Monitoring of Emissions from Barnett Shale Natural Gas Production Facilities for Population Exposure Assessment

Final Report

Prepared for

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1. INTRODUCTION

The Barnett Shale Study was conducted to provide a better understanding of population exposure to air toxics associated with gas production operations in the Barnett Shale region of North Texas. The data from this study is intended to supplement existing data and on-going air quality monitoring and health risk assessments by the Texas Commission on Environmental Quality (TCEQ).

1.1 Background

The Barnett Shale is a geological formation that stretches from Dallas to west of Fort Worth and southward, covering at least 5,000 square miles and 18 counties in the Fort Worth Basin (see Figure 1-1). Oil and gas experts have suggested that it may be the largest onshore natural gas field in the US, containing not only natural gas but also condensate and light oil. Figure 1-2 illustrate the distribution of natural gas/oil wells in the counties that are considered to be a part of the Barnett Shale formation (from Texas Commission on Environmental Quality Barnett Shale Formation Monitoring Report, January 2010). The primary sources of emissions in the Barnet Shale gas production areas include compressor engine exhausts (typically internal combustion engines), oil and condensate tank vents, production well fugitives, well drilling and hydraulic fracturing, natural gas processing and transmission fugitives. According to a preliminary study examining emission inventory assumptions (Armendariz, 2009), the higher HAPs emissions are expected from compressor engine exhausts, followed by condensate and oil tanks, well drilling and transmission fugitives.

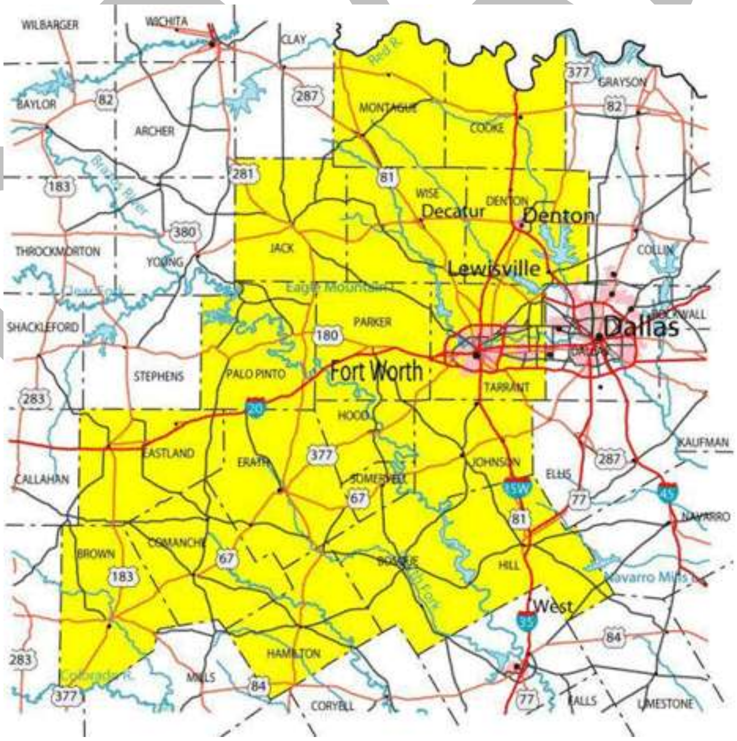

Figure 1-1. Barnet Shale coverage map

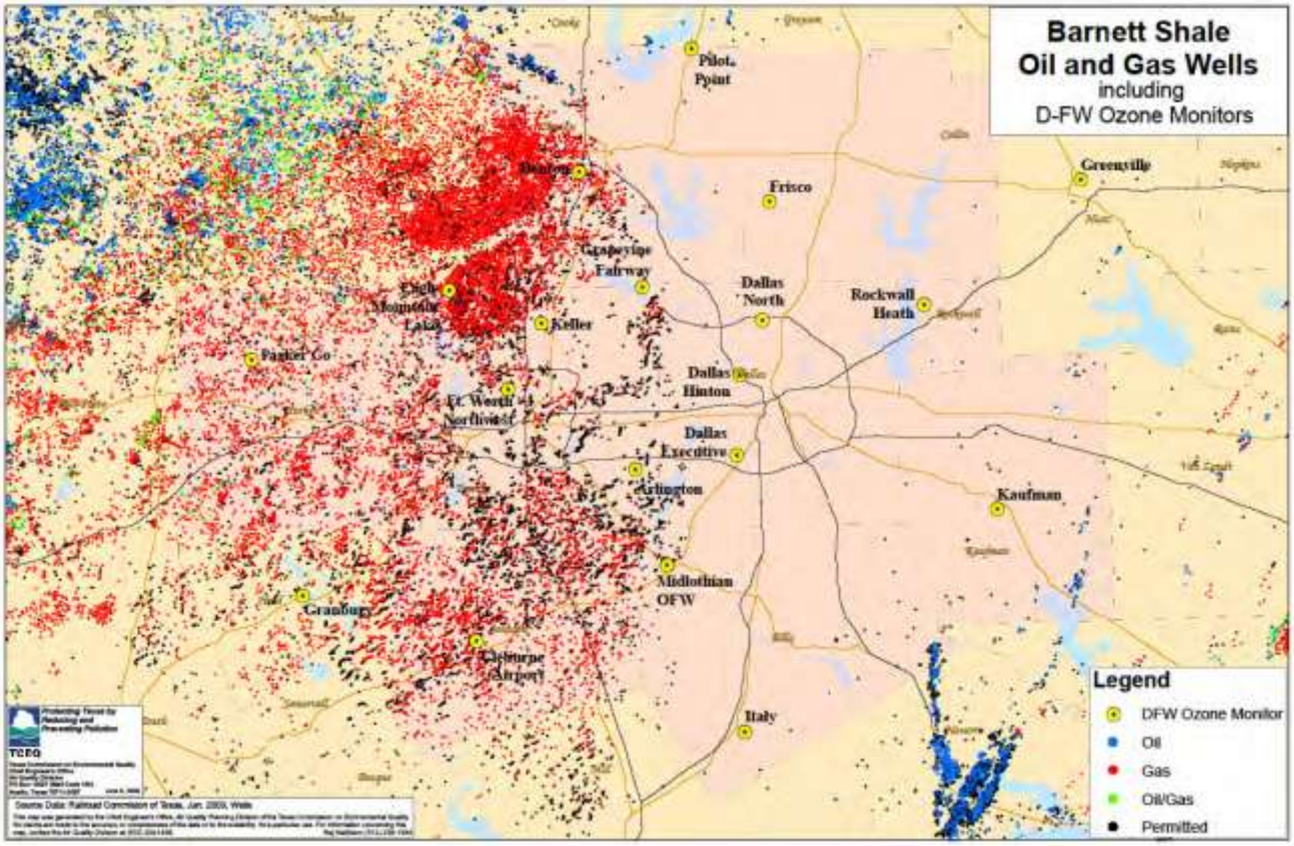

Figure 1-2. Barnet Shale oil and gas wells (from TCEQ Report, 2010, http://www.tceq.state.tx.us/assets/public/implementation/barnett_shale/2010.01.27-BarnettShaleMonitoringReport.pdf)

In response to public complaints and health concerns, the Texas Commission on Environmental Quality (TCEQ) conducted ambient air quality monitoring in Denton, Wise, Parker, Hood, Johnson, and Tarrant Counties in three phases during August, October, and November 2009 (TCEQ Report, 2010). During Phase I (August 24 – 28, 2009) two teams surveyed the area using GasFindIR cameras to identify potential emission sources within the five counties. The GasFindIR camera is a hand-held, battery-operated, passive infrared imaging system designed for real-time detection of multiple hydrocarbon gases. In addition to its VOC detection capabilities, the GasFindIR camera is also a thermal imagery device. Surveys of potential emission sources were conducted both on- and off-site and supplemented with collection of instantaneous canister samples ("grab samples"). Potential sampling locations for future monitoring efforts were identified. During Phase II (October 9 - 16, 2009) TCEQ staff used several different sampling methodologies to identify emission sources and collect downwind measurements. Off-site monitoring was conducted at locations identified during Phase I and at additional sites identified in the field during Phase II. Sampling was also conducted in several residential areas located in close proximity to natural gas-related processes and facilities. Monitoring of reduced sulfide compounds (RSC) was conducted during Phase III (November 16 – 20, 2009) in the area of potential sources of these compounds. A total of 94 monitoring sites were surveyed with air samples collected at 73 sites. GasFindIR images were recorded at 43 monitoring sites and 75 instantaneous canister samples were collected at 58 monitoring sites. Real time gas chromatograph (RTGC) samples were analyzed at 20 monitoring sites and RTGC RSC data were obtained at 15 sites.

The primary analytical targets for TCEQ's monitoring project were benzene and carbon disulfide (CS_2). In addition, a number of other volatile organic compounds (VOC) were quantified from canister "grab samples" (TCEQ Report, 2010). Benzene was detected above the air monitoring comparison value (AMCV) of 180 ppb (concentration above which short-term health effects might be observed) at two sites. However, these samples were collected on sites with malfunctioning (or inadvertently left open) pressure relief valves. The levels of benzene were reduced to below 1 ppb after appropriate measures were taken by site operators (TCEQ Report, 2010). Benzene was detected above the long-term AMCV of 1.4 ppb at 21 monitoring sites, which raised concerns about elevated short-term levels of benzene contributing to long-term cumulative exposures (TCEQ Memorandum, 2010). Carbon disulfide was detected above the short-term AMCV of 10 ppb in three of 69 instantaneous canisters samples with concentrations of 20 ppb, 12 ppb, and 19 ppb. These concentrations of carbon disulfide are well below known health effect levels and would not be expected to cause adverse health effects (TCEQ Memorandum, 2010). No other RSCs were detected. The TCEQ followed these initial monitoring efforts with longer-term monitoring in the area, starting with the community of DISH. Currently (as of Nov 2, 2010) five automatic air monitoring gas chromatographs (Auto GCs) were established in the Barnet Shale area (http://www.tceq.state.tx.us/compliance/monitoring/air/monops/agc/agc_barnett.html).

The characterization of a community's exposure to air pollutants is a complex task. Exposures to toxic air contaminants (TAC) 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 that affect the transport and dispersion of emissions. Gas production wells in the Barnett Shale area number in the thousands and are spread over a large areas of North Texas. Available data show large variations in production levels of both natural gas and condensate within the Barnett Shale area that are likely reflected in the spatial variations in magnitude and composition of gas production emissions. Emissions can occur during various stages in the life of any single well and along various points of the production stream from extraction of raw gas at the well to distribution of commercial grade natural gas at central gathering and processing plants. In addition to release of raw gas from various pressure relief valves, emissions from gas production operations include combustion emissions from compressors and diesel-powered trucks during well installation and removal of condensate from the well tanks. These variations are also accompanied by changes in the chemical and physical nature of the mixture of pollutants during transport in the atmosphere.

Recognizing the needs for additional data regarding emissions from gas production facilities in the Barnet Shale area and their impact on population exposures, Mickey Leland National Urban Air Toxics Research Center issued a request for proposal (RFP) in November

2009 that called for a short-term (seven months) focused study that would lead to better understanding of air toxic emissions in the area and potential population exposures of residents in this area. The technical plan for this study acknowledges that most air toxics contaminants are not unique to a single source or source type, and that attribution of a particular source(s) to a community's exposure can be difficult to quantify and distinguish from contributions of the same TAC from other nearby sources or transport from urban areas upwind of the study area. Furthermore, ambient measurements at several randomly selected locations within such a large area, with numerous scattered points of emissions with potentially widely varying composition and rates of emissions, are unlikely to yield results that would be particularly useful for exposure assessment. Similarly, grab samples near a malfunctioning pressure relief valve would not be representative of the typical exposure concentrations in the region. The study design attempts to balance these challenges with the practical limitations (e.g., measurements for one community during a single season) imposed by available project resources so that results and conclusions from the study would be more generally applicable and complementary to on-going exposure assessments in the Barnett Shale area. However, the conclusions drawn from this study should be considered tentative and supported by a larger study or data from other studies covering all seasons that provides statistical confirmation of the study results.

1.2 Research Objectives

The purpose of this study was to provide a better understanding of the potential contributions of emissions from gas production operations to population exposure to air toxics in the Barnett Shale region. The following technical objectives were addressed in two phases.

1. Characterize the chemical composition of emissions related to natural gas production operations in the Barnett Shale area.
2. Estimate the potential emissions impact from various types of natural gas production facilities by measuring the associated pollutant gradients from the point of emissions.
3. Determine the ambient concentrations of selected air toxics within a community in the Barnett Shale region, and, to the extent possible, apportion the contributions of emissions from gas production operations to the measured exposure concentrations.

In the first phase of this study we characterized the emissions from major gas production facilities in the Barnett Shale area. An initial survey was performed using a mobile sampling vehicle to identify facilities with measureable emissions. Source-oriented samples were collected at several facilities with confirmed emissions measured with our continuous survey monitors. Continuous measurements were also made around the facilities to characterize the spatial variations in pollutant concentrations near the facilities.

In the second phase we conducted saturation monitoring (multiple fixed-ambient sampling locations) downwind of gas production areas. One location was near a well with emissions from condensate tanks that were well characterized during Phase 1. A single private residence was located a short distance downwind of this well and was away from other emission sources that might interfere with the measured gradient of emissions from the well. The measurement at this site serves as a case study of the pollutant gradient from a well characterized emission source at various distances downwind of the source relative to the upwind pollutant concentrations. The second facility was a gas compressor station located near a small community. The spatial variations in pollutant concentrations were determined at various distances and directions from the source, sites adjacent to nearby roadways and a background site located upwind of the community. The measured volatile organic compounds were apportioned to sources using the Chemical Mass Balance receptor model. The study results were placed in context by comparing the measured pollutant concentrations to comparable data from elsewhere is the Barnett Shale area and from urban areas of the Dallas-Fort Worth.

2. EXPERIMENTAL METHODS

2.1 Phase 1 – Sample Collection for Characterization of Emission Sources

Phase 1 of the study was conducted in April 15 – 23, 2010, and included mobile sampling with continuous monitors to select appropriate emission sources for monitoring and time-integrated (over 1-hr) sampling of volatile organic compounds and related air pollutants at selected facilities to determine chemical source profiles. We selected Wise County for our monitoring area, based on the fact that the wells in this County produce significant quantities of condensate (Railroad Commission of Texas website, Production data Query system, http://webapps.rrc.state.tx.us/PDQ/generalReportAction.do.). For example, for the period of September-December 2009 the total natural gas production in Wise County was 69,983,018 MCF and total condensate 274,875 BBL. In comparison, production in the top natural gas producers, Johnson and Tarrant Counties was 171,919,278 and 182,139,429 MCF of gas, respectively, but only 15,407 and 14,777 BBL of condensate, respectively. It is known that the "wet gas" contains higher concentrations of aliphatic and aromatic hydrocarbons.

The selection of the gas production facilities for monitoring was based on surveying candidate sites using our mobile monitoring system, which includes real-time estimates of VOC, using a portable photoionization detector (PID) monitor (RAE Systems Model PGM-7240 (ppbRAE)), continuous NO with a 2B Technologies model 400 instrument, and $PM_{2.5}$ mass using a TSI DustTrack. Additionally, a GasFindIR camera from FLIR Systems Co., Ltd. became available on April 20, and was used to document gas leaks and other fugitive emissions. Wind speed and direction were also monitored during sample collection. Approximately two dozen well sites were surveyed in the areas surrounding Rhome, Decatur, Aurora, Boyd, New Fairview, Alvord, Bridgeport, Runaway Bay, Chico, Paradise, and Allison. We also made measurements near the fencelines of gas compression/processing plants near Rhome, Chico, Bridgeport, Allison, and New Fairview. Although there were several active fracturing operations in the area we were unable to get closer than 200-300 m from the drill pads, and access to downwind locations was unavailable.

Table 2-1 shows the facilities selected for source sampling and the type of samples collected at these sites. Figure 2-1 shows the map of the area selected for monitoring

Table 2-1. List of source samples

Sample ID	**Location**	**date/time**	**type**	**Met data**	**Notes**
Star Shell 1	403 Star Shell Rd., Decatur	4/16/10; 800-900	VOC, DNPH	T = 18C, RH= 77%, Wind 0.5m/s SE	Next to gas well condensate tank
Star Shell 2, Replicate	403 Star Shell Rd., Decatur	4/21/10; 1330-1430	VOC, DNPH	T = 31C, RH= 45%, Wind <0.5m/s	Next to gas well condensate tank
Star Shell 3	403 Star Shell Rd., Decatur	5/13/10; 840-845	VOC	T = 22C, RH= 66%, Wind 1m/s SE	Downwind of gas well while truck servicing tanks
Shale Creek 1	Orloff Rd, W of Forest Lawn Rd., Rhome	4/20/10; 1120-1220	VOC, DNPH	T = 25C, RH= 50%, Wind <0.5m/s	Near large compressor station adjacent to residential community
Shale Creek 2	Shale Creek, Rhome	4/20/10; 1614-1714	VOC, DNPH	T = 21C, RH= 51%, Wind 0.5m/s SE	On access road to compressor station
Shale Creek 3	Shale Creek, Rhome	5/13/10; 1330	VOC	T = 21C, RH= 64%, Wind <0.5m/s	Grab sample; residence yard during lawn mowing
John Day	John Day Road, south of Rhome	4/20/10; 1754-1854	VOC, DNPH	T = 23C, RH= 48%, Wind <0.5m/s	Adjacent to two gas wells with compressors
Background	CR 2513, Decatur	4/21/10; 906-1006	VOC, DNPH	T = 22C, RH= 63%, Wind 3.5m/s S	Background site, away from gas wells and traffic
Plant	Decatur, CR 2610	4/21/10; 1107-1207	VOC, DNPH	T = 26C, RH= 53%, Wind 2m/s SE	Near Burlington compressor station
Allison	Decatur, CR 2513	4/22/10; 835-935	VOC, DNPH	T = 19C, RH= 77%, Wind <0.5m/s	Next to 4-tank gas well
I-287	Decatur, I-287 freeway	5/13/10; 1000-1005	VOC	T = 21C, RH= 67%, Wind 1m/s SE	Grab sample, at downwind edge of busy highway

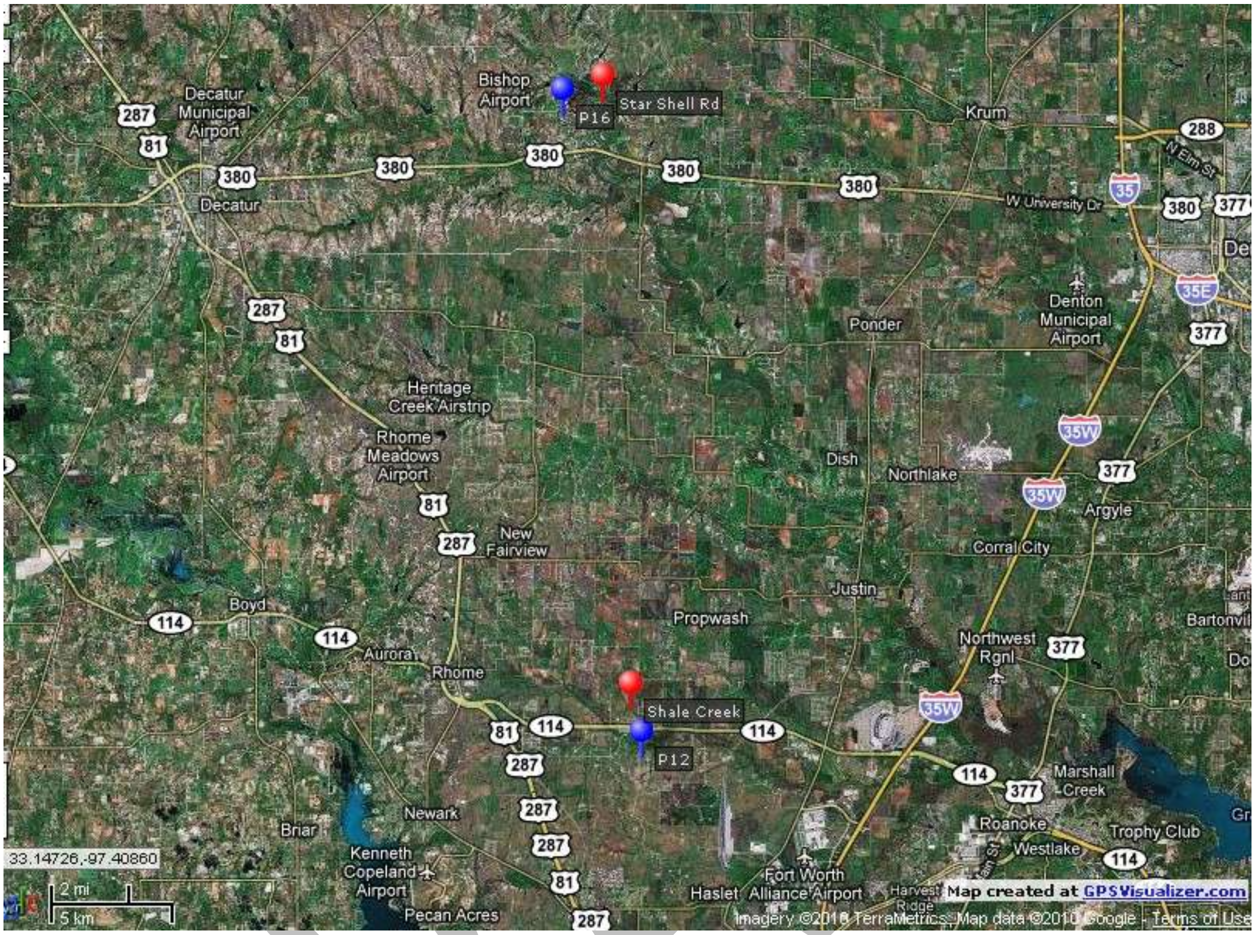

Figure 2-1. Map of the area selected for monitoring. Location of saturation and gradient monitoring sites are marked with red pins. Blue pins indicate the corresponding upwind background sites.

Star Shell Road site is located on private residential property, approximately 100 m from the house (see Figure 2-2, A, B and C). This 2-tank well site showed high intermittent PID readings, up to 5 ppm. We collected 1-hour canister VOC and active carbonyl samples on 4/16 and 4/21/10 next to the facility fence (see Figure 2-2) and also two corresponding grab samples in passivated canisters at a peak in PID readings. In addition, one VOC grab sample was collected near the house on 5/13/10 when a tanker truck was servicing the well (i.e. removing condensates from the tanks). The Star Shell site was selected for long-term monitoring during phase 2 of the study.

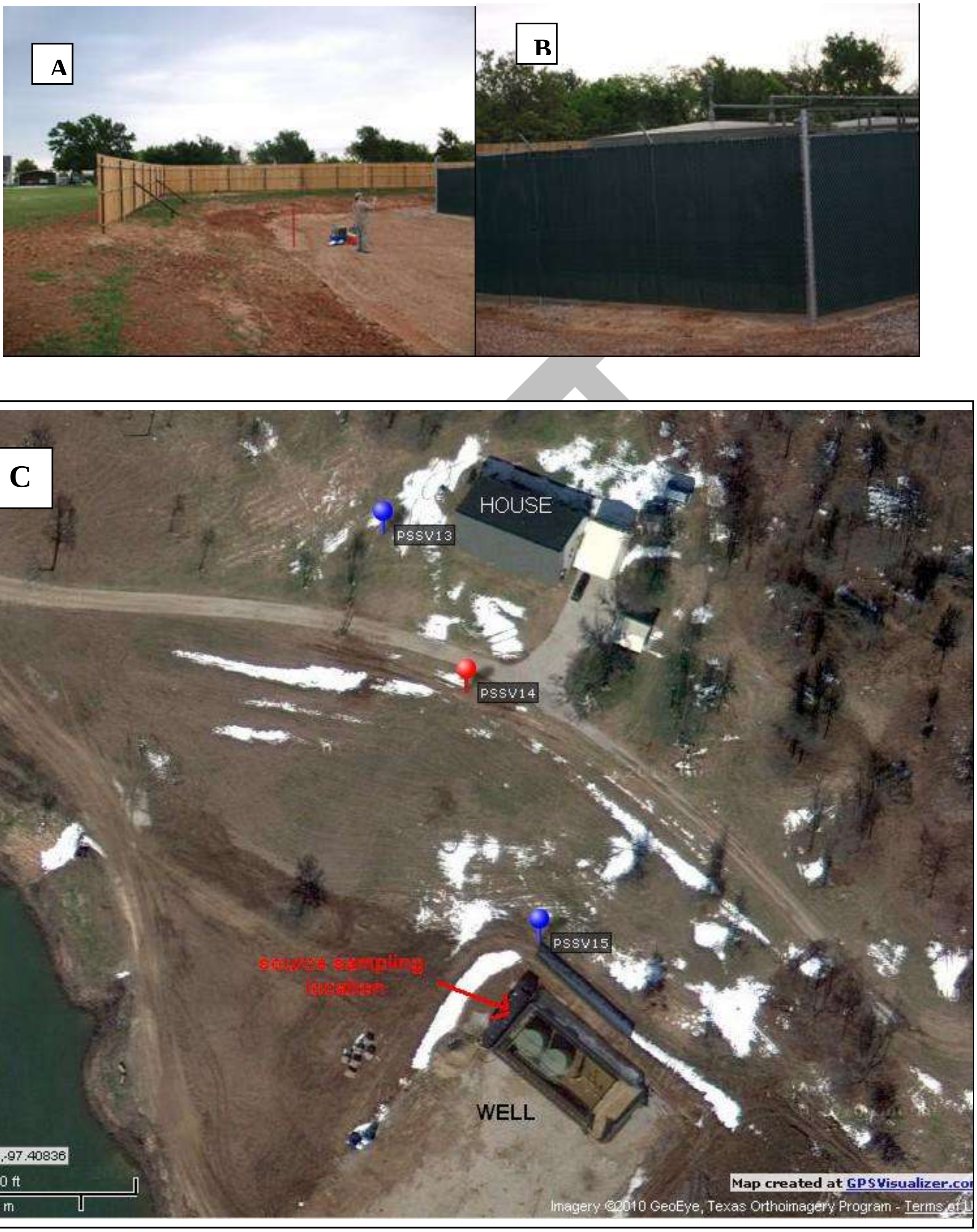

Figure 2-2. Star Shell Road source sample collection site. A: sampling site in relation to the fenced condensate tanks and house; B: fenced condensate tanks. C: aerial view showing monitoring site locations.

Shale Creek sampling sites were located in the community situated next to a compressor station in Rhome. The community of Shale Creek is located on 330 acres with over 1000 single family home sites (http://www.shalecreekcommunity.com/community.html). At present, around 250-300 houses are occupied. The compressor station is situated near the southwest edge of the community and is screened from the community by a sound wall (see Figure 2-3). In addition, there are several wells in the surrounding area. Shale Creek 1 samples were collected at a location just north-east of the compressor station (corner of Forest Lawn and Orloff Rds.) and the Shale Creek 2 location was on the west side near the entrance to the compressor station, just outside of the fenced area. Since this is a Devon lease, access to the compressor site or downwind area was not possible. There was some truck traffic around the compressor station, so we also recorded continuous NO and $PM_{2.5}$ concentrations during the VOC sampling. In addition one grab VOC sample (Shale Creek 3) was collected when the resident of a house used for passive monitoring was mowing his lawn with a gasoline-powered mower.

Figure 2-3. A: West side of the compressor station near Shale Creek. B: the sound screening wall around the east side of the compressor station, facing Shale Creek community.

The John Day samples were collected next to two wells located south of Rhome on John Day Road. Both wells have compressors (or generators) on site. We recorded some IR camera readings, but PID readings were consistently below detection and NO, $PM_{2.5}$ and CO were all near background. Winds during time of sampling were from the southeast at 0 – 2 m/sec. The samples were collected downwind at a distance of 15 - 20 m from the condensate tanks, as measured with a laser rangefinder.

On April 21, we collected several canister and carbonyl samples, along with continuous NO, $PM_{2.5}$, and CO data, in the Star Shell Rd. area. One set was collected away from any wells on CR 2513 near CR 2618 to represent the area background. Another set of samples (Plant) was collected downwind of a compressor station (Flin #1) located on CR 2610. The IR camera showed some emissions from this station, however, it was quite windy (4 to 6 m/sec from SSE).

The Allison samples were collected next to a 4-tank site on the CR 2513, not far from the Star Shell site. The IR camera showed some emissions from one of the tanks which had an un-latched hatch cover and the PID recorded intermittent readings up to 1 ppm.

We also collected a VOC grab sample approximately 50'east of I-287 freeway in Decatur. The traffic was moderately heavy with many heavy-duty diesel trucks.

The samples included canister samples for VOC characterization (EPA Method TO-15) and 2,4-dinitrophenyl hydrazine (DNPH) impregnated SepPak cartridges for carbonyl compound collection (EPA Method TO-11A). In general, we collected 1 hr samples with the exception of a few "grab samples" collected over a few seconds. A Davis Instruments meteorology package was deployed to measure wind speed, wind direction, relative humidity, and temperature during sampling.

2.2 Phase 2 – Saturation Monitoring

During Phase 1 of the study we selected the Shale Creek community (see description above) for exposure measurements in Phase 2 of the study. We also selected a residential property at 403 Star Shell Road. This property is located downwind of a gas well and two condensate tanks that we had characterized during phase 1. Measurements at these sites included 7-day integrated passive samples for oxides of nitrogen (NOx), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), BTEX (benzene, toluene, ethylbenzene and xylenes), 1,3-butadiene, CS_2 and carbonyl compounds (formaldehyde, acetaldehyde and acrolein) using the passive samplers. Additionally, 7-day integrated Teflon and quartz filters were collected with portable Airmetrics MiniVol samplers at 7 sites for $PM_{2.5}$ mass, elements, organic carbon (OC) and elemental carbon (EC) and polycyclic aromatic hydrocarbons (PAH) analyses. Table 2-2 shows the sampling sites and the type of samples collected at each site.

Table 2-2. Long-term sampling sites

Site ID	Location	Passive	Active	Notes
PSSV01	12004 Forest Lawn.	VOC, A, NOx, SO_2	Q/T	set up on 4/22
PSSV02	12650 Forest Lawn.	VOC, A, NOx, SO_2	Q/T	set up on 4/22
PSSV03	12931 Kingsgate.	VOC, A, NOx, SO_2	Q/T	GFI (outlet in garage) blew shortly after 4/29 filter change, no samples for week. Reset on 5/6.
PSSV04	12702 Carpenter.	VOC,A, NOx, SO_2	Q/T	set up on 4/23
PSSV05	12329 Shine Ave.	VOC,A, NOx, SO_2	Q/T	set up on 4/23
PSSV06	12424 Steelwood	VOC,A, NOx, SO_2	Q/T	set up on 4/23
PSSV07	12029 Shine Ave	VOC,A, NOx, SO_2	no	Set up on 4/29
PSSV08	Barrier at end of Orloff Rd, near intersection with Forest Lawn (NE corner of CS)	VOC,A, NOx, SO_2	no	set up on 4/23

Site ID	Location	Passive	Active	Notes
PSSV09	SE of the compressor station, on the boundary fence near entrance to Shale Creek.	VOC,A, NOx, SO_2	no	set up on 4/22
PSSV10	Next to the County Line Road near Hwy 114.	VOC,A, NOx, SO_2	no	set up on 4/23
PSSV11	W side of Shale Creek compressor station. Across dirt road from fenced tank area.	VOC,A, NOx, SO_2	no	Set up on 4/29.
PSSV12	Warbler Lane, 1 mile S of Shale Creek community. On road sign S of Robin Ln.	VOC,A, NOx, SO_2	no	Set up on 4/29. No NOx installed week of 4/29.
PSSV13	403 Star Shell Rd., on wire fence W of residence	VOC,A, NOx, SO_2	no	set up on 4/22
PSSV14	403 Star Shell Rd., on wire fence S of residence	VOC,A, NOx, SO_2	Q/T	set up on 4/22
PSSV15	403 Star Shell Rd., on wood fence N side of gas well	VOC,A, NOx, SO_2	no	set up on 4/22
PSSV16	S end of Star Shell Rd, ~200m E of CR2513, on wood fence post W of gate for London Petr. Well	VOC,A, NOx, SO_2	no	Set up on 4/29.

A: aldehydes (by DNPH Radiello cartridges); Q/T: quartz/Teflon filters

On April 22 we installed passive samplers and a set of active mini-vol samplers (PSSV13, 14 and 15) at the 403 Star Shell Road property. We installed three passive sampler sets at different distances from the condensate tanks: one passive set was put on a wooden fence near the condensation tanks (~ 17 m from the tanks), second on a barbed-wire fence surrounding the house (~ 50 m from the 1st passive) and third on the same fence, but further away from the source (~ 30 m from the 2nd passive). All passive sets were downwind from the source when the wind was from the prevailing SE direction. Also, two mini-vol filter samplers (requiring power), one with quartz filter and one with Teflon filter were installed at the SE corner of the residential property, downwind of the well. In addition, one set of passive samplers (PSSV16) was installed on 4/29/10 on the south end of Star Shell Road, upwind from the Aruba well and tanks (see Figure 2-2C).

Samplers were installed at Shale Creek on 4/22-4/23, with the exception of PSSV07, PSSV11, and PSSV12 which were added a week later, on 4/29/10. Samplers PSSV01 – 06 were installed in the backyard of private residential properties and included one set of passive and one set of active samplers each. Site PSSV07 was installed on 4/29 and included passive samplers only. In addition, one set of passive samplers (PSSV08) was installed at the dead end of Orloff Rd, where the canister and DNPH samples were collected during Phase 1 (Shale Creek 1). Another set (PSSV09) was installed on the compressor station boundary fence (SE corner) near entrance to Shale Creek, and another one (PSSV10) on the SE edge of the community next to Country Line Road, near Hwy 114. On 4/29 two more passive sets were added: PSSV11 on west side of Shale Creek compressor station, just across the dirt road leading to the station, and PSSV12 in a small residential area ~1 mile south of the Shale Creek community to characterize the upwind background concentrations. Figure 2-4 maps the locations of the saturation monitoring sites in the Shale Creek Community and Figure 2-5 shows the typical passive and active sampler installations.

Figure 2-4. Map of Shale Creek community sampling sites. Red pins indicate sites with passive (NOx, SO2, BTEX, and aldehydes) and active filter samplers. Blue pins had only passive samplers.

Figure 2-5. Typical Shale Creek community sampling sites, A = site PSSV03, B = site PSSV04

2.3 Sampling and Analytical Methods

2.3.1 Continuous Methods for Gaseous Pollutants

NO/NOx or NO2

Nitric oxide (NO) is typically measured continuously by the chemiluminescence nitric oxide-ozone method (OCM). This method is based on the gas-phase chemical reaction of NO with ozone. Standard sensitivity instruments have detection limits of about 0.5 to 3 ppb (60 sec averaging times) and are suitable for air quality monitoring in urban and suburban areas, however they are rather large and heavy for mobile monitoring and require substantial power. A compact 12V NO monitor sold by 2B Technologies (Model 400) which has sensitivity and resolution as low as 2 ppb was used instead. The detection method uses UV absorption technology to determine the depletion of ozone by NO and calculates the NO concentration by assuming a 1:1 stoichiometric ratio for the NO/O_3 reaction cycle. In laboratory and field use we have found this instrument to be equivalent to the chemiluminescence method for NO concentrations greater than 20 ppb.

Volatile Organic Compounds.

A RAE Systems Model PGM-7240 (ppbRAE) portable PID monitor was used to continuously monitor ambient levels of VOC that are detectable by PID. The monitor is equipped with a 10.6 eV photoionization (PID) detector and responds to certain organic and inorganic gases that have an ionization potential of less than 10.6 eV, which includes 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 < 5-second response and lower detection limit of ~20 ppb. Because the total response of the PID depends upon the specific mix of VOC's, the response must be calibrated to the expected mix of VOC. Isobutylene is the normal calibration gas but the PID response can be adjusted to one of several specific VOC species or 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. Instruments utilizing flame ionization detection (FID) are sensitive to a broader range of hydrocarbons, but do not provide the sensitivity and rapid response time required for ambient exposure monitoring.

2.3.2 Continuous PM Mass

PM2.5 Mass

The TSI DustTrak 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. Because it is sensitive, requires low flow rates, offers good time resolutions, and is portable and relatively inexpensive, the TSI DustTrak nephelometer is well suited for continuous onboard PM measurements in this study. It can be fitted with inlet of varying size-cuts. We equipped the monitor for this project with a $PM_{2.5}$ inlet.

The reported PM mass concentration is factory-calibrated using the respirable fraction of an Arizona Road Dust standard (ISO 12103-1, A1), which consists of primarily silica particles (70%) that are provided with some particle size specifications. The mass scattering efficiency depends on particle shapes, size distribution, and composition (index of refraction). By volume, the standard consists of 1–3% particles with diameter less than 1000 nm (1 µm), 36–44% with diameter less than 4000 nm (4 µm), 83–88% with diameter less than 7000 nm (7 µm), and 97–100% with diameter less than 10,000 nm (10 µm). This standard contains a larger quantity of coarse 2500 nm (>2.5 µm) particles than are usually found in ambient aerosol. $PM_{2.5}$ has a higher mass scattering efficiency, so the DustTrak overestimates $PM_{2.5}$ for smaller, chain aggregate soot particles. The laser diode used by the DustTrak has a wavelength of 780 nm, which limits the smallest detectable particle to about 100 nm. Combustion aerosols typically have a mass median diameter between 100 nm and 300 nm. Although direct optical light scattering of particles in this size range is limited, it has been shown to correlate reasonably well with gravimetric mass from vehicle exhaust samples.

2.3.3 Meteorological Parameters

A Davis Instruments meteorology package was deployed to measure wind speed, wind direction, relative humidity, and temperature during sampling at fixed locations unless data is available from existing meteorological equipment. Time-integrated data were recorded at 10-minute intervals by a dedicated datalogger. Self-contained, compact HOBO U10 temperature and relative humidity loggers was also deployed to provide T and RH data for correction of passive measurements.

2.3.4 Time-Integrated Particle Sampling

2.3.4.1 Mini-Volume Particle Samples

MiniVol portable $PM_{2.5}$ air samplers from AirMetrics Corporation were used for particle sampling for 7 continuous days (see Figure 2-6). 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 inlet tube conducts air to a twin cylinder diaphragm pump. From the pump, air is forced through a standard rotameter (0-10 L/minute) where it is exhausted to the atmosphere inside the sampler housing. An elapsed time meter is used to totalize the time the sampler is operated within the flow and voltage specification. Particles are collected on either Teflon or pre-fired quartz 47 mm filters that can be analyzed gravimetrically for mass or by thermal/optical reflectance (TOR) for organic and elemental carbon (OC and EC).

The following substrates were used for this program:

- 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 samplers are 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. Each sampler has two battery packs to allow for 'continuous' field sampling; while the sampler is operating on one battery (up to 24 sampling hours on a single charge), the other battery is charged using an AC power adaptor. During the Harbor 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 used fielding this study.

AirMetricMinivol 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 and aldehydes
(size of a roll of pennies)

Figure 2-6. Samplers used in the Phase 2 of the study.

2.3.5 Time-Integrated Gaseous Pollutant Sampling

2.3.5.1 Canister VOC Sampling

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/MS/FID method, as described below. The canisters are considered clean if the target compound concentrations are less than 0.05 ppbv each. The canister sampling systems are 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.

2.3.5.2 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. Depending on the type of sorbent (C18, or silica gel, (Si) in the cartridge, the ambient measurement results are subject to various artifacts due to interaction with ozone (Tejada, 1986). To prevent this, the samplers are equipped with potassium iodide (KI) denuder, as recommended by the EPA Method TO-11A (US EPA, 1999)

2.3.5.3 Passive Sampling

The ability of passive samplers to collect analytes over extended periods of time allows for potentially high sensitivity for low concentration 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. We employed five different types of passive samplers each with a unique adsorbent and method of analysis. The NO_x and SO_2 samplers are manufactured by Ogawa and Co. The VOC and aldehyde samplers are manufactured by Radiello (see Figure 2-6). The analysis methods are listed in the table below:

Manufacturer	Target Pollutant	Analysis Method
Ogawa	NO_2/NOx	Colorimetry for nitrite
Ogawa	SO_2	Ion Chromatography
Radiello	VOC	Thermal Desorption/GC/MS
Radiello	Aldehyde	HPLC/UV

The basic principle employed 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). 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.

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:

$$\text{Concentration} = \frac{\text{Mass of Analyte}}{\text{Sampling Rate} * \text{Sampling Time}}$$

The sampling rate for every analyte is calculated experimentally since pumps are not used in passive collection. Radiello[1] and Ogawa and Company[2] supply these sampling rates for a number of commonly collected compounds. These sampling rates have been validated in our chamber experiments for NO_x, formaldehyde, acrolein, BTEX, and SO_2 (Fujita et al., 2009a). The sampling rate for pentane, isopentane and CS_2 is not available from Radiello and was determined experimentally in our lab as described below (Section 2.4). Mass of analyte is calculated after the average blank result is subtracted from the analytical result. Sampling time is the amount of time that the sampler was exposed. While lengthening the exposure time corresponds to an increase in sensitivity, it should be noted that exposure time is generally limited to 14 days due to the capacity of the adsorbents.

Ogawa Passive Samplers for NOx, NO2 and SO2

Ogawa Passive Sampling Systems (Rupprecht and Patashnick Co., Inc.) were used for monitoring NOx, 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 are calculated by subtracting NO_2 from NOx concentrations. Sampling and analysis are 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:

$$\alpha_{NO} = \frac{10000}{(-0.78 \cdot P \cdot RH) + 220} \qquad \alpha_{NO2} = \frac{10000}{(0.677 \cdot P \cdot RH) + (2.009 \cdot T) + 89.8}$$

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

Where PN and PT are the vapor pressure of water in mmHg at 20 C and ambient temperature, respectively. α_{SO2} is determined from tables provided by the manufacturer, and varies from 44 - 35 ppb-min/ng for the temperature range 0 – 40C.

Radiello Diffusive Samplers for VOCs

Radiello diffusive samplers (adsorbing cartridge code R145) were used for passive sampling of benzene, toluene, ethylbenzene, xylenes (BTEX), n-hexane, n-heptane and other

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[1] Information about Radiello Passive Samplers can be found at http://www.radiello.com.
[2] Information and sales for Ogawa passive samplers can be found at http://www.ogawausa.com/.

higher mw alkanes. Radiello samplers with Carbopack X (R141), which have been shown to significantly reduce the desorption of 1,3-butadiene were used for sampling 1,3-butadiene, carbon disulfide, pentane and iso-pentane. The Radiello samplers are insensitive to humidity within the range 10-90% RH and wind speed between 0.1 and 10 m/s. The actual value used for the sampling rate is calculated based on ambient temperature during sampling using the following equation:

$$QT = Q298(T/298)^{1.5}$$

Where QT is the sampling rate at ambient temperature T in oK and Q298 is the reference value at 25 ^{o}C. This produces a variation of ± 5% for ± 10 ^{o}C variation from 25 ^{o}C.

Radiello Diffusive Samplers for Carbonyl Compounds

We used Radiello diffusive samplers to passively collect carbonyl compounds. A stainless steel net cartridge filled with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated florisil (Code 165) are used. Carbonyl compounds react with 2,4-DNPH forming corresponding 2,3-dinitrophenylhydrazones. Sampling rate varies from value at 25 ^{o}C according to the following equation:

$$QT = Q298(T/298)^{0.35}$$

This produces a variation of ± 1% for ± 10 ^{o}C variation from 25 ^{o}C. The hydrazones are extracted and analyzed by HPLC with UV detection.

2.3.6 Laboratory Analysis of Time-Integrated Samples

2.3.6.1 Laboratory Analysis of Passive Samples

Radiello VOC samplers. All Radiello passive samples (Carbograph 4, R145 and Carbopack X, R141) were analyzed by the thermal desorption-cryogenic preconcentration method, followed by high-resolution gas chromatographic separation and mass spectrometric detection (GC/MS) of individual compounds. The Gerstel Thermal Desorption System (TDS) unit, equipped with Cooled Injection System (CIS) and 20–position autosampler, attached to the Varian Saturn 2000GC/MS, was used for the purpose of 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 employed to achieve separation of the target species. Experimental conditions are shown in Table 2-3. For calibration of the GC/MS a set of Radiello passive samplers were prepared by loading the cartridges with a known amount of gaseous calibration standards (57 VOCs from PAMS standard (Restek), BTEX and carbon disulfide from Scott Specialty Gases). Four different concentrations (plus one blank) were used to construct calibration curves.

Table 2-3. GC/MS conditions for thermal desorption of Radiello VOC cartridges

Radiello diffusion samplers	*Carbograph 4 (R145)*	*Carbopack X (R141)*
Analyzed compounds	n-hexane cyclohexane n-heptane toluene benzene ethylbenzene o-, m- and p- xylenes n-octane	isopentane pentane 1,3-butadiane carbon disulfide
Thermal desorption conditions		
Head pressure	17 psi	10 psi
Carrier gas	Helium	Helium
Split flow	50 ml/min	50 ml/min
TDSA parameters:		
Initial temperature	20 °C	20 °C
End temperature	340 °C	320 °C
Desorption time	10 min	5 min
Split	Splitless	Splitless
CIS parameters:		
Initial temperature	-150 °C	-150 °C
End temperature	320	280
Desorption time	10 min	5 min
Split	Split	Split
GC/MS conditions		
Column temperature program	3 min at 40 °C, 3°C/min to 120 °C, 20°C/min to 280 °C, 1.3 min at 280 °C	5 min at 1 °C, 7°C/min to 200 °C, 1.5 min at 200 °C
Detector	Ion trap MS, 280 °C	Ion trap MS, 280 °C

Radiello aldehyde cartridges are eluted with 2 ml of acetonitrile (ACN) and filtered before analysis. The aldehydes derivatives are 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 Ogawa NO_2 and NO_x pads are extracted and mixed with a solution of sulfanilamide and N-(1-Naphthyl)-ethylenediamine dihydrochoride to produce a colored nitrite solution which is analyzed on a Technicon (Tarrytown, NY) TRAACS 800 Automated Colorimetric System (AC). The Ogawa SO_2 pads are extracted in 8 ml of deionized-distilled water (DDW), 1.75% hydrogen peroxide is added and sulfate are measured with the Dionex 2020i (Sunnyvale, CA) ion chromatograph (IC). These analyses were performed by the Environmental Analysis Facility (EAF) of DRI.

2.3.6.2 Laboratory Determination of n-Pentane and iso-Pentane Sampling Rates

As mentioned in Section 2.3.5.3, Radiello supply the sampling rates for a number of commonly collected compounds. However, for C4 hydrocarbons only 1,3-butadiane sampling rate was published and no sampling rates for C5 hydrocarbons were provided. Since our canister samples collected at Star Shell Road show high abundance of C4 and C5 hydrocarbons, we determined the sampling rates for these species in a laboratory experiment. Passive Radiello R141 samplers were exposed in a 100-liter flow-through chamber (Figure 2-7) with known concentrations of selected C4 and C5 hydrocarbons. The chamber consists of a 100 liter half-cylindrical shape framed with Teflon rods and sheeting. An internal fan ensures a well-mixed atmosphere and emulates 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. Stainless steel ports are built into the base for test atmosphere inflow, exhaust, a temperature and relative humidity (RH) probe, and sampling applications. The atmosphere is created by diluting certified gas standards (Scott Specialty Gases) with zero air using an Environics 9100 Ambient Monitoring Calibration System. Zero air is generated using an Aadco 737 pure air generator outfitted with several scrubbing filters. The diluted gas mixture was run through the humidifier (Figure 2-7, c) in order to regulate humidity in the exposure chamber at 50%. The relative humidity, temperature, pressure and wind velocity were constantly recorded by DAVIS Weather Monitor (Figure 2-7, d). C4 (butane and iso-butane) and C5 (iso-pentane and pentane) concentrations generated in the exposure chamber were independently verified twice a day by sampling the chamber atmosphere with 1 L canisters (for 4 hours) and analyzed by GC/FID. Analysis of canisters and continuous monitoring of all parameters showed that the generated C4 and C5 hydrocarbon concentrations, temperature, relative humidity, pressure and wind velocity were very stable during whole chamber experiment. 20 R141 samplers were placed in the chamber filled with equilibrated atmosphere (equilibration time ~ 5 hours) and exposed for four periods of time (1, 3, 5 and 7 days, see Table 2-4). Passive samples were analyzed directly by thermal desorption GC/MS as described above (see Section 2.3.6.1) and sampling rates were calculated from following equation:

$$C_{[\mu g/m^3]} = m_{[\mu g]} \times 10^6 / (Q_{[ml/min]} \times t_{[min]})$$

where:
C = the average concentration over the exposure time in $\mu g/m^3$
m = mass of analyte in μg
t = exposure time in *minutes*

Experimentally measured C, t, and m parameters were applied to determine the sampling rates of C4 and C5 hydrocarbons. The sampling rates for n-butane and iso-butane reveals marked back-diffusion with sampling rates exponentially declining over time. The sampling rates for n-pentane and iso-pentane (Table 2-4) showed some decreasing diffusion rates as exposure time increased from 1 to 7 days, evidence that slight back-diffusion takes place during sampling and that sampling rates may need to be adjusted depending on exposure time. The sampling rates obtained for 7-days exposure have been used to calculate the average concentration of target compounds for this study.

Table 2-4. Exposure time, mass of analytes and sampling rates calculated for iso-pentane and n-pentane.

Number of Radiello samplers	*Exposure time*	*Mass of analyte [µg]*		*Sampling rates [ml/min]*	
		Isopentane	Pentane	Isopentane	Pentane
3	1 day	1.36	0.86	70.2	47.03
5	3 days	3.01	2.58	53.1	48.2
5	5 days	3.49	3.33	37.5	37.9
5	7 days	4.38	4.92	38.3	40.5
5	blanks	<DL	<DL	-	-

DL-detection limit

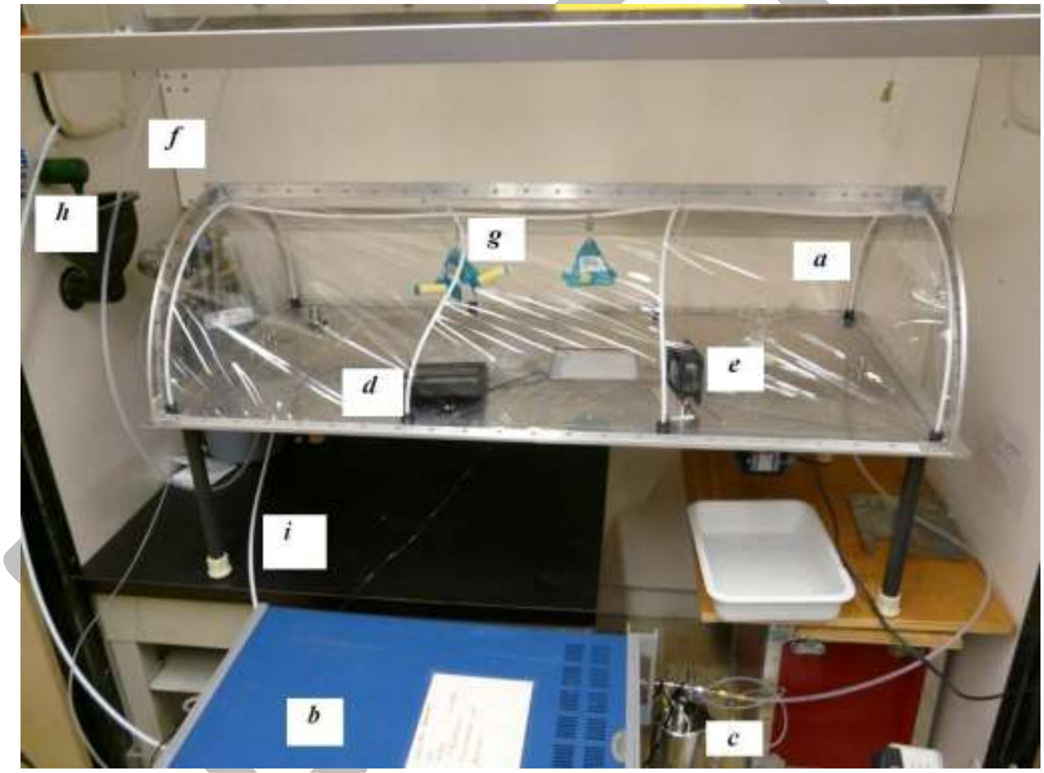

Figure 2-7. Exposure chamber system: (a) Teflon chamber, (b) Environics 9100 Ambient Monitoring Calibration System, (c) humidifier, (d) DAVIS Weather Monitor, (e) fan, (f) self regulating exhaust line, (g) Radiello diffusion samplers placed in Radiello yellow diffusion bodies, (h) Teflon line from zero air generator Aadco 737, (i) Teflon line for collecting canister samples

2.3.6.3 Laboratory Analysis of Canister VOC samples

Canister samples were analyzed for BTEX, 1,3-butadiene, hexane, CS_2 and other VOC species 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 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.

2.3.6.4 Laboratory Analysis of DNPH Cartridges

The hydrazones are separated and quantified per EPA Method TO-11A using a high performance liquid chromatograph (Waters 2690 Alliance HPLC System with 996 Photodiode Array Detector). After sampling, the cartridges are eluted with acetonitrile. An aliquot of the eluent is transferred into a 2-ml septum vial and injected with an autosampler into a Polaris C18-A 3µm 100 x 2.0 mm HPLC column. Since our HPLC system is equipped with the photodiode array detector, the identification of carbonyl compounds is much more accurate than with standard UV/VIS detector. Also, the sensitivity of the analysis is enhanced by using the photodiode array detector.

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 converts 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. 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 very 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 (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.

2.3.6.5 Laboratory Analysis of Time-integrated PM Samples for PM Mass, Elements and Carbon

Batch samples collected during the field study were retrieved or weekly from the sampling sites, placed in climate-controlled storage, and periodically returned to DRI for analysis by the Environmental Analysis Facility (EAF) or Organic Analysis Laboratory(OAL).

Gravimetric Analysis. Unexposed and exposed Teflon-membrane filters are equilibrated at a temperature of 20±5 °C and a relative humidity of 30±5% for a minimum of 24 hours prior to weighing. Weighing is 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 mg, the balance is re-calibrated. If the difference exceeds ±15 mg, 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 ±0.015 mg. Pre- and post-weights, check weights, and re-weights (if required) are recorded on data sheets as well as being directly entered into a database via an RS232 connection. All PM$_{2.5}$ Teflon filters will be analyzed for mass.

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) (Chow et al., 1993; Chow et al., 2001). Samples are collected in this method on quartz filters. A section of the filter sample 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 CO2 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. EC and OC are thus distinguished based upon the refractory properties of EC using a thermal evolution carbon analyzer with optical 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 nonoxidizing helium atmosphere, and at 550^{o}C (EC1), 700^{o}C (EC2), and 850^{o}C (EC3) in an oxidizing atmosphere. The IMPROVE method uses variable hold times of 150-580 seconds at each heating stage so that carbon responses return to baseline values.

Elements. Energy Dispersive X-ray Fluorescence (EDXRF) analysis was performed on Teflon-membrane filters for elemental analysis using PANalytical Epsilon 5 EDXRF analyzer (Watson et al., 1999). Two types of EDXRF standards are used for calibration, performance testing, and auditing: (1) vacuum-deposited thin-film elements and compounds from Micromatter Co. (Deer Harbor, WA), and (2) polymer films. The vacuum deposit standards cover all elements except for Ir, Ta, Zr, and Hf (which may be determined by interpolation) and are used as calibration standards. The polymer film and National Institute of Standards and Technology (NIST) standards are used as QC standards. During EDXRF analysis, filters are removed from their Petri slides, and loaded into holders for entry into the x-ray analysis chamber. A QC standard and a replicate from a previous analysis are analyzed with each set of 10 filters. When a QC value differs from specifications by ± 10% or more, or when a replicate value differs from the original value (where values exceed 10 times the detection limits) by ±10% or more, the previous 10 filters are reanalyzed.

2.3.6.6 Laboratory Analysis of Time-integrated PM Samples for Particulate PAHs

After taking a punch for TOR analysis, quartz filters were spiked with the following deuterated internal standards: chrysene-d$_{12}$, pyrene-d$_{12}$, benz[a]anthracene-d$_{12}$, benzo[a]pyrene-d$_{12}$, benzo[e]pyrene-d$_{12}$, benzo[k]fluoranthene-d-$_{12}$, benzo[g,h,i]perylene-d$_{12}$, coronene - d$_{12}$. The samples were extracted with dichloromethane (twice) utilizing pressurized fluid extraction method with Accelerated Solvent Extractor (Dionex Corporation, Sunnyvale, CA). The extracts were then concentrated by rotary evaporation at 20°C under gentle vacuum to ~1 ml and filtered through 0.45 mm Acrodiscs (Gelman Scientific), rinsing the sample flask twice with 1 ml dichloromethane (CH_2Cl_2) each time. Approximately 100 µl of toluene was added to the sample and CH_2Cl_2 /hexane was evaporated under a gentle stream of nitrogen. The extracts were analyzed for PAH using the Varian 1200 triple quadrupole gas chromatograph/mass spectrometer (GC/MS/MS) system with CP-8400 autosampler, operating in EI and multiple ion detection (MID) mode. Splitless injections (1 µL) were made onto a phenylmethylsilicone fused-silica capillary column (30 m, 0.25 mm id, 0.25 µm film thickness; Chrompack Factor four VF-5ms). The GC operating conditions were as follows: 85ºC for 2 min; 12ºC/min to 200ºC; 8ºC/min to 320ºC; hold at 320ºC for 8 min. Samples were quantified by comparing the response of the deuterated internal standards to the analyte of interest. Analyte response was referenced to five-point calibration curves created from standard solutions made with certified PAH mixtures purchased from Sigma -Aldrich, Inc., ACCU Standards, Ultra SCI and CDN, Inc. The National Institute of Standards and Technology Standard Reference Materials (SRM 1941 and 2260a) served as reference standards for QA/QC purposes. Compounds for which authentic standards were not available were quantified based on the response factor of standards most closely matched in structure and retention characteristics.

2.4 Quality Assurance and Data Validation

Success of the project was evaluated in terms of: 1) accuracy, precision, validity, and completeness of acquired data; and 2) extent to which data can be used to meet stated project objectives. In particular, the DRI field operators conducted regular flow and calibration checks. In addition, DRI routinely conducts interlaboratory comparisons with the ARB and the South Coast Air Quality Management District. This final report discusses accomplishments with respect to the data qualification statement described in the QA/QC plan (Zielinska et al., 2010).

The accuracy of the continuous gas monitoring instruments used in this project was checked at DRI prior to and following field use using certified gas standards. During the field study, the zero levels and air flow rates were checked daily and adjusted when necessary.

The passive sampling methods employed in this project, except for the Radiello R141 passive VOC samplers discussed in Section 2.3.6.2, have been previously subjected to validation by comparison to other, well established methods and by collection and analysis of replicate samples (Fujita et al., 2009a, 2009b) Active sampling was carried out using widely accepted methods and following established SOPs (available upon request).

All analytical data was reviewed and validated prior to calculation of summary values presented in this report. Problems that occurred during sample collection or sample analysis were indicated using a system of coded data flags, and data from flagged samples were subjected to additional review and excluded where appropriate.

2.5 VOC Source Apportionment

The Chemical Mass Balance (CMB) receptor model was applied in this study to apportion the source contributions to volatile organic compound concentrations in the Barnett Shale area. The CMB model consists of a least-squares solution to a set of linear equations that expresses each receptor concentration of a chemical species as a linear sum of products of source profile species and source contributions. The source profile species and the receptor concentrations, each with uncertainty estimates, serve as input data to the CMB model. Input data uncertainties are used both to weight the relative importance of the input data to the model solution and to estimate uncertainties of the source contributions. The output consists of the contributions of each source type to both total and individual ambient VOC concentrations and the propagated uncertainties.

While the application of the CMB receptor model is relatively straightforward given these input data, assessment of the validity of source contribution estimates is not. The uncertainty in the source composition profile may only account for measurement uncertainties in the selected profiles and may not reflect the actual real-world variability of the source compositions. Testing and sampling protocols and a number of other factors affect the emission rates and chemical composition of gaseous and particulate pollutants from various combustion sources. CMB results can also vary with the specific procedures used to derive the composite profiles and uncertainties and the choice of source profiles and fitting species. Thus, the uncertainties derived by the CMB model are insufficient alone to assess the true validity of the apportionment results.

Version 8 of the DRI/EPA CMB receptor model[3] was used to apportion hydrocarbon compounds to the several source categories (motor vehicle exhaust, 2-stroke gas engine exhaust, biogenic, natural gas, and condensate tank emissions). The source composition profiles were normalized to the sum of the 13 organic species reported in Table 3-3 and composite profiles were derived by averaging the normalized fractions to give equal weight to all members of the composite. The uncertainties were set to the larger of the analytical uncertainties or one σ variability in species abundances among members of a composite.

Source profiles were derived from the VOC canister samples collected during phase 1 of this study and augmented with additional profiles prepared by DRI for other projects. Profiles created specifically for the study area were 1) a composite of two samples from the venting condensate tank at Star Shell Rd, 2) a composite of fugitive emissions from 2 condensate tanks with open ‘thief hatches’ (Allison and Star Shell 3 in Table 2-1), 3) a mixed on-road motor vehicle exhaust profile based on the sample collected along Hwy 287 (I-287) in Decatur, and 4) a profile for small gasoline engines based on the Shale Creek 3 sample in Table 2-1. We also attempted to create profiles representing downwind emissions from gas compression plants, but the canister samples collected from these locations proved to be too dilute to distinguish from the regional background. Various profiles representing gasoline and diesel engine vehicle exhaust, fugitive and combustion emissions from natural gas and LPG operations were collected and evaluated until a default set of chemical profiles (Table 2-5) were selected based upon best CMB model performance among the alternative source profiles.

The CMB program proportionally combined these default profiles to provide the best reconstruction of the measured hydrocarbon composition from each ambient air sample, and outputs the amount of each species that is attributed to each source. The results were then reduced to 5 source categories by adding together the apportionments to TANK_VENT and TANK_FUG as Condensate Tanks and combining the HDDIESEL, LDGAS, and HWY_MIXED

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[3] http://www.epa.gov/scram001/receptor_cmb.htm

sources as Motor Vehicles, since it was difficult for the program to distinguish between sources in these categories due to the limited number of chemical species available.

Table 2-5. List of VOC default source profiles used for CMB receptor modeling.

Profile name	Emissions source represented	Origin
TANK_VENT	Condensate tank vent gas	Phase 1 of this project
TANK_FUG	Condensate tank fugitive emissions	Phase 1 of this project
LAWNMWR	Small 2-stroke gas engines	Phase 1 of this project
HWY_MIXED	mixed fleet highway emissions	Phase 1 of this project
HDDIESEL	Heavy duty diesel exhaust	NREL/DOE Weekend Ozone Study[4] – Los Angeles, 2000
LDGAS	Light duty gasoline exhaust	NREL/DOE Weekend Ozone Study – Los Angeles, 2000
CTCNG	Compressed natural gas	1998 Central Texas On-Road Hydrocarbon Study[5]

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[4] Eric M. Fujita, E.M., Campbell, D.E., Stockwell, W., Keislar, R.E., Zielinksa, B., Sagebiel, J.C., Goliff, W., Keith, M., and Bowen, J.L. (2002). Weekend/Weekday Ozone Observations In The South Coast Air Basin - Final Report. Desert Research Institute, Reno, NV Prepared for National Renewable Energy Laboratory.

[5] Fujita, E.M., R.E. Keislar, J.L. Bowen, W. Goliff, F. Zhang, L.H. Sheetz, M.D. Keith, J.C. Sagebiel, and B. Zielinska (1999). 1998 Central Texas On-Road Hydrocarbon Study. Final report prepared for the Texas Department of Transportation, Austin, TX.

3. RESULTS AND DISCUSSION

3.1 Characterization of Emission Sources (Phase 1)

We conducted an initial survey in Phase 1 to identify facilities with measureable emissions and collect source-oriented samples to characterize the chemical composition of the emissions. Continuous measurements were also made around the facilities to determine the spatial variations in pollutant concentrations near the facilities. All relationships discussed in Sections 3.1 and 3.2 relate to the raw data collected during this study and need to be confirmed with additional data and supported by a statistical analysis.

3.1.1 Volatile Organic Compounds

Table 3-1 shows the list of compounds that were quantified from canisters. Figures 3-1A and B shows the concentrations of more abundant components (above 2 ppb in at least one sample) in the source-oriented samples listed in Table 2-1. For clarity of presentation the samples are divided into High (Star Shell 1, 2, Allison, and Shale Creek 3) and Low (Shale Creek 1, 2, John Day, Background, Star Shell 3, Gas Plant, I-287) VOC concentrations. Figures High A and Low A show hydrocarbons from C2 (acetylene) to C6 (n-hexane) and Figures High B and Low B show hydrocarbons from C6 (methylcyclopentane) to C12 (n-dodecane). The full data set is presented in electronic form in Excel format in Final Database.

Figures 3-2A and B show the same data in percentages of total VOC emissions. The Star Shell 1, 2 and Allison samples represent the VOC emissions from the malfunctioning condensate tanks at the separate well sites. The VOC emitted along with methane consist mostly of lower molecular weight (mw) hydrocarbons, including ethane, propane, iso-butane, butane, iso-pentane, pentane and n-hexane. Higher mw hydrocarbons are much less abundant and include methylcyclopentane, benzene, cyclohexane, 2-methylhexane, n-hexane, n-heptane, methylcyclohexane and n-octane (as the most abundant species in this group). Although the hydrocarbon concentrations of three source samples vary, their composition is very consistent. Variations in the three samples are related to the rate of emissions from the tank and meteorology conditions that affect patterns of dispersion and dilution, as well as location of the sampling sites relative to the tanks. The fourth sample, Shale Creek 3, was affected by emissions from a gasoline-powered lawn mower. The contributions of lower mw hydrocarbons to total non-methane hydrocarbons (TNMHC) are much lower and higher mw hydrocarbons are relatively more abundant than in the three gas well source samples. Also, unsaturated and aromatic hydrocarbons (ethene, propene, benzene, toluene, m/p- and o –xylenes) are more abundant in these emissions.

Low concentration samples (Figure 3-1B) were collected in the vicinity of compressor stations (Shale Creek 1, 2, Gas Plant) or functioning wells (John Day), as well as local background sample (Background), freeway dominated sample (I-287) and when a tanker truck was servicing the condensate tanks at Star Shell Road (Star Shell 3). The VOC concentrations in these samples are much lower than the samples in Figure 3-1A High A and B. The compositions of the first five samples (Shale Creek 1, 2, John Day, Background and Gas Plant) (Figure 3-2A) are similar to the natural gas source samples (Star Shell 1,2 and Allison). Star Shell 3 and I-287 samples show higher contributions of ethene, aromatic and higher mw hydrocarbons, which is consistent with motor vehicle exhaust emissions and composition of the Shale Creek 3 sample (lawn mower emission).

Table 3-1. List of VOC canister species quantified for this study

Peak No.	Acronym	Compound	Peak No.	Acronym	Compound
1	acetyl	Acetylene	36	hexa2m	2-methylhexane
2	ethene	Ethene	37	pen23m	2,3-dimethylpentane
3	ethane	Ethane	38	cyhexe	cyclohexene
4	lprope	Propene	39	hx3m_cp13	3-methylhexane + 1,3-dimethylcyclopentane
5	lpropa	Propane	40	hep1e	1-heptene
6	lbud13	1,3-butadiene	41	pa224m	2,2,4-trimethylpentane
7	lbut1e	1-butene	42	n_hept	n-heptane
8	lc2but	c-2-butene	43	p2e23m	2,3-dimethyl-2-pentene
9	libute	Isobutylene	44	mecyhx	methylcyclohexane
10	lt2but	t-2-butene	45	pa234m	2,3,4-trimethylpentane
11	lbutan	n-butane	46	tolue	toluene
12	libuta	iso-butane	47	hep2me	2-methylheptane
13	lipent	iso-pentane	48	hep4me	4-methylheptane
14	lnpent	n-pentane	49	hep3me	3-methylheptane
15	pente1	1-pentene	50	n_oct	n-octane
16	b1e2m	2-methyl-1-butene	51	etbz	ethylbenzene
17	i_pren	Isoprene	52	mp_xyl	m&p-xylene
18	t2pene	t-2-pentene	53	styr	styrene
19	c2pene	c-2-pentene	54	o_xyl	o-xylene
20	b2e2m	2-methyl-2-butene	55	n_non	n-nonane
21	bu22dm	2,2-dimethylbutane	56	iprbz	isopropylbenzene
22	cpente	cyclopentene	57	n_prbz	n-propylbenzene
23	cpenta	cyclopentane	58	a_pine	alpha-pinene
24	bu23dm	2,3-dimethylbutane	59	m_etol	3-ethyltoluene
25	pena2m	2-methylpentane	60	p_etol	4-ethyltoluene
26	pena3m	3-methylpentane	61	bz135m	1,3,5-trimethylbenzene
27	p1e2me	2-methyl-1-pentene	62	o_etol	o-ethyltoluene
28	n_hex	n-hexane	63	n_dec	n-decane
29	t2hexe	t-2-hexene	64	bz123m	1,2,3-trimethylbenzene
30	c2hexe	c-2-hexene	65	indan	indan
31	hxdi13	1,3-hexadiene (trans)	66	detbz13	1,3-diethylbenzene
32	mcypna	methylcyclopentane	67	detbz14	1,4-diethylbenzene
33	pen24m	2,4-dimethylpentane	68	n_bubz	n-butylbenzene
34	benze	benzene	69	n_unde	n-undecane
35	cyhexa	cyclohexane	70	cs2	carbon disulfide

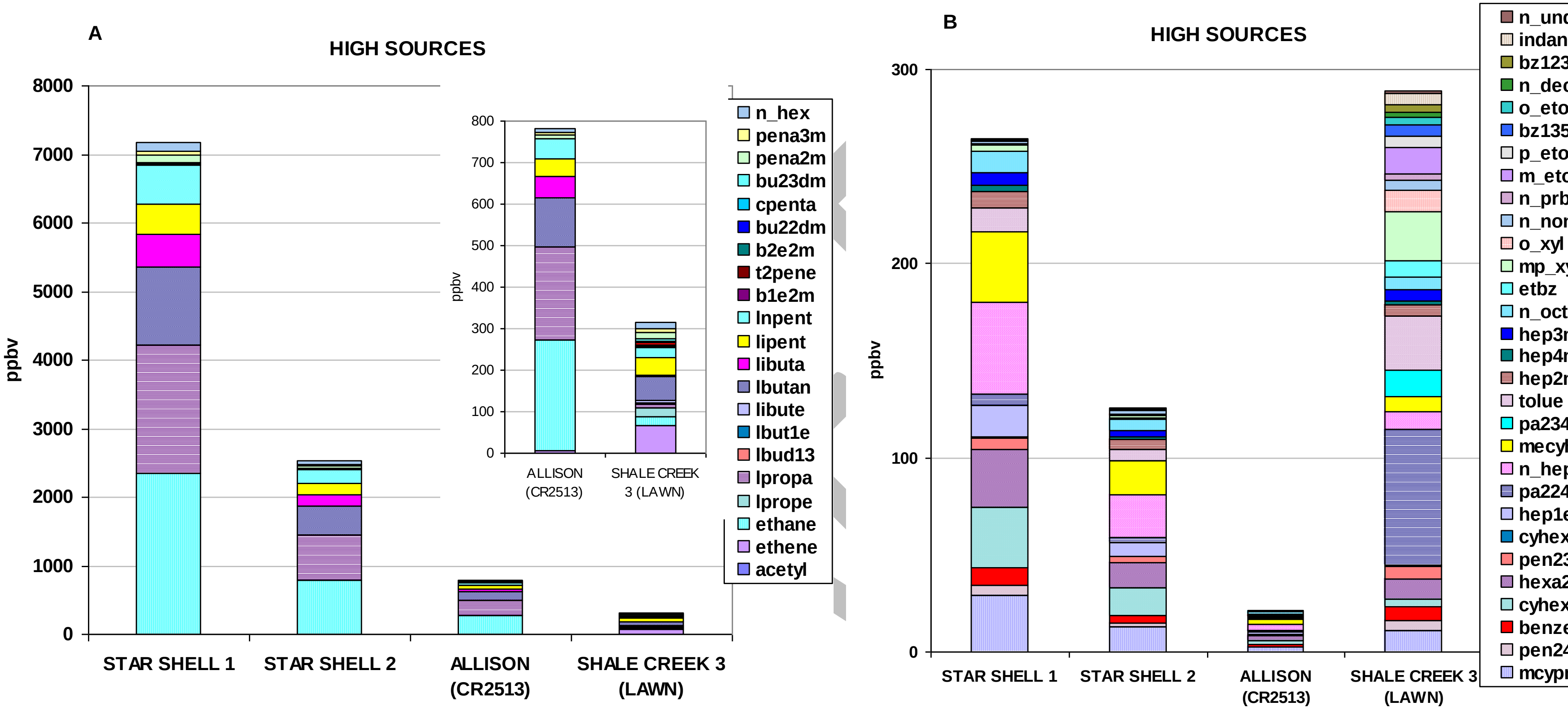

Figure 3-1A. VOC concentrations in source-oriented canister samples. High A and B: high concentration source-oriented samples; See Table 3-1 for compound's names

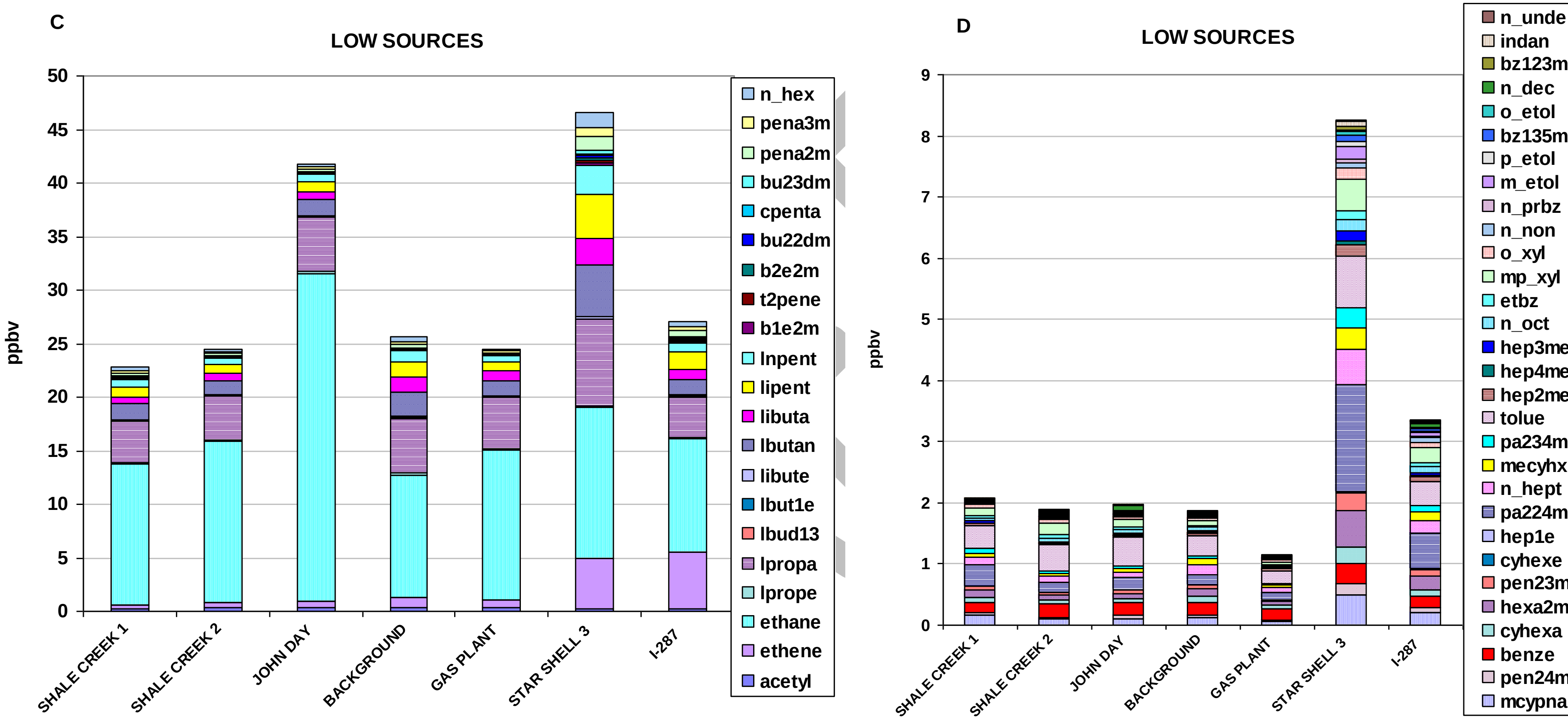

Figure 3-1B. VOC concentrations in source-oriented canister samples. Low A and B: low concentrations source-oriented samples. See Table 3-1 for compound's names

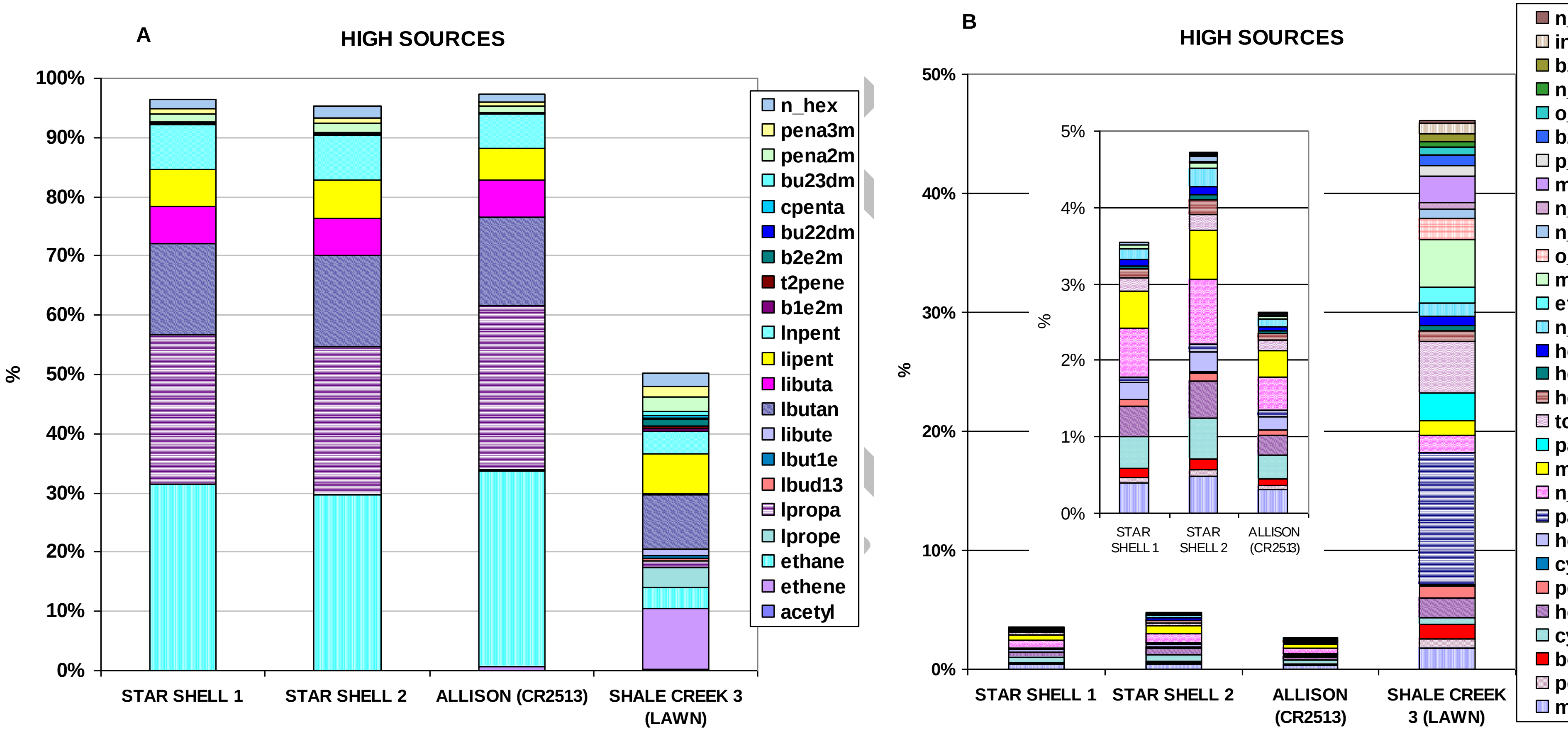

Figure 3-2A. Percentage contribution of individual VOC to total non-methane hydrocarbons in high A and B source-oriented category. See Table 3-1 for compound’s names

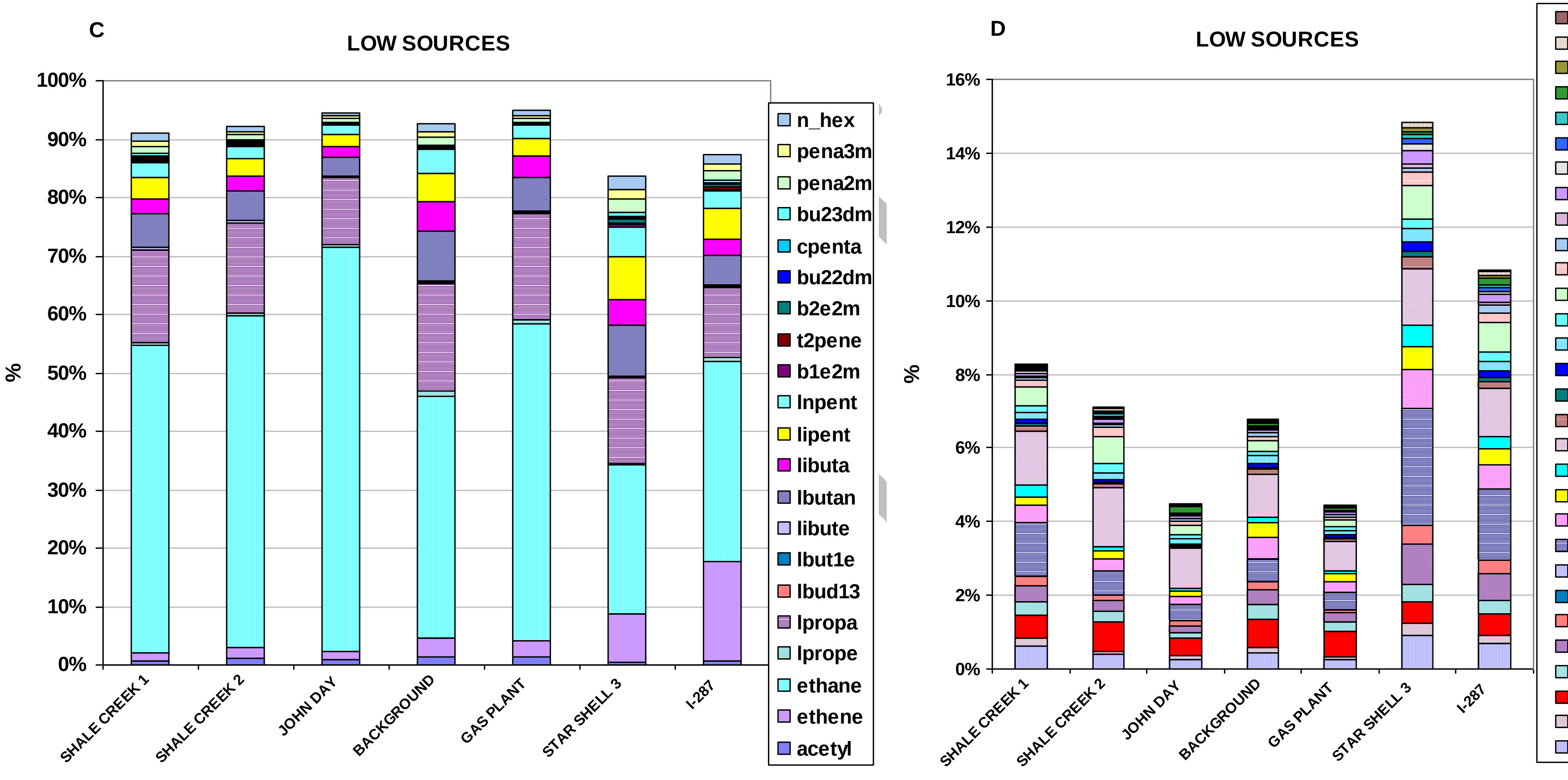

Figure 3-2B. Percentage contribution of individual VOC to total non-methane hydrocarbons in low C and D source-oriented category. See Table 3-1 for compound’s names

Carbon disulfide is not shown on these figures, since its concentrations were very low – in the range of 0.03 – 0.05 ppbv. Slightly higher concentrations were recorded in the grab samples collected at the peak of emissions from the Star Shell Rd tanks (1.8 and 0.45 ppbv). However, when integrated over an hour, the corresponding concentrations in Star Shell samples 1 and 2 were 0.04 and 0.05 ppbv, respectively.

Figure 3-3 shows the concentrations of carbonyl compounds in the source-oriented samples collected in Phase 1. The composition and concentrations of carbonyls in all high and low concentration samples are very similar to background sample with acetone, formaldehyde and acetaldehyde being the most abundant species. No acrolein was detected. This indicates that carbonyl compounds are not present in the emissions from natural gas production facilities and are formed mostly from photochemical transformation of gas phase hydrocarbons.

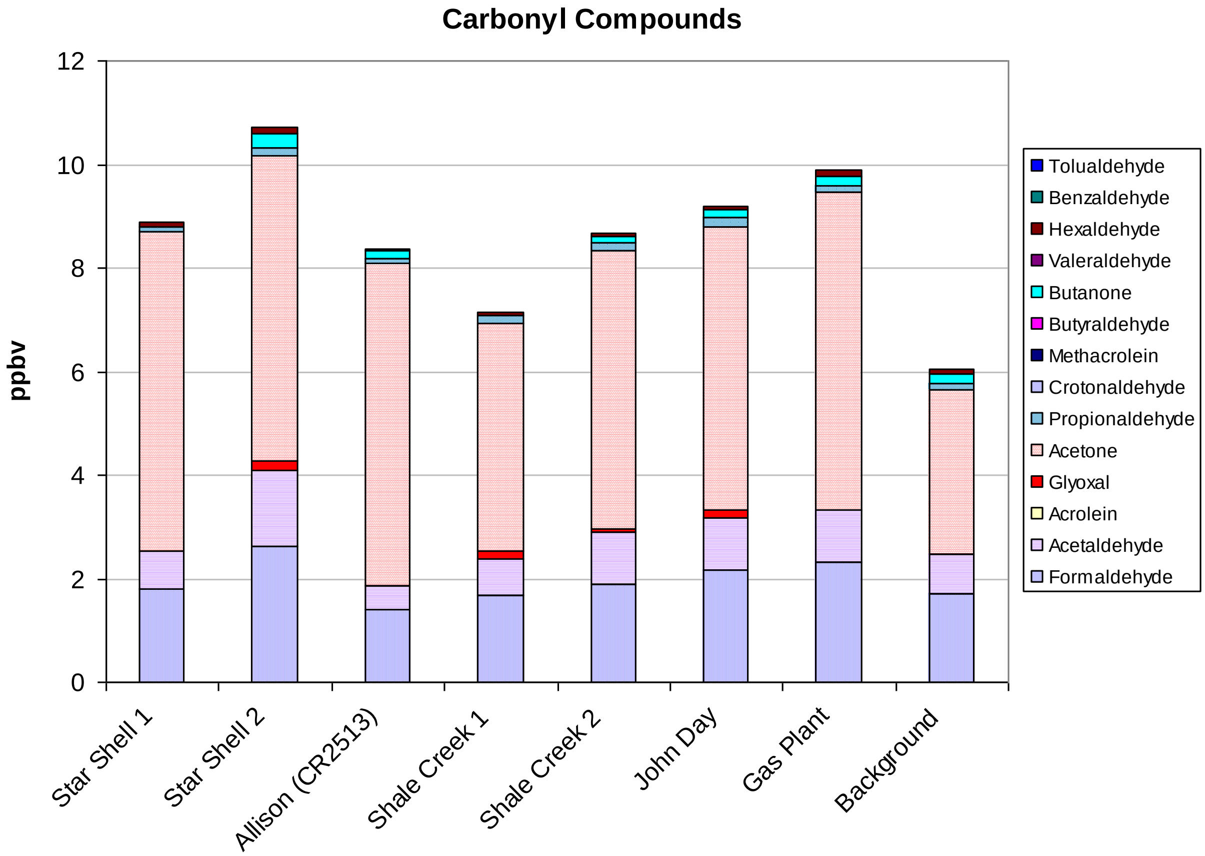

Figure 3-3. Carbonyl compounds concentrations in the source samples

3.1.2 Continuous data

During the Phase 1 collection of near-source canister and DNPH samples, NO, CO, and $PM_{2.5}$ (estimated from light scattering) concentrations were measured continuously along with meteorological data. NO and CO were consistently below the detection limits of the instruments (25 ppb and 500 ppb, respectively) and $PM_{2.5}$ never exceeded background levels. This is not surprising since NO and CO are primary emissions from fuel combustion and are not expected to be emitted by gas wells or storage tanks. The low levels observed at the John Day Rd site and near the gas processing plants where compressor engines were operating indicates that emissions from those facilities were either dispersing too rapidly to be detected or were being transported away from our sampling locations. VOC levels monitored with the handheld PID were generally below detection except near the Star Shell Rd and Allison condensate tanks where frequent large peaks were observed. However this measurement is not quantitative due to variable response of PID to different organic compounds and was only used to observe the relative variations in concentration and verify that our sampling location was downwind of the source. An example of the PID data is shown in Figure 3-4.

The continuous monitors were also used during our survey of potential source sampling locations to identify locations where pollutant concentrations were above local background. Other than the two venting tanks where source samples were collected and slightly elevated VOC concentrations observed intermittently downwind of the TARGA gas plant near Chico, we did not detect any other ‘hotspots’.

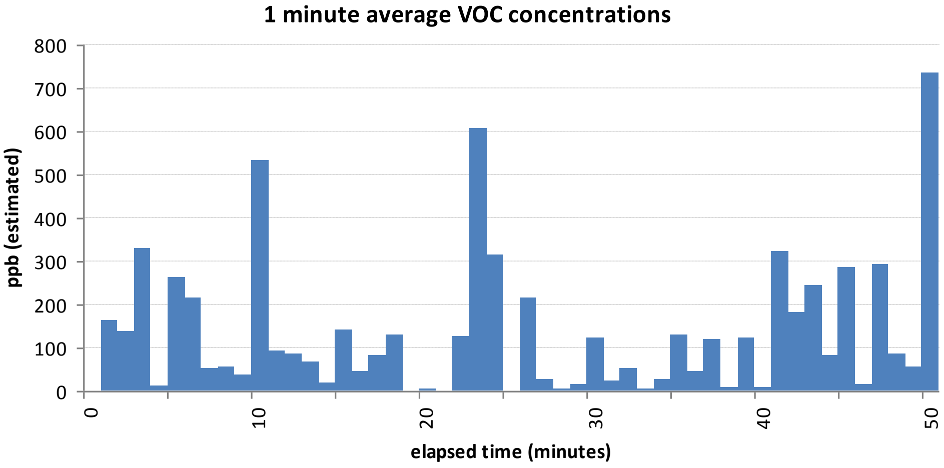

Figure 3-4. VOC levels estimated by PID during a source sample near venting condensate tank.

During the survey, a 'GasFindIR' camera that provides infra-red video images tuned to detect hydrocarbon emissions was used to identify the source of detected emissions, or to look for emissions from sources from a distance. This method proved useful for identifying the point of emissions at the two condensate tanks where samples were collected. Video images showed that the emissions from the tank at 403 Star Shell Rd were mainly from the vent pipe on top of the tank (see Fig 3-5) while at the Allison (CR 2513) tank battery emissions were from an unsecured hatch. The plumes are difficult to spot in still images, but clearly visible in the video footage. At the Shale Creek gas plant no elevated VOC concentrations were detected from the nearest accessible locations, but the camera indicated continuous HC plumes emanating from structures within the plant. The density of the plumes from the plant could not be gauged because the structures were apparently quite hot and tended to flood the infrared image.

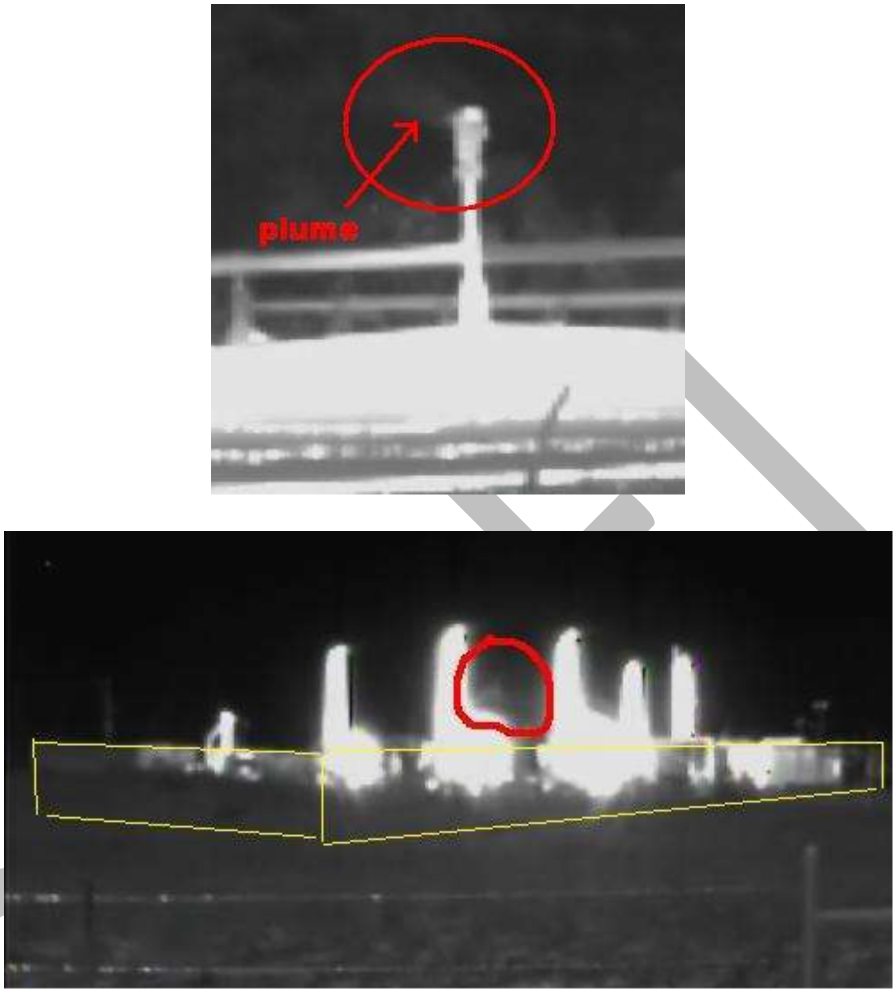

Figure 3-5. Infrared images of VOC plumes from the vent pipe on top of condensate tank (top) and Shale Creek gas plant (bottom). The fenceline of the plant has been outlined in yellow.

3.2 Downwind Gradient Experiment (Phase 2)

In the second phase we conducted 7-day time-integrated sampling for four consecutive weeks at multiple locations downwind of gas production areas. One location was near a well with emissions from condensate tanks that were characterized during Phase 1. The measurements at this private residence at 403 Star Shell Rd serve as a case study of the pollutant gradients at increasing distance downwind of the well tanks relative to the upwind background pollutant concentrations. Figure 2-2 shows the locations of the sampling sites in relation to the gas well and two condensate tanks.

The weekly average levels of VOC in Figure 3-6 shows consistently lower values downwind of the well, especially for the lower molecular weight alkanes. The data are ordered by position relative to PSSV15, the site closest to the tanks. Site to the right of PSSV15 is PSSV16 that was located about one mile downwind to represent the local background. Data from PSSV15 were invalidated for Week 3 and are not shown and sampling at PSSV16 did not begin until the second week. One Radiello VOC sample (for higher mw hydrocarbons) from site PSSV14 for week 2 was lost, thus only data for 1,3-butadiane, n-pentane iso-pentane and n-hexane (quantified from R141) are available for this sample.

In contrast, the corresponding data for carbonyl compounds in Figure 3-7 show much more uniform concentrations among the four sampling locations. Although carbonyl compounds are directly emitted from motor vehicles, a greater portion of these compounds in the ambient air are due to chemical transformation of hydrocarbons in the atmosphere.

The pollutant gradients can be seen more clearly in Figure 3-8 by normalizing all of the concentrations values at the downwind and upwind sites to the site closest to the tanks (PSSV15). This plot is for the week of May 13 when data are valid for all sites. The downwind site, PSSV16, is shown at -100 m distance for clarity of presentation, although its actual distance from the tanks was approximately 1600 m (~ 1 mile). All of the alkanes show a similar sharp decrease of 60 to 80% from site closest to the tanks (~17 m from the tanks) to the next downwind site (~ 67 m from the tanks). Concentrations at the second downwind sites (~ 110 m from the tanks) were only slightly lower than the first downwind site. This steep decrease in concentration is very similar to that observed in the 2009 API Exposure Classification Project, where measured downwind pollutant concentrations decreased to upwind background levels within about 100m of a roadway (Fujita et all, 2009b). In contrast to alkanes, the concentration gradients were not as steep and more variable for the BTEX species. This is likely due the greater local background ambient concentrations of BTEX, especially benzene as indicated by the higher values obtained for BTEX at PSSV16 relative to alkanes. In addition, 1,3-butadiene does not show appreciable gradient, as this specie is not emitted from condensate tanks or gas wells.

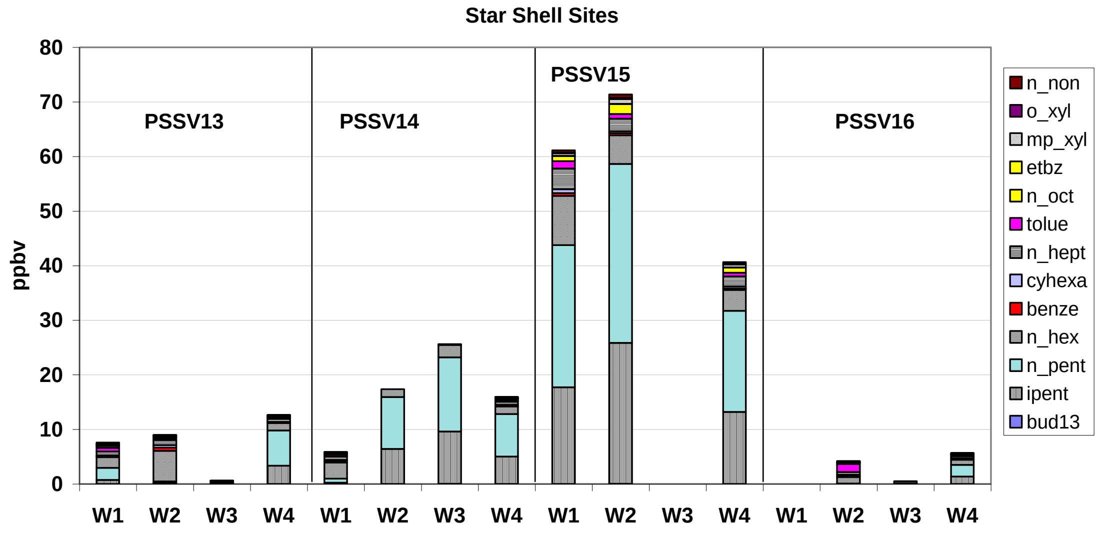

Figure 3-6. VOC concentrations in passive samples (W1,2,3,4 – week number). Star Shell area (PSSV13 - ~100 m from tanks, PSSV14:~67 m from tanks; PSSV15: 17 m from tanks and PSSV16: ~1600 m upwind of tanks)

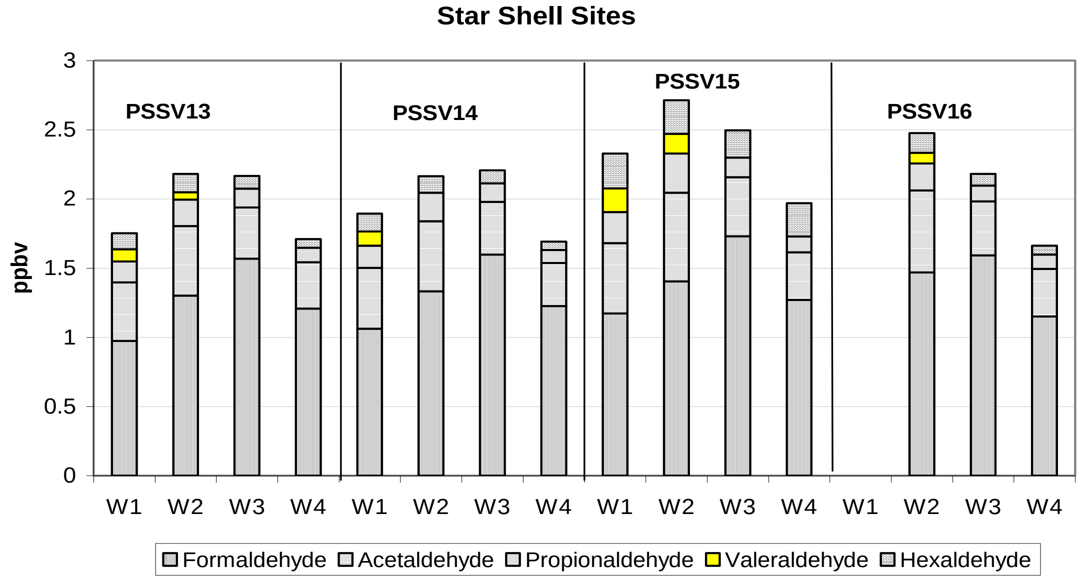

Figure 3-7. Carbonyl concentrations in passive samples. Star Shell Road (PSSV13 - ~100 m from tanks, PSSV14:~67 m from tanks; PSSV15: 17 m from tanks and PSSV16: ~1600 m upwind of tanks).

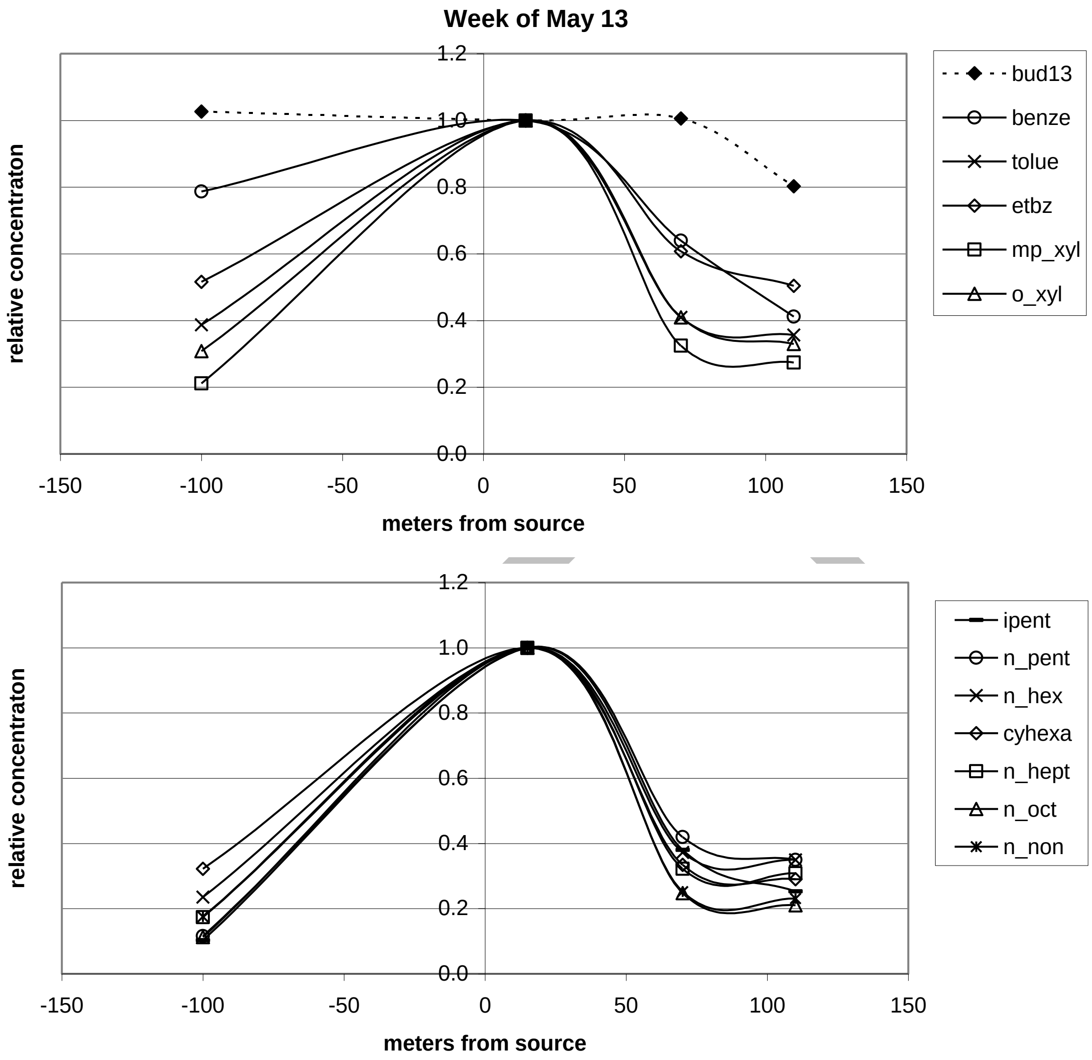

Figure 3-8. The relative concentration gradient from PSSV15 site during week of May 13, 2010 (week 4). Top panel shows 1,3-butadiene and BTEX and the lower panel shows alkanes. The downwind site, PSSV16, is shown at -100 m distance for clarity of presentation, although its actual distance from the tanks was approximately 1600 m.

3.3 Community Saturation Monitoring (Phase 2)

The second facility was a gas compressor station located near a small community of Shale Creek in Rhome (see Section 2.1.2 and Figure 2-4). This community is a cluster of approximately 250 occupied houses with the compressor station located approximately 200 m west-southwest of the community. We did not have access to the compressor station or its downwind area, so only monitoring at the fence line was possible. This station has several compressors and condensation tanks within the facility. There is also increased truck traffic around the station and several gas wells in the area surrounding the community. The spatial variations in pollutant concentrations were determined at various distances and directions from the source, sites adjacent to nearby roadways and a background site located upwind of the community. The measured volatile organic compounds were apportioned to sources using the Chemical Mass Balance receptor model. The study results were placed in context by comparing the measured pollutant concentrations to comparable data from elsewhere is the Barnett Shale area and from urban areas of the Dallas-Fort Worth.

The passive and active monitors were located at the backyards of volunteer's houses (sites PSSV01- PSSV07, see Section 2.2). We also installed passive only sites at the dead end of Orloff Rd at the north-east corner of Shale Creek (PSSV08), on the compressor station boundary fence (south-east corner) near entrance to Shale Creek (PSSV09), next to the Country Line Road, near Hwy 114 (PSSV10), on west side of Shale Creek compressor station, just across the dirt road leading to the station (PSSV11) and 1 mile south of Shale Creek community (PSSV12).

3.3.1 Meteorological data over monitoring period

A Davis Instruments meteorology package was installed at the PSSV01 passive site at the Shale Creek community on April 23, 2010 and was operating over 4 weeks of sampling. Table 3-2 shows the weekly mean of meteorology parameters from data collected at site PSSV01 and Figure 3-9 displays the frequency of wind direction at this site.

As the Table 3-2 and Figure 3-9 shows, the predominant wind direction is from south/south east at this site. The west or south-west component is less prevalent. However, with exception of week 3, the wind speed was not very high, on average close to 1 m/s, with longer period of calm weather. Week 3 was characterized by higher wind speed, predominantly from south/southeast direction. Consequently, the VOC concentrations were the lowest during this week. Conversely, $PM_{2.5}$, OC and ammonium sulfate concentrations were the highest which may indicate transport from Dallas/Forth Worth metropolitan area.

Table 3-2 Weekly mean of meteorology parameters from data collected at site PSSV01

week	T (C)	RH (%)	wind speed (m/s)	Easterly wind vector (m/s)	Northerly wind vector (m/s)	RWD*
Apr 22 - Apr 29	18.0	58.7	1.0	-0.09	-0.34	SSE
Apr 29 - May 6	20.1	61.3	1.1	0.00	-0.68	S
May 6 - May 13	22.5	62.9	2.0	0.53	-1.31	SSE
May 13 - May 20	21.9	77.9	0.7	0.25	-0.09	ESE
Negative wind vectors indicate prevailing wind from opposite direction. **Resultant Wind Direction*						

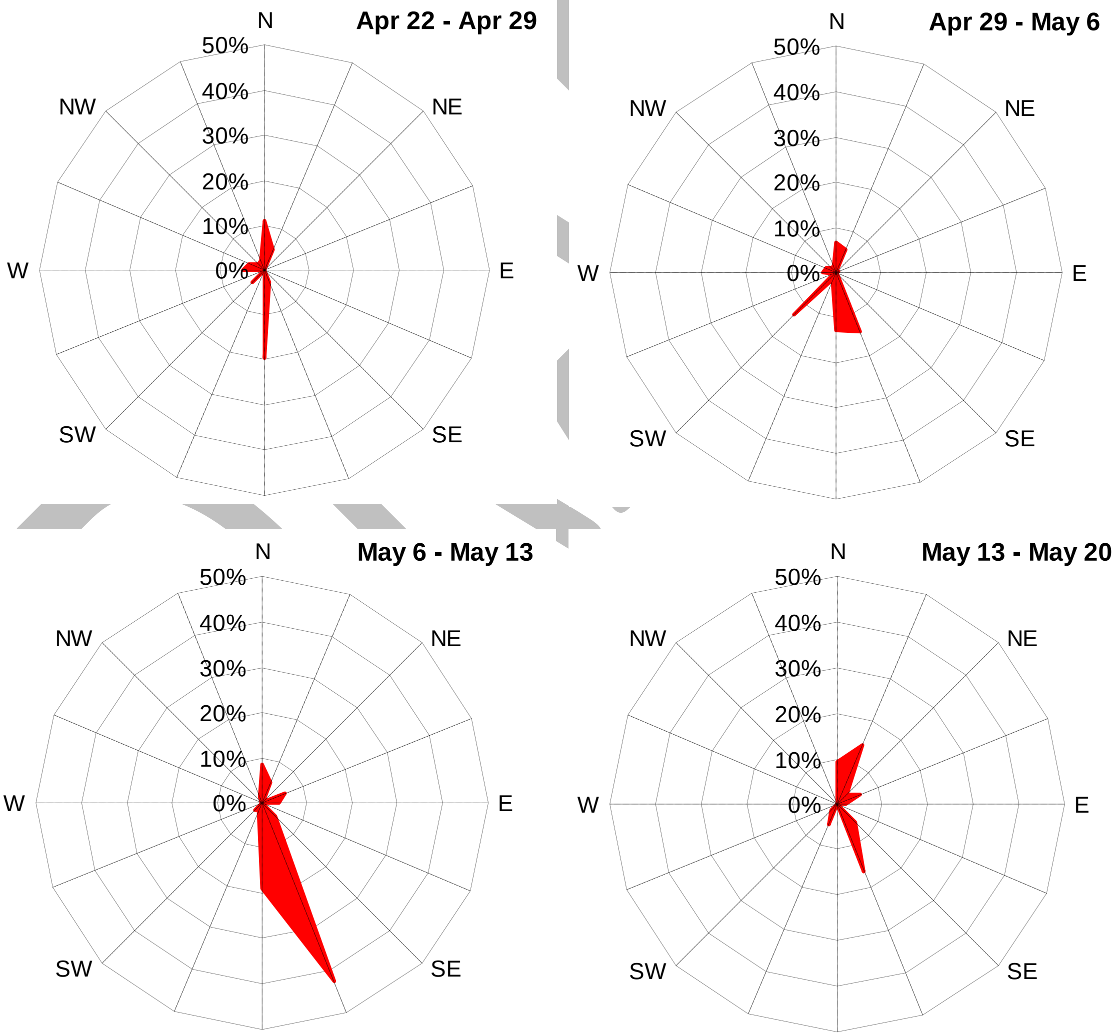

Figure 3-9. Frequency of wind direction at site PSSV01

3.3.2 Volatile Organic Compounds

For the Shale Creek community the concentrations were generally low (Figure 3-10 and 3-11). They were especially low during week 3 of sampling when the winds were mostly from the southeast and were stronger than during other weeks (see Figure 3-9). Table 3-3 shows the 28-days mean concentrations of VOC species quantified by passive Radiello cartridges (R141 and 145 combined) in Shale Creek community sites, listed in the order of increasing distance from the compressor station (see Figure 2-4). Sites PSSV11 and PSSV09 are situated next to the station on west and east site, respectively. Site PSSV10 is next to the County Line Road and site PSSV12 is situated around 1 mile south of Shale Creek, across from highway 114 (see Figure 2-1).

Although the differences in concentrations of total quantified VOC is very small, some individual species shows larger differences, but not always consistent with the distance from the compressor station. For example, Figure 3-12 shows the average concentrations for benzene (A) and n-pentane (B). Benzene concentrations are decreasing from two sites closest to the station (PSSV09 and PSSV11), but are increasing again for a distant site PSSV07. PSSV10 is close to the road, so it may be influenced by motor vehicle emissions. Concentrations of n-pentane are more uniform, although they are lower for more distant sites PSSV05 and PSSV07. Also, background site PSS12, far away from Shale Creek community shows the lowest concentrations for majority of quantified compounds. Table 3-3 and Figure 3-12 also show the corresponding data (i.e. averaged over the same sampling period) from TCEQ auto GC sites in Forth Worth and DISH (calculated from daily average values obtained from TCEQ website (http://www.tceq.state.tx.us/compliance/monitoring/air/monops/agc/agc_barnett.html/). For comparison, TCEQ Exposure Screening Levels (ESL), long-term health-related exposure levels, are also listed in Table 3-3.

The concentrations of iso-pentane and n-pentane as measured from passive Radiello R141 samplers may be slightly underestimated, since (as discussed in Section 2.3.6.1) the sampling rates for these species (Table 2-4) showed some decreasing diffusion rates as exposure time increased from 1 to 7 days, evidence that slight back-diffusion takes place during sampling, especially for iso-pentane. Passive samples at sites PSSV07, PSSV11, 12 and 16 were established in week 2 of the monitoring, thus the data for week 1 are missing. All VOC data are submitted in electronic format (in Excel) with this report.

Figure 3-11 shows the carbonyl compound concentrations in all passive samples collected over monitoring period. Although we analyzed passive samples for all 14 carbonyl species, the concentrations of 5 aldehydes are reported, since diffusion rates are published for these species only. Acrolein was not detected in any of the samples. Data from Week 2 at PSSV02, 03, 05 and 10 are missing due to the error in installation of the sampling media at those sites. Concentrations of carbonyl compounds were low and consistent with active sampling performed in Phase 1. The most abundant aldehyde in all samples is formaldehyde, followed by acetaldehyde. There is no indication of carbonyl compounds emissions from natural gas production facilities.

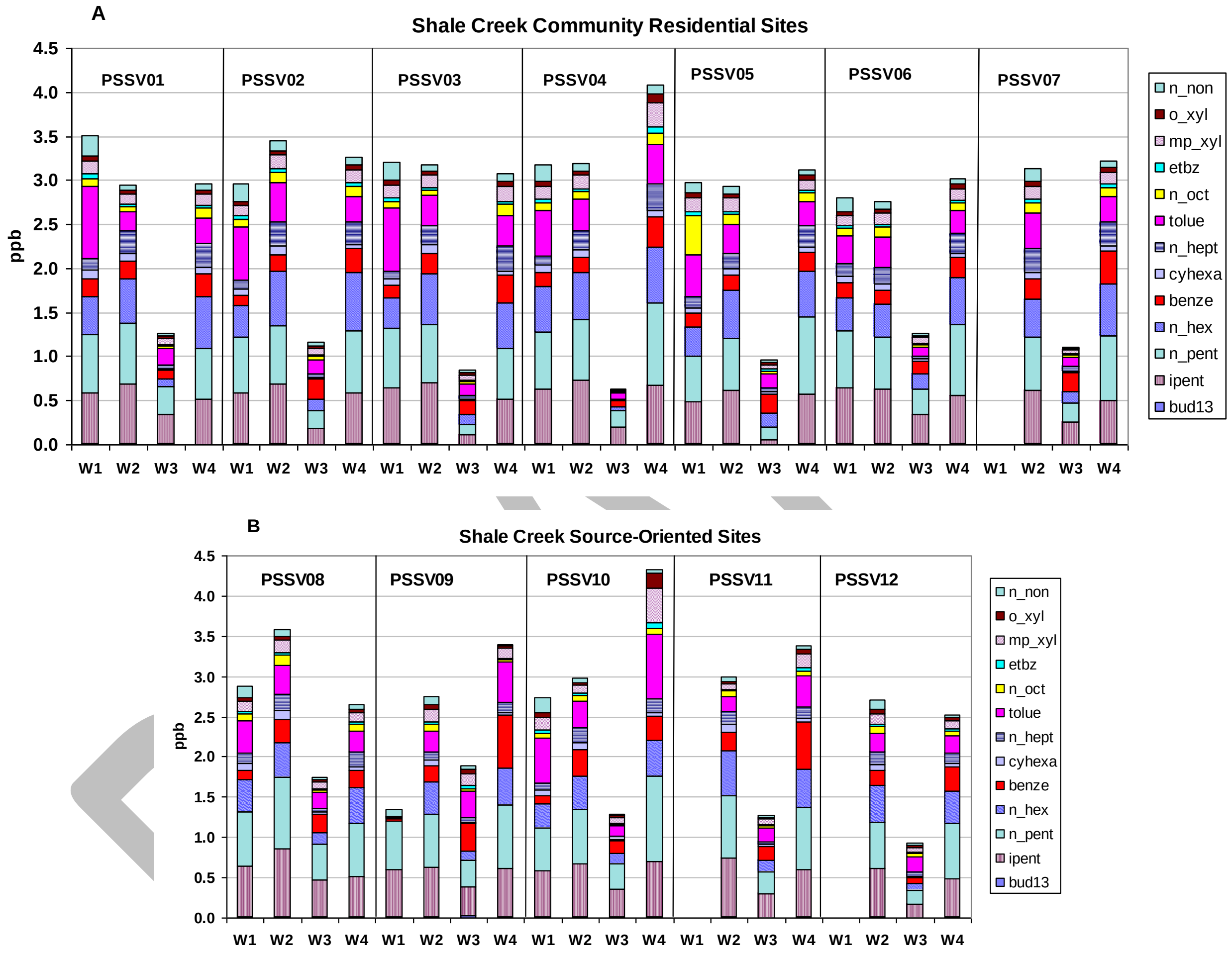

Figure 3-10. VOC concentrations in passive samples (W1,2,3,4 – week number). A: Residential sites in Shale Creek (SC) community (PSSV01-07); B: Source oriented sites in and around Shale Creek (PSSSV08: NE corner of SC; PSSV09: SE corner of compressor station, boundary fence; PSSV10: County Line Rd; PSSV11: W side of compressor station; PSSV12: 1 mile S of SC)

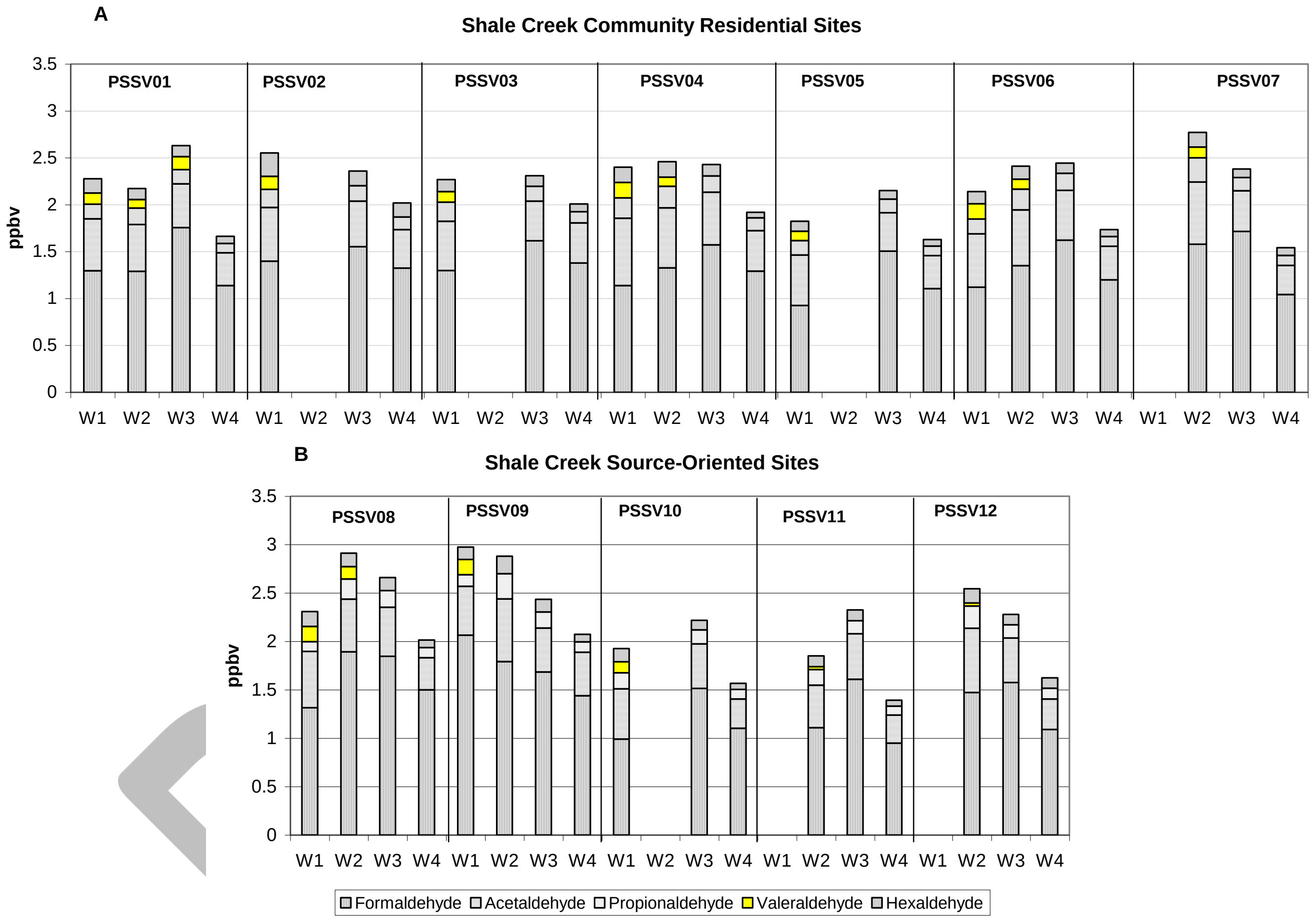

Figure 3-11. Carbonyl concentrations in passive samples. A: Residential sites in Shale Creek (SC) community (PSSV01-07); B: Source oriented sites in and around Shale Creek (PSSSV08: NE corner of SC; PSSV09: SE corner of compressor station, boundary fence; PSSV10: County Line Rd; PSSV11: W side of compressor station; PSSV12: 1 mile S of SC).

Table 3-3 Average 28-day VOC concentrations at Shale Creek sites, listed in the order of increasing distance from the compressor station

Site	1,3-butadiene	Iso-pentane	n-pentane	n-hexane	Benzene	Cyhexane	n-heptane	Toluene	n-octane	Ethylbenzene	M,p-xylene	o-xylene	n-nonane	Total VOC*
PSSV11	0.008	0.539	0.608	0.395	0.329	0.053	0.115	0.245	0.052	0.026	0.106	0.037	0.039	2.550
PSSV09	0.018	0.539	0.595	0.246	0.305	0.032	0.069	0.273	0.044	0.023	0.107	0.034	0.064	2.348
PSSV08	0.012	0.608	0.669	0.353	0.217	0.070	0.133	0.305	0.081	0.027	0.121	0.042	0.081	2.718
PSSV03	0.009	0.487	0.508	0.393	0.206	0.058	0.155	0.388	0.073	0.031	0.125	0.046	0.097	2.576
PSSV02	0.009	0.508	0.547	0.440	0.202	0.053	0.172	0.377	0.089	0.033	0.124	0.046	0.113	2.713
PSSV06	0.010	0.537	0.582	0.362	0.179	0.055	0.146	0.250	0.079	0.028	0.109	0.042	0.083	2.461
PSSV04	0.009	0.551	0.616	0.430	0.186	0.059	0.162	0.348	0.074	0.035	0.150	0.059	0.089	2.769
PSSV05	0.010	0.422	0.533	0.391	0.188	0.057	0.148	0.306	0.174	0.032	0.118	0.046	0.071	2.497
PSSV07	0.009	0.447	0.521	0.385	0.272	0.051	0.198	0.264	0.081	0.029	0.111	0.042	0.079	2.488
PSSV01	0.009	0.528	0.560	0.404	0.189	0.064	0.179	0.379	0.072	0.031	0.116	0.042	0.098	2.671
PSSV10	0.011	0.566	0.649	0.317	0.227	0.053	0.120	0.452	0.057	0.043	0.187	0.077	0.077	2.837
PSSV12	0.008	0.415	0.481	0.319	0.180	0.042	0.117	0.213	0.057	0.027	0.094	0.040	0.062	2.054
Mean Residential	0.009	0.497	0.552	0.401	0.203	0.057	0.166	0.330	0.092	0.031	0.122	0.046	0.090	2.597
Ft. Worth autoGC	0.046	0.976	0.705	0.263	0.135	0.058	0.127	0.366	0.043	0.039	0.122	0.042	0.024	2.946
DISH autoGC	0.003	1.236	1.075	0.445	0.124	0.091	0.124	0.178	0.039	0.014	0.055	0.014	0.016	3.413
ESL**	4.5	120	120	57	1.4	100	85	330	75	290	42	42	200	

*Total VOC = sum of concentrations of compounds listed in the table.

**ESL= TCEQ long-term Exposure Screening Level

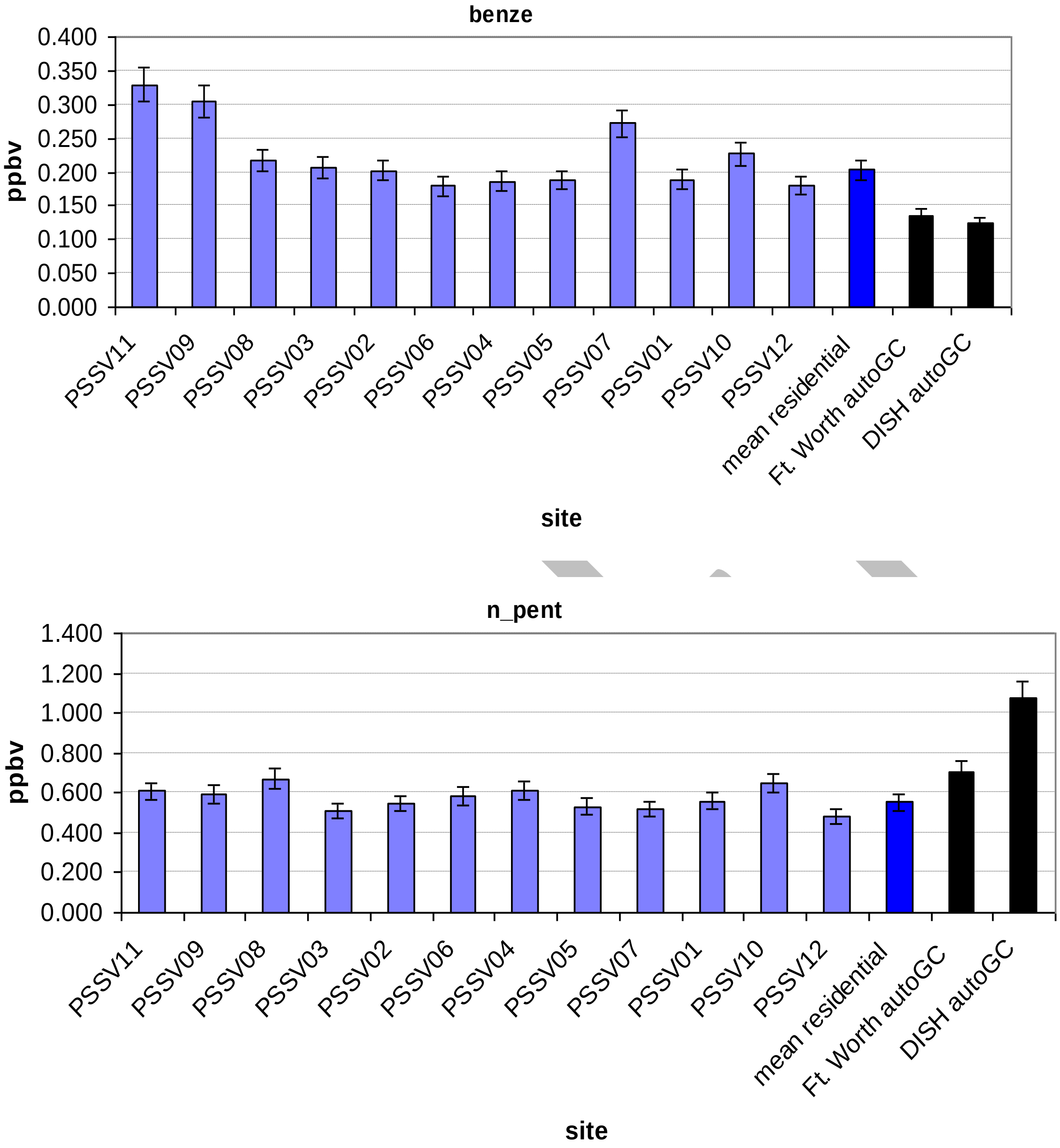

Figure 3-12 Average over 28-days benzene (A) and n-pentane (B) concentrations at Shale Creek community sites, ordered according to increased distance from the compressor station. Corresponding data from TCEQ autoGC sites are included for comparison.

3.3.3 Oxides of Nitrogen and Sulfur Dioxide

Figure 3-13 shows mean (averaged over 4-week monitoring period) NO and NO_2 concentrations in all passive samples collected at Shale Creek Community. SO_2 concentrations are very low, at or below the detection limit of the method (not shown). NO concentrations, which indicate diesel or gasoline engine emissions, are higher than NO_2 concentrations, which is a photochemical oxidation product of NO. Site PSSV09 situated at the south-east corner of the compressor station shows the highest NO concentrations, consistent with contribution of emissions from diesel engine powered compressors. Also, site PSSV10 located next to County Line Rd. and PSSV11 located at the west side of compressor station show higher NO concentrations. Background site PSSV12 shows the lowest NO values.

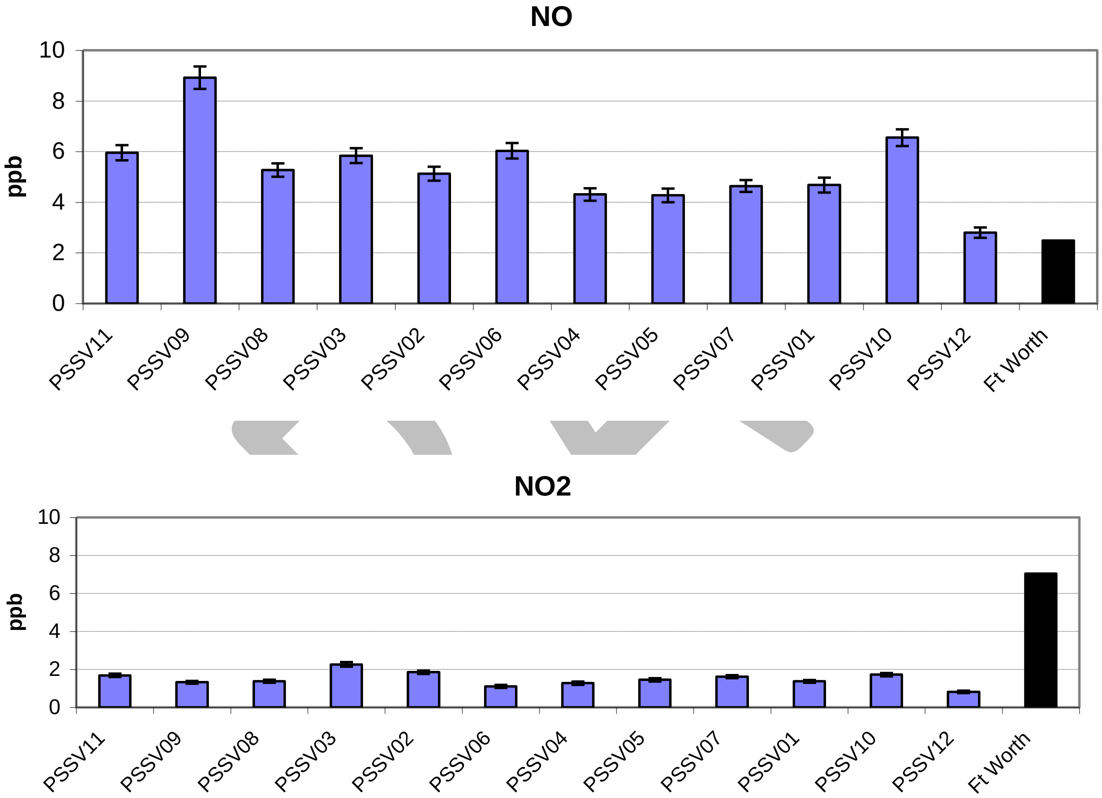

Figure 3-13. Mean NO and NO2 concentrations over sampling period. PSSV01-PSSV-07: residential sites in Shale Creek (SC) community; PSSSV08: NE corner of SC; PSSV09: SE corner of compressor station, boundary fence; PSSV10: County Line Rd; PSSV11: W side of compressor station; PSSV12: 1 mile S of SC;. Sites are ordered according to increased distance from the compressor station

3.3.4 Particulate Matter Data

PM$_{2.5}$ filter samples were collected in parallel with passive samples at the 6 residential locations in the Shale Creek community (these samplers require power). Teflon filters were analyzed for PM$_{2.5}$ mass and elements and quartz filters were analyzed for organic carbon (OC), elemental carbon (EC) and polycyclic aromatic hydrocarbons (PAH). Both Teflon and quartz filters from the first week of monitoring at the PSSV02 site were lost due to the sampler malfunction and one Teflon filter sample from this site (4/29-5/06) was invalidated due to the insect contamination. At the site PSSV03 both filter from week 2 were lost due to the power outage and quartz filters from week 1, and 3 were lost due to filter clogging. All data were submitted with this report in electronic format (Excel).

The plots in Figure 3-14 A, B and C show the concentrations of PM$_{2.5}$ mass, OC and EC, respectively, for four weeks of sampling at the sites with active mini-vol sampling, i.e. 6 residential sites in Shale Creek community (PSSV01-06) and one site at 403 Star Shell Road (PSSV14). Figure 3-15 A and B shows four week mean and maximum concentrations of PM$_{2.5}$ mass, OC and EC at all sites (OC/EC data not shown for site PSV03, since only week 4 data are available). The concentrations of PM$_{2.5}$ mass and OC were well correlated. Note that OC indicates mass of carbon contained in organic species, and not organic species mass (OM). Assuming OM/OC ratio ~ 2 (El-Zanan et al, 2005, 2009; Lowenthal et al, 2009) OM contributes in the range of 30-50% to PM$_{2.5}$ mass. EC concentrations were very low, below 0.5 ug/m3 and their contributions to PM$_{2.5}$ mass were in the range of 4-8%. In contrast to VOC data, PM$_{2.5}$ and OC concentrations were the highest in week 3 in all monitoring sites, when the predominant wind was from southeasterly direction (see Section 3.4). This may indicate transport from the Dallas/Forth Worth metropolitan area.

The Teflon filters were also analyzed for elements by XRF to determine the main component of PM$_{2.5}$ besides OC and EC. Figure 3-16 shows the concentrations of soil elements (adjusted for oxide forms, El-Zanan et al., 2005) and ammonium sulfate (estimated from sulfur concentration). Whereas soil components were the most abundant in week 2, ammonium sulfate was the main component of PM2.5 during week 3, as was the case for OC. Ammonium sulfate is a secondary atmospheric transformation product and is an indication of greater transport from Dallas/Fort Worth metropolitan area during the third week. A large fraction of the OC may have been associated with secondary organic aerosols transported from the urban areas.

After removing a punch for OC/EC analysis, the quartz filters were analyzed for PAH by GC/MS method. Table 3-4 list PAH quantified for this study and Figure 3-17 shows the concentrations of most abundant PAH in these samples. As mentioned previously, some samples from sites PSSV02 and PSSV03 were lost due to the power outage/sampler malfunction. The concentrations of PAH in all samples were extremely low, in the range of picograms/m^3, close to the instrument detection limit. The most abundant PAH in most of the samples included 1,7-dimethylphenenathrene, 7,12-dimethylbenzo(a)anthracene, methylphenanthrene isomers, phenanthrene and chrysene. These methylated PAH are present in diesel engine exhaust (Zielinska et al., 2004 a,b).

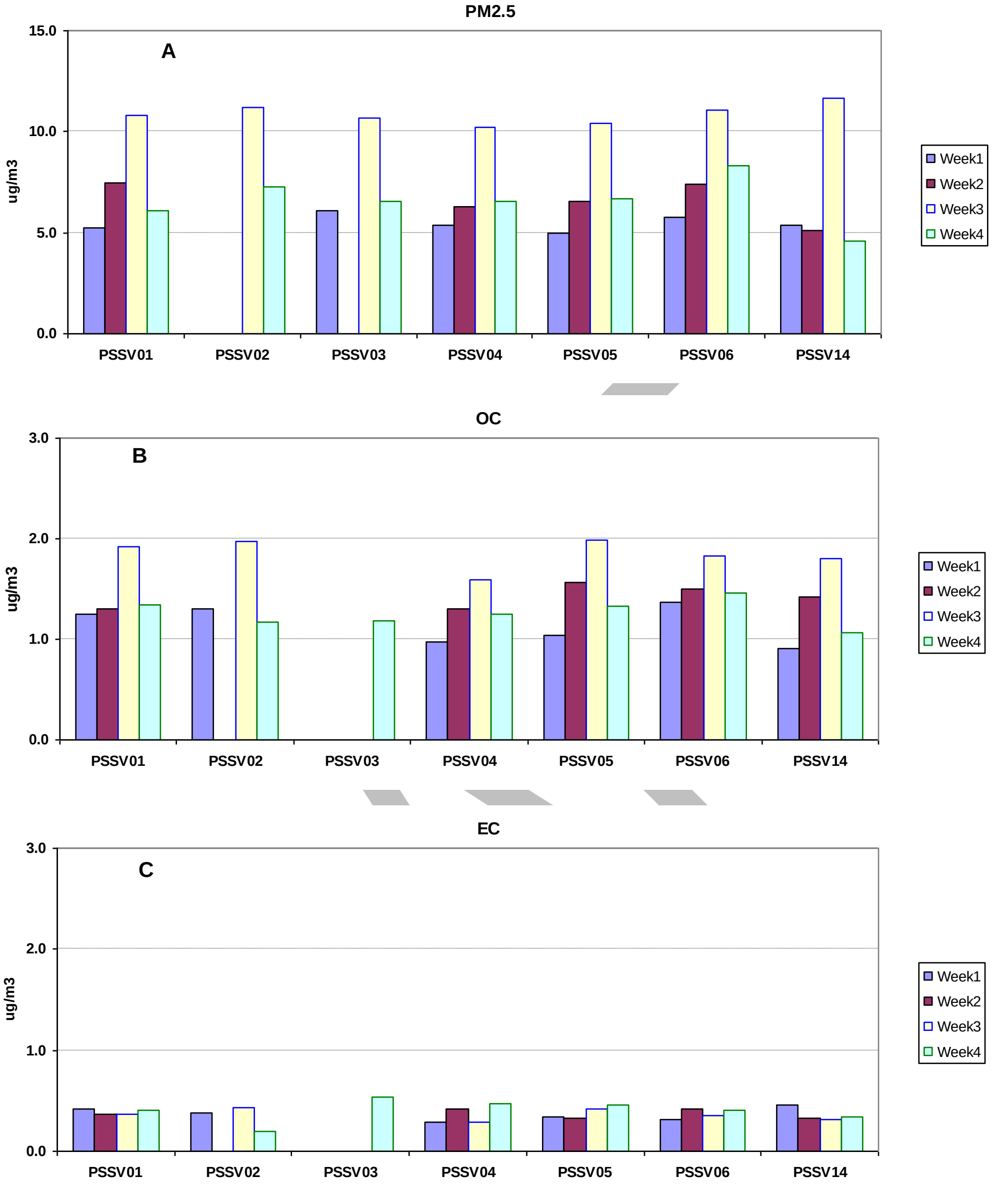

Figure 3-14. PM2.5 mass (A), organic carbon (B) and elemental carbon (C) data for all four weeks of sampling at PSSV01-06 (shale Creek) and PSSV14 (Star Shell Rd) sites

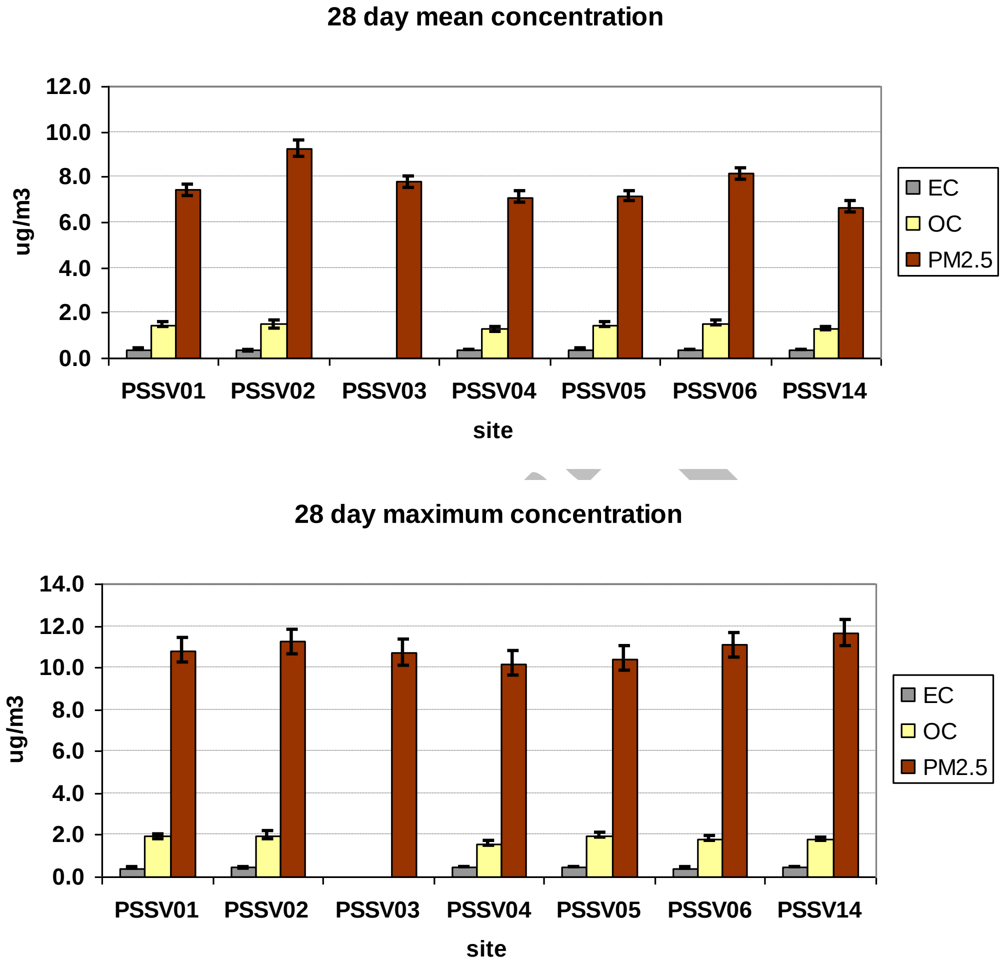

Figure 3-15. Mean and maximum $PM_{2.5}$ mass, OC and EC concentrations over monitoring period

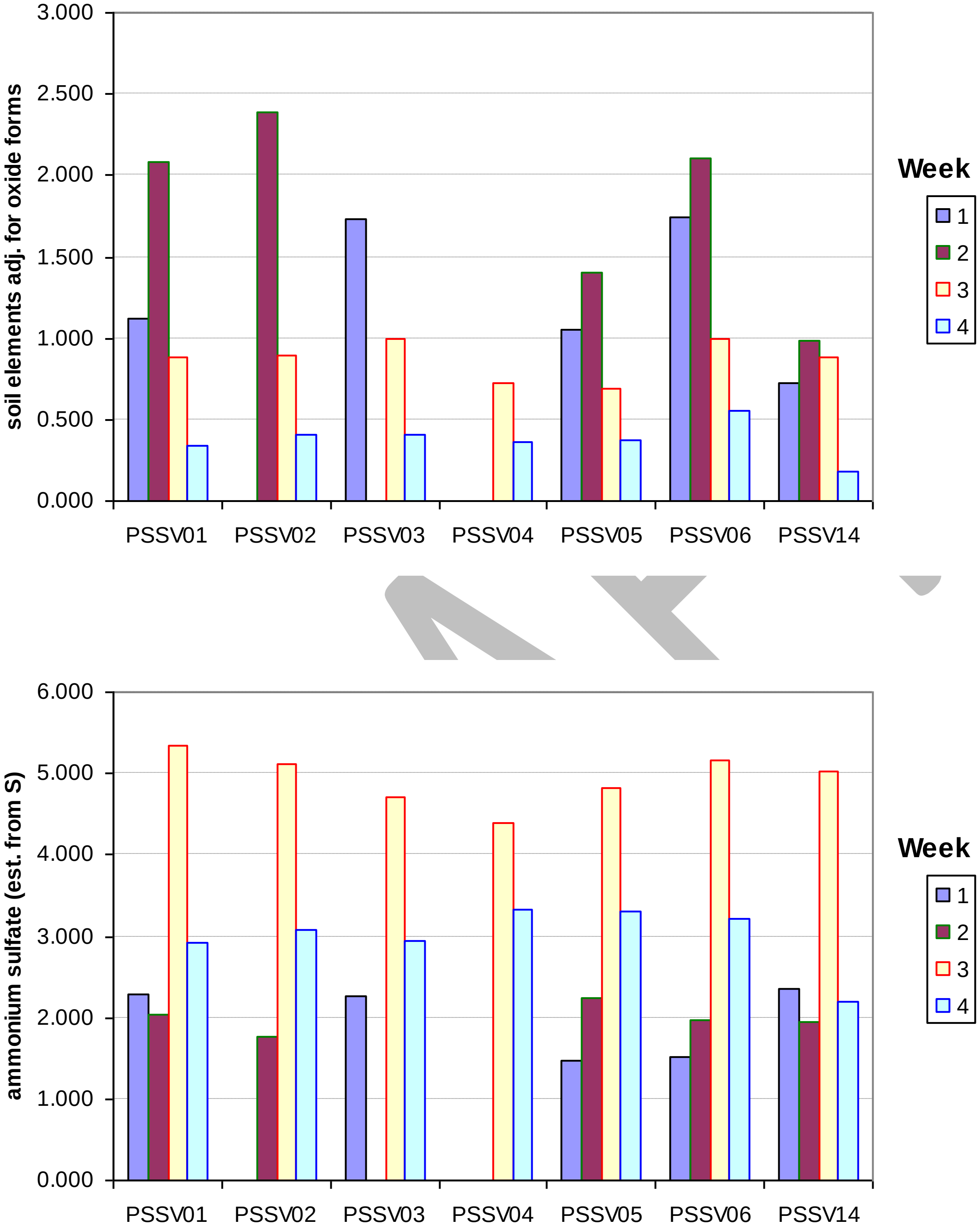

Figure 3-16. Concentrations (in ug/m3) of soil elements adjusted for oxide forms (top panel) and ammonium sulfate (lower panel) estimated from sulfur concentration.

Table 3-4. List of PAH with their mnemonics quantified from quartz filters

Mnemonic	Compound	Mnemonic	Compound
chrysn	Chrysene	bghifl	Benzo(ghi)fluoranthene
dbth	Dibenzothiophene	cp_cdpyr	Cyclopenta(c,d)pyrene
phenan	Phenanthrene	baanth	Benz(a)anthracene
anthra	Anthracene	dmban712	7,12-dimethylbenz(a)anthracene
m_2phen	3-methylphenanthrene	bbfl	Benzo(b)fluoranthene
m_3phen	2-methylphenanthrene	bjfl	Benzo(j)fluoranthene
m_2anth	2-methylanthracene	bkfl	Benzo(k)fluoranthene
m_9phen	9-methylphenanthrene	bepyrn	Benzo(e)pyrene (BeP)
mpht_1	1-methylphenanthrene	bapyrn	Benzo(a)pyrene (BaP)
m_9ant	9-methylanthracene	peryle	Perylene
dm17ph	1,7-dimethylphenanthrene	in123pyr	Indeno[123-cd]pyrene
dm36ph	3,6-dimethylphenanthrene	dbacan	Dibenzo(ac)anthracene
fluora	Fluoranthene	dbahan	Dibenzo(ah)anthracene
pyrene	Pyrene	bbchr	Benzo(b)chrysene
retene	Retene	pic	Picene
bafluo	Benzo(a)fluorene	bghipe	Benzo(ghi)perylene
bbfluo	Benzo(b)fluorene	anthan	Anthanthrene
m_4pyr	4-methylpyrene	dbalpyr	Dibenzo(a,l)pyrene
m_1pyr	1-methylpyrene	corone	Coronene
bntiop	Benzonaphthothiophene	dbaepyr	Dibenzo(a,e)pyrene
bzcphen	Benzo(c)phenanthrene	dbaipyr	Dibenzo(a,i)pyrene

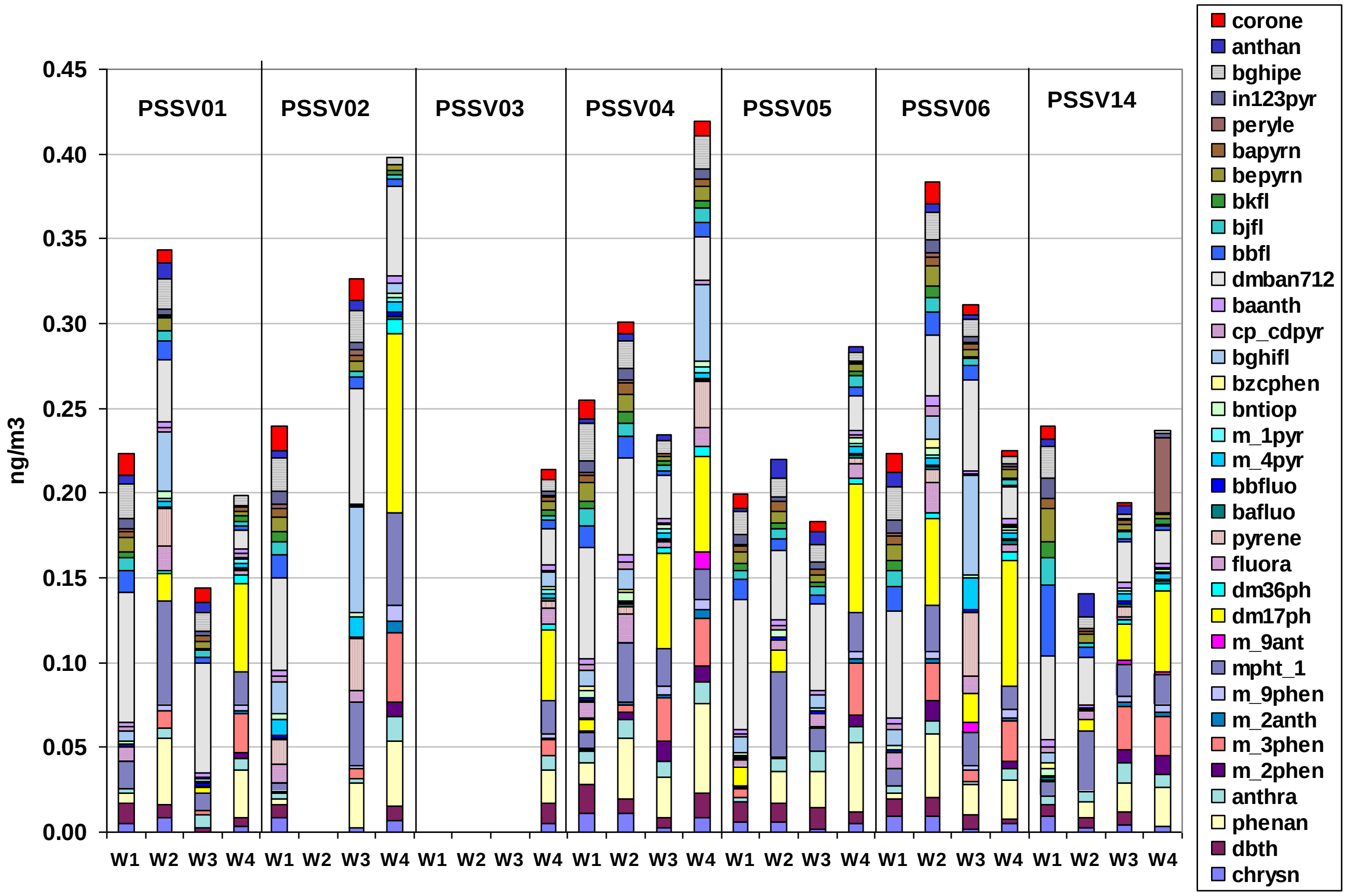

Figure 3-17. Concentrations of PAH measured in residential sites

3.4 VOC Source Apportionment Results

The Chemical Mass Balance (CMB) receptor model was applied in this study to apportion the source contributions to volatile organic compound concentrations in the Barnett Shale area. Good model performance was achieved for 90% of the ambient sample data from the Shale Creek area using the default set of source profiles and fitting species, and the relative contributions attributed to the source categories was similar for all sites within the community, giving a high degree of credibility to the model results. Performance was not as good for the Star Shell Road sites (PSSV15 and 16) and satisfactory results could not be obtained for any of the samples from site 14, possibly due to local emissions from an unrepresented source. However, those sites were only included as a demonstration of model sensitivity.

For the sum of all measured hydrocarbons, the dominant source category at the Shale Creek residential sites was motor vehicle emissions to which 46 ± 14% was attributed. Combined natural gas and condensate tank emissions were estimated to contribute about the same amount; 43 ± 5%. Small gasoline engines (e.g. lawnmowers) accounted for about 17 ± 7% of the total, although it is likely that this may include some mis-apportioned automobile exhaust since the profiles are quite similar. Apportionments for the sites nearest the gas processing plant or the highway fell within the range of the residential sites, except for higher condensate tank influence at sites 08, 09 and 11, which are nearest the gas plant. As expected, the apportionments for the sites at 403 Star Shell Rd are much more strongly dominated by condensate tank emissions (70 – 80%), with very little motor vehicle contribution. See Table 3-5 and Figure 3-18.

Examining the apportionments for individual organic compounds, the model predicts that about 70% of isopentane is due to engine emissions, while 70 – 80% of benzene is attributed to fugitive emissions of natural gas. Xylenes are almost entirely attributed to motor vehicle emissions at most sites, except at the Star Shell Rd site which is far from any public roads. In summary, CMB results indicate that motor vehicle exhaust is the dominant source of VOC in the Shale Creek community, but emissions from natural gas extraction make a substantial contribution to some hydrocarbons < C7 (see Figure 3-19)

Table 3-5. CMB source apportionment of the sum of measured HC species. Shale Creek sites are listed in the order of increasing distance from the compressor station

	performance statistics			average source apportionment				
SITE	**r2**	**chi2**	**%mass apportioned**	**motor vehicles**	**small gas engines**	**condensate tanks**	**natural gas**	**unidentified**
PSSV11	0.98	0.80	103	26 ± 25%	18 ± 23%	30 ± 25%	29 ± 16%	0%
PSSV09	0.83	5.49	88	10 ± 15%	29 ± 27%	33 ± 30%	20 ± 17%	8%
PSSV08	0.97	0.88	103	19 ± 4%	21 ± 16%	40 ± 11%	25 ± 7%	0%
PSSV03	0.96	1.02	105	56 ± 35%	13 ± 9%	5 ± 6%	32 ± 14%	0%
PSSV02	0.96	0.96	106	44 ± 46%	17 ± 12%	16 ± 20%	30 ± 9%	0%
PSSV06	0.97	0.71	104	46 ± 28%	15 ± 10%	21 ± 18%	22 ± 10%	0%
PSSV04	0.97	0.55	104	41 ± 46%	22 ± 35%	18 ± 11%	24 ± 20%	0%
PSSV05	0.88	3.02	106	29 ± 17%	27 ± 16%	22 ± 19%	27 ± 6%	0%
PSSV07	0.97	0.47	106	61 ± 40%	8 ± 10%	11 ± 17%	26 ± 15%	0%
PSSV01	0.96	0.62	106	50 ± 41%	9 ± 18%	21 ± 14%	27 ± 19%	0%
PSSV10	0.98	0.47	102	30 ± 25%	28 ± 31%	17 ± 11%	29 ± 19%	0%
PSSV12	0.98	0.56	105	36 ± 37%	16 ± 10%	26 ± 14%	27 ± 9%	0%
avg resid.				46 ± 14%	17 ± 7%	16 ± 6%	27 ± 5%	0%
PSSV16	0.93	2.45	97	11 ± 15%	7 ± 10%	66 ± 72%	20 ± 28%	0%
PSSV15	0.92	7.30	90	0 ± 0%	4 ± 0%	86 ± 4%	0 ± 0%	10%
PSSV14	unable to make satisfactory apportiomnents							
PSSV13	0.87	1.60	94	17 ± 31%	-6 ± 13%	58 ± 72%	15 ± 26%	16%

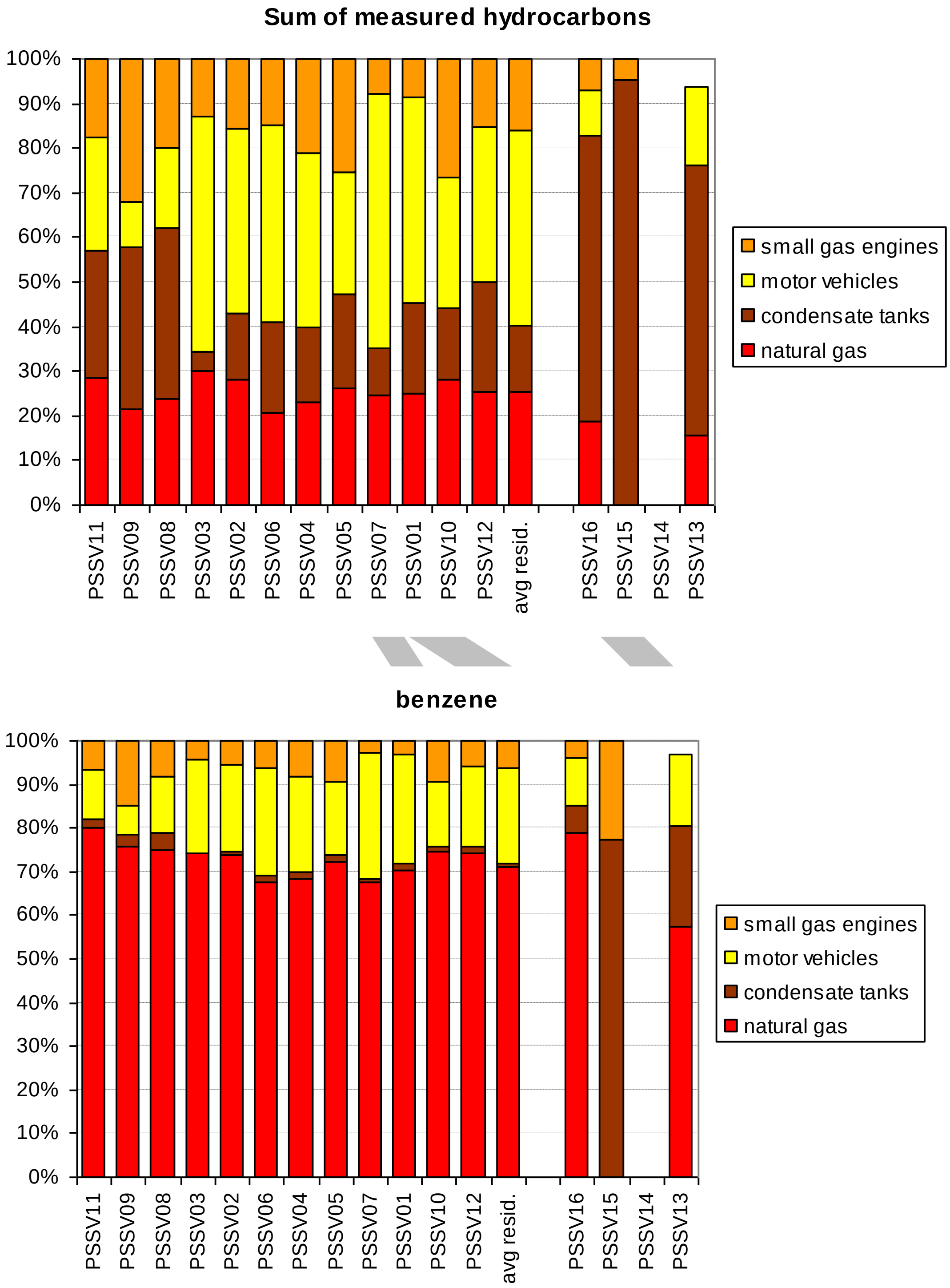

Figure 3-18. Mean relative contributions of 5 source categories to total hydrocarbons (top) and benzene (bottom), for each monitoring site.

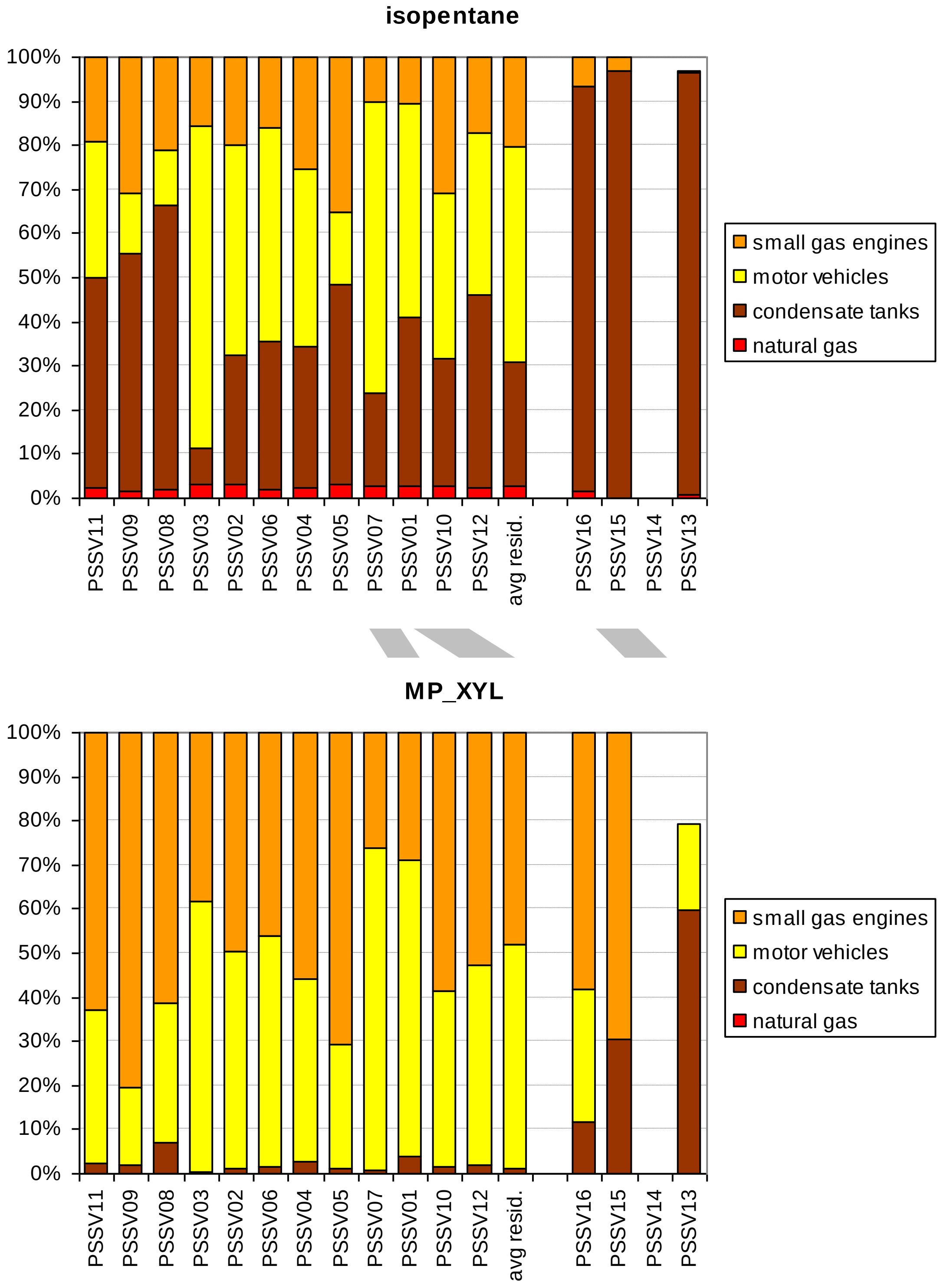

Figure 3-19. Mean relative contributions of 5 source categories to isopentane (top) and mp-xylene (bottom), for each monitoring site.

4. SUMMARY AND RECOMMENDATIONS

The purpose of this study was to provide a better understanding of the potential contributions of emissions from gas production operations to population exposure to air toxics in the Barnett Shale region. The specific technical objectives of this study were as follows:

1. Characterize the chemical composition of emissions related to natural gas production operations in the Barnett Shale area.
2. Estimate the potential emissions impact from various types of natural gas production facilities by measuring the associated pollutant gradients from the point of emissions.
3. Determine the ambient concentrations of selected air toxics within a community in the Barnett Shale region, and, to the extent possible, apportion the contributions of emissions from gas production operations to the measured exposure concentrations.

Technical objective #1 was accomplished in the Phase 1 of the study. Based on the canister samples collected during this phase, we were able to construct chemical profiles that are characteristic for venting condensate tank emissions, fugitive emissions from gas production facilities, mixed on-road motor vehicle emissions and small gasoline engine emissions, such as lawn mowers. These profiles were used in the source apportionment reported in Section 3.5.
From the data gathered in Phase 1, it was observed that:

- ✓ The most abundant non-methane VOC species emitted from the condensate tank adjacent to gas wells were ethane, propane, n-butane, iso-butane, iso-pentane, and n-pentane. These species account for over 90% of VOC emissions (see Figure 3-2, High A)
- ✓ The remaining ~10% included mostly of 2- and 3-methylpentane, n-hexane, methyl-cyclopentane, cyclohexane, 2-methylhexane, 1-heptene, methyl-cyclohexane, n-heptane and n-octane (see Figure 3-2, High A and High B)
- ✓ Aromatic hydrocarbons, such as benzene, toluene and xylenes were much less abundant and accounted for approximately 0.1 – 0.2% of non-methane VOC emissions (see Figure 3-2, High B)
- ✓ Carbon disulfide was present in very low concentrations in 1-hr canister samples, below 0.05 ppb
- ✓ Carbonyl compounds were not emitted from the condensate tanks located next to the gas wells

Technical objective #2 was accomplished by conducting passive monitoring at the Star Shell Rd site. We deployed three sets of passive samplers at increasing distances downwind and one set upwind from the venting condensate tanks. Major conclusions from these measurements include:

- ✓ There was a steep, exponential decrease in emission concentrations from the site closest to an emission source (~17m from the condensate tank) to the next downwind site located

~67 m from the tank. The concentrations of emissions from the tank decreases to near background levels at the distance of ~ 100 m (see Figure 3-8)

- This steep decrease in concentration is very similar to that observed in other studies (for example, in the 2009 API Exposure Classification Project, Fujita et al., 2009b), where measured downwind pollutant concentrations decreased to upwind background levels within about 100m of a roadway.

Technical objective #3 was accomplished by performing saturation monitoring over 4 weeks period at the Shale Creek community. Major conclusions include:

- The average concentrations of species measured by passive VOC Radiello samples were low, generally below 1 ppb. These concentrations are comparable or slightly higher to those measured by TCEQ over the same time period with continuous autoGCs in Forth Worth and DISH (see Table 3-3 and Figure 3-12). These concentrations are also much lower than those specified by the short- and long-term AMCVs (for example, 180 and 1.4 ppbv, respectively, for benzene)
- The compressor stations adjacent to the Shale Creek community was typically downwind of the community and observed gradients in pollutant concentrations were small and cannot be unambiguously associated with the compressor station. Higher concentrations were observed at a few sites that are in closer proximity to roadways.
- Source apportionment performed for Shale Creek community by Chemical Mass Balance (Section 3-5) indicated that for the sum of measured VOC (13 species) the dominant source category was motor vehicle emissions to which 46 ± 14% was attributed. Combined natural gas and condensate tank emissions were estimated to contribute about the same amount; 43 ± 5%. Small gasoline engines (e.g. lawnmowers) accounted for about 17 ± 7% of the total
- Apportionments for the sites nearest the compressor station or the highway fell within the range of the residential sites, except for higher condensate tank influence at sites PSSV08, 09 and 11, which are nearest the gas plant and where higher influence of combined condensate tank and natural gas emissions was observed (see Table 3-5).
- For individual organic compounds, the CMB receptor model predicts that about 70% of iso-pentane is due to engine emissions, while 70 – 80% of benzene is attributed to fugitive emissions of natural gas (see Figure 3-18 and 3-19).

There are several caveats regarding these general conclusions:

- Due to contractual constraints, the study was performed in April-May when the temperatures were not high and winds were mostly from southeasterly directions, usually in the range of 1 – 2 m/s (see Section 3-4). Results may differ if the study had been performed in the winter or summer months.
- Approximately two dozen well sites were surveyed in Wise County in the areas surrounding Rhome, Decatur, Aurora, Boyd, New Fairview, Alvord, Bridgeport, Runaway Bay, Chico, Paradise, and Allison. This survey was certainly not complete, taking into account thousands of well sites and compressor stations active in the Barnett Shale area. Thus, this study should be regarded as a pilot study

✓ We were denied access to the active well sites and compressor stations in the area. This forced us to perform fenceline monitoring in the Phase 1 of this study, which might result in rather incomplete and limited source profiles that were used for the source apportionment.

✓ The conclusions drawn from this study should be considered tentative and supported by a larger study or data from other studies covering all seasons that provides statistical confirmation of the study results. In additional to data for other seasons, spatial pollutant gradients should be obtained for other communities in the region. The samples that were collected in this study for source composition profiles were obtained at the fence line due to access restrictions. More source specific composition profiles should be obtained from samples collected directly at the point of emissions. Data from this and other related studies should be used to evaluate air quality modeling for the Barnett Shale and Dallas-Fort Worth area region.

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