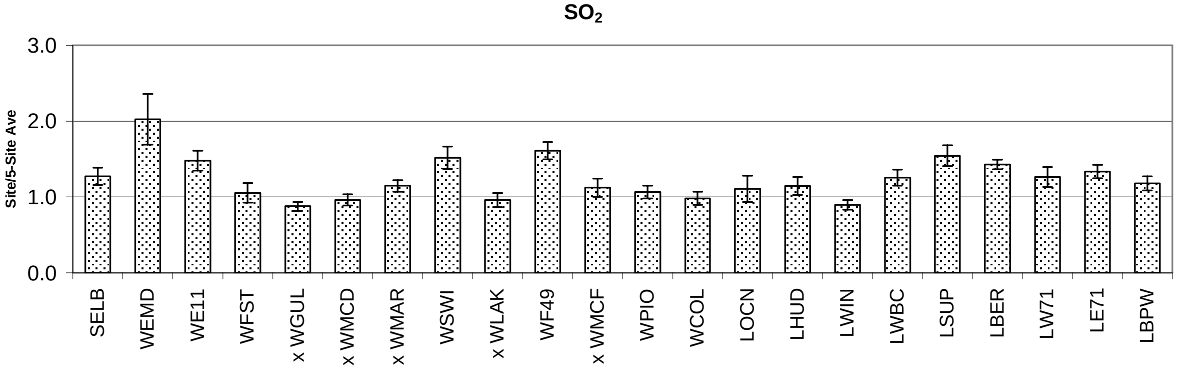

Figure ES-6**.** SO_2 mixing ratios normalized to the mean of the residential sampling sites in Wilmington. Uncertainties are standard errors of the mean ratios.

The annual average mixing ratios (ppbv) of BTEX tended to be higher near roadways, but this association was not as strong as for NOx. Average BTEX levels in the Harbor Communities were generally comparable or less than at other air monitoring locations in the basin. Toluene levels were higher at two locations where use of solvent was observed in the immediate area.

While the annual average mixing ratios of formaldehyde and acetaldehyde were slightly higher near roadways, site-to-site variations were relatively small within the study area and were comparable or slightly lower than annual mean levels measured elsewhere in the SoCAB during MATES-III and at the routine air toxic monitoring site during 2007. These results suggest that secondary formation of these aldehydes within the SoCAB have greater contributions to the annual average levels than local contributions near roadways, especially over sampling durations of seven days.

Hypothesis #3. *Ambient concentrations of black carbon serve as a surrogate for diesel particulate matter and can be correlated to proximity to heavy duty truck traffic and day-of-week variations in diesel truck traffic.*

Diesel particulate carbon (DPC) concentrations were estimated at each site from the measured EC concentrations times the slope of the correlation between total carbon and EC at the near-road sampling locations for each season (Figure ES-7). TC and EC are well correlated (R^2 between 0.8 and 0.9) with slopes between 1.5 and 2.2. Using these regression results, we estimated the upper-bound ambient concentrations of DPC from the average EC concentrations at each site. Diesel particulate matter (DPM) was estimated from the following relationship:

Diesel Particulate Matter (DPM) = EC + 1.46 (DPC-EC)

where 1.46 is the ratio of diesel particulate organic matter (DPOM) to DPC from the Gasoline/Diesel PM Split dynamometer testing of diesel trucks in the Riverside, CA area (El-Zanan et al., 2008). Metals have a minor contribution to DPM and can be excluded in the above DPM calculation. This estimation for DPM was specifically developed for this study and may not be applicable for other areas, especially when residential wood burning or wildfires are significant contributors to ambient $PM_{2.5}$ concentrations.

The estimated annual average concentrations of DPM (from the EC surrogate method) at the residential sampling sites were similar to those determined in MATES-III at the West Long Beach and North Long Beach monitoring sites using the Chemical Mass Balance receptor model during (Figure ES-8) and are comparable or lower than at other MATES-III sites in the SoCAB. However, higher concentrations of DPM as well as EC and NOx were measured at sites in closer proximity to diesel truck traffic. We recently measured on-road concentrations of black carbon on highways in the South Coast Air Basin for a separate study (Fujita et al. 2008). The results of that study, shown in Figure 4-6, show that higher concentrations of DPM are also likely in other parts of the SoCAB near major truck routes from the port area to the Inland Empire along SR-91, I-605, SR-60 and out of the basin along I-5 and I-10.

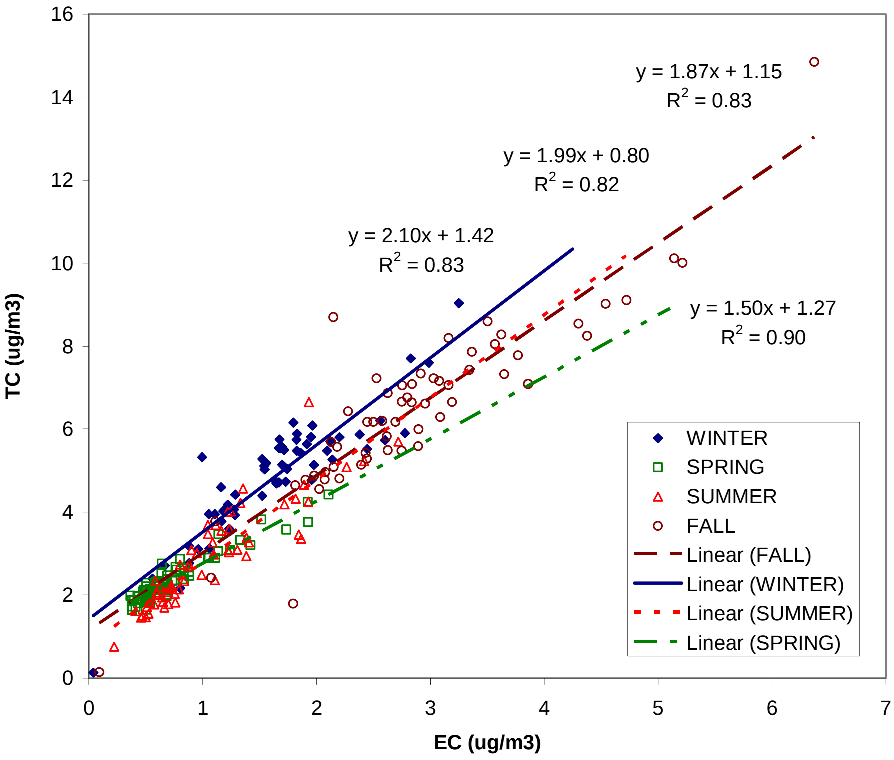

Figure ES-7. Correlations of TC and EC by season.

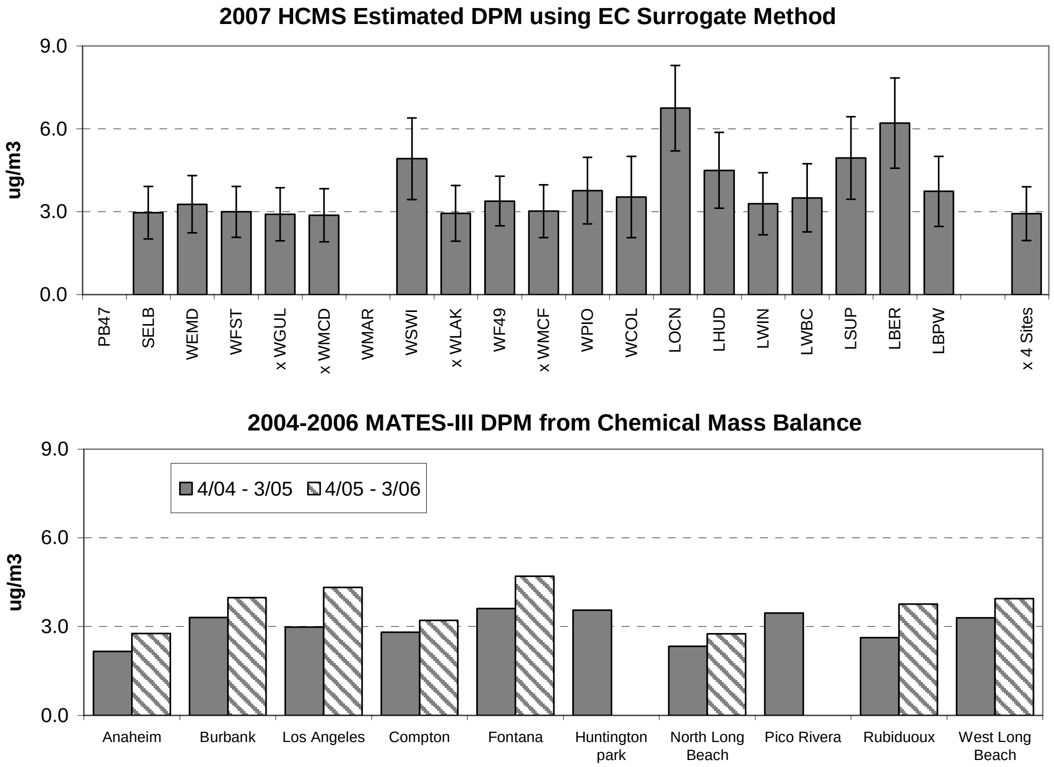

Figure ES-8. Estimated annual mean diesel particulate matter concentrations (µg/m^3) and standard errors of the four seasonal means during 2007 HCMS and MATES-III.

Hypothesis #4. *The existing air quality monitoring in the area is not adequate to characterize the spatial variations in cumulative exposure within the community.*

This hypothesis is true with respect to the sharp gradient in pollutant concentrations that occur near roadways (i.e., NOx, CO, DPM). However, the existing SCAQMD monitoring stations in North Long Beach and West Long Beach are representative of the annual mean concentrations in residential areas of the community that are located greater than 300 meters from the truck routes (I-710 freeway and arterial streets leading to the port area).

Hypothesis #5. *Seasonal variations in meteorological conditions affect the pattern and magnitude of ambient concentrations of toxic air contaminants.*

This hypothesis is true for primary pollutants. Ambient concentrations are higher in the fall by as much as a factor of 4 to 6 for NOx and DPM compared to spring, which had the lowest concentrations. Fall concentrations were about factor of three higher compared to summer and nearly equal to winter concentrations. Concentrations at near-road sampling sites were about 2-4 times higher than the community mean in all season. There is less seasonal variation in aldehyde concentrations due to contributions of increased atmospheric formation of these compounds during spring and summer. The synoptic meteorological conditions during the fall result in periods of stagnation and buildup of higher pollutant concentrations and colder temperatures during winter results in stronger inversions (during nighttime and early morning) and correspondingly larger pollutant gradients near roadways.

1. INTRODUCTION

The Harbor Community Monitoring Study (HCMS) was conducted to characterize the spatial variations in concentrations of toxic air contaminants (TACs) and their co-pollutants within the communities of Wilmington, West Long Beach, and San Pedro in California's South Coast Air Basin (SoCAB). These communities were chosen for this study because of the high density of emission sources in the area and close proximity of residents to these emission sources. These sources include the Ports of Los Angeles and Long Beach, petroleum refineries, intermodal rail facilities and diesel trucks (high traffic volumes associated with the movement of goods from one of the busiest port complexes in the world). The HCMS consisted of three types of air pollution sampling: a high density ("saturation") air monitoring network of 23 sampling locations operated by the Desert Research Institute, mobile sampling by the University of California, Los Angeles and California Air Resources Board (CARB), and a network of particle counters operated by the University of Southern California. HCMS was conducted during 2007 concurrently with on-going monitoring programs in the study area by the South Coast Air Quality Management District (SCAQMD) and the Ports of Los Angeles and Long Beach.

1.1 Background

Urban and regional air monitoring programs typically consist of a relatively limited number of widely spaced monitoring stations within a given airshed. While these monitoring networks are generally adequate to characterize the spatial variations of secondary pollutants such as ozone, nitrogen dioxide, and nitrate and sulfate particles, they are less effective for determining the range of exposure to directly emitted pollutants such as CO, diesel PM and other toxic air contaminants. The costs of traditional monitoring technologies also pose limitations on the number of monitoring locations that can be established for special studies to assess community level exposures to toxic air contaminants (TAC). This raises concerns about the adequacy of such assessments because exposure concentrations can vary substantially in space and time due to variations in proximity to sources of emissions, magnitude and specific mix of emissions and meteorological conditions.

Annual average outdoor concentrations of air toxic contaminants in the SoCAB have been obtained by the SCAQMD since 1989 at five sites (Azusa, Burbank, Los Angeles-North Main, North Long Beach and Riverside-Rubidoux). Samples are collected for 24 hours every 12th day, and are analyzed for volatile air toxics (e.g., BTEX, 1,3-butadiene, aldehydes, halogenated hydrocarbons), metals, and particulate polyaromatic hydrocarbons. These long-term monitoring sites represent neighborhood or urban-scale concentrations and do not provide the spatial resolution necessary to fully characterize variations in pollutant concentrations within a community and the potential for disproportionate exposure in certain communities due to their proximity to pollutant sources. Several special studies have been conducted in the South Coast Air Basin to provide more detailed estimates of ambient levels and potential health risks of air toxics. Other studies have characterized higher exposures on and near roadways.

1.1.1 Community-Scale Exposure and Risk Assessment Studies in SoCAB

Special monitoring programs have been conducted in California to characterize the ambient air toxic concentrations and potential exposures to certain susceptible populations and within communities that may experience disproportionate impacts due to their proximity to pollutant sources. The objectives of these monitoring programs and research studies were to characterize the ambient air toxic concentrations within communities and potential exposures to certain susceptible populations. In addition to ambient measurements, these projects typically included development of toxics emission inventories and air dispersion modeling to estimate ambient levels and potential health risks of air toxics.

ARB Community Monitoring in Wilmington

The California Air Resources Board conducted air toxics monitoring in Wilmington during 2001 and 2002 as part of the larger statewide evaluation of the adequacy of the State's air quality monitoring network as required by the Children's Environmental Health Protection Act (SB25) (CARB, 2003). Monitoring was conducted at the Wilmington Park Elementary School (Wilmington School) and the data were compared to data from long-term SCAQMD air monitoring sites in downtown Los Angeles and North Long Beach. Additional monitoring was conducted at the Hawaiian Avenue Elementary School (Hawaiian School) to obtain information about the air quality impact of particulate matter (PM_{10}) emissions from a freeway, a refinery, and the Port of Los Angeles that are all located within a half mile of the school.

The study did not find large differences between most pollutants at Wilmington School and the long-term monitoring site in North Long Beach. Concentrations of PM_{10} were higher at the Wilmington School site than North Long Beach and were similar to the PM_{10} levels measured in downtown Los Angeles during the same time period. The potential cancer risk associated with air pollution at Wilmington School site was lower than the downtown Los Angeles site, but similar to the North Long Beach site. The estimated cancer risk at downtown Los Angeles was 23% higher than Wilmington School or North Long Beach. The main toxic pollutants associated with cancer risk at all three sites were primarily from motor vehicles. However, these estimates of risk did not include diesel particulate matter.

ARB Diesel Particulate Matter Exposure Assessment Study for the Ports of Los Angeles and Long Beach

The California Air Resources Board conducted an exposure assessment study to evaluate the impacts from PM emissions from diesel-fueled engines associated with port activities at the Port of Los Angeles (POLA) and Long Beach (POLB) (CARB, 2006). The combined diesel PM emissions from the ports were estimated to be about 1760 tons per year in 2002, which accounted for about 21 percent of all diesel PM emissions in the South Coast Air Basin. Emissions from ship activities (transiting, maneuvering, and hotelling) accounted for 73 percent of diesel PM emissions within the port and coastal waters, followed by 10% for cargo handling, 14% for commercial harbor craft vessels, 2% for in-port heavy-duty trucks and 1% for in-port locomotives.

The U.S. EPA Industrial Source Complex Short Term Version 3 (ISCST3, Version 02035) Gaussian plume dispersion model was used to estimate the downwind dispersion of diesel PM exhaust emission resulting from the activities at the POLA and POLB. The modeled diesel PM concentrations were used to estimate the potential cancer risk levels and other health effects within the downwind communities. The potential cancer risks were estimated based on the annual average concentration of diesel PM predicted by the model and a cancer potency factor developed by California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA). The estimated risk from diesel PM emissions from the ports were 500 excess lifetime cancers per million population near the port boundaries and 50 in a million for distances greater than 15 miles. These risk estimates are lower than those obtained in the MATES-II study because the CARB assessment includes only emissions from the ports while the MATES-II simulated diesel emissions from all sources (e.g., port activities and freeway emissions).

Multiple Air Toxics Exposure Study–III (MATES-III)

The Multiple Air Toxics Exposure Study–III (MATES-III) was conducted by the SCAQMD over two years ending in March 2006 (SCAQMD, 2008). The study was preceded by similar studies in 1986 and 1998 (SCAQMD, 2000). The monitoring components of the MATES-III consisted of a network of 10 fixed sites where toxic air contaminants were monitored once every three days from April 2004 through March 2006 and a microscale study which utilized mobile platforms to sample at five additional locations.

The carcinogenic risk from air toxics in the SoCAB, based on the average concentrations at the fixed monitoring sites, was about 1,200 per million[2]. About 94% of the risk was attributed to emissions associated with mobile sources, and about 6% of the risk was attributed to toxics emitted from stationary sources (e.g., dry cleaners and chrome plating operations). Diesel exhaust was the major contributor to air toxics risk, accounting on average for about 84% of the total. The air toxics risk at the ten fixed monitoring sites ranged from 870 to 1,400 cancer cases per million. Sites with higher levels of risk included Burbank, Central Los Angeles, Inland Valley San Bernardino, Huntington Park, and West Long Beach. The site with the lowest risk was Anaheim.

The modeling results showed that the highest air toxics risk was at the ports. The cancer risk in modeling grid cells near the ports ranged from about 1,100 to 3,700 in a million. In addition to the ports, an area of elevated risk is shown near the Central Los Angeles area with grid cells ranging from about 1,400 to 1,900 per million. There are also higher levels of risk that track transportation corridors and freeways. Compared to previous studies of air toxics in the SoCAB, this study found a decreasing risk for air toxics exposure, with the estimated Basin-wide population-weighted risk down by 8% from the analysis done for the MATES II time period. The ambient air toxics data from the ten fixed monitoring locations also demonstrated a reduction in air toxic levels and risks. Overall, there were decreases in air toxics risk of varying magnitude throughout most of the Basin, with the exceptions of the areas directly downwind of the ports and those areas heavily impacted by activities associated with goods movement. The model comparison shows an increase in air toxics risk occurred in the immediate areas encompassing the ports of more than 800 in a million between the two periods. This increase correlates with the increased container movement of cargo containers through the ports and increased goods movement that occurred between the MATES II and MATES III time periods.

1.1.2 On-Road and Near-Road Exposure Studies

Several studies (Wallace, 1987; Chan et al., 1991; Weisel et al., 1992; Jo and Choi, 1996; Duffy and Nelson, 1997; Jo and Park; 1999; Leung and Harrison, 1999) have found that individuals are exposed while commuting to levels of VOC several fold higher than the corresponding ambient concentrations measured at nearby traditional (neighborhood-scale) monitoring sites. In a study of ozone precursors in the South Coast Air Basin, Fujita et al.

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[2] This risk refers to the expected number of additional cancers in a population of one million individuals that are exposed over a 70-year lifetime.

(2003a) found that concentrations of black carbon[3] (BC) and nitrogen oxides (NO_x) were about ten times higher on roadways than at regional air monitoring sites, and that volatile organic compounds (VOC) and carbon monoxide (CO) were factors of two to four higher on roadways. Westerdahl et al. (2005) also found that concentrations of ultrafine PM (< 100 nm), nitrous oxide (NO), BC and CO on freeways were frequently ten times higher than on residential streets. Others have shown that traffic-related pollutants disperse rapidly downwind of the roadway (Zhu et al., 2002). These results suggest that the exposure to air pollutants for commuters and urban pedestrians would be underestimated by using fixed-site monitoring data or predicted concentrations from grid-based air quality simulation models.

Investigators from the Desert Research Institute measured on-road concentrations of volatile air toxics, $PM_{2.5}$ mass, black carbon, and polycyclic organic matter (POM) in California's South Coast Air Basin during summer 2004 and winter 2004/5 (Fujita et al., 2006). An important impetus for this study was to conduct the measurements during the MATES-III field study. The average and upper range of black carbon concentrations were highest on those routes with a higher proportion of truck traffic. The concentration ranges for BC show as much as an order of magnitude higher average concentration on the road than at three near-road residential neighborhood sites, and the peak 1-minute averages on roadways with high amounts of truck traffic can be as much as two orders of magnitude higher than peak neighborhood concentrations. The average 1-minute $PM_{2.5}$ mass concentrations for on-road exposures are about 2-6 times higher than at the three near-traffic residential sites. The spatial patterns of on-road pollutant concentrations indicated that gasoline vehicles were the predominant source of volatile mobile source air toxics (MSAT) such as 1,3-butadiene and BTEX (sum of benzene, toluene, ethylbenzene and xylenes).

1.1.3 Contributions of Gasoline and Diesel Exhaust to Ambient PM

The Gasoline/Diesel PM Split Study, sponsored by the U.S. Department of Energy, was conducted to assess the sources of uncertainties in using an organic compound-based chemical mass balance (CMB) receptor model to quantify the relative contributions of emissions from gasoline (or spark ignition, SI) and diesel (or compression ignition, CI) engines to the ambient concentrations of fine particulate matter ($PM_{2.5}$) (Fujita et al., 2007a; Fujita et al., 2007b; Lough et al., 2007a; Lough et al., 2007b). In this study, several groups worked cooperatively on sample collection and quality assurance aspects of the study. The Desert Research Institute and the University of Wisconsin worked independently to perform chemical and data analysis and source apportionment. Source testing included 59 light-duty vehicles (including two diesel vehicles) and 34 heavy-duty diesel vehicles. Ambient sampling included daily 24-hour $PM_{2.5}$ samples for twenty-eight days during summer 2001 at two air quality monitoring stations in the SoCAB plus samples at several regional urban locations and along freeway routes and surface streets with varying proportions of automobile and truck traffic.

On-road measurements of $PM_{2.5}$ mass (gravimetric) concentrations were consistently lower on Sundays and were very similar to levels measured on Sundays at the monitoring stations in Los Angeles and Azusa and an upwind background location in Venice. On-road levels of $PM_{2.5}$ were about 2 to 2.5 times higher on weekdays than on Sundays. The weekday-weekend

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[3] In this report BC refers to light absorbing carbon determined by methods such as an aethalometer, photoacoustic, or other instruments that measure light absorption that can be interpreted as BC when divided by assumed mass absorption efficiency. Elemental carbon (EC) refers to refractory carbon determined by thermal evolution methods.

differences are more apparent with total carbon and even more so for elemental carbon. On-road concentrations of total carbon were 3-4 times higher than ambient concentrations at the Los Angeles and Azusa monitoring stations. Furthermore, on-road concentrations of elemental carbon were about an order of magnitude higher than at the monitoring stations. While CI engine exhaust was the dominant source of total carbon (TC) and EC at the air monitoring stations at Azusa and downtown Los Angeles, samples from a regional park in the central part of the South Coast Air Basin showed nearly equal apportionment of CI and SI. About 70 percent of organic carbon in the ambient samples collected at the two fixed monitoring sites could not be apportioned to directly-emitted PM emissions.

1.2 Study Objectives and Hypotheses

The disproportionate impacts that may be experienced by certain communities due to their proximity to pollutant sources have caused policy makers to consider whether current regulatory practices allow greater air pollution exposures in some communities compared to others. The concept of environmental justice (EJ) is intended to address this concern and the need for guidelines for assessing air pollutant impacts at the neighborhood scale. The communities of Wilmington, Long Beach, and San Pedro are located in to one of the largest industrial and commercial areas of Southern California and the potential for disproportionate health impacts to these communities has drawn considerable interest from policy makers and community advocates. The California Air Resources Board selected this area for a saturation monitoring study because of its proximity to many stationary, area and mobile sources, existing detailed inventory of emissions (Sax, 2004), recent community-scale monitoring by the ARB (ARB, 2003), and both near-source dispersion and regional air quality modeling of for the area (Isakov, 2004; Venkatram, 2004). Additionally, the South Coast Air Quality Management District measured elemental carbon intermittently during 1997 to 2003 at several sites in the Long Beach/Wilmington area as part of the implementation Rule 1158 and recently conducted the Multiple Air Toxics Exposure Study–III (MATES-III).

The saturation monitoring program by Desert Research Institute was primarily designed to characterize the spatial variations in annual average concentrations of selected pollutants with long-term exposure impacts (e.g., selected TACs and criteria pollutants) within the study area. Measurements included oxides of nitrogen (NOx), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) using Ogawa passive samplers and VOC (benzene, toluene, ethylbenzene, and xylenes), aldehydes (formaldehyde and acetaldehyde), and hydrogen sulfide (H_2S) using Radiello passive samplers. Additionally, Teflon and quartz filters were collected with portable Airmetrics MiniVol samplers and analyzed for $PM_{2.5}$ mass and organic carbon (OC) and elemental carbon (EC). The time-integrated sampling was supplemented with continuous measurements of VOC, $PM_{2.5}$ and black carbon at four sites during three of the four sampling seasons. Data from the saturation monitoring program were used to: characterize the spatial gradients in concentrations of air toxics within the communities adjacent to the Ports relative to the sources of emissions; evaluate the adequacy of existing routine air quality monitoring to characterize exposure concentrations within the community; correlate ambient concentrations of NOx, black carbon and $PM_{2.5}$ with proximity to truck traffic; and evaluate lower cost monitoring techniques and approaches for characterizing neighborhood-level exposures to toxic air contaminants. The spatial variations in concentrations of TACs measured during the HCMS were compared to data from the Multiple Air Toxics Exposure Study–III (MATES-III) (SCAQMD, 2008) and to relevant data from monitoring sites in the port area and elsewhere in the basin.

The objectives of the study were to: 1) collect spatially-resolved data in order to identify hot spots of selected pollutants, 2) characterize the magnitude and spatial extent of the hot spots and their relative importance compared to a regional background; 3) collect data of sufficient spatial and temporal resolution to allow comparison with fine-scale modeling results; and 4) demonstrate and evaluate the use of passive samplers. These technical objectives can be rephrased into the following specific hypotheses.

6. Passive monitoring methods can be used to measure 1-week average ambient concentrations of selected pollutants with sensitivity and precision comparable to conventional monitoring methods (averaged over the same period).
7. Gradients in pollutant concentrations exist within the Harbor Communities (i.e., measurable variations in ambient concentrations) and can be related to a location's proximity to emissions from either stationary or mobile sources.
8. The existing air quality monitoring in the area is not adequate to characterize the spatial variations in cumulative exposure within the community.
9. Ambient concentrations of black carbon are correlated to proximity to truck traffic and day-of-week variations in diesel truck traffic volume.
10. Seasonal variations in meteorology affect the pattern and magnitude of ambient concentrations of toxic air contaminants.

2. EXPERIMENTAL APPROACH AND METHODS

The term “saturation monitoring” refers to ambient air monitoring for the purpose of establishing detailed spatial variations in pollutant concentrations at the community scale. The objectives of this type of monitoring in the context of health risk assessments is to determine the annual average air toxics concentrations at a sufficient number of locations within the community to: 1) establish the spatial variations in annual average air toxic concentrations; 2) identify the potential influence of air toxic emission hotspots on the community’s exposure; and 3) characterize the gradients in air toxic concentrations from these hotspots. The HCMS saturation monitoring by DRI consisted of the 23 sites listed in Table 2-1. The table also includes monitoring stations that were operated during the study period by the SCAQMD and the Port of Los Angeles and Port of Long Beach and sites where USC measured ultrafine particles concentrations. Figure 2-1 shows the locations of the HCMS sampling sites and other air monitoring stations within the study area.

The core set of measurements at the 20 sites indicated in Figure 2-1 as yellow dots included oxides of nitrogen (NOx) and sulfur dioxide (SO_2) using Ogawa passive samplers and VOC (benzene, toluene, ethylbenzene and xylenes) and carbonyl compounds (formaldehyde and acetaldehyde) using Radiello passive samplers. Additionally, 7-day integrated Teflon and quartz filters were collected with portable Airmetrics MiniVol samplers and analyzed for $PM_{2.5}$ mass and organic carbon (OC) and elemental carbon (EC). Nitrogen dioxide (NO_2) and hydrogen sulfide (H_2S) were also measured at three core sampling sites using Ogawa and Radiello passive samplers, respectively, (indicated as vertical line within the site symbols). In addition to the 20 core sites, full sets of passive measurements (including NO_2 but not H_2S) were made at three additional near-roadway locations (indicated as horizontal line within the site symbols). Temperature and relative humidity were monitored continuously at four sampling sites and averages of the four measurements were used to apply temperature and relative humidity corrections to the Ogawa and Radiello passive sampling data. The time-integrated sampling was supplemented with continuous measurements of VOC, $PM_{2.5}$ and black carbon at four sites during three of the four sampling seasons. Passive samples were also collected for NOx, SO_2, VOC and aldehydes at University of Southern California during the summer and fall seasons for comparisons with the data collected in the Harbor area.

Samples were collected during the HCMS for four consecutive weeks in four seasons in 2007: 2/13/07 to 3/13/07 (winter), 5/15/07 to 6/12/07 (spring), 7/31/07 to 8/28/07 (summer), and 11/13/07 to 12/11/07 (fall). This sampling schedule was used in order to maximize the number of sampling sites with the resources available while providing sufficient data to determine representative annual mean ambient concentrations of TACs. The annual means based upon this approach consist of 112 days of data.[4] The ambient NO and CO data from the North Long Beach air monitoring station for the years 1990 to 2004 were used to evaluate the validity of this approach. Figure 2-2 shows the annual means based upon means of the twelve monthly means ± two standard errors. Also shown are three alternative estimates of the annual means derived from the four monthly means with one month taken from each quarter. The three estimates of the annual means based on four subsets of the monthly means lay within one standard error of the annual means (based on all 12 months).

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[4] By comparison, the every sixth day sampling schedule used in routine PM monitoring by state and local agencies includes 61 days of data.

Table 2-1. Harbor Communities Monitoring Study – Monitoring Sites

Site ID	Operator(s)	Site Name	Site Address	City	Latitude	Longitude
LBER	DRI, USC	Berns Forklift	1250 W. 17th Street,	Long Beach	33^{O} 47' 16" N	118^{O} 12' 29" W
LOCN	DRI, USC	Orange County Nursery	2377 W. Willow St.	Long Beach	33^{O} 48' 18" N	118^{O} 13' 21" W
LWBC	DRI, USC	Westside Baptist Church	1490 W. 23rd Street	Long Beach	33^{O} 47' 55" N	118^{O} 12' 44" W
LSUP	DRI, USC	Superior Electric	1700 W. Anaheim Street	Long Beach	33^{O} 46' 57" N	118^{O} 13' 01" W
LWIN	DRI	Private Residence #1	3595 Santa Fe Ave.	Long Beach	33° 47' 01" N	118° 12' 13" W
LBPW	DRI	Long Beach Public Works	901 Anaheim Street	Long Beach	33^{O} 47' 01" N	118^{O} 12' 13" W
LE71	DRI	E of 710 freeway	Pico at Pacific Coast Highway & Anaheim	Long Beach	33° 47' 16" N	118° 12' 28" N
LW71	DRI	W of 710 freeway	Gale St. btwn 16th & 17th Streets	Long Beach	33° 45' 02" N	118° 17' 17" N
SELB	DRI	Private Residence #11	415 W. Elberon Ave	San Pedro	33° 47' 29" N	118° 14' 51" N
WCOL	DRI	Private Residence #4	1318 E. Colon St.	Wilmington	33° 47' 47" N	118° 16' 29" N
WGUL	DRI	Private Residence #2	1659 Gulf Ave.	Wilmington	33° 47' 38" N	118° 15' 37" N
WLAK	DRI	Private Residence #3	1510 Lakme Ave.	Wilmington	33° 47' 09" N	118° 16' 16" N
WMCD	DRI	Private Residence #6	1148 McDonald Ave.	Wilmington	33° 47' 08" N	118° 15' 08" N
WMCF	DRI	Private Residence #5	1122 McFarland Ave.	Wilmington	33° 47' 02" N	118° 15' 52" N
WMAR	DRI, USC	Private Residence #7	1027 N. Marine Ave.	Wilmington	33° 46' 48" N	118° 14' 55" N
WPIO	DRI	Private Residence #8	719 Pioneer Ave.	Wilmington	33^{O} 46' 48" N	118^{O} 14' 55" W
WFST	DRI	Private Residence #10	1027 W. F St.	Wilmington	33° 46' 29" N	118° 16' 46" N
WE11	DRI	Llewellyn Supply Co.	507 N. Figueroa St.	Wilmington	33° 45' 57" N	118° 15' 22" W
WF49	DRI, USC	LA Fire Stn #49	400 Yacht St. - Berth 194	Wilmington	33^{O} 45' 57" N	118^{O} 15' 22" W
WEMD	DRI	Private Residence #9; W of 110 freeway	1443 Emden St.	Wilmington	33° 49' 55" N	118° 14' 24" W
CDAS	SCAQMD	Del Amo Elementary School	21228 ½ Water St.	Carson	33^{O} 49' 55" N	118^{O} 14' 24" W
SMST	SCAQMD	San Pedro - Math, Science, & Tech Center	2201 Barrywood,	San Pedro	33^{O} 45' 53" N	118^{O} 17' 47" W
LNLB	SCAQMD	N. Long Beach	3648 N. Long Beach Blvd,	Long Beach	33^{O} 49' 25" N	118^{O} 11' 19" W
LHUD	SCAQMD, DRI, USC	Hudson School Maintenance	2425 Webster Ave.	Long Beach	33^{O} 48' 09" N	118^{O} 13' 12" W
LJCF	SCAQMD, USC	Wilmington-MATES	1903 Santa Fe Ave.	Long Beach	33^{O} 47' 35" N	118^{O} 13' 07" W
LBPW	SCAQMD	Long Beach Public Works	901 Anaheim Street	Long Beach	33^{O} 47' 01" N	118^{O} 12' 13" W
WSWI	SCAQMD, DRI, USC	So. Wilmington	207 N. Fries	Wilmington	33^{O} 46' 16" N	118^{O} 15' 52" W
LSLB	SCAQMD	S. Long Beach	1305 E. Pacific Coast Hwy.	Long Beach	33^{O} 47' 32" N	118^{O} 10' 31" W
PB47	PoLA, DRI, USC	Port of LA - Berth 47	Berth 47	POLA	33^{O} 42' 54" N	118^{O} 16' 28" W
PTIT	PoLA	Terminal Island Treatment Plant	Terminal Island Treatment Plant	POLA	33^{O} 44' 47" N	118^{O} 15' 54" W
SLHP	PoLA	SP - Liberty Hills Plaza	Liberty Hills Plaza Building	San Pedro	33^{O} 44' 21" N	118^{O} 16' 50" W
WSPP	PoLA, USC, SCAQMD	Saints Peter & Paul School	Saints Peter & Paul School	Wilmington	33^{O} 47' 26" N	118^{O} 15' 52" W
PLBI	PoLB	Port of Long Beach - Inner Harbor	Canal Ave. & 12th St.	POLB	33^{O} 46' 54" N	118^{O} 12' 49" W
PLBO	PoLB, USC	Port of Long Beach - Outer Harbor	east end of Navy MOLE pier	POLB	33^{O} 44' 40" N	118^{O} 13' 05" W
USCP	USC, DRI	Particle Instrumentation Unit	USC campus	Los Angeles	34^{O} 01' 09" N	118^{O} 16' 39" W

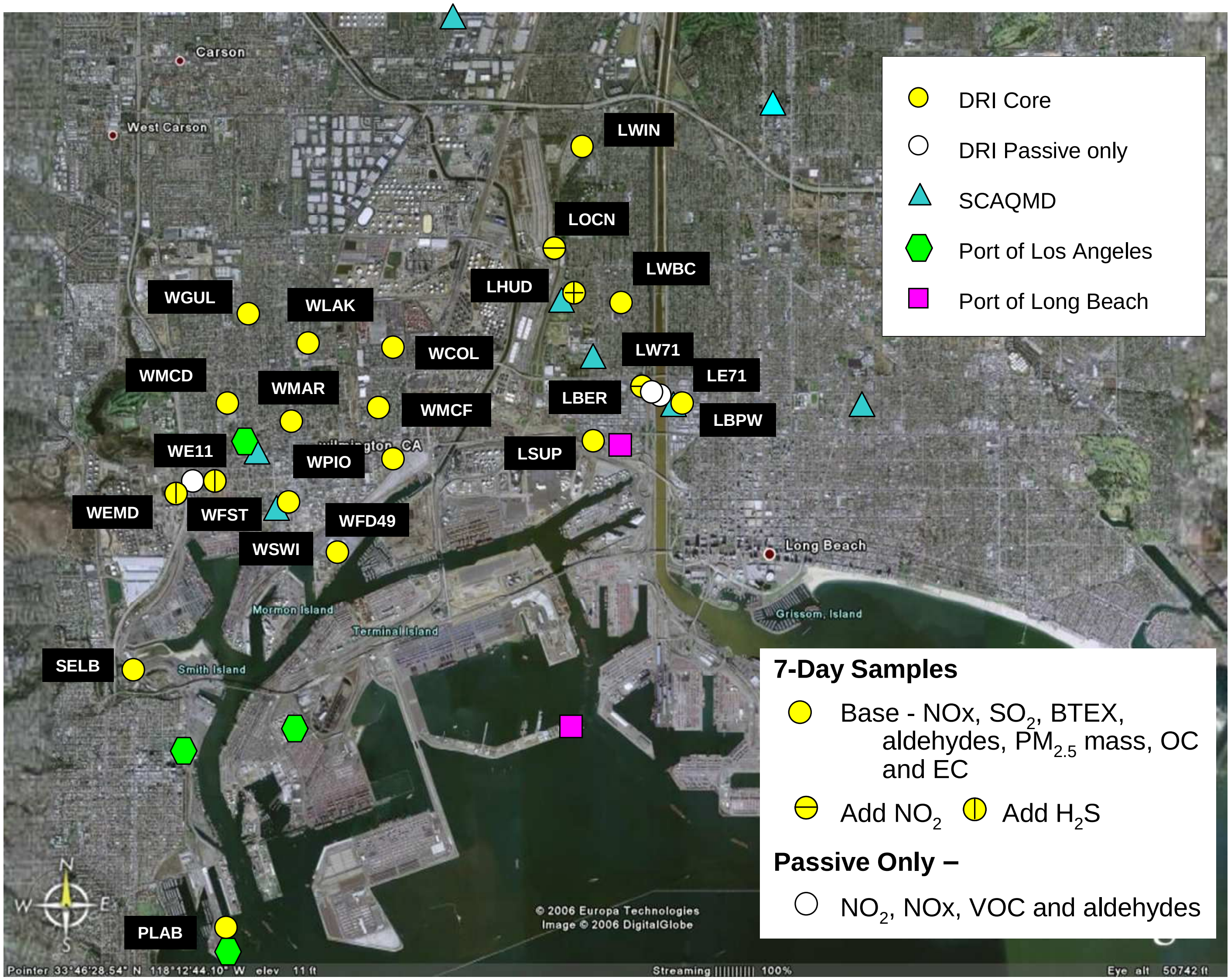

Figure 2-1. HCMS saturation monitoring sites relative to monitoring sites operated by the SCAQMD, Port of Los Angeles and Port of Long Beach.

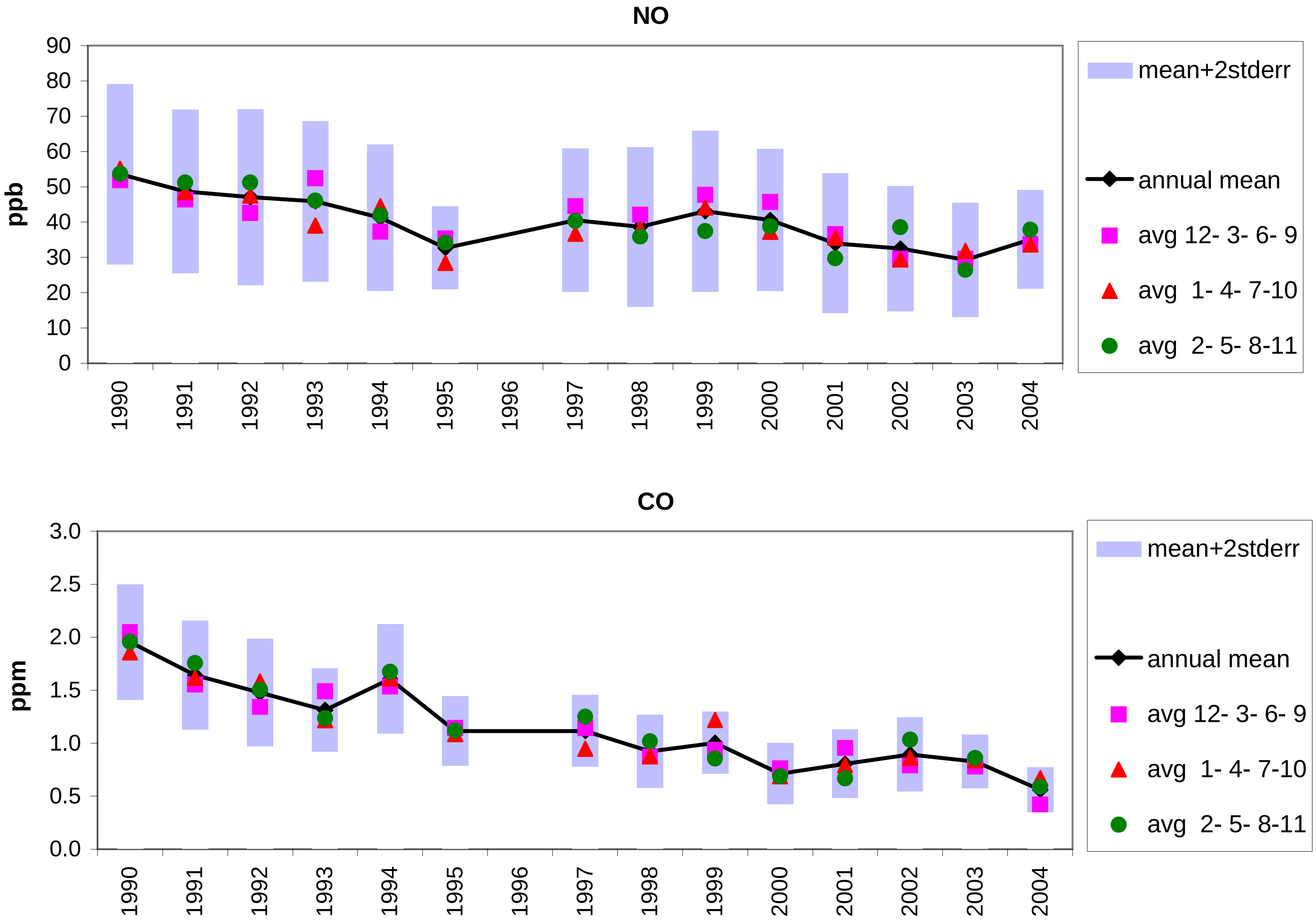

Figure 2-2. Annual means of the twelve monthly mean NO and CO mixing ratios at the N. Long Beach monitoring station versus three estimates of the annual means by using various one month subsets from each calendar quarter.

2.1 Monitoring Network Design and Objectives

The magnitude and locations of emission sources and patterns of dispersion and transport of pollutants were considered in the selection of appropriate sampling locations. We examined the spatial mapping in Figure 2-3 of annual average diesel particulate matter (DPM) concentrations as modeled by the California Air Resources Board (CARB, 2006). This spatial mapping was produced by CARB as part of a risk assessment study for the port area and includes the locations of stationary emission sources. The wind roses in Figure 2-4 were derived from data collected by the ARB in 2001-2 at the Wilmington Park Elementary School and were used to infer the general pattern of atmospheric transport in the study area.[5] Winds in the area are almost exclusively from 135 (southeast) to 315 degrees (northwest) throughout the year. Winds are most frequently from the northwest during winter, southeast during summer and west during spring and fall. Winds are typically calm overnight and switch from northerly during the morning to southerly in the afternoon. This flow reversal is less pronounced during the winter. The westerly component of the wind peaks during mid-afternoons throughout the year.

The saturation monitoring network consisted of sites that were intended to represent varying spatial scales relative to emission sources. Neighborhood-scale sampling sites represent an area of the community with relatively uniform land use within 0.5 to 4 kilometers. Microscale sampling sites characterize higher roadside exposures within several meters to 100 meters from I-710 and I-110. Middle scale (100 m to 0.5 km) sampling sites characterize near-road exposures and higher exposures that may be observed near major stationary sources. Urban-scale represents the upwind boundary that may contain a mix of aged urban emissions during periods of onshore flow following the morning offshore flow.

Figure 2-3 shows the locations of the HCMS sites overlain on the spatial mapping of modeled DPM concentrations. There were two main clusters of sampling sites in the HCMS saturation monitoring network, one in West Long Beach and the other throughout Wilmington. The cluster in Long Beach was designed primarily to characterize the impact of diesel emissions from truck traffic near the port along the I-710 Freeway (Figure 2-5) and near the Intermodal Container Transfer Facility (ICTF) near the north end of the Terminal Island Freeway (Figure 2-6). DRI's continuous black carbon and $PM_{2.5}$ measurements were concentrated in this area and are aligned from I-710 at Anaheim Street to near the ICTF along a northwest direction (LBPW-DRI, LBER, LHUD and LOCN). Three of the SCAQMD monitoring sites were also located along a similar trajectory. Passive-only measurements were made at the east (LE71) and west (LW71) edges of I-710 between Pacific Coast Highway and Anaheim Street. A core sampling site was located adjacent to Pacific Coast Highway, which carries a high volume of truck traffic. Two additional core sites were located in residential areas of West Long Beach (LWIN and LWBC).

The cluster in Wilmington included six neighborhood sites spaced throughout the community (WGUL, WLAK, WMCD, WMAR, WMCF, and WCOL). Two additional sites were located near Harry Bridges Blvd (WSWI) and Alameda Street (WPIO) to measure potential impact of diesel traffic. Another site was located at the north end of the Port of Los Angeles (WF49) to characterize the transport of emissions from the port area. A group of two core sites and one passive-only site was located downwind of a refinery (Figure 2-7). The passive only site

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[5] Wilmington School is located about 800 m east of the HCMS sampling site labeled WMCF, which is located near the center of the study area.

was located on the east edge of the I-110 freeway (WE11). One core site was near the fence line of the refinery (WEMD) and the other was located about 1.2 km east on the other side of the I-110 freeway (WFST).

The wind roses indicated that the potential for transport of emissions from the port area to San Pedro is less than to the areas north and east of the port area. Accordingly, our coverage in this area is not as extensive as in the other two communities. The monitoring network included one site in the residential area of San Pedro (SELB) across the street from the Port of Los Angeles China Shipping Terminal and the Yang Ming Intermodal Facility and another site collocated with the Port of Los Angeles Boundary Site on Berth 47 (PB47).

Final site selections were based upon proximity to intended locations, available access, and adherence to the following siting criteria.

- Access to a secure area and small amount of electrical power. Suitable locations included backyard of a private residence, flat roof of a one-story public or commercial building, fire station, or place of business, or locked fenced area.
- At least 270 degrees of unrestricted air flow around the sampler including the most frequent wind directions. Airflow was considered restricted if the distance between an obstacle (e.g., walls of buildings, trees and shrubs) and the samplers was less than twice the height that the obstacle protrudes above the sampler. Samplers were located 2 to 15 meters above ground level and 20 meters from the drip lines of trees.
- Neighborhood-scale sampling sites were located at least one city block away from major arterial surface streets and at least 500 meters from freeways and potential stationary sources of toxic air contaminants (e.g., fuel service stations and auto body shops).

2.2 Community Outreach and Participation

The saturation monitoring relied greatly on community volunteers that offered their residences or businesses for many of our sampling sites. The Air Resources Board held several meetings with the local community to publicize the objectives and scope of the proposed study and provided reports of progress during the study. Public meeting were held prior to (April 25, 2006), during (January 10, 2007 and August 1, 2007), and after (April 17, 2008) the field study. The meetings were held in the evening at the Wilmington Senior Citizen's Center and included presentations by ARB staff and HCMS researchers followed by open discussion. The ARB also established a web site for the HCMS at http://www.arb.ca.gov/research/mobile/hcm/hcm.htm to post relevant project information.

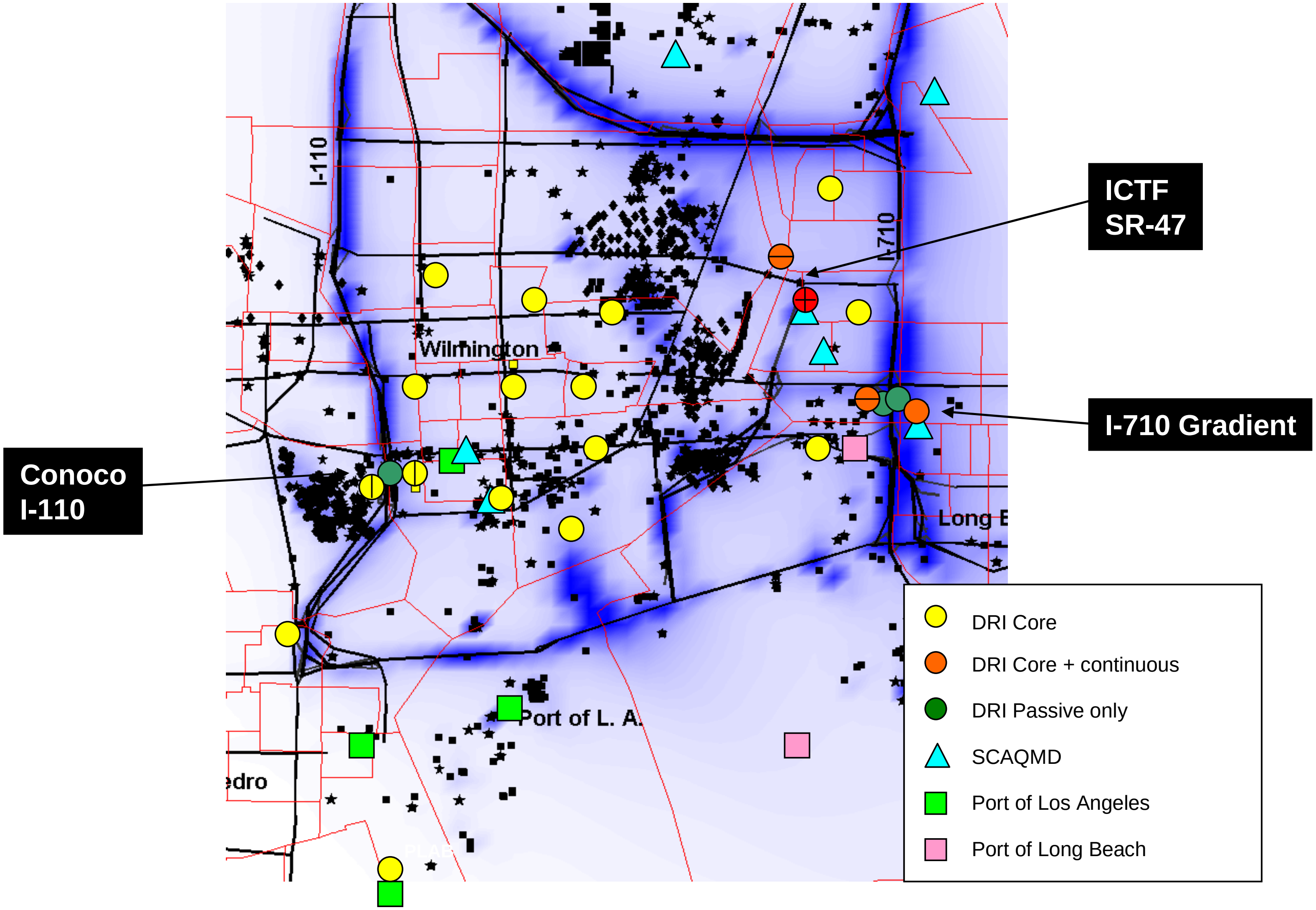

Figure 2-3. Locations of HCMS sites on spatial mapping of ARB's modeling estimate of annual average DPM concentrations. Black symbols indicate locations of stationary emission sources.

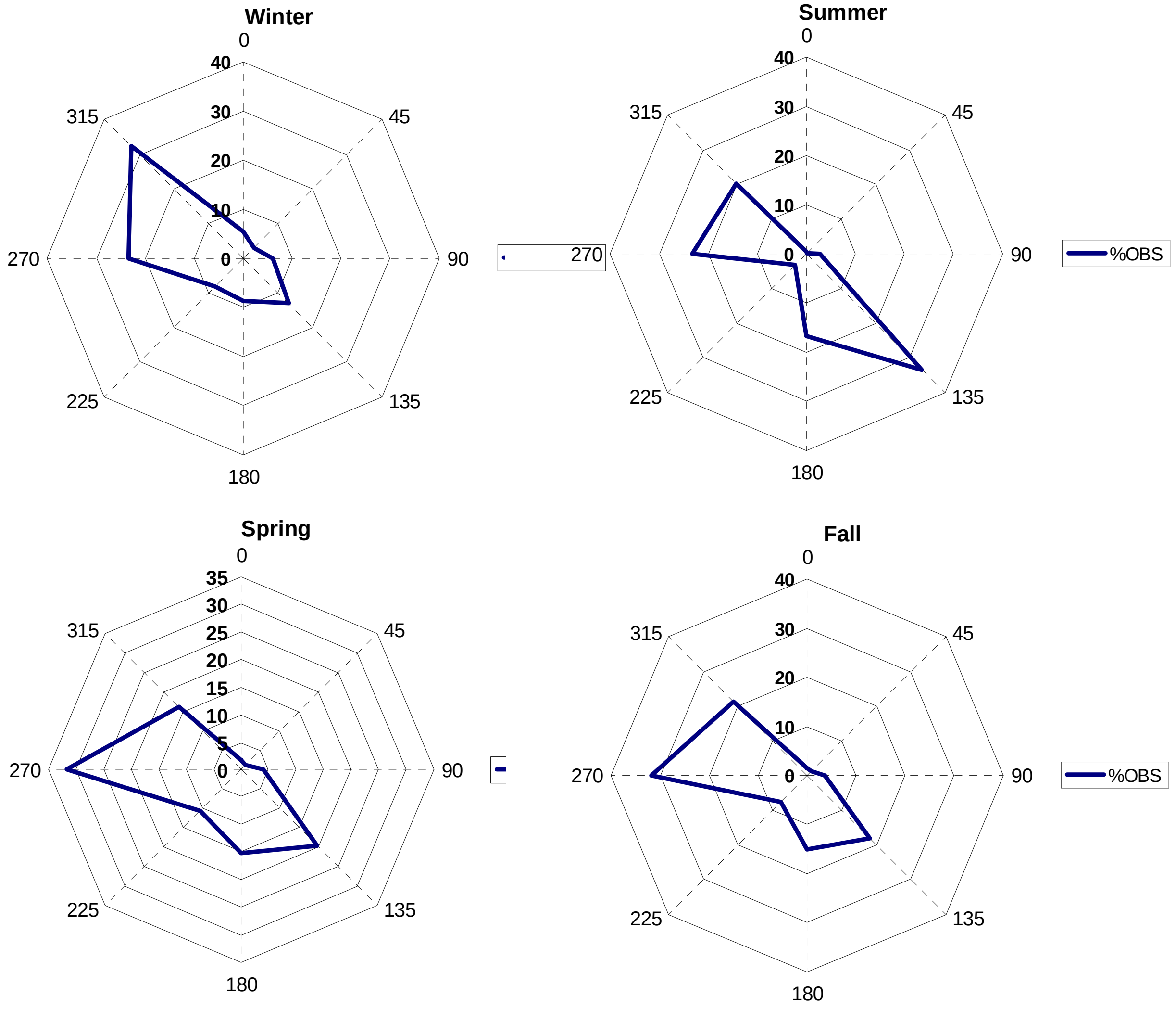

Figure 2-4. Seasonal wind patterns at Wilmington Park Elementary School, August 2001 to July 2002 (CARB, 2003).

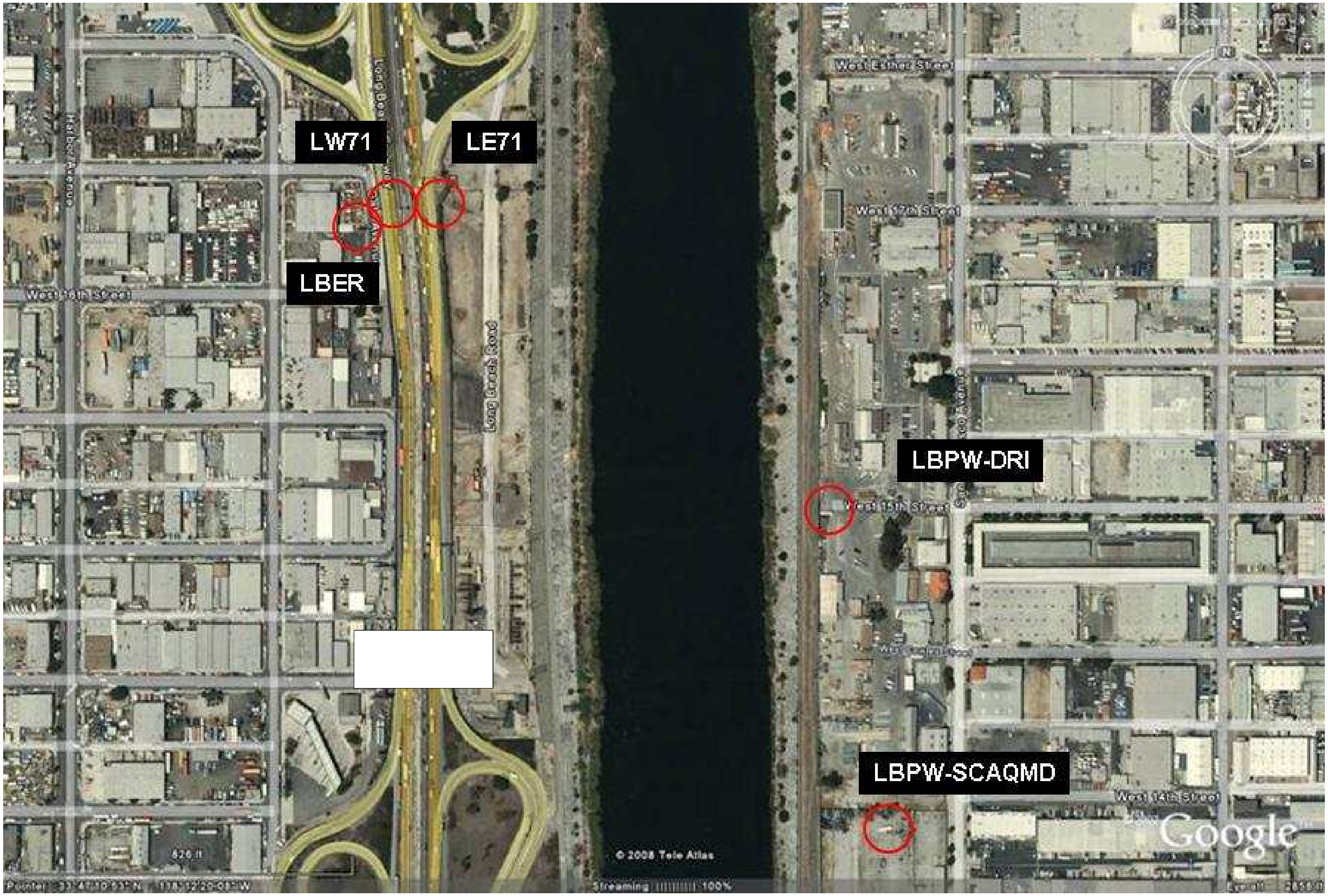

Figure 2-5. Location of HCMS sampling sites selected to determine pollutant gradients near I-710.

Figure 2-6. Locations of HCMS sampling sites at the north end of the Terminal Island Freeway (SR-103) and near the Intermodal Container Transfer Facility (ICTF).

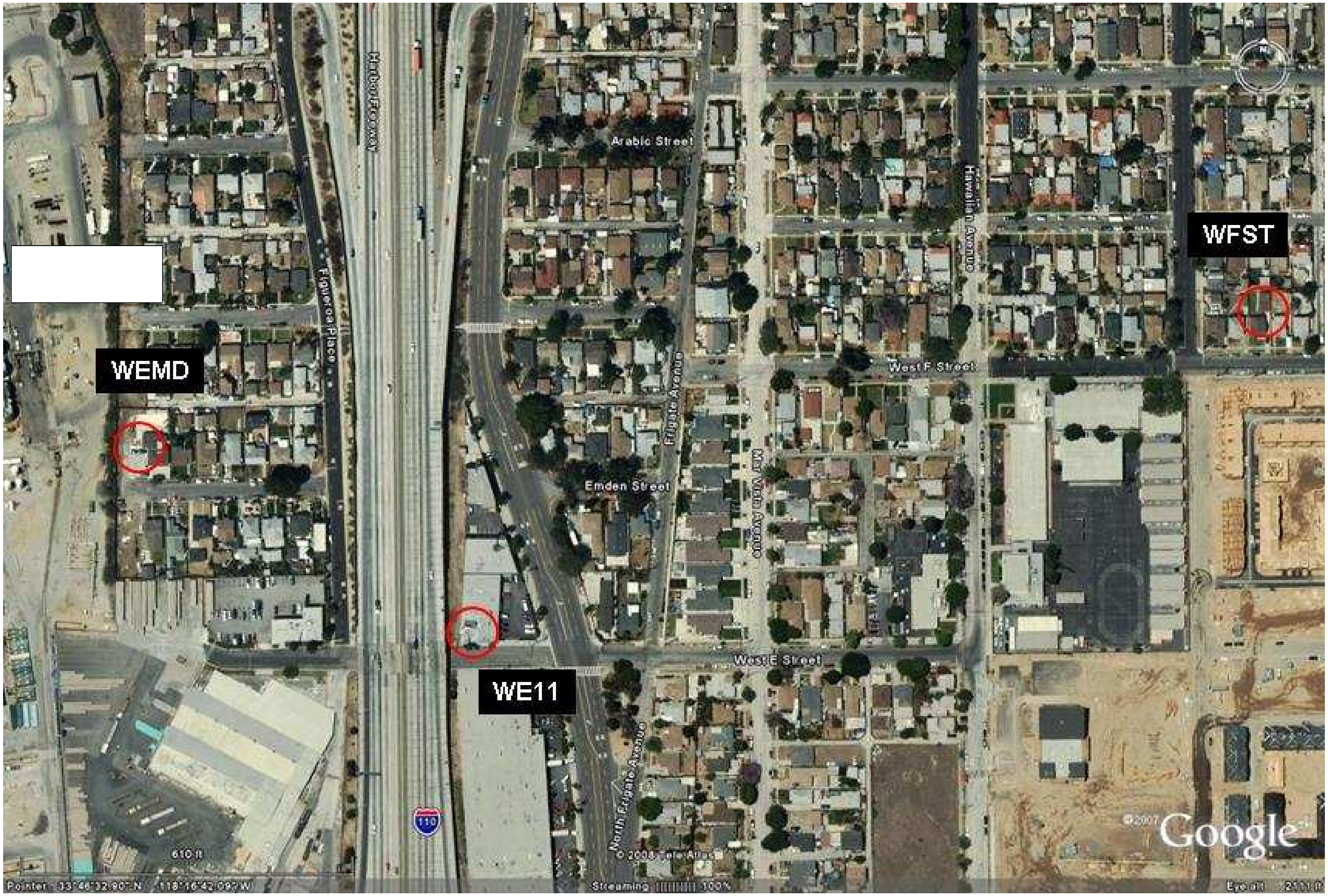

Figure 2-7. Sampling sites near a refinery and I-110.

2.3 Measurement Methods

This section describes the measurement methods used by DRI during the HCMS. Table 2-2 summarizes the measured parameters, sampling and analysis methods, integration period, and the project objectives for measurement sensitivity and precision. These data quality objectives are either that published by the manufacturer or determined in past studies. An important objective of this study was to evaluate and document the precision, accuracy, and sampling rates of the passive sampling methods. This evaluation was conducted in the following three phases.

1. Laboratory Evaluations. Precision, accuracy, and sampling rates for the passive sampling methods were evaluated in the laboratory using a flow-through chamber with known pollutant concentrations.
2. Pilot Study. The accuracies of the passive measurements under field conditions were determined prior to the main study at the SCAQMD N. Long Beach monitoring station. The 7-day time-integrated passive measurements were compared to continuous monitors or established time-integrated sampling and analysis methods. The 7-day integrated aerosol samples were also compared with the averages of the seven corresponding 24-hour aerosol samples for gravimetric $PM_{2.5}$ mass, OC and EC.
3. Collocated Measurements and SCAQMD Data Comparison during HCMS. One HCMS sampling site was collocated with an existing SCAQMD monitoring station for quality assurance. Triplicate passive samples were collected at this site during the winter and summer seasons to determine measurement precision and compared to the District's continuous data for NOx, NO_2 and SO_2 and to the daily 24-hour integrated canister samples (for BTEX and 1,3-butadiene) and DNPH samples (for carbonyl compounds) collected and analyzed by DRI. The continuous measurements of $PM_{2.5}$ and BC by DRI and SCAQMD were also compared.

DRI also evaluated collocated measurements made by the UCLA mobile monitoring van at the SCAQMD Hudson monitoring station. The results and conclusions of the measurement evaluations are summarized in Section 3.

2.3.1 Passive Sampling Methods

The basic principle employed in passive sampling is diffusion of gaseous pollutants across a surface to an adsorbing material on which the pollutant of interest accumulates over time according to Fick's law. The continual adsorption of the pollutant from the air maintains a concentration gradient near the surface that allows uptake of the pollutant to occur without any forced air movement (i.e., no pump or fan is required). After sampling, the collected pollutant is desorbed from the sampling media by thermal or chemical means and analyzed quantitatively. The average concentration of the pollutant in the air to which the sampler was exposed can be calculated from the following relationship:

$$Concentration = \frac{AnalyteMass}{SamplingRate \times Time}$$

The sampling rate can be determined theoretically or experimentally and is regulated by Fick's Law of Diffusion. Fick's first law, Equation 1, describes the rate of diffusion, J, of a solute across a surface area, A, and following a path length, L.

$$J = DA \times \frac{C}{L} \qquad [1]$$

Table 2-2. Measurements for the HCMS saturation monitoring program and data quality objectives.

Species measured	Sampling Methods	Instrument/Analysis Methods	Integration period	Minimum Detection Limits and Precision [1]
Passive Time-Integrated Sampling Methods				
NO_2 and NOx	Ogawa passive sampler	colorimetry for nitrite	7 days	0.32 ppb/7days
SO_2	Ogawa passive sampler	ion chromatography for sulfate	7 days	0.54 ppb/7days
BTEX	Radiello passive sampler	thermal desorption onto GC/MS	7 days	benzene - 0.015 ppbv (8.3%) *
				toluene - 0.002 ppbv (8.3%) *
				ethylbenzene - 0.002 ppbv (9.1%) *
				xylenes - 0.002 ppbv (11.3%) *
				1,3-butadiene - evaluated in this study
Carbonyl Compounds	Radiello passive sampler	HPLC/UV	7 days	formaldehyde - 0.07 ppbv (13.8%) *
				acetaldehyde - 0.05 ppbv (15.9%) *
				acrolein - 0.12 ppbv (16.5%) *
H_2S	Radiello passive sampler	spectrophotometry	7 days	0.2 ppb (8.7%) *
Active Time-Integrated Sampling Methods				
$PM_{2.5}$ mass (Teflon)	AirMetric Mini-Vol Sampler at 5 lpm	gravimetry	7 days	0.3 ug/m^3 (5%)
$PM_{2.5}$ OC/EC (Quartz)		IMPROVE TOR		0.3 ug/m^3 (5%)
Speciated toxic VOC	DRI OAL 7-channel can sampler	GC/MS	24 hours	0.05 ppbv (10%)
Speciated aldehydes	DRI OAL 7-channel DNPH sampler	HPLC-UV	24 hours	0.1 ppbv (10%)
Continuous Monitoring Methods				
Total VOC (estimated)	photo-ionization	RAE systems ppbRAE	1 min	30 ppb
Black carbon	photoacoustic	DRI portable PA	1 min	0.1 ug/m^3
$PM_{2.5}$ mass (estimated)	light scattering	TSI DustTrak	1 min	1.0 ug/m^3

[1] Precision estimates are one standard deviations or two standard deviations (indicated by *)

Assuming the blank value of the media is zero, the concentration C is that of the ambient compound of interest. D is the coefficient of diffusion and is dependent on the affinity of the adsorbing material for the analyte. Theoretical calculation of the coefficient of diffusion is possible, but the real world dependencies regulating its value are extensive and ambient tests are required for validation. Therefore, experimental determination of sampling rates in chambers and controlled field studies is usually preferred (Sunesson, 2007).

Several different geometries of passive samplers have been developed to control the diffusion rates according to Fick's first law. Thus sampling rates can be varied depending on the desired exposure time and expected ambient concentrations of the compounds of interest. Since the coefficient of diffusion, D and the concentration, C, are known, the sampling rate is proportional to the diffusive path area, A, and inversely proportional to the path length, L. Figure 2-8 shows three different geometries of passive monitors. The tube geometry is best for low sampling rates, while the shield (e.g., Ogawa) and radial geometry (e.g., Radiello) were developed for applications where higher diffusion rates were desired.

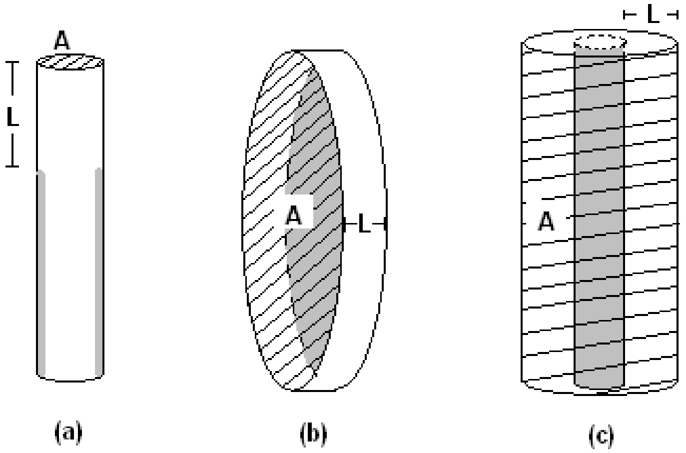

Figure 2-8. Schematics of (a) tube, (b) shield, and (c) radial geometry passive samplers with path length, L; Dashed area represents diffusive path area, A; Grey area represents adsorbent surface.

The HCMS used six different types of passive sampler, each with a unique combination of adsorbent and method of analysis (Table 2-3). The sampling rate for every analyte is calculated experimentally since pumps are not used in passive collection. Radiello[6] and Ogawa and Company[7] supply these sampling rates for a number of commonly collected compounds. These sampling rates were validated at DRI in chamber experiments for NO_x, formaldehyde, acrolein, BTEX, SO_2, and H_2S. Because 1,3-butadiene is more volatile than the other the BTEX compounds, it is more prone to back diffusion (desorption). The sampling rate for 1,3-butadiene and extent of back diffusion was determined experimentally in the laboratory.

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[6] Information about Radiello passive samplers can be found at http://www.radiello.com.

[7] Information about Ogawa passive samplers can be found at http://www.ogawausa.com/.

Table 2-3. HCMS Passive Sampling Methods

Pollutant	**Manufacturer**	**Diffusive Body**	**Adsorbent**	**Analytical Method**
NO_2	Ogawa	Ogawa Passive Sampler	Triethanolamine	Colorimetry for nitrite
NOx	Ogawa	Ogawa Passive Sampler	Triethanolamine + PTIO	Colorimetry for nitrite
SO_2	Ogawa	Ogawa Passive Sampler	Triethanolamine	Ion Chromatography for sulfate
H_2S	Radiello	Code 120-1, polycarbonate and blue microporous polyethylene cylindrical diffusive body	Code 170, microporous polyethylene and impregnated with zinc acetate	Visible spectrometry
VOC	Radiello	Code 120-2, polycarbonate and yellow microporous polyethylene cylindrical diffusive body	Code 145, ss net cylindrical cartridge, o.d. 4.8 mm packed with 350 mg of 35-50 mesh graphitic charcoal (Carbograph 4)	Thermal Desorption GC/MS
Carbonyl	Radiello	Code 120-1, polycarbonate and blue microporous polyethylene cylindrical diffusive body	Code 165, ss net cylindrical cartridge, o.d. 5.9 mm with 900 mg of 35-50 mesh DNPH coated florisil	HPLC-UV

Ogawa Passive Samplers for NOx, NO_2 and SO_2

Ogawa Passive Sampling Systems (Rupprecht and Patashnick Co., Inc.) were used for monitoring NOx, NO_2, and SO_2. NOx, and SO_2 were collected over weeklong periods using pre-coated 14.5 mm sampling pads, deployed in personal sampling bodies. NO concentrations were calculated by subtracting NO_2 from NOx concentrations. Sampling and analysis were performed according to manufacturer protocols (Ogawa & Co., USA, Inc., http://www.rpco.com/assets/lit/lit03/amb3300_00312_protocolno.pdf). For the Ogawa samplers the sampling rate conversion factor α (ppb-min/ng) is given by the equations:

$$\alpha_{NOx} = \frac{10000}{(-0.78 \cdot P \cdot RH) + 220} \qquad \alpha_{NO2} = \frac{10000}{(0.677 \cdot P \cdot RH) + (2.009 \cdot T) + 89.8}$$

$$\text{where } P = \left(\frac{2P_N}{P_T + P_N} \right)^{2/3}$$

and RH is the relative humidity in percent, T is the air temperature in ^oC, and P_N and P_T are the vapor pressure of water in mmHg at 20 ^oC and ambient temperature, respectively. α_{SO2} was determined from tables provided by the manufacturer, and varies from 44 - 35 ppb-min/ng for the temperature range 0 – 40 ^oC. The Ogawa NO_2 and NO_x pads were extracted and mixed with a solution of sulfanilamide and N-(1-Naphthyl)-ethylenediamine dihydrochoride to produce a colored nitrite solution which was analyzed on a Technicon (Tarrytown, NY) TRAACS 800 Automated Colorimetric System (AC). The Ogawa SO_2 pads were extracted in 8 ml of deionized-distilled water (DDW), 1.75% hydrogen peroxide is added and sulfate was measured with a Dionex 2020i (Sunnyvale, CA) ion chromatograph (IC). These analyses were performed by the Environmental Analysis Facility (EAF) of DRI.

Radiello Diffusive Samplers for VOCs

Unlike other samplers that use axial diffusion from one surface to another, Radiello samplers use radial diffusion over a microporous cylinder into an absorbing inner cylinder, which gives about a 100 times higher uptake rate. Radiello diffusive samplers (adsorbing cartridge code 145) were used for passive sampling of benzene, toluene, ethylbenzene, and xylenes (BTEX). Sampling of 1,3-butadiene was evaluated in the laboratory and during the Pilot Test in Long Beach. VOC samples were collected over weeklong periods using stainless steel net cylinders (3x8 um mesh, 4.8 mm diameter x 60 mm length) packed with Carbograph 4 (350 mg) and deployed in the diffusive sampling bodies, according to the manufacturer's procedures (http://www.radiello.com). The Radiello samplers are insensitive to humidity within the range 10-90% RH and wind speed between 0.1 and 10 m/s. Sampling rates were calculated based on ambient temperature during sampling using the following equation:

$$Q_T = Q_{298}(T/298)^{1.5}$$

where Q_T is the sampling rate at ambient temperature T in ^oK and Q_{298} is the reference value at 25 ^oC. This produces a variation of ± 5% for ± 10 ^oC variation from 25 ^oC. As a side note, meteorological conditions summarized for 2007 at the two Port of Long Beach sites were outside the RH bounds 8 and 14% of the time, outside the wind speed bounds about 1% of the time, and outside (generally below) the 15-35 ^oC air temperature range about 35 to 50% of the time. However, even at 10 ^oC, which occurs with some regularity, the sampling rate would be less than 8% below the 25 ^oC base rate.

All VOC passive samples were analyzed by the thermal desorption-cryogenic pre-concentration method, followed by high-resolution gas chromatographic separation and mass spectrometric detection (GC/MS) of individual compounds. A Gerstel ThermoDesorption System (TDS) unit, equipped with 20–position autosampler, attached to the Varian Saturn 2000 GC/MS system, was used for sample desorption and cryogenic preconcentration. A 60 m (0.32 mm i.d., 0.25 mm film thickness) DB-1 capillary column (J&W Scientific, Inc.) was used to achieve separation of the target species. For calibration of the GC/MS, a set of standard Carbograph 4 cartridges were prepared by spiking the cartridges with a known amount of gaseous calibration mixture of benzene, toluene, ethylbenzene, o-, m- and p- xylene (BTEX) and 1, 3–butadiene, purchased from Scott Specialty Gases. Three different concentrations (plus one blank) were used to construct calibration curves.

Radiello Diffusive Samplers for Carbonyl Compounds

Radiello diffusive samplers consisting of a stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated florisil (Code 165) were used to passively collect carbonyl compounds. Sampling rates vary from the value at 25 ^{o}C according to the following equation:

$$Q_T = Q_{298}(T/298)^{0.35}$$

This produces a variation of ± 1% for ± 10 ^{o}C variation from 25 ^{o}C. Carbonyl compounds react with 2,4-DNPH forming corresponding 2,3-dinitrophenylhydrazones. The hydrazones were extracted and analyzed with a Waters 2690 Alliance System HPLC with 996 Photodiode Array UV Detector. The VOC and carbonyl compound analyses were performed by the Organic Analytical Laboratory (OAL) of DRI.

Despite the widespread use of the DNPH methods, interferences and sampling artifacts have been associated with the methods. The analytical method is well established, and questions regarding the accuracy of the DNPH method are mainly concerned with sampling. The major concerns are: 1) incomplete collection of carbonyls, 2) loss of carbonyl compounds by physical processes such as adsorption or chemical reaction with co-pollutants such as ozone, and 3) conversion of the hydrazone during sampling and subsequent storage. Radiello acknowledges the potential for ozonolysis of dinitrophenylhydrazones on active supporting materials such as silica gel, but claim that ozonolysis is less important on the code 165 cartridge, packed with coated florisil. Apart from acetaldehyde, the ozone effect becomes relevant only at levels higher than 100 ppb as an average over the entire exposure period. Sampling rates for acetaldehyde are lower by about 10 and 25 percent at ozone levels of 50 and 100 ppb, respectively. A recent study found that although active sampling on commercial DNPH cartridges was adequate for the measurement of formaldehyde, low recovery (< 60%) was observed for acetaldehyde for a sampling duration greater than 8 hours. The recovery decreased with increasing sampling time (Herrington et al., 2007). Thus, even the traditional method for measuring acetaldehyde is not particularly quantitative.

Acrolein is known to rearrange on DNPH cartridges to an unknown degradation product (acrolein-X) (Tejada, 1986). Disappearance of the acrolein hydrazone in the analytical sample matrix correlates quantitatively almost on a mole for mole basis with the growth of acrolein-X, and the sum of acrolein and acrolein-X appears to be invariant with time (Tejada, 1986). This process of rearrangement is sufficiently rapid that most of the acrolein may convert to acrolein-X, unless the sample is analyzed within a few hours. The problem is compounded by the fact that acrolein-X co-elutes in our HPLC analysis with another common carbonyl compound, butyraldehyde. The UV spectra from the photodiode array detector show that there is substantial overlap in the chromatographic retention time of acrolein-X with butyraldehyde. Thus, the sum of acrolein and butyraldehyde represents an upper-bound estimate of acrolein that was originally present in the sample.

DRI's Organic Analytical Laboratory recently performed experiments to determine if a more accurate measurement of acrolein could be obtained by post-analysis reprocessing of the HPLC spectra. This work was done for the Health Effects Institute for samples collected in the Los Angeles area for another project during summer and fall/winter 2004 (Fujita et al., 2008). An acrolein-X standard was generated by collecting a known concentration of acrolein onto a DNPH cartridge and letting it remain in the sample matrix long enough for part of the acrolein to convert to acrolein-X. The concentration of acrolein-X was calculated as the difference between the known amount of acrolein deposited on the DNPH cartridge and concentration determined from HPLC analysis. The apparent concentration of acrolein-X (from the peak identified as butyraldehyde) detected in the analysis is equivalent to the concentration of acrolein collected on the DNPH cartridge. A 'standard' for acrolein-X was generated in this manner. Several mixtures containing varying relative amounts of acrolein-X and butyraldehyde were analyzed to obtain spectra for which the correct proportions were known. Then, using an iterative solution process, peaks from the spectra of the two pure compounds were added together to obtain the closest match to the spectrum of each mixture, as shown in Figure 2-9. The scaling factors applied to the spectra from the acrolein-X and butyraldehyde spectra to obtain the best fit indicated the estimated amounts of each compound in the mixture.

Results from this experiment were quite good, yielding agreement to within 20% of the actual concentrations for all mixtures except those where the concentration of butyraldehyde was much higher (e.g. 10x) than acrolein. We applied the same technique to the previously analyzed HPLC data from samples collected in the Los Angeles area for a previous study (Fujita et al., 2008) in order to estimate the concentrations of acrolein and butyraldehyde in each sample. Comparing the sum of the two separated compounds to the original concentration of unresolved acrolein-X + butyraldehyde for each sample showed very strong correlations and good agreement, but there is some indication of bias due to variations in the instrument response over time. Although chemical standards are analyzed during each analysis run in order to compensate for variations in detector response, no standard for acrolein-X is available for routine use so there is some uncertainty connected with the reprocessing of the spectra using standards analyzed at a later time. However, Figure 2-10 indicates that the effect is relatively small even over a period of many months.

Radiello Diffusive Samplers for Hydrogen Sulfide

Radiello chemiadsorbing cartridges (code 170) were used for passive sampling of hydrogen sulfide (H_2S). The cartridge is made of microporous polyethylene and impregnated with zinc acetate. H_2S is chemiadsorbed by zinc acetate and transformed into stable zinc sulfide. The sulfide is recovered by extraction with water. In contact with ferric chloride in a strongly acid solution, it reacts with N,N-dimethyl-p-phenylendiammonium ion to yield methylene blue. Methylene blue is quantified by visible spectrometry. The sampling rate Q_{298} at 298 K (25°C) and 1013 hPa is 0.096 ± 0.005 $\text{ng}\cdot\text{ppb}^{-1}\cdot\text{min}^{-1}$. The sampling rate varies from its value at 25 ^{o}C according to the following equation:

$$Q_T = Q_{298}(T/298)^{3.8}$$

This produces a variation of ± 13 % for ± 10 ^{o}C variation from 25 ^{o}C. The sampling rate is invariant with humidity in the range 10-90% and with wind speed between 0.1 and 10 m/sec.

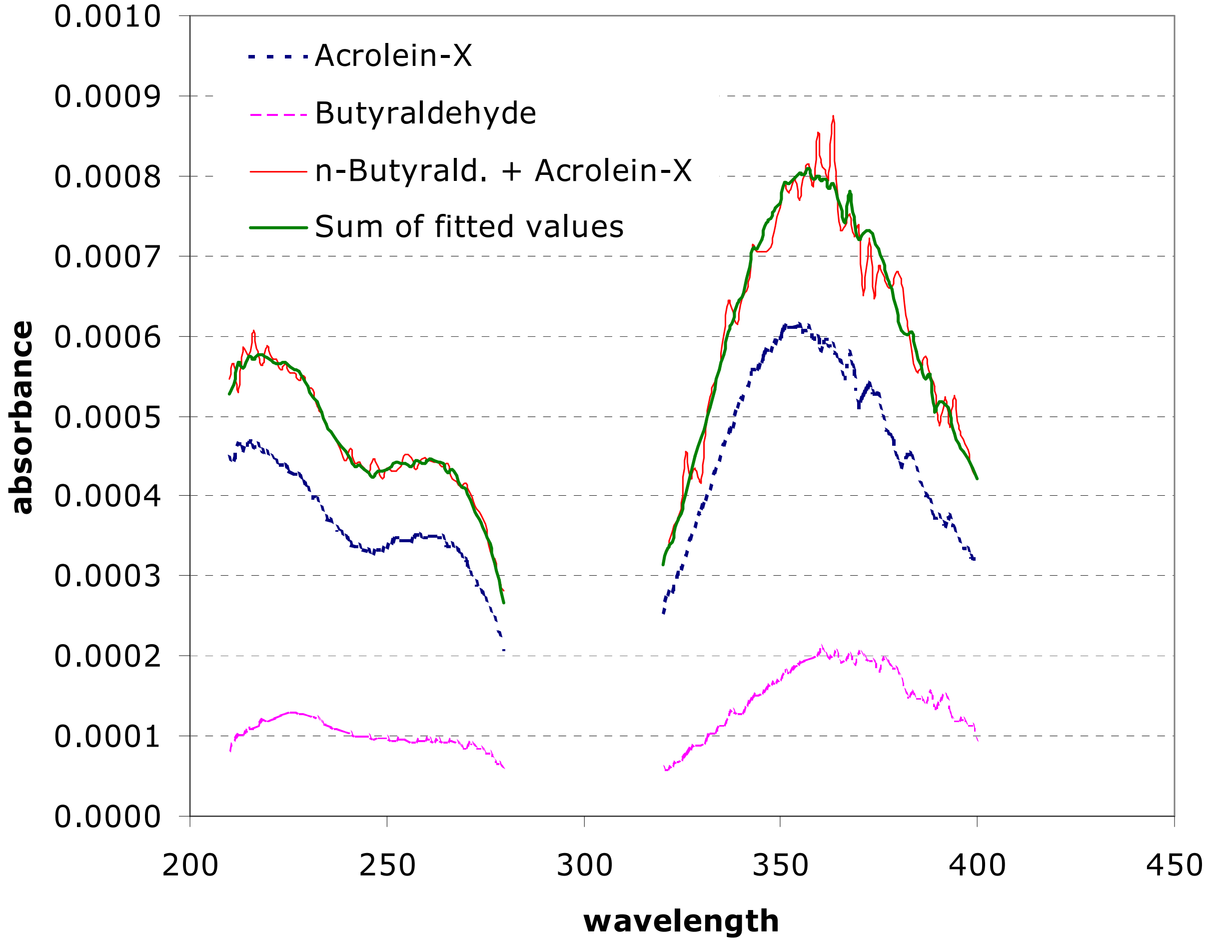


Figure 2-9. Sample of results of curve fitting program to reconstruct acrolein data from original spectrum. Absorbance is in units of cm^{-1}.

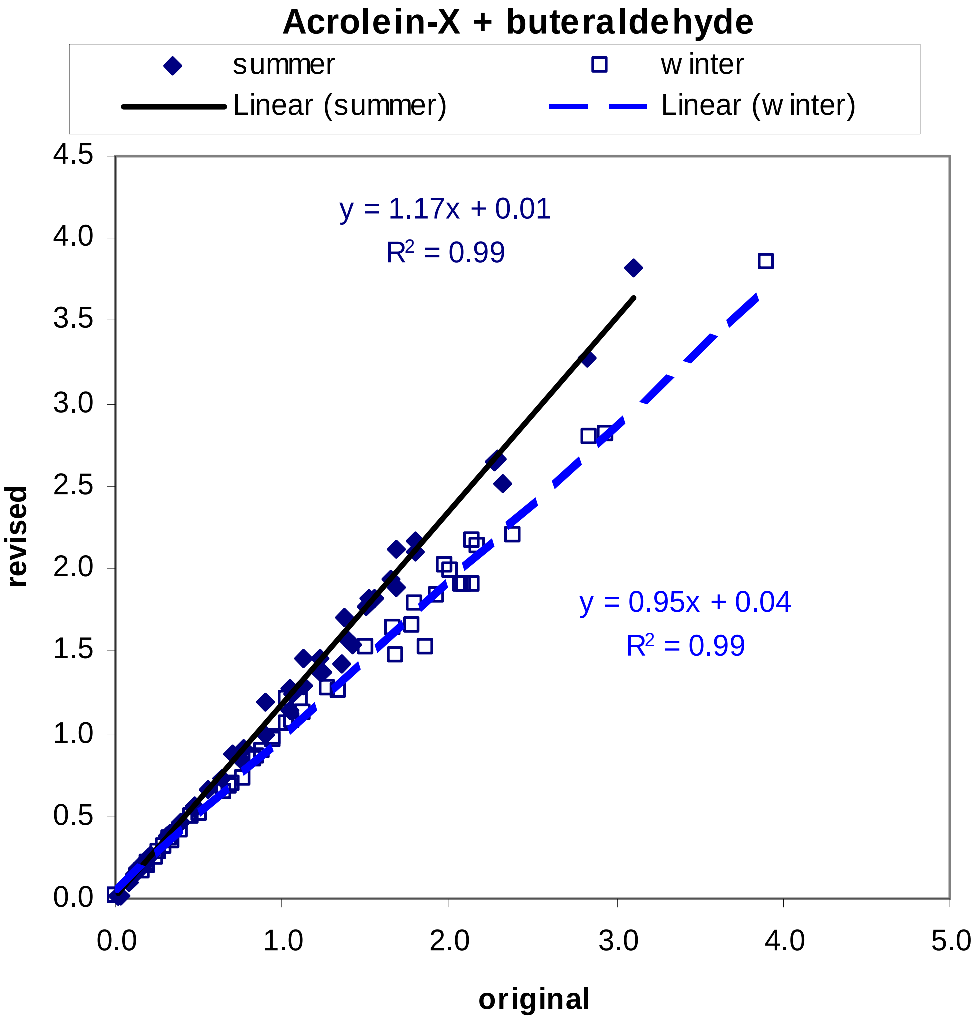


Figure 2-10. Regression plot comparing reconstructed sum of acrolein-X and butyraldehyde to original, unresolved total (DNPH adduct in µg/sample). Data from the two field sampling periods are grouped separately due to differences in instrument calibration.

2.3.2 Collection and Analysis of Time-Integrated MiniVol Particle Samples

MiniVol portable $PM_{2.5}$ air samplers from AirMetrics Corporation were used for particle sampling for seven continuous days coincident with the passive samples. The sampler is equipped with an inlet containing an impactor unit with 2.5-µm particle cut point and a flow control system capable of maintaining a constant flow rate within the design specifications of the inlet. The impactor is designed for a 50% collection efficiency for particles of aerodynamic diameter of 2.5 µm or less at a flow rate of 5 L/minute. The following substrates were used in the HCMS:

- Gelman (Ann Arbor, MI) polymethylpentane ringed, 2.0 mm pore size, 47 mm diameter PTFE Teflon-membrane Teflo filters (#RPJ047) for particle gravimetric mass and elements.
- Pallflex (Putnam, CT) 47 mm diameter pre-fired quartz-fiber filters (#2500 QAT-UP) for organic and elemental carbon measurements

The portable aerosol samplers were specially equipped to operate from both AC and DC power sources. In the DC mode, the sampler is attached to a charged battery pack prior to field sampling, making the sampler siting independent of external power. During the pilot study we experienced a number of equipment failures with the AeroMetrics Mini-Vol filter samplers, even though they had been individually tested before deployment. In subsequent testing at DRI, we determined that the problems were primarily related to failure of the internal battery and/or charging system over the course of the week-long sampling period. The rechargeable lead-acid batteries provided by the manufacturer are not well-suited to (or intended for) long-term continuous use. To rectify the problem, a direct power system, using a switch-mode 12V power supply in place of the battery system, was tested and proved reliable over period of 5 weeks of continuous operation. As a result, we decided to purchase and install these direct power systems in all of the samplers to be used for the main field study. The new systems are also lighter in weight and require only about 300 mA of 110V line power to operate (less than a 40W light bulb).

Gravimetric Mass

Unexposed and exposed Teflon-membrane filters were equilibrated at a temperature of 20 °C and a relative humidity of 30 % for a minimum of 24 hours prior to weighing. Weighing was performed on a Cahn 31 electro microbalance with ± 0.001 mg sensitivity. The charge on each filter is neutralized by exposure to a polonium source for 30 seconds prior to the filter being placed on the balance pan. The balance is calibrated with a 20 mg Class M weight and the tare is set prior to weighing each batch of filters. After every 10 filters are weighed, the calibration and tare are re-checked. If the results of these performance tests deviate from specifications by more than ± 5 µg, the balance is re-calibrated. If the difference exceeds ± 15 µg, the balance is recalibrated and the previous 10 samples are re-weighed. At least 30% of the weights are checked by an independent technician and samples are re-weighed if these check-weights do not agree with the original weights within ± 15 µg.

Elemental and Organic Carbon

Elemental carbon (EC) and organic carbon (OC) were measured by thermal optical reflectance (TOR) method using the IMPROVE (Interagency Monitoring of Protected Visual Environments) temperature/oxygen cycle (IMPROVE TOR). A section of the quartz filter is placed in the carbon analyzer oven such that the optical reflectance or transmittance of He-Ne laser light (632.8 nm) can be monitored during the analysis process. The filter is first heated under oxygen-free helium purge gas. The volatilized or pyrolyzed carbonaceous gases are carried by the purge gas to the oxidizer catalyst where all carbon compounds are converted to carbon dioxide. The CO_2 is then reduced to methane, which is quantified by a flame ionization detector (FID). The carbon evolved during the oxygen-free heating stage is defined as “organic carbon”. The sample is then heated in the presence of helium gas containing 2 percent of oxygen and the carbon evolved during this stage is defined as “elemental carbon”. Some organic compounds pyrolyze when heated during the oxygen-free stage of the analysis and produce additional EC, which is defined as pyrolyzed carbon (PC). The formation of PC is monitored during the analysis by the sample reflectance or transmittance. EC and OC are thus distinguished based upon the refractory properties of EC using a thermal evolution carbon analyzer with optical (reflectance or transmittance) correction to compensate for the pyrolysis (charring) of OC. Carbon fractions in the IMPROVE method correspond to temperature steps of 120^{o}C (OC1), 250^{o}C (OC2), 450^{o}C (OC3), and 550^{o}C (OC4) in a non-oxidizing helium atmosphere, and at 550^{o}C (EC1), 700^{o}C (EC2), and 850^{o}C (EC3) in an oxidizing atmosphere.

The system is calibrated by analyzing samples of known amounts of methane, carbon dioxide, and potassium hydrogen phthalate (KHP). The FID response is ratioed to a reference level of methane injected at the end of each sample analysis. Performance tests of the instrument calibration are conducted at the beginning and end of each day's operation. Intervening samples are re-analyzed when calibration changes of more than ±10% are found. Known amounts of reagent grade crystal sucrose and KHP (certified by the American Chemical Society) are committed to TOR as a verification of the organic carbon fractions. Fifteen different standards are used for each calibration. Widely accepted primary standards for elemental and/or organic carbon are still lacking. Results of the TOR analysis of each filter are entered into the DRI data base.

2.3.3 Active Sampling of Gaseous Air Toxics for Quality Assurance

Speciated air toxics include canister sampling for VOC (benzene, toluene, ethylbenzene, m- & p-xylene, o-xylene (i.e., BTEX), 1,3-butadiene, and DNPH-coated Sep Pak cartridges sampling for carbonyl compounds (formaldehyde, acetaldehyde, acrolein).

Canister Samples for VOC

The canisters were cleaned prior to sampling 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 UHP humid zero air to ~15 psig is used. One canister out of the ten per lot was filled with humidified UHP zero air and analyzed by the GC-FID/MS method, as described below. The canisters were considered clean if target compound concentrations are less than 0.05 ppbv each. The canister sampling systems were cleaned prior to field sampling by purging with humidified zero air for 48 hours, followed by purging with dry UHP zero air for one hour and certified clean.

Canister samples were analyzed for BTEX and 1,3-butadiene using gas chromatography/mass spectrometry according to EPA Method TO-15. The GC-FID/MS system includes a Lotus Consulting Ultra-Trace Toxics sample preconcentration system built into a Varian 3800 gas chromatograph with flame ionization detector (FID) coupled to a Varian Saturn 2000 ion trap mass spectrometer. The Lotus preconcentration system consists of three traps. Mid- and heavier weight hydrocarbons are trapped on the front trap consisting of 1/8” nickel tubing packed with multiple adsorbents. Trapping is performed at 55 ºC and eluting is performed at 200 ºC. The rear traps consist of two traps: empty 0.040” ID nickel tubing for trapping light hydrocarbons and a cryo-focusing trap for mid and higher weight hydrocarbons isolated in the front trap. The cryo-focusing trap is built from 6’ x 1/8” nickel tubing filled with glass beads. Trapping of both rear traps occurs at -180 ºC and eluting at 200 ºC. Light hydrocarbons are deposited to a Varian CP-Sil5 column (15m x 0.32mm x 1µm) plumbed to a column-switching valve in the GC oven, then to a Chrompack Al_2O_3/KCl column (25m x 0.53mm x 10µm) leading to the flame ionization detector for quantitation of light hydrocarbons. The mid-range and heavier hydrocarbons cryo-focused in the rear trap are deposited to a J&W DB-1 column (60m x 0.32mm x 1µm) connected to the ion trap mass spectrometer. The GC initial temperature is 5 ºC held for approximately 9.5 minutes, then ramps at 3 ºC/min to 200 ºC for a total run time of 80 minutes.

Calibration of the system is conducted with a mixture that contained the most commonly found hydrocarbons (75 compounds from ethane to n-undecane, purchased from Air Environmental) in the range of 0.2 to 10 ppbv. Three point external calibrations are run prior to analysis, and one calibration check is run every 24 hours. If the response of an individual compound is more then 10% off, the system is recalibrated. Replicate analysis is conducted at least 24 hours after the initial analysis to allow re-equilibration of the compounds within the canister.

DNPH Cartridges Samples for Carbonyl Compounds

Formaldehyde, acetaldehyde and acrolein were 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 the exhaust is drawn through the cartridge, carbonyls in the sample are captured by reacting with DNPH to form hydrazones. These hydrazones are separated and quantified per EPA Method TO-11A using a high performance liquid chromatograph (Waters 2690 Alliance System with 996 Photodiode Array Detector). Since acrolein undergoes summarization when reacted with DNPH on the silica-gel cartridges and forms two products, both peaks were identified and quantified and the total concentration was reported. The peak overlapping with butyraldehyde was corrected as described in the previous section. For commercial 2,4-dinitrophenylhydrazine (DNPH) cartridges (Waters Sep-Pak XpoSure Aldehyde Sampler), DRI analyzed 5% of the purchased cartridges to ascertain the blank variability.

2.3.4 Continuous Measurements

DustTrak Nephelometer for PM2.5 Mass.

TSI DustTrak nephelometers were used to measure light scattering that is interpreted as PM mass. The DustTrak Aerosol Monitor is a portable, battery-operated, laser-photometer that measures 90° light scattering (different from the total light scattering measured by an integrating nephelometer) and reports it as PM mass concentration. The laser diode used by the DustTrak has a wavelength of 780 nm, which limits the smallest detectable particle to about 0.1 µm. The reported PM mass concentration is factory-calibrated using the respirable fraction of an Arizona Road Dust standard (ISO 12103-1, A1). The mass scattering efficiency depends on particle shapes, size distribution, and composition (index of refraction). The ISO 12103–1, A1 standard consists of primarily silica particles (70%) that are provided with some particle size specifications. By volume, the standard consists of 1–3% particles with diameter less than 1 µm, 36–44% with diameter less than 4 µm, 83–88% with diameter less than 7 µm, and 97–100% with diameter less than 10 µm. This standard contains a larger quantity of coarse (>2.5 µm) particles than are usually found in urban ambient aerosol. $PM_{2.5}$ has a higher mass scattering efficiency, so the DustTrak overestimates $PM_{2.5}$ for smaller, chain aggregate soot particles. During the Gasoline/Diesel PM Split Study, the DustTrak was found to exceed gravimetric mass concentrations of the on-road ambient samples by a factor of 2.24 with an R^2 of 0.75 (Fujita et al., 2007).

Photoacoustic Black Carbon Analyzer

The photoacoustic black carbon instrument used in the HCMS was developed at DRI and has been described in several publications (Arnott, Moosmüller, et al., 1999; Arnott, Moosmüller, et al., 2000). Briefly, light from a 1047 nm laser is power-modulated at the operating frequency of an acoustical resonator. Sample air is continuously drawn through the resonator at a flow rate of 1 – 3 liters per minute (lpm). Light absorbing aerosol (black carbon) will absorb some of the laser power, slightly heating the aerosol (typically much less than 1 ^{o}C). The heat transfers very rapidly from the aerosol to the surrounding air and increases the local pressure. The pulsing laser contributes to a standing acoustic wave in the resonator. The acoustic wave is measured with a microphone as a measure of the light absorption. For the operating conditions of the resonator, and the laser wavelength used, the light absorption measurement is linearly proportional to the mass concentration of the black carbon aerosol in the sample air. The constant of proportionality has been inferred from correlations of black carbon measurements with elemental carbon as determined by the TOR method, and an efficiency factor of 5 square meters per gram is used to go from aerosol light absorption to estimated black carbon mass concentration. No filters are needed for the photoacoustic measurement, and the flow rate is not used in the calculation of aerosol mass concentration. The flow rate must only be sufficient to adequately sample the air with minimal particle loss in the instrument and sample lines. The resolution of the instrument for a 3-second averaging time is usually 2.5 Mm^{-1} for light absorption, corresponding to 0.5 microgram per cubic meter for black carbon mass concentration. The resolution scales as the square root of sampling time, so for example, a resolution of 0.25 micrograms per cubic meter can be obtained for a 9-second averaging time. The photoacoustic measurement does not receive interference from exhaust gases, in our experience so far, and it is a zero-based measurement when no light absorbing aerosols are present.

Portable PID Monitor for estimates of total VOC

A RAE Systems Model PGM-7240 (ppbRAE) portable photoionization detector (PID) was used to continuously monitor ambient VOC levels. The monitor is equipped with a 10.6 eV PID and responds to certain organic and inorganic gases that have an ionization potential of less than 10.6 eV, which includes aromatic hydrocarbons, olefins, and higher molecular weight alkanes. It does not respond to light hydrocarbons such as methane, ethane, and propane or to acetylene, formaldehyde or methanol. The monitor has less than a 5-second response time and a lower detection limit of 20 ppb. Because the total response of the PID depends upon the specific mix of VOCs, the response must be calibrated to the expected mix of VOC. Isobutylene is the calibration gas and the PID response can be adjusted to one of several specific VOC species or a standard mixtures of VOC such as gasoline. We have developed empirical relationships between the PID response to urban air and the sum of VOC species from the canister VOC data.

Carbon Monoxide

Carbon monoxide and carbon dioxide were continuously measured at one site with a TSI Model 8854 monitor. This portable instrument has a resolution of 1 ppm and accuracy of 3%

from 0 to 5000 ppm for CO_2. CO was measured by an electrochemical cell and CO_2 was measured by an NDIR optical absorption method. This instrument also records ambient temperature and relative humidity.

Temperature and Relative Humidity Sensors

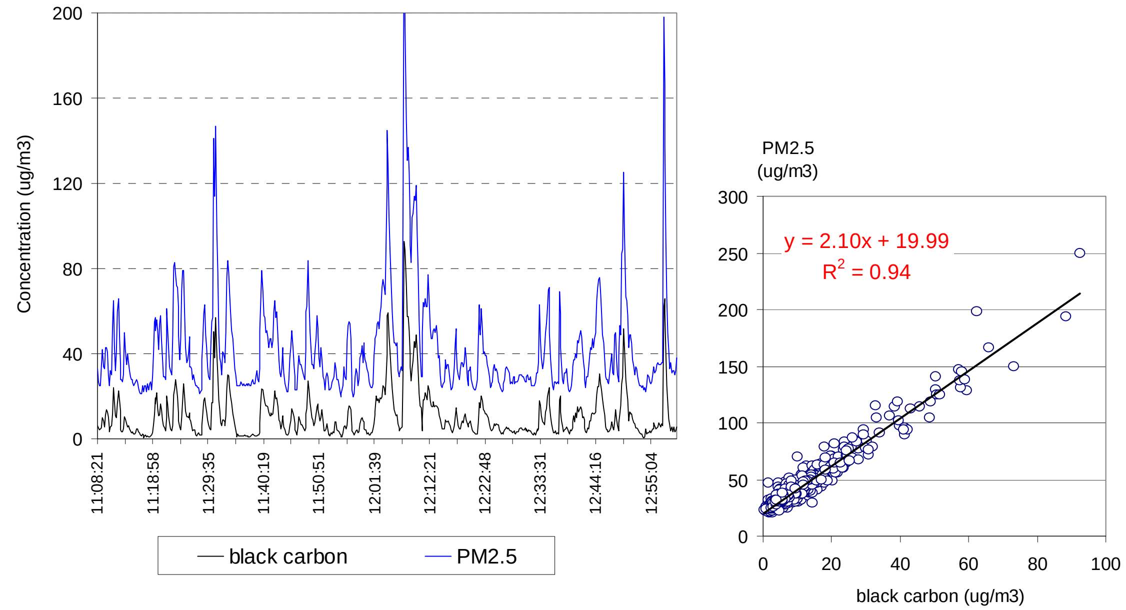
Onset Computing HOBO U10 temperature/humidity loggers were used to monitor temperature and relative humidity (RH). The sensor has a range of -20 to 70 °C and 25 to 95% RH with an accuracy of ±0.4 °C and ±3.5 % RH. The averaging time can be adjusted from 1 second to 12 hours. The sensor can store up to 52,000 data points (360 days @ 10-minute average) and has a battery life of approximately 1 year.

2.4 Elemental Carbon as a Surrogate for Diesel Particulate Matter

Diesel particulate matter (DPM) is composed of a center core of elemental carbon (EC) coated with organic compounds, as well as small amounts of sulfate, nitrates, metals, and other trace elements. There is no direct method for measuring DPM in ambient air as it contains many of the chemical components that are also emitted by other combustion sources (e.g., gasoline vehicles). Ambient concentrations of EC in the South Coast Air Basin have been primarily attributed to diesel exhaust. Surrogate calculations of DPM have been based on the fraction of ambient EC attributed to diesel engine exhaust by source apportionment methods and the fraction of the total mass of diesel particles determined to be EC in direct source measurements. In the Multiple Air Toxics Exposure Study in the South Coast Air Basin (MATES-II, SCAQMD, 2000), EC measurements were used to estimate DPM concentrations using the following relationships: approximately 67% of EC in the ambient air in the Los Angeles area originates from diesel engine exhaust (Gray, 1986), and the average EC fraction of diesel particles was 64%. Therefore, in the MATES-II study, the South Coast Air Quality Management District calculated DPM concentrations from EC measurements by multiplying a measured EC concentration by 67% and dividing by the fraction of DPM mass accounted for by EC (64%), that is, DPM concentration = (EC * 0.67)/0.64, or DPM = EC * 1.04. Using a 1998 emissions inventory for the South Coast Air Basin, the conversion from EC to DPM is a factor of 1.24 (MATES-II, SCAQMD, 2000).

The estimation of DPM from EC was recently updated (Fujita et al, 2006) using data from the Gasoline/Diesel PM Split Study. Source apportionment results showed that diesel exhaust was the dominant source of TC and EC at the Azusa and downtown Los Angeles (Fujita et al, 2007b). Time series plots were used to characterize the spatial and temporal variations in BC and PM mass data relative to expected dominance of diesel or gasoline vehicle traffic near the monitoring sites. The time-series in the upper panel in Figure 2-11 is from several traverses at the Port of Long Beach. BC was closely correlated to the PM with peak 10-second average BC levels exceeding 80 $\mu g/m^3$. The peak 10-second $PM_{2.5}$ concentration in the Terminal Island area of 118 $\mu g/m^3$ was ten times the local background $PM_{2.5}$ concentration of about 12 $\mu g/m^3$. The bottom panel shows the changes in ambient BC and $PM_{2.5}$ at the Pasadena Rose Bowl parking lot starting a few minutes before the end of a professional soccer match to about an hour after the match when the parking lot had nearly emptied. PM concentrations increased sharply immediately after the vehicles began leaving the parking lot and then continued to increase gradually while the vehicles cleared the lot. However, there was no corresponding increase in concentrations of BC. Scatterplots of BC with PM in Figure 2-11 show the strong correlations between diesel exhaust and ambient concentrations of BC for diesel exhaust dominated aerosol.

Terminal Island, Tuesday 7/10/01 1105-1300



Rose Bowl after Soccer Game, Fri 7/14/01 2030-2208

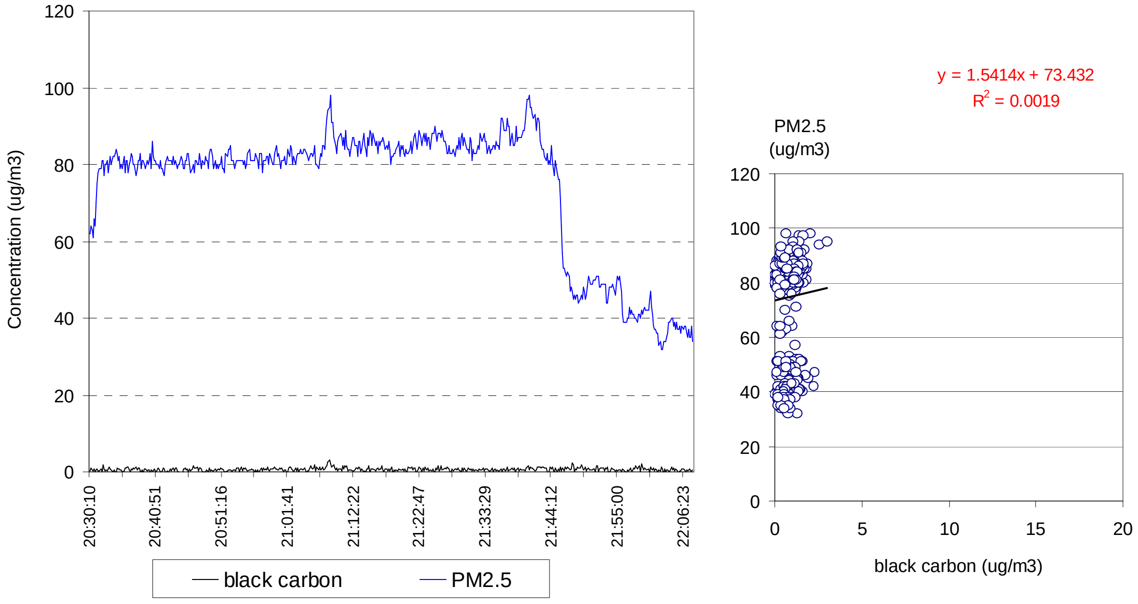


Figure 2-11. Time-series and linear-regression plots of real-time BC and PM data collected in diesel (top) and gasoline (bottom) vehicle dominated environments during the Gasoline Diesel PM Split Study (Fujita et al., 2007b).

DPM was estimated from the slope of the regression of the DustTrak $PM_{2.5}$ versus photoacoustic black carbon data from on-road measurements in diesel dominated traffic at Terminal Island (the linear regression with R^2 of 0.94 is shown in the top panel in Figure 2-11). The resulting DustTrak PM data were then adjusted using the ratio of time-averaged DustTrak to corresponding Teflon filter gravimetric mass for that sample. The following relationship between DPM and EC(IMPROVE protocol) was derived:

$$DPM = EC^{amb}\left[\left(\frac{\overline{BC}}{EC}\right)\left(\frac{\partial DT}{\partial BC}\right)\left(\frac{PM_{2.5}}{\overline{DT}}\right)\right]^{diesel} = EC^{amb}\left[.83\times 2.1\times .59\right] = 1.03\times EC^{amb}$$

Where:

EC^{amb} = ambient EC at site of interest

$\frac{\overline{BC}}{EC}$ = ratio of mean photoacoustic black carbon to time-integrated EC in diesel-dominated area.

$\frac{\partial DT}{\partial BC}$ = slope of regression line for DustTrak $PM_{2.5}$ vs. BC data in diesel-dominated area

$\frac{PM_{2.5}}{\overline{DT}}$ = ratio of time-integrated gravimetric mass concentration to mean DustTrak $PM_{2.5}$ estimate in diesel-dominated area.

The multiplying factor of 1.03 is similar to the factor used in MATES-II to estimate DPM from EC. In this study, diesel particulate carbon (DPC) concentrations were estimated from the measured EC concentrations times the slope of the correlation between total carbon and EC at the near road sampling locations for each season. Diesel particulate matter (DPM) was estimated from the following relationship:

Diesel Particulate Matter (DPM) = EC + 1.46 (DPC-EC)

where 1.46 is the ratio of diesel particulate organic matter (DPOM) to DPC from the Gasoline/Diesel PM Split dynamometer testing of diesel trucks in the Riverside, CA area (El-Zanan et al., 2008). Metals have a minor contribution to DPM and can be excluded in the above calculation.

3. RESULTS

The Harbor Communities Monitoring Study (HCMS) saturation monitoring was conducted to characterize the magnitude and spatial gradients in concentrations of toxic air contaminants relative to emission sources, to evaluate the adequacy of exiting routine air quality monitoring for characterizing exposure concentration within the study area, and to evaluate the use of passive samplers for application in community-level exposure assessments. The results of the HCMS saturation monitoring program are presented in this section with respect to the following study hypotheses.

1. Passive monitoring methods can be used to measure 1-week average ambient concentrations of selected pollutants with sensitivity and precision comparable to conventional monitoring methods averaged over the same period.
2. Gradients in pollutant concentrations exist within the Harbor Communities (i.e., measurable variations in ambient concentrations) and can be related to a location's proximity to emissions from either stationary or mobile sources.
3. The existing air quality monitoring in the area is not adequate to characterize the spatial variations in cumulative exposure within the community.
4. Ambient concentrations of black carbon are correlated to proximity to truck traffic and day-of-week variations in diesel truck traffic volume.
5. Seasonal variations in meteorology affect the pattern and magnitude of ambient concentrations of toxic air contaminants.

3.1 Assessment of Data Quality

The diffusive samplers and analytical methods that were used in the HCMS are in Table 3-1. An assessment of the quality of the data produced by these samplers was critical to the objectives of the HCMS. The data quality assessments conducted prior to and during the monitoring program included laboratory evaluations using a flow-through chamber with known pollutant concentrations, evaluations under field conditions during a pilot study in North Long Beach, and replicate sampling during the main study at the SCAQMD Hudson monitoring site in West Long Beach.

3.1.1 Laboratory Evaluation of Passive Sampling Methods

The passive samplers that were used in the HCMS were evaluated under controlled conditions in the laboratory to verify sampling rates, precision, accuracy, and validity of measurements for periods extending up to seven days. The following passive samplers were evaluated: Ogawa NOx and NO_2; Radiello H_2S; Radiello VOC sampler for BTEX and 1,3-butadiene; and Radiello carbonyl sampler for formaldehyde, acetaldehyde and acrolein. The laboratory evaluations were conducted by Brooks Mason, a graduate student at the University of Nevada, Reno/Desert Research Institute, as part of a Masters Degree research project under the supervision of Drs. Barbara Zielinska and Eric Fujita. Technical support for this effort was provided by Katarzyna Rempala, Michael Keith and Larry Sheetz of the Organic Analytical Laboratory (OAL) and Steve Kohl and Edward Hackett of the Environmental Analysis Facility. David Campbell supported the operation of the continuous instruments. The experimental details and results of the laboratory evaluations are described in a draft manuscript, which is included in

Appendix A of this report. A summary of the paper is presented here to place these results in context with the other components of the quality assurance program for HCMS.

Table 3-1. Diffusive samplers and analytical methods used in the HCMS with manufacturer supplied minimum detection limits for 7-day exposures.

Pollutant	**Diffusive Body**	**Adsorbent**	**Analytical Method**	**MDL (168 hours exposure)**
NO_2	Ogawa 3300 Sampler	Triethanolamine	Colorimetry for nitrite	0.32 ppb
NOx	Ogawa 3300 Sampler	Triethanolamine + PTIO	Colorimetry for nitrite	0.32 ppb
SO_2	Ogawa 3300 Sampler	Triethanolamine	Ion Chromatography for sulfate	0.54 ppb
H_2S	Radiello 120-1, polycarbonate and blue microporous polyethylene cylindrical diffusive body	Radiello 170, microporous polyethylene and impregnated with zinc acetate	Visible spectrometry	0.14 ppb
VOC	Radiello 120-2, polycarbonate and yellow microporous polyethylene cylindrical diffusive body	Radiello 145, ss net cylindrical cartridge, o.d. 4.8 mm packed with 350 mg of 35-50 mesh graphitic charcoal (Carbograph 4)	Thermal Desorption GC/MS	benzene 0.05 etbenzene 0.02 toluene 0.02 xylenes 0.02 (ug/m^3)
Carbonyl Compounds	Radiello 120-1, polycarbonate and blue microporous polyethylene cylindrical diffusive body	Radiello 165, ss net cylindrical cartridge, o.d. 5.9 mm with 900 mg of 35-50 mesh DNPH coated florisil	HPLC-UV	formaldehyde 0.1 acetaldehyde 0.1 acrolein 0.3 (ug/m^3)

The passive samplers were exposed in a 100-liter flow-through chamber with known concentrations of target gases. The chamber shown in Figure 3-1 was designed and built specifically for this evaluation. The interior of the chamber is constructed almost entirely out of Teflon. The chamber floor contains multiple ports designated for gaseous inflow, outflow, and continuous analysis of the atmosphere inside the chamber. Temperature and relative humidity inside the chamber was monitored continuously and a small fan ensured a well-mixed atmosphere. Passive samplers were exposed in the flow-through chamber in triplicate to known pollutant concentrations for 3- and 7-day periods. Gaseous flow into the chamber was controlled by an Environics 9100 ambient monitoring calibration system, which mixed a standard mixture of gas with dilution air supplied by an Aadco 737 pure air generator. With the exception of the first set of experiments involving NO_2 and NO, the calibration system was connected to an APC Back-UPS to protect the experiment from power surges. Input flow was 2.5 L/min and chamber conditions were set at 24 ^{o}C and 50% relative humidity.

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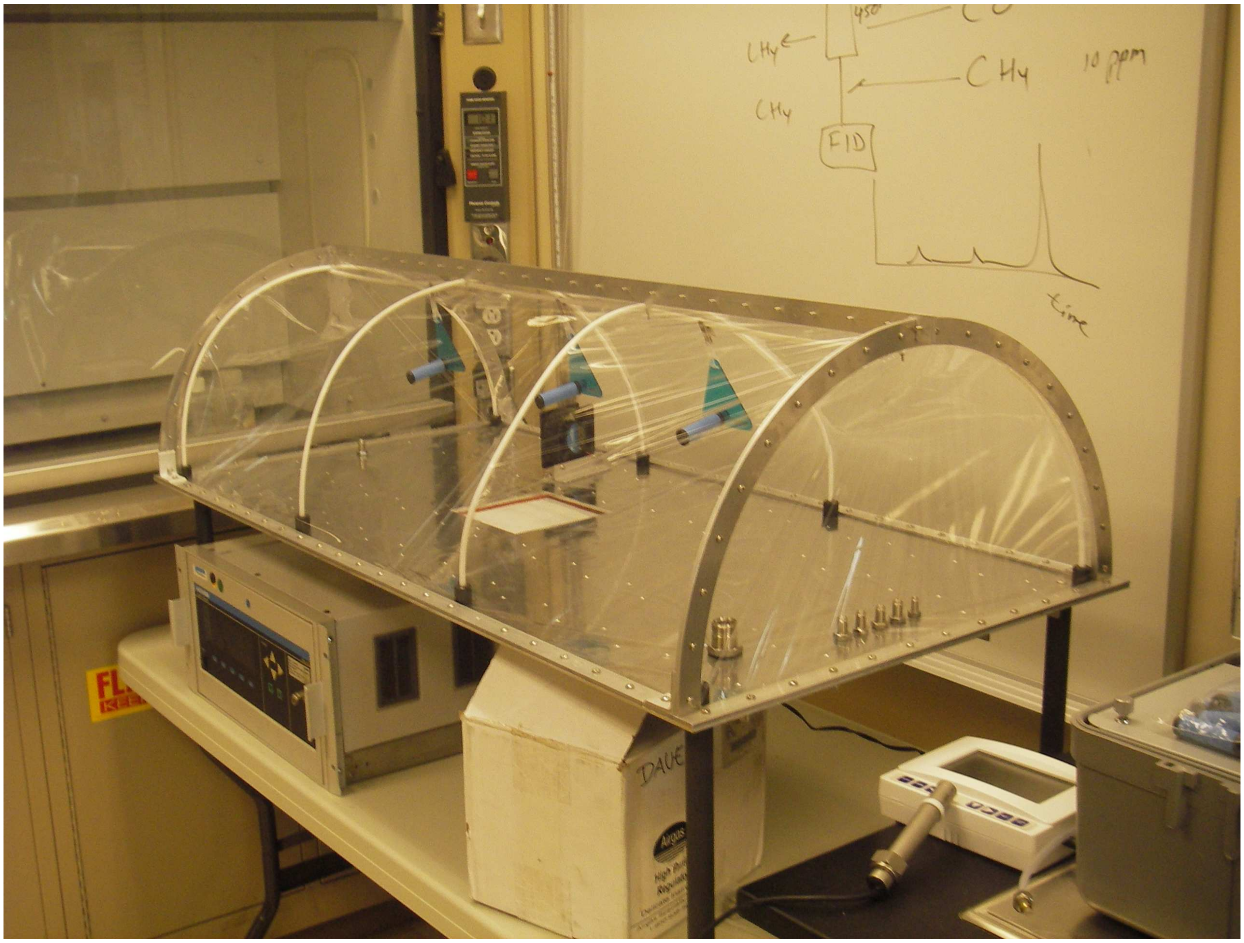

Figure 3-1. 100-liter atmospheric chamber used for evaluation of passive monitoring methods.

The sampling rates provided by Ogawa and Radiello were used to calculate the corresponding mixing ratios, which were compared to data from the alternative measurement methods (i.e., Horiba NOx analyzer, canister or DNPH cartridge samples) and the nominal concentrations of the diluted standards. The process of diluting the standard gases is reasonably precise resulting in stable mixing ratios of the diluted standard. Therefore, the diluted standards could have served as reference values assuming that there were no leaks in the chamber and no interruption in the input flow due to power failures. The alternative methods provided checks on the stability of the nominal mixing ratios of the diluted standards and condition of the exposure chamber. The canister and DNPH samples were collected four times for about 2 hours each during the 7 days of exposure and the NOx and PID analyzers were run continuously during the NOx and BTEX exposures, respectively. Averages of the continuous NOx and NO_2 data provided a second set of reference values. Although useful in monitoring the condition of the chamber, the PID data are not sufficiently accurate to use as a second reference due to baseline drifts. Results of the laboratory evaluations are shown in Table 3-2. The replicate precision is given in the table as the standard deviation of three replicate passive samples (RSD).

Table 3-2. Chamber pollutant mixing ratios (ppbv) and relative standard deviations measured by three replicate passive samples over seven-day periods versus the reference methods.

Compounds	n	Passive Sample[1]	Passive RSD (%)	Reference Value[2]	Percent Δ[3]
NO	3	18.3 ± 0.5	2.7%	17.20	6%
NO_2	3	21.5 ± 0.3	1.4%	21.80	-1%
H_2S	3	1.99 ± 0.04	2.0%	2.10	-5%
benzene	3	2.10 ± 0.24	11.4%	2.57	-18%
toluene	3	2.24 ± 0.11	4.9%	2.37	-5%
ethylbenzene	3	1.80 ± 0.12	6.7%	1.28	41% or (-6%) [4]
m,p-xylene	3	0.89 ± 0.04	4.5%	1.02	-13%
o-xylene	3	0.38 ± 0.02	5.3%	0.43	-12%
formaldehyde	3	5.08 ± 0.36	7.1%	5.20	-2%

[1] Mean value ± standard deviation

[2] Reference method is by Horriba NO/ NO_x analyzer for NO, NO_2, by 24-hour time-integrated canisters for BTEX and by dilution of standards by Environics 9100 for formaldehyde and H_2S

[3] Percent difference of the passive result compared to the reference result.

[4] Using our experimentally determined sampling rate of 37.4 ml/min rather than 25.7 ml/min published by Radiello, the concentration of ethylbenzene was 1.2 rather than 1.8 ppbv, which is within 6 percent of the reference canister value.

All of the passive measurements showed good replicate precision with %RSD ranging from 1.4 to 11.4 percent, and were generally in good agreement with reference values. Additional experiments for the Radiello VOC sampler revealed that, in general, replicate precision improved with exposure time. NO and NO_2 concentrations measured passively by the Ogawa NO_2 and NOx samplers were within 6% and 1% of the concentration measured by the Horriba Analyzer with replicate precision of 3% and 1%, respectively. BTEX concentrations measured by the Radiello VOC sampler were within 20% of the canister measurements with replicate precisions within 11% of the mean except of ethylbenzene, which was about 40 % higher for the passive measurement. This difference is related to differences between the sampling rate reported by Radiello for ethylbenzene and rate in our laboratory evaluation (explained further below). The Radiello aldehyde sampler measured formaldehyde to within 2% of the nominal concentration with replicate precision of 7%. The mean chamber concentration of the Radiello H_2S sampler was within 5% of the nominal concentration with a 2% standard deviation of the mean.

Verifying the sampling rates of the passive samplers was a major objective of the laboratory evaluations. The sampling rates for benzene and toluene determined in this experiment were within 20% of those published by Radiello. For xylenes, the sampling rates are within 20% for 4- and 7-day exposure times. A significantly higher sampling rate was measured than that reported by Radiello for ethylbenzene for all exposure times. Experimentally determined sampling rates for ethylbenzene was 37.4 ml/min versus 25.7 ml/min published by Radiello (see Table 3 in Appendix A). Using our higher experimentally determined sampling rate the concentration of ethylbenzene in Table 3-2 was 1.2 rather than 1.8 ppbv, which is within 6 percent of the reference canister value. The experimentally determine sampling rate_was used to determine ethylbenzene concentrations for the main HCMS, which results in concentrations that are a factor of 0.69 lower than using the rate published by Radiello. The sampling rates for all BTEX compounds were stable for storage times of up to 14 days at -18º C. Percent standard deviations for all 7-day exposed samples, irrespective of storage time, were 14, 8, 9, 11, and 13% for benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene, respectively.

As with BTEX, the replicate precision of passive 1,3-butadiene measurements increases markedly with exposure time. 1,3-Butadiane was stable during storage of up to14 days at -18º C and the percent standard deviation for all samples exposed for 7 days was 24%. However, the experimentally determined sampling rate for 1,3-butadiene showed an exponentially decreasing trend, declining by 73% and 86% from the original value for 4- and 7-day exposures, respectively. The loss is likely due to back diffusion. Consequently, passive measurements with the Radiello VOC sampler with Carbograph 4 will substantially underestimate the true ambient concentrations of 1,3-butadiene. Therefore, results for 1,3-butadiene are not quantitative and are not reported in the HCMS.

3.1.2 Pilot Study Evaluations

DRI conducted a pilot study during a one-week period beginning on August 16, 2006 at the SCAQMD N. Long Beach monitoring station (located at 3648 N. Long Beach Blvd.) to determine the accuracy of the passive measurements for NO_2, NOx, SO_2, H_2S, benzene, toluene, ethylbenzene, xylenes, 1,3-butadiene, formaldehyde, acetaldehyde, and acrolein under field conditions. The passive measurements were compared with the SCAQMD continuous NOx, NO_2 and SO_2 data and time-integrated samples collected and analyzed by DRI for organic air toxics using more established methods. We also compared the 7-day integrated aerosol samples with corresponding averages of the daily 24-hour aerosol samples for gravimetric $PM_{2.5}$ mass and organic and elemental carbon.

Passive samplers were exposed for a 7-day period. The passive samplers were deployed at a height of approximately 2 meters above the instrument platform on the roof of the station, along a line running parallel to Long Beach Blvd. approximately 10 meters east of the street side roofline of the building. The passive samplers were protected from settling dust and rain by transparent plastic canopies, as shown in Figure 3-2. A minimum distance of 6" was maintained between adjacent samplers. In order to determine the potential influence of air flow on the passive sampling methods, the samplers were deployed in two groups with an oscillating electric fan providing constant air flow at approximately 3 mph (1.3 m/s) across one group. Each sampling group consisted of three passive samplers of each pollutant in order to also evaluate measurement precision. The passive methods were evaluated by comparison with either continuous measurements (for NO/NOx, and SO_2) or with an alternative time-integrated measurement method. 24-hour canister and DNPH cartridge samples were collected on a daily basis beginning at noon each day.

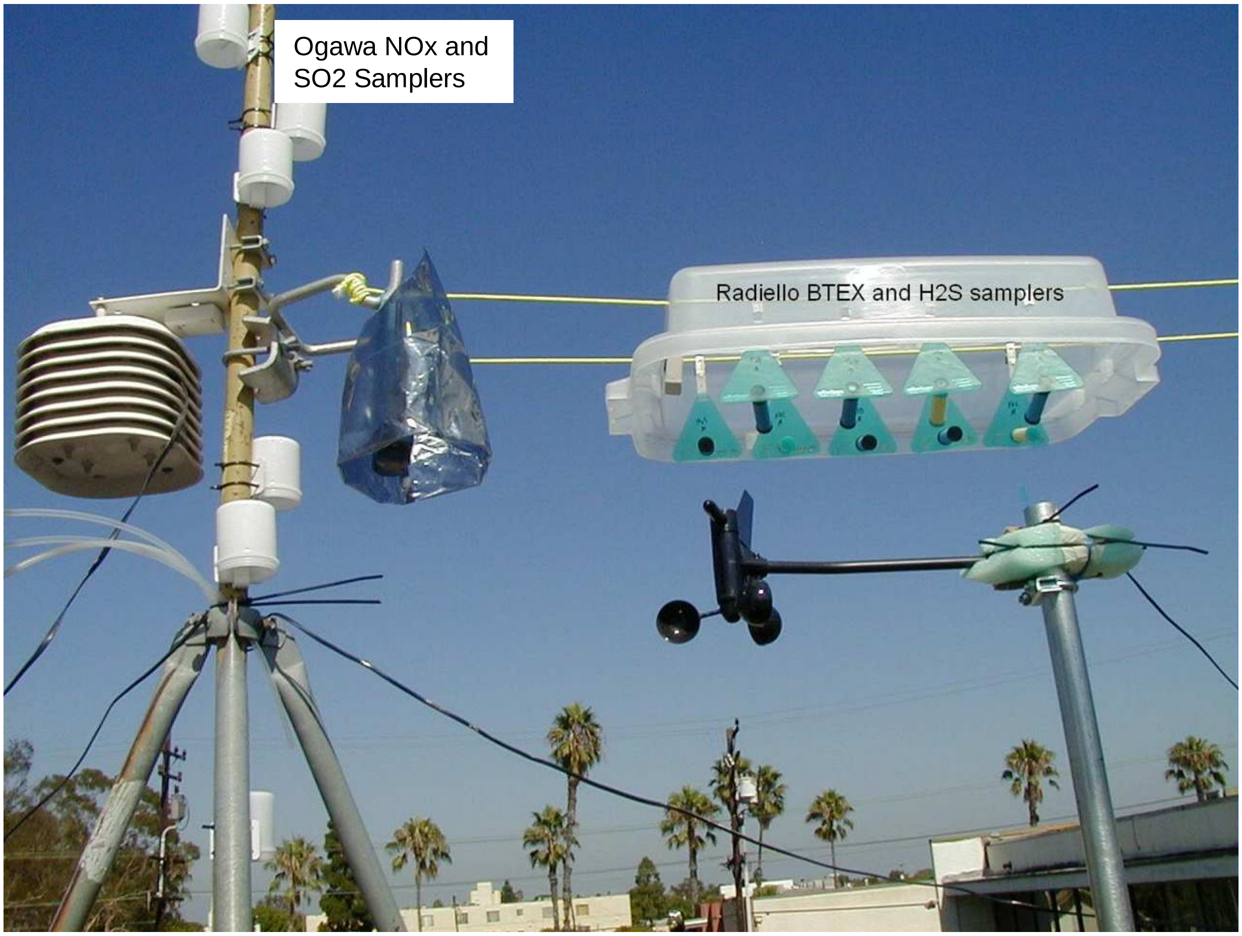

Figure 3-2. Deployment of passive samplers at the SCAQMD N. Long Beach station.

MiniVol portable $PM_{2.5}$ air samplers from AirMetrics Corporation were used for particle sampling for periods up to one week in duration. Particles were collected on Teflon (for subsequent gravimetric analysis for mass) and on pre-fired quartz 47 mm filters (for subsequent analysis by thermal/optical reflectance (TOR) for organic and elemental carbon (OC and EC). Ten MiniVol PM2.5 samplers were positioned on the instrument platform adjacent to the passive samplers. The sampler inlets were positioned 1 meter above the platform (see Figure 3-3). These samplers were aligned into two groups, each consisting of three units collecting a single filter sample for the entire 7-day period and two units collecting 24-hour samples on alternating days. One group of samplers was loaded with Teflon filters for gravimetric mass analysis and the other with quartz filters for TOR carbon analysis. The 24-hour filters were changed daily to provide a week-long series of daily samples. The week-long sample results were compared with the averages from the daily filter samples for gravimetric mass analysis and carbon.

Continuous monitoring instruments measuring CO & CO_2 (TSI Q-Trak model 8854), $PM_{2.5}$ light scattering (TSI DustTrak nephelometer), and VOC portable PID monitors (RAE Systems Model PGM-7240) were deployed inside a climate-controlled enclosure on the rooftop platform. In addition, black carbon (BC) was monitored continuously with two photoacoustic instruments. The time-averaged optical BC measurements were compared to EC measurements from the time-integrated quartz filter samples. The ppbRAEs collected ambient air via Teflon inlet tubing, and the DustTrak used a conductive aluminum inlet tube to minimize particle losses. The Qtrak, which is a passive instrument, had its probe attached to the base of the enclosure to avoid direct sunlight. The two photoacoustic instruments were located inside the station building. Conductive copper inlet tubing was used to draw sample air from the rooftop platform.

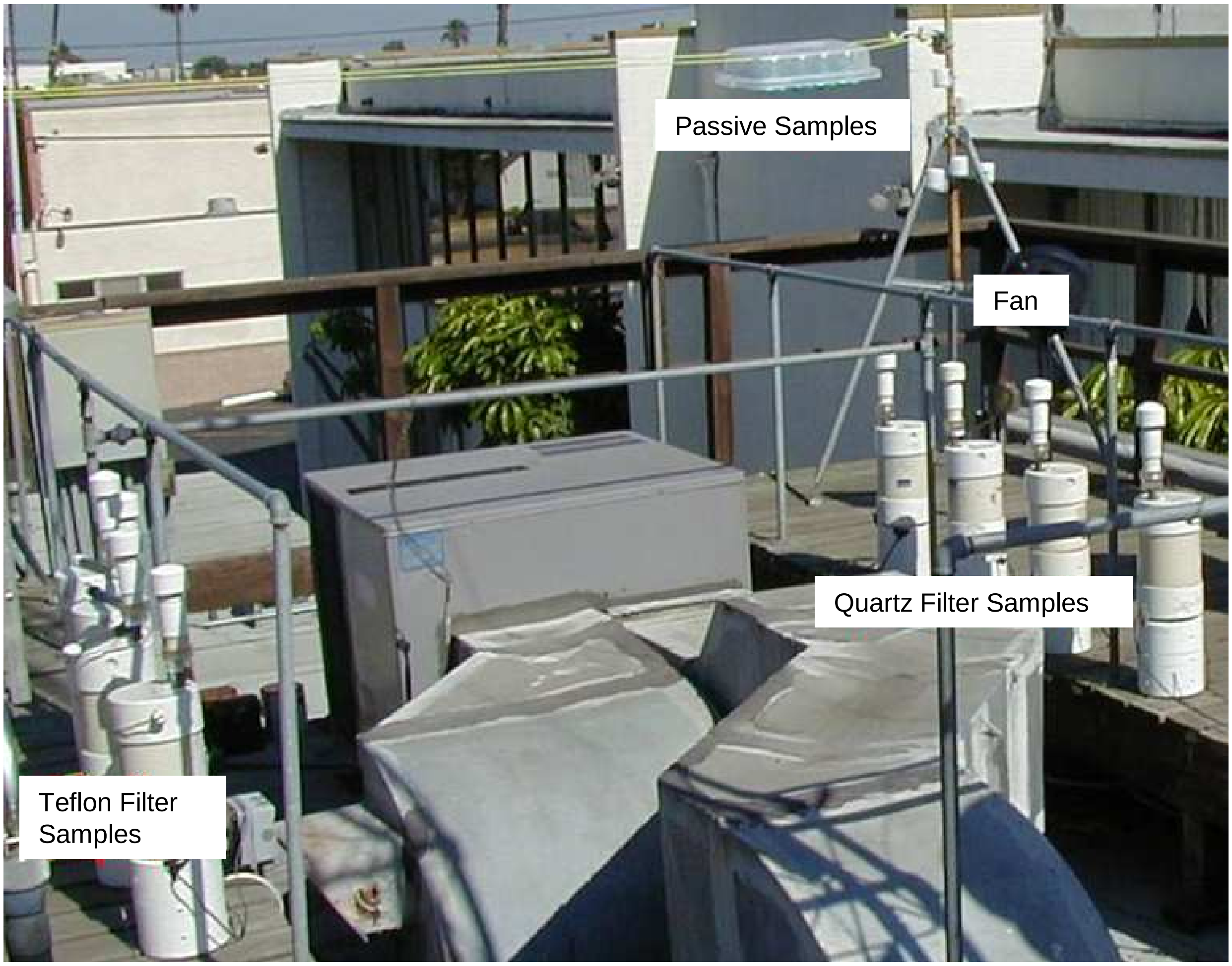

Figure 3-3. Deployment of active filter samplers (MiniVols) at the N. Long Beach station.

Concentrations of air toxics and criteria pollutants were relatively low at the North Long Beach AQMD station during the week of the pilot study measurements (Table 3-3). Annual average and annual maximum 24-hour measurements during 2002 to 2004 are shown in Table 3-4 for comparison. The concentrations of all measured pollutants during the pilot study were well below the annual averages, with the exception of $PM_{2.5}$ which was slightly lower. The upper chart in Figure 3-4 shows a consistent diurnal pattern dominated by westerly winds mid-day that typically reached a maximum of about 2 m/s. Winds were calm overnight. The lower chart shows high nighttime RH that decreased with warmer temperatures and the onset of the daytime winds.

Table 3-3. Daily 24-hour average pollutant values measured by the SCAQMD and DRI during the pilot study at the N. Long Beach Monitoring Station.

SCAQMD N. Long Beach Monitoring Station Data

	NO (ppb)		NO_2 (ppb)		NOx (ppb)		SO_2 (ppb)		CO (ppb)	
Date	24-hr	HrMax	24-hr	HrMax	24-hr	HrMax	24-hr	HrMax	24-hr	HrMax
8/16/06	8.2	27.0	14.6	31.0	22.7	58.0	0.6	7.0	0.4	0.8
8/17/06	8.7	28.0	18.4	38.0	27.1	66.0	1.9	10.0	0.2	0.5
8/18/06	6.2	23.0	13.5	27.0	19.6	50.0	1.9	12.0	0.1	0.3
8/19/06	4.1	12.0	9.8	22.0	13.9	34.0	1.2	6.0	0.1	0.3
8/20/06	5.2	28.0	11.2	33.0	16.5	61.0	0.7	6.0	0.2	0.5
8/21/06	16.8	54.0	24.2	45.0	41.1	98.0	2.5	8.0	0.3	0.7
8/22/06	26.0	93.0	28.6	55.0	54.8	136.0	3.3	12.0	0.5	1.1
Mean	**10.8**	**93.0**	**17.2**	**55.0**	**28.0**	**136.0**	**1.7**	**12.0**	**0.3**	**1.1**

DRI Pilot Study Data

	$PM_{2.5}$	HCHO	Acetal	WS (m/s)	
Date	µg/m^3	ppb	ppb	24-hr	HrMax
8/16/06	13.6	0.5	0.1	2.4	5.8
8/17/06	18.5	2.1	4.9	2.3	5.5
8/18/06	15.7	0.5	0.2	2.7	6.3
8/19/06	15.3	0.6	0.4	2.7	5.5
8/20/06				2.4	7.1
8/21/06	15.1	1.5	0.4	2.5	6.0
8/22/06	19.5	1.3	0.3	2.0	6.2
Mean	**16.3**	**1.1**	**1.0**	**2.4**	**7.1**

Table 3-4. Historical annual summary of daily 24-hour average pollutant concentrations measured at the N. Long Beach air quality station.

Year	NO ppb	NO_2 ppb	SO_2 ppb	CO ppm	$PM_{2.5}$ µg/m^3	Benzene ppb	Form ppb	Acet ppb
24-Hour Mean								
2002	32	30	2	0.9	20	0.71	2.9 [1]	0.9 [1]
2003	31	29	2	0.8	18	0.71	2.8	1.1
2004	35	28	5	0.6	18	0.55	2.8	1.2
24-Hour Max								
2002	197	68	8	3.0	63	2.10	7.6	2.5
2003	224	78	8	3.0	115	1.60	6.0	2.6
2004	224	70	13	3.0	67	1.50	5.8	3.0

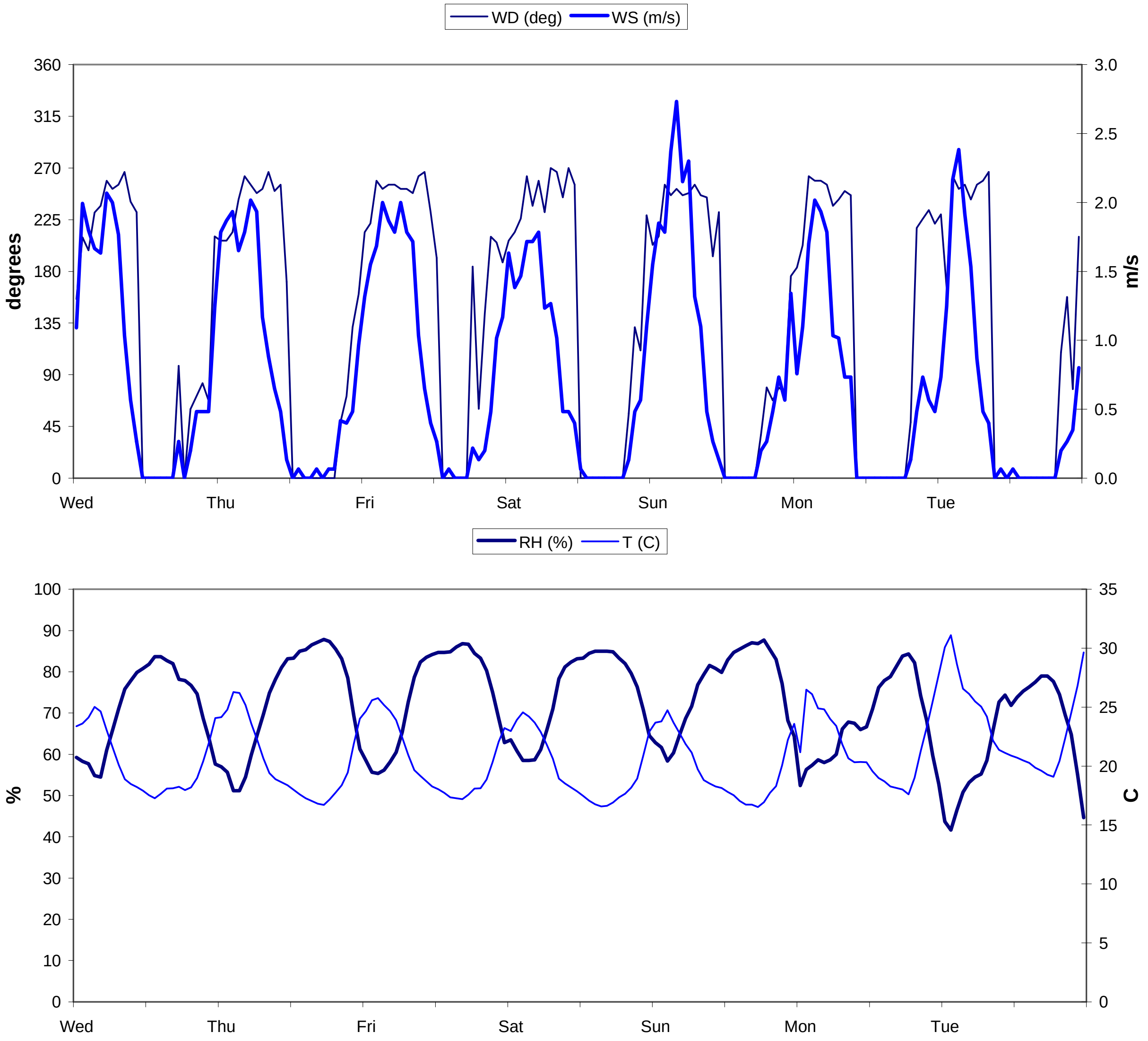

Figure 3-4 Hourly averaged wind speed, direction, relative humidity, and temperature during the pilot study. Data begin at 12:00 noon on Wednesday, so unlabeled tick marks indicate midnight.

Passive Measurements

Each type of passive sampler was deployed in triplicate into two sampling groups to examine the effect of air movement on sampling rates and to establish measurement precision. Data from the 7-day passive samples were compared to the corresponding time-averaged data from the SCAQMD continuous analyzers or 7-day averages of the daily 24-hour integrated canister and DNPH samples. Of particular interest in this pilot study was the potential effect of calm condition on the sampling rates of the passive samplers. As shown in Figure 3-4, winds were calm (zero m/s or below detection) every night for about 8-10 hours starting at approximately 9 to 10 pm. Although no quantitative information on the impact of air flow on the sampling rate of the passive methods is provided by the manufacturers, Radiello states that the sampling rate is "invariant with wind speed between 0.1 and 10 m/s". To examine the effect of air movement on the sampling rate of the passive samplers, one group of triplicate samples received airflow across them from an electric fan (1.3 m/s above ambient), while the other group was exposed to the prevailing ambient winds (0 to 2 m/s). Results of the passive sampling during the Pilot Study are summarized in Table 3-5 for NO (NOx-NO_2), NO_2, SO_2, H_2S, BTEX and carbonyl compounds. Despite the calm conditions overnight, the two groups of triplicate measurements (with and without the fan) were not statistically different for any of the passive sampler measurement types.

Passive measurements of NO and NO_2 showed good replicate precision with an average coefficient of variation (standard deviation/mean) of 8%. Blank values were consistent and low compared to the samples. Both SO_2 and H_2S showed replicate precision that were comparable to the limit of detection of the measurements. The Ogawa samplers (without enhanced air movement) measured mean concentrations for NO, NO_2 and SO_2 approximately 20% below those evaluated by the continuous analyzers at the SCAQMD site but with good replicate precision given the low levels. This may have to do with the positioning of sampling lines onsite. The North Long Beach monitoring station occupies a building located next to a busy road. The inlets for the continuous monitoring equipment maintained by SCAQMD are street side whereas the passive monitors were located about 30 feet further downwind at the other end of the rooftop. Vehicle emissions along Long Beach Blvd. may occasionally result in higher pollutant concentration gradients from roadside to locations further back from the road.

The correction of standard sampling rates to actual sampling conditions may be another potential source of the apparent bias. Sampling rates Q given by the manufacturers of the passive samplers were measured at 25 ^{o}C and 1 atm. The dependence of Q on atmospheric pressure is linear. This correction is typically within ± 1.5% and can be ignored. On the other hand, Q depends exponentially on temperature variations. Beside thermodynamic effects, temperature can also affect the kinetics or reaction velocities between analytes and chemiadsorbing substrates. As a sensitivity check, we determined the hourly sampling rates corrected for the average temperature and pressure for each hour. The hourly NOx concentrations were weighted by the hourly sampling rate corrections and summed over the one week period and compared to week-long average NOx concentration weighted by the sampling rate correction derived from the average T and P during the week. The differences were within 2-3%.

Passive measurements for BTEX showed good replicate precision with %RSD ranging from 5 to 15 percent. The comparison of the passive samplers to the canister methods produced variable results. Passive measurements of xylenes and toluene were within 20% of the reference method and ethylbenzene was about 30% higher. Note that the Radiello published sampling rate was used for calculating passive ethylbenzene concentration; if the DRI experimentally determined sampling rate were used, ethylbenzene concentration would be 0.12 ppbv or within 10% of reference value. These results support the use of our experimentally determined sampling rate for determining the concentrations of ethylbenzene for samples collected in the main study.

The passive measurements of aldehydes showed good replicate precision with standard deviations ranging from 0.01 to 0.12 ppbv. The percent standard deviations for formaldehyde, acetaldehyde and acrolein were 6%, 3%, and 37%, respectively. The Radiello aldehyde sampler was in good agreement with the active DNPH method for formaldehyde (12%), but results for acetaldehyde (-43%) and acrolein (-79%) were considerably different. The DNPH method is prone to sampling artifacts due to presence of ambient ozone concentrations. Consequently, ozone is normally denuded from the sample prior to collection on DNPH cartridges. Since ozone denudation is unrealistic for passive sampling, active DNPH sampling in the pilot study was not denuded to compare the effects on each type of media. The mean ozone concentration during the pilot study was calculated from hourly average data at 26.9 ppbv. Radiello has published data which suggests that acetaldehyde is much more vulnerable than formaldehyde to ozonolysis on their media (www.radiello.com). Furthermore, evidence in the past few years suggests that active DNPH samples are subject to low collection efficiencies for acetaldehyde for sampling times of 24 hours or greater (Herrington et al., 2007). Acrolein (sum of acrolein and acrolein-X) mean concentration as measured by Radiello was 49 pptv, which is well below its published limit of quantitation. It is not possible to assess the significance of the differences of these low values.

Table 3-5. Pollutant mixing ratios (ppbv) measured by passive samplers over a seven-day period during the Pilot Study versus the reference methods.

Compounds	n	Ambient Winds[1]	Fan-Induced Winds[1]	Passive RSD (%)	Reference Value[2]	Amb-Fan Percent Δ [3]	Amb-Ref Percent Δ [4]
NO	3	8.1 ± 0.8	8.5 ± 0.6	8.5%	10.8	-4%	-25%
NO_2	3	14.1 ± 0.5	14.4 ± 1.2	5.9%	17.2	-2%	-18%
SO_2	3	1.4 ± 0.2	1.2 ± 0.2	15.5%	1.7	16%	18%
H_2S	3	0.31 ± 0.15	0.26 ± 0.08	39.6%	NA	18%	NA
benzene	3	0.29 ± 0.03	0.29 ± 0.01	6.9%	0.37	0%	-22%
toluene	3	1.31 ± 0.22	1.19 ± 0.17	15.5%	1.09	-10%	20%
ethylbenzene	3	0.17 ± 0.01	0.18 ± 0.01	5.7%	0.13	-6%	31% or (-8%) [5]
m,p-xylene	3	0.46 ± 0.04	0.49 ± 0.01	5.4%	0.45	-6%	2%
o-xylene	3	0.18 ± 0.01	0.20 ± 0.01	5.3%	0.18	-11%	0%
formaldehyde	3	1.23 ± 0.04	1.27 ± 0.12	6.4%	1.10	-3%	12%
acetaldehyde	3	0.59 ± 0.01	0.59 ± 0.03	3.4%	1.04	0%	-43%
acrolein	3	0.05 ± 0.02	0.03 ± 0.01	36.7%	0.24	50%	-79%

[1] Mean value ± standard deviation

[2] Reference methods are SCAQMD analyzers for NO/NO_2 and SO_2, and DRI time-integrated canisters and active DNPH cartridges.

[3] Percent difference of results for ambient and fan-induced winds.

[4] Percent difference of the passive result (without fan) compared to the reference result.

[5] Using our experimentally determined sampling rate of 37.4 ml/min rather than 25.7 ml/min published by Radiello reduced values by factor of 0.69.

Time-Integrated Particle Measurements

The MiniVol filter samplers were used to collect $PM_{2.5}$ samples on Teflon and quartz filters over both 24-hour and 7-day time periods. One pair of samplers collected a contiguous series of 24-hour samples (noon to noon). Another set of samplers, comprised of three replicates for both Teflon and quartz filters, sampled continuously on the same filters for the entire week. Precision of the weekly $PM_{2.5}$ gravimetric and TOR measurements were estimated from the three replicate 7-day filter samples. Results for the numerical average of the 24-hour concentrations obtained from the daily samplers were compared to the 7-day samples to identify any measurement issues that arise from sampling for such an extended period on a single filter substrate. The data are summarized in Table 3-6.

The $PM_{2.5}$ mass was measured on the three replicate 7-day samples to 3 percent of the mean. The average mass measured on the three replicate 7-day Teflon filters was about 13 percent lower than the average of the six 24-hour samples. The single missing invalid sample is unlikely to explain this difference, considering the narrow range of the other six 24-hour $PM_{2.5}$ mass measurements. However, looking at the organic carbon data, which did have complete contemporaneous measurements, the difference in average $PM_{2.5}$ mass concentration for the seven daily samples versus the 7-day sample of 2.2 $\mu g/m^3$ is similar to the higher average OC concentration of the daily quartz filters versus the 7-day sample of 2.5 $\mu g/m^3$. In contrast, 7-day average of elemental carbon (EC) concentrations is similar to the averages of the seven daily samples for both TOR and TOT methods (see also Figure 3-5). This suggests that OC is volatilized to a greater extent during 7 days of sampling as compared to the daily samples and this difference is also reflected in the gravimetric mass measurements. These discrepancies illustrate the effect of sampling conditions and sample handling on the measured aerosol mass. Additionally, OC and EC are operationally defined values that depend on the specific analytical method and protocol.

Table 3-6. Measurements of Teflon and quartz filters during August 2006 Pilot Study at N. Long Beach and comparison to continuous monitors. All units are $\mu g/m^3$.

Start Date	Day	Duration (hrs)	$PM_{2.5}$ Mass (grav)	TC (TOR)	OC (TOR)	EC (TOR)	EC (TOT)	Photo-acoustic BC (532nm)	Photo-acoustic BC (870nm)	DustTrak $PM_{2.5}$
16-Aug	Wed	24	13.6	4.0	3.4	0.6	0.5	0.9		
17-Aug	Thu	24	18.5	7.2	5.6	1.7	1.1	0.7	0.7	52
18-Aug	Fri	24	15.7	4.9	4.0	0.9	0.1	0.7	0.5	49
19-Aug	Sat	24	15.3	6.5	5.7	0.8	0.5	0.4	0.2	48
20-Aug	Sun	24		4.8	4.0	0.8	0.6	0.5	0.3	42
21-Aug	Mon	24	15.1	5.6	4.7	0.9	0.7	1.0	1.0	38
22-Aug	Tue	24	19.5	9.7	7.4	2.2	1.8	1.3	1.5	57
Mean Daily			**16.3**	**6.1**	**5.0**	**1.1**	**0.8**	**0.8**	**0.7**	**47.8**
unc of mean			0.5	0.4	0.3	0.1	0.5			
16-Aug	7day	168	14.0	4.2	2.8	1.3	0.9			
16-Aug	7day	168	14.1	3.4	2.2	1.3	0.8			
16-Aug	7day	86-122	14.2	3.1	2.4					
Mean 7-day			**14.1**	**3.6**	**2.5**	**1.3**	**0.8**			
unc of mean			0.4	0.2	0.1	0.2	0.7			
% avg dev			3%	5%	4%	14%	80%			
7day - daily			**-2.2**	**-2.5**	**-2.5**	**0.2**	**0.1**			
% difference			-13%	-41%	-51%	16%	10%			

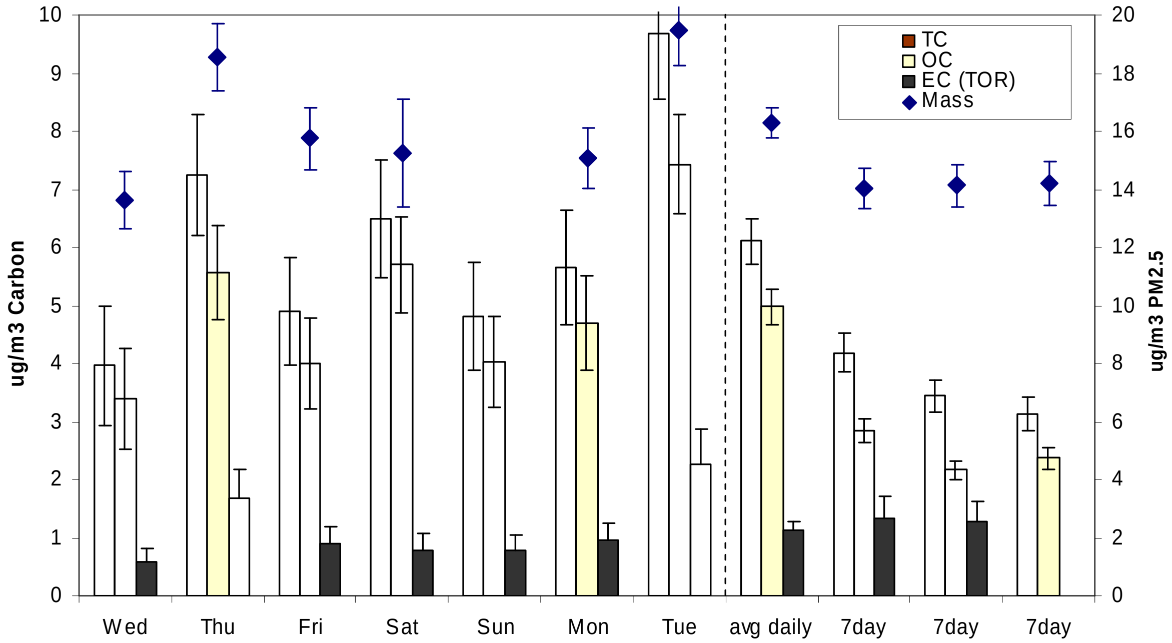

Figure 3-5. Measured 24-hour concentrations of $PM_{2.5}$ mass, total carbon, organic carbon, and elemental carbon for daily and 7-day filter samples. Error bars show the combined standard error of mean for replicates and analytical measurement uncertainty.

Continuous Measurements

Scatterplots of the photoacoustic BC concentrations are shown versus the TOR and TOT EC in Figure 3-6. Note that for this discussion we will use the term BC in reference to the optical measurement and EC for the thermal evolution method. There is a fair amount of scatter in the correlations due to the low ambient levels of black carbon. The higher IMPROVE-TOR EC values relative to the photoacoustic BC may be related to greater retention in the IMPROVE protocol of OC prior to the oxidizing stages and either underestimation of the pyrolysis correction by TOR due to pyrolyzed material beneath the surface of the filter or overestimation of the TOT pyrolysis correction due to the higher absorption efficiency of pyrolyzed carbon. Figure 3-7 shows the time series of BC and $PM_{2.5}$ mass concentrations. The values roughly track each other and the peak BC concentrations are always coincident with peak $PM_{2.5}$ mass concentrations estimated by light scattering. The scatterplot in Figure 3-8 shows modest correlation between the DustTrak and gravimetric mass data with an R^2 of 0.68. The DustTrak results exceed gravimetric mass measurements by a large factor of about 2.8.

Figure 3-9 shows the time series plot of hourly averaged BTEX concentration estimated by portable PID and carbon monoxide by passive electrochemical method. The three estimates are widely scattered and irregularly track each other. Data from the second PID instrument have been adjusted for zero drift (13 ppb correction). Most of the PID data were below the MDL of the instruments (20 ppb). The instrument has sensitivity close to 1 ppbv above the MDL. Accuracy is a concern due to baseline drift and bias between two PID on the order of 20-40 ppbv. However, the PID was used in the study to primarily detect plumes with high VOC concentrations that may be associated a particular source(s). It is important to note that the PID responds differently to different mixtures with high sensitivity to aromatic compounds, moderate sensitivity to olefins and no response to low molecular weight alkanes, which may be the primary constituent of refinery emissions.

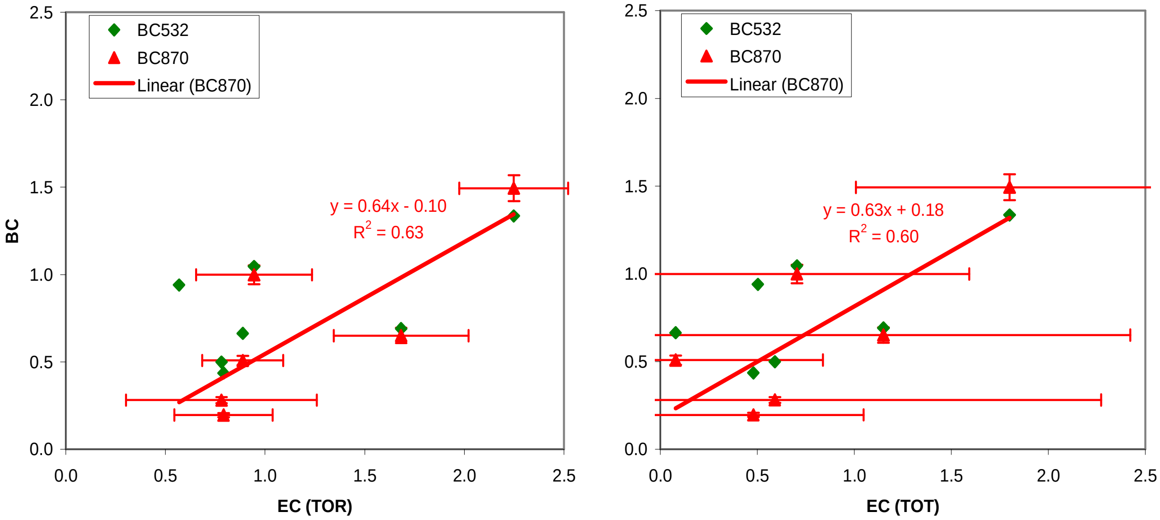

Figure 3-6. Comparison of 24-hour elemental carbon concentrations (µg/m^3) from quartz filters to mean continuous black carbon measured by photoacoustic method at 2 wavelengths. Error bars indicate the analytical measurement uncertainties.

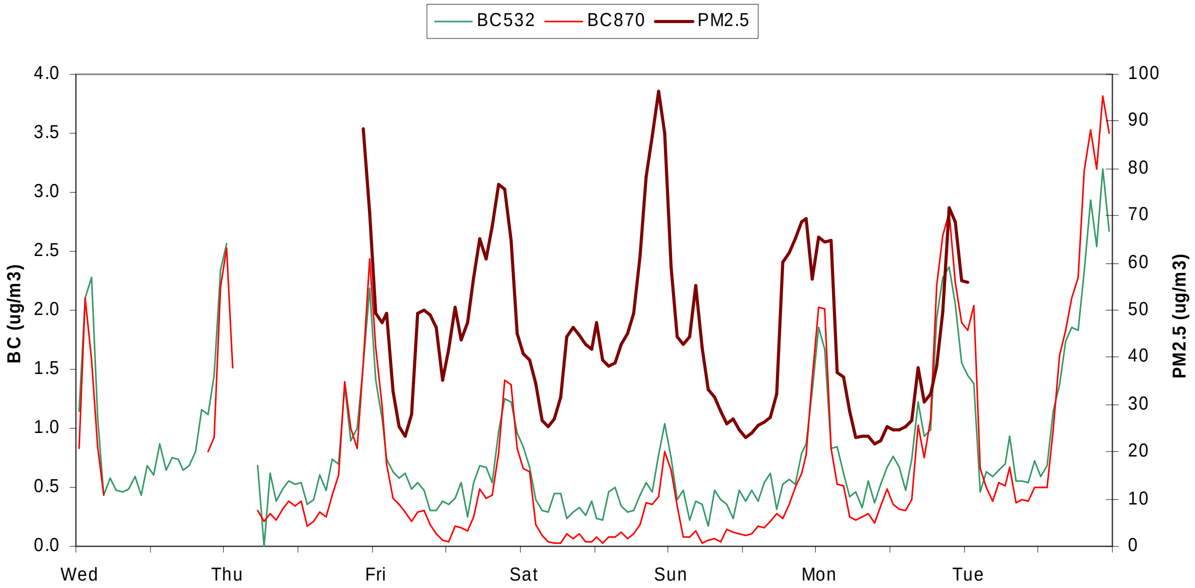

Figure 3-7. Time series plot of hourly black carbon at two wavelengths and $PM_{2.5}$ mass estimated by light scattering. Unlabeled tick marks indicate midnight.

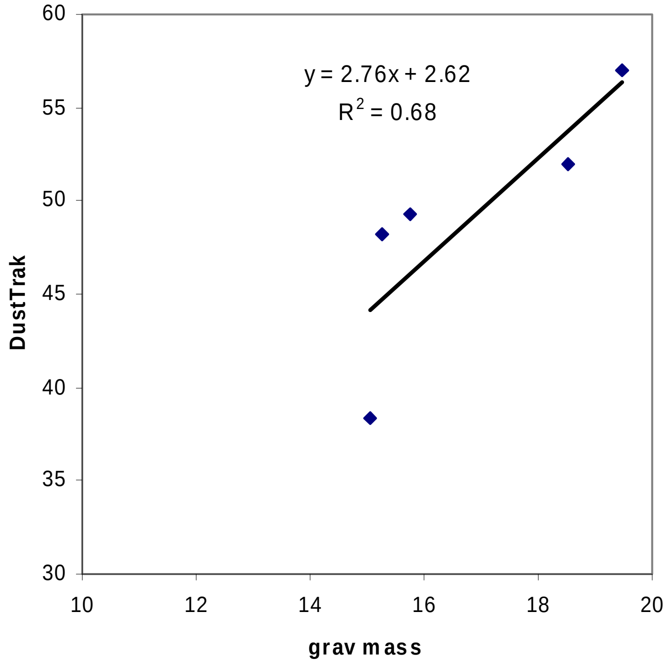

Figure 3-8 Correlation of 24-hour mean continuous mass concentration from DustTrak instrument to reference measurement (gravimetric mass from Teflon filters).

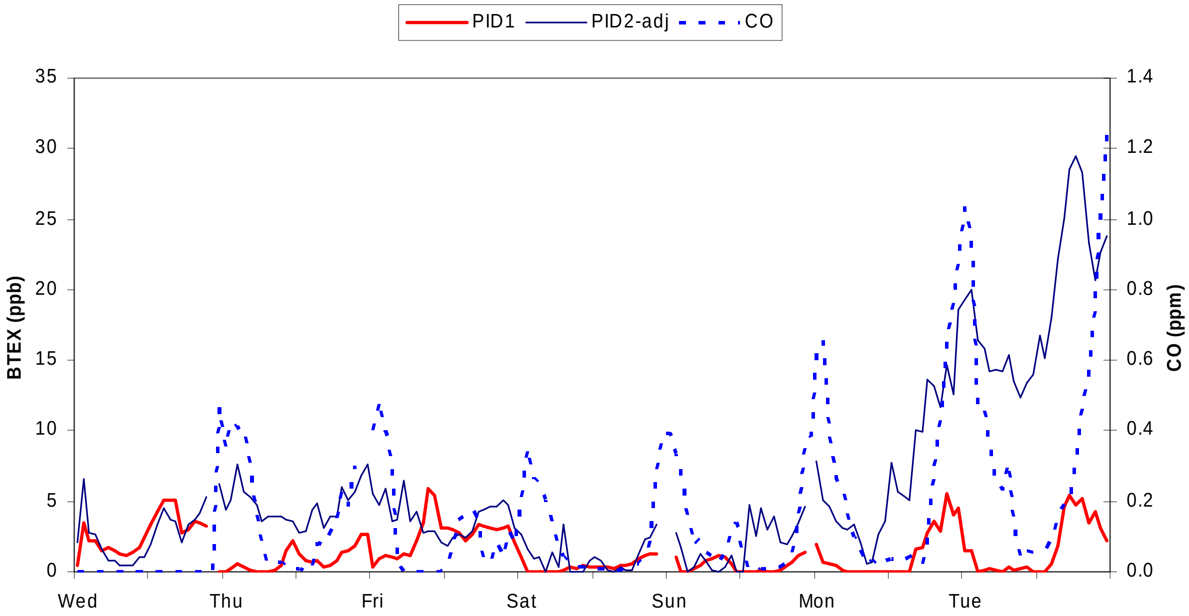

Figure 3-9. Time series plot of hourly averaged BTEX concentration estimated by portable PID and carbon monoxide by passive electrochemical method. Data from the second PID instrument have been adjusted for zero drift (13 ppb correction).

3.1.3 HCMS Quality Assurance Data

The SCAQMD Hudson monitoring site was used in the HCMS as a quality assurance site. In addition to the primary passive samples (7-day Ogawa samplers for NO_2, NOx, SO_2 and Radiello samplers for BTEX, 1,3-butadiene, formaldehyde, acetaldehyde and acrolein) and 7-day mini-volume aerosol samples for $PM_{2.5}$ mass and OC and EC, DRI collected two additional sets of replicate samples during the winter and summer sampling periods to establish the precision of the passive measurements. Daily 24-hour canister and DNPH samples were also collected for two weeks in winter and summer to compare the passive measurements with methods that are commonly used in other air monitoring programs. Additionally during the winter and summer sampling periods, the continuous data from the TSI DustTrak and DRI photoacoustic instruments were averaged and compared to the corresponding filter-based gravimetric mass and carbon measurements.

The Hudson site was selected as the quality assurance site in order to utilize the District's routine criteria pollutants and air toxics measurements which are collected with traditional methods. Collocating with similar measurements enabled a more complete assessment of the HCMS data and the comparability of the measurements being made by various methods and investigators, including the UCLA mobile monitoring van. The following preliminary data were provided by the SCAQMD and compared with corresponding HCMS data.

1. Hourly NO and NOx (Horiba APNA-360).
2. Hourly CO (Horiba APMA-370).
3. Hourly SO_2 (Monitor Labs 8850).
4. Hourly black carbon (Magee Scientific aethalometer).
5. Hourly $PM_{2.5}$ mass (Thermo Electron Corp 1400A TEOM).
6. Hourly wind speed and direction, temperature and relative humidity.
7. Every sixth day canister and DNPH cartridge data.

The SCAQMD data were used for initial review of the HCMS data to identify and diagnose potential problems in the monitoring program.

<u>Replicate Precision of Passive Measurements</u>

Radiello VOC, aldehyde, and H_2S samplers as well as Ogawa NOx and SO_2 samplers were deployed in triplicate at the Hudson monitoring site during 28 days during the winter (2/13/07-3/13/07) and summer (7/31/07-8/28/07) sampling seasons (four sets of triplicates per season). The summary of these results in Table 3-7 includes the ranges and means of the four 7-day samples in each season and the mean, % relative difference, standard deviation and 90th percentile of the differences of the individual replicate to means of the three replicates. The precision of the passive measurements during the main study are consistent with the earlier laboratory evaluation and pilot study and are equal to or exceed the HCMS data quality objectives in Table 2-2. The practical consequence of these results is that any spatial differences in pollutant concentrations within the HCMS saturation monitoring network that are greater than two times the mean difference in the replicates are significant with respect to precision of the measurement. The comparisons of alternative measurement methods in the next two subsections examine measurement accuracy and the significance of regional differences in pollutant concentrations.

Table 3-7. Minimum, maximum and mean of the four 7-day samples in each season and the mean and % relative differences of the individual replicate samples to the mean of the replicates.

	7-day Mixing Ratios (ppbv)			Differences of Replicates			
	Min	Max	Mean	Mean	%RD	SD	90%
Winter							
Nitrogen Oxides (NOx)	54.4	91.6	73.0	2.0	2.8%	2.8	6.9
Nitorgen Dioxide (NO_2)	21.7	34.4	28.5	1.5	5.3%	1.3	3.4
Sulfur Dioxide (SO_2)	0.77	1.60	1.09	0.11	9.8%	0.07	0.20
Hydrogen Sulfide (H_2S)	0.59	0.98	0.76	0.04	4.8%	0.01	0.05
Benzene	0.530	0.687	0.607	0.014	2.3%	0.015	0.040
Toluene	1.185	2.296	1.728	0.039	2.3%	0.033	0.081
Ethylbenzene	0.211	0.417	0.337	0.008	2.4%	0.007	0.015
Xylenes	0.985	1.737	1.408	0.031	2.2%	0.029	0.072
1,3-Butadiene	0.019	0.030	0.026	0.001	4.8%	0.001	0.003
Formaldehyde	1.75	3.51	2.65	0.06	2.2%	0.03	0.10
Acetaldehyde	0.83	2.63	1.88	0.05	2.8%	0.06	0.13
Acrolein	0.013	0.047	0.028	0.015	52.0%	0.013	0.032
Summer							
Nitrogen Oxides (NOx)	25.5	33.4	29.4	0.6	2.2%	0.5	0.9
Nitorgen Dioxide (NO_2)	14.8	25.1	19.5	1.0	4.9%	1.1	2.6
Sulfur Dioxide (SO_2)	0.35	1.53	0.99	0.20	19.8%	0.19	0.35
Hydrogen Sulfide (H_2S)	0.75	0.79	0.93	0.12	12.5%	0.06	0.20
Benzene	0.251	0.445	0.347	0.026	7.5%	0.014	0.035
Toluene	0.853	1.256	1.045	0.044	4.2%	0.027	0.071
Ethylbenzene	0.177	0.238	0.208	0.014	6.7%	0.010	0.026
Xylenes	0.568	0.781	0.692	0.063	9.2%	0.051	0.138
1,3-Butadiene	0.052	0.063	0.057	0.005	8.3%	0.003	0.010
Formaldehyde	0.91	2.33	1.76	0.12	6.7%	0.06	0.17
Acetaldehyde	0.61	0.92	0.73	0.03	4.7%	0.02	0.06
Acrolein	-0.010	0.062	0.010	0.005	47.4%	0.021	0.022

Passive versus Active Measurements

Daily 24-hour canister and DNPH samples were collected by DRI for two and three weeks in the winter and summer sampling season, respectively, for comparison with the passive measurements. Table 3-8 summarize the comparisons between the 7-day passive measurements with the corresponding averages of the seven 24-hour active samples. Although Table 3-8 shows all of the data collected, the comparisons between passive and active measurements were considered valid only if six or more 24-hour samples were collected during the corresponding 7-day passive sampling period. This criterion was met for the winter samples. However, the 24-hour canister measurements were not complete for the summertime weeks due to high humidity, which caused the canister sampler to plug and restrict sample flow during the 24-hour periods. The valid comparisons are shaded in Table 3-8. The averages of the valid samples are shown in Figure 3-10. The uncertainty bars are the average deviations from the mean of the valid 7-day average samples. The two measurements are equivalent for all BTEX species within the range of uncertainty. The canister measurements of 1,3-butadiene were about three times higher than the Radiello (Carbograph 4) passive measurements, which is consistent with the laboratory evaluations that confirmed less than quantitative retention on the adsorbent due to back diffusion.

Table 3-8. Comparison of passive and active measurements.

				Weekly			Seasonal		
Analyte	Season	Week	Sampling Overlap	Active Mean	Passive Mean & SD	P/A Ratios	Mean Active	Mean Passive	P/A
Benzene	Winter	III	100%	0.581	0.561 ± 0.009	0.97	0.70	0.61	0.86
	Winter	IV	100%	0.825	0.651 ± 0.004	0.79			
	Summer	I	43%	0.212	0.251 ± 0.030	1.18	0.30	0.35	1.18
	Summer	II	71%	0.254	0.445 ± 0.049	1.75			
	Summer	III	57%	0.426	0.361 ± 0.022	0.85			
Toluene	Winter	III	100%	1.536	1.553 ± 0.028	1.01	1.93	1.71	0.89
	Winter	IV	100%	2.322	1.877 ± 0.025	0.81			
	Summer	I	43%	0.808	0.853 ± 0.060	1.06	0.89	1.09	1.23
	Summer	II	71%	0.753	1.256 ± 0.077	1.67			
	Summer	III	57%	1.101	1.152 ± 0.067	1.05			
Ethylbenzene	Winter	III	100%	0.314	0.329 ± 0.002	1.05	0.37	0.37	1.00
	Winter	IV	100%	0.431	0.417 ± 0.010	0.97			
	Summer	I	43%	0.105	0.186 ± 0.025	1.77	0.13	0.22	1.63
	Summer	II	71%	0.097	0.232 ± 0.027	2.38			
	Summer	III	57%	0.200	0.238 ± 0.012	1.19			
m,p-Xylene	Winter	III	100%	1.049	1.006 ± 0.008	0.96	1.26	1.11	0.88
	Winter	IV	100%	1.473	1.221 ± 0.020	0.83			
	Summer	I	43%	0.310	0.450 ± 0.087	1.45	0.37	0.52	1.39
	Summer	II	71%	0.311	0.557 ± 0.086	1.79			
	Summer	III	57%	0.498	0.548 ± 0.040	1.10			
o-Xylene	Winter	III	100%	0.412	0.421 ± 0.003	1.02	0.51	0.47	0.92
	Winter	IV	100%	0.602	0.517 ± 0.007	0.86			
	Summer	I	43%	0.117	0.192 ± 0.040	1.64	0.14	0.21	1.50
	Summer	II	71%	0.113	0.223 ± 0.040	1.98			
	Summer	III	57%	0.198	0.227 ± 0.021	1.15			
1,3-butadiene	Winter	III	100%	0.094	0.028 ± 0.003	0.30	0.10	0.03	0.29
	Winter	IV	100%	0.105	0.028 ± 0.001	0.27			
	Summer	I	43%	0.055	0.054 ± 0.005	0.99	0.07	0.06	0.82
	Summer	II	71%	0.047	0.063 ± 0.005	1.33			
	Summer	III	57%	0.105	0.052 ± 0.005	0.50			
Formaldehyde	Winter	III	100%	4.415	2.472 ± 0.097	0.56	4.97	2.99	0.60
	Winter	IV	100%	5.517	3.510 ± 0.069	0.64			
	Summer	II	86%	2.310	2.326 ± 0.209	1.01	2.47	1.62	0.66
	Summer	III	100%	2.636	0.915 ± 0.142	0.35			
Acetaldehyde	Winter	III	100%	1.658	2.632 ± 0.159	1.59	1.91	2.47	1.29
	Winter	IV	100%	2.164	2.305 ± 0.003	1.07			
	Summer	II	86%	0.985	0.920 ± 0.037	0.93	0.97	0.76	0.78
	Summer	III	100%	0.960	0.607 ± 0.051	0.63			
Acrolein	Winter	III	100%	0.104	0.479 ± 0.058	4.62	0.12	0.36	3.01
	Winter	IV	100%	0.134	0.237 ± 0.005	1.77			
	Summer	II	86%	0.020	0.020 ± 0.004	0.99	0.02	0.02	0.97
	Summer	III	100%	0.023	0.022 ± 0.006	0.96			

Notes: Only sample pairs with > 6/7 days of overlap are accepted for comparison (shown shaded)
Ozone denuder used on active DNPH samples during summer only.

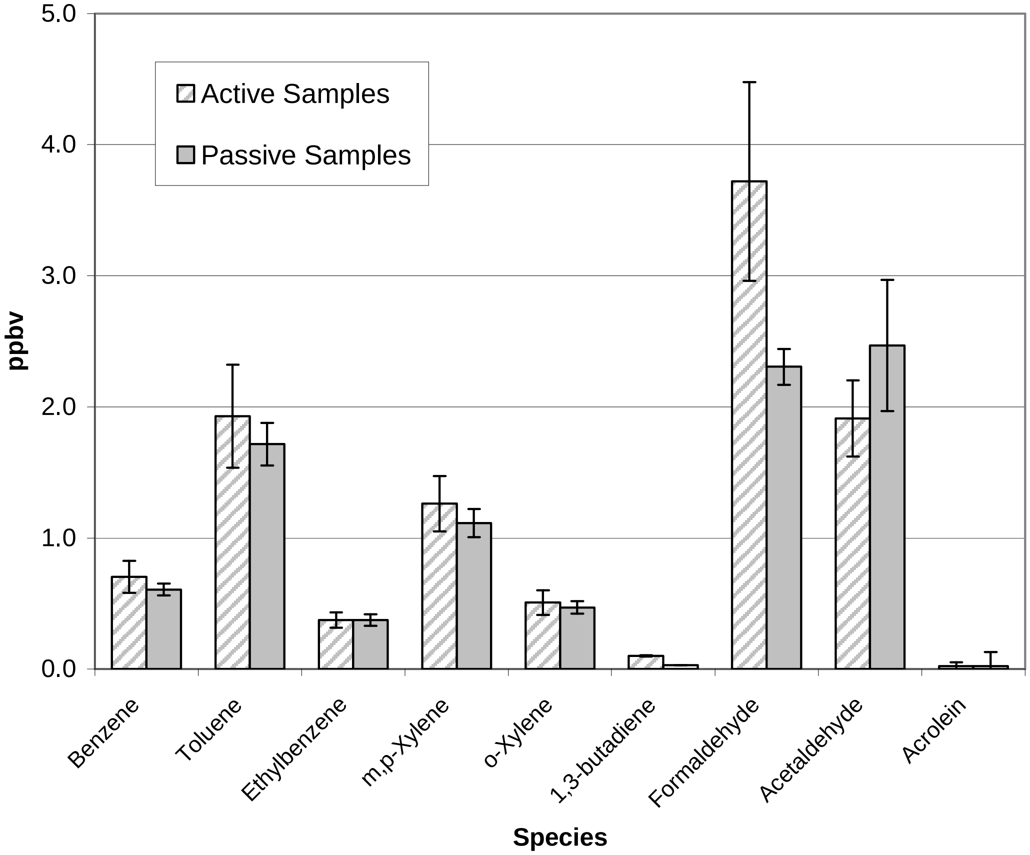

Figure 3-10. Comparison of active versus passive sampling measurements at the Hudson site using sample pairs with six or more days of overlap within each weekly sampling period.

Poorer agreement was obtained for comparison between passive and active measurements of aldehydes than for BTEX. Formaldehyde concentrations measured by the passive sampler were lower than active sampling in both seasons by about as much as 40%. These differences cannot be attributed solely to reactions with ozone (no ozone denuder for passive samplers) since one of the two pairs of summer samples had good agreement. Compared to the corresponding active samples, two of the passive acetaldehyde samples agreed well on average, but one had 60% higher and one had 40% lower values. As noted earlier in the methods sections, acetaldehyde is lost during passive measurements at moderate ozone concentrations. However, low collection efficiency was recently reported by (Herrington et al., 2007) for active acetaldehyde samples.

Active sampling methods are also used in other air monitoring programs in the area, including the SCAQMD Multiple Air Toxics Exposure Study (MATES) and Photochemical Assessment Monitoring Stations Network and CARB Air Toxics Monitoring Network. The SCAQMD collected 24-hour canister and DNPH every sixth day at the Hudson monitoring site. Thus, the DRI passive measurements can be indirectly compared to the SCAQMD active measurements. Figure 3-11a shows comparisons of DRI and SCAQMD 24-hour 1,3-butadiene, benzene and toluene during the winter season. Similar comparisons are shown in Figure 3-11b for ethylbenzene and xylenes. Figure 3-12a and 3-12b show the comparisons of DRI and SCAQMD 24-hour formaldehyde and acetaldehyde during winter and summer seasons, respectively. However, it must be noted that the collection of 24-hour active samples by DRI began at about noon and SCAQMD's samples began at midnight. Start times by DRI coincides with collection of the passive samples, which must be started manually. Each SCAQMD sample overlaps in time with the second 12 hours of one DRI sample and the first 12 hours of the following day's sample. While these comparisons are not quantitative, they indicate that DRI and SCAQMD measured comparable range of pollutant concentrations during the two week periods. DRI canister values for the substituted aromatic compounds (i.e. ethylbenzene and xylenes) were slightly higher than SCAQMD's values.

Comparisons of Continuous Measurements

Collocated measurements were made during the winter and summer seasons at the Hudson monitoring sites by DRI and SCAQMD. DRI's NOx and SO_2 data from the Ogawa passive samples are compared to data from the SCAQMD continuous monitors (Figure 3-13). Seven-day integrated PM mass from the Teflon filters are compared to corresponding continuous TEOM measurements by the SCAQMD and estimates of $PM_{2.5}$ from light scattering measurements by DRI with a TSI DustTrak. The SCAQMD operated the TEOM in the winter season but not in summer. Conversely, the District operated the Aethalometer during summer but not in winter. DRI's photoacoustic measurements were compared to the SCAQMD's Aethalometer measurements during the summer and DRI's DustTrak data were compared to SCAQMD's TEOM data during winter.

Comparisons of data from DRI's 7-day time-integrated sampling versus the corresponding time-averaged SCAQMD continuous measurements at Hudson site are summarized in Table 3-9. NOx and NO data from the passive samples agree well with time-averaged data from the AQMD NOx analyzer. However, most of the AQMD SO_2 values were below the detection limit of their instrument. In comparison, the 7-day average SO_2 values from the passive samples were 1.1 and 1.6 ppb. The AQMD $PM_{2.5}$ concentrations exceeded the 7-day integrated gravimetric mass (from the Teflon filter) by nearly a factor of two.

The time series plot in Figure 3-14 shows that the hourly-averaged DustTrak measurements generally track the SCAQMD TEOM data. While the two data sets are reasonably correlated without significant bias when averaged over a 24-hour period (Figure 3-15), the hourly averages are poorly correlated. The series of plots in Figure 3-16 show correlations for subsets of data corresponding to 0600-0900, 1300-1600, and 2000 to 0500 compared to the correlation of all data. The plot in Figure 3-17 shows that visible light scattering efficiencies as function of particle size peak in the range of 0.4 to 0.8 µm. This size range corresponds to freshly emitted particle from vehicle exhaust while accumulation mode and coarse particles have much lower scattering efficiencies. The ratios of the DustTrak to the corresponding TEOM data are largest during the commute period and lowest during the afternoon. These variations are consistent with the diurnal variations in the particle size distribution of urban aerosols and the relationship between light scattering efficiency and particle size shown in Figure 3-17. Figures 3-18 and 3-19 show that the Aethalometer and photoacoustic black carbon data are well correlated. There is a consistent bias (photoacoustic lower than Aethalometer) related to the light absorption efficiency assumed in the black carbon mass calculation.

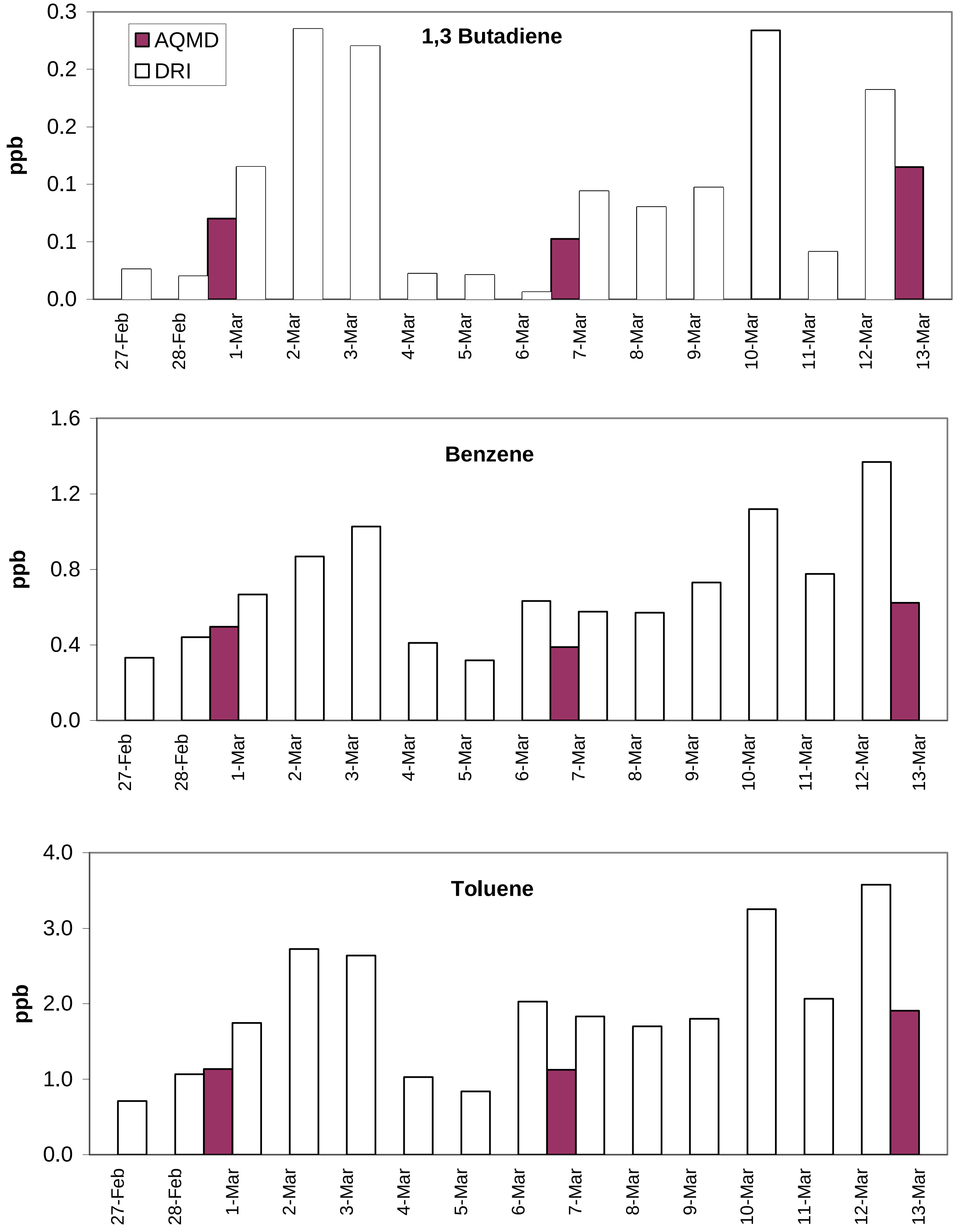

Figure 3-11a. Comparisons of DRI (noon to noon) and SCAQMD (midnight to midnight) 24-hour 1,3-butadiene, benzene and toluene during the winter season.

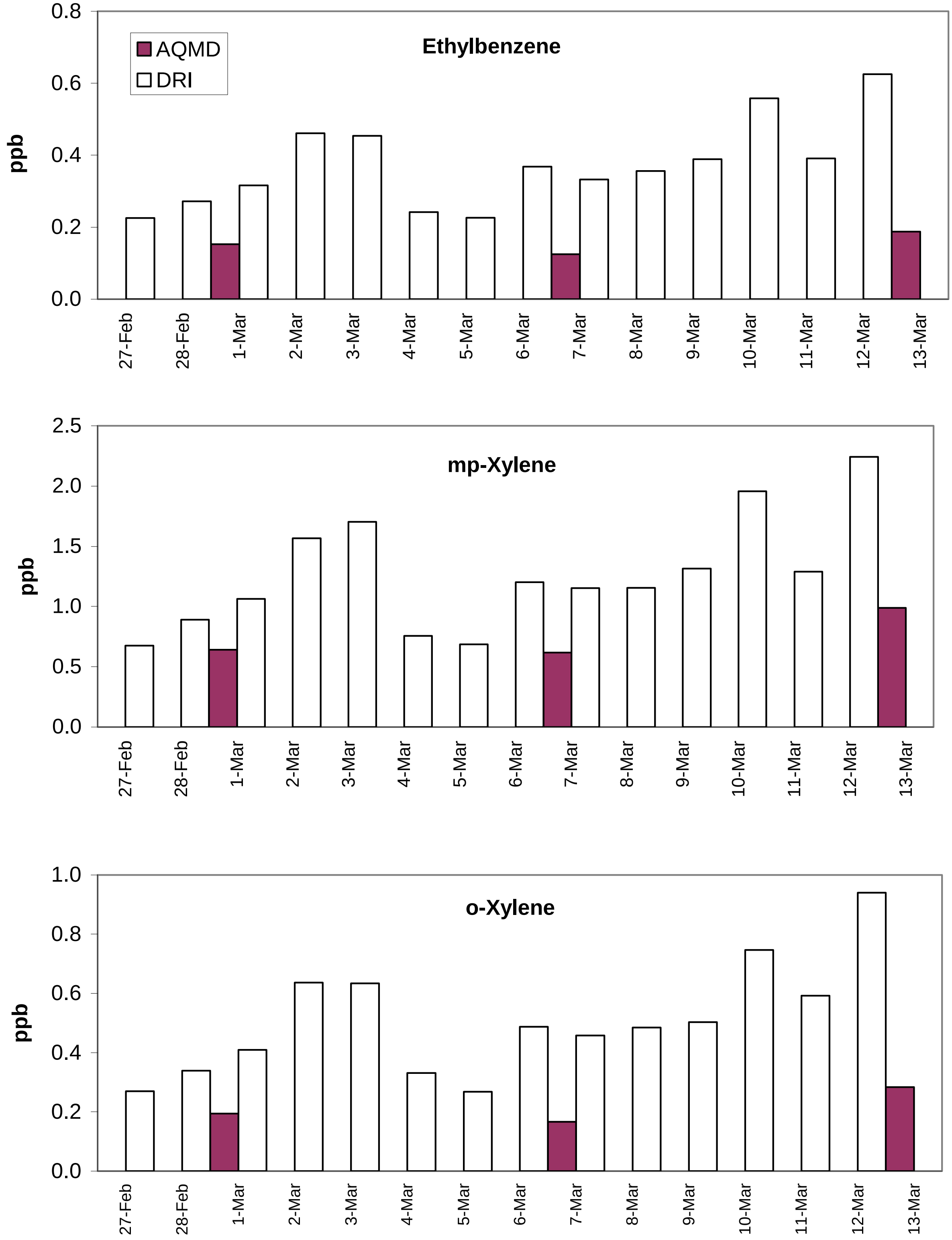

Figure 3-11b. Comparisons of DRI (noon to noon) and SCAQMD (midnight to midnight) 4-hour ethylbenzene and xylenes during winter season.

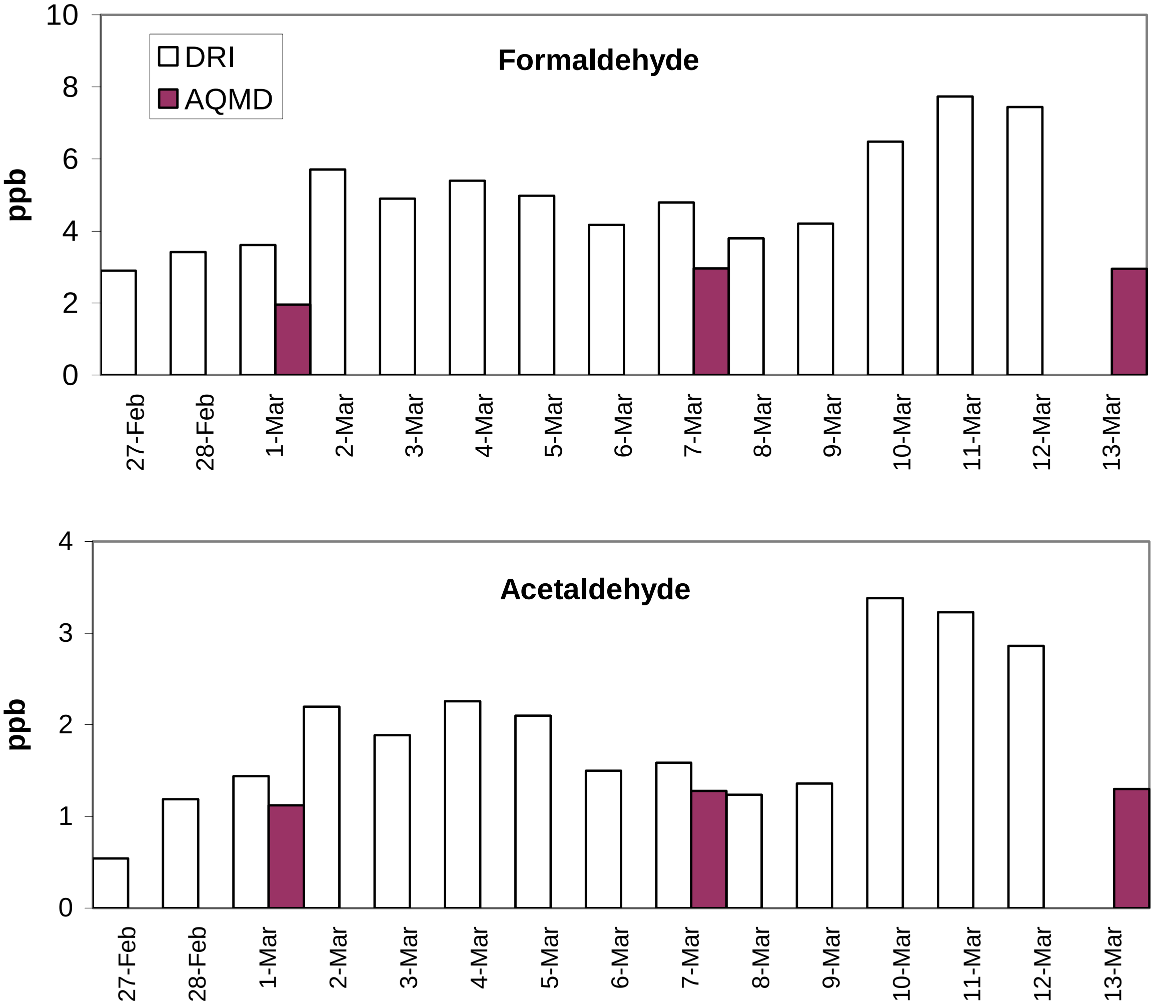

Figure 3-12a. Comparisons of DRI (noon to noon) and SCAQMD (midnight to midnight) 24-hour formaldehyde and acetaldehyde during winter season.

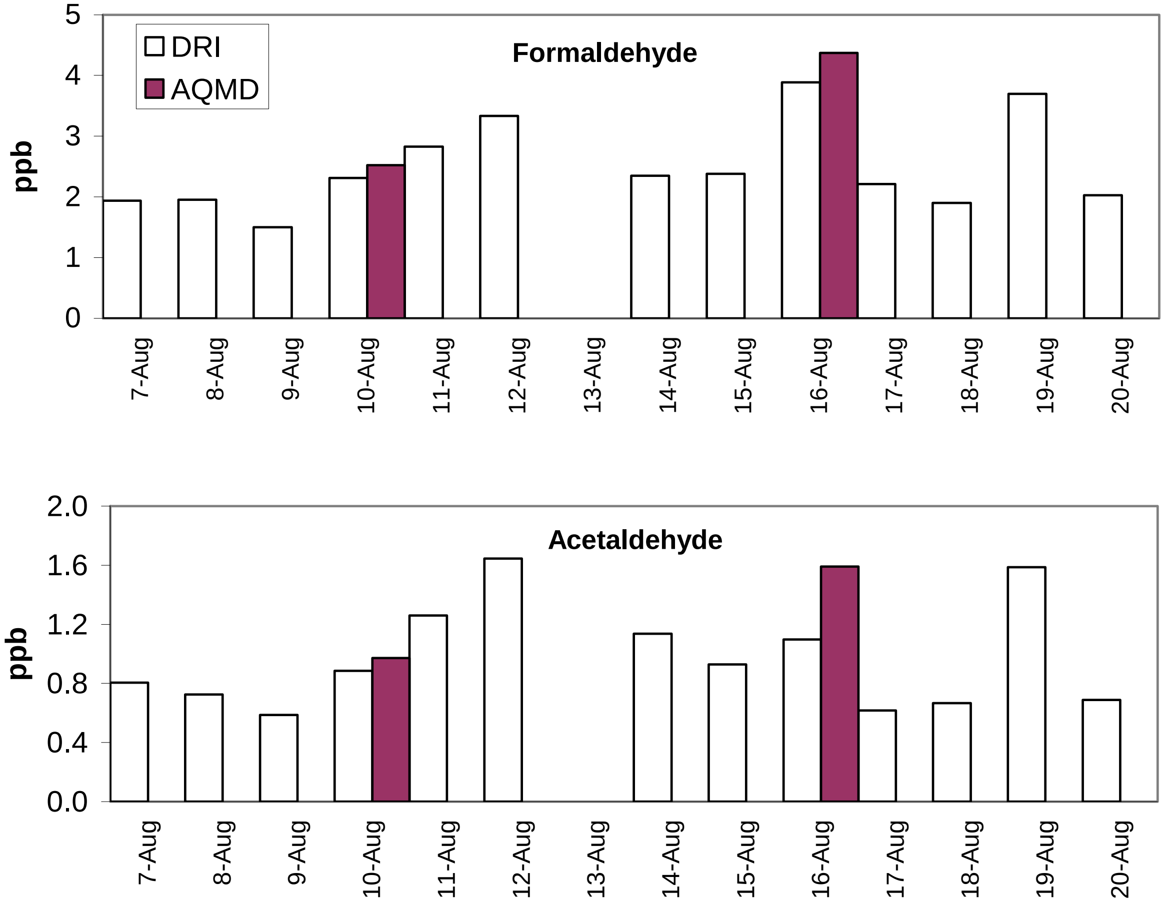

Figure 3-12b. Comparisons of DRI (noon to noon) and SCAQMD (midnight to midnight) 24-hour formaldehyde and acetaldehyde during summer season.

Table 3-9. Comparisons of data from DRI time-integrated sampling with time-averaged SCAQMD continuous measurements at Hudson site during winter season.

Duration	Start Date	Data Source	NOx ppb	NO ppb	SO_2 ppb	CO ppm	$PM_{2.5}$ ug/m^3	TC ug/m^3	T °F	RH %
7-day	2/28/2007	AQMD [1]	76.0	42.1	-0.8	0.6	27.7		59.4	38.9
7-day	2/28/2007	DRI	73.2	43.8	1.1			4.8		
7-day	2/28/2007	DRI/AQMD	0.96	1.04						
7-day	3/6/2007	AQMD	84.2	33.8		0.7	30.9		63.7	58.7
7-day	3/6/2007	DRI	72.7	38.3	1.6		15.7	5.8		
7-day	3/6/2007	DRI/AQMD	0.86	1.14			0.51			

Notes

DRI NOx, NO and SO_2 data are from passive sampling

DRI $PM_{2.5}$ are gravimetric mass from Teflon filters and AQMD are from TEOM.

DRI TC data are TOR-IMPROVE analysis of quartz filters.

[1] Only 6.7 days of data were received from SCAQMD for this week.

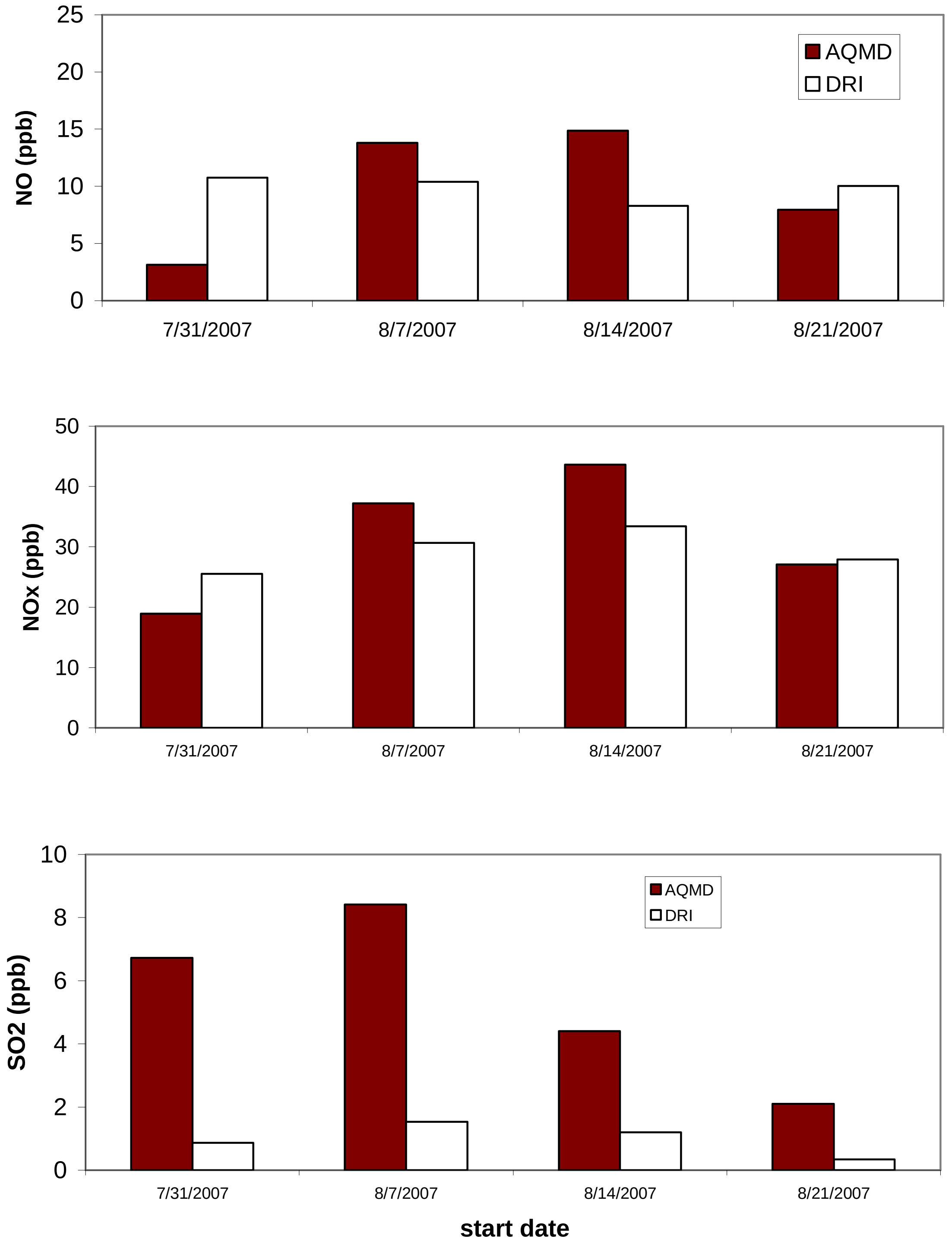

Figure 3-13. Comparisons of data from DRI time-integrated sampling with time-averaged SCAQMD continuous measurements at Hudson site during summer season. Passive measurements show less variability than AQMD results, which may be an artifact of the continuous analyzers having less measurement precision (e.g., the continuous SO_2 measurements have 10 ppb precision and the mean results are from averaging concentrations of 0 and 10 ppb).

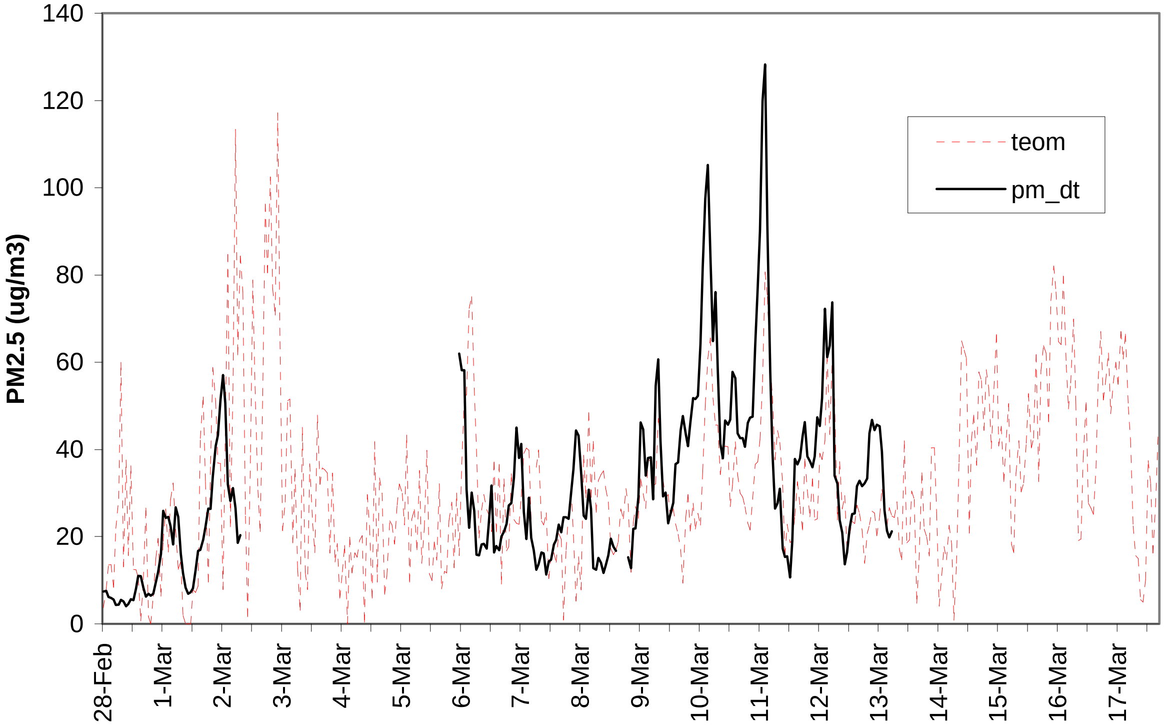

Figure 3-14. Time series of hourly $PM_{2.5}$ by TEOM (SCAQMD) and TSI DustTrak (DRI) at the Hudson site during the winter season.

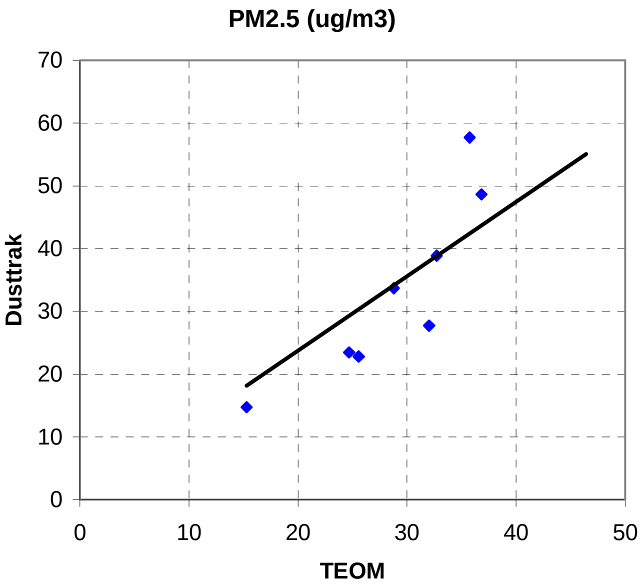

Figure 3-15. Scatterplots of 24-hour average SCAQMD TEOM and DRI DustTrak $PM_{2.5}$ mass ($\mu g/m^3$) at the Hudson site during winter season.

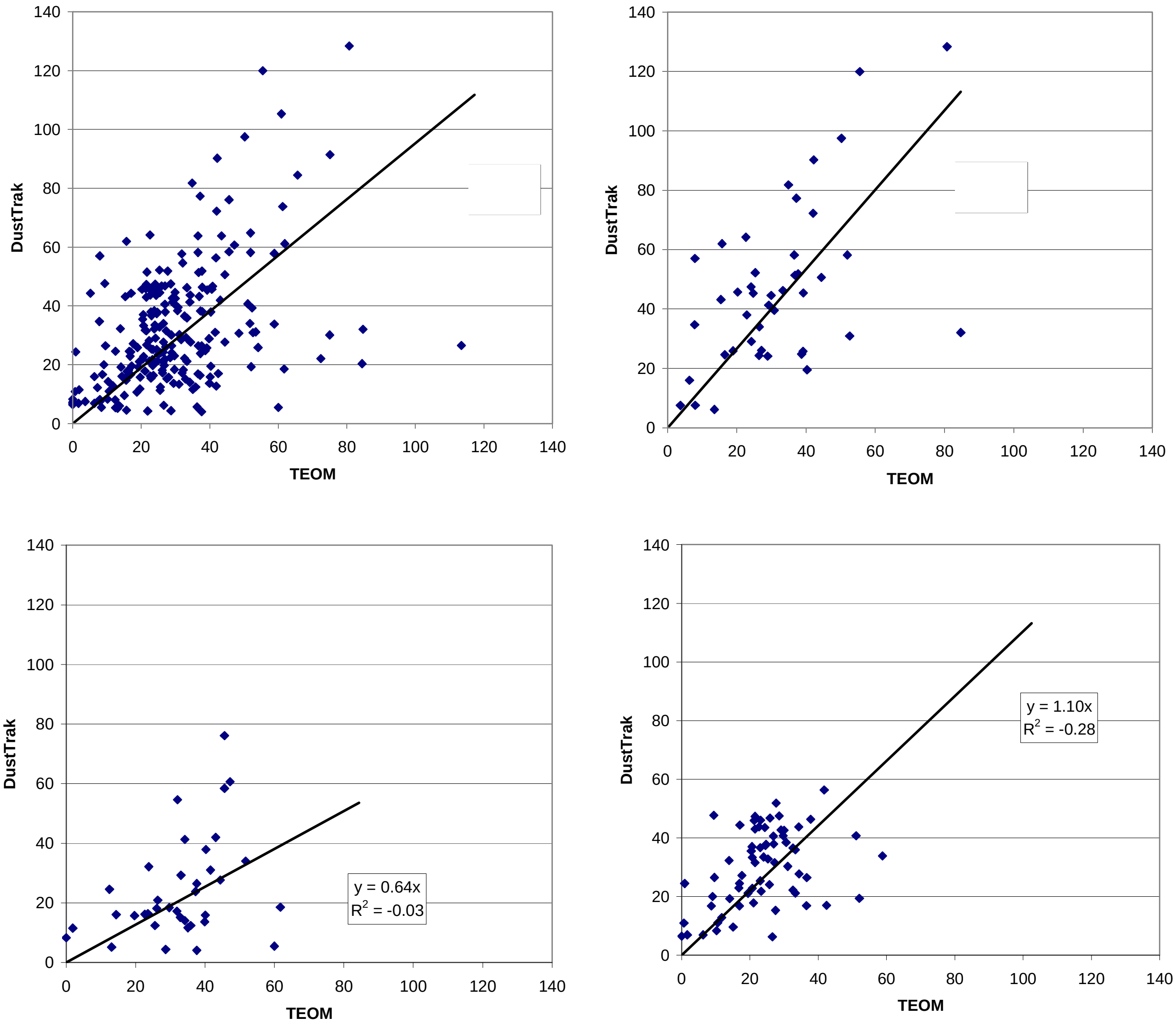

Figure 3-16. Scatterplots of hourly SCAQMD TEOM and DRI DustTrak PM2.5 mass (µg/m3) at the Hudson site during winter season. Data included are all (upper left), 0600-0900 (upper right), 1300-1600 (lower left) and 2000-0500 (lower right).

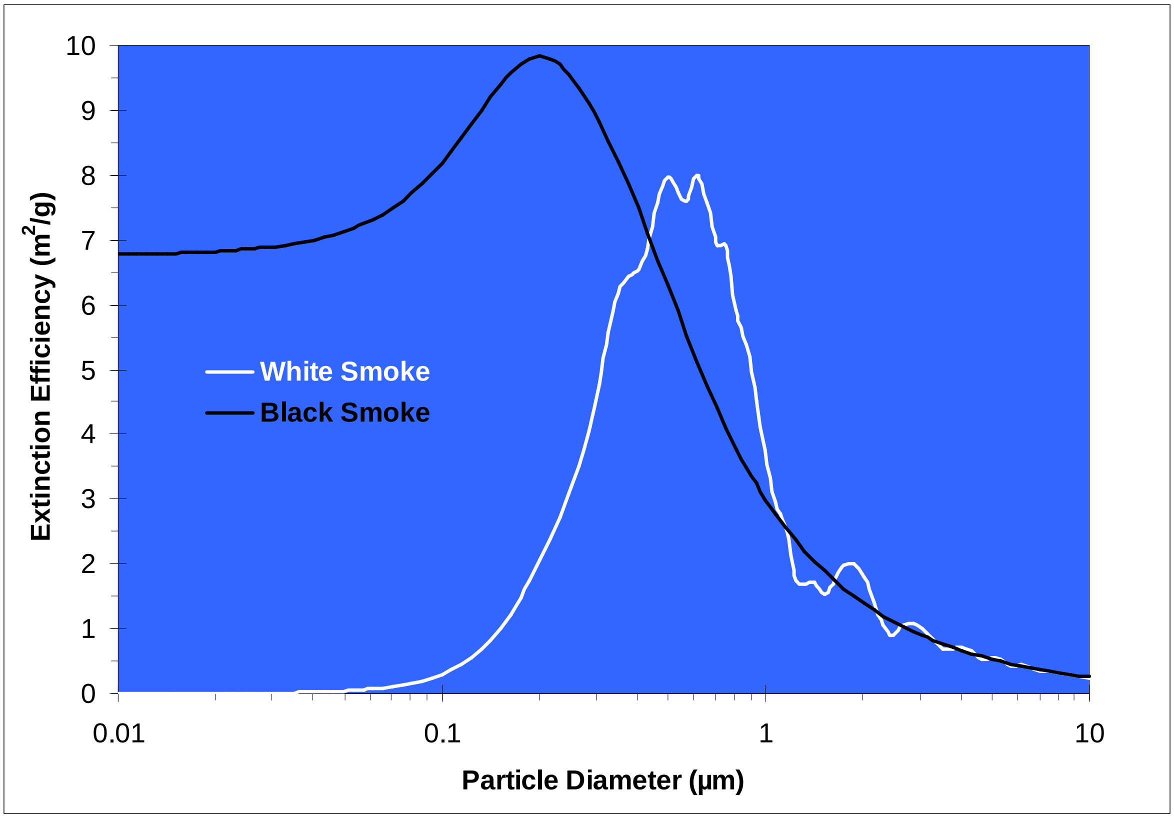

Figure 3-17. Visible light extinction efficiencies as function of particle size for white and black smoke. Other assumptions in the calculation are a particle mass density of 1250 kg/m^3 and a wavelength of 550 nm, corresponding to the peak of both solar radiation and eye sensitivity.

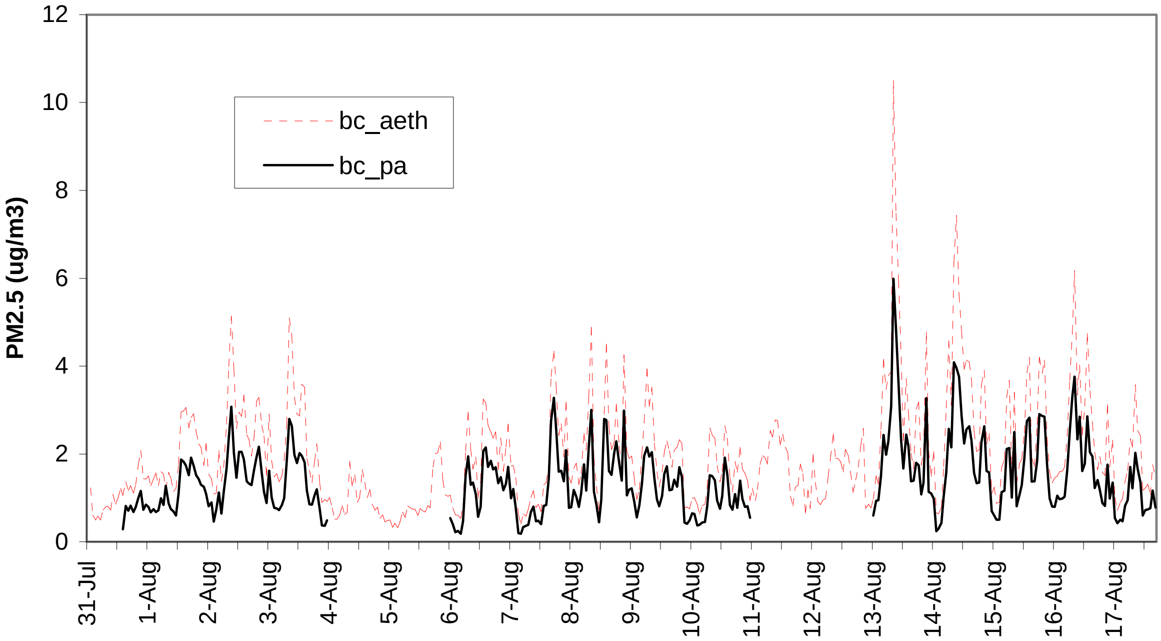

Figure 3-18. Time series of hourly black carbon (µg/m^3) by Aethalometer (SCAQMD) and photoacoustic (DRI) at the Hudson site during the summer season.

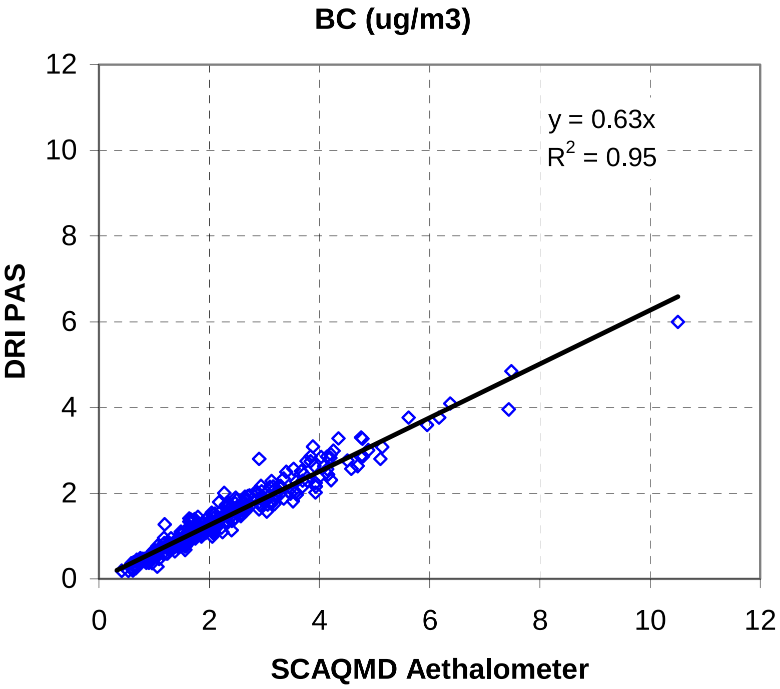

Figure 3-19. Scatterplots of 24-hour average SCAQMD Aethalometer and DRI photoacoustic (PAS) black carbon (µg/m^3) at the Hudson site during summer season.

3.1.4 UCLA and SCAQMD Measurement Comparisons at the Hudson Site

DRI compared collocated measurements made for several hours by UCLA in the mobile sampling platform at the Hudson sites during March 7, 2007. Table 3-10 summarizes the comparisons of hourly-averaged data from the continuous measurements by DRI, UCLA and SCAQMD at Hudson site. The UCLA CO analyzer measures lower values than AQMD but most of the measurements were close to detection limits. UCLA's NOx data compared well with AQMD's measurements. UCLA's hourly-averaged DustTrak measurements exceeded DRI's values by about 30 percent, on average. The top panel in Figure 3-20 shows comparisons of 10-minute averaged measurements by DRI and UCLA. Note, however, that a $PM_{2.5}$ inlet was used by DRI while UCLA used a PM_{10} inlet. As expected from the differing PM size cuts, most of the UCLA values exceed those reported by DRI. However, there were some cases during lower PM concentrations when DRI's values exceeded UCLA values. The difference may also be due to differing heights of the sampling inlets. The sample inlet for the DRI DustTrak was located on the roof of the District monitoring shed, while the inlet for the UCLA DustTrak was at vehicle level. The lower panel in Figure 3-21 shows that the DRI photoacoustic and UCLA Aethalometer black carbon data track each other well. However, the scatterplot in Figure 2-24 shows only moderate correlations between the two datasets for black carbon with slightly higher values for the photoacoustic.

Table 3-10. Comparisons of hourly-averaged data from continuous measurements by DRI, UCLA and SCAQMD at Hudson site on March 7, 2007.

Parameter	Group	10:00	11:00	12:00	13:00	14:00	MEAN	RATIO
CO (ppm)	UCLA	0.2	0.2				0.2	
	SCAQMD	0.6	0.4				0.5	0.42
NO (ppb)	UCLA	40.6	36.0				38.3	
	SCAQMD	46.2	27.2				36.7	1.04
NOx (ppb)	UCLA	92.7	92.5				92.6	
	SCAQMD	95.2	70.2				82.7	1.12
BC (ug/m3)	UCLA	4.6	3.5	1.5	3.8	2.5	3.2	
	DRI	4.9	4.4	1.8	4.4	3.4	3.8	0.84
PM (ug/m3)	UCLA	30.2	29.0	9.5	25.9	25.6	24.0	
	DRI	28.9	19.8	16.9	12.4	13.7	18.3	1.31
	SCAQMD	39.8	23.4		35.9	39.9	34.8	0.69
T (oC)	UCLA	24.9	25.6	26.0	26.5	25.9	25.8	
	SCAQMD	23.1	24.4		24.9	23.7	24.0	1.07
RH (%)	UCLA	40.8	37.1	28.4	30.8	28.4	33.1	
	SCAQMD	45.5	43.3		41.1	36.8	41.7	0.79

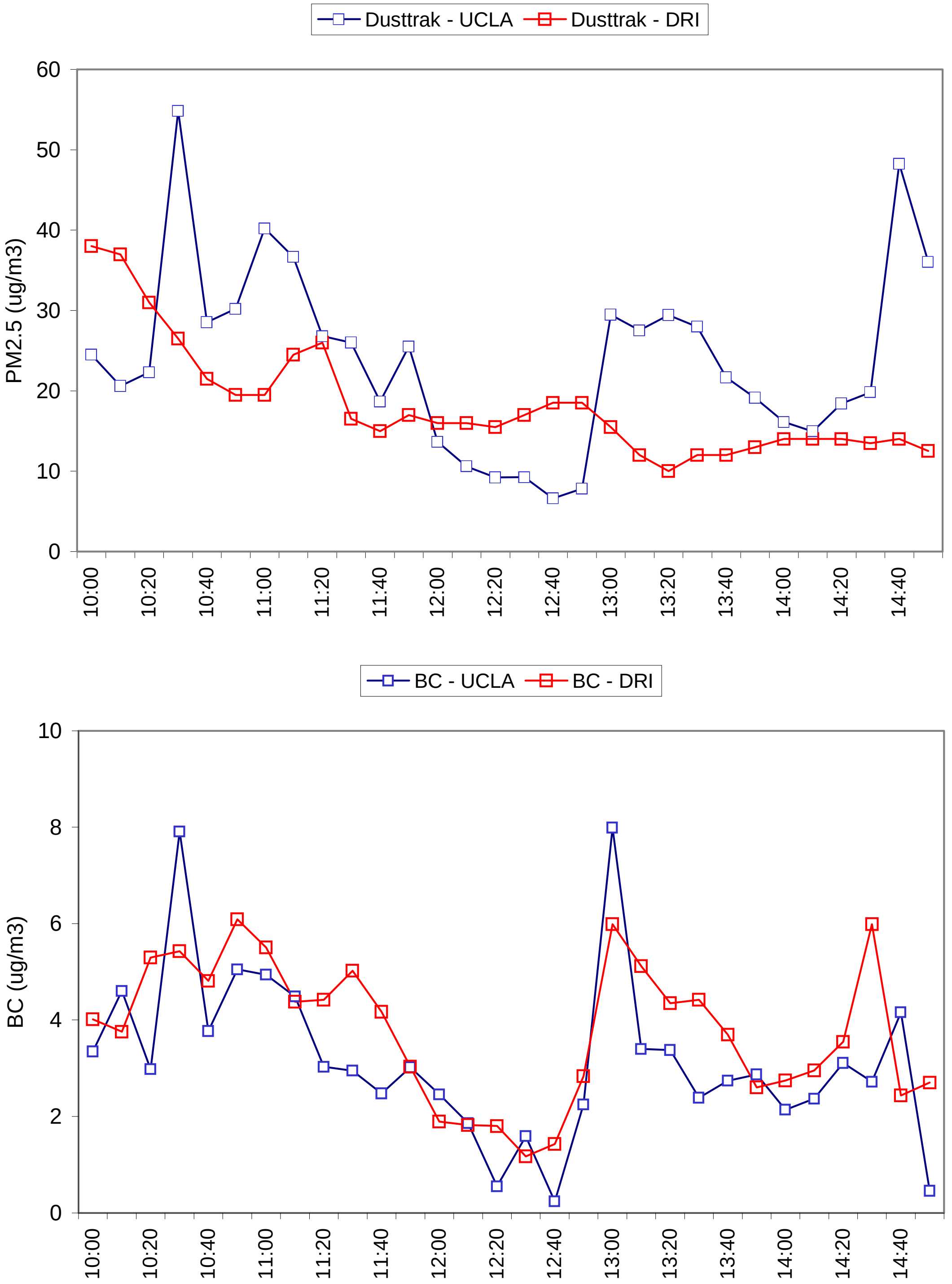

Figure 3-20. Comparisons of 10-minute averaged measurements by DRI and UCLA at the Hudson site on March 7, 2007. Top panel shows DustTrak measurements by DRI with $PM_{2.5}$ inlet and UCLA with PM_{10} inlet and lower panel shows black carbon data for DRI by the photoacoustic instrument and UCLA by Aethalometer.

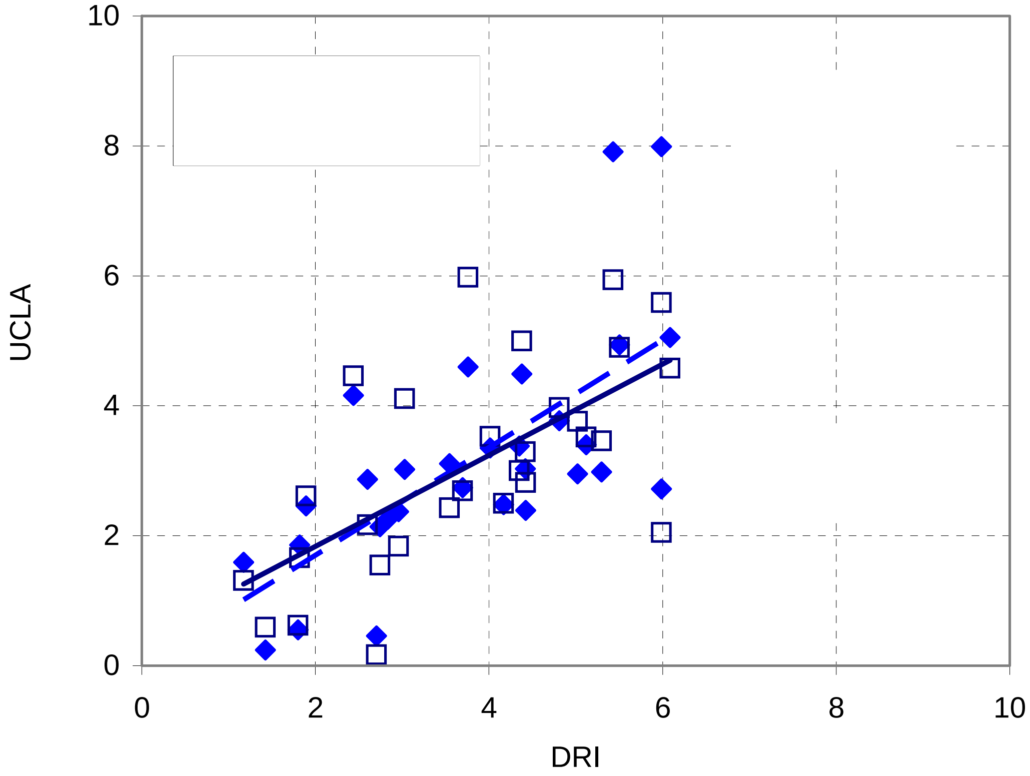

Figure 3-21. Scatterplot of 10-minute averaged black carbon measurements by DRI (BC) and UCLA (BC_hs) at the Hudson site on March 7, 2007.

3.2 Spatial Variations in Annual Mean Concentrations of Air Toxic Contaminants and Related Pollutants

This section presents the estimated annual mean concentrations of TACs and related air pollutants from the HCMS saturation monitoring program. The saturation monitoring network consisted of 7-day time-integrated sampling for four consecutive weeks in four seasons during 2007 (Winter - 2/13 to 3/13, Spring - 5/15 to 6/12, Summer - 7/31 to 8/28, and Fall - 11/13 to 12/11) at 23 locations within the communities of West Long Beach, Wilmington and San Pedro (Figure 3-1). These HCMS results were compared to similar data from the recent Multiple Air Toxics Exposure Study–III (MATES-III) conducted by the SCAQMD (SCAQMD, 2008). The MATES-III monitoring network included sites near the HCMS area and elsewhere in the basin (Figure 3-2).

Estimates of annual averages of TACs and related pollutants concentrations are presented in this section in tables and in bar charts. The sampling sites are listed in the tables roughly from west to east (left to right in the bar charts). First letter in site identification corresponds to community (e.g., W for Wilmington, L for Long Beach). The five sampling sites that are located within the residential areas of Wilmington are identified in the tables with an x in front of the site identifications. The average pollutant concentrations at these sites were used to represent the Wilmington community average for comparisons to concentrations measured in the residential areas of San Pedro and West Long Beach and near stationary and mobile sources.

The uncertainties in the tables for annual mean concentrations from the HCMS, MATES-III and the long term air toxics monitoring program are standard errors of the means (standard deviations divided by the square root of the number of observations). Seasonal variations in ambient pollutant concentrations due to changes in meteorological conditions (factors of 2 to 4) are far greater than measurement precision. Therefore, the standard errors of the annual means reflect the seasonal variations in pollutant concentrations and the numbers and time integrations (7-day versus 24-hours) of the samples used to estimate the annual means (maximum of 16 seven-day integrated samples equaling 112 total days for the HCMS, up to 121 24-hour samples every third day for MATES-III and 30 24-hour samples every twelfth day for the air toxics monitoring program).

The standard errors of the mean concentrations are appropriate measures of the significance of differences in annual average concentrations over multiple years. However, they are not appropriate measures of the significance of spatial variations in concentrations in the context of community-scale saturation monitoring during a fixed sampling interval. Proximity of the sampling site to emission sources and measurement precision are the main factors in the spatial variations in pollutant concentrations. We examined the spatial variations in pollutant concentrations by normalizing each 7-day sample to the mean concentrations of the five Wilmington residential sampling sites for the corresponding 7-day period. These normalized values exhibited little seasonal variations and had standard errors that were similar to the measurement precision. These ratios provide a direct measure of the spatial variations in pollutant concentrations within the study area and a more relevant measure of the statistical significance of the differences.

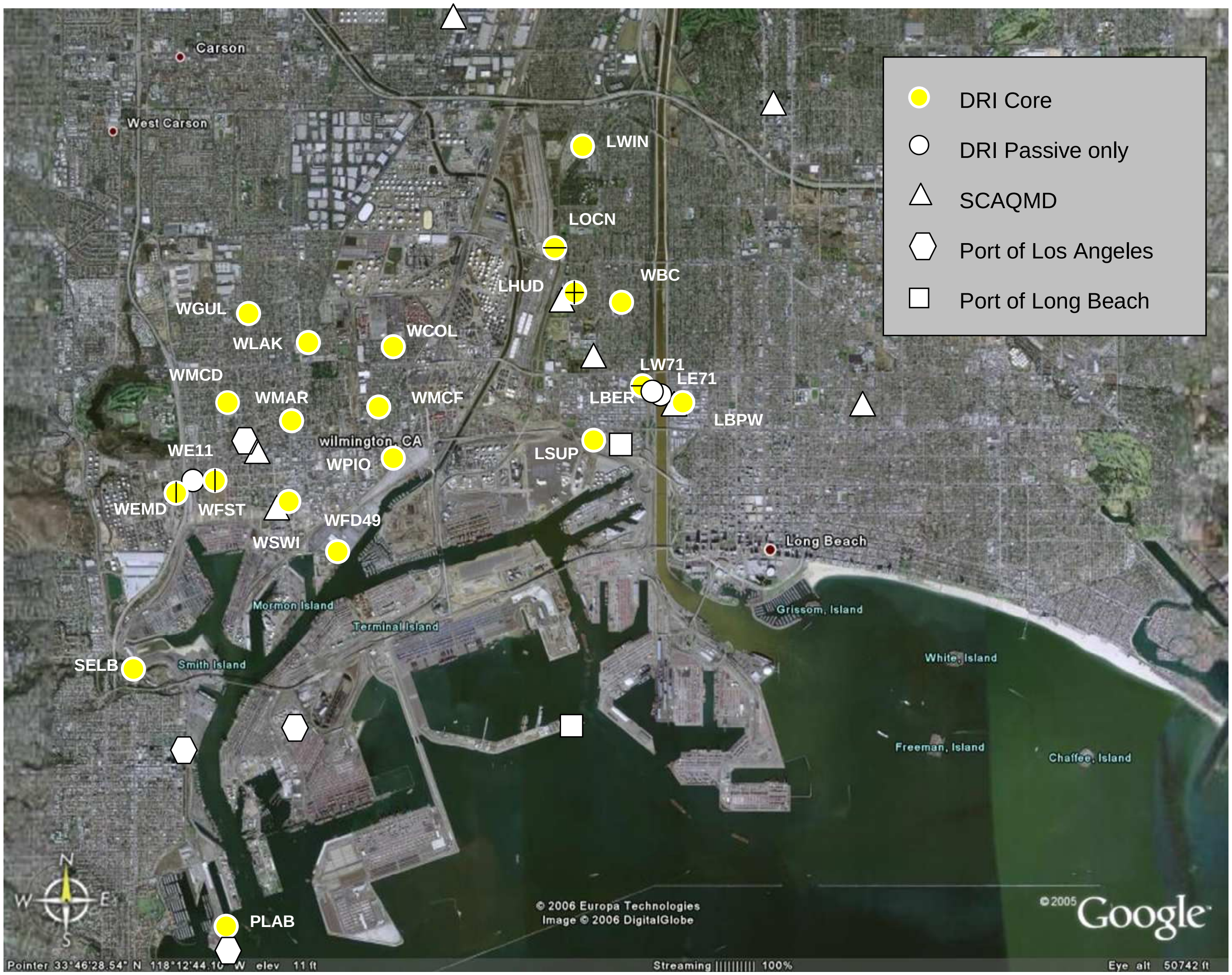

Figure 3-22. Map of the Harbor Communities Monitoring Study monitoring sites. Symbol for DRI core site with a horizontal line also includes measurement of NO_2 and a vertical line includes H_2S.

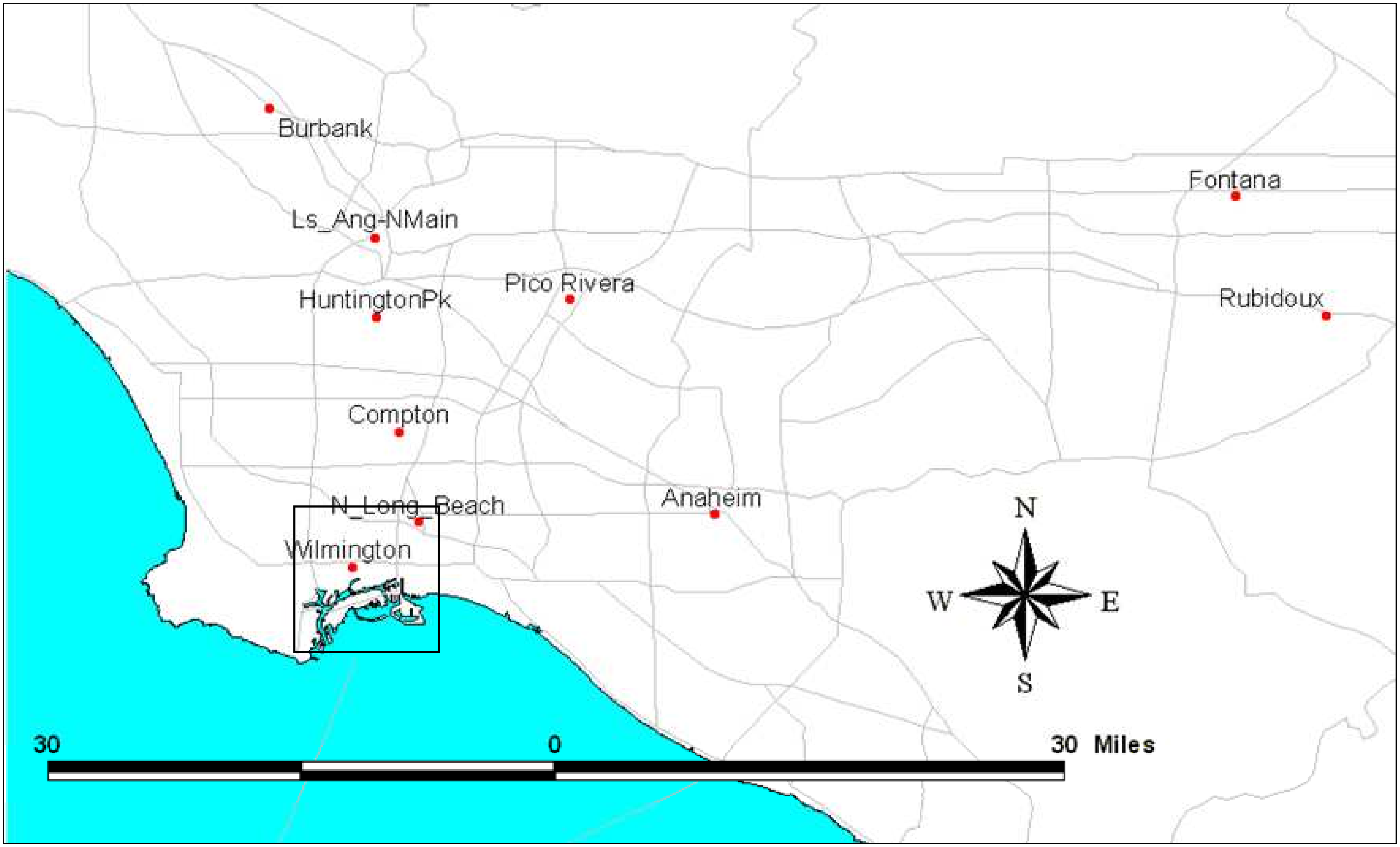

Figure 3-23. Map showing locations of ten MATES-III fixed monitoring sites in the South Coast Air Basin relative to the Harbor Communities Monitoring Study area shown as a rectangular box.

3.2.1 Annual Mean Mixing Ratios of NOx, SO_2 and H_2S.

Table 3-11 and Figure 3-24 show the estimated annual means and standard errors of the NOx and SO_2 mixing ratios. Based on the sites in Wilmington with complete monitoring periods for NOx and SO_2, the six residential sites with the lowest pollution levels were averaged and deemed to represent the neighborhood-scale pollutant levels in Wilmington. Figure 3-25 shows the mean and standard errors of the 7-day samples normalized to the mean of the six Wilmington residential sampling sites. NOx levels were uniformly lower at the six Wilmington community sampling sites (ratio to six-site mean ranging from 0.94 to 1.04) and at the residential sampling site in San Pedro (ratio of 1.01 ± 0.03) The two passive only sites on the east (LE71) and west (LW71) edges of the I-710 freeway had annual average NOx levels 3.03 ± 0.25 and 3.72 ± 0.23 times higher, respectively, than the Wilmington Community mean. The near-road site (LBER) located about 18 m west of the LW71 site, and the LBPW site located about 300 m east of the freeway, had NOx levels 2.20 ± 0.18 and 1.23 ± 0.04 times higher than the Wilmington Community mean. The spatial variations in NOx levels for sampling sites near the I-710 freeway are consistent with sharp decreases in concentrations with distance from the roadway. Note that the ratio to the NOx levels at LBPW to the Wilmington Community mean is comparable to the two sampling sites in the residential areas of West Long Beach, LWIN (1.23 ± 0.04) and LWBC (1.15 ± 0.04). These ratios indicate that NOx levels are higher (significant within two standard errors) in the residential area of West Long Beach compared to Wilmington, presumably due to closer proximity to the I-710 freeway. Higher NOx levels were also measured at LSUP (adjacent to Pacific Coast Highway), WE11 (west edge of the I-110 freeway), LHUD (near east edge of the Terminal Island Freeway), and LOCN (near the ICTF) with ratios to Wilmington Community mean of 1.78 ± 0.06, 1.77 ± 0.11, 1.33 ± 0.04, and 1.65 ± 0.10, respectively.

Table 3-11. Annual average levels of NOx, SO_2 and H_2S measured at HCMS sites in 2007.

HCMS Sites		NOx	SO_2	H_2S
	SELB	38.3 ± 5.2	0.9 ± 0.5	
	WEMD	40.0 ± 5.6	1.7 ± 1.0	1.3 ± 0.7
	WE11	60.9 ± 6.0	1.2 ± 0.6	
x	WFST	40.0 ± 5.9	0.7 ± 0.4	1.2 ± 0.7
x	WGUL	35.6 ± 4.6	0.7 ± 0.4	
x	WMCD	39.9 ± 6.1	0.7 ± 0.3	
x	WMAR	38.4 ± 5.8	0.8 ± 0.4	
	WSWI	46.4 ± 6.6	1.1 ± 0.6	
x	WLAK	38.6 ± 5.8	0.8 ± 0.4	
	WF49	44.3 ± 6.5	1.3 ± 0.7	
x	WMCF	40.8 ± 5.8	0.9 ± 0.5	
	WPIO	45.7 ± 6.9	0.9 ± 0.4	
	WCOL	47.3 ± 6.7	0.7 ± 0.3	
	LOCN	57.8 ± 6.1	0.8 ± 0.4	
	LHUD	51.4 ± 7.6	0.8 ± 0.4	1.4 ± 0.8
	LWIN	48.9 ± 7.8	0.6 ± 0.3	
	LWBC	43.1 ± 5.7	1.0 ± 0.5	
	LSUP	67.4 ± 9.9	1.3 ± 0.7	
	LBER	78.5 ± 9.2	1.0 ± 0.5	
	LW71	132.7 ± 14.8	1.0 ± 0.6	
	LE71	101.5 ± 8.9	1.0 ± 0.5	
	LBPW	48.4 ± 7.5	0.9 ± 0.5	

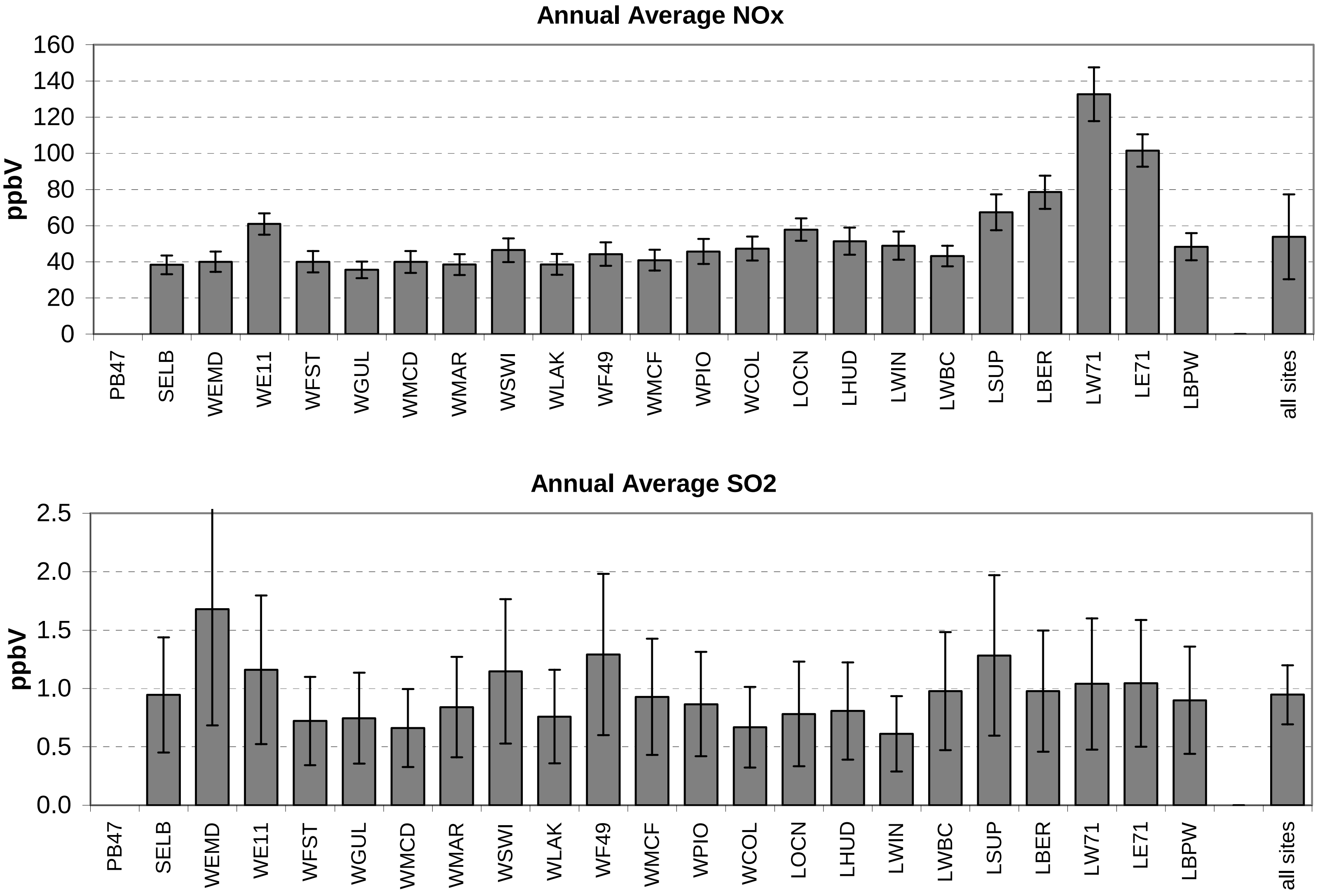

Figure 3-24. Estimated annual mean NOx and SO_2 mixing ratios (ppbv) during the 2007 HCMS. Uncertainties are standard errors of the means based on up to 16 samples.

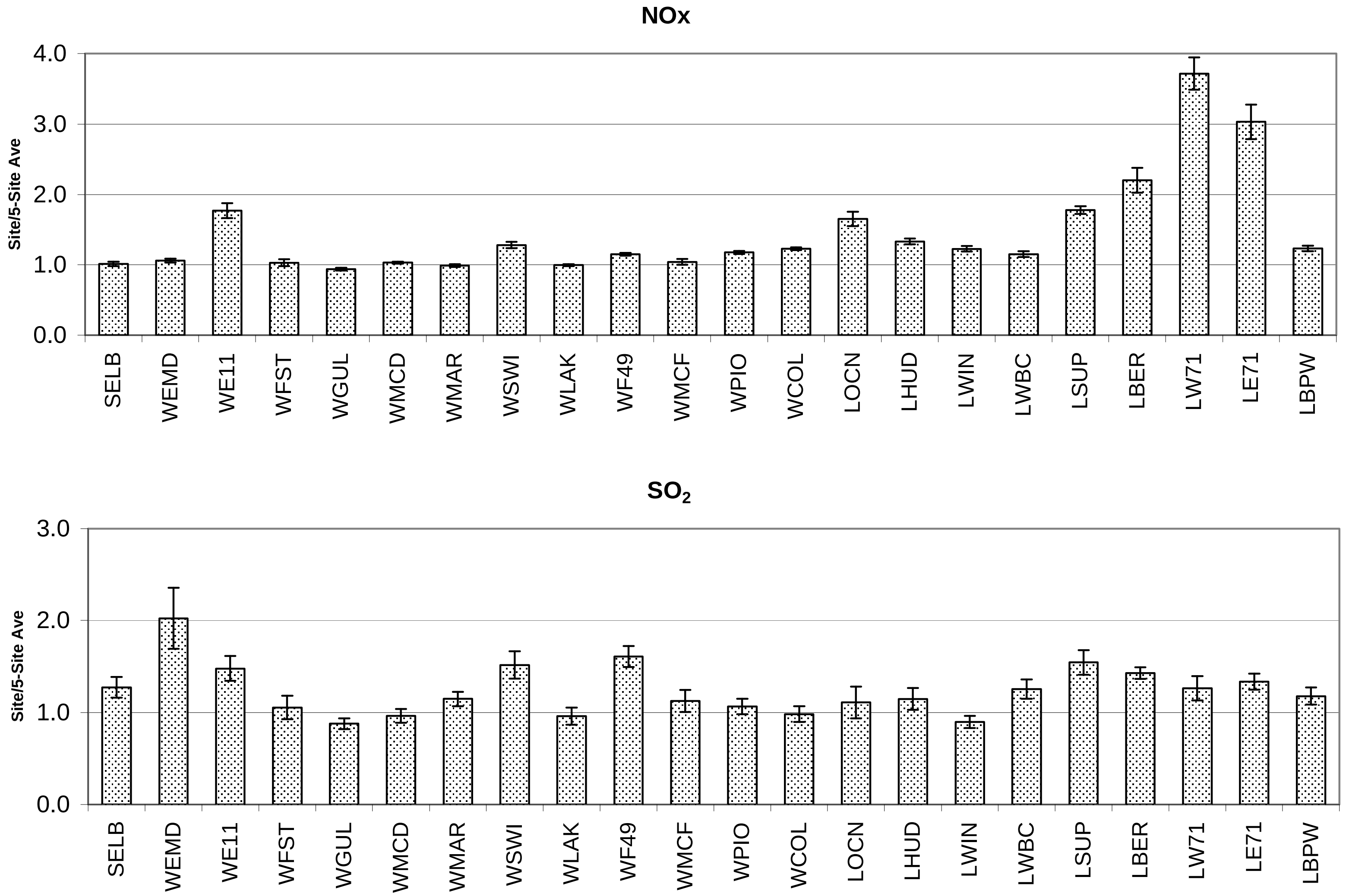

Figure 3-25**.** NOx and SO$_2$ mixing ratios normalized to the mean of six residential sampling sites in Wilmington. Uncertainties are standard errors of the mean ratios.

Ambient levels of SO_2 were highest at WEMD, which is adjacent to the east boundary of a refinery. The mean ratio of SO_2 levels measured at this site to the Wilmington Community mean was 2.02 with higher variability than at the other sites (SE of ± 0.33). The second highest site was E110 (ratios of 1.48 ± 0.13), which is about 400 m east of WEMD. SO_2 levels dropped to levels comparable to the Wilmington Community mean at WFST (1.05 ± 0.13), about 800 m east of WEMD. A desulfurization unit is located near the east edge of the refinery and is likely the source of the higher SO_2 levels at WEMD. The pattern in Figure 3-25 is consistent with higher SO_2 levels nearer to the port due to emission from ships and diesel trucks. Ratios to the Wilmington Community mean are higher (significant to two SE) at WSWI (1.52 ± 0.15), WF49 (1.61 ± 0.11), LSUP (1.54 ± 0.14), LBER (1.43 ± 0.06).

3.2.2 Annual Mean Mixing Ratios of Volatile Organic Toxic Air Contaminants

The annual mean mixing ratios (ppbv) for benzene, toluene, ethylbenzene and xylenes (BTEX) and standard errors of the means are shown in Table 3-12. The 2007 HCMS data are compared to data from the ten fixed MATES-III monitoring sites that operated during April 2004 to March 2006 and to the 2007 data from the routine air toxics monitoring network. The annual average mixing ratios (ppbv) of BTEX tended to be higher near roadways, but this association was not as strong as it was for NOx. Highest levels of toluene were measured at WCOL and WPIO. Local source impacts are the probable explanation in each case. The rear of residence, WPIO, is adjacent to a commercial/light industrial area. On one occasion, DRI personnel observed workers splitting wood with a gas-powered log splitter. WCOL is located next to a small furniture shop. Otherwise, the spatial pattern of annual average concentrations for the toluene, ethylbenzene and xylenes were similar to benzene. The annual mean mixing ratios of benzene are shown in Figure 3-26 relative to the MATES-III data. The mean of the six Wilmington community sites and the two nearest MATES-III sites, North Long Beach and West Long Beach are all near 0.5 ppbv. Furthermore, the range in annual average mixing ratios of benzene in the study area during the HCMS is similar to the range of values measured elsewhere in the SoCAB during MATES-III. Comparisons of the annual averages measured during 2007 at the three routine air toxics monitoring sites with the two prior years during MATES-III show a slight decreasing trend for BTEX.

Table 3-13 shows the annual average ambient levels of aldehydes measured at HCMS sites in 2007 compared to MATES-III sites operated from April 2004 to March 2006 and to SCAQMD/ARB air toxics monitoring sites in 2007. While the annual average mixing ratios of formaldehyde and acetaldehyde were slightly higher near roadways, site-to-site variations were relatively small within the study area and were comparable or slightly lower than annual mean levels measured elsewhere in the SoCAB during MATES-III and at the routine air toxic monitoring site in 2007 as shown in Figures 3-27 and 3-28. These results suggest that secondary formation of these aldehydes within the SoCAB have greater contributions to the annual average levels than local contributions near roadways, especially over sampling durations of seven days. Acrolein levels were generally below the method detection limit of 0.15 ppbv.

Table 3-12. Estimate annual average mixing ratios (ppbv) of BTEX ± standard errors of the mean at HCMS sites in 2007 compared to annual averages for the MATES-III sites during April 2004 to March 2006 and for the routine air toxics monitoring sites in 2007.

Monitoring Program/ Site	Benzene	Toluene	Xylenes	Ethylbenzene [1]		1,3Butadiene
				Radiello Rate	DRI Rate	
HCMS 2007						
SELB	0.37 ± 0.05	1.19 ± 0.20	0.98 ± 0.14	0.46 ± 0.16	0.32 ± 0.11	
WEMD	0.40 ± 0.06	1.18 ± 0.16	0.89 ± 0.13	0.35 ± 0.11	0.24 ± 0.08	
WE11	0.49 ± 0.07	1.36 ± 0.18	1.01 ± 0.13	0.44 ± 0.16	0.30 ± 0.11	
x WFST	0.53 ± 0.08	1.61 ± 0.20	1.33 ± 0.18	0.54 ± 0.16	0.37 ± 0.11	
x WGUL	0.47 ± 0.08	1.60 ± 0.26	1.21 ± 0.15	0.55 ± 0.19	0.38 ± 0.13	
x WMCD	0.49 ± 0.07	1.45 ± 0.18	1.21 ± 0.17	0.52 ± 0.18	0.36 ± 0.12	
x WMAR	0.52 ± 0.08	1.52 ± 0.20	1.31 ± 0.17	0.58 ± 0.19	0.40 ± 0.13	
WSWI	0.45 ± 0.08	1.29 ± 0.19	1.13 ± 0.16	0.52 ± 0.18	0.36 ± 0.12	
x WLAK	0.46 ± 0.06	1.26 ± 0.18	1.06 ± 0.15	0.40 ± 0.12	0.27 ± 0.08	
WF49	0.42 ± 0.07	1.15 ± 0.17	0.91 ± 0.14	0.38 ± 0.13	0.27 ± 0.09	
x WMCF	0.48 ± 0.07	1.49 ± 0.21	1.19 ± 0.15	0.53 ± 0.18	0.36 ± 0.13	
WPIO	0.61 ± 0.08	2.86 ± 0.51	1.77 ± 0.18	0.73 ± 0.20	0.50 ± 0.14	
WCOL	0.50 ± 0.07	3.59 ± 0.47	1.45 ± 0.17	0.50 ± 0.10	0.35 ± 0.07	
LOCN	0.49 ± 0.09*	1.35 ± 0.22*	0.98 ± 0.17*	0.28 ± 0.05*	0.20 ± 0.03*	
LHUD	0.54 ± 0.08	1.47 ± 0.20	1.09 ± 0.16	0.32 ± 0.05	0.22 ± 0.03	
LWIN	0.46 ± 0.07	1.31 ± 0.20	0.95 ± 0.16	0.26 ± 0.04	0.18 ± 0.03	
LWBC	0.54 ± 0.09	1.46 ± 0.24	0.98 ± 0.17	0.43 ± 0.16	0.30 ± 0.11	
LSUP	0.55 ± 0.09	1.78 ± 0.30	1.14 ± 0.21	0.38 ± 0.09	0.26 ± 0.06	
LBER	0.62 ± 0.09	1.71 ± 0.20	1.26 ± 0.17	0.49 ± 0.14	0.34 ± 0.10	
LW71	0.72 ± 0.09	1.72 ± 0.19	1.37 ± 0.18	0.52 ± 0.15	0.36 ± 0.10	
LE71	0.67 ± 0.08	1.61 ± 0.17	1.22 ± 0.16	0.47 ± 0.14	0.32 ± 0.10	
LBPW	0.52 ± 0.10	1.40 ± 0.23	1.00 ± 0.17	0.44 ± 0.17	0.30 ± 0.12	
x 6-site mean	0.48 ± 0.07	1.49 ± 0.21	1.22 ± 0.16	0.52 ± 0.17	0.36 ± 0.12	
ARB Air Toxic 2007						
Los Angeles N. Main	0.53 ± 0.07	1.64 ± 0.21	1.01 ± 0.08	0.21 ± 0.03		0.12 ± 0.02
N. Long Beach	0.41 ± 0.06	1.15 ± 0.18	0.69 ± 0.06	0.16 ± 0.02		0.09 ± 0.02
Rubidous	0.40 ± 0.05	1.26 ± 0.16	0.73 ± 0.06	0.16 ± 0.02		0.08 ± 0.02
MATES-III 4/04 - 3/05						
Anaheim	0.44 ± 0.03	1.55 ± 0.11	0.96 ± 0.04	0.20 ± 0.01		0.08 ± 0.01
Burbank	0.73 ± 0.04	2.68 ± 0.15	1.68 ± 0.06	0.34 ± 0.02		0.15 ± 0.01
Los Angeles N. Main	0.59 ± 0.03	1.84 ± 0.09	1.19 ± 0.04	0.25 ± 0.01		0.12 ± 0.01
Compton	0.82 ± 0.06	2.89 ± 0.24	1.97 ± 0.10	0.40 ± 0.03		0.20 ± 0.02
San Bernardino	0.49 ± 0.02	1.73 ± 0.10	0.97 ± 0.03	0.21 ± 0.01		0.08 ± 0.00
Huntington park	0.76 ± 0.05	2.87 ± 0.18	1.79 ± 0.07	0.36 ± 0.03		0.17 ± 0.01
North Long Beach	0.56 ± 0.03	1.60 ± 0.10	1.04 ± 0.04	0.22 ± 0.02		0.12 ± 0.01
Pico rivera	0.57 ± 0.03	1.97 ± 0.12	1.19 ± 0.04	0.26 ± 0.02		0.12 ± 0.01
Rubiduoux	0.45 ± 0.02	1.53 ± 0.09	0.84 ± 0.03	0.18 ± 0.01		0.08 ± 0.01
West Long Beach	0.57 ± 0.04	1.98 ± 0.16	1.15 ± 0.06	0.27 ± 0.02		0.10 ± 0.01
MATES-III 4/05 - 3/06						
Anaheim	0.42 ± 0.03	1.45 ± 0.12	0.86 ± 0.05	0.20 ± 0.02		0.04 ± 0.01
Burbank	0.69 ± 0.04	2.49 ± 0.15	1.56 ± 0.06	0.35 ± 0.02		0.12 ± 0.01
Los Angeles N. Main	0.57 ± 0.03	1.80 ± 0.10	1.13 ± 0.04	0.26 ± 0.01		0.09 ± 0.01
Compton	0.78 ± 0.06	2.72 ± 0.22	1.81 ± 0.09	0.41 ± 0.03		0.14 ± 0.02
San Bernardino	0.49 ± 0.02	1.69 ± 0.08	0.88 ± 0.03	0.22 ± 0.01		0.04 ± 0.00
North Long Beach	0.48 ± 0.03	1.40 ± 0.10	0.85 ± 0.04	0.20 ± 0.02		0.07 ± 0.01
Rubiduoux	0.43 ± 0.02	1.49 ± 0.09	0.77 ± 0.03	0.19 ± 0.01		0.04 ± 0.01
West Long Beach	0.50 ± 0.03	1.56 ± 0.12	0.91 ± 0.04	0.22 ± 0.02		0.06 ± 0.01

* Based on estimation of missing 7-day measurements.

[1] The sampling rate for ethylbenzene determined experimentally in this study were 1.5 times higher than published by Radiello. Ethylbenzene values are 30% lower using the sampling rate determined experimentally by DRI.

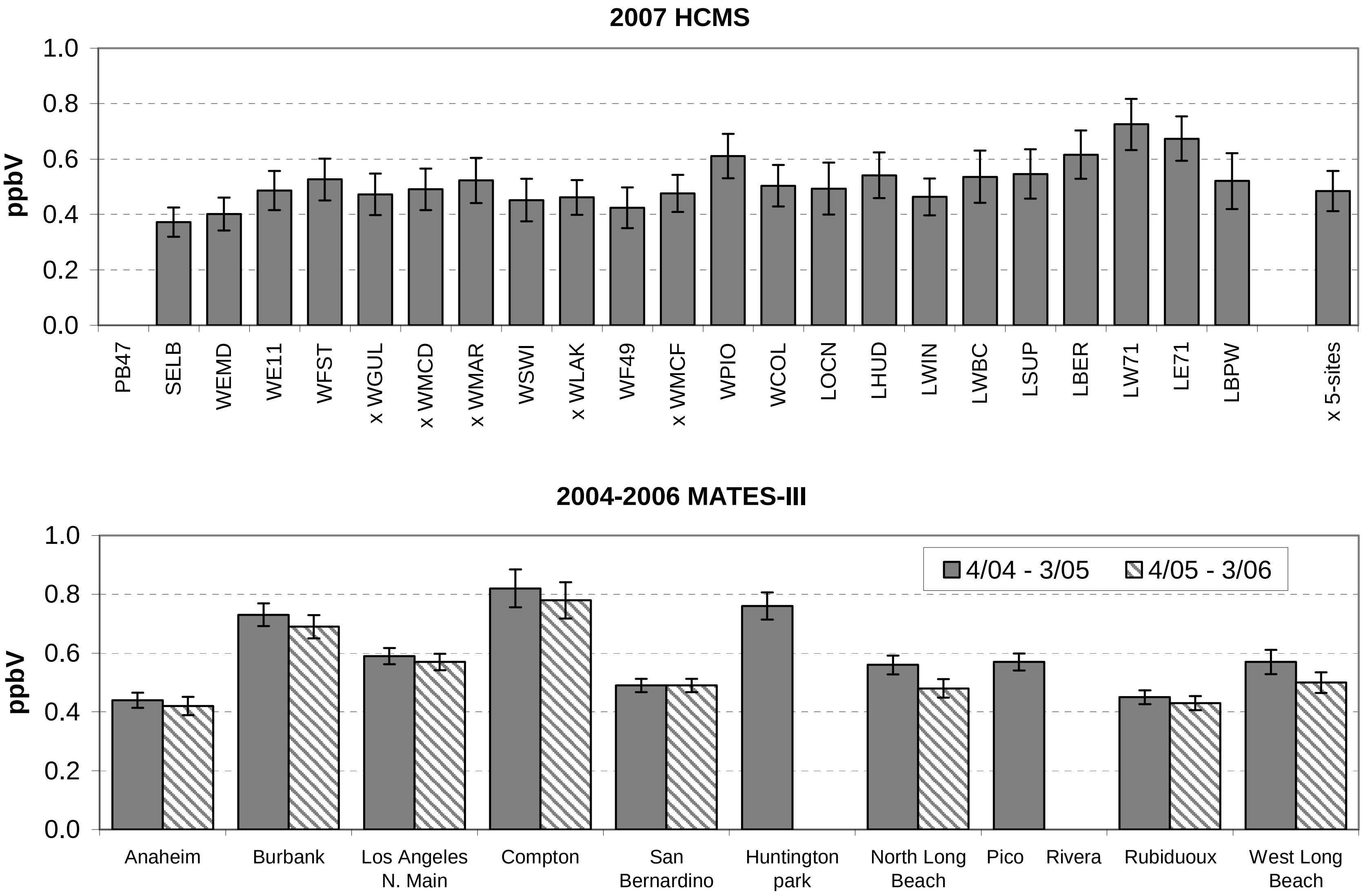

Figure 3-26. Annual average benzene mixing ratios (ppbv) during the HCMS and MATES-III. Uncertainties are standard errors of the means based on up to 16 samples for HCMS and up to 121 samples per year for MATES-III.

Table 3-13. Estimated annual average mixing ratios (ppbv) of aldehydes at HCMS sites in 2007 compared to measurements at MATES-III sites during April 2004 to March 2006 and the routine air toxics monitoring sites in 2007.

Monitoring Program/Site	**Formaldehyde**	**Acetaldehyde**	**Acrolein**
HCMS 2007			
SELB	1.89 ± 0.21	1.04 ± 0.16	0.1 ± 0.3
WEMD	1.86 ± 0.18	1.04 ± 0.19	0.5 ± 0.4
WE11	1.97 ± 0.18	1.01 ± 0.16	0.2 ± 0.3
x WFST	1.98 ± 0.20	1.05 ± 0.17	0.3 ± 0.3
x WGUL	1.80 ± 0.20	1.03 ± 0.19	0.1 ± 0.3
x WMCD	1.97 ± 0.19	1.21 ± 0.21	0.1 ± 0.3
x WMAR	2.02 ± 0.22	1.16 ± 0.20	0.3 ± 0.3
WSWI	1.88 ± 0.24	1.14 ± 0.23	0.1 ± 0.3
x WLAK	1.83 ± 0.20	1.11 ± 0.21	0.1 ± 0.3
WF49	1.80 ± 0.24	1.08 ± 0.22	0.1 ± 0.3
x WMCF	1.87 ± 0.19	1.08 ± 0.19	0.1 ± 0.3
WPIO	2.17 ± 0.17	1.20 ± 0.22	0.1 ± 0.3
WCOL	2.17 ± 0.22	1.09 ± 0.18	0.3 ± 0.3
LOCN	1.96 ± 0.26*	1.13 ± 0.23*	0.4 ± 0.3
LHUD	1.96 ± 0.18	1.19 ± 0.20	0.3 ± 0.3
LWIN	2.05 ± 0.23	1.16 ± 0.19	0.1 ± 0.3
LWBC	2.09 ± 0.21	1.20 ± 0.20	0.1 ± 0.3
LSUP	2.35 ± 0.23	1.14 ± 0.20	0.1 ± 0.3
LBER	2.43 ± 0.23	1.18 ± 0.19	0.4 ± 0.3
LW71	2.48 ± 0.25	1.24 ± 0.21	0.1 ± 0.3
LE71	2.20 ± 0.17	1.20 ± 0.17	0.1 ± 0.3
LBPW	2.00 ± 0.27	1.10 ± 0.21	0.0 ± 0.3
x 6-site mean	1.91 ± 0.20	1.11 ± 0.20	0.2 ± 0.3
ARB Air Toxic 2007			
Los Angeles N. Main	5.87 ± 0.55	0.94 ± 0.13	0.75 ± 0.07
N. Long Beach	2.33 ± 0.17	0.81 ± 0.09	0.87 ± 0.06
Rubidous	2.88 ± 0.29	1.08 ± 0.13	0.51 ± 0.05
MATES-III 4/04 - 3/05			
Anaheim	2.91 ± 0.11	1.28 ± 0.06	NA
Burbank	3.73 ± 0.13	1.96 ± 0.08	NA
Los Angeles N. Main	4.47 ± 0.17	2.09 ± 0.10	NA
Compton	3.17 ± 0.12	1.56 ± 0.07	NA
San Bernardino	3.39 ± 0.18	1.79 ± 0.10	NA
Huntington park	4.08 ± 0.14	1.33 ± 0.08	NA
North Long Beach	3.84 ± 0.14	1.30 ± 0.06	NA
Pico rivera	3.49 ± 0.12	1.68 ± 0.07	NA
Rubiduoux	3.47 ± 0.16	1.64 ± 0.08	NA
West Long Beach	3.19 ± 0.15	1.41 ± 0.07	NA
MATES-III 4/05 - 3/06			
Anaheim	2.99 ± 0.12	1.31 ± 0.06	NA
Burbank	3.84 ± 0.15	1.95 ± 0.08	NA
Los Angeles N. Main	4.02 ± 0.17	1.69 ± 0.07	NA
Compton	2.94 ± 0.15	1.52 ± 0.09	NA
San Bernardino	3.81 ± 0.18	1.98 ± 0.09	NA
North Long Beach	3.56 ± 0.15	1.31 ± 0.06	NA
Rubiduoux	3.53 ± 0.16	1.75 ± 0.08	NA
West Long Beach	3.36 ± 0.14	1.43 ± 0.08	NA

* Based on estimation of missing 7-day measurements.

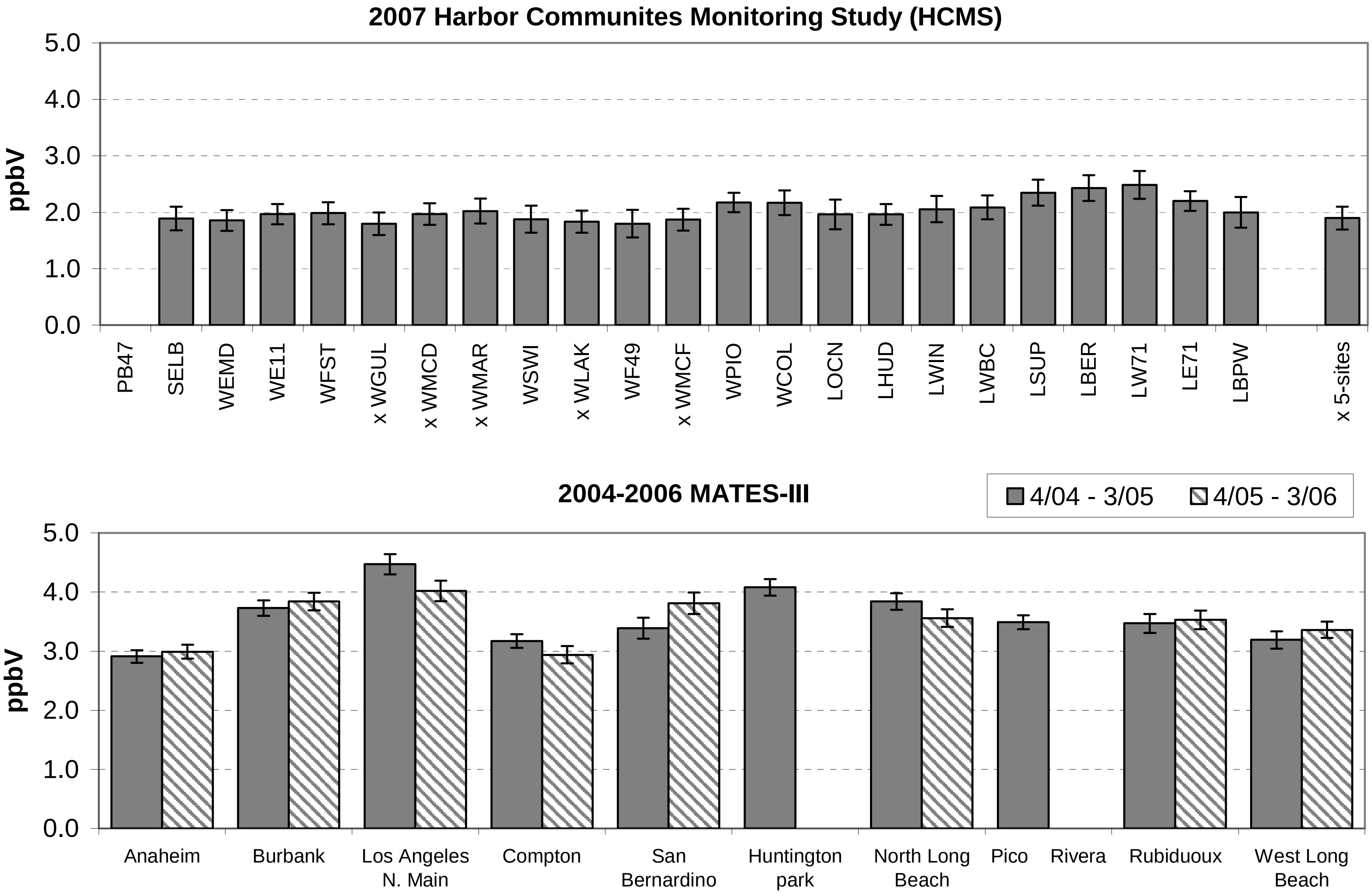

Figure 3-27. Estimated annual average formaldehyde mixing ratios (ppbv) during 2007 HCMS and MATES-III. Uncertainties are standard errors of the means based on up to 16 samples for HCMS and up to 121 samples per year for MATES-III.

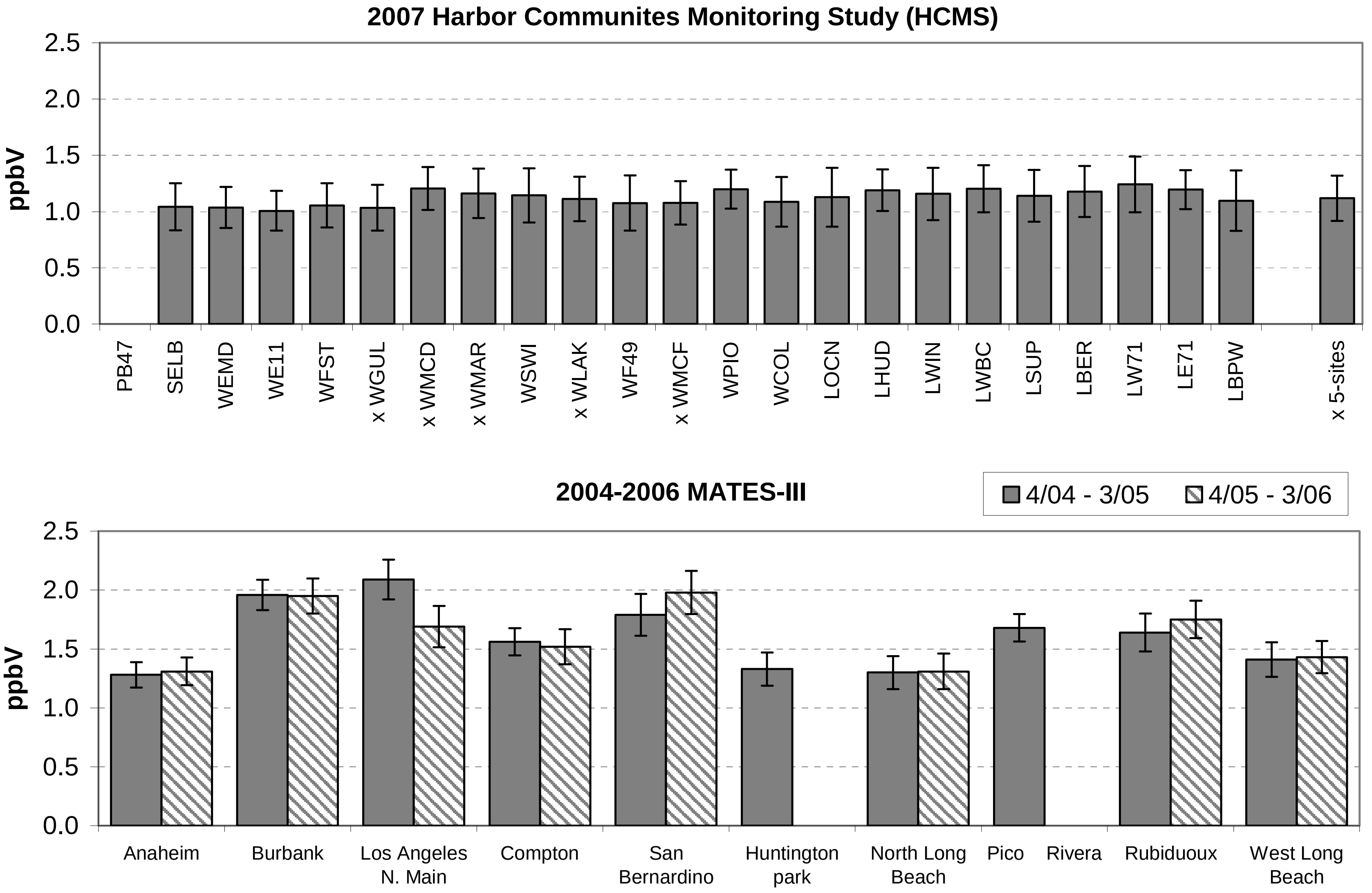

Figure 3-28. Estimated annual average acetaldehyde mixing ratios (ppbv) during HCMS and MATES-III. Uncertainties are standard errors of the means based on up to 16 samples for HCMS and up to 121 samples per year for MATES-III.

3.2.3 Annual Mean Concentrations of Particulate Matter

Unlike passive samples that had nearly complete data capture during the HCMS, data for particulate matter were incomplete for several sites due to disruptions in electrical power and sampler malfunctions resulting from high humidity conditions. An alternative approach was required to minimize the effect of missing data on the annual mean concentrations of $PM_{2.5}$ mass, OC and EC. Missing values were estimated for sampling sites with more than two missing values in a single season. First, ratios of the concentrations for each valid sample to the average concentrations at all samples (except the Port of Los Angeles boundary site) for the 7-day sampling period were determined. Missing values for a given site were then estimated by multiplying its mean ratio with the mean concentration of all samples for that 7-day sampling period. The asterisks in Table 3-6 indicate the estimated annual means that are based on this approach. The uncertainties in the estimated missing value is the standard error of the mean times the mean concentration of all samples in a sampling period. The annual averages for particulate matter concentrations were based on the four seasonal averages. Thus, they have higher standard errors of the mean rather than averages of the 16 seven-day integrated samples.

The estimated annual mean $PM_{2.5}$, TC and EC concentrations from the HCMS are compared in Table 3-14 to the MATES-III annual averages for April 2004 to March 2005, April 2005 to March 2006, and to 2007 data for the routine air toxic monitoring program. Results for elemental carbon were qualitatively similar to NOx with higher concentrations closer to roadways. As shown earlier for NOx, we examined the spatial variations in $PM_{2.5}$, TC and EC concentrations by normalizing each sample to the mean concentrations of the corresponding 7-day samples from four Wilmington residential sampling sites. The mean ratios and standard errors are shown in Figure 3-29 and Table 3-15.

EC levels were uniformly lower at the four Wilmington community sampling sites (ratio to four-site mean ranging from 0.92 to 1.01) and at the residential sampling site in San Pedro (ratio of 1.08 ± 0.08). The EC concentrations at LBER and LBPW (about 18 m west and 300 m east of the I-710 freeway, respectively) were 2.26 ± 0.13 and 1.24 ± 0.08 times higher than the Wilmington Community mean, respectively. As with NOx, the spatial variations in EC concentrations near the I-710 freeway are consistent with sharp decrease in pollutant concentrations with distance from the roadway. Higher EC concentrations were significantly higher at LOCN (near the ICTF), LSUP (adjacent to Pacific Coast Highway), LHUD (near east edge of the Terminal Island Freeway), WSWI (near the north end of the Port of Los Angeles) and with ratios to Wilmington Community mean of 2.62 ± 0.26, 1.76 ± 0.11, 1.64 ± 0.28, and 1.85 ± 0.11, respectively. EC concentrations are also slightly higher in the residential areas of West Long Beach (ratios of 1.09 ± 0.04 for LWIN and 1.08 ± 0.07 for LWBC presumably due to closer proximity to the I-710 freeway. The spatial variations in TC and $PM_{2.5}$ concentrations were very similar to EC, but the differences in concentrations of TC and $PM_{2.5}$ between residential and near-source sampling locations are less than for EC. Local vehicle emissions are superimposed on the contributions of other sources of $PM_{2.5}$ which appear to be more spatially uniform. These results suggest that most of the contributions to $PM_{2.5}$ are regional rather than local.

Table 3-14. Annual average measurements of particulate matter at HCMS sites in 2007 compared to MATES-III sites during April 2004 to March 2006.

Program and Site	PM$_{2.5}$	TC	EC	DPC [1]	DPM [2]	DPC/TC	DPM/PM$_{2.5}$
HCMS 2007							
SELB	12.8 ± 2.0	3.4 ± 0.8	1.3 ± 0.4	2.4 ± 0.8	3.0 ± 1.0	72.0%	23.1%
WEMD	13.4 ± 2.5 *	3.7 ± 0.8	1.4 ± 0.4	2.7 ± 0.9	3.3 ± 1.0	72.5%	24.3%
WFST	14.4 ± 3.1	4.0 ± 0.9	1.3 ± 0.4	2.5 ± 0.8	3.0 ± 0.9	61.2%	20.9%
x WGUL	12.9 ± 2.5 *	3.8 ± 0.9 *	1.2 ± 0.4 *	2.4 ± 0.8 *	2.9 ± 1.0 *	62.1%	22.6%
x WMCD	13.1 ± 2.3	3.6 ± 0.9	1.2 ± 0.4	2.4 ± 0.8	2.9 ± 1.0	65.1%	21.8%
WSWI	14.1 ± 2.6 *	4.7 ± 1.0 *	2.1 ± 0.6 *	4.0 ± 1.2 *	4.9 ± 1.5 *	86.6%	34.9%
x WLAK	12.5 ± 2.8	3.6 ± 0.9	1.3 ± 0.4	2.4 ± 0.8	2.9 ± 1.0	66.3%	23.5%
WF49	13.9 ± 2.6 *	3.6 ± 0.6	1.4 ± 0.4	2.8 ± 0.7	3.4 ± 0.9	77.3%	24.3%
x WMCF	13.5 ± 2.7 *	3.7 ± 0.8 *	1.3 ± 0.4 *	2.5 ± 0.8 *	3.0 ± 1.0 *	67.6%	22.4%
WPIO	15.4 ± 3.0	4.5 ± 1.1	1.6 ± 0.5	3.1 ± 1.0	3.8 ± 1.2	68.9%	24.4%
WCOL	14.5 ± 2.5	4.4 ± 1.3	1.5 ± 0.6	2.9 ± 1.2	3.5 ± 1.5	65.4%	24.4%
LOCN	16.4 ± 2.9 *	6.0 ± 1.1 *	2.9 ± 0.6 *	5.5 ± 1.3 *	6.7 ± 1.5 *	92.0%	41.1%
LHUD	14.8 ± 3.3	4.8 ± 1.2 *	1.9 ± 0.6 *	3.7 ± 1.1 *	4.5 ± 1.4 *	76.0%	30.4%
LWIN	14.9 ± 2.8 *	3.9 ± 1.0	1.4 ± 0.5	2.7 ± 0.9	3.3 ± 1.1	68.3%	22.1%
LWBC	14.7 ± 3.8	4.2 ± 1.1 *	1.5 ± 0.5 *	2.9 ± 1.0 *	3.5 ± 1.2 *	67.7%	23.8%
LSUP	15.8 ± 2.7	5.1 ± 1.1 *	2.1 ± 0.6 *	4.1 ± 1.2 *	4.9 ± 1.5 *	79.3%	31.3%
LBER	15.5 ± 1.9	5.8 ± 1.2	2.7 ± 0.7	5.1 ± 1.3	6.2 ± 1.6	87.8%	40.1%
LBPW	14.4 ± 2.7	4.2 ± 1.1	1.6 ± 0.5	3.1 ± 1.0	3.7 ± 1.3	73.6%	25.8%
Port of LA 2007							
Wilmington (WC)	13.7		1.6				
Coastal Boundary (CB)	10.4		1.2				
San Pedro (SPC)	11.3		1.5				
Source-dominated (SD)	12.4		2.2				
SCAQMD 2007							
Los Angeles N. Main	16.7						
North Long Beach	14.6						
MATES-III 4/04 - 3/05							
Anaheim	17.7 ± 0.9	7.2 ± 0.3	1.2 ± 0.1		2.2		12.1%
Burbank	21.3 ± 1.2	9.5 ± 0.4	1.8 ± 0.1		3.3		15.6%
Los Angeles N. Main	19.4 ± 1.0	8.2 ± 0.3	1.6 ± 0.1		3.0		14.2%
Compton	19.5 ± 1.0	8.7 ± 0.4	1.6 ± 0.1		2.8		13.2%
San Bernardino	21.4 ± 1.3	9.4 ± 0.4	1.8 ± 0.1		3.6		16.1%
Huntington park	22.4 ± 1.2	10.5 ± 0.5	2.2 ± 0.2		3.6		15.3%
North Long Beach	18.5 ± 0.9	7.7 ± 0.4	1.5 ± 0.1		2.3		12.2%
Pico Rivera	20.7 ± 1.1	9.0 ± 0.3	2.0 ± 0.1		3.5		16.0%
Rubiduoux	23.4 ± 1.4	8.0 ± 0.4	1.5 ± 0.1		2.6		11.6%
West Long Beach	18.4 ± 0.9	8.3 ± 0.5	2.0 ± 0.2		3.3		16.2%
MATES-III 4/05 - 3/06							
Anaheim	17.4 ± 0.9	7.9 ± 0.4	1.5 ± 0.1		2.8		15.9%
Burbank	20.6 ± 0.9	10.7 ± 0.4	2.1 ± 0.1		4.0		19.5%
Los Angeles N. Main	18.0 ± 0.9	10.3 ± 0.4	2.0 ± 0.1		4.3		22.3%
Compton	18.2 ± 0.9	8.7 ± 0.4	1.8 ± 0.1		3.2		17.0%
San Bernardino	21.7 ± 1.2	10.7 ± 0.4	2.2 ± 0.1		4.7		20.6%
North Long Beach	17.1 ± 0.9	8.3 ± 0.4	1.5 ± 0.1		2.8		15.8%
Rubiduoux	22.4 ± 1.3	9.2 ± 0.4	1.8 ± 0.1		3.8		16.4%
West Long Beach	18.3 ± 0.9	9.1 ± 0.5	2.1 ± 0.2		3.9		20.4%

[1] Diesel Particulate Carbon

[2] Diesel Particulate Matter

* Indicates more than two missing values in any single season.

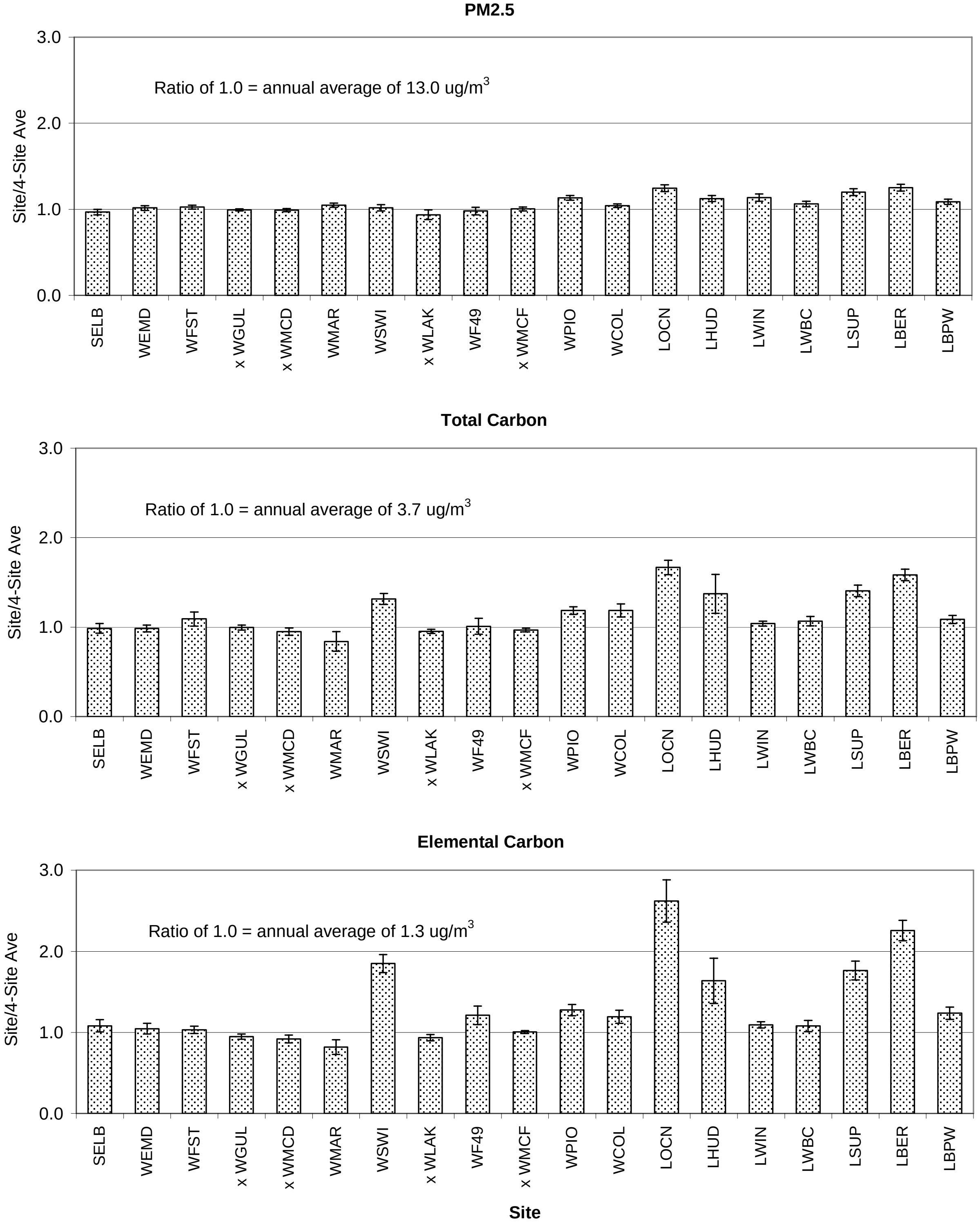

Figure 3-29. Mean of the 7-day integrated $PM_{2.5}$, TC and EC concentrations normalized to the mean of four residential sampling sites in Wilmington. Uncertainties are standard errors of the mean ratios.

Table 3-15. Mean of the 7-day integrated $PM_{2.5}$, TC and EC concentrations normalized to the mean of four residential sampling sites in Wilmington. Uncertainties are standard errors of the mean ratios.

	PM2.5		**TC**		**EC**	
Site	**n**	**Ratio ± SE**	**n**	**Ratio ± SE**	**n**	**Ratio ± SE**
SELB	16	0.96 ± 0.03	13	0.99 ± 0.05	13	1.10 ± 0.07
WEMD	12	1.01 ± 0.03	14	0.98 ± 0.04	14	1.05 ± 0.06
WFST	15	1.02 ± 0.02	14	1.07 ± 0.05	14	1.04 ± 0.04
WGUL	12	0.99 ± 0.01	12	0.99 ± 0.04	12	0.96 ± 0.04
WMCD	14	0.99 ± 0.02	16	0.94 ± 0.04	16	0.93 ± 0.05
WMAR	10	1.04 ± 0.02	7	0.82 ± 0.10	7	0.83 ± 0.09
WSWI	8	1.02 ± 0.04	9	1.31 ± 0.06	9	1.85 ± 0.11
WLAK	14	0.93 ± 0.05	16	0.95 ± 0.03	16	0.95 ± 0.04
WF49	8	0.98 ± 0.04	13	1.01 ± 0.09	13	1.22 ± 0.11
WMCF	11	1.00 ± 0.03	13	0.96 ± 0.03	13	1.02 ± 0.03
WPIO	13	1.13 ± 0.03	15	1.18 ± 0.04	15	1.28 ± 0.06
WCOL	12	1.04 ± 0.02	15	1.17 ± 0.07	15	1.20 ± 0.08
LOCN	11	1.25 ± 0.04	10	1.67 ± 0.08	10	2.62 ± 0.26
LHUD	12	1.12 ± 0.03	11	1.33 ± 0.16	11	1.63 ± 0.25
LWIN	12	1.13 ± 0.04	16	1.03 ± 0.02	16	1.10 ± 0.03
LWBC	14	1.06 ± 0.03	11	1.05 ± 0.04	11	1.09 ± 0.06
LSUP	15	1.20 ± 0.04	10	1.39 ± 0.06	10	1.77 ± 0.11
LBER	13	1.25 ± 0.04	14	1.59 ± 0.06	14	2.27 ± 0.12
LBPW	14	1.08 ± 0.03	14	1.09 ± 0.04	14	1.25 ± 0.07

3.3 Estimation of Diesel Particulate Matter (DPM)

Diesel particulate carbon (DPC) concentrations were estimated at each site from the measured EC concentrations times the slope of the correlation between total carbon and EC at the near road sampling locations shown in Figure 3-9 for each season. TC and EC are well correlated (R^2 between 0.8 and 0.9) with a slopes between 1.5 and 2.2. Using these regression results, we estimated the upper-bound ambient concentrations of DPC from the average EC concentrations at each site. Diesel particulate matter (DPM) was estimated from the following relationship:

Diesel Particulate Matter (DPM) = EC + 1.46 (DPC-EC)

where 1.46 is the ratio of diesel particulate organic matter (DPOM) to DPC from the Gasoline/Diesel PM Split dynamometer testing of diesel trucks in the Riverside, CA area (El-Zanan et al., 2008). Metals have a minor contribution to DPM and can be excluded in the above DPM calculation.

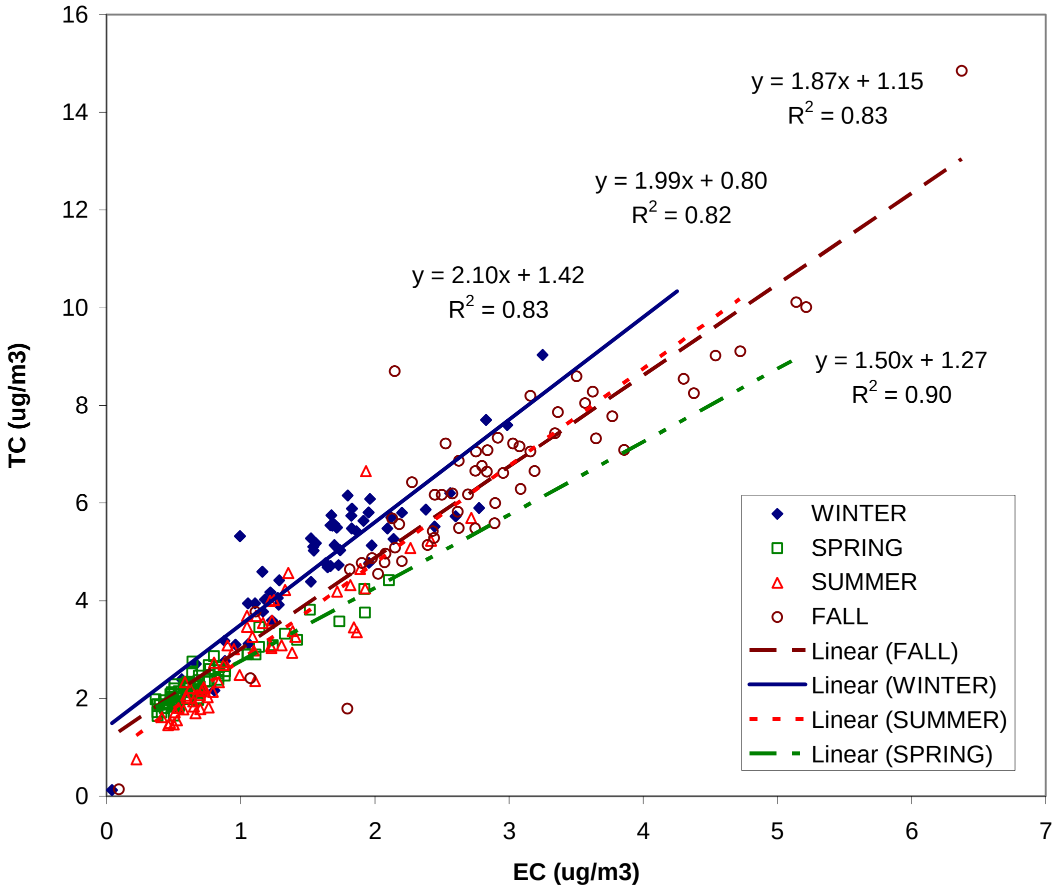

Figure 3-30. Correlations of TC and EC by season. Diesel particulate carbon (DPC) is estimated by multiplying the measured EC times the slope of the associated seasonal regression between TC and EC.

Table 3-14 shows the DPC and DPM estimates for the HCMS sampling sites as well as the DPC/TC and DPM/$PM_{2.5}$ ratios. The contributions of diesel exhaust to ambient $PM_{2.5}$ were derived by SCAQMD for MATES-III using the Chemical Mass Balance receptor model. Figure 3-31 compares the MATES-III apportionments of the DPM contributions with the DPM contributions at the HCMS sampling sites from the EC surrogate method. The annual average concentrations of DPM at the HCMS residential sampling sites are similar to those measured during MATES-III at the West Long Beach and North Long Beach monitoring sites and are comparable or lower than at other MATES-III sites in the SoCAB. However, as discuss earlier, higher concentrations of DPM as well as EC and NOx were measured at sites in closer proximity to diesel truck traffic. Higher concentrations of DPM are also likely in other part of the SoCAB near major truck routes from the port area to the Inland Empire along SR-91, I-605, SR-60 and out of the basin along I-5 and I-10.

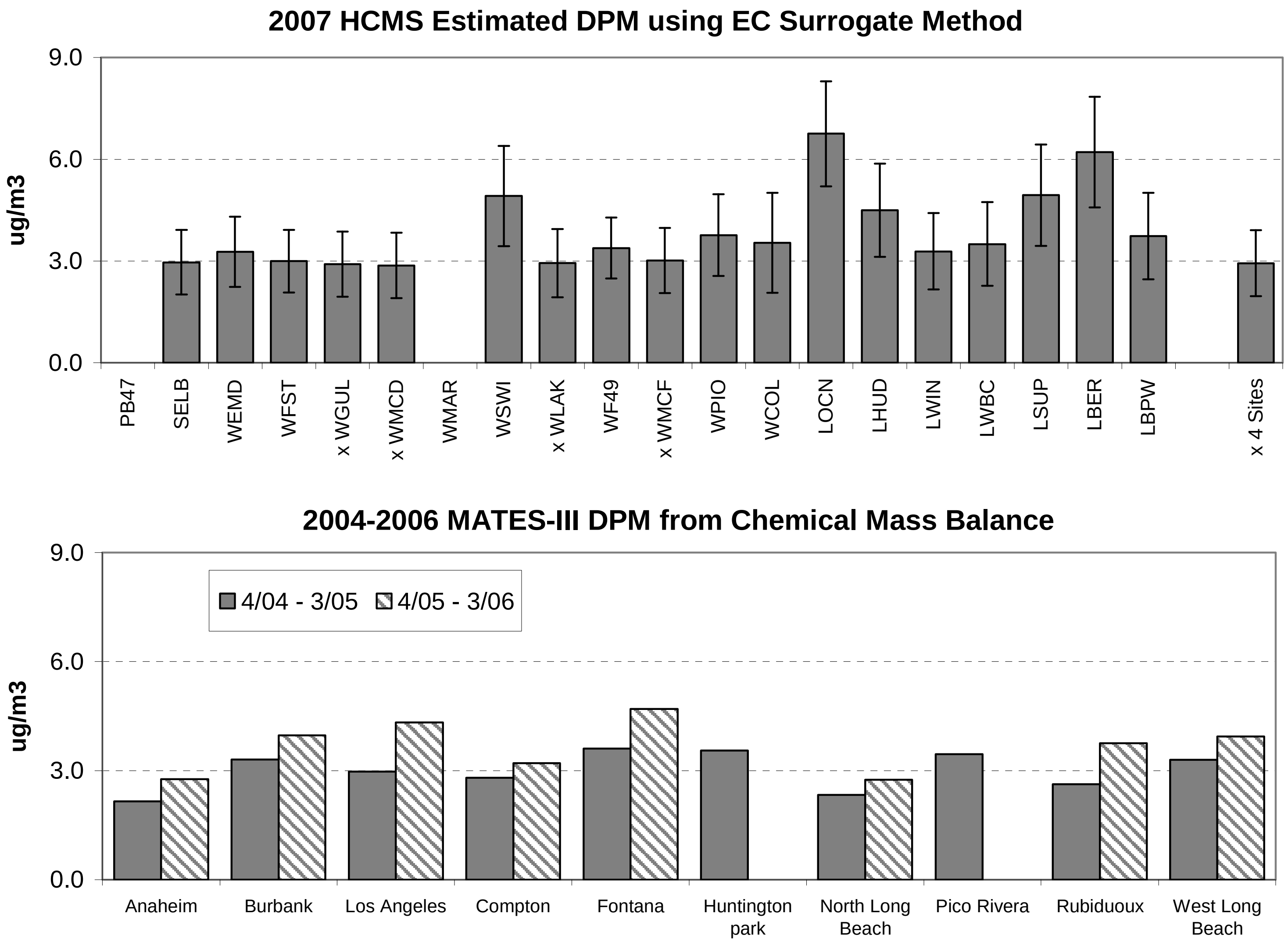

Figure 3-31. Estimated annual mean diesel particulate matter concentrations ($\mu g/m^3$) and standard errors of the four seasonal means during the HCMS and MATES-III.

3.4 Day of Week and Diurnal Variations in $PM_{2.5}$ and Black Carbon Concentrations

Figure 3-32 and 3-33 show the time series of hourly averaged photoacoustic black carbon (µg/m^3) and estimated DustTrak $PM_{2.5}$ mass at the near-road sampling sites during winter and summer seasons, respectively. Each hourly average consists of a minimum of 75 percent of the 1-minute averages for the hour. The time series for BC and DustTrak $PM_{2.5}$ are generally well correlated and especially at LBER and LOCN, which are the two sites located nearest to diesel traffic. Note the substantially lower BC concentrations on Sundays when heavy duty diesel truck traffic is much lower. Periods of higher PM/BC ratios were observed, most noticeably during February 21-22 and March 10-12. These higher ratios agree with the 7-day integrated filter-based carbon and PM measurements.

Figure 3-34 and 3-35 show the diurnal variations of the hourly-averaged photoacoustic BC and estimated (uncorrected) DustTrak $PM_{2.5}$ mass concentrations (µg/m^3), respectively. The box and whisker plots indicate the distributions of the hourly averages during the winter field study. The diurnal patterns for BC and $PM_{2.5}$ are similar at all three sites reflecting both time variations in traffic volumes and degree of atmospheric mixing and dispersion. BC concentrations are highest at BFL during the day reflecting the higher diesel truck traffic near this site. While the mean PM concentrations are also higher at LBER, the maximum concentrations are higher at both LBPW and LHUD than LBER for all hours. This again suggests that there may be episodes of higher PM concentrations when the major contribution to PM may be other than local diesel traffic.

3.5 Seasonal Variations

In addition to the spatial and temporal patterns of pollutant emissions, changes in meteorological conditions are a dominant factor in the diurnal, day-to-day and seasonal variations in pollutant concentrations. During summer, the sea-land breeze is strong during the day with a weak land-sea breeze at night. Owing to the high summer temperatures and extensive urbanization in the SoCAB, the land surface temperature does not usually fall below the water temperature at night and nocturnal and morning winds are less vigorous than daytime winds. The land surface cools sufficiently to create surface inversions with depths as shallow as ~50 m. Surface heating usually erodes the surface and marine layers within a few hours after sunrise each day resulting in lower pollutant concentrations during the day. Summertime flow patterns in the SoCAB are from the west and south during the morning, switching to predominantly westerly winds by the afternoon. The prevailing winds in the study area are affected by the Palos Verdes Hills, which are located west of the study area. The wind roses in Figure 2-4 show that winds in Wilmington are almost exclusively from 135 (southeast) to 315 degrees (northwest) throughout the year. Winds are most frequently from the northwest during winter, southeast during summer and west during spring and fall. Winds near the ports are typically calm overnight and switch from northerly during the morning to southerly in the afternoon. The semi-permanent combination of Pacific anticyclone and ‘thermal’ low pressure that extends up from Mexico into the Central Valley of California in summer begins to break down in fall. The cold/dry penetrations that affect the southern California coast do not typically begin until early December (late fall). These cold/dry penetrations are usually associated with northwesterly flow, and the SoCAB is usually scoured of pollutants during these episodes. The synoptic weather situations that favor increases in pollution (as measured by $PM_{2.5}$ concentrations) appear to be the quiescent periods during the fall season where steady-state high pressure (anticyclones) covers the southern half of California.

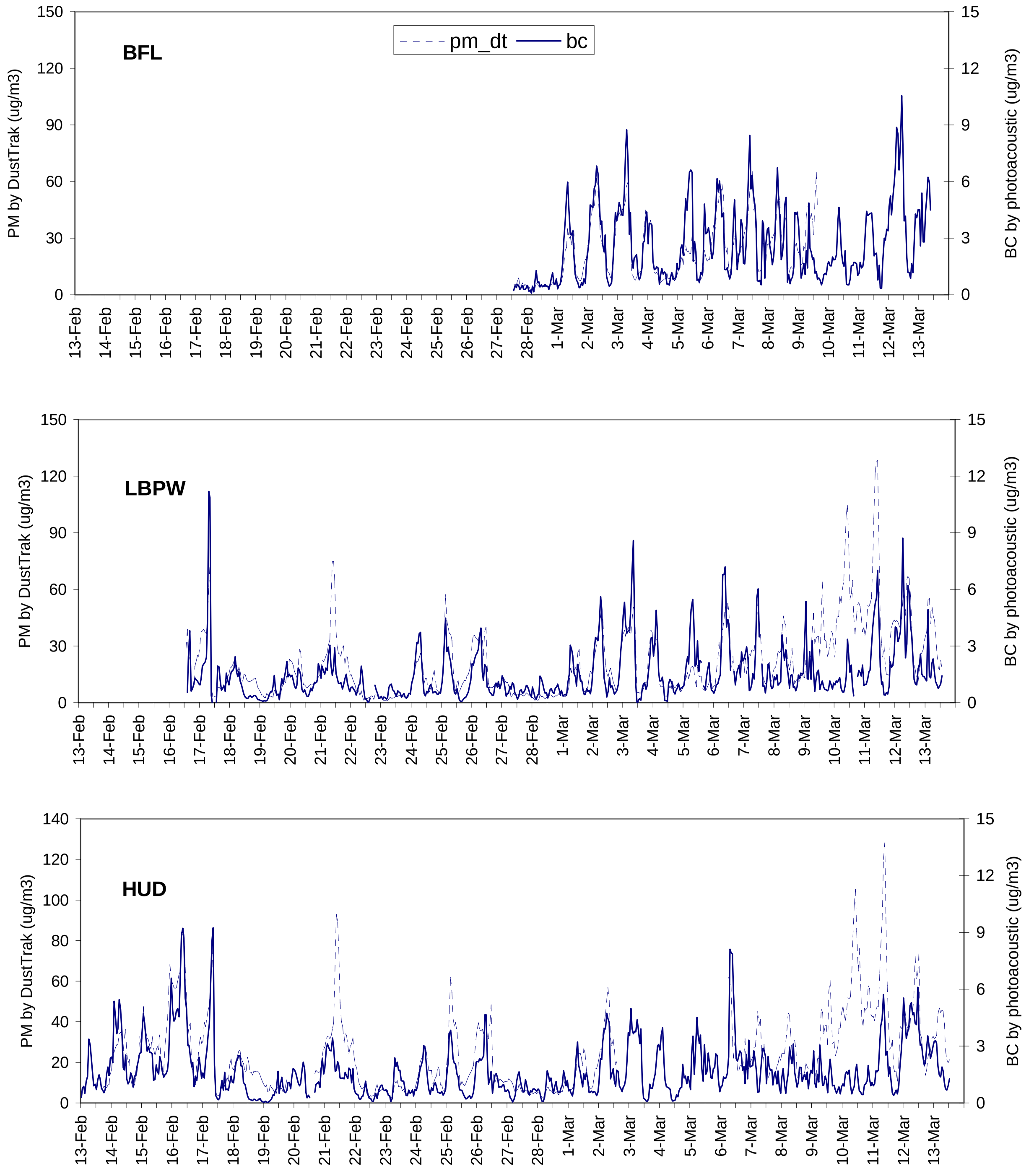

Figure 3-32. Time series of hourly averaged photoacoustic black carbon (µg/m^3) and estimated DustTrak PM$_{2.5}$ mass (uncorrected) at near-road sampling sites during winter season. Each hourly average consists of a minimum of 75 percent of the 1-minute averages for the hour. Sundays are February 18 and 25 and March 4 and 11.

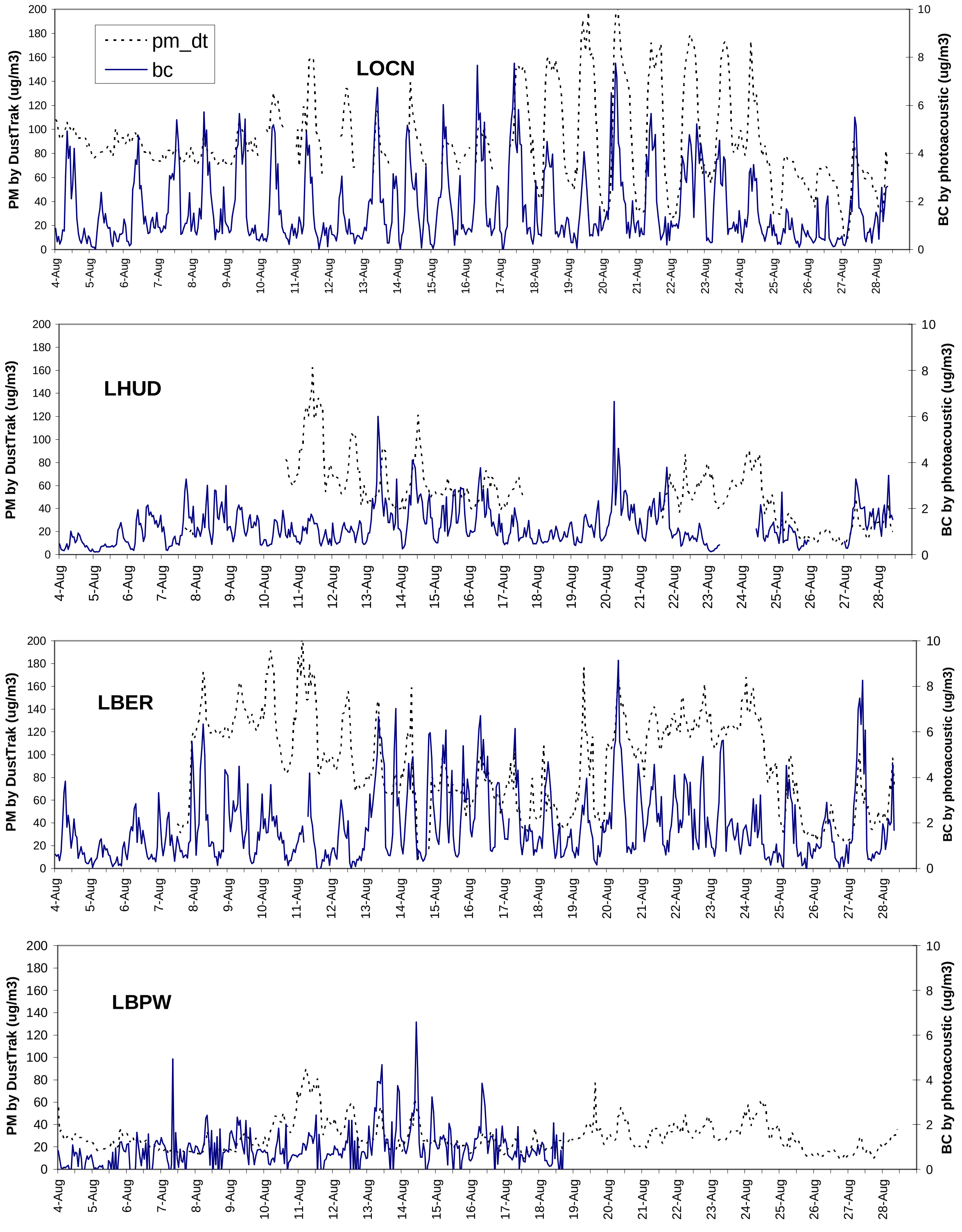

Figure 3-33. Time series of hourly averaged photoacoustic black carbon (µg/m^3) and estimated DustTrak PM$_{2.5}$ mass (uncorrected) at near-road sampling sites during summer season. Each hourly average consists of a minimum of 75 percent of the 1-minute averages for the hour. Sundays are August 5, 12, 19, and 26.

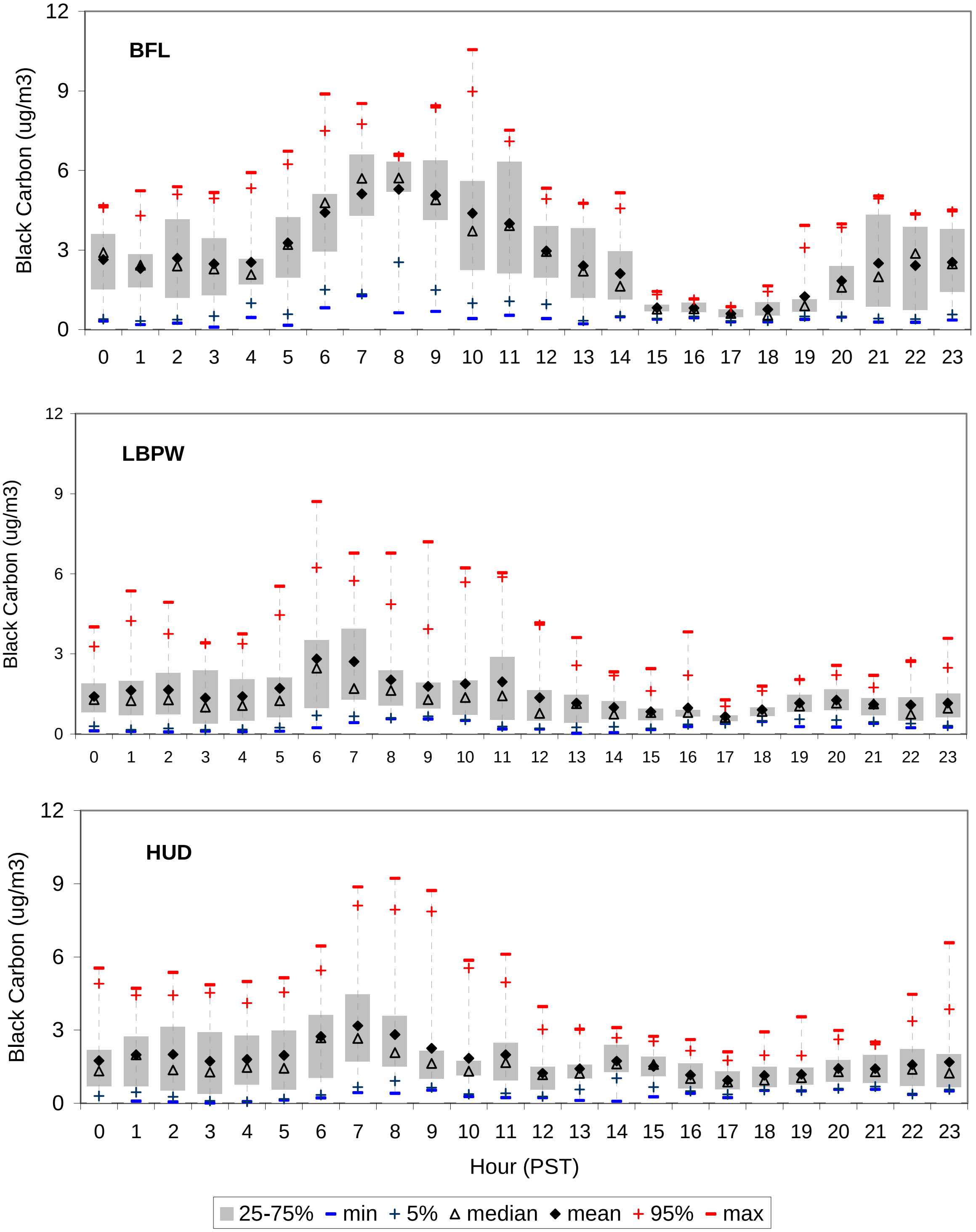

Figure 3-34. Diurnal variations of hourly-averaged photoacoustic black carbon (µg/m^3) during winter season. Each hourly average consists of a minimum of 75 percent of the 1-minute averages for the hour. The box and whisker plots indicate the distributions of the hourly averages during the winter field study.

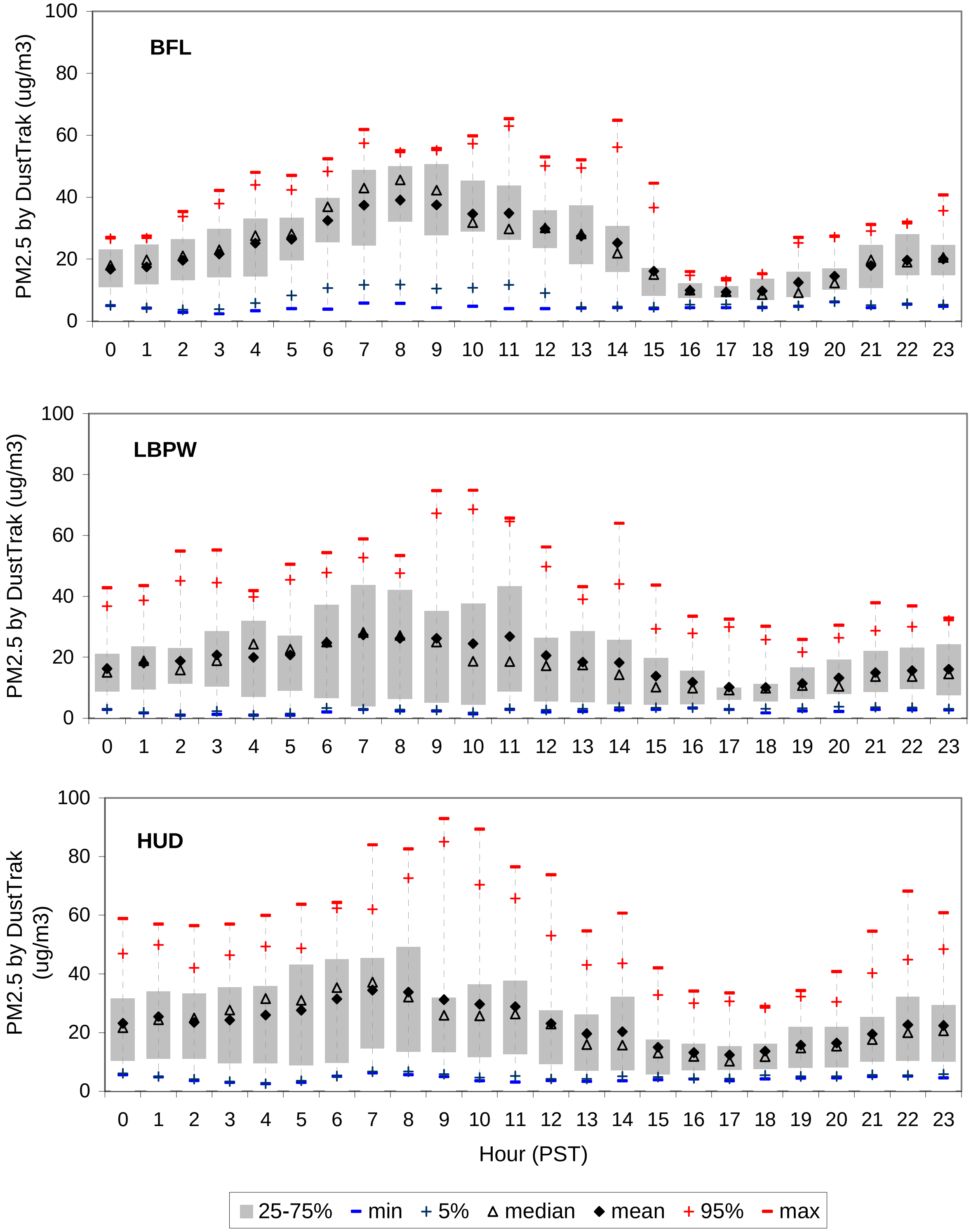

Figure 3-35. Diurnal variations of hourly-averaged estimated (uncorrected) DustTrak $PM_{2.5}$ mass ($\mu g/m^3$) during winter season. Each hourly average consists of a minimum of 75 percent of the 1-minute averages for the hour. The box and whisker plots indicate the distributions of the hourly averages during the winter field study.

The SoCAB climate in 2007 was characterized by nearly normal seasonal temperatures and lower than average precipitation during the first three months of the year. Figure 3-36 shows the actual and normal monthly mean maximum and minimum temperatures and precipitation in southwestern California in 2007. Red bars indicate the four 4-week HCMS sampling periods (2/13 to 3/13, 5/15 to 6/12, 7/31 to 8/28, and 11/13 to 12/11).

Tables 3-16 to 3-27 show the seasonal and annual mean concentrations for NOx, SO_2, BTEX, formaldehyde, acetaldehyde, $PM_{2.5}$, EC, DPC and DPM. Ambient concentrations are generally higher during the winter and fall seasons for all species due to period of stagnation. However the range of concentrations is larger during these seasons due to occasional passage of cold fronts that reduce the basin's pollution levels. Within this general pattern, there are distinctive seasonal differences that appear to be pollutant specific.

The seasonal mean mixing ratios of NOx were about 3 to 4 times higher during fall and winter than during spring and summer. The NOx levels throughout Wilmington were consistently higher during the fall than winter by about 50 to 75%. In contrast, NOx levels during fall and winter were similar in West Long Beach and are highest near the I-710 freeway during winter. BTEX and NOx had similar seasonal variations. The synoptic meteorological conditions that lead to periods of stagnation during the fall result in buildup of higher pollutant concentrations over a larger area, while colder temperatures during winter results in stronger nighttime and early morning inversions, which result in larger pollutant gradients near emission sources such as the I-710 freeway.

Elemental carbon concentrations were also higher and more spatially uniform during the fall and had larger gradients near sources in the other three seasons. $PM_{2.5}$ concentrations are about a factor of two higher during the fall than during the other three seasons at nearly all sites. While the seasonal mean NOx levels were a factor of 2-4 higher in winter than in spring and summer, $PM_{2.5}$ concentrations were slightly lower in winter than in spring and summer. The contrasting seasonal variations of NOx and $PM_{2.5}$ are likely due to greater contributions of secondary PM component (nitrates, sulfates and organic aerosol) during the warmer months of the year. Formaldehyde and acetaldehyde levels were higher during winter and fall, which indicate a greater contribution of primary sources of these aldehydes than atmospheric formation. SO_2 levels were generally low throughout the study area and were often near the limit of detection of the measurement method. While seasonal variations were not large, SO_2 levels were highest during winter and lowest during spring.

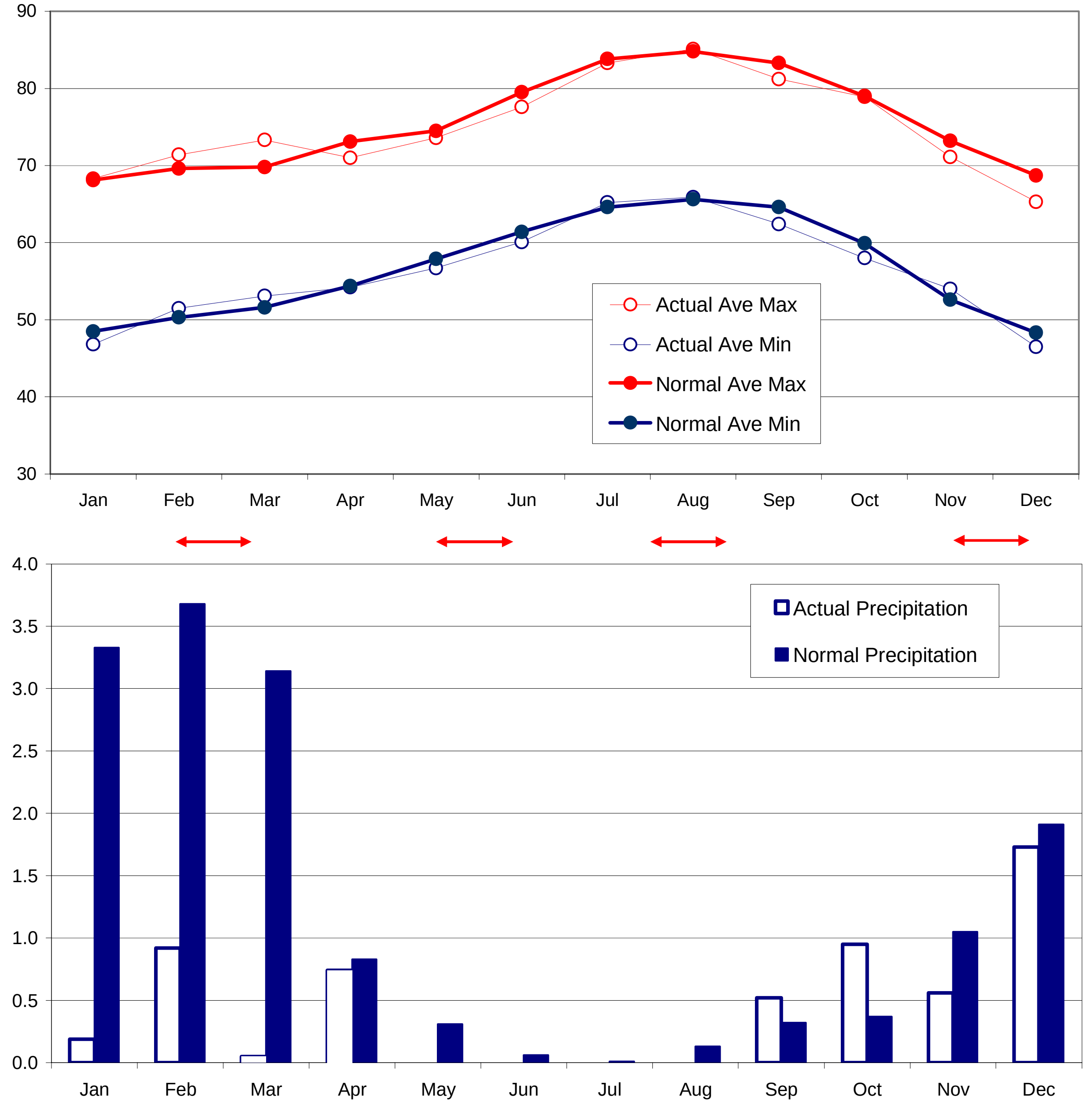

Figure 3-36. Actual and normal monthly mean maximum and minimum temperatures in ^{o}F (upper panel) and precipitation in inches (lower panel) in southwestern California in 2007. Red bars indicate the four 4-week HCMS sampling periods (2/13 to 3/13, 5/15 to 6/12, 7/31 to 8/28, and 11/13 to 12/11).

Table 3-16. Seasonal and annual average NOx (ppb).

Site	Winter	Spring	Summer	Fall	Annual	% Data
PB47			21.0 ± 2.0	53.2 ± 6.0		50%
SELB	45.3 ± 6.2	17.4 ± 0.9	26.6 ± 2.8	64.0 ± 4.8	38.3 ± 5.0	100%
WEMD	44.0 ± 4.5	19.9 ± 1.8	26.1 ± 2.6	70.0 ± 5.0	40.0 ± 5.3	100%
WE11	70.1 ± 4.3	38.3 ± 2.1	45.0 ± 2.4	90.0 ± 5.7	60.9 ± 5.6	100%
WFST	49.0 ± 4.7	18.1 ± 4.0	23.7 ± 2.7	69.3 ± 4.4	40.0 ± 5.6	100%
WGUL	44.1 ± 4.9	18.1 ± 0.2	22.9 ± 2.3	57.1 ± 0.6	36.7 ± 4.4	94%
WMCD	45.8 ± 9.4	17.9 ± 0.9	24.2 ± 2.4	71.7 ± 4.0	39.1 ± 6.5	88%
WMAR	44.6 ± 5.0	16.6 ± 0.9	24.2 ± 2.5	68.3 ± 5.2	38.4 ± 5.5	100%
WSWI	48.9 ± 4.3	25.5 ± 3.1	28.8 ± 2.5	82.5 ± 8.8	46.3 ± 6.7	94%
WLAK	46.4 ± 4.6	17.1 ± 0.9	23.3 ± 2.3	67.8 ± 4.9	38.6 ± 5.4	100%
WF49	52.9 ± 0.2	20.3 ± 1.2	26.9 ± 3.4	76.9 ± 8.5	44.3 ± 7.4	81%
WMCF	56.3 ± 17.1	18.1 ± 1.0	24.1 ± 2.4	64.8 ± 4.1	40.8 ± 6.5	100%
WPIO	56.0 ± 5.3	20.4 ± 0.7	26.5 ± 2.1	79.7 ± 7.0	45.7 ± 6.5	100%
WCOL	62.3 ± 8.6	22.1 ± 1.2	27.5 ± 2.5	77.2 ± 5.4	47.3 ± 6.4	100%
LOCN	71.9 ± 6.3	36.7 ± 3.5	37.3 ± 1.7	85.1 ± 7.2	55.7 ± 6.5	88%
LHUD	70.4 ± 6.2	22.3 ± 1.0	29.1 ± 1.8	83.8 ± 4.0	51.4 ± 7.0	100%
LWIN	63.6 ± 6.9	20.0 ± 1.0	26.0 ± 2.4	86.0 ± 9.0	48.9 ± 7.5	100%
LWBC	59.1 ± 6.3	20.5 ± 1.3	27.0 ± 2.4	65.9 ± 4.4	43.1 ± 5.4	100%
LSUP	88.4 ± 8.9	29.7 ± 0.7	39.0 ± 3.0	112.4 ± 12.1	66.0 ± 10.0	94%
LBER	95.1 ± 10.3	41.9 ± 4.1	54.8 ± 9.7	122.3 ± 9.8	78.5 ± 9.2	100%
LW71	170.0 ± 14.9	87.1 ± 7.6	77.4 ± 12.1	196.3 ± 9.2	132.7 ± 14.2	100%
LE71	129.4 ± 7.5	72.3 ± 4.7	68.8 ± 4.1	135.3 ± 9.1	101.5 ± 8.5	100%
LBPW	63.7 ± 10.5	20.9 ± 1.0	25.8 ± 2.1	83.0 ± 9.6	49.9 ± 7.8	94%

Table 3-17. Seasonal and annual average SO_2 (ppb).

Site	Winter	Spring	Summer	Fall	Annual	% Data
PB47			2.07 ± 0.99	1.20 ± 0.36		44%
SELB	1.36 ± 0.52	0.58 ± 0.08	0.87 ± 0.30	0.96 ± 0.30	1.1 ± 0.2	88%
WEMD	3.51 ± 0.64	0.77 ± 0.05	1.19 ± 0.16	1.25 ± 0.12	1.7 ± 0.3	100%
WE11	2.00 ± 0.32	0.58 ± 0.09	0.90 ± 0.36	1.16 ± 0.12	1.2 ± 0.2	94%
WFST	0.92 ± 0.41	0.34 ± 0.15	0.75 ± 0.30	0.88 ± 0.13	0.8 ± 0.1	81%
WGUL	1.01 ± 0.14	0.48 ± 0.04	0.93 ± 0.12	0.56 ± 0.25	0.7 ± 0.1	100%
WMCD	0.68 ± 0.10	0.55 ± 0.11	0.78 ± 0.28	0.63 ± 0.35	0.8 ± 0.1	81%
WMAR	1.14 ± 0.22	0.63 ± 0.15	0.77 ± 0.28	0.83 ± 0.29	0.8 ± 0.1	100%
WSWI	1.69 ± 0.34	0.50 ± 0.30	1.46 ± 0.39	0.94 ± 0.22	1.3 ± 0.2	81%
WLAK	1.18 ± 0.20	0.52 ± 0.06	0.62 ± 0.36	0.73 ± 0.18	0.9 ± 0.1	88%
WF49	2.03 ± 0.03	0.76 ± 0.17	0.99 ± 0.43	1.39 ± 0.33	1.3 ± 0.2	75%
WMCF	1.48 ± 0.29	0.49 ± 0.05	0.95 ± 0.18	0.79 ± 0.15	0.9 ± 0.1	100%
WPIO	1.08 ± 0.20	0.56 ± 0.07	1.05 ± 0.19	0.77 ± 0.17	0.9 ± 0.1	100%
WCOL	0.94 ± 0.35	0.47 ± 0.07	0.58 ± 0.34	0.68 ± 0.15	0.8 ± 0.1	81%
LOCN	1.23 ± 0.25	0.28 ± 0.16	1.19 ± 0.44	0.43 ± 0.15	1.0 ± 0.2	63%
LHUD	1.10 ± 0.21	0.65 ± 0.08	0.87 ± 0.34	0.61 ± 0.33	0.9 ± 0.1	88%
LWIN	0.91 ± 0.16	0.35 ± 0.12	0.52 ± 0.30	0.67 ± 0.02	0.8 ± 0.1	81%
LWBC	1.28 ± 0.26	0.63 ± 0.06	1.14 ± 0.41	0.86 ± 0.15	1.0 ± 0.1	94%
LSUP	1.67 ± 0.61	0.90 ± 0.07	1.86 ± 0.27	0.70 ± 0.06	1.3 ± 0.2	94%
LBER	1.47 ± 0.26	0.85 ± 0.11	1.08 ± 0.40	0.50 ± 0.31	1.2 ± 0.1	81%
LW71	1.33 ± 0.24	0.40 ± 0.23	1.51 ± 0.28	0.92 ± 0.29	1.2 ± 0.1	88%
LE71	1.52 ± 0.33	0.85 ± 0.06	1.09 ± 0.36	0.71 ± 0.14	1.1 ± 0.1	94%
LBPW	1.10 ± 0.07	0.65 ± 0.09	1.06 ± 0.18	0.78 ± 0.47	0.9 ± 0.1	81%

Table 3-18. Seasonal and annual average Benzene (ppb).

Site	**Winter**	**Spring**	**Summer**	**Fall**	**Annual**	**% Data**
PB47			0.20 ± 0.08	0.48 ± 0.07		50%
SELB	0.37 ± 0.03	0.17 ± 0.34	0.27 ± 0.04	0.68 ± 0.05	0.37 ± 0.05	100%
WEMD	0.41 ± 0.03	0.16 ± 0.42	0.31 ± 0.06	0.74 ± 0.06	0.40 ± 0.06	100%
WE11	0.48 ± 0.02	0.19 ± 0.47	0.39 ± 0.03	0.89 ± 0.10	0.49 ± 0.07	100%
WFST	0.63 ± 0.04	0.19 ± 0.40	0.38 ± 0.07	0.91 ± 0.10	0.53 ± 0.08	100%
WGUL	0.55 ± 0.05	0.20 ± 0.33	0.34 ± 0.06	0.92 ± 0.11	0.47 ± 0.08	94%
WMCD	0.54 ± 0.03	0.20 ± 0.34	0.31 ± 0.06	0.91 ± 0.09	0.49 ± 0.07	100%
WMAR	0.60 ± 0.04	0.20 ± 0.44	0.32 ± 0.04	0.97 ± 0.10	0.52 ± 0.08	100%
WSWI	0.44 ± 0.02	0.19 ± 0.38	0.31 ± 0.08	0.86 ± 0.09	0.45 ± 0.08	94%
WLAK	0.56 ± 0.04	0.20 ± 0.29	0.31 ± 0.06	0.78 ± 0.06	0.46 ± 0.06	100%
WF49	0.46 ± 0.01	0.16 ± 0.34	0.30 ± 0.07	0.79 ± 0.06	0.42 ± 0.07	88%
WMCF	0.52 ± 0.03	0.20 ± 0.37	0.34 ± 0.06	0.84 ± 0.08	0.48 ± 0.07	100%
WPIO	0.81 ± 0.06	0.24 ± 0.30	0.41 ± 0.03	0.98 ± 0.08	0.61 ± 0.08	100%
WCOL	0.63 ± 0.02	0.20 ± 0.38	0.33 ± 0.04	0.86 ± 0.13	0.50 ± 0.07	100%
LOCN		0.17 ± 0.00	0.36 ± 0.04	0.92 ± 0.09	0.49 ± 0.09*	81%
LHUD	0.61 ± 0.04	0.20 ± 0.38	0.36 ± 0.06	0.95 ± 0.11	0.54 ± 0.08	94%
LWIN	0.55 ± 0.06	0.22 ± 0.43	0.28 ± 0.05	0.80 ± 0.10	0.46 ± 0.07	100%
LWBC	0.54 ± 0.04	0.26 ± 0.38	0.34 ± 0.07	1.15 ± 0.11	0.54 ± 0.09	94%
LSUP	0.64 ± 0.10	0.26 ± 0.56	0.32 ± 0.06	0.99 ± 0.09	0.55 ± 0.09	94%
LBER	0.66 ± 0.03	0.28 ± 0.39	0.44 ± 0.06	1.09 ± 0.14	0.62 ± 0.09	100%
LW71	0.72 ± 0.03	0.41 ± 0.39	0.57 ± 0.04	1.20 ± 0.15	0.72 ± 0.09	94%
LE71	0.68 ± 0.01	0.41 ± 0.25	0.49 ± 0.07	1.12 ± 0.09	0.67 ± 0.08	100%
LBPW	0.53 ± 0.05	0.15 ± 0.65	0.43 ± 0.14	1.12 ± 0.14	0.52 ± 0.10	94%

Table 3-19. Seasonal and annual average Toluene (ppb).

Site	**Winter**	**Spring**	**Summer**	**Fall**	**Annual**	**% Data**
PB47			0.63 ± 0.35	1.26 ± 0.24		44%
SELB	1.49 ± 0.45	0.44 ± 0.10	1.01 ± 0.07	2.03 ± 0.36	1.19 ± 0.20	94%
WEMD	1.37 ± 0.26	0.42 ± 0.05	1.00 ± 0.25	1.92 ± 0.11	1.18 ± 0.16	100%
WE11	1.50 ± 0.26	0.53 ± 0.13	1.18 ± 0.15	2.21 ± 0.24	1.36 ± 0.18	100%
WFST	2.04 ± 0.27	0.64 ± 0.17	1.30 ± 0.18	2.48 ± 0.10	1.61 ± 0.20	100%
WGUL	1.66 ± 0.33	1.36 ± 0.88	1.13 ± 0.18	2.45 ± 0.18	1.60 ± 0.26	94%
WMCD	1.79 ± 0.29	0.72 ± 0.22	1.02 ± 0.16	2.25 ± 0.15	1.45 ± 0.18	100%
WMAR	1.83 ± 0.30	0.67 ± 0.12	1.04 ± 0.16	2.52 ± 0.12	1.52 ± 0.20	100%
WSWI	1.46 ± 0.10	0.42 ± 0.07	1.15 ± 0.27	2.16 ± 0.18	1.29 ± 0.19	94%
WLAK	1.76 ± 0.33	0.56 ± 0.10	0.96 ± 0.17	1.94 ± 0.14	1.26 ± 0.18	94%
WF49	1.36 ± 0.04	0.49 ± 0.11	0.89 ± 0.19	1.97 ± 0.12	1.15 ± 0.17	88%
WMCF	1.68 ± 0.27	0.68 ± 0.12	1.31 ± 0.41	2.30 ± 0.38	1.49 ± 0.21	100%
WPIO	3.31 ± 0.26	1.01 ± 0.23	3.75 ± 1.85	3.37 ± 0.42	2.86 ± 0.51	100%
WCOL	3.36 ± 0.72	3.39 ± 1.32	4.17 ± 1.10	3.45 ± 0.89	3.59 ± 0.47	100%
LOCN	1.21 ± 0.58*	0.48 ± 0.11	1.32 ± 0.29	2.14 ± 0.17	1.35 ± 0.22*	81%
LHUD	1.73 ± 0.24	0.63 ± 0.23	1.11 ± 0.10	2.33 ± 0.22	1.47 ± 0.20	94%
LWIN	1.70 ± 0.27	0.54 ± 0.09	0.93 ± 0.12	2.09 ± 0.42	1.31 ± 0.20	100%
LWBC	1.58 ± 0.20	0.59 ± 0.15	1.15 ± 0.25	2.88 ± 0.44	1.46 ± 0.24	94%
LSUP	1.71 ± 0.22	0.75 ± 0.07	1.34 ± 0.16	3.30 ± 0.53	1.78 ± 0.30	94%
LBER	1.93 ± 0.16	0.76 ± 0.12	1.44 ± 0.23	2.70 ± 0.16	1.71 ± 0.20	100%
LW71	1.84 ± 0.14	0.92 ± 0.17	1.47 ± 0.13	2.68 ± 0.21	1.72 ± 0.19	94%
LE71	1.81 ± 0.16	0.94 ± 0.22	1.23 ± 0.12	2.47 ± 0.21	1.61 ± 0.17	100%
LBPW	1.57 ± 0.24	0.61 ± 0.41	1.20 ± 0.38	2.52 ± 0.24	1.40 ± 0.23	94%

Table 3-20. Seasonal and annual average Ethylbenzene (ppb). [1]

Site	Winter	Spring	Summer	Fall	Annual	% Data
PB47			0.24 ± 0.15	0.35 ± 0.14		50%
SELB	0.18 ± 0.05	0.06 ± 0.01	0.21 ± 0.05	0.82 ± 0.35	0.32 ± 0.11	100%
WEMD	0.19 ± 0.03	0.05 ± 0.01	0.13 ± 0.02	0.59 ± 0.24	0.24 ± 0.08	100%
WE11	0.20 ± 0.02	0.07 ± 0.01	0.18 ± 0.03	0.77 ± 0.37	0.30 ± 0.11	100%
WFST	0.28 ± 0.04	0.07 ± 0.01	0.20 ± 0.02	0.94 ± 0.31	0.37 ± 0.11	100%
WGUL	0.22 ± 0.03	0.12 ± 0.05	0.19 ± 0.02	0.90 ± 0.43	0.38 ± 0.13	94%
WMCD	0.24 ± 0.04	0.11 ± 0.05	0.15 ± 0.02	0.95 ± 0.37	0.36 ± 0.12	100%
WMAR	0.25 ± 0.03	0.10 ± 0.02	0.19 ± 0.02	1.04 ± 0.40	0.40 ± 0.13	100%
WSWI	0.16 ± 0.06	0.06 ± 0.01	0.21 ± 0.03	0.92 ± 0.35	0.36 ± 0.12	94%
WLAK	0.24 ± 0.04	0.08 ± 0.01	0.15 ± 0.03	0.63 ± 0.25	0.27 ± 0.08	100%
WF49	0.11 ± 0.07	0.07 ± 0.01	0.14 ± 0.01	0.61 ± 0.25	0.27 ± 0.09	88%
WMCF	0.23 ± 0.02	0.09 ± 0.01	0.19 ± 0.06	0.95 ± 0.40	0.36 ± 0.13	100%
WPIO	0.36 ± 0.03	0.17 ± 0.04	0.32 ± 0.09	1.16 ± 0.41	0.50 ± 0.14	100%
WCOL	0.31 ± 0.04	0.20 ± 0.06	0.28 ± 0.04	0.60 ± 0.24	0.35 ± 0.07	100%
LOCN	0.14 ± 0.07*	0.06 ± 0.01	0.17 ± 0.01	0.34 ± 0.02	0.20 ± 0.03*	81%
LHUD	0.24 ± 0.03	0.10 ± 0.05	0.11 ± 0.04	0.37 ± 0.02	0.22 ± 0.03	94%
LWIN	0.22 ± 0.03	0.06 ± 0.01	0.13 ± 0.02	0.31 ± 0.06	0.18 ± 0.03	100%
LWBC	0.21 ± 0.03	0.07 ± 0.02	0.16 ± 0.03	0.67 ± 0.39	0.30 ± 0.11	94%
LSUP	0.14 ± 0.07	0.10 ± 0.01	0.19 ± 0.01	0.56 ± 0.14	0.26 ± 0.06	94%
LBER	0.26 ± 0.02	0.09 ± 0.01	0.20 ± 0.01	0.80 ± 0.30	0.34 ± 0.10	100%
LW71	0.20 ± 0.07	0.11 ± 0.02	0.23 ± 0.02	0.80 ± 0.30	0.36 ± 0.10	94%
LE71	0.25 ± 0.02	0.11 ± 0.02	0.19 ± 0.02	0.74 ± 0.32	0.32 ± 0.10	100%
LBPW	0.21 ± 0.03	0.08 ± 0.05	0.16 ± 0.05	0.69 ± 0.41	0.30 ± 0.12	94%

[1] Calculation of mixing ratios is based on the experimentally determined sampling rate.

Table 3-21. Seasonal and annual average Xylenes (ppb).

Site	Winter	Spring	Summer	Fall	Annual	% Data
PB47			1.07 ± 0.46	0.81 ± 0.06		50%
SELB	1.07 ± 0.28	0.35 ± 0.04	0.99 ± 0.22	1.50 ± 0.25	0.98 ± 0.14	100%
WEMD	1.18 ± 0.18	0.31 ± 0.04	0.64 ± 0.12	1.43 ± 0.20	0.89 ± 0.13	100%
WE11	1.25 ± 0.10	0.39 ± 0.08	0.94 ± 0.18	1.46 ± 0.29	1.01 ± 0.13	100%
WFST	1.80 ± 0.23	0.43 ± 0.07	1.03 ± 0.11	2.06 ± 0.21	1.33 ± 0.18	100%
WGUL	1.38 ± 0.15	0.63 ± 0.23	1.01 ± 0.11	2.03 ± 0.05	1.21 ± 0.15	94%
WMCD	1.51 ± 0.21	0.68 ± 0.30	0.73 ± 0.09	1.92 ± 0.22	1.21 ± 0.17	100%
WMAR	1.58 ± 0.16	0.65 ± 0.16	0.91 ± 0.11	2.11 ± 0.23	1.31 ± 0.17	100%
WSWI	1.37 ± 0.16	0.35 ± 0.05	1.03 ± 0.15	1.82 ± 0.15	1.13 ± 0.16	94%
WLAK	1.44 ± 0.26	0.47 ± 0.07	0.78 ± 0.15	1.56 ± 0.27	1.06 ± 0.15	100%
WF49	1.38 ± 0.06	0.40 ± 0.07	0.65 ± 0.07	1.42 ± 0.21	0.91 ± 0.14	88%
WMCF	1.40 ± 0.11	0.54 ± 0.08	0.99 ± 0.31	1.82 ± 0.25	1.19 ± 0.15	100%
WPIO	2.18 ± 0.19	1.08 ± 0.28	1.47 ± 0.26	2.36 ± 0.27	1.77 ± 0.18	100%
WCOL	1.88 ± 0.23	0.97 ± 0.28	1.18 ± 0.13	1.75 ± 0.47	1.45 ± 0.17	100%
LOCN	0.90 ± 0.99*	0.37 ± 0.06	0.83 ± 0.06	1.53 ± 0.30	0.98 ± 0.17*	81%
LHUD	1.42 ± 0.16	0.53 ± 0.26	0.76 ± 0.03	1.57 ± 0.33	1.09 ± 0.16	94%
LWIN	1.33 ± 0.19	0.36 ± 0.06	0.63 ± 0.07	1.48 ± 0.44	0.95 ± 0.16	100%
LWBC	1.28 ± 0.15	0.43 ± 0.14	0.73 ± 0.13	1.64 ± 0.57	0.98 ± 0.17	94%
LSUP	1.12 ± 0.39	0.58 ± 0.08	0.98 ± 0.03	1.87 ± 0.61	1.14 ± 0.21	94%
LBER	1.61 ± 0.13	0.57 ± 0.10	1.06 ± 0.05	1.80 ± 0.51	1.26 ± 0.17	100%
LW71	1.74 ± 0.16	0.73 ± 0.11	1.25 ± 0.14	1.86 ± 0.54	1.37 ± 0.18	94%
LE71	1.58 ± 0.10	0.68 ± 0.09	0.95 ± 0.15	1.67 ± 0.49	1.22 ± 0.16	100%
LBPW	1.26 ± 0.18	0.42 ± 0.28	0.81 ± 0.25	1.65 ± 0.33	1.00 ± 0.17	94%

Table 3-22. Seasonal and annual average Formaldehyde (ppb)

Site	**Winter**	**Spring**	**Summer**	**Fall**	**Annual**	**% Data**
PB47			1.78 ± 0.36	1.58 ± 0.32		56%
SELB	2.39 ± 0.34	1.63 ± 0.18	1.62 ± 0.33	1.92 ± 0.69	1.89 ± 0.21	100%
WEMD	2.61 ± 0.42	1.58 ± 0.05	1.36 ± 0.13	1.81 ± 0.31	1.86 ± 0.18	94%
WE11	2.68 ± 0.47	1.78 ± 0.19	1.57 ± 0.21	1.84 ± 0.29	1.97 ± 0.18	100%
WFST	2.76 ± 0.40	1.64 ± 0.12	1.65 ± 0.29	1.88 ± 0.47	1.98 ± 0.20	100%
WGUL	2.66 ± 0.33	1.51 ± 0.10	1.41 ± 0.28	1.54 ± 0.52	1.80 ± 0.20	94%
WMCD	2.76 ± 0.34	1.54 ± 0.10	1.57 ± 0.18	2.00 ± 0.49	1.97 ± 0.19	100%
WMAR	2.96 ± 0.44	1.53 ± 0.04	1.58 ± 0.31	2.02 ± 0.49	2.02 ± 0.22	100%
WSWI	2.69 ± 0.38	1.43 ± 0.16	1.34 ± 0.19	2.02 ± 0.56	1.88 ± 0.24	81%
WLAK	2.64 ± 0.29	1.49 ± 0.11	1.25 ± 0.26	1.95 ± 0.49	1.83 ± 0.20	100%
WF49	3.11 ± 0.34	1.52 ± 0.10	1.33 ± 0.21	1.89 ± 0.65	1.80 ± 0.24	88%
WMCF	2.52 ± 0.37	1.66 ± 0.06	1.41 ± 0.22	1.89 ± 0.58	1.87 ± 0.19	100%
WPIO	2.83 ± 0.30	1.76 ± 0.11	1.89 ± 0.08	2.15 ± 0.44	2.17 ± 0.17	94%
WCOL	2.90 ± 0.38	1.96 ± 0.12	1.78 ± 0.35	2.03 ± 0.67	2.17 ± 0.22	100%
LOCN		1.75 ± 0.19	1.57 ± 0.27	2.11 ± 0.66	1.96 ± 0.26*	81%
LHUD	2.68 ± 0.38	1.65 ± 0.12	1.76 ± 0.24	1.75 ± 0.48	1.96 ± 0.18	100%
LWIN	2.73 ± 0.43	1.69 ± 0.18	1.89 ± 0.34	1.91 ± 0.72	2.05 ± 0.23	100%
LWBC	2.68 ± 0.38	1.69 ± 0.24	1.70 ± 0.22	2.28 ± 0.63	2.09 ± 0.21	100%
LSUP	3.10 ± 0.56	1.98 ± 0.15	1.98 ± 0.14	2.51 ± 0.66	2.35 ± 0.23	94%
LBER	3.30 ± 0.39	1.93 ± 0.19	1.96 ± 0.22	2.40 ± 0.55	2.43 ± 0.23	94%
LW71	3.12 ± 0.39	2.28 ± 0.30	1.88 ± 0.39	2.82 ± 0.68	2.48 ± 0.25	94%
LE71	2.89 ± 0.25	1.95 ± 0.23	1.70 ± 0.22	2.25 ± 0.42	2.20 ± 0.17	100%
LBPW	3.00 ± 0.65	1.19 ± 0.40	1.86 ± 0.18	2.20 ± 0.56	2.00 ± 0.27	94%

Table 3-23. Seasonal and annual average Acetaldehyde (ppb)

Site	**Winter**	**Spring**	**Summer**	**Fall**	**Annual**	**% Data**
PB47			0.53 ± 0.14	1.07 ± 0.15		56%
SELB	1.55 ± 0.41	0.52 ± 0.05	0.71 ± 0.11	1.39 ± 0.29	1.04 ± 0.16	100%
WEMD	1.92 ± 0.37	0.28 ± 0.15	0.64 ± 0.08	1.31 ± 0.17	1.04 ± 0.19	100%
WE11	1.63 ± 0.41	0.51 ± 0.09	0.56 ± 0.09	1.32 ± 0.16	1.01 ± 0.16	100%
WFST	1.81 ± 0.39	0.52 ± 0.09	0.70 ± 0.10	1.19 ± 0.21	1.05 ± 0.17	100%
WGUL	1.83 ± 0.38	0.44 ± 0.09	0.56 ± 0.03	1.40 ± 0.22	1.03 ± 0.19	94%
WMCD	1.94 ± 0.43	0.52 ± 0.07	0.61 ± 0.09	1.75 ± 0.36	1.21 ± 0.21	100%
WMAR	1.99 ± 0.37	0.46 ± 0.07	0.62 ± 0.09	1.58 ± 0.34	1.16 ± 0.20	100%
WSWI	1.98 ± 0.44	0.28 ± 0.17	0.61 ± 0.08	1.69 ± 0.31	1.14 ± 0.23	88%
WLAK	1.81 ± 0.46	0.43 ± 0.06	0.49 ± 0.05	1.72 ± 0.33	1.11 ± 0.21	100%
WF49	2.47 ± 0.28	0.41 ± 0.06	0.58 ± 0.09	1.54 ± 0.29	1.08 ± 0.22	88%
WMCF	1.71 ± 0.42	0.45 ± 0.06	0.55 ± 0.07	1.60 ± 0.33	1.08 ± 0.19	100%
WPIO	1.81 ± 0.50	0.51 ± 0.09	0.55 ± 0.08	1.77 ± 0.32	1.20 ± 0.22	94%
WCOL	1.68 ± 0.39	0.55 ± 0.12	0.62 ± 0.09	1.50 ± 0.38	1.09 ± 0.18	100%
LOCN		0.52 ± 0.03	0.66 ± 0.06	1.87 ± 0.42	1.13 ± 0.23*	81%
LHUD	1.91 ± 0.41	0.47 ± 0.06	0.78 ± 0.05	1.60 ± 0.42	1.19 ± 0.20	100%
LWIN	1.83 ± 0.36	0.48 ± 0.09	0.80 ± 0.07	1.51 ± 0.43	1.16 ± 0.19	100%
LWBC	1.78 ± 0.35	0.47 ± 0.11	0.71 ± 0.06	1.86 ± 0.40	1.20 ± 0.20	100%
LSUP	1.86 ± 0.42	0.48 ± 0.09	0.63 ± 0.08	1.77 ± 0.32	1.14 ± 0.20	94%
LBER	1.71 ± 0.36	0.44 ± 0.07	0.76 ± 0.08	1.80 ± 0.35	1.18 ± 0.19	100%
LW71	1.98 ± 0.44	0.50 ± 0.10	0.78 ± 0.10	1.89 ± 0.34	1.24 ± 0.21	94%
LE71	1.70 ± 0.38	0.54 ± 0.09	0.85 ± 0.04	1.70 ± 0.30	1.20 ± 0.17	100%
LBPW	1.69 ± 0.55	0.30 ± 0.11	0.82 ± 0.15	1.72 ± 0.32	1.10 ± 0.21	94%

Table 3-24. Seasonal and annual average $PM_{2.5}$ (µg/m^3)

Site	Winter	Spring	Summer	Fall	Annual	% Data
PB47			12.3 ± 0.6	17.1 ± 9.1		38%
SELB	9.4 ± 0.5	11.3 ± 0.6	12.0 ± 0.6	18.6 ± 0.9	12.8 ± 2.0	100%
WEMD	10.2 ± 0.5	11.7 ± 0.6	11.1 ± 0.6 *	20.8 ± 1.0	13.4 ± 2.5 *	75%
WFST	10.1 ± 0.5	11.7 ± 0.6	12.2 ± 0.6	23.5 ± 1.2	14.4 ± 3.1	94%
WGUL	8.2 ± 0.4	12.1 ± 0.6	11.2 ± 0.6	20.1 ± 2.9 *	12.9 ± 2.5 *	75%
WMCD	10.1 ± 0.5	11.4 ± 0.7	11.1 ± 0.6	19.9 ± 1.0	13.1 ± 2.3	88%
WMAR	10.4 ± 0.6 *	11.9 ± 0.7 *	11.6 ± 0.6	21.1 ± 1.1	0.0 ± 0.0 *	63%
WSWI	10.6 ± 1.0 *	12.2 ± 0.6	11.6 ± 1.1	21.9 ± 2.1	14.1 ± 2.6 *	50%
WLAK	10.4 ± 0.5	12.0 ± 0.6	7.4 ± 0.4	20.3 ± 1.0	12.5 ± 2.8	88%
WF49	10.5 ± 1.0 *	11.3 ± 0.6	12.1 ± 0.6	21.8 ± 2.1 *	13.9 ± 2.6 *	50%
WMCF	9.8 ± 0.5	11.6 ± 0.6	11.0 ± 0.7 *	21.4 ± 1.1	13.5 ± 2.7 *	69%
WPIO	11.3 ± 0.6	13.2 ± 0.7	12.7 ± 0.6	24.4 ± 1.2	15.4 ± 3.0	81%
WCOL	11.1 ± 0.8	13.4 ± 0.7	11.6 ± 0.6	21.8 ± 1.1	14.5 ± 2.5	75%
LOCN	12.4 ± 0.6 *	14.3 ± 0.7	13.9 ± 0.7	25.1 ± 1.3	16.4 ± 2.9 *	69%
LHUD	10.0 ± 0.5	12.7 ± 0.6	12.0 ± 0.6	24.6 ± 1.2	14.8 ± 3.3	81%
LWIN	11.3 ± 0.6	12.6 ± 0.6	12.2 ± 0.6 *	23.3 ± 1.2	14.9 ± 2.8 *	75%
LWBC	9.0 ± 0.5	11.4 ± 0.6	12.6 ± 0.6	25.8 ± 1.3	14.7 ± 3.8	88%
LSUP	13.6 ± 0.7	13.7 ± 0.7	12.1 ± 0.6	23.7 ± 1.2	15.8 ± 2.7	94%
LBER	12.3 ± 1.6	14.3 ± 0.7	14.3 ± 0.7	21.0 ± 1.1	15.5 ± 1.9	81%
LBPW	11.5 ± 1.7	11.8 ± 0.6	11.9 ± 0.6	22.6 ± 1.1	14.4 ± 2.7	88%

Table 3-25. Seasonal and annual average elemental carbon (µg/m^3)

Site	Winter	Spring	Summer	Fall	Annual	% Data
PB47			1.1 ± 0.1	2.5 ± 0.7		38%
SELB	1.3 ± 0.1	0.6 ± 0.1	0.9 ± 0.1	2.4 ± 0.1	1.3 ± 0.4	88%
WEMD	1.5 ± 0.1	0.6 ± 0.1	0.9 ± 0.1	2.6 ± 0.2	1.4 ± 0.4	88%
WFST	1.4 ± 0.1	0.5 ± 0.1	0.9 ± 0.1	2.3 ± 0.2	1.3 ± 0.4	88%
WGUL	1.6 ± 0.1	0.5 ± 0.1	0.7 ± 0.1	2.2 ± 0.6 *	1.2 ± 0.4 *	75%
WMCD	1.5 ± 0.1	0.5 ± 0.1	0.7 ± 0.1	2.2 ± 0.1	1.2 ± 0.4	100%
WMAR	0.8 ± 0.1	0.4 ± 0.1 *	0.6 ± 0.1 *	1.5 ± 0.2	0.0 ± 0.0 *	44%
WSWI	2.2 ± 0.1 *	1.0 ± 0.1	1.5 ± 0.1	3.8 ± 0.2 *	2.1 ± 0.6 *	56%
WLAK	1.4 ± 0.1	0.5 ± 0.1	0.7 ± 0.1	2.4 ± 0.1	1.3 ± 0.4	100%
WF49	1.7 ± 0.4	0.7 ± 0.1	1.1 ± 0.1	2.3 ± 0.1	1.4 ± 0.4	81%
WMCF	1.6 ± 0.1	0.6 ± 0.1	0.8 ± 0.1	2.3 ± 0.4 *	1.3 ± 0.4 *	81%
WPIO	1.6 ± 0.1	0.7 ± 0.1	1.1 ± 0.1	3.1 ± 0.2	1.6 ± 0.5	94%
WCOL	1.1 ± 0.1	0.7 ± 0.1	0.9 ± 0.1	3.5 ± 0.2	1.5 ± 0.6	94%
LOCN	3.3 ± 0.7 *	1.8 ± 0.1	2.2 ± 0.5	4.5 ± 0.3	2.9 ± 0.6 *	63%
LHUD	2.3 ± 0.1	0.8 ± 0.1	1.3 ± 0.2 *	3.3 ± 0.2	1.9 ± 0.6 *	69%
LWIN	1.5 ± 0.1	0.6 ± 0.1	0.9 ± 0.1	2.7 ± 0.2	1.4 ± 0.5	100%
LWBC	1.5 ± 0.1	0.6 ± 0.1	1.0 ± 0.2 *	3.0 ± 0.2	1.5 ± 0.5 *	69%
LSUP	2.3 ± 0.1	0.9 ± 0.1	1.5 ± 0.1	3.8 ± 0.4 *	2.1 ± 0.6 *	63%
LBER	2.9 ± 0.3	1.4 ± 0.1	2.0 ± 0.1	4.5 ± 0.3	2.7 ± 0.7	88%
LBPW	1.8 ± 0.1	0.7 ± 0.1	0.9 ± 0.1	3.0 ± 0.2	1.6 ± 0.5	88%

Table 3-26. Seasonal and annual average diesel particulate carbon ($\mu g/m^3$).

Site	Winter	Spring	Summer	Fall	Annual	% Data
PB47			2.3 ± 0.2	4.7 ± 1.3		38%
SELB	2.7 ± 0.2	0.8 ± 0.2	1.7 ± 0.2	4.5 ± 0.3	2.4 ± 0.8	88%
WEMD	3.2 ± 0.2	0.9 ± 0.2	1.8 ± 0.2	4.8 ± 0.3	2.7 ± 0.9	88%
WFST	3.0 ± 0.2	0.8 ± 0.2	1.7 ± 0.2	4.3 ± 0.4	2.5 ± 0.8	88%
WGUL	3.4 ± 0.2	0.7 ± 0.2	1.4 ± 0.2	4.0 ± 1.0 *	2.4 ± 0.8 *	75%
WMCD	3.2 ± 0.2	0.7 ± 0.2	1.4 ± 0.2	4.1 ± 0.2	2.4 ± 0.8	100%
WMAR	1.8 ± 0.2	0.6 ± 0.2 *	1.1 ± 0.2 *	2.7 ± 0.3	0.0 ± 0.0 *	44%
WSWI	4.6 ± 0.2 *	1.5 ± 0.2	2.9 ± 0.2	7.1 ± 0.3 *	4.0 ± 1.2 *	56%
WLAK	3.0 ± 0.2	0.8 ± 0.2	1.4 ± 0.2	4.5 ± 0.3	2.4 ± 0.8	100%
WF49	3.6 ± 0.6	1.0 ± 0.2	2.2 ± 0.2	4.3 ± 0.3	2.8 ± 0.7	81%
WMCF	3.3 ± 0.2	0.8 ± 0.2	1.5 ± 0.2	4.2 ± 0.8 *	2.5 ± 0.8 *	81%
WPIO	3.3 ± 0.2	1.1 ± 0.2	2.2 ± 0.2	5.7 ± 0.3	3.1 ± 1.0	94%
WCOL	2.3 ± 0.2	1.1 ± 0.2	1.8 ± 0.2	6.5 ± 0.4	2.9 ± 1.2	94%
LOCN	6.9 ± 0.5 *	2.7 ± 0.2	4.3 ± 0.9	8.3 ± 0.5	5.5 ± 1.3 *	63%
LHUD	4.9 ± 0.3	1.1 ± 0.2	2.6 ± 0.4 *	6.1 ± 0.4	3.7 ± 1.1 *	69%
LWIN	3.1 ± 0.2	0.9 ± 0.2	1.7 ± 0.2	5.1 ± 0.3	2.7 ± 0.9	100%
LWBC	3.1 ± 0.2	0.9 ± 0.2	1.9 ± 0.3 *	5.6 ± 0.3	2.9 ± 1.0 *	69%
LSUP	4.8 ± 0.3	1.3 ± 0.2	3.0 ± 0.2	7.1 ± 0.7 *	4.1 ± 1.2 *	63%
LBER	6.0 ± 0.3	2.1 ± 0.2	3.9 ± 0.2	8.4 ± 0.5	5.1 ± 1.3	88%
LBPW	3.9 ± 0.2	1.0 ± 0.2	1.8 ± 0.2	5.6 ± 0.3	3.1 ± 1.0	88%

Table 3-27. Seasonal and annual average diesel particulate matter ($\mu g/m^3$).

Site	Winter	Spring	Summer	Fall	Annual	% Data
PB47			3.3 ± 0.3	6.9 ± 1.9		38%
SELB	4.0 ± 0.3	1.2 ± 0.3	2.5 ± 0.3	6.5 ± 0.4	3.0 ± 1.0	88%
WEMD	4.7 ± 0.3	1.3 ± 0.3	2.7 ± 0.3	7.0 ± 0.4	3.3 ± 1.0	88%
WFST	4.4 ± 0.3	1.2 ± 0.3	2.5 ± 0.3	6.2 ± 0.7	3.0 ± 0.9	88%
WGUL	4.9 ± 0.3	1.0 ± 0.3	2.1 ± 0.3	5.9 ± 1.5 *	2.9 ± 1.0 *	75%
WMCD	4.7 ± 0.3	1.0 ± 0.3	2.1 ± 0.3	6.0 ± 0.4	2.9 ± 1.0	100%
WMAR	2.6 ± 0.3	0.8 ± 0.3 *	1.6 ± 0.3 *	4.0 ± 0.5	0.0 ± 0.0 *	44%
WSWI	6.8 ± 0.4 *	2.2 ± 0.3	4.2 ± 0.3	10.4 ± 0.5 *	4.9 ± 1.5 *	56%
WLAK	4.4 ± 0.3	1.2 ± 0.3	2.0 ± 0.3	6.5 ± 0.4	2.9 ± 1.0	100%
WF49	5.2 ± 0.8	1.4 ± 0.3	3.3 ± 0.3	6.3 ± 0.4	3.4 ± 0.9	81%
WMCF	4.8 ± 0.3	1.2 ± 0.3	2.2 ± 0.3	6.2 ± 1.1 *	3.0 ± 1.0 *	81%
WPIO	4.8 ± 0.3	1.6 ± 0.3	3.2 ± 0.3	8.4 ± 0.5	3.8 ± 1.2	94%
WCOL	3.4 ± 0.3	1.6 ± 0.3	2.6 ± 0.3	9.4 ± 0.6	3.5 ± 1.5	94%
LOCN	10.0 ± 0.7 *	3.9 ± 0.3	6.2 ± 1.3	12.2 ± 0.7	6.7 ± 1.5 *	63%
LHUD	7.1 ± 0.4	1.7 ± 0.3	3.8 ± 0.6 *	9.0 ± 0.5	4.5 ± 1.4 *	69%
LWIN	4.5 ± 0.3	1.3 ± 0.3	2.5 ± 0.3	7.5 ± 0.4	3.3 ± 1.1	100%
LWBC	4.6 ± 0.3	1.2 ± 0.3	2.8 ± 0.5 *	8.1 ± 0.5	3.5 ± 1.2 *	69%
LSUP	7.0 ± 0.4	2.0 ± 0.3	4.4 ± 0.3	10.3 ± 1.0 *	4.9 ± 1.5 *	63%
LBER	8.8 ± 0.4	3.1 ± 0.3	5.7 ± 0.3	12.2 ± 0.7	6.2 ± 1.6	88%
LBPW	5.6 ± 0.3	1.4 ± 0.3	2.6 ± 0.3	8.2 ± 0.5	3.7 ± 1.3	88%

4. DISCUSSION AND CONCLUSIONS

The Harbor Community Monitoring Study (HCMS) was conducted to characterize the spatial variations in concentrations of toxic air contaminants (TACs) and their co-pollutants within the communities of Wilmington, West Long Beach, and San Pedro in California's South Coast Air Basin (SoCAB). The saturation monitoring component of the HCMS had five hypotheses.

Hypothesis #1. *Passive monitoring methods can be used to measure 1-week average ambient concentrations of selected pollutants with sensitivity, accuracy and precision comparable to conventional monitoring methods.*

This hypothesis is generally true with a few exceptions. The detection limits and precision specified by the manufacturer for compounds quantified in the HCMS are compared in Table 4-1 to the mean values measured during the study at the HCMS quality assurance site. Mean ambient concentrations were well above the detection limits during the study for all compounds with the exception of SO_2, H_2S, and acrolein. The replicate precisions measured during the HCMS were better than 10 percent for compounds with ambient concentrations greater than five times the limit of detection. The results for 1,3-butadiene from passive samplers with Carbograph 4 were not quantitative due to back diffusion and are not reported in the HCMS.

Table 4-1. Seven-day average mixing ratios (ppbv) of passive measurements at the Hudson Monitoring Station and measurement precision based on replicate samples.

	DQO [1]		HCMS Winter			HCMS Summer		
	MDL	Precision	Mean	Precision [2]		Mean	Precision [2]	
	ppbv	%	ppbv	ppbv	%	ppbv	ppbv	%
Nitrogen Oxides (NOx)	0.32		73.0	2.03	2.8%	29.4	0.65	2.2%
Nitorgen Dioxide (NO_2)	0.32		28.5	1.50	5.3%	19.5	0.96	4.9%
Sulfur Dioxide (SO_2)	0.54		1.1	0.107	9.8%	1.0	0.196	19.8%
Hydrogen Sulfide (H_2S)	0.20	8.7%	0.8	0.036	4.8%	0.9	0.117	12.5%
Benzene	0.015	8.3%	0.6	0.014	2.3%	0.3	0.026	7.5%
Toluene	0.002	8.3%	1.7	0.039	2.3%	1.0	0.044	4.2%
Ethylbenzene	0.002	9.1%	0.3	0.008	2.4%	0.2	0.014	6.7%
Xylenes	0.002	11.3%	1.4	0.031	2.2%	0.7	0.063	9.2%
Formaldehyde	0.07	13.8%	2.7	0.06	2.2%	1.8	0.12	6.7%
Acetaldehyde	0.05	15.9%	1.9	0.05	2.8%	0.7	0.03	4.7%
Acrolein	0.120	16.5%	0.028	0.015	52.0%	0.010	0.005	47.4%

[1] Data quality objectives (DQO) are based upon manufacturers' specifications for 7-day exposure period and one standard deviation precision.

[2] Mean of the absolute differences between average of triplicates and individual sample (12 values per season).

Note: Shaded values denote mean ambient values that are less than five times the minimum detection limit (MDL).

The accuracy of the passive measurements were evaluated in the laboratory using a flow-through chamber with known pollutant concentrations, and in the field during a pilot study and again during the summer and winter seasons of the main study. The field evaluations compared the 7-day integrated passive measurements with corresponding time averages of continuous NOx and SO_2 measurements or averages of seven consecutive 24-hour canisters and DNPH cartridge samples. The results summarized in Table 4-2 show that most passive measurements were in reasonable agreement with the measurements methods that are commonly used in state and local monitoring air programs. The accuracy of passive measurements of acrolein and H_2S could not be evaluated during this study as their ambient concentrations were often below the limits of detection.

Table 4-2. Assessments of accuracy of passive measurements using standards and comparisons with reference methods and commonly used active sampling methods.

	Lab Evaluation		Pilot Study		HCMS Winter	
Compounds	Reference Value (ppbv)	Passive-Ref % Δ	Reference Value (ppbv)	Passive-Ref % Δ	Reference Value (ppbv)	Passive-Ref % Δ
Nitrogen Oxides (NOx)	17.20	6.2%	10.8	-24.6%	80.1	-8.9%
Nitorgen Dioxide (NO_2)	21.80	-1.4%	17.2	-17.9%	42.2	-24.5%
Sulfur Dioxide (SO_2)			1.7	18.2%		
Hydrogen Sulfide (H_2S)	2.10	-5.2%				
Benzene	2.57	-18.3%	0.37	-21.6%	0.70	-13.8%
Toluene	2.37	-5.5%	1.09	20.2%	1.93	-11.1%
Ethylbenzene	1.28	41% or (-6%)[1]	0.13	31% or (-8%)[1]	0.37	0.1%
m,p-Xylenes	1.02	-12.7%	0.45	2.2%	1.26	-11.7%
o-Xylene	0.43	-12.2%	0.18	0.0%	0.51	-7.5%
Formaldehyde	5.20	-2.3%	1.10	11.8%	4.97	-38.9%
Acetaldehyde			1.04	-43.3%	1.91	31.0%
Acrolein			0.24	-79.2%		

[1] Using our experimentally determined sampling rate of 37.4 ml/min rather than 25.7 ml/min published by Radiello, which reduced values by factor of 0.69.

Passive measurements of NOx were in good agreement (± 6%) with time-averaged continuous NO data during the laboratory evaluations. Passive NOx measurements were consistently lower than SCAQMD's NOx analyzer by about 15 to 20% during the pilot study, but these differences may be related to occasional concentration gradients from vehicles passing by the monitoring station because the inlet for District continuous monitors was located at the front of building and passive samplers were at the back. Passive SO_2 measurements were within 20% of the District continuous monitor, which is comparable to its precision during the summer HCMS. Passive measurements of NOx were generally in good agreement with SCAQMD's NOx analyzer during the main study when ambient levels were above the detection limit of the continuous analyzers.

Verifying the sampling rates of the passive samplers was a major objective of the laboratory evaluations. The experimentally determined sampling rates for benzene, toluene xylenes were within 20% of those published by Radiello. A significantly higher sampling rate than that reported by Radiello was measured for ethylbenzene. Experimentally determined sampling rates for ethylbenzene was 37.4 ml/min versus 25.7 ml/min published by Radiello. The experimentally determined sampling rate was used to determine ethylbenzene concentrations for the main HCMS, which results in concentrations that are a factor of 0.69 lower than using the rate published by Radiello. The passive samples for all BTEX compounds were stable for storage times of up to 14 days at -18º C. Passive measurements of BTEX species were generally within ± 15% of corresponding samples collected by active sampling methods that are commonly used in state and local monitoring programs.

Passive measurements of formaldehyde and acetaldehyde were in good agreement with diluted standards for the laboratory evaluations. Passive sampler values were slightly higher during pilot study for formaldehyde compared to time-averaged DNPH samples. However, one out of the seven 24-hour DNPH samples was invalid. Acetaldehyde measured by the passive sampler was 43% lower than values obtained by active sampling on DNPH cartridges. Acetaldehyde had poor accuracy probably due to effects from ozonolysis and from low collection efficiencies, which may also apply to “reference” samples collected actively on DNPH cartridges.

Passive sampling methods for NOx, NO_2, SO_2, H_2S, BTEX and formaldehyde are viable alternatives to continuous instruments or active sampling methods and are especially applicable for saturation monitoring and assessment of personal exposures. The ability of passive methods to collect samples over long exposure times allows for monitoring of ambient concentrations with comparable or better limits of detection and precision than active sampling methods. Passive monitors have no pumps or other moving parts and are very compact and portable. No special training is required for their deployment and operation. The low associated labor means that passive monitoring is often cost-effective over other methods of measurement. Laboratory analysis costs are the main expense for this type of monitoring. We provide basic standard operating procedures for the Ogawa and Radiello passive samplers in Appendix B and C, respectively, which can be tailored to specific projects.

Hypothesis #2. *Gradients in pollutant concentrations exist within the Harbor Communities (i.e., measurable variations in ambient concentrations) and can be related to a location’s proximity to emissions from either stationary or mobile sources.*

This hypothesis is true for NOx, SO_2, and elemental carbon, and is less so for $PM_{2.5}$. Annual average NOx and EC concentrations were 2 to 4 times higher at sampling sites located near diesel truck traffic than the mean concentrations at the sites in residential areas of the study area (Figure 4-1). The spatial variations of NOx and EC concentrations near the I-710 freeway are consistent with sharp decreases in pollutant concentrations with distance from the roadway. The EC concentrations at LBER and LBPW (about 18 m west and 300 m east of the I-710 freeway, respectively) were 2.26 ± 0.13 and 1.24 ± 0.08 times higher than the Wilmington Community mean, respectively. The sampling site 300 m downwind of I-710 (LBPW) had slightly higher EC concentrations to the two residential sites in west Long Beach (ratios of 1.09 ± 0.04 for LWIN and 1.08 ± 0.07 for LWBC). These results are qualitatively consistent with the ARB’s modeling estimates of DPM concentrations in 2002 (CARB, 2006) shown in Figure 2-3. EC concentrations were also significantly higher at LOCN (near the ICTF), LSUP (adjacent to

Pacific Coast Highway), LHUD (near east edge of the Terminal Island Freeway), WSWI (adjacent to W. Harry Bridges Blvd. at the north boundary of Port of Los Angeles) with ratios to Wilmington Community mean of 2.62 ± 0.26, 1.76 ± 0.11, 1.64 ± 0.28, and 1.85 ± 0.11, respectively. EC levels were uniformly lower at the four Wilmington community sampling sites and at the residential sampling site in San Pedro.

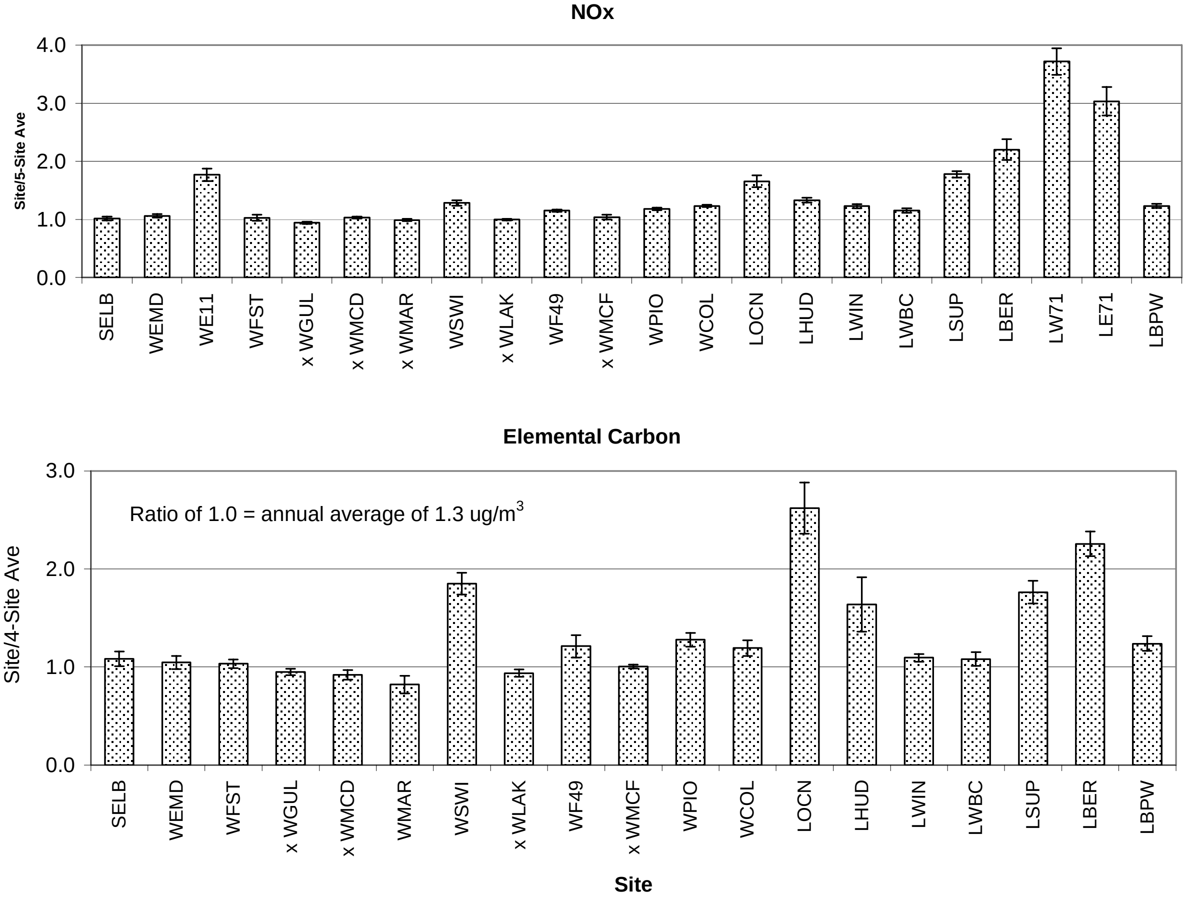

Figure 4-1**.** NOx and EC concentrations normalized to the mean of the residential sampling sites in Wilmington (identified with x). Uncertainties are standard errors of the mean ratios.

The spatial variations of $PM_{2.5}$ concentrations between residential and near-source sampling locations are far less than for EC (figure 4-2). Note that the average EC concentration was 1.3 $\mu g/m^3$ compared to 13.0 $\mu g/m^3$ for $PM_{2.5}$. The contributions of diesel exhaust are superimposed on the contributions of other sources of $PM_{2.5}$ from both within and outside the study area. In addition to direct emissions of particulate matter from motor vehicles (primary emissions), ambient $PM_{2.5}$ consists of nitrates, sulfates, and organic aerosols that are formed in the atmosphere (secondary pollutants) from NOx, SO_2, and volatile and semi-volatile organic compounds, respectively. Secondary pollutants are formed at varying rates that allow time for dispersion. Thus, atmospheric concentrations of secondary pollutants tend to be more uniform spatially than concentrations of primary pollutants, which can be significantly higher near sources of emissions (e.g., spatial variations for NOx and EC in Figure 4-1). Directly-emitted PM from outside the study area that has been well mixed during transport into the study area can also contribute to the apparent background concentrations in addition to dispersion and dilution of local emissions. The results in Figure 4-2 show that the roadside gradients in $PM_{2.5}$ are relatively small and that contributions of $PM_{2.5}$ from outside the study area may be large relative to local contributions.

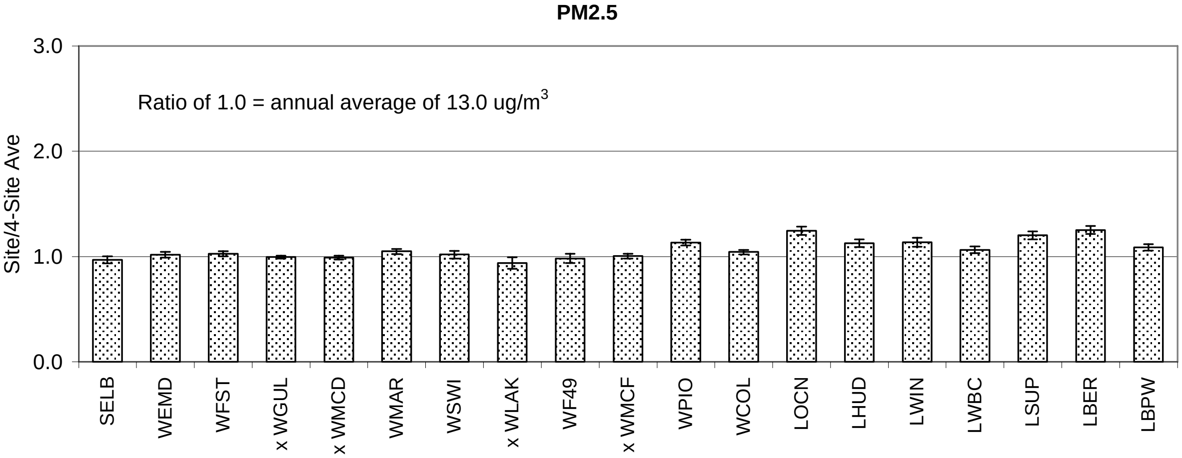

Figure 4-2**.** $PM_{2.5}$ concentrations normalized to the mean of the residential sampling sites in Wilmington (identified with x). Uncertainties are standard errors of the mean ratios.

The spatial pattern of SO_2 concentrations is consistent with higher levels occurring near a refinery (WEMD) and the port (e.g., WSWI, WF49, LSUP) (Figure 4-3). Annual mean mixing ratios of SO_2 were highest at the site adjacent to the east boundary of a refinery (2.02 ± 0.33 higher than the Wilmington Community mean) and dropped to 1.48 ± 0.13 about 400 m east of refinery. SO_2 levels were comparable to the Wilmington Community at the site about 800 m east of refinery (1.05 ± 0.13).

The annual average mixing ratios (ppbv) of BTEX tended to be higher near roadways, but this association was not as strong as for NOx. Levels of BTEX at the site adjacent to the refinery were similar to other residential sites. Average BTEX levels in the Harbor Communities were generally comparable or less than at other air monitoring locations in the basin. Toluene levels were higher at two locations where use of solvent was observed in the immediate area.

While the annual average mixing ratios of formaldehyde and acetaldehyde were slightly higher near roadways, site-to-site variations were relatively small within the study area and were comparable or slightly lower than annual mean levels measured elsewhere in the SoCAB during MATES-III and at the routine air toxic monitoring site during 2007. These results suggest that secondary formation of these aldehydes within the SoCAB have greater contributions to the annual average levels than local contributions near roadways over sampling durations of seven days.

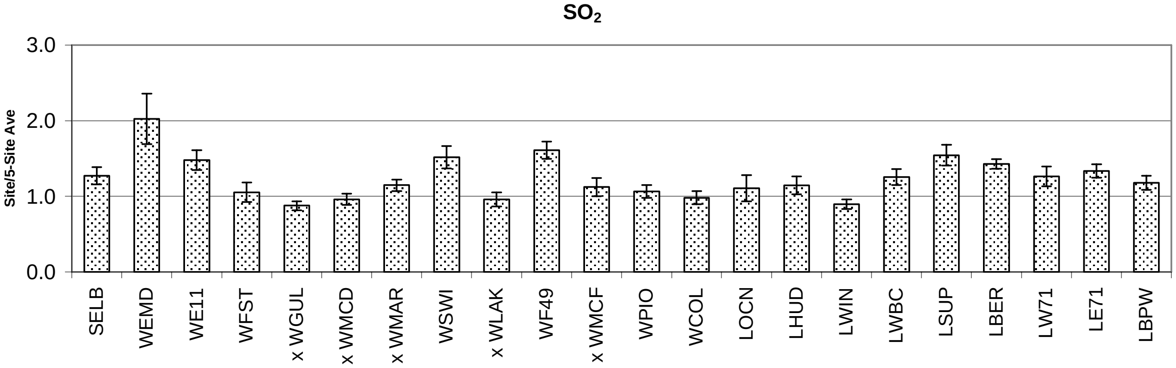

Figure 4-3**.** SO_2 mixing ratios normalized to the mean of the residential sampling sites in Wilmington. Uncertainties are standard errors of the mean ratios.

Hypothesis #3. *Ambient concentrations of black carbon serve as a surrogate for diesel particulate matter and can be correlated to proximity to heavy duty truck traffic and day-of-week variations in diesel truck traffic.*

Diesel particulate carbon (DPC) concentrations were estimated at each site from the measured EC concentrations times the slope of the correlation between total carbon and EC at the near road sampling locations shown in Figure 4-4 for each season. TC and EC are well correlated (R^2 between 0.8 and 0.9) with slopes between 1.5 and 2.2. Using these regression results, we estimated the upper-bound ambient concentrations of DPC from the average EC concentrations at each site. Diesel particulate matter (DPM) was estimated from the following relationship:

Diesel Particulate Matter (DPM) = EC + 1.46 (DPC-EC)

where 1.46 is the ratio of diesel particulate organic matter (DPOM) to DPC from the Gasoline/Diesel PM Split dynamometer testing of diesel trucks in the Riverside, CA area (El-Zanan et al., 2008). Metals have a minor contribution to DPM and can be excluded in the above DPM calculation. This estimation for DPM was specifically developed for this study and may not be applicable for other areas, especially when residential wood burning or wildfires are significant contributors to ambient $PM_{2.5}$ concentrations.

The estimated annual average concentrations of DPM (from the EC surrogate method) at the residential sampling sites were similar to those determined in MATES-III at the West Long Beach and North Long Beach monitoring sites using the Chemical Mass Balance receptor model (Figure 4-5) and are comparable or lower than at other MATES-III sites in the SoCAB. However, higher concentrations of DPM as well as EC and NOx were measured at sites in closer proximity to diesel truck traffic. We recently measured on-road concentrations of black carbon on highways in the South Coast Air Basin for a separate study (Fujita et al. 2008). The results of that study shown in Figure 4-6 show that higher concentrations of DPM are also likely in other part of the SoCAB near major truck routes from the port area to the Inland Empire along SR-91, I-605, SR-60 and out of the basin along I-5 and I-10.

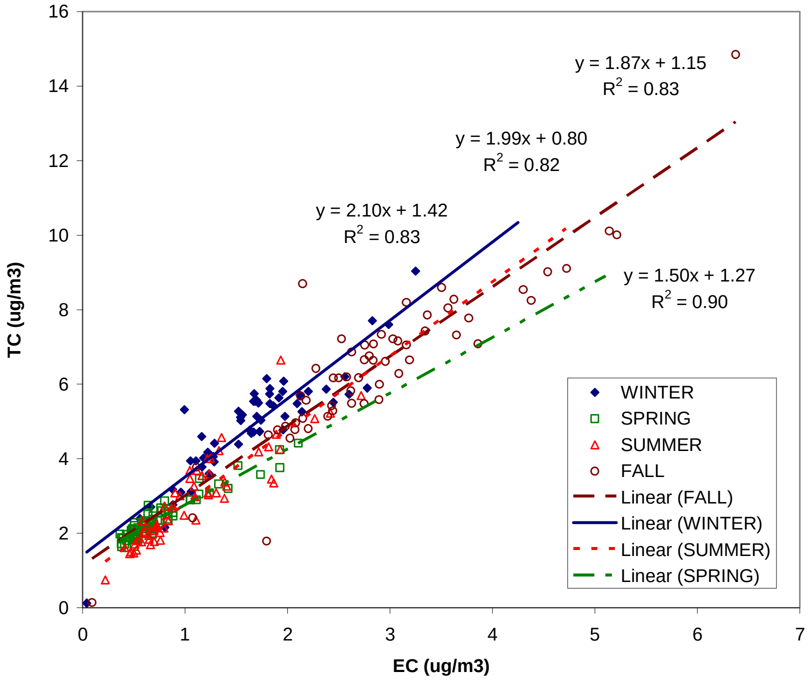

Figure 4-4. Correlations of TC and EC by season.

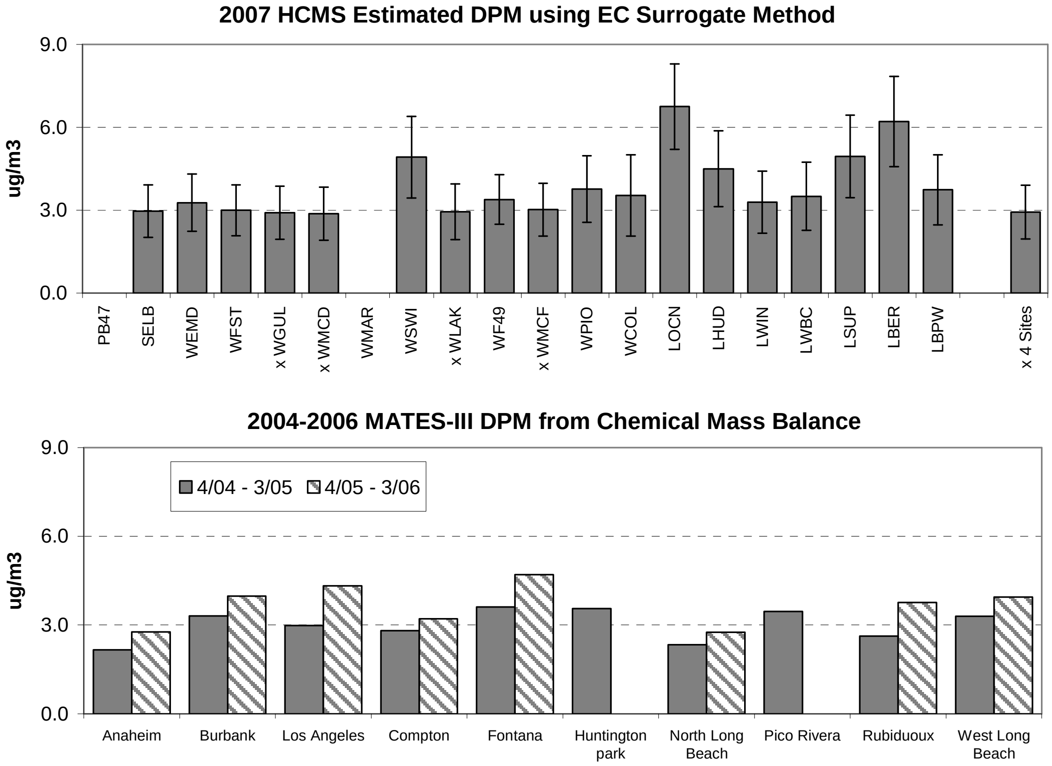

Figure 4-5. Estimated annual mean diesel particulate matter concentrations (μg/m^3) and standard errors of the four seasonal means during 2007 HCMS and MATES-III.

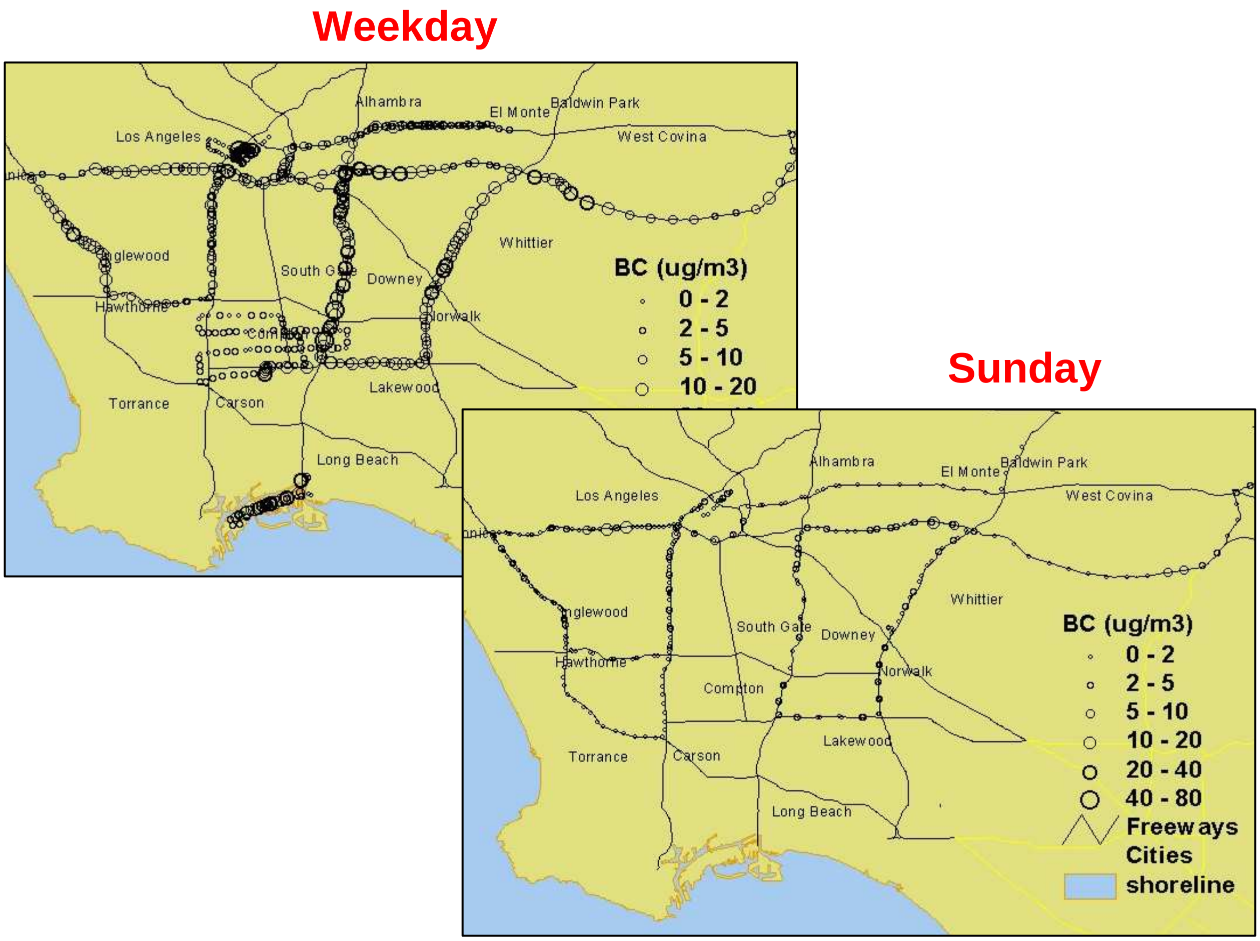

Figure 4-6. On-road concentrations of black carbon (1-minute averages) measured on highways in the South Coast Air Basin on a weekday and Sunday. (Source: Fujita et al. 2008).

Hypothesis #4. *The existing air quality monitoring in the area is not adequate to characterize the spatial variations in cumulative exposure within the community.*

This hypothesis is true with respect to the sharp gradient in pollutant concentrations that occur near roadways (i.e., NOx, CO, DPM). However, the existing SCAQMD monitoring stations in North Long Beach and West Long Beach are representative of the annual mean concentrations in residential areas of the community that are located greater than 300 meters from the truck routes (I-710 freeway and arterial streets leading to the port area).

Hypothesis #5. *Seasonal variations in meteorological conditions affect the pattern and magnitude of ambient concentrations of toxic air contaminants.*

This hypothesis is true for primary pollutants. Ambient concentrations are higher in the fall by as much as a factor of 4 to 6 for NOx and DPM compared to spring, which had the lowest concentrations. Fall concentrations were about factor of three higher compared to summer and nearly equal to winter concentrations. Concentrations at near-road sampling sites were about 2-4 times higher than the community mean in all seasons. There is less seasonal variation in aldehyde concentrations due to contributions of increased atmospheric formation of these compounds during spring and summer. The synoptic meteorological conditions during the fall result in periods of stagnation and buildup of higher pollutant concentrations and colder temperatures during winter results in stronger inversions (during nighttime and early morning) and correspondingly larger pollutant gradients near roadways.

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APPENDIX A

Application and Evaluation of Passive Samplers for Assessment of Community Exposure to Toxic Air Contaminants and Related Pollutants

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ABSTRACT

Several types of passive monitors were evaluated for their use in the Harbor Communities Monitoring Study, a saturation monitoring campaign in the communities of Wilmington, Long Beach, and San Pedro, CA during 2007. Preliminary evaluation took place in a small atmospheric chamber to test the accuracy of diffusion rates published by the manufacturers and to measure replicate precision. Chamber experiments found the monitors to be accurate and highly precise during seven day periods. Additional chamber experiments were conducted to evaluate the stability of volatile organic compounds on Carbograph 4 during and after exposure. Secondarily, the passive monitors were evaluated in a one week pilot study in Long Beach, CA to assess the effects of environmental factors such as varying pollutant concentration and low wind speed. Finally, in conjunction with the Harbor Communities Monitoring Study, passive monitors underwent quality assurance experiments to evaluate their replicate precision and measurement accuracy during the course of the study. Although some interferences were observed to affect the rates of diffusion during evaluation, the monitors showed an overall ability to effectively measure ambient level pollution. The high sensitivity, precision and accuracy of the samplers coupled with the lack of need for pumps, electricity, and general maintenance should guarantee a niche for them in future studies.

1. INTRODUCTION

The Harbor Communities Monitoring Study (HCMS) was conducted to characterize the spatial variations in concentrations of toxic air contaminants (TACs) and their co-pollutants within the California communities of Wilmington, parts of Carson, West Long Beach, and San Pedro. These communities were chosen because of the various emission sources in the area and the close proximity of residents to these emission sources. These include the Ports of Los Angeles and Long Beach, petroleum refineries, intermodal rail facilities and the greatest concentration of diesel traffic in the Los Angeles metropolitan area. The study consisted of three types of air pollution sampling: a saturation monitoring network operated by the Desert Research Institute, mobile sampling by the University of California, Los Angeles and California Air Resources Board, and a network of particle counters operated by the University of Southern California. HCMS was conducted during 2007 concurrently with complementary monitoring programs in the study area by the South Coast Air Quality Management District (SCAQMD) and the Ports of Los Angeles and Long Beach.

The saturation monitoring by Desert Research Institute was designed to establish the spatial variations of annual average concentrations of selected TACs and copollutants within the study area. The saturation monitoring network consisted of 7-day time-integrated sampling at twenty sites for four consecutive weeks in four seasons during 2007. Measurements included NO_x and SO_2 using Ogawa passive samplers and VOC (benzene, toluene, ethylbenzene, xylenes and 1,3 butadiene) and carbonyl compounds (formaldehyde, acetaldehyde and acrolein) using Radiello passive samplers. Additionally, 7-day integrated Teflon and quartz filters were collected with portable AirMetric MiniVol samplers and analyzed for $PM_{2.5}$ mass and organic and elemental carbon. NO_2 and H_2S (using Radiello passive samplers) were also be measured at three sampling sites, and full sets of passive measurements (including NO_2 but not H_2S) were made at three additional near-roadway locations.

The basic principle of passive sampling is diffusion of gaseous pollutants across a surface to an adsorbing material on which the pollutant of interest accumulates over time. The continual adsorption of the pollutant from the air maintains a concentration gradient near the surface that allows uptake of the pollutant to occur without any forced air movement (i.e., no pump or fan is required). While electricity demands and moving parts make active and continuous monitoring technologies a challenge for personal exposure assessment, passive monitors are unobtrusive and costs for sample collection are low. The ability of passive samplers to collect analytes over extended periods of time allows for the measurement of trace pollutants. Sensitivity is limited only by the amount of time for which a sampler can be exposed and the blank value of the analyte on an unexposed adsorbent surface. After sampling, the collected pollutant is desorbed from the sampling media by thermal or chemical means and analyzed quantitatively. The average concentration of the pollutant in the air to which the sampler was exposed is calculated by dividing the mass of pollutant measured analytically by the product of sampling rate and sampling time.

The Ogawa Sampler has been used in a number of studies, mostly in urban environments (Singer et al., 2004; Mukerjee et al., 2004). The Radiello sampler, developed over a decade ago for assessment of benzene exposure (Cocheo et al., 1996), has been evaluated for collection of VOCs with Carbograph 4 and other adsorbents (Vardoilakis et al., 2001; Bruno et al., 2004;

Strandberg et al., 2005; Strandberg et al., 2006). Sampling rates of diffusive samplers cannot be directly measured and must be experimentally determined. The sampling rates are supplied by Radiello (http://www.radiello.com) and Ogawa and Company (http://www.ogawausa.com) for a number of commonly collected compounds. The Radiello aldehyde and H_2S sampler have been used in studies but little work has been done to independently evaluate the sampling rates published by Radiello. Measured diffusion rates can vary with environmental factors including temperature, relative humidity, wind speed, concentration of analyte, and the concentration of chemically or physically interfering species. Recent interest in 1,3-butadiene has spurred the development of a passive method for this suspected carcinogen (Martin et al.; 2004; Strandberg et al., 2005; Strandberg et al., 2006).

The accuracy and precision of the passive sampling methods used in the HCMS were evaluated in three phases. First, we evaluated the sampling rates of the passive sampling methods for NO_2, NOx, H_2S, benzene, toluene, ethylbenzene, xylenes, and formaldehyde in the laboratory using a flow through chamber with known pollutant concentrations. A pilot study was then conducted during a one-week period beginning on August 16, 2006 at the South Coast Air Quality Management District (SCAQMD) North Long Beach monitoring station to determine replicate precision of the passive measurements under field conditions. The passive measurements were compared with the SCAQMD continuous NO_x, NO_2 and SO_2 data and time-integrated samples were collected and analyzed by DRI for organic air toxics using established "reference" methods. The passive samplers were evaluated during the main field study by collecting replicate samples and by comparing results to corresponding active sampling methods.

3. EXPERIMENTAL METHODS

3.1 Equipment and Analysis

Ogawa passive samplers were used for monitoring NO_x, NO_2, and SO_2. NO_x and SO_2 were collected over weeklong periods using precoated 14.5 mm sampling pads, deployed in personal sampling bodies. NO concentrations were calculated by subtracting NO2 from NOx concentrations. Sampling and analysis were performed according to manufacturer protocols (Ogawa & Co., USA, Inc., http://www.ogawausa.com/protocol.html). The Ogawa NO_2 and NOx pads were extracted and mixed with a solution of sulfanilamide and N-(1-Naphthyl)-ethylenediamine dihydrochoride to produce a colored nitrite solution which was analyzed on a Technicon (Tarrytown, NY) TRAACS 800 Automated Colorimetric System (AC). The Ogawa SO_2 pads were extracted in 8 ml of deionized-distilled water (DDW), 1.75% hydrogen peroxide were added and sulfate were measured with the Dionex 2020i (Sunnyvale, CA) ion chromatograph (IC). These analyses were performed by the Environmental Analysis Facility (EAF) of DRI.

Benzene, toluene, ethylbenzene, and xylenes (BTEX) were passively collected over weeklong periods using Radiello diffusive samplers consisting of stainless steel mesh cylinders (3x8 um mesh, 4.8 mm diameter x 60 mm length) packed with Carbograph 4 (350 mg). The cartridges were deployed in the diffusive sampling bodies according to the manufacturer's instruction (http://www.radiello.com). Collection of 1,3-butadiene was also evaluated. Radiello VOC cartridges were analyzed on a Varian 3800 gas chromatograph with Saturn 2000 mass spectrometry (MS) detection equipped with a Gerstel TDSA-3 thermal desorption unit. Initial desorption was set for five minutes at 300 °C before transfer onto a Tenax trap cooled to -150

°C. Sample was split 15:1 in order to reduce analytical loading in the MS. After preconcentration on the trap, the sample was injected at 240 °C onto a 60m, widebore, Phenometrix ZB-1 for separation before MS detection.

Radiello diffusive samplers were used to passively collect carbonyl compounds. Stainless steel net cartridges filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated florisil were used. Carbonyl compounds react with 2,4-DNPH forming corresponding dinitrophenylhydrazones. 24-hour time averaged Waters Sep-Pac DNPH cartridges and Radiello aldehyde cartridges were eluted with 2 ml of acetonitrile (ACN) and filtered before analysis. The samples were then separated and analyzed on a Waters 2695 equipped with a Waters 996 photodiode array detector. The mobile phase was water and acetonitrile run on a Varian Polaris 3u C18-A 150 x 4.6mm column according to EPA method TO-11A (US EPA, 1999). The VOC and carbonyl compound analyses were performed by the Organic Analytical Laboratory (OAL) of DRI.

Radiello chemiadsorbing cartridges were used for passive sampling of hydrogen sulfide (H2S). The cartridge is made of microporous polyethylene and impregnated with zinc acetate. H2S is chemiadsorbed by zinc acetate and transformed into stable zinc sulfide. Radiello H_2S samples were eluted with a 10.5 ml ferric chloride-amine solution to yield methylene blue, which was analyzed with a Bausch and Laumb Spectronic 20 visible spectrometer at 665 nm. Calibration was completed using a calibration kit from Radiello: RAD-171 (www.radiello.com).

Passive VOC samples were compared to corresponding canister samples analyzed according to the EPA Method TO-15 using a Varian 3800 gas chromatograph interfaced to a Varian Saturn 2000 ion trap mass spectrometer (MS) and flame ionization detector (FID). Canisters were preconcentrated using a Lotus Ultra Trace Toxics System-MS-TO15 before injection onto a Varian CP fused silica 60m widebore column with MS detection for BTEX and an Agilent Alumina 30m megabore column with FID detection for 1,3-butadiene (US EPA, 1999). Calibration of the system was conducted with a VOC mixture (purchased from AiR Environmental) that contained the most commonly found hydrocarbons (including BTEX and 1,3-butadiene). Passive carbonyl compound samples were compared to corresponding samples collected with Sep-Pak cartridges which have been impregnated with an acidified 2,4-dinitrophenylhydrazine (DNPH) reagent (Waters, Inc), according to the EPA Method TO-11A (US EPA, 1999). The cartridges were analyzed by high performance liquid chromatograph (Waters 2690 Alliance System with 996 Photodiode Array Detector) for separation and quantification of the hydrazones.

Acrolein is known to rearrange on DNPH cartridges to an unknown degradation product (acrolein-X) This process of rearrangement is sufficiently rapid that most of the acrolein may convert to acrolein-X, unless the sample is analyzed within a few hours. The problem is compounded by the fact that acrolein-X co-elutes in the HPLC analysis with another common carbonyl compound, butyraldehyde. The UV spectra from the photodiode array detector show that there is substantial overlap in the chromatographic retention time of acrolein-x with butyraldehyde. Thus, the sum of acrolein and butyraldehyde represents an upper-bound estimate of acrolein that was originally present in the sample. In order to circumvent this problem, DRI's Organic Analytical Laboratory recently performed experiments, as part of a separate study to determine if a more accurate measurement of acrolein concentration could be obtained by post-analysis reprocessing of the HPLC spectra (Fujita et al., 2006). This procedure was used to estimate the "total" acrolein for both Radiello passive samples and DNPH cartridges.

3.2 Laboratory Evaluation

The passive samplers were evaluated under controlled conditions in the laboratory to verify sampling rates, precision, accuracy, and validity of measurements for periods extending up to seven days. Passive samplers were exposed in a 100-liter flow-through chamber with known concentrations of selected TACs. The chamber consists of a 100 liter half-cylindrical shape framed with steel and Teflon rods and lined with Teflon sheeting. An internal fan ensured a well-mixed atmosphere and a wind speed of 1.0 m/s. The flow-through chamber was constructed to minimize potential losses to walls and other surfaces over exposure periods. Seven stainless steel ports were built into the flooring: 1 for flow of the atmosphere into the chamber, 1 for exhaust, 1 for a temperature and relative humidity probe, and 4 possible ports for sampling. The atmospheres were created by diluting certified gas standards with zero air using an Environics 9100 Ambient Monitoring Calibration System. Zero air was generated using an Aadco 737 pure air generator outfitted with several scrubbing filters. This system is evaluated regularly for purity as it is used for canister cleaning. The diluted atmosphere was then split: half of the flow was humidified until saturation and half was diverted around the humidifier and then combined again with the saturated air to form a 50% RH mixture. The humidified test atmosphere was fed directly to the chamber at 2.5 liters per minute. A self-regulating exhaust line leads from the chamber to a hood. Exposure tests were delayed 2 hours after flow began to allow for atmospheric equilibrium within the chamber. See **Figure 1** for chamber schematic.

Chamber tests were used to evaluate the published sampling rates of Ogawa NO_x and NO_2 samplers and Radiello volatile organic compounds (VOCs), aldehyde and hydrogen sulfide (H_2S) samplers **(Table 1)**. The samplers were deployed in triplicate and exposed to atmospheres of constant temperature, humidity, and concentrations typical of an urban atmosphere for seven day periods. Due to several unplanned power outages during the first chamber test, the Ogawa NO_2/NO_x samplers were exposed to 100% RH conditions and some variation in NO_x concentrations. All other evaluations were conducted with battery backups to prevent future problems arising from power outages. Nominal concentrations determined by the Environics 9100 were used for sampling rate evaluation if dilution occurred directly from a certified standard (H2S). In other cases, an established comparison method was used to determine chamber concentration (VOC). In some cases, both conventions were observed (aldehyde, NO_x, NO_2).

Additional experiments were used to evaluate the collection efficiency of the Radiello VOC sampler for 1,3-butadiene and to evaluate the published sampling rates for BTEX. If suitable for 1,3-butadiene, experimental calculation of a sampling rate is possible by measuring the chamber test atmosphere with an established method. The sampling rate for 1,3-butadiene is not available from Radiello and was determined experimentally. Previous studies have shown that 1,3-butadiene is susceptible to backdiffusion on passive adsorbents (Strandberg, 2005; Strandberg, 2006). In order to check the stability of 1,3-butadiene and BTEX on the cartridge during and after exposure, samplers were deployed in triplicate in 6 groups. Triplicate groups were removed from the chamber and analyzed immediately after 1, 4, and 7 days. The other 3 groups were exposed for the full seven days, stored in a freezer at -18ºC, and analyzed after 1, 7, and 14 days. Chamber concentration was measured independently by time-averaged canister sampling at 8.3ml/min sample flow for 24 hours each.

3.3 Pilot Study

A pilot study was conducted during a week in August 2006 at the SCAQMD North Long Beach monitoring station to determine the replicate precision of the passive samplers for NO_2, NO_x, SO_2, H_2S, BTEX, 1,3-butadiene, formaldehyde, acetaldehyde, and acrolein under field conditions. The passive measurements were compared with the SCAQMD continuous NO_x, NO_2 and SO_2 data, and with time-integrated samples collected and analyzed by DRI for organic air toxics using Waters DNPH cartridges for carbonyls and NO_x-denuded canisters for VOCs according to EPA Methods TO-11A and TO-15, respectively. All sampler inlets and passive samplers were located on the station's rooftop instrument platform. All daily samples were integrated over 24 hours beginning at noon each day.

Passive samplers were exposed for a one week period. The passive samplers were deployed at a height of approximately 2 meters above the instrument platform on the roof of the station, along a line running parallel to Long Beach Blvd. approximately 10 meters from the street side roofline of the building. The passive samplers were protected from settling dust and rain by transparent plastic canopies. A minimum distance of 6" was maintained between adjacent samplers. Another objective of the pilot study was to understand the effect that stagnant air might have on diffusion rates since the Long Beach/Wilmington area is characterized by low nocturnal winds. Radiello publishes that its sampling rates are invariant from .1-10m/s (www.radiello.com). In order to determine the potential influence of air flow on diffusion rates, the samplers were deployed in two groups with an oscillating electric fan providing constant easterly air flow at approximately 3 mph (1.3 m/s) across one group. Each group consisted of three of each type of sampler for evaluation of measurement precision. Time-integrated canister and DNPH cartridge samples were collected on a daily basis using samplers designed by DRI, which were deployed on the rooftop platform with inlets located along the same line as the passive samplers (near the group without the electric fan).

3.4 Harbor Communities Monitoring Study Quality Assurance

Quality assurance was conducted at a site in northeast Wilmington for two weeks each, in the summer and winter seasons. During these periods, Ogawa passive samplers for NO_x and SO_2 and Radiello passive samplers for VOCs, aldehydes, and H_2S were deployed in triplicate to determine replicate precision. Passive diffusion rates were tested by comparison with more common active sampling. SO_2 and NO_x were measured with co-located continuous analyzers. 24-hour NO_x-denuded canisters and DNPH cartridges were collected to measure VOCs and aldehydes.

4. RESULTS

The sampling rates of the Ogawa and Radiello passive samplers were evaluated in this study under controlled laboratory conditions and in the field during an initial pilot study and during the main HCMS. Measurement accuracy was assessed by comparison with reference methods, which included EPA-certified continuous gas monitors and time-integrated samples collected by active sampling methods. The precision of passive sampling methods were determined by replicate sampling during all three phases of the evaluation.

4.1 Laboratory Evaluation

The chamber concentrations measured by Ogawa and Radiello passive samplers during 7 day exposures were consistently accurate when compared with reference values (**Table 2**). NO and NO_2 concentrations measured passively by the Ogawa NO_2/NOx sampler were within 6% and 1% of the concentration measured by the Horriba Analyzer with replicate precision of 3% and 1%, respectively. BTEX concentrations measured by the Radiello VOC sampler were within 20% of the canister measurements with the exception of ethylbenzene. Replicate precisions were within 11% of the mean. The Radiello aldehyde sampler measured formaldehyde to within 2% of the nominal concentration with replicate precision of 7%. The Radiello H_2S sampler evaluated a mean chamber concentration within 5% of the nominal concentration and with a 2% standard deviation of the mean.

Additional experiments for the Radiello VOC sampler revealed that in general, replicate precision increases with exposure time (**Figure 2**). BTEX chamber concentrations were measured in the 0-3 ppbv range for all compounds. Benzene, toluene, and ethylbenzene showed increasing sampling rates for decreasing exposure times and the xylenes showed mixed trends over exposure time. Replicate precision for all of the compounds shows a decreasing trend with sampling time but for benzene, toluene, and ethylbenzene, the data is precise enough to distinguish a negative trend in diffusion rates with longer exposure times (**Figure 2**). Radiello has published sampling rates for the BTEX compounds and reports them to be invariant from 8 hours to 14 days (7 day maximum for benzene) (www.radiello.com). For benzene and toluene, the sampling rates measured here are within 20% of those published by Radiello for all exposure times. For xylenes, the sampling rates are within 20% for only 4 and 7 day exposure times and for ethylbenzene, a significantly higher sampling rate was measured than that reported by Radiello for all exposure times (**Table 3**). Storage tests showed good reproducibility for samples stored up to 14 days at -18º C (**Figure 3**). BTEX experimental mean sampling rates as a function of storage time are shown in **Table 3**. For all compounds, sampling rates were stable for storage times of up to 14 days at -18º C. Percent standard deviations for all 7 day exposed samples, irrespective of storage time, were 14, 8, 9, 11, and 13% for benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene, respectively.

1,3-butadiene chamber concentration during the 7 day period was measured by canisters at 1.8 ppbv. It should be noted that the sampling rates in **Figures 4 and 5** were calculated experimentally based on this concentration. The mean passive sampling rate for 1, 4, and 7 day exposures was 4.9, 1.3, and 0.7 ml/min, respectively (Table 3). The sampling rate shows an exponentially decreasing trend, declining by 73% and 86% from the original value for 4 and 7 day exposures, respectively. The replicate precision increases markedly with exposure time as with BTEX (**Figure 4**). The mean sampling rates of 1,3-butadiene as a function of storage time are shown in **Figure 5**. The sampling rate was relatively consistent during storage of up to14 days at -18º C. The percent standard deviation for all samples exposed for 7 days was 24%.

4.2 Pilot Study

Concentrations of air toxics were low at the Long Beach AQMD station during the week of the pilot study measurements (**Table 4**). Meteorological data for the sampling period is shown in **Figure 6**. The upper chart shows the strong, consistent diurnal pattern dominated by westerly winds mid-day and stagnant air at night. The lower chart indicates high nighttime RH that decreased with the onset of the daytime winds. The following sections describe the results of comparisons between active time-integrated or continuous sampling methods and corresponding passive or continuous measurements, as well as evaluations of measurement precision.

The replicate precision for benzene, toluene, ethylbenzene, m-, p-, and o-xylene, formaldehyde, acetaldehyde, NO, NO_2, and SO_2 was evaluated by the passive samplers to be under 17% standard deviation of the mean in all cases. It should be noted that the percent standard deviations for acrolein and H_2S (37, and 47%, respectively) were measured under pptv ambient concentrations which were below or near the published limits of detection. The comparison of the constant airflow samplers with those exposed to ambient winds was excellent for all compounds. The concentrations measured by the ambient samplers were within 16% of those under controlled winds for all compounds except H_2S and acrolein (**Table 4**). An anemometer positioned directly above the ambient passive samplers confirmed that winds were undetectable for a significant period of time every night during exposure (**Figure 6**). Nevertheless, there was no correlation between wind speed and sampling rate observed.

The comparison of the ambient samplers to the reference methods produced variable results. For BTEX, all compounds were within 31% of the canister measured concentrations. M-, p-, and o-xylenes were both measured passively to be within 2% of the reference method (Table 4). The Radiello aldehyde sampler performed well for formaldehyde (12%) but the results for acetaldehyde (43%) and acrolein (79%) were considerably different than those measured by the active DNPH cartridges (Table 4). Ozone concentrations are a concern for aldehyde scavenging when sampling with DNPH and as such, active samples are usually ozone-denuded. Since ozone denudation is unrealistic for passive sampling, active DNPH sampling in the pilot study was not denuded to compare the effects on each type of media. The mean ozone concentration during the pilot study was calculated from hourly average data at 26.9 ppbv (**Figure 7**). Radiello has published data which suggests that acetaldehyde is much more vulnerable than formaldehyde to ozonolysis on their media, but only at ozone concentrations of greater than 100 ppbv (www.radiello.com). Furthermore, evidence in the past few years suggests that active DNPH samples are subject to low collection efficiencies for acetaldehyde for sampling times of 24 hours or greater (Herrington et al., 2007). Acrolein mean concentration as measured by Radiello was 49 pptv, which is well below its published limit of quantitation. The percent standard deviations for formaldehyde, acetaldehyde and acrolein were 4%, 2%, and 37%, respectively. The Ogawa samplers measured mean concentrations for NO, NO_2 and SO_2 approximately 20% below those evaluated by the continuous analyzers at the SCAQMD site with high replicate precision (**Table 4**). This may have to do with the positioning of sampling lines onsite. The North Long Beach monitoring station occupies the rooftop of a building located next to a busy road. The inlets for the continuous monitoring equipment maintained by SCAQMD are street side whereas the passive monitoring occurred downwind, about 30 feet at the other end of the rooftop. It seems likely that a negative concentration gradient from the dilution of vehicle emissions accounts for these differences.

4.3 Harbor Communities Monitoring Study

The Harbor Communities Monitoring Study took place in Wilmington, CA during four, 28-day seasons in 2007. Saturation monitoring at 23 sites for air toxics was accomplished using Ogawa and Radiello passive samplers. During the winter (2/13/07-3/13/07) and summer (7/31/07-8/28/07) seasons, a site in northeast Wilmington was equipped with measurement equipment for quality assurance of passive sampling. Radiello VOC, aldehyde, and H2S samplers as well as Ogawa NOx and SO2 samplers were deployed in triplicate during these seasons. The following sections describe the results of comparisons between active time-integrated or continuous sampling methods and corresponding passive or continuous measurements, as well as evaluations of measurement precision.

Radiello VOC samplers exhibited high accuracy and precision during most QA periods. In total, 4 weeks were accounted for by reference methods: 2 during the winter period and 2 during the summer period. During the winter, BTEX concentrations were low (**Table 5a**). During the week 02/27/07-03/06/07, Radiello passive samplers were accurate with differences between the passive samples and the averaged 24-hour canister measurements of less than 5% for BTEX. The percent standard deviations were all below 2%. The replicate precisions for the week of 3/6/07-3/13/07 were all measured below 2% as well. The passive VOC samplers, however, were not as accurate for the second week, but all concentrations were within 21% of the reference method (**Table 5b**). In the summer, VOC comparisons and replicate precisions were worse than in winter (**Table 5c and 5d**). It should be noted, however, that 24-canister measurements were not complete for the summertime weeks due to equipment failures. For weeks 08/07/07-08/14/07 and 08/14/07-08/21/07, canister measurements accounted for 5 and 4 of the 7 days for each week, respectively. Radiello aldehyde samplers exhibited less accuracy during the QA periods then the VOC samplers. In total, 4 weeks were accounted for by 24-hour, ozone-denuded DNPH cartridges; Two weeks were sampled in each season. Replicate precision was excellent over all weeks. Percent standard deviations were under 15% for all aldehydes samples and under 6% in the winter weeks alone. However, the passive concentrations generally underestimated the concentrations measured by active DNPH methods, sometimes by 50% or more (**Table 5**). It is difficult to attribute such inaccuracies to ozonolysis even though active DNPH samples were denuded at the QA site (**Figure 8 and 9**). During the two summertime weeks, when ozone is at its maximum, we would expect to see the two worst comparisons with the ozone-denuded, reference method. However, the week of 08/07/07-08/14/07 showed the best comparison of all four weeks. It is believed that the data during the QA study demonstrate a balance between two environmental influences on the sampling rate of aldehydes. These influences are ozonolysis, which affects all passive aldehydes, and the low collection efficiency for active acetaldehyde samples noted by Herrington (Herrington et al., 2007). Ogawa NOx and NO2 samplers demonstrated high replicate precision and good agreement with the reference measurement during the four QA periods. The continuous monitoring instrumentation for SO_2 was down during the QA periods, but replicate precision of the passive measurement is high throughout. For most compounds, it is apparent that replicate precision was higher in winter than summer. This could be due to increased air motions associated with summertime heating of the boundary layer.

5. DISCUSSION AND CONCLUSIONS

Chamber experiments confirmed the accuracy of the sampling rates provided by Ogawa and Radiello and high replicate precision of the passive samplers during 7 day exposure periods. For ethylbenzene, the observed sampling rate was 42% higher than that published by Radiello, but all others were within 20%. The Ogawa NOx and NO_2 samplers performed the best in chamber evaluations. Observed sampling rates were within 6% of those published and percent standard deviations were below 3% of the mean for both compounds. Additional experiments for the Radiello VOC sampler show that in general, longer exposure times result in an increase in replicate precision and measurement accuracy. Since the decline in replicate precision with short exposure times is likely due to decreased analytical loading, precision may be increased by sampling in high concentration environments. BTEX on the adsorbent, Carbograph 4, is stable for at least 14 days when stored in a freezer at -18º C. Replicate precision was excellent for all 7-day exposed samples with varying storage times. The Radiello VOC sampler packed with Carbograph 4 is unsuitable for sampling of 1,3-butadiene. Sampling rates for one day are markedly lower than those published for other VOC and we conclude that this is because of backdiffusion. 1,3-butadiene does appear to be stable on the adsorbent when stored in a freezer. This is likely due to improved stability at low temperatures on Carbograph 4.

In most cases, Radiello and Ogawa passive samplers in field experiments were accurate and highly precise. The Radiello VOC sampler was in most cases within 20% of the reference canister method for BTEX with the exception of the first summer QA week. Ethylbenzene, however, continually shows less accurate results than the other BTEX compounds. The Radiello aldehyde sampler was the most problematic of any of the samplers. Formaldehyde was measured effectively in the laboratory and in the pilot study, but in the QA, there was an interference with aldehyde collection which may be in part attributable to ozone reacting across the double bond. Ozone scavenging can be prevented with a denuder using active methods, but in passive methods, there is no such option. Discrepancies in acetaldehyde concentration during the main study indicate a problem with the collection efficiency of active DNPH samples seen in other studies (Herrington et al., 2007). More work is needed to better evaluate these influences on the passive method. The Radiello H2S sampler showed consistently high replicate precision and high accuracy in chamber experiments. More work should be conducted to evaluate its accuracy in field environments. The Ogawa NO2, NOx, and SO2 samplers compared well with continuous NOx and SO2 instrumentation during field evaluations. The 20% discrepancy between the passive method and the continuous data during the pilot study are likely explained by a dilution gradient of vehicle exhaust.

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Table 1
Nominal pollutant mixing ratios and reference methods used in chamber experiments

Sampler Type	Analyte	Nominal	Comparison
Ogawa NO_2	NO_2	25 ppb	Horriba NO/NOx Analyzer
Ogawa NO_x	NO_x	54 ppb	Horriba NO/NOx Analyzer
Radiello Aldehyde	Formaldehyde	5 ppb	Waters DNPH by HPLC
Radiello VOC	BTEX	1.5 ppb	Canister GC/MS
Radiello H_2S	H_2S	2 ppb	N/A

Table 2
Chamber pollutant mixing ratios (ppbv) measured by passive samplers over seven day periods versus the reference methods

Compounds	n	Passive Sample[1]	Reference Value[2]	Percent Δ[3]
NO	3	(17.64 - 18.64) 18.26 ± 0.54	17.20	6%
NO_2	3	(21.23 - 21.80) 21.49 ± 0.29	21.80	1%
formaldehyde	3	(4.68 - 5.38) 5.08 ± 0.36	5.20	2%
benzene	3	(1.82 - 2.30) 2.10 ± 0.24	2.57	18%
toluene	3	(2.18 - 2.37) 2.24 ± 0.11	2.37	5%
ethylbenzene	3	(1.70 - 1.91) 1.80 ± 0.12	1.28	41%
m,p-xylene	3	(0.84 - 0.92) 0.89 ± 0.04	1.02	13%
o-xylene	3	(0.37 - 0.40) 0.38 ± 0.02	0.43	12%
hydrogen sulfide	3	(1.96 - 2.04) 1.99 ± 0.04	2.10	5%

[1] Range of passive values given in parenthesis followed by mean value ± standard deviation

[2] Reference method is by Horriba NO/ NO_x analyzer for NO, NO_2, by 24-hour time-integrated canisters for BTEX and by Environics 9100 for formaldehyde and H_2S

[3] Percent difference of the passive result compared to the reference result

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Table 3
Reference and mean experimentally determined sampling rates (ml/min) and their ratios

Exposure (days)	Storage (days)	1,3-butadiene	benzene	toluene	ethylbenzene	m,p_xylenes	o_xylene
Reference Rates		NA	27.8	30.0	25.7	26.6	24.6
<u>Experimentally Determined</u>							
1	0	4.9 ± 0.7	31.8 ± 3.3	35.0 ± 4.0	44.7 ± 4.0	15.2 ± 9.6	11.0 ± 10.1
4	0	1.3 ± 0.2	30.4 ± 4.5	32.8 ± 2.8	45.5 ± 1.4	27.7 ± 2.5	22.2
7	0	0.7 ± 0.1	22.4 ± 2.6	29.3 ± 1.4	36.6 ± 2.6	23.5 ± 1.1	21.6 ± 0.8
7	1	0.6	20.6	29.4	38.0	24.8	23.6
7	7	0.6	21.4 ± 2.4	33.6	37.8 ± 1.6	24.6 ± 2.7	23.7 ± 3.2
7	14	0.7 ± 0.1	24.4 ± 1.8	33.2 ± 2.5	32.0 ± 2.0	29.1 ± 2.5	28.1 ± 2.5
<u>Expt/Ref Ratios</u>							
1	0		1.14 ± 0.12	1.17 ± 0.13	1.74 ± 0.15	0.57 ± 0.36	0.45 ± 0.41
4	0		1.09 ± 0.16	1.09 ± 0.09	1.77 ± 0.05	1.04 ± 0.09	0.90
7	0		0.80 ± 0.09	0.98 ± 0.05	1.42 ± 0.10	0.88 ± 0.04	0.88 ± 0.03
7	1		0.74	0.98	1.48	0.93	0.96
7	7		0.77 ± 0.09	1.12	1.47 ± 0.06	0.93 ± 0.10	0.96 ± 0.13
7	14		0.88 ± 0.06	1.11 ± 0.08	1.24 ± 0.08	1.09 ± 0.09	1.14 ± 0.10

Table 4
Pollutant mixing ratios (ppbv) measured by passive samplers with ambient and induced winds versus the reference methods during a pilot study at the North Long Beach monitoring station

Compounds	n	Ambient Winds¹	Fan-Induced Winds¹	Reference Value²	Amb-Fan Percent Δ [3]	Amb-Ref Percent Δ [4]
NO	3	(7.33 - 8.93) 8.14 ± 0.80	(8.11 - 9.25) 8.51 ± 0.64	10.80	4%	25%
NO_2	3	(13.55 - 14.61) 14.12 ± 0.53	(13.12 - 15.56) 14.36 ± 1.22	17.20	2%	18%
SO_2	3	(1.15 - 1.53) 1.39 ± 0.21	(1.16 - 1.19) 1.18 ± 0.02	1.70	16%	18%
formaldehyde	3	(1.18 - 1.26) 1.23 ± 0.04	(1.19 - 1.41) 1.27 ± 0.12	1.10	3%	12%
acetaldehyde	3	(0.58 - 0.60) 0.59 ± 0.01	(0.56 - 0.62) 0.59 ± 0.03	1.04	0%	43%
acrolein	3	(0.03 - 0.06) 0.05 ± 0.02	(0.02 - 0.04) 0.03 ± 0.01	0.24	50%	79%
benzene	3	(0.25 - 0.31) 0.29 ± 0.03	(0.29 - 0.30) 0.29 ± 0.01	0.37	0%	22%
toluene	3	(1.11 - 1.55) 1.31 ± 0.22	(1.02 - 1.36) 1.19 ± 0.17	1.09	10%	20%
ethylbenzene	3	(0.15 - 0.18) 0.17 ± 0.01	(0.17 - 0.18) 0.18 ± 0.01	0.13	6%	31%
m,p-xylene	3	(0.42 - 0.48) 0.46 ± 0.04	(0.48 - 0.50) 0.49 ± 0.01	0.45	6%	2%
o-xylene	3	(0.17 - 0.19) 0.18 ± 0.01	(0.19 - 0.20) 0.20 ± 0.01	0.18	11%	0%
hydrogen sulfide	3	(0.16 - 0.46) 0.31 ± 0.15	(0.16 - 0.31) 0.26 ± 0.08	NA	18%	NA

[1] Range of passive values given in parenthesis followed by mean value ± standard deviation

[2] Reference method is by SCAQMD continuous analyzers for NO, NO_2 and SO_2, by 24-hour time-integrated Waters DNPH cartridges, and by 24-hour time-integrated canisters for BTEX. No reference method was used for H_2S concentration

[3] Percentage difference between ambient and fanned samples as compared to their mean

[4] Percentage difference between ambient and reference samples as compared to reference value

Table 5
Replicate precisions of passive sampling during the winter and summer HCMS and measurement comparisons with reference methods

Compounds	Passive[1]	Reference[2]	Percent Δ[3]	Passive[1]	Reference[2]	Percent Δ[3]
Winter 2007	02/27/07 - 03/06/07			03/06/07 - 03/13/07		
benzene	0.561 ± 0.009	0.581	3.3%	0.651 ± 0.004	0.825	21.1%
toluene	1.553 ± 0.028	1.536	1.1%	1.877 ± 0.025	2.322	19.2%
ethylbenzene	0.329 ± 0.002	0.314	4.9%	0.417 ± 0.010	0.431	3.4%
m,p-xylene	1.006 ± 0.008	1.049	4.1%	1.221 ± 0.020	1.473	17.1%
o-xylene	0.421 ± 0.003	0.412	2.1%	0.517 ± 0.007	0.602	14.2%
formaldehyde	2.52 ± 0.10	4.42	43.0%	3.55 ± 0.07	5.52	35.7%
acetaldehyde	2.68 ± 0.16	1.66	61.5%	2.33 ± 0.00	2.16	7.7%
acrolein	0.49 ± 0.06	BDL	NA	0.24 ± 0.00	BDL	NA
NO_2	29.4 ± 1.9	34.0	13.5%	34.4 ± 1.4	50.5	31.8%
NOx	73.2 ± 0.3	76.0	3.7%	72.7 ± 1.7	84.2	13.6%
SO_2	1.1 ± 0.1	NA	NA	1.6 ± 0.2	NA	NA
Summer 2007	08/07/07 - 08/14/07			08/14/07 - 08/21/07		
benzene	0.443 ± 0.049	0.254	74.0%	0.363 ± 0.022	0.426	14.8%
toluene	1.250 ± 0.076	0.753	66.1%	1.158 ± 0.067	1.101	5.2%
ethylbenzene	0.231 ± 0.027	0.097	137.1%	0.239 ± 0.012	0.200	19.5%
m,p-xylene	0.555 ± 0.085	0.311	78.5%	0.552 ± 0.040	0.498	10.9%
o-xylene	0.222 ± 0.040	0.113	97.2%	0.228 ± 0.021	0.198	15.6%
formaldehyde	2.33 ± 0.21	2.31	0.9%	0.91 ± 0.14	2.64	65.4%
acetaldehyde	0.92 ± 0.04	0.98	6.4%	0.61 ± 0.05	0.96	37.0%
acrolein	0.02 ± 0.00	BDL	NA	0.02 ± 0.01	BDL	NA
NO_2	20.2 ± 1.9	25.0	19.0%	25.1 ± 3.0	29.7	15.5%
NOx	30.7 ± 0.9	45.0	31.8%	33.4 ± 0.6	50.2	33.4%
SO_2	1.5 ± 0.1	NA	NA	1.2 ± 0.1	NA	NA

[1] Mean passive value and standard deviations of three replicates.
[2] Reference methods were EPA-certified continuous analyzers for NO_2 and NOx or averages of seven consecutive 24-hour DNPH cartridge and canister samples.
[3] Percent difference of passive method as compared to reference value.

List of Figures

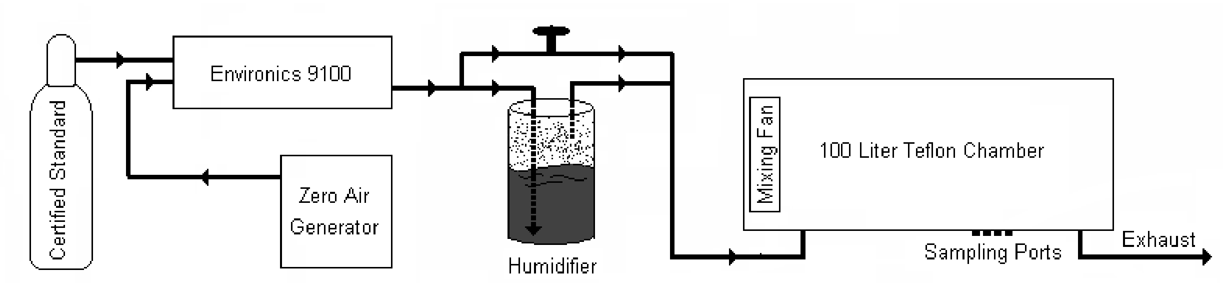


Figure 1.

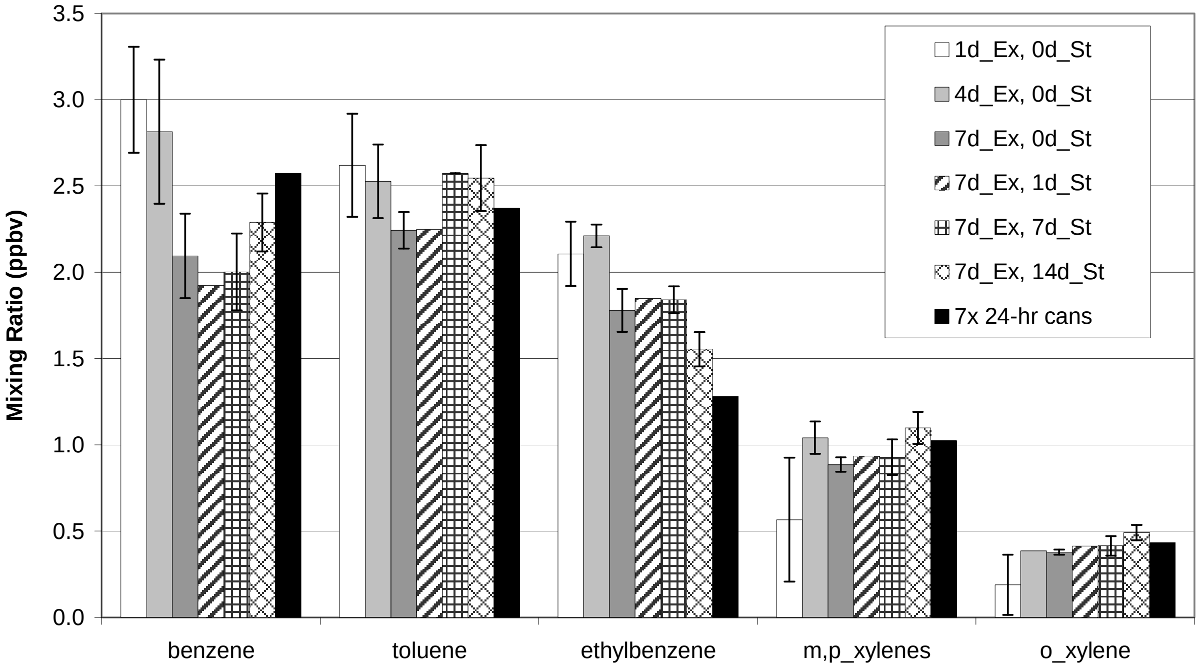
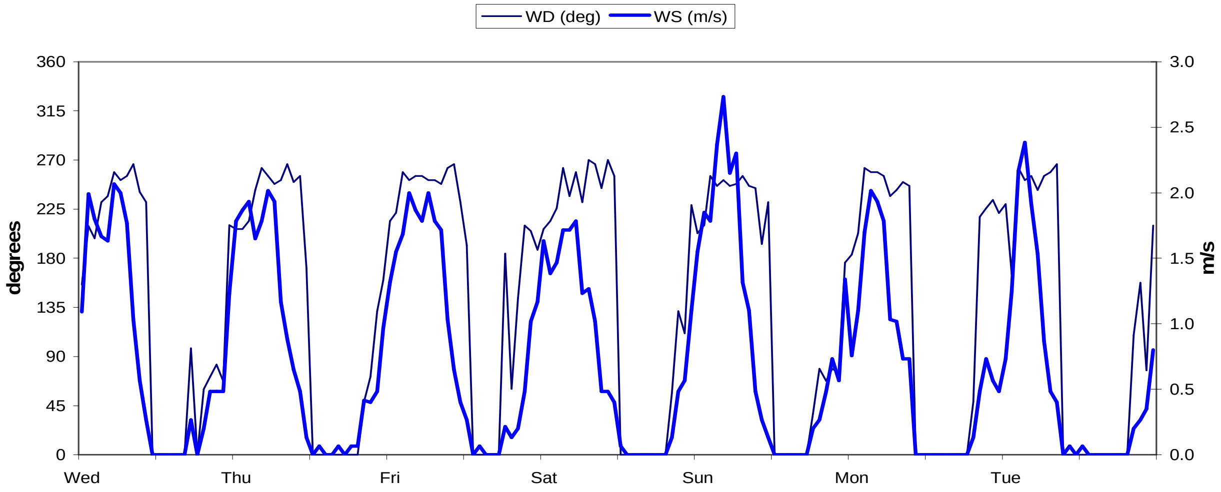


Figure 2.



WD (deg)
WS (m/s)
degrees
m/s
360
315
270
225
180
135
90
45
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3.0
2.5
2.0
1.5
1.0
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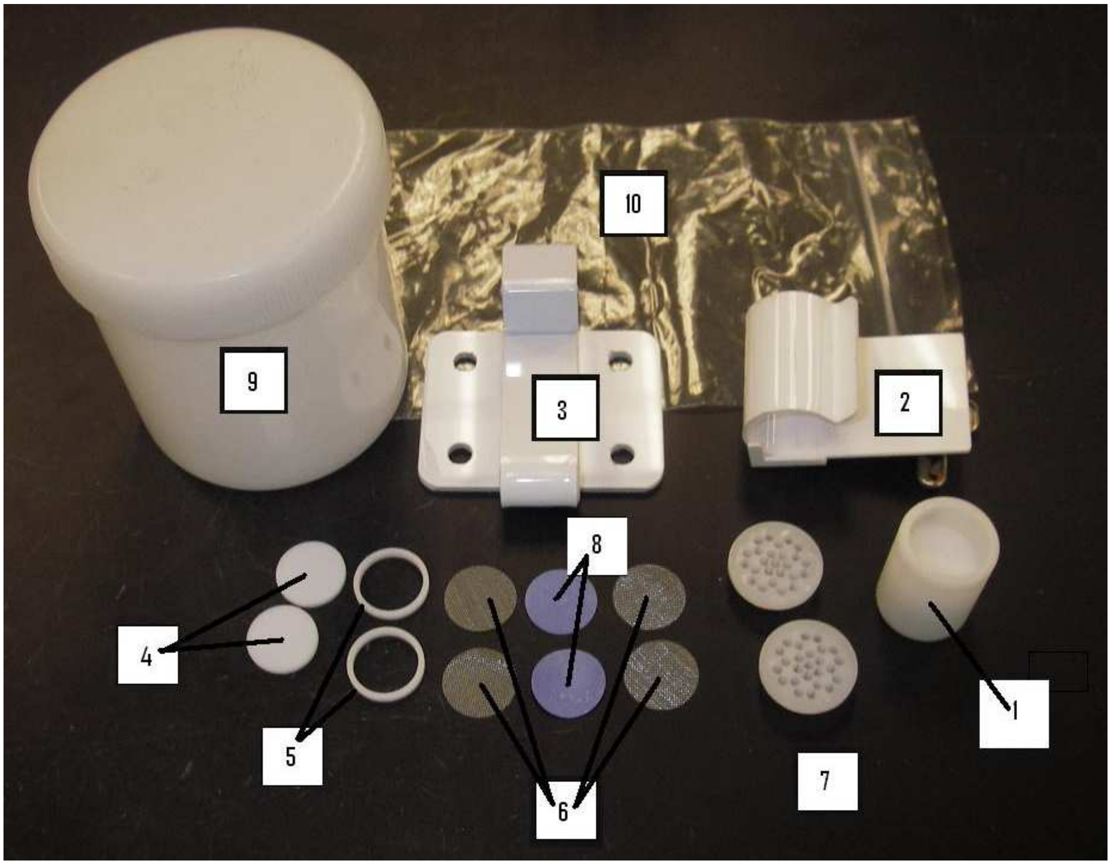
Wed
Thu
Fri
Sat
Sun
Mon
Tue

Figure 3.

Appendix B

Standard Operating Procedure for Ogawa Passive Monitors



Equipment List - Ogawa Passive Sampler

ID #	Description	Quantity
1	Sampler Housing	1
2	Sampler Holder	1
3	Mounting Bracket	1
4	Solid Pad	2
5	Pad Retaining Ring	2
6	Stainless Screen	4
7	Diffuser End Cap	2
8	Pre-Coated Collection Pad	2
9	Shelter/Vial	1
10	Sample Bag	1

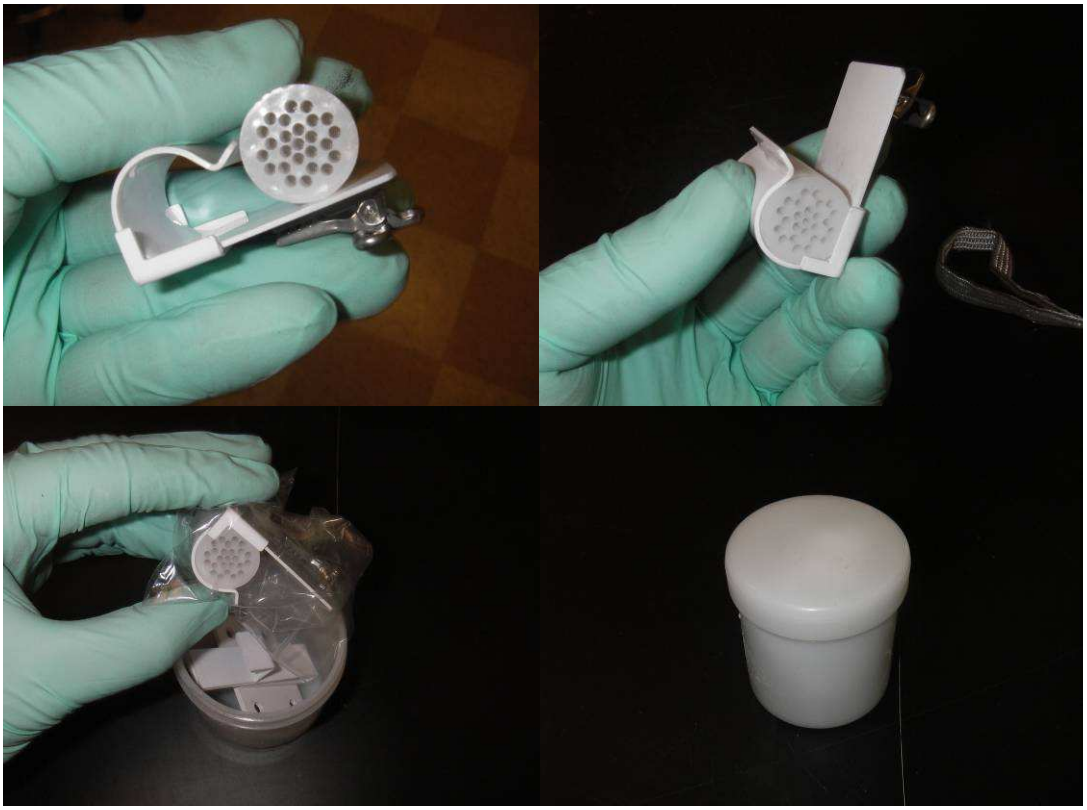
The Ogawa *Pre-Coated Collection Pads* come in a few varieties depending on the application. Specific information on the correct parts for each monitoring application can be found at the company website (www.ogawausa.com).

Assembly of the Ogawa Passive Sampler should be completed in a clean, indoor environment devoid of dust and then transported to the sampling site. Dirt and oils from your skin can affect the Ogawa Sampler if contact is made with the *collection pads* so gloves and/or a sterile pair of tweezers should be used for assembly.

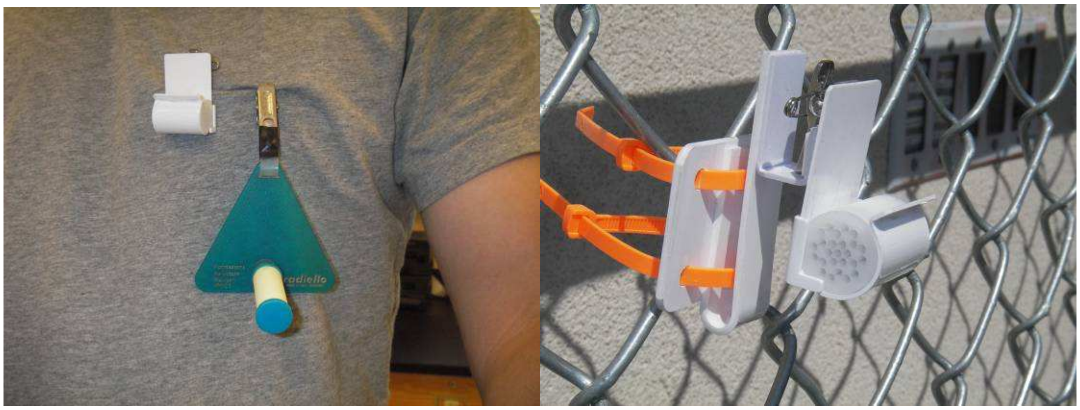
To assemble, remove the Ogawa *Sampler Housing* from the *Sampler Holder* and the *Opaque Vial*. Remove the *Diffuser End Cap* from one side of the *Sampler Housing* and remove the two stainless screens behind the *Diffuser End Cap*. The *Solid Pad* and *Pad Retaining Ring* should be visible inside of the sampler and should not be removed. If they come loose, just insert the *Solid Pad* into the *Sampler Housing* first and then slide the *Pad Retaining Ring* above it to hold it in place.

The *Pre-Coated Collection Pads* will come sealed in a vial and a resealable aluminum envelope. Remove one *Collection Pad* from the vial with the tweezers and place it in between the two *Stainless Screens*. Insert this assembly into the *Sampler Housing* taking care that it sits level on top of the *Retaining Ring*. The fit should be loose. If it feels snug, then remove and try again. Then, snap the *Diffusion End Cap* into place. Repeat this process on the other end of the *Sampler Housing* if two measurements are being conducted. See below.

After assembling the *Sampler Housing*, insert it into the *Sampler Holder* as shown below. The assembled sampler should now be sealed into the *Sample Bag*, removing as much as air as possible to prevent contamination. Place the bag inside the *Opaque Vial* with the *Mounting Bracket*, screw on the lid, and transport to the sampling site. See Below.



At the sampling site, remove the Ogawa Sampler from the *Opaque Vial* and *Sample Bag*. Attach the sampler to clothing for personal exposure or to the *Mounting Bracket* for ambient monitoring as shown below.

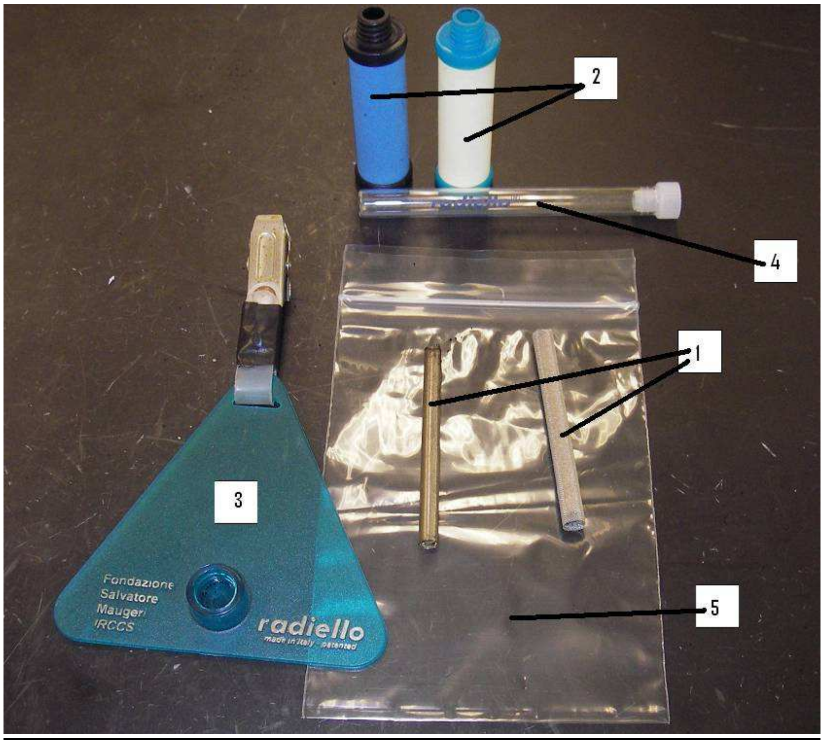


The *Mounting Bracket* can be easily attached to objects such as fences and poles with zip ties. If sampling outdoors, the *Opaque Vial* should be used as a shelter. It can easily be slipped over the *Mounting Bracket* and sampler as shown below. Keep the *Opaque Vial* lid and sealed *Sample Bag* for later. Note time and date when sampling begins.

Make sure to note the time and date when sampling ends. After sampling, remove the *Opaque Vial* and sampler from the *Mounting Bracket*. Seal the Ogawa Sampler inside the *Sample Bag* removing as much air as possible and store the *Sample Bag* inside the capped *Opaque Vial*. The Exposed Sampler inside the *Opaque Vial* should be stored in a freezer or in a cooler on blue ice for transportation to a laboratory for analysis.

Appendix C

Standard Operating Procedure for Radiello Passive Monitors



Equipment List - Radiello Passive Sampler

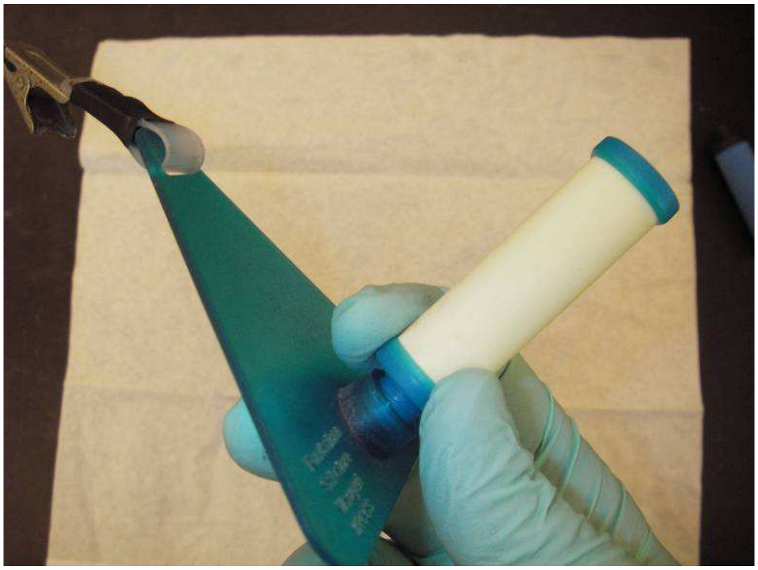
ID #	Description	Quantity
1	Radiello Adsorbing Cartridge	1
2	Diffusive Body	1
3	Supporting Plate	1
4	Glass Vial	1
5	Sample Bag	1

The *Radiello Adsorbing Cartridges* and *Diffusive Bodies* come in a few varieties depending on the application. Specific information on the correct parts for each monitoring application can be found at the company website (www.radiello.com).

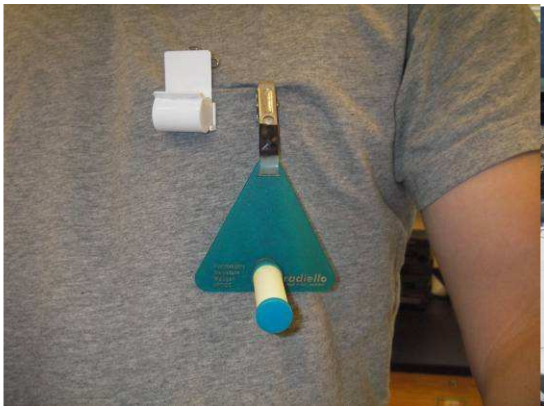
Assembly of the Radiello Passive Sampler is simple and should be completed at the location where sampling will take place. Dirt and oils from your skin can affect the Radiello Sampler if contact is made with the porous midsections of the *Diffusive Body* or with the *Adsorbing Cartridge* so gloves should be worn during assembly.

The *Adsorbing Cartridge* will arrive sealed in the *Glass Vial* and may be wrapped in plastic in addition. Remove the plastic wrapper, if necessary, and the cap from the *Glass Vial*. Slide the *Adsorbing Cartridge* into the *Diffusive Body* as shown below. Try to handle the *Diffusive Body* from the hard plastic ends. If the opening of the *Glass Vial* is mated with the opening on the *Diffusive Body*, transfer can be made without touching the *Adsorbing Cartridge*. The *Glass Vial* will be used later to store the exposed cartridge so re-cap it to prevent contamination.

Next, screw the *Diffusive Body* into the *Supporting Plate* as shown below. Be careful, to ensure the threads are aligned properly before tightening. The fit should be snug, but do not over-tighten as this can result in breaking the *Supporting Plate* or the *Diffusive body*. Screw the assembly together upside-down to ensure that the *Adsorbing Cartridge* is not protruding from the end of the *Diffusive Body* during tightening.



Assembly of the Radiello Passive Sampler is now complete. Use the metal clip to attach the sampler to clothing for personal exposure monitoring or to another object for ambient monitoring. If monitoring is being done outside where the sampler may be exposed to rain, care must be taken to attach the sampler under an overhanging feature. Plastic shelters can be fashioned easily from disposable cups or other containers but make sure not to inhibit airflow from reaching the sampler. Note start time and date. See below.




After exposure, note end time and date. Sampler should be taken down by unscrewing the D*iffusive Body* from the *Supporting Plate*. Slide exposed *Adsorbing Cartridge* back into *Glass Vial* by mating the two openings. Recap the *Glass Vial* containing the *Adsorbing Cartridge* and seal it into the *Sample Bag*. Remove as much air as possible from the *Sample Bag* to prevent contamination. Place the *Sample Bag* into a freezer or cooler containing blue ice for transportation to a laboratory for analysis.