ANALYSIS OF CCROPS VOC DATA FOR HAPS COMPOUNDS
FINAL REPORT

Prepared for

Clark County Department of Air Quality and Environmental Management
500 S Grand Central Pkwy Las Vegas, NV 89155-5210(702) 455-5942

Prepared by

Wendy S. Goliff
Division of Atmospheric Sciences
DESERT RESEARCH INSTITUTE
2215 Raggio Parkway
Reno, NV 89512

June 19, 2007

Executive Summary

Clark County, the most populous of Nevada's 17 counties with 1.9 million residents and 70 percent of the state's population, is one of the fastest-growing areas in the country, with more than 5,000 people moving there each month. It is also the destination of 38.2 million tourists a year (2005). The continued growth of southern Nevada threatens the air quality of its citizens.

Hazardous air pollutants (HAPs) can cause adverse effects to human health or the environment. Section 112 of the Clean Air Act (CAA), as amended in 1990, identifies 189 of these pollutants, including substances that cause cancer, neurological, respiratory, and reproductive effects. In regard to chemical characteristics, the HAPs consist of vapor phase organics (e.g., toluene, benzene), particulate organics (e.g., polycyclic aromatic hydrocarbons [PAHs]), and metal compounds (e.g., lead and cadmium) (Kyle et al., 2001).

The Desert Research Institute (DRI) provided laboratory analytical support for the Clark County Department of Air Quality Management as part of their Clark County Regional Ozone and Precursor Study (CCROPS) during the summer of 2005. Ten (10) HAPs (which are also ozone precursors) were quantified as part of this study (Table ES-1).

Table ES-1. Hydrocarbons on the HAPs list identified and quantified for CCROPS.

Benzene	n-hexane	Toluene	o-xylene
1,3-butadiene	methyl-t-butyl ether	2,2,4-trimethylpentane	
Ethylbenzene	styrene	M,p-xylene	

Eight of the ten compounds shared common sources, while the remaining two, 2,2,4-trimethylpentane and MTBE, did not correlate well with the other compounds, indicating that the eight had additional sources other than mobile sources, such as being used as solvents for industrial applications. Comparison of the three sampling locations showed that MTBE concentrations were dominated by transport from upwind locations such as surface waters and abandoned gasoline stations, while the remaining HAPs studied were dominated by local sources. None of the HAPs compounds showed any correlation with surface wind direction or aloft wind direction, although the data was sparse for the aloft wind direction.

For all ten HAPS compounds analyzed in this study, each showed anti-correlation with surface wind speed. When wind speeds were higher, concentrations of HAPs were lower due to increased ventilation, and when wind speeds were lower, concentrations were higher due to low ventilation allowing the buildup of pollutants.

Benzene and 1,3-butadiene possessed average concentrations greater than the Cancer Risk of one in a million threshold during the CCROPS field campaign. The remaining HAPs quantified during CCROPS had concentrations below health thresholds listed by USEPA.

The concentrations of HAPs studied here in the Las Vegas area during the CCROPS field campaign were most similar to levels in southern California, with the exception of MTBE, which is no longer detected by CARB (as of 2005).

Recommendations

As was noted by the T&B Systems report "Clark County Regional Ozone & Precursor Study", monsoonal activity (known as the Southwest monsoon or the Mexican monsoon) and troughing (an elongated region of relatively low atmospheric pressure, often associated with a front) dominated for much of the summer of 2005, resulting in long periods of clean conditions that precluded intensive monitoring. Therefore, the Clark County Department of Air Quality & Environmental Management should not make any policy decisions regarding Hazardous Air Pollutants based on the CCROPS field campaign.

It is recommended that the Clark County Department of Air Quality & Environmental Management conduct a separate field campaign to measure HAPs in the Las Vegas area. The field campaign should be multi-year to allow for annual variability, with sampling during each season to study seasonal variability. If a weekday/weekend effect study is desired, sampling should take place during at least 12 weekends to acquire a robust dataset. During any sampling campaign, Jean, Nevada remains a good upwind location, JD Smith a good urban site, and Joe Neal a suitable suburban site.

Table of Contents

List of Tables

List of Figures

Introduction

Clark County, the most populous of Nevada's 17 counties with 1.9 million residents and 70 percent of the state's population, is one of the fastest-growing areas in the country, with more than 5,000 people moving there each month. It is also the destination of 38.2 million tourists a year (2005). The continued growth of southern Nevada threatens the air quality of its citizens.

Hazardous air pollutants (HAPs) can cause adverse effects to human health or the environment. Section 112 of the Clean Air Act (CAA), as amended in 1990, identifies 189 of these pollutants, including substances that cause cancer, neurological, respiratory, and reproductive effects. In regard to chemical characteristics, the HAPs consist of vapor phase organics (e.g., toluene, benzene), particulate organics (e.g., polycyclic aromatic hydrocarbons [PAHs]), and metal compounds (e.g., lead and cadmium) (Kyle et al., 2001).

The Clark County Department of Air Quality and Environmental Management routinely monitors the criteria pollutants: particulate matter less than ten microns in diameter (PM_{10}) and fine particulates less than 2.5 microns in diameter ($PM_{2.5}$), carbon monoxide (CO), and ozone (O_3) as well as oxides of nitrogen (NO_X), and sulfur dioxide (SO_2), and non-criteria pollutants such as ammonia (NH_3), and hydrogen sulfide (H_2S). However, volatile organic compounds (VOCs) and most hazardous air pollutants (HAPs) are not monitored on a routine basis.

On April 15, 2004, the EPA designated Clark County as a nonattainment area for failing to meet the new eight-hour ozone standard. It designated Clark County a Sub Part 1 nonattainment area, which is the least severe of the possible classifications. However, the designation means Clark County has until 2009 to meet the eight-hour ozone standard. They are also charged with preparing attainment and maintenance State Implementation Plans and ensuring the implementation of effective control strategies. Therefore, during the summer of 2005, Clark County DAQEM conducted a field program as part of the Clark County Regional Ozone and Precursor Study to collect data during high ozone events, including meteorological parameters and concentrations of ozone and its precursors, as well as NOx and nitric acid.

The Desert Research Institute (DRI) provided laboratory analytical support for the Clark County Department of Air Quality Management as part of their Clark County Regional Ozone and Precursor Study (CCROPS). The objective of the work performed by DRI was to provide analysis of canister samples for speciated volatile organic compounds. The specific objective was to provide ambient concentrations for speciated non-methane organic compounds (in the C_2-C_{11} range). And because this was an ozone study, gas phase ozone precursors were targeted for analysis.

Canister samples were analyzed using gas chromatography with mass spectrometry (GC/MS) in accordance with the EPA method TO-15 for volatile organic compounds (PAMs) rather than for hazardous air pollutants (HAPs), and with gas chromatography with flame ionization detection (GC/FID) for C_2-C_4 compounds. Because there is some overlap between the PAMs list and the HAPs list, a small number of HAPs were quantified as part of this study (Table 1).

Table 1. Hydrocarbons on the HAPs list identified and quantified for CCROPS.

Compound	Lifetime (HO)[†]	Compound	Lifetime
benzene[b]	9.5 days	toluene[b]	2.1 days
1,3-butadiene[d]	2.1 hours	2,2,4-trimethylpentane[b]	3.5 days
ethylbenzene[d]	18.5 hours	m-xylene[a]	5.9 hours
n-hexane[d]	1.04 days	p-xylene[c]	10.7 hours
methyl-t-butyl ether[b]	3.9 days	o-xylene[c]	11.4 hours
styrene[a]	2.4 hours		

[†] For a 12-h daytime average OH radical concentration of 2.0×10^6 molecule cm^{-3} (Prinn et al., 2001)
[a] Atkinson,R, *Atmos Envir.* **34** (2000) 2063-2101
[b] Atkinson, R., and J. Arey, *Chem.Rev*., **103** (2003) 4603-4638.
[c] Atkinson, R.; Aschmann, S.M, *Int. J. Chem. Kinet.* **21** (1989)
[d] Atkinson, R. *Chem. Rev.* 86 (1986)

The Jean, Nevada site was chosen as the background location, and indeed analysis of the data showed that its air was relatively clean. Canisters were also filled at JD Smith, located at 1301B E Tonopah Avenue in North Las Vegas, NV. Joe Neal, 6651 Azure Drive, Las Vegas, NV was chosen as the downwind location for canister sampling. Analysis of the data showed that the Joe Neal site is too close to local sources to be considered a downwind site, and that in future ozone studies in Clark County, the "downwind location" should be established farther downwind from the urban center.

VOCs emitted into the atmosphere react at varying rates, so their radius of impact will be local, regional, and in some cases global, depending on their atmospheric lifetimes. For example, 1,3-butadiene, with a lifetime of 2.1 hours, will degrade over a local scale relatively close to its source, and toluene, with an estimated lifetime of 1.9 days, will degrade over a regional scale. The greater the atmospheric lifetime of a compound, the more dilution and dispersion will reduce the impact of products of atmospheric transformations.

For reaction of a VOC with OH radicals, NO_3 radicals and O_3, the lifetime is given by $\tau = 1/(k_X[X])$, where k_X is the rate constant for reaction of species X with the VOC, and [X] is the ambient atmospheric concentration of species X (X = OH, NO_3 or O_3). Lifetimes for the compounds presented here are listed in Table 1.

Methyl *tert*-butyl ether (MTBE) was used primarily as an oxygenate in unleaded gasoline to improve combustion efficiency and reduce exhaust emissions of carbon monoxide (CO) and reactive hydrocarbons. MTBE was emitted into ambient air through tailpipe exhaust, and evaporation and spillage of gasoline. With a lifetime of almost four days, MTBE can be transported to more rural and remote locations before it is removed from the atmosphere by oxidation or rainout. MTBE has been measured at a ponderosa pine plantation in the Sierra Nevada mountains by Schade et al. (2002) at levels ranging from <0.01 ppbv (below their detection limit) to 0.5 ppbv. In California, the California Air Resources Board (CARB) measured MTBE in urban regions in 1995–1996, reporting a range of 1 to 11 ppbv in the Los Angeles Area (California Environmental Protection

Agency, 1997, p. 675–680). Starting in 2000, a number of states have banned the use of MTBE in gasoline because of groundwater contamination, including Nevada and California in 2004, and Arizona in 2005.

The objective of this study is to perform data analyses of the ten HAPs (which in this case are VOCs) quantified during the CCROPS field project for commonality of sources, the contribution of transport versus local sources and the influence of meteorology on HAPs concentrations.

Methodology

For this study, the following tasks were performed: 1) commonality of sources was determined for the 10 HAPs quantified during the CCROPS; 2) the three sites monitored for VOCs were compared and contrasted; 3) investigating the contribution of transport relative to local sources of pollutants; samples were collected at an upwind site (Jean, NV) as well as two other sites in the Las Vegas metropolitan area; the concentrations of the HAPs concentrations at the upwind site serve as background relative to local sources in Las Vegas; and 4) analysis of the CCROPS VOC data with respect to meteorological variables, e.g., wind direction.

Results

Commonality of sources

Tables 2 through 4 show the correlation coefficients (R^2) of n-hexane and the aromatic compounds to 1,3-butadiene. The best correlations (0.67 and higher) were found at JD Smith, the urban center site. This indicates that the JD Smith site was closest to the sources of these HAPs. Poorer correlations were found at Joe Neal, the downwind location. At Jean, Nevada, the R^2 values are below 0.1 for every compound except benzene, indicating no correlation at the upwind location, which is expected given the relatively short lifetime of 1,3-butadiene.

Table 2. Correlation coefficient for n-hexane and the aromatic compounds with respect to 1,3-butadiene at JD Smith.

Compound	**R^2**	**Compound**	**R^2**
benzene	0.92	toluene	0.87
styrene	0.67	m,p-xylene	0.86
ethylbenzene	0.77	o-xylene	0.88
n-hexane	0.74		

Table 3. Correlation coefficient for n-hexane and the aromatic compounds with respect to 1,3-butadiene at Joe Neal.

Compound	R^2	Compound	R^2
benzene	0.54	toluene	0.34
styrene	0.20	m,p-xylene	0.40
ethylbenzene	0.32	o-xylene	0.44
n-hexane	0.23		

Table 4. Correlation coefficient for n-hexane and the aromatic compounds with respect to 1,3-butadiene at Jean.

Compound	R^2	Compound	R^2
benzene	0.25	toluene	0.02
styrene	0.09	m,p-xylene	0.02
ethylbenzene	0.01	o-xylene	0.05
n-hexane	0.001		

The HAPs compounds MTBE and isooctane (2,2,4-trimethylpentane) did not correlate well with the other HAPs measured in this study. Because these two compounds have only one source, mobile sources (e.g., cars and light trucks, large trucks and buses), this indicates that the other compounds share additional sources.

Because MTBE dissolves easily in water and does not "cling" to soil very well, the likeliest source of MTBE is transport from areas where MTBE is in surface waters such as lakes and reservoirs (http://www.epa.gov/mtbe/faq.htm#movement). MTBE has been shown to volatilize from surface waters at rates which depend upon the speed of the water flow and the wind speed above the water (Pankow et al., 1996). Other possible sources of MTBE are abandoned gasoline stations.

Comparison of the VOC monitoring sites.

Figure 1 shows MTBE concentrations at each sampling site. The lifetime of MTBE is long enough that transport from California to the Clark County area is possible. The values at the Jean location are comparable to the urban and downwind locations, indicating that transport is a major source of MTBE in Clark County.

Figure 1. MTBE concentrations at each sampling site.

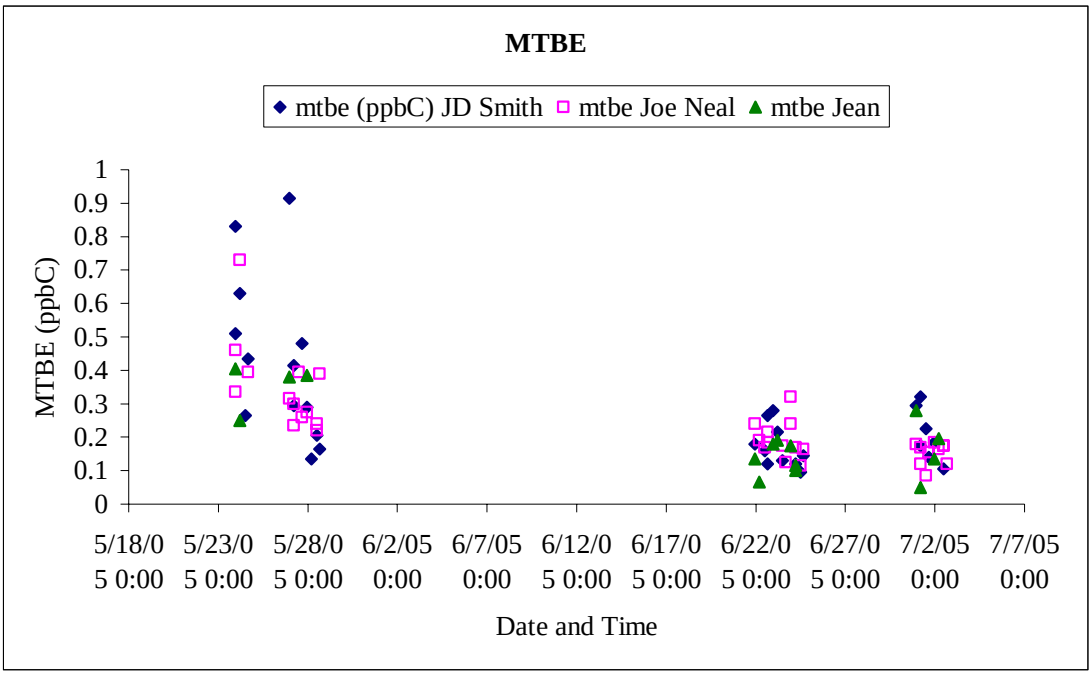
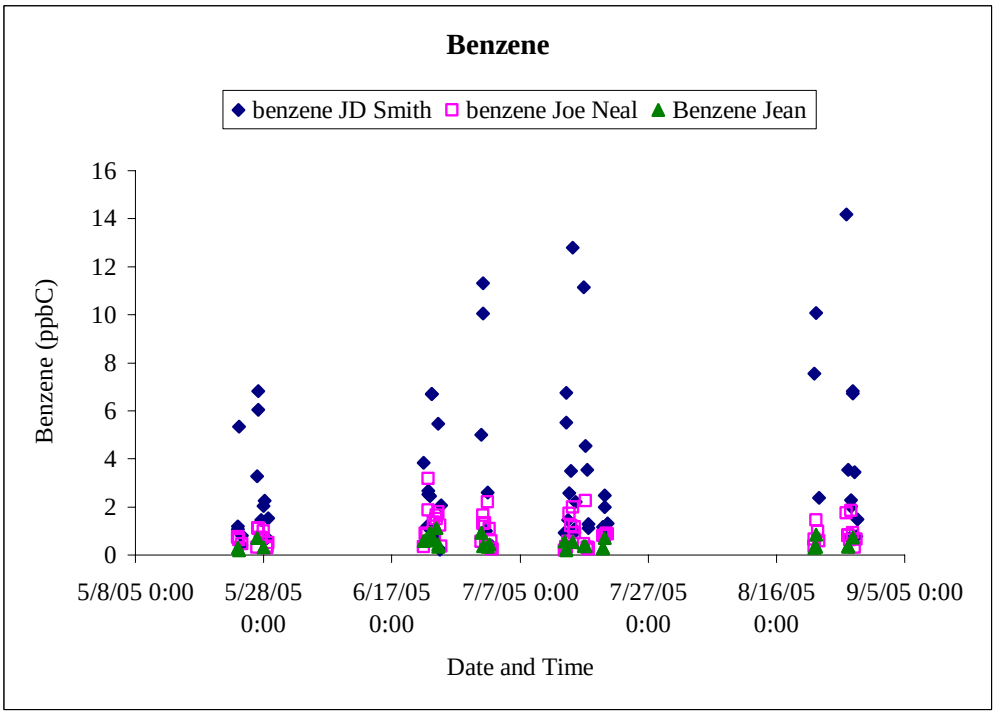


Figure 2 shows benzene concentrations at the three sampling sites. Benzene also has a long enough lifetime in the atmosphere for transport to occur from upwind locations. However, benzene levels at the urban center (JD Smith) were often an order of magnitude higher than at Jean, Nevada, indicating significant local sources of benzene.

Figure 2. Benzene concentrations at each sampling site.



Isooctane, with a lifetime of 3.5 days, and toluene, with a lifetime of 2.1 days, may be transported into the Clark County region from upwind sources. However, Figures 3 and 4 show elevated levels of isooctane and toluene at JD Smith compared to Jean, Nevada, indicating significant local source emissions such as vehicle emissions and evaporative emissions from gasoline.

The remaining compounds studied here have sufficiently short lifetimes such that their concentrations degrade significantly while transported from upwind locations. Therefore local emissions will be the dominant factor in their concentrations in Clark County. And indeed Figure 5 shows 1,3-butadiene concentrations an order of magnitude higher at JD Smith than Jean, Nevada.

Average Concentrations and Exposure Limits

Table 5 shows the average concentrations of the 10 HAPs compounds studied here, as well as their minimum and maximum concentrations, during the CCROPS field campaign during the summer of 2005 at the JD Smith and Joe Neal sites. The average concentrations of benzene and 1,3-butadiene are above the Cancer Risk level 1 in a million as determined by the USEPA. The remaining compounds are below the health risk levels for inhalation reference concentration and chronic minimal risk level as determined by the USEPA.

Tables 6 through 10 list the concentrations of 1,3-butadiene, benzene, toluene, ethyl benzene, m,p-xylene, o-xylene, and styrene, respectively at Las Vegas during CCROPS as well as in California cities (northern, central and southern). (California cities data from http://www.arb.ca.gov/adam/toxics/sitesubstance.html) 1,3-butadiene concentrations are comparable to each California city list, while the remaining compounds are mostly similar in concentration to southern California (the Burbank site). Table 11 shows concentrations of MTBE as compared to other cities, US and international. Las Vegas levels of MTBE are most similar to the Sierra Nevada mountains (a location with no local sources of MTBE).

Overview of meteorological conditions during the CCROPS field campaign.

Overall the 2005 ozone season in southern Nevada appears to have been one of anomalies. Very few clear-cut interbasin transport events took place in the manner reported in the Ozone Characterization Study. There were also at least two unusually long "clean" periods resulting from troughing or monsoonal activity that precluded intensive monitoring activities for extended periods. Conversely, an ozone episode took place in late June that was characterized by some of the highest concentrations ever recorded in Clark County. This event was associated with a severe wildfire smoke event that also produced high PM concentrations. Another "surprise" single day ozone event took place on a Sunday in early June that appears to be associated with weekend tourist traffic leaving of Clark County during meteorological conditions particularly conducive to the development of high ozone (Bush et al., 2006).

Table 5. HAPs concentrations as measured during the CCROPS field campaign.

	Compound	Average concentration (mg/m^3)	Minimum concentration (mg/m^3)	Maximum concentration (mg/m^3)	Health Numbers (mg/m^3)
JD Smith	benzene	0.0019	0.0001	0.0077	1.3×10^{-4} [a]
	1,3-butadiene	0.0002	8.8×10^{-6}	0.0009	4×10^{-4} [a]
	ethylbenzene	0.0013	4.3×10^{-6}	0.0063	1[b]
	n-hexane	0.0016	7.8×10^{-5}	0.0065	0.2[b]
	methyl-t-butyl ether	0.0002	6.9×10^{-5}	0.0007	3[b]
	styrene	0.0002	9×10^{-6}	0.001	1[b]
	toluene	0.0066	0.0002	0.029	0.4[b]
	2,2,4-trimethylpentane	0.0021	3.3×10^{-5}	0.010	none
	M,p-xylene	0.0049	0.0002	0.019	0.4[c]
	o-xylene	0.0016	4.3×10^{-6}	0.0068	0.4[c]
Joe Neal	benzene	0.0005	0.0001	0.0017	1.3×10^{-4} [a]
	1,3-butadiene	4.5×10^{-5}	2.2×10^{-6}	0.0002	4×10^{-4} [a]
	ethylbenzene	0.0003	2.6×10^{-5}	0.0040	1[b]
	n-hexane	0.0005	5.3×10^{-5}	0.0020	0.2[b]
	methyl-t-butyl ether	0.0002	6.1×10^{-5}	0.0005	3[b]
	styrene	8.5×10^{-5}	4.3×10^{-6}	0.0011	1[b]
	toluene	0.0017	0.0002	0.0090	0.4[b]
	2,2,4-trimethylpentane	0.0005	1.9×10^{-5}	0.0045	none
	M,p-xylene	0.0010	8.7×10^{-5}	0.0153	0.4[c]
	o-xylene	0.0004	4.3×10^{-6}	0.0037	0.4[c]

[a] Cancer Risk level 1 in a million (mg/m^3)

[b] RfC (inhalation reference concentration): An estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure of a chemical to the human population through inhalation (including sensitive subpopulations), that is likely to be without risk of deleterious noncancer effects during a lifetime.

[c] The Agency for Toxic Substances and Disease Registry (ATSDR) chronic minimal risk level (MRL)

Table 6. Comparison of Las Vegas 1,3-butadiene concentrations with California cities.

Compound	Average concentration (ppb)	Minimum concentration (ppb)	Maximum concentration (ppb)
LV-JD Smith (2005)	0.10	0.004	0.43
Burbank-W Palm Avenue (2005)	0.196	0.02	0.73
San Francisco-Arkansas Street (2005)	0.053	0.02	0.19
Fresno-1st Street (2005)	0.101	0.02	0.47
Roseville-N Sunrise Blvd (2005)	0.051	0.02	0.22

Table 7. Comparison of Las Vegas benzene concentrations with California cities.

Compound	Average concentration (ppb)	Minimum concentration (ppb)	Maximum concentration (ppb)
LV-JD Smith (2005)	0.59	0.05	3.55
Burbank-W Palm Avenue (2005)	0.83	0.2	2.2
San Francisco-Arkansas Street (2005)	0.23	0.07	0.74
Fresno-1st Street (2005)	0.408	0.07	1.5
Roseville-N Sunrise Blvd (2005)	0.244	0.08	0.68

Table 8. Comparison of Las Vegas toluene concentrations with California cities.

Compound	Average concentration (ppb)	Minimum concentration (ppb)	Maximum concentration (ppb)
LV-JD Smith (2005)	1.77	0.08	13.4
Burbank-W Palm Avenue (2005)	2.73	0.4	6.6
San Francisco-Arkansas Street (2005)	0.68	0.1	2.5
Fresno-1st Street (2005)	1.01	0.1	3.2
Roseville-N Sunrise Blvd (2005)	0.8	0.1	3.3

Table 9. Comparison of Las Vegas ethyl benzene concentrations with California cities.

Compound	Average concentration (ppb)	Minimum concentration (ppb)	Maximum concentration (ppb)
LV-JD Smith (2005)	0.31	0.002	2.9
Burbank-W Palm Avenue (2005)	0.36	0.1	1.1
San Francisco-Arkansas Street (2005)	0.11	0.1	0.4
Fresno-1st Street (2005)	0.15	0.1	0.5
Roseville-N Sunrise Blvd (2005)	0.11	0.1	0.3

Table 10. Comparison of Las Vegas m,p-xylene concentrations with California cities.

Compound	Average concentration (ppb)	Minimum concentration (ppb)	Maximum concentration (ppb)
LV-JD Smith (2005)	1.13	0.10	8.77
Burbank-W Palm Avenue (2005)	1.32	0.1	4.0
San Francisco-Arkansas Street (2005)	0.33	0.1	1.4
Fresno-1st Street (2005)	0.52	0.1	1.8
Roseville-N Sunrise Blvd (2005)	0.32	0.1	1.1

Table 11. Comparison of Las Vegas o-xylene concentrations with California cities.

Compound	Average concentration (ppb)	Minimum concentration (ppb)	Maximum concentration (ppb)
LV-JD Smith (2005)	0.38	0.002	3.14
Burbank-W Palm Avenue (2005)	0.44	0.05	1.2
San Francisco-Arkansas Street (2005)	0.1	0.05	0.5
Fresno-1st Street (2005)	0.18	0.05	0.6
Roseville-N Sunrise Blvd (2005)	0.1	0.05	0.4

Table 12. Comparison of Las Vegas styrene concentrations with California cities.

Compound	Average concentration (ppb)	Minimum concentration (ppb)	Maximum concentration (ppb)
LV-JD Smith (2005)	0.05	0.004	0.47
Burbank-W Palm Avenue (2005)	0.14	0.05	0.6
San Francisco-Arkansas Street (2005)	0.05	0.05	0.1
Fresno-1st Street (2005)	0.06	0.05	0.2
Roseville-N Sunrise Blvd (2005)	0.05	0.05	0.05

Table 13. Comparison of Las Vegas MTBE concentrations with California and other cities.

Compound	Average concentration (ppb)	Minimum concentration (ppb)	Maximum concentration (ppb)
LV-JD Smith (2005)	0.06	0.02	0.23
Los Angeles (1995-1996)	4	0.4	13.2
Sierra Nevada Mountains (2002)	0.3	<0.01	0.5
Porto Alegre, Brazil (1996-1997)[a]	15.6	--	--
Southern Taiwan (all sites) (2003-2004)[b]	6.74	*	40.3
Northwestern Taiwan (Hsinchu City)[c] (2001)	5.7	0.5	10.2

*below detection limit

[a] Grosjean et al. 1998

[b] Hsieh et al.

[c] Chang et al.

During the sampling period of May 25 -28, 2005 a high ridge of pressure which had started on May 20 weakened, and by the 28th a subtropical low in the southern Baja became a more dominant synoptic feature as it started injecting moisture and less stability into the Southwest.

During June 22-24 regional flow remained southwesterly while the air mass stabilized somewhat due to the ridging influence to the east. Unfortunately, the interface zone contained a stronger pressure gradient, which manifested itself with breezy afternoon local winds.

During July 1-2 stagnant conditions prevailed with the best inter-basin transport conditions of the summer. An outbreak of wildfires in southern Nevada, Arizona and Utah a few days before resulted in polluted conditions in the Las Vegas area.

July 14-20 consisted of an extended period of record high temperatures in the Las Vegas area, and throughout the Southwest U.S. The air mass was stable and rather stagnant, featuring light flow and high-level subsidence capping. The intense surface heating during the afternoons likely increased the depth of the boundary layer in the study area and induced local flow regimes.

During August 22 flow trajectories had turned far enough from the southeasterly monsoonal direction to set up inter-basin transport flow. However, the well-ventilated composition of the air mass precluded the formation of any pollutants to transport.

August 27-28 consisted of the southerly flow resulting in inter-basin type flow with a westerly component. The influx of the ridge was enough to stabilize air mass, but pollution levels upwind in California never materialized enough to provide a significant source. The closer proximity of the trough and the lateness of the season probably were probably responsible for the poor development in California.

CCROPS VOC data and meteorological variables

The HAPs compounds studied here were compared to three meteorological variables: surface and aloft wind direction and surface wind speed. Compounds with longer lifetimes such as benzene and MTBE may reach the free troposphere and be transported by aloft winds. Only the Jean, Nevada had both VOCs and aloft wind direction measured simultaneously, so only this site is considered here for the aloft wind direction. Figures 6 through 8 show concentrations of MTBE, benzene and 2,2,4-trimethylpentane respectively versus surface wind direction. No correlations between these compounds and surface wind direction is evident. Figures 9 and 10 show MTBE and benzene respectively versus aloft wind direction at Jean, Nevada, but no correlation is evident, although it should be noted that the data is sparse.

Figure 3. Isooctane concentrations at each sampling site.

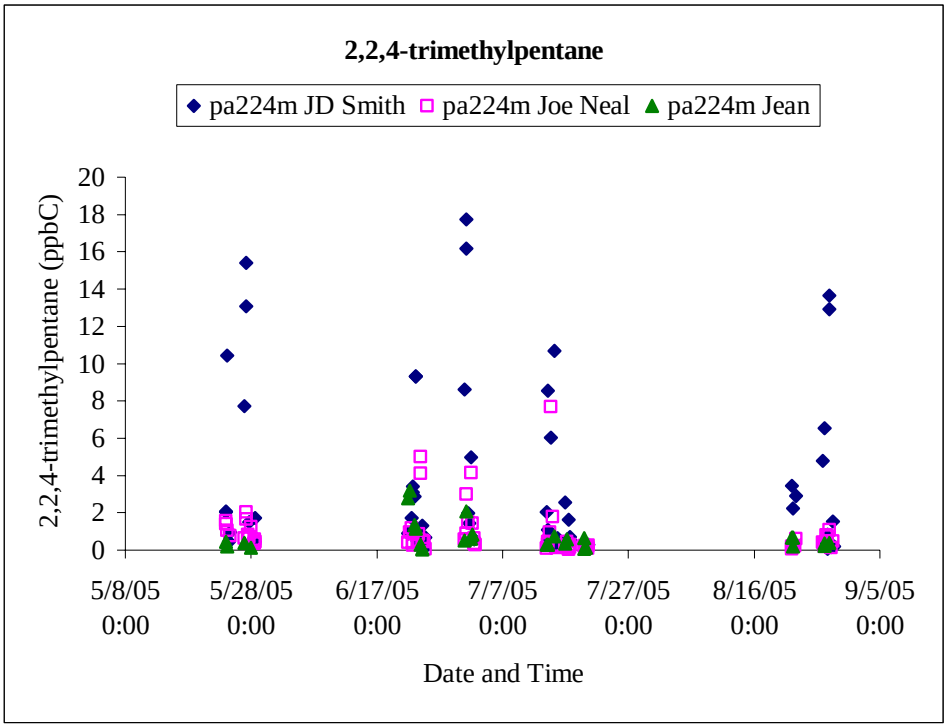


Figure 4. Isooctane concentrations at each sampling site.

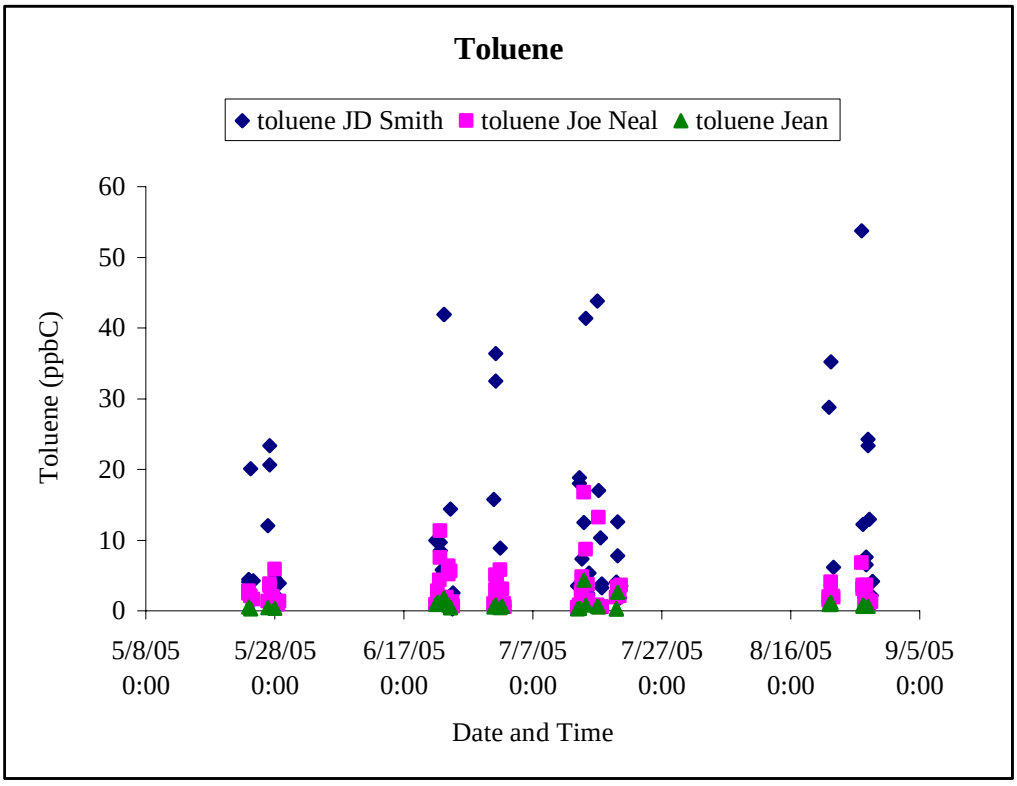


Figure 5. 1,3-butadiene at all three sampling sites.

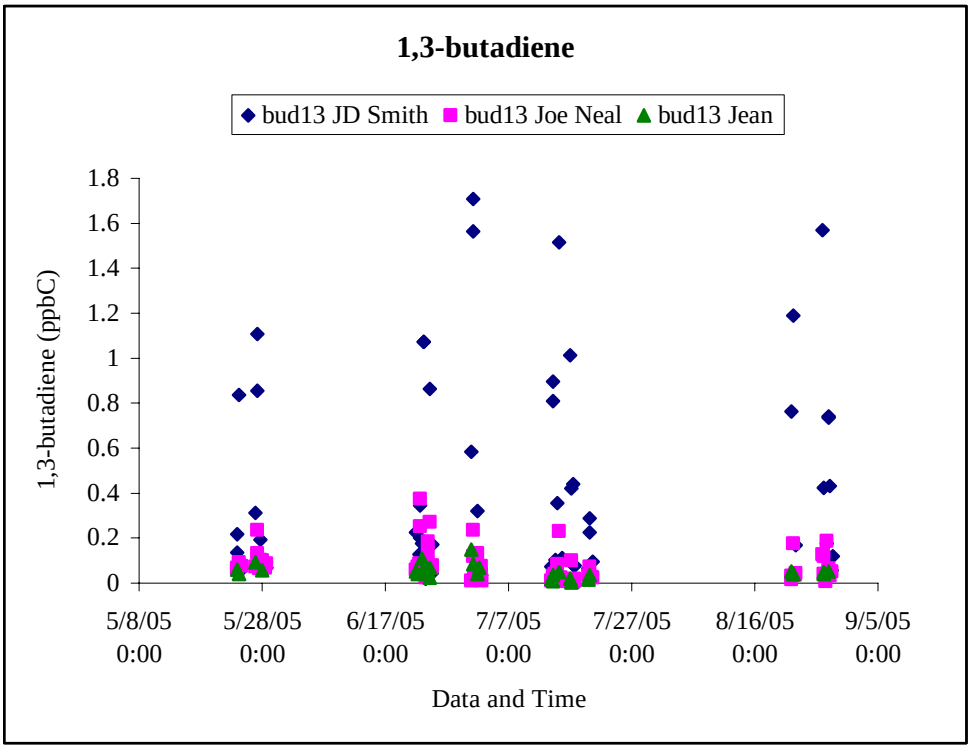


Figure 6. MTBE versus surface wind direction at each sampling site.

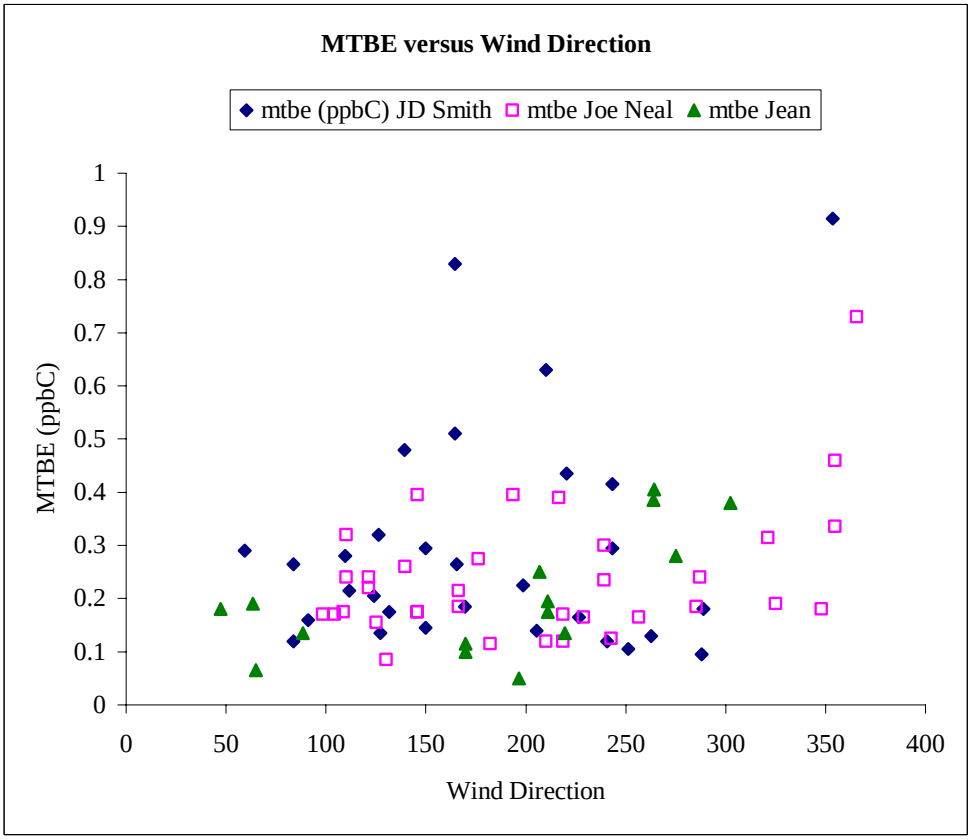


Figure 7. Benzene versus surface wind direction at each sampling site.

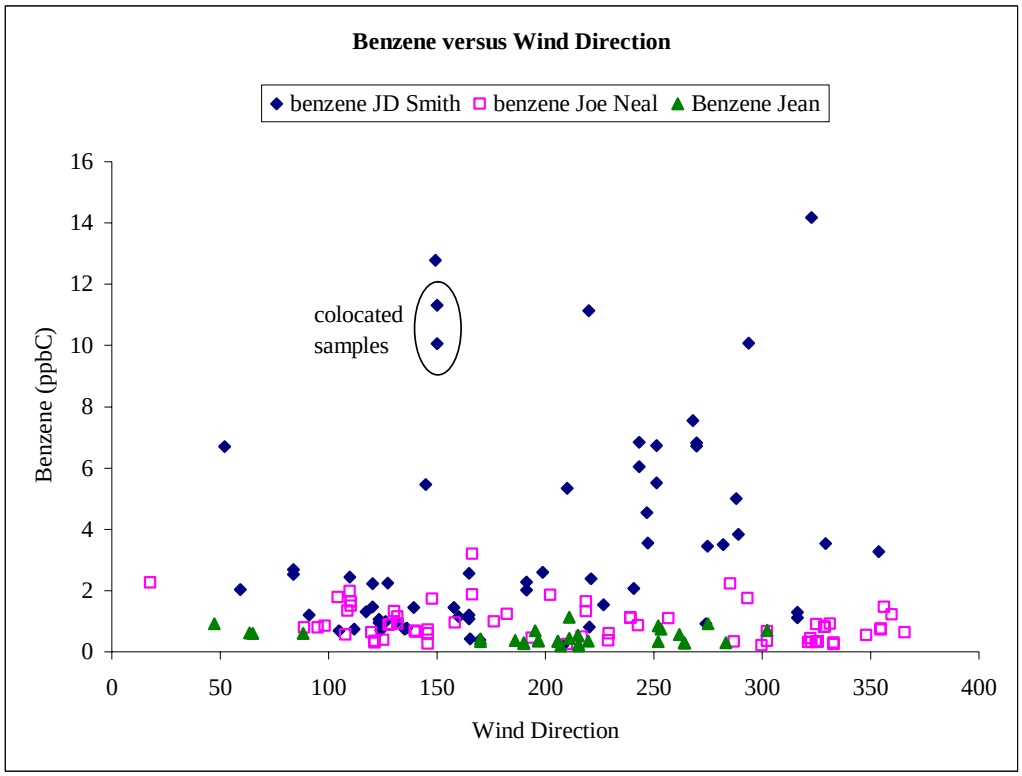


Figure 8. 2,2,4-trimethylpentane versus surface wind direction at each sampling site.

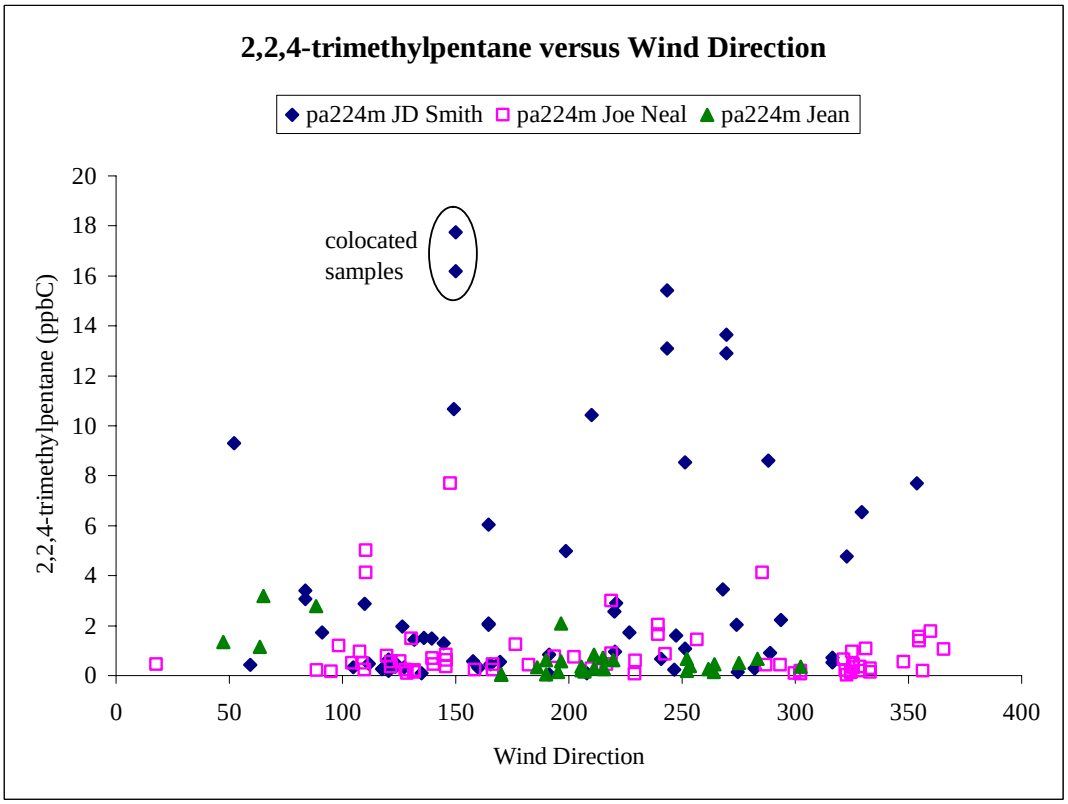


Figure 9. MTBE versus aloft wind direction at Jean, NV

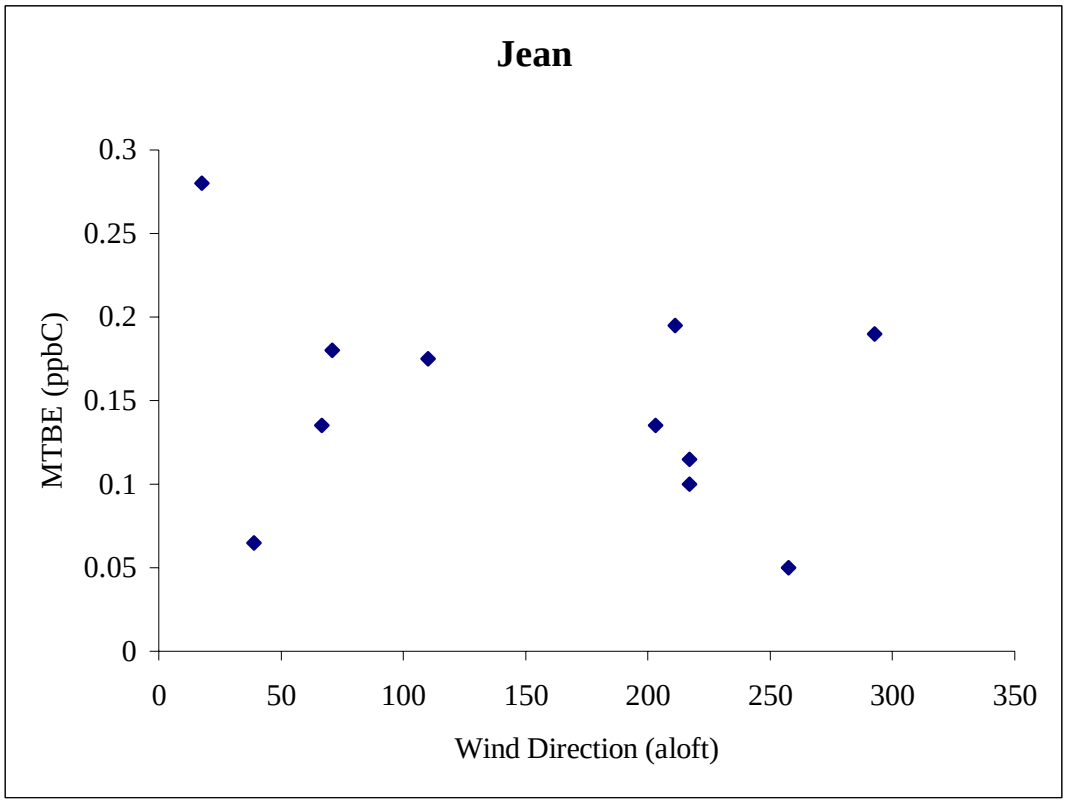
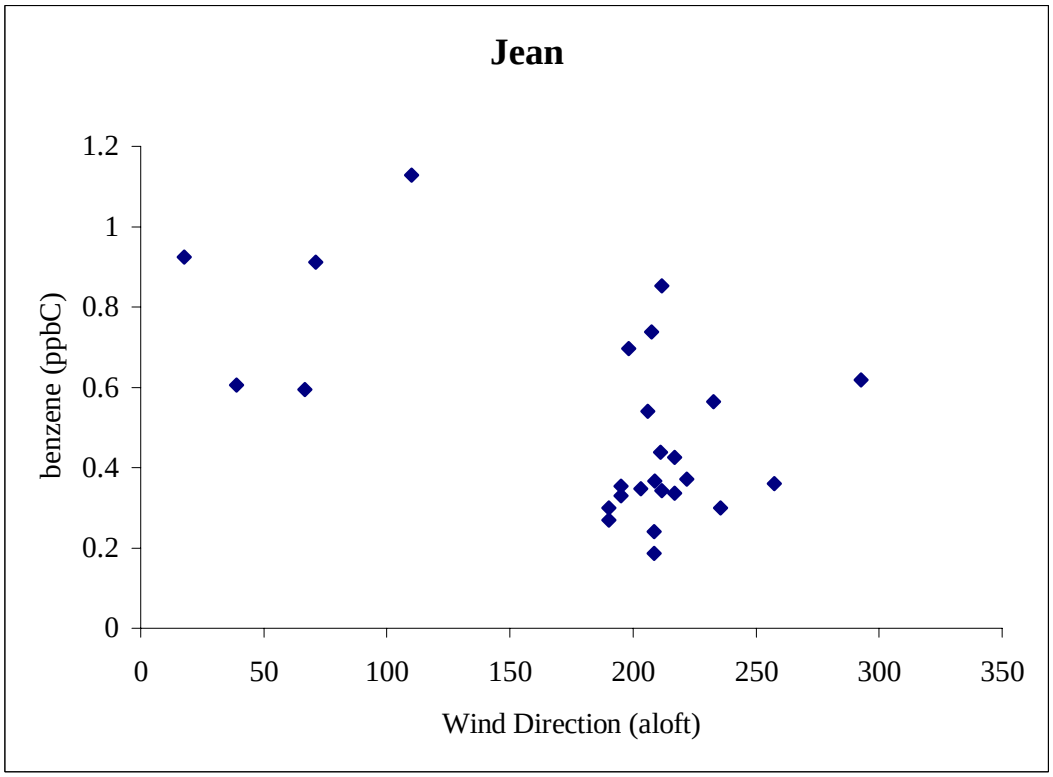


Figure 10. Benzene versus aloft wind direction at Jean, NV.



Surface Winds

Surface wind speeds control the degree of ventilation in the boundary layer. Calm or light winds produce weak ventilation and allow more emissions to accumulate in a given volume of air, resulting in higher pollutant concentrations. Conversely, higher wind speeds provide higher ventilation, resulting in lower pollutant concentrations. This can be seen in figures 11 through 20, in which anti-correlation between each measured HAPs concentrations and wind speed is observed. (MTBE concentrations were not analyzed for the month of August due to technician error.)

Figure 11. 1,3-butadiene and wind speed versus date and time at JD Smith.

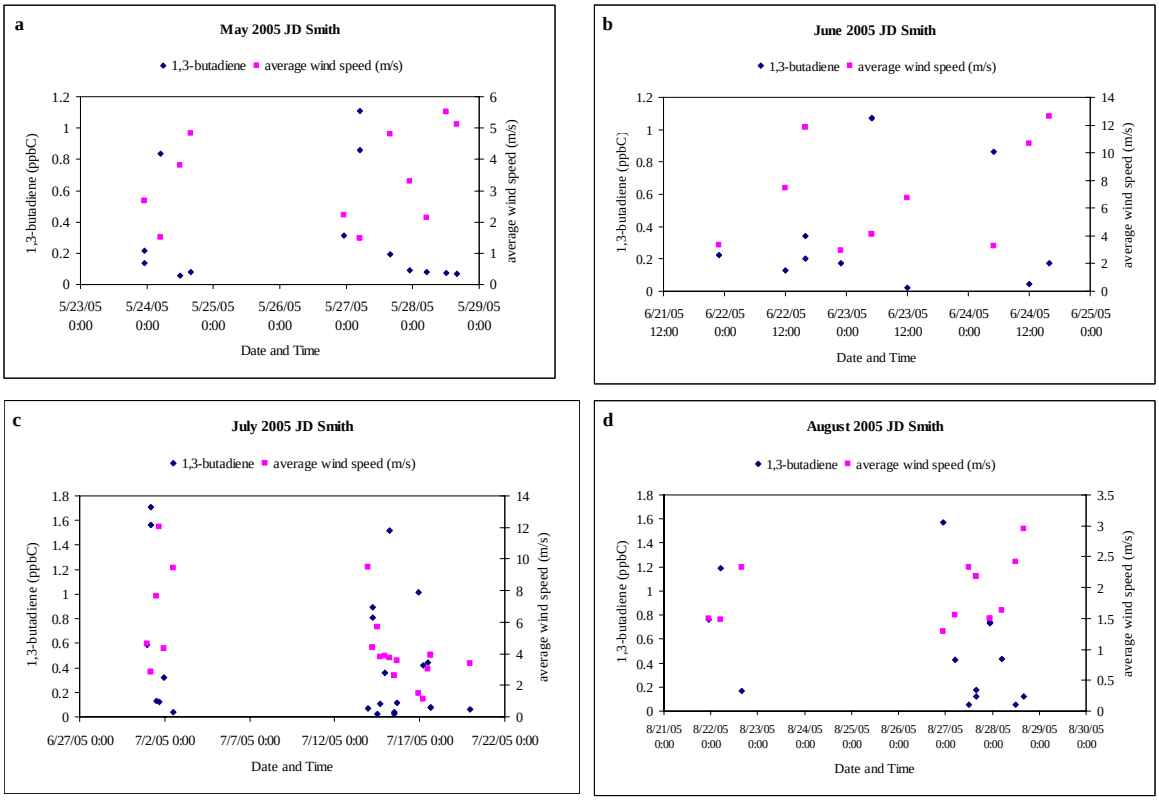


Figure 12. N-hexane and wind speed versus date and time at JD Smith.

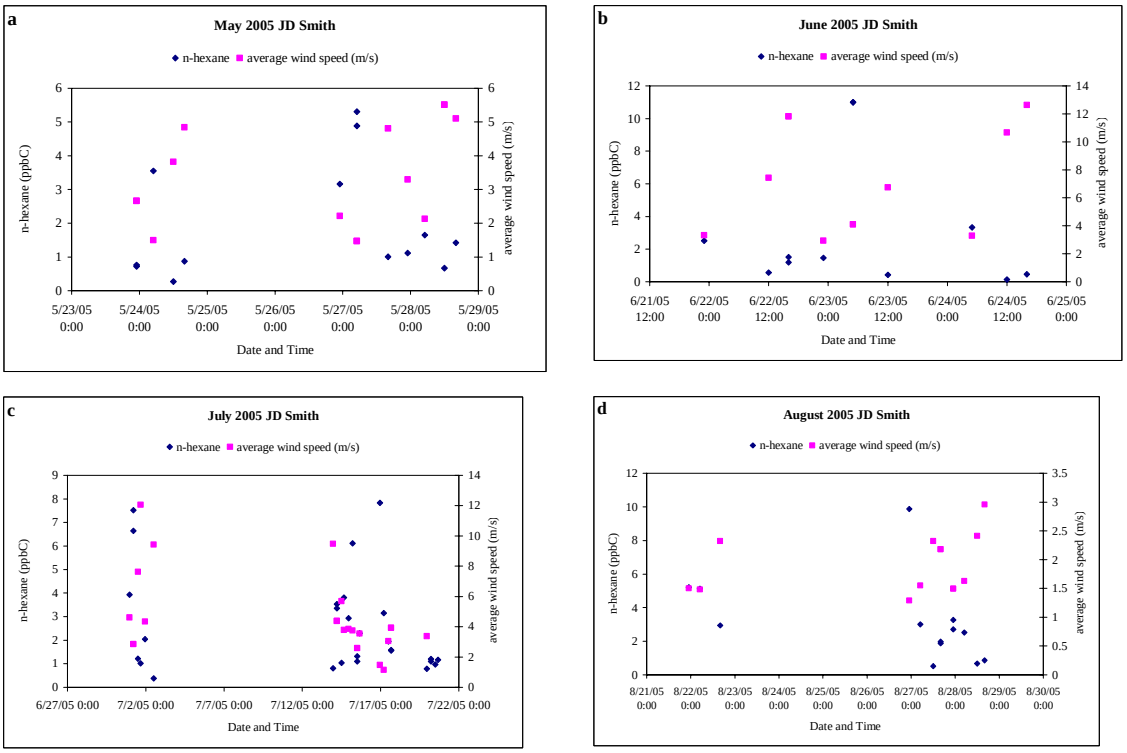


Figure 13. 2,2,4-trimethylpentane and wind speed versus date and time at JD Smith.

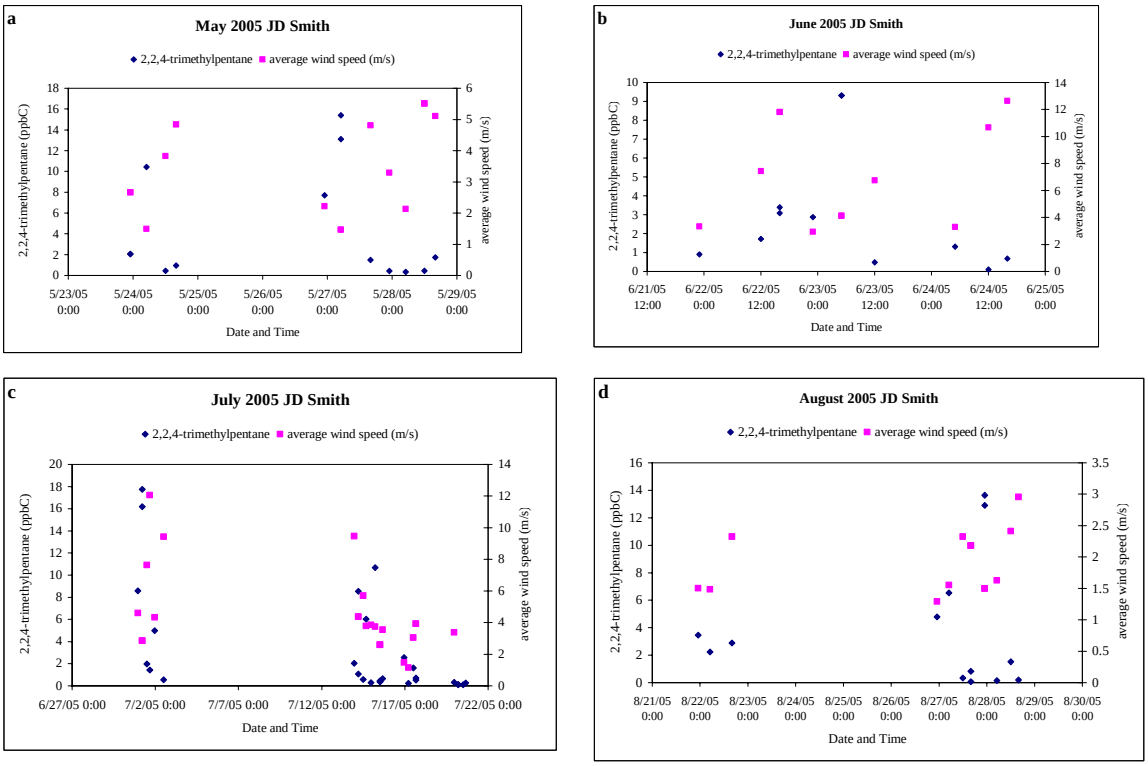


Figure 14. Benzene and wind speed versus date and time at JD Smith.

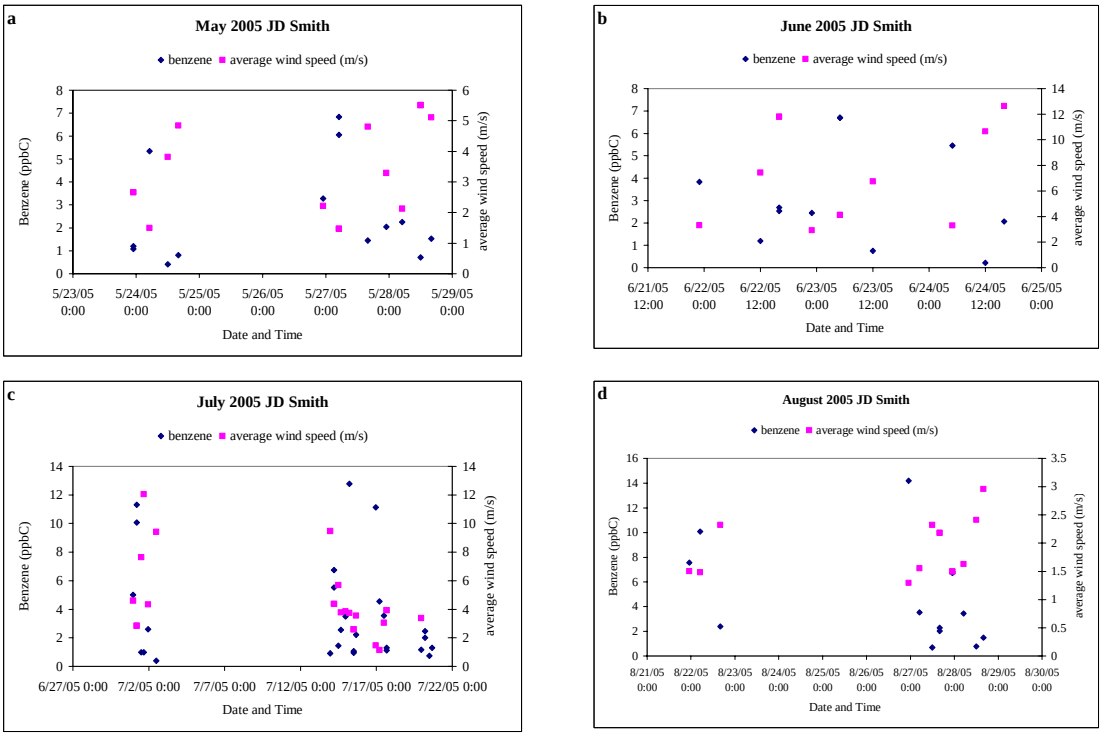


Figure 15. Toluene and wind speed versus date and time at JD Smith.

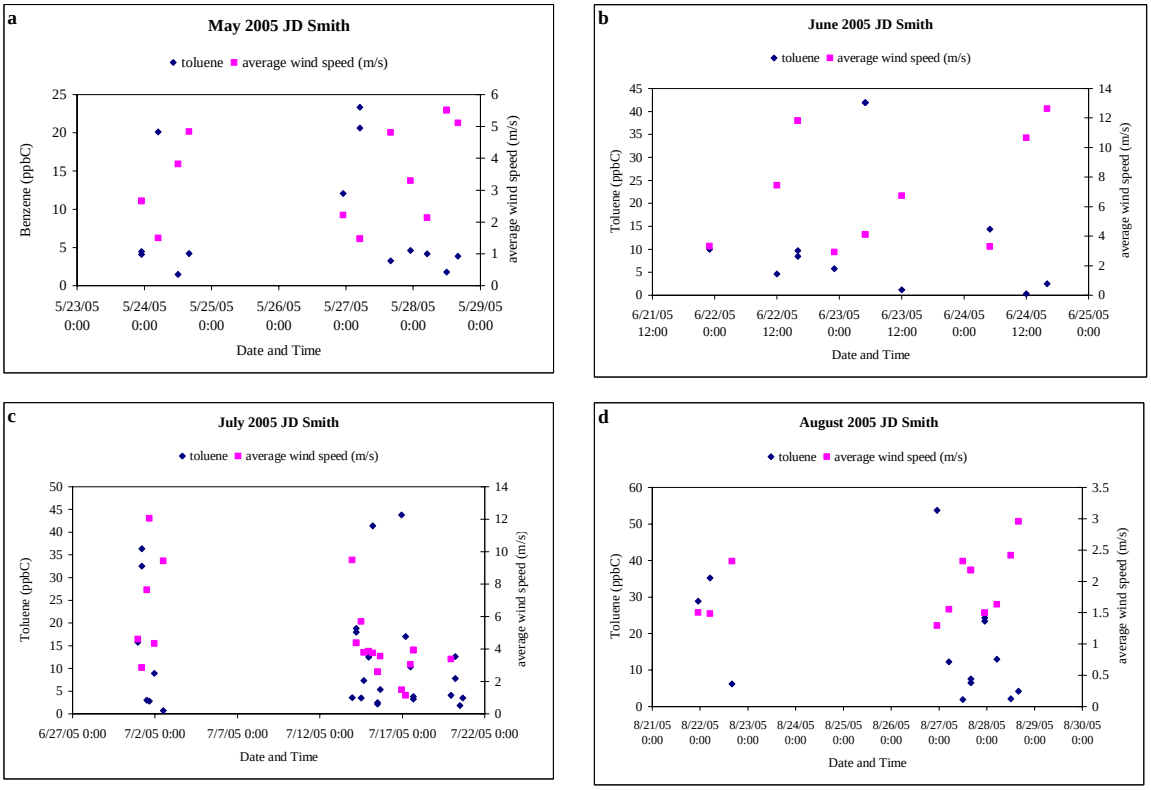


Figure 16. Ethyl benzene and wind speed versus date and time at JD Smith.

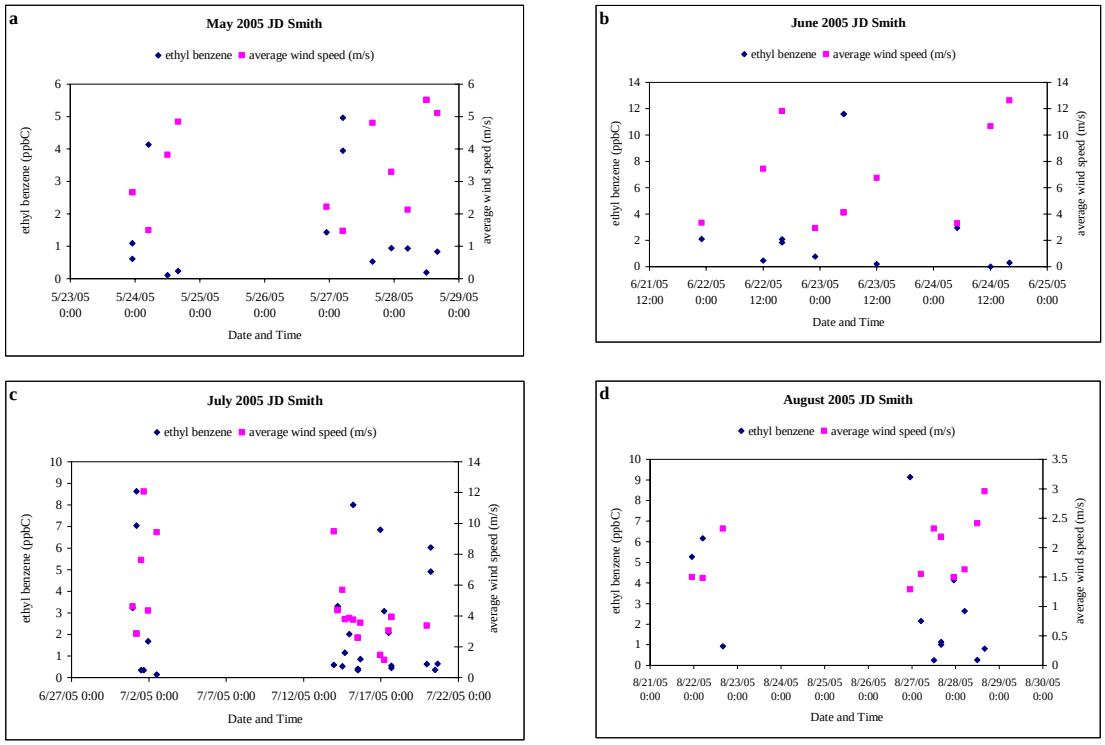


Figure 17. M,p-xylene and wind speed versus date and time at JD Smith.

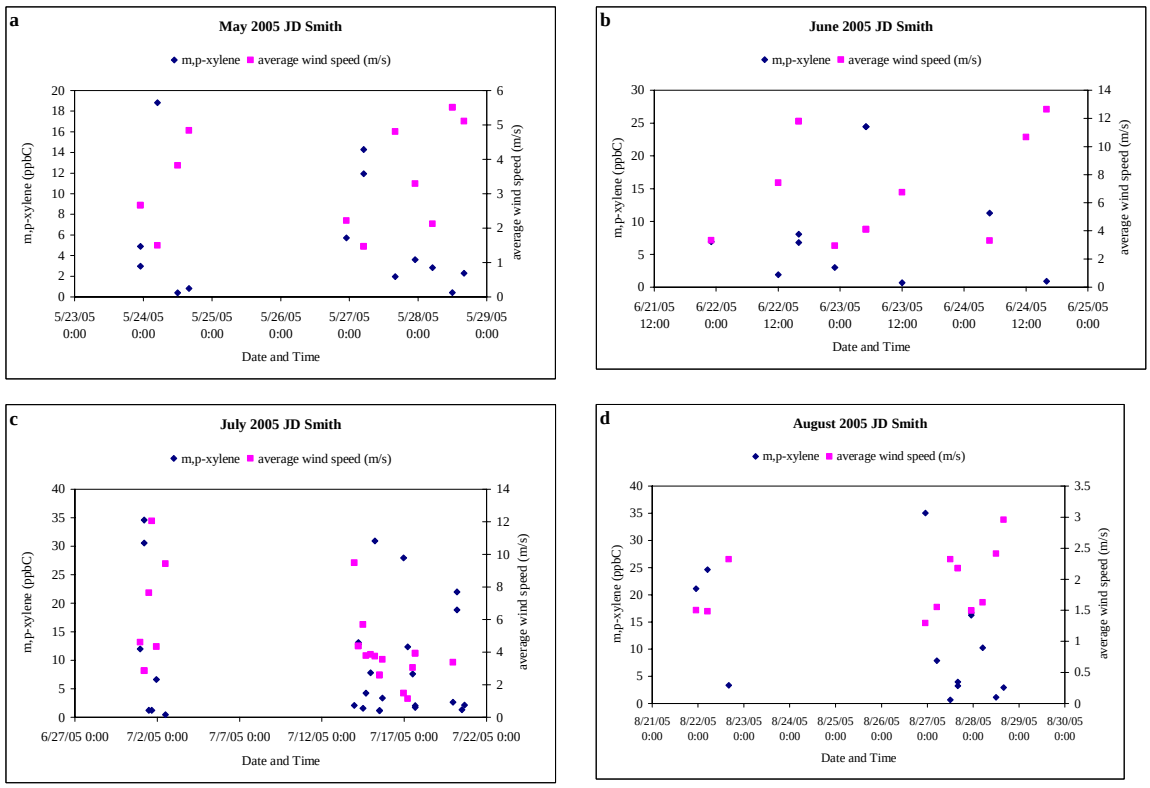


Figure 18. O-xylene and wind speed versus date and time at JD Smith.

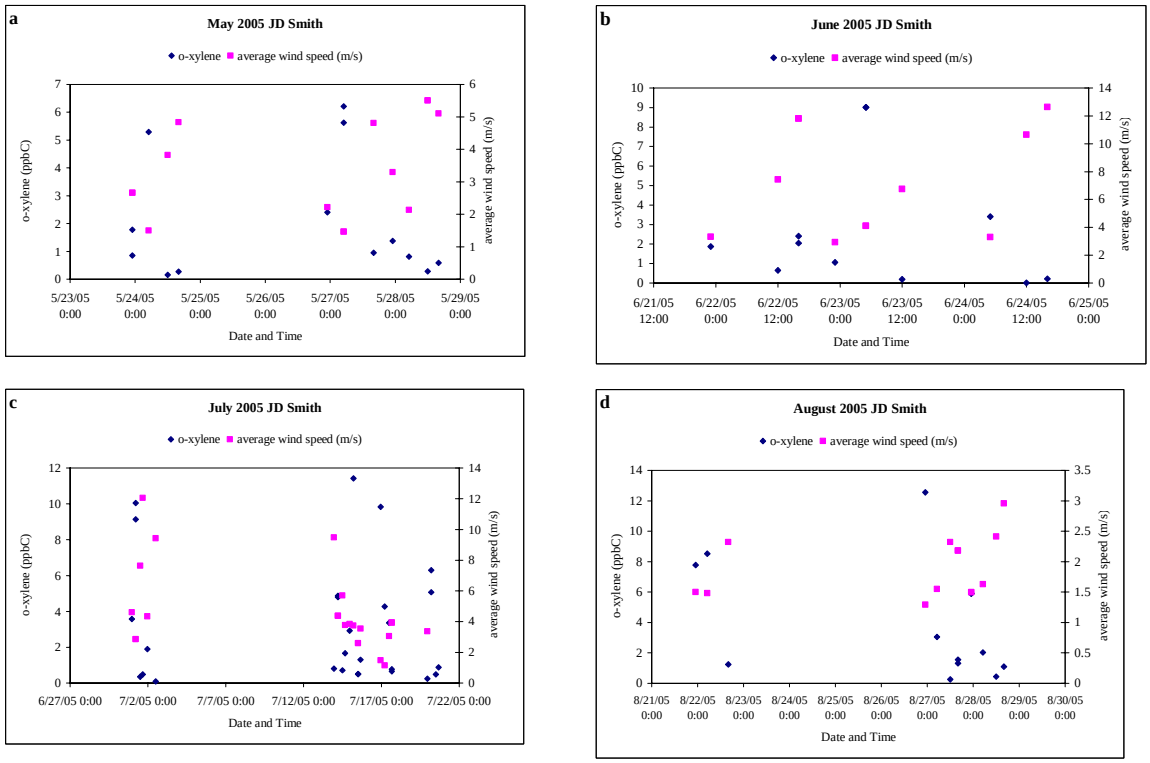


Figure 19. Styrene and wind speed versus date and time at JD Smith.

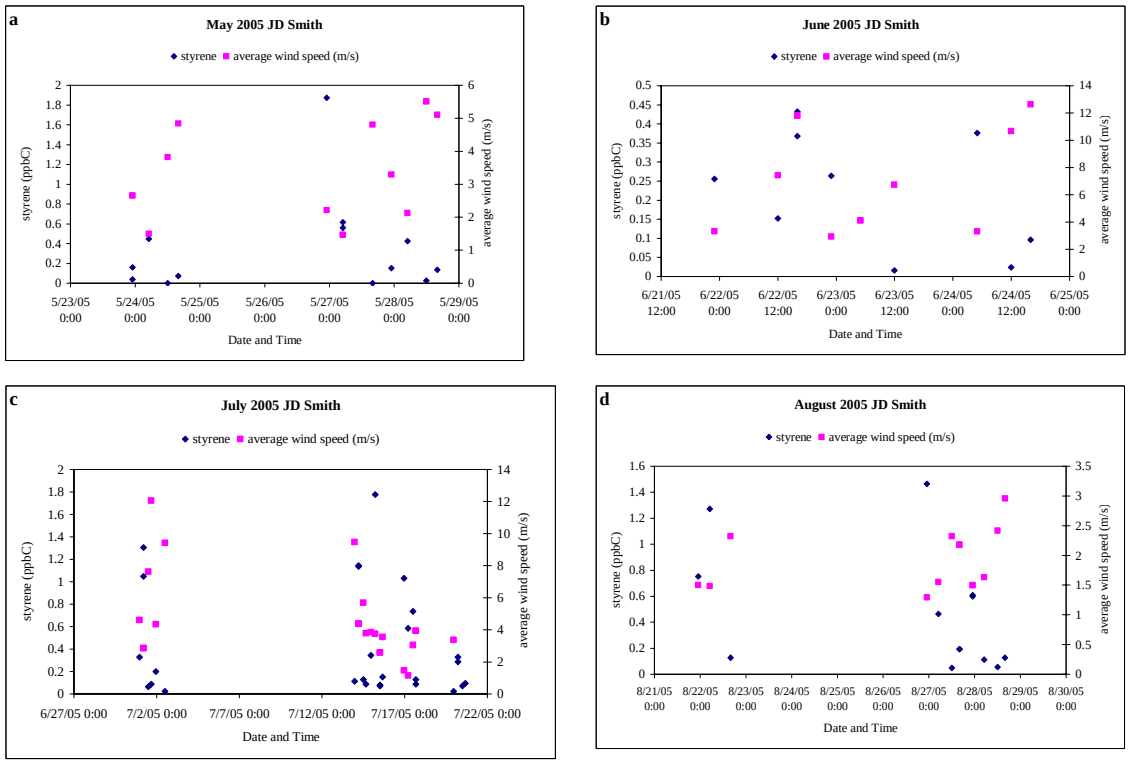
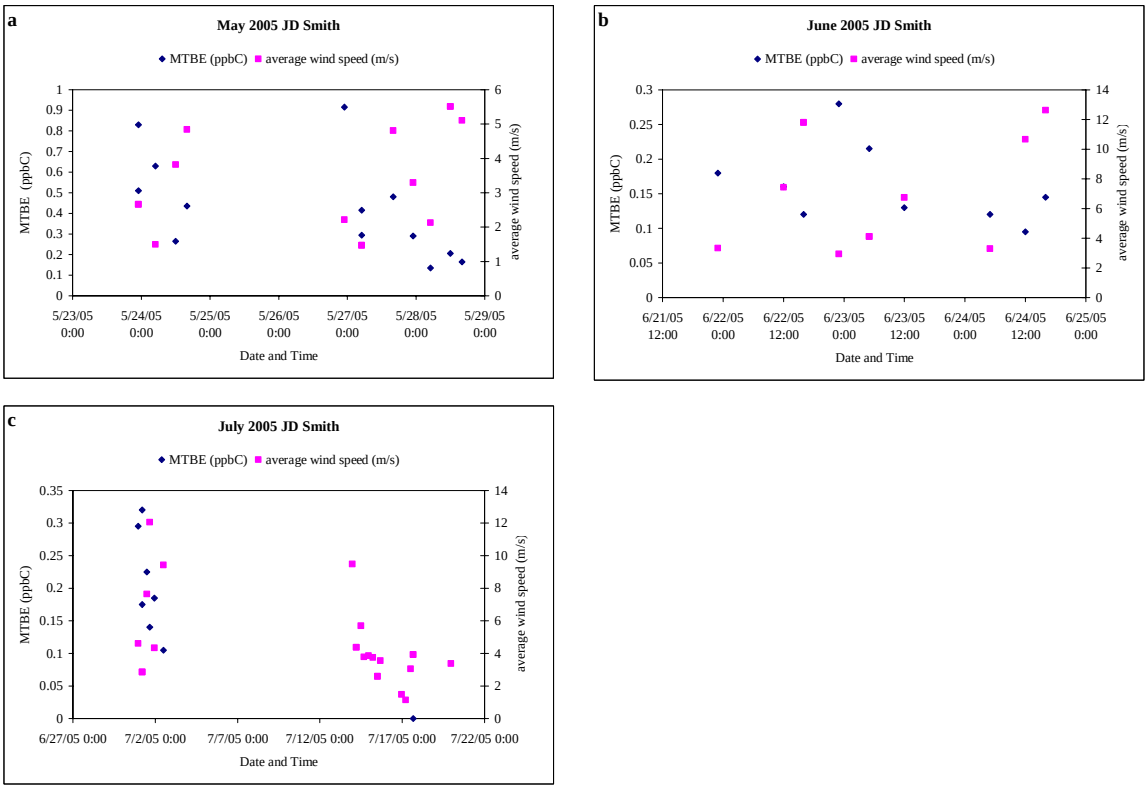


Figure 20. MTBE and wind speed versus date and time at JD Smith.



Conclusions

Ten HAPs compounds were quantified during the CCROPS field campaign during the summer of 2005. Eight of the ten compounds shared common sources, while the remaining two, isooctane and MTBE, did not correlate well with the other compounds, indicating that the eight had additional sources other than mobile sources, such as being used as solvents for industrial applications. Comparison of the three sampling locations showed that MTBE concentrations were dominated by transport from upwind locations such as surface waters and abandoned gasoline stations, while the remaining HAPs studied were dominated by local sources. None of the HAPs compounds showed any correlation with surface wind direction or aloft wind direction, although the data was sparse for the aloft wind direction.

For all ten HAPS compounds analyzed in this study, each showed anti-correlation with surface wind speed. When wind speeds were higher, concentrations of HAPs were lower due to increased ventilation, and when wind speeds were lower, concentrations were higher due to low ventilation allowing the buildup of pollutants.

Benzene and 1,3-butadiene possessed average concentrations greater than the Cancer Risk of one in a million threshold during the CCROPS field campaign. The remaining HAPs quantified during CCROPS had concentrations below health thresholds listed by USEPA.

The concentrations of HAPs studied here in the Las Vegas area during the CCROPS field campaign were most similar to levels in southern California, with the exception of MTBE, which is no longer detected by CARB (as of 2005).

Recommendations

As was noted by the T&B Systems report "Clark County Regional Ozone & Precursor Study", monsoonal activity (known as the Southwest monsoon or the Mexican monsoon) and troughing (an elongated region of relatively low atmospheric pressure, often associated with a front) dominated for much of the summer of 2005, resulting in long periods of clean conditions that precluded intensive monitoring. Therefore, the Clark County Department of Air Quality & Environmental Management should not make any policy decisions regarding Hazardous Air Pollutants based on the CCROPS field campaign.

It is recommended that the Clark County Department of Air Quality & Environmental Management conduct a separate field campaign to measure HAPs in the Las Vegas area. The field campaign should be multi-year to allow for annual variability, with sampling during each season to study seasonal variability. If a weekday/weekend effect study is desired, sampling should take place during at least 12 weekends to acquire a robust dataset. During any sampling campaign, Jean, Nevada remains a good upwind location, JD Smith a good urban site, and Joe Neal a suitable suburban site.

References

Atkinson, R. (1986) Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions *Chem. Rev.* **86.**

Atkinson, R., and J. Arey (2003) Atmospheric degradation of volatile organic compounds, *Chem. Rev.*, **103**, 4603-4638.

Atkinson, R.; Aschmann, S.M, (1989) Rate constants for the gas-phase reactions of the OH radical with a series of aromatic hydrocarbons at 296 ± 2 K *Int. J. Chem. Kinet.* **21.**

Atkinson,R, (2000) Atmospheric Chemistry of VOCs and NO_x, *Atmos Envir.* **34** 2063-2101.

Bush D., Baxter R., Knuth W., Lehrman D., Fransioli P., Yoho D., Goliff W., Fitz D. (2006). Clark County Regional Ozone & Precursor Study Final Report. Prepared for the Clark County Department of Air Quality & Environmental Management.

California Environmental Protection Agency. 1997. Toxic air contaminant identification list summaries, "Methyl Tert.-Butyl Ether". California Environ. Protection Agency, Air Resour. Board, Stationary Source Div., Sacramento.

Chang C.-C., Lo S.-J., Lo J.-G., Wang J.-L. 2003. Analysis of methyl *tert*-butyl ether in the atmosphere and implications as an exclusive indicator of automobile exhaust. *Atmos Envir* **37,** 4747–4755.

Grosjean E., Rasmussen R. A., Grosjean D., 1998. *Atmos Envir*. **32**, 20, 3371-3379.

Hsieh L.-T., Yang H.-H., Chen H.-W. 2006. Ambient BTEX and MTBE in the neighborhoods of different industrial parks in Southern Taiwan. *J. Hazardous Materials*, **128**, 2-3, 106-115.

Kyle, A.D., C.C. Wright, J.C. Caldwell, P.A. Buffler, and T.J. Woodruff. 2001. Evaluating the health significance of hazardous air pollutants using monitoring data. *Public Health Rep*. **116**(1):32–44.

Pankow, J.F., Rathbun, R.E., Zogorski, J.S. 1996. Calculated Volatilization Rates of Fuel Oxygenate Compounds From Rivers and Streams. *Chemosphere*, **33**, 921-937.

Prinn, R.G., J. Huang, R.F. Weiss, D.M. Cunnold, P.J. Fraser, P. G. Simmonds, A. McCulloch, C. Harth, P. Salameh, S. O'Doherty, R.H. J. Wang, L. Porter, and B.R. Miller (2001) Evidence for substantial variations in atmospheric hydroxyl radicals in the past two decades, *Science*, **292**, 1882-1888.