

Draft Final Report

Impact of Wildfire Events on Clark County's Air Quality in 2005 and 2008

Prepared for:

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Table of Contents

1. Introduction and Background	1
1.1 Semi Volatile Organic Compounds Wood Smoke Tracers	2
1.2 Volatile Organic Compound Wood Smoke Emissions	5
1.3 Study Objectives.....	8
1.4 Study Description	8
2. Experimental.....	8
2.1 2005 Sample Collection.	8
2.2 2008 Field Study.....	10
2.2.1 Sampling Sites and Sampling Periods	10
2.2.2 Sampling Procedures	13
2.2.3 Continuous Gas Chromatography.....	15
2.2.4 Aircraft Sampling.....	18
2.3 Sample Analysis	20
2.3.1 Canister Sample Analysis	20
2.3.2 Carbonyl Sample Analysis.....	20
2.3.3 Filter Sample Analysis.....	21
2.3.3.1 Analysis of quartz filters for organic and elemental carbon (OC/EC).....	21
2.3.3.2 Analysis of quartz filters for wood smoke tracers.....	22
2.3.3.3 Analysis of Teflon filters for PM mass	23
2.3.3.4 Analysis of Teflon filters for elements.....	24
2.3.3.5 Analysis of Teflon filters for ions	25
2.3.3.6 Analysis of Teflon filters for soluble potassium	26
2.3.4 Synoptic Meteorology during Sampling Events in 2008	26
3. Results and discussion	28
3.1 Results from the 2005 Filter Analysis.....	29
3.1.1 Chemical Analyses.....	29
3.1.2 Satellite Images	35
3.1.3 Ozone and Levoglucosan Correlations in 2005 Study.....	39
3.2 Results from the 2008 Study	42
3.2.1 Canister Samples.....	42
3.2.2 Carbonyl Samples	48
3.2.3 Aircraft VOC and Carbonyl Samples	50
3.2.4 Filter Samples	53
3.2.4.1 PM2.5 mass and organic/elemental carbon (OC/EC).....	53
3.2.4.2 Water soluble ions.....	54
3.2.4.3 Elements	57
3.2.4.4 Organic biomass burning tracers.....	57
3.2.5 Ozone and Levoglucosan Correlations in 2008 Study.....	62
3.2.6 Continuous GC VOC Data.....	65

3.2.6.1	Mean, median concentrations and comparison with canister data	65
3.2.6.2	Temporal and diurnal variations.....	70
3.2.6.3	IOP #3.....	74
3.2.7	Data Quality	78
4.	Conclusions and recommendations for future work	81
5.	References.....	83

Table of Tables

Table 1.1.	Chemical compositions and emission factors for wildland fires	6
Table 3.1.	List of filter samples analyzed for biomass smoke tracers	29
Table 3.2	List of VOC (with their mnemonics) analyzed from canisters	42
Table 3.3	List of carbonyl compounds analyzed for this study	48
Table 3.4.	Aircraft sampling dates and times	50
Table 3.5	List of wood smoke tracers with their mnemonics, quantified for 2008 study.....	57
Table 3.6.	Mean, median and maximum concentrations (in ppbv) of VOCs during the monitoring period	65
Table 3.7.	Daily concentrations of VOC measured in Apex (AP), JD Smith (JD), Jean (JN), Joe Neal (JO, primary and collocated) and Walter Johnson (WJ) sites of the Clark County Air Quality monitoring sites and 24-hour average, min, and max concentrations measured at DRI Southern Nevada Science Center	66
Table 3.8	Total number of samples collected during three IOP events.....	78

Table of Figures

Figure 2.1.	Clark County monitoring stations: JN: Jean, AP: Apex, BC: Boulder City and MQ: Mesquite.....	9
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Figure 2.2. Las Vegas area monitoring stations. JO: Joe Neal, LO: Lone Mountain, CR: E. Craig Road, PV: Palo Verde, WJ: Walter Johnson, CC: City Center, JD: JD Smith, SA: Sunrise Acres, PM: Paul Mayer, OR: Orr, WW: Winterwood, ES: East Sahara, GV: Green Valley and HN: Handerson	10
Figure 2.3. Satellite image of the Clower fire, affecting the Clark County area on June 23-26.....	12
Figure 2.4. Location of the monitoring site at Desert Research Institute (DRI-SNSC) (Google Earth).....	16
Figure 2.5. Schematic of the online continuous gas chromatography system.....	17
Figure 2.6. Sequence of sampling and analysis of ambient samples.....	18
Figure 3.1. Biomass burning tracers for all analyzed Clark County samples.....	32
Figure 3.2. Resin acid concentrations in the Clark County samples analyzed for biomass burning tracers. The inset shows samples with very low abundance of resin acids.	33
Figure 3.3. Methoxy-phenol concentrations in the Clark County samples.....	34
Figure 3.4. Wild fire locations on June 23, 2005.....	36
Figure 3.5. Wild fire locations on June 29, 2005.....	37
Figure 3.6. Wild fire locations on June 30, 2005.....	38
Figure 3.7. Corrected average (24 hr) ozone and levoglucosan concentrations at the SA site (A); and correlation between these concentrations (B). Red dotted trend line shows the correlation with the outlier (7/2) removed.....	40
Figure 3.8. Corrected maximum (1 hr) ozone and 24- hr levoglucosan concentrations at the SA site (A); and correlation between these concentrations (B).....	41
Figure 3.9. The most abundant VOC from canister samples collected during three IOP events (6/3/08, 6/23 – 6/26/08 and 7/9 – 7/10/08). A: light VOC, C2-C6; B: heavier VOC, C6-C12; C: furan derivatives and chloromethane. See Table 3.3. for compound mnemonics.	45
Figure 3.10. Correlations between pentane and iso-pentane (A); ethane and propene (B); and ethane and acetylene (C). Black trend line includes all data for IOP #1,2, and 3 and red trend line - data for IOP#2 (6/23-6/24/08) only.....	46
Figure 3.11. Correlations between benzene and toluene for all IOPs (A); for IOP#2 (B) and for IOP#3 (C). D: correlations between toluene and m/p-xylenes.	47

Figure 3.12 Carbonyl compound concentrations in Walter Johnson (WJ) and Joe Neal (JO) sites. F = front cartridge, B = back-up cartridge.....	49
Figure 3.13. Correlations between formaldehyde, acetaldehyde (A) and acetone (B); black trend line includes all data for IOP #1,2, and 3 and red trend line - data for IOP#2 (6/23-6/24/08) only	49
Figure 3.14. The most abundant VOC from canister samples collected during two aircraft flights (6/3/08, 6/24 and 7/9/08). A: light VOC, C2-C6; B: heavier VOC, C6-C12; C: furan derivatives and chloromethane. See Table 3.3 for compound mnemonics.....	52
Figure 3.15 Carbonyl compound concentrations from the aircraft samples. F = front cartridge, B = back-up cartridge	53
Figure 3.16. Concentrations of PM _{2.5} , OC and EC (A) and contribution of TC to PM _{2.5} (B).....	55
Figure 3.17. Concentrations of sulfates (SO ₄), nitrates (NO ₃) chlorine (Cl), ammonium (NH ₄) and soluble potassium (K).....	56
Figure 3.18. Concentrations of the major elements in filter samples	58
Figure 3.19. Wood smoke tracers (A) and levoglucosan (B) in filter samples.....	60
Figure 3.20. Resin acids (A) and methoxy-phenols (B) in the filter samples.....	61
Figure 3.21 Relations between 24-hr sum of 1-hr ozone concentrations and corresponding levoglucosan concentrations for all sites and all IOPs.	63
Figure 3.22. Relations between average 24-hr ozone sum and levoglucosan concentrations for all measured sites during IOP# 2	64
Figure 3.23. Hourly mean, minimum and maximum concentrations of benzene (in ppbv) measured at DRI-SNSC and daily benzene concentrations (in ppbv) at the five DAQEM sites	68
Figure 3.24. Hourly mean, minimum and maximum concentrations of ethylbenzene (in ppbv) measured at DRI-SNSC and daily o-xylene concentrations (in ppbv) at the five DAQEM sites	68
Figure 3.25. Hourly mean, minimum and maximum concentrations of o-xylene (in ppbv) measured at DRI-SNSC and daily o-xylene concentrations (in ppbv) at the five DAQEM sites	69
Figure 3.26. Hourly mean, minimum and maximum concentrations of o-ethyl-toluene (in ppbv) measured at DRI-SNSC and daily o-ethyl-toluene concentrations (in ppbv) at the five DAQEM sites	69

Figure 3.27 Daily variation of benzene and toluene concentrations (in ppbv).....	71
Figure 3.28 Daily variation of 2-,3- and 4-methyl-heptane, <i>n</i> -octane and <i>n</i> -nonane concentrations (in ppbv)	71
Figure 3.29 Daily variation of ethylbenzene concentrations (in ppbv)	72
Figure 3.30 Daily variation of m-, p- and o-xylene and styrene concentrations (in ppbv)	72
Figure 3.31 Daily variation of m-, p- and o-methyl-toluenes and, 1,2,4- and 1,3,5-trimethyl-benzenes concentrations (in ppbv).....	73
Figure 3.32 Day of the week variation of selected VOCs	73
Figure 3.33 Diurnal variations of average benzene, toluene, m-/p-xylene and o-xylene	74
Figure 3.34 Mean 24-h concentrations of benzene and toluene from July 3, 2008 to July 19, 2008.....	75
Figure 3.35 Hourly variation of benzene during July 8-11, 2008 (Event 1), July 11-15, 2008 (Event 2) and August 11-15, 2008 (Event 3).....	76
Figure 3.36 Hourly variation of toluene during July 8-11, 2008 (Event 1), July 11-15, 2008 (Event 2) and August 11-15, 2008 (Event 3).....	76
Figure 3.37 Variation of toluene/benzene ratio during July 8-11, 2008 (Event 1), July 11-15, 2008 (Event 2) and August 11-15, 2008 (Event 3)	77
Figure 3.38. A: Collocated light VOC (C2 – C6) and B: heavier VOC (C6-C11) canister samples (see Table 3.2 for compound mnemonics) collected at the Joe Neal site.	79
Figure 3.39. Collocated filter samples analyzed for the biomass tracers.....	80
Figure 3.40. Collocated filter samples analyzed for PM mass, OC and EC	80

1. INTRODUCTION AND BACKGROUND

Biomass combustion emissions are receiving increasing attention as sources of primary and precursors of secondary air pollutants. A number of epidemiological studies have found associations between biomass combustion emissions and health effects, such as decreasing lung function, respiratory symptoms, asthma, cardiovascular diseases, etc. Emissions from biomass fires have significant impact on chemical and physical properties of the atmosphere and can affect visibility and Earth's climate. A number of studies have shown that biomass combustion emissions influence cloud formation, ozone levels, total amount of particulate matter, chemical composition of atmosphere, etc.

Biomass combustion arising from natural fires, prescribed burns, and residential wood combustion contribute significant amounts of particulate matter (PM), inorganic species (e.g. CO, CO₂, elements, ions), and volatile organic compounds (VOC) to the troposphere (Crutzen and Andreae, 1990). Wood smoke emissions from residential fireplaces have been shown to be a major source of PM in a number of communities in the United States (Schauer et al., 1996; Schauer and Cass, 2000; Tanner, 2005). In addition, wood smoke emissions from wildfires and prescribed burns are responsible for occasional severe episodes of air pollution (Fraser and Lakshmanan, 2000; Phuleria et al., 2005). Biomass combustion smoke is a mixture of gaseous and particulate organic compounds with complex chemical composition (Oros and Simoneit, 2001; Oros and Simoneit, 2001; Gao et al., 2003). Variability in combustion emissions arises from environmental differences such as fuel composition and structure, the fire intensity, aeration, ambient and vascular moisture, duration of smoldering and flaming conditions, and the physical surroundings such as the slope of the ground. Several studies have been conducted to characterize the organic composition of the PM

emissions from residential wood combustion (McDonald et al., 2000; Fine et al., 2001; Schauer et al., 2001; Fine et al., 2002; Fine et al., 2004), however only few studies have been done on wildland fuels (Hays et al., 2002) and in-situ prescribed burns (Lee et al., 2005; Mazzoleni et al., 2007).

1.1 Semi Volatile Organic Compounds Wood Smoke Tracers

Major pyrolysis products arising from cellulose, lignin, and resins have been proposed as tracers for biomass combustion emissions (Hawthorne et al., 1988; Simoneit et al., 1993; Simoneit et al., 1999; Fraser and Lakshmanan, 2000). Levoglucosan, a pyrolysis product of cellulose and hemicellulose, has been proposed as a molecular marker for the long-range transport of biomass combustion aerosols (Fraser and Lakshmanan, 2000; Zdrahal et al., 2002).

A comprehensive study of several individual semi-volatile organic compounds (SVOC) was conducted to examine compositional similarities and differences between biomass types and combustion conditions (Mazzoleni et al., 2007). Of these individual compounds, levoglucosan was found to be the dominant species in most source samples. Other abundant compounds included methoxylated phenols, resin acids, and methoxy acids. The total SVOC identified for source types ranged from approximately 5-80% of the PM_{2.5} gravimetric mass. Highest percentages of PM_{2.5} were identified for prescribed burns, white pine needles, grasses, straws, and mixed woods.

Levoglucosan has been widely reported to be very abundant compared to other individual organic compounds in biomass smoke but reported concentrations are highly variable in biomass source emissions (Fine et al., 2001; Nolte et al., 2001; Schauer et al.,

2001; Fine et al., 2002; Hays et al., 2002; Sheesley et al., 2003). In the study of Mazzoleni et al. (2007), the overall range of levoglucosan was from approximately 3% to 36% of $PM_{2.5}$ mass, with the highest percentage observed for grasses, white pine needles, straws, and mixed woods.

Methoxylated phenols, guaiacols and syringols, arising from pyrolysis of wood lignin are commonly found in biomass combustion emissions. In the lignin of hardwoods, structural units consist of both guaiacyl and syringyl types in similar proportions, but in softwoods guaiacyl units are the predominant structural unit. Thus, during pyrolysis of coniferous lignin, syringols are generally not formed, but during pyrolysis of deciduous lignin guaiacols and syringols are formed (McDonald, 2000). Many researchers have included these compounds in source characterization analyses of residential woods (McDonald et al., 2000; Fine et al., 2001; Schauer et al., 2001; Fine et al., 2002; Hays et al., 2002). Mazzoleni et al. (2007) reported that in addition to hardwoods, sagebrush and grasses emit both guaiacols and syringols, but pine needles (especially white pine needles) have a high PM fraction of guaiacols with very little syringols, similar to softwoods. The prescribed burn samples collected in mixed coniferous forests (in Yosemite National Park, CA, and Toiyabye National Forest near Lake Tahoe, NV) also had a high percentage of PM represented by guaiacols and very little represented by syringols, while the prescribed burn samples of desert brushes of central rural Nevada have considerable weight fractions of syringol, similar to the sagebrush source test. However, methoxy phenols are low molecular weight semi-volatile polar aromatic compounds, and are distributed between the gas and particle phases. Thus, many of the methoxy phenols are found in higher percentages in the gas phase than in the particle

phase, depending upon molecular weight, and the analysis of filter PM samples only, does not necessarily reflect the true concentrations of guaiacols and syringols.

Methoxy acids (vanillic, homovanillic and syringic acids), also originating from pyrolysis of wood lignin, were identified in biomass combustion source samples and in-field prescribed burn samples (Mazzoleni et al, 2007). In general, methoxy acids were found in low abundance for residential wood combustion and wildland fuels. An unusually large fraction of PM was accounted for by homovanillic acid in the prescribed burn samples collected north of Lake Tahoe, NV.

Resin acids are generally found in low abundance in particulate carbon emissions from coniferous woods. Most source characterization tests have been focused on residential wood combustion, however Hays et al. (2005) collected fresh green biomass for a series of source emission tests, which resulted in much higher concentrations of resin acids in the emissions than reported previously. This was done to simulate wildland fires in nature, rather than residential wood combustion. Mazzoleni et al. (2007) also found high resin acid concentrations in the in-field prescribed burn samples, especially in north of Lake Tahoe. Moisture may play an important role in abundance of the resin acids compared to other carbonaceous species. Prescribed burn samples collected north of Lake Tahoe, showed a much higher abundance of resin acids compared to laboratory wildland fuel source tests where fuels were pre-conditioned for several months before combustion.

The large variations in abundance of molecular markers for biomass combustion between residential woods, wildland fuels, and in-field prescribed burns are due to the complex nature of combustion chemistry. Additional factors such as water content, plant structure, and combustion temperature not only affect the SVOC characterization, but also

affected the organic/elemental carbon (OC/EC) ratio, CO emission rate, and total particulate carbon emission rate.

1.2 Volatile Organic Compound Wood Smoke Emissions

A substantial amount of volatile organic compounds (VOC) is released during biomass combustion. It has been reported (McDonald et al., 2000) that the highest emissions of total VOC were observed from burning hardwood in the woodstove (21.8 g/kg). However, VOC data from the wild and prescribed fires are rather sparse. Table 1.1 lists the ranges of major components of wildland fires, expressed as emission factors that are defined as the mass of compound released per mass of dry fuel consumed, in units of g/kg. Temperate forest and rangeland data are mostly from the US and Canada. As Table 1.1 shows, wildland fires emit large amounts of PM_{2.5} and reactive VOC. Total emissions of VOC exceed that of PM_{2.5} and account for 1 -2% of fuel carbon burned. Oxygenated VOC (OVOC) account for ~60 – 70% of total non-methane hydrocarbons (TNMHC) emissions and are dominated by methanol, acetic acid, formic acid and formaldehyde. Alkenes are second in importance in wildland fire emissions, followed by aromatics (benzene, toluene, ethylbenzene, o-, m- and p- xylenes, so called BTEX) and alkanes.

Furans are formed from the decomposition of wood cellulose upon heating, and constitute from 5 to 10 % of the total C₂-C₁₂ VOC from softwood and hardwood emissions (McDonald et al., 2000). The structures of the pentose, xylose and arabinose, commonly found in wood structure favor the production of 2-methylfuran, 2,5-dimethylfuran and 2-ethylfuran. It has been reported that furan and acetonitrile come mostly from wildfire, whereas 2-methylfuran, 2,5-dimethylfuran, 2-ethylfuran originates mainly from wild fires and also from agricultural residue burning (Andrea, 1997).

Table 1.1. Chemical compositions and emission factors for wildland fires

Compound or Compound Class	Emission Factors (g/kg)	
	Temperate forest	Temperate rangeland
PM _{2.5}	11.7	9.7
Organic carbon (wt % of PM _{2.5})	45 - 55	40 - 70
Elemental carbon (wt % of PM _{2.5})	4 - 8	4 - 10
Elemental Species (wt % of PM _{2.5}):	~ 3	~ 6
- Potassium (K, wt % of PM _{2.5})	~ 1	~ 3
- Chloride (Cl, wt % of PM _{2.5})	0.3	2
CO	89.6 ± 13.2	69 ± 17
CO ₂	1619 ± 112	1684 ± 45
Alkanes (C ₂ -C ₁₀)	0.8	0.4
Alkenes (C ₂ -C ₉)	2.2	1.8
Aromatics (BTEX)	0.64	0.42
Oxygenated VOC (OVOC):	10.9 – 12.9	Na
-Methanol	0.31 – 2.03	0.14
-Formic acid	1.17	Na
-Acetic acid	3.11	Na
-Formaldehyde	2.25	Na
-Acetaldehyde	0.24	0.25
-Acetone	0.347	0.25
-Acrolein (propenal)	0.123	0.08
-Furan	0.445	0.1
-2-methyl-furan	0.521	Na
-3-methyl-furan	0.052	Na
-2,5-dimethyl-furan	0.053	Na
-Benzofuran	0.038	Na

Na = not available; BTEX = benzene, toluene, ethyl benzene and xylenes

In addition, it has been reported that biomass burning of wood and savanna grass is the main source of tropospheric acetonitrile and contributes significantly to tropospheric acetaldehyde and acetone (de Gouw et al., 2003; Jost et. al., 2003). Methyl chloride has been specifically identified in the smoke from pine needles and oak leaves (Rasmussen et al., 1980).

The air quality impact of wildfire emissions occurs not only through emissions of primary pollutants (CO, CO₂, PM, VOC, elements, NO_x) but also by the production of secondary pollutants, i.e. ozone and secondary organic aerosol (SOA), when VOC and NO_x undergo photochemical processing during transport through the atmosphere. The main VOC compounds emitted by wildland fires, i.e. oxygenated VOC and alkenes are highly reactive and their atmospheric lifetimes due to the reactions with OH radicals or photolysis is short, ranging from minutes to several days. This gives the wildland fire emissions significant potential to influence tropospheric chemistry and degrade air quality. VOC – NO_x photochemistry leads to ozone formation on time scale of hours to days over local and intercontinental distances (Pfister et al., 2008). Maximal incremental reactivity factors (MIR) for furan, 2-methylfuran, 2-ethylfuran and 2,5-dimethylfuran are 9.03; 8.2; 7.01; 7.78 gmO₃/gmVOC, respectively (SAPRC Atmospheric Chemical Mechanisms and VOC Reactivity Scales, <http://pah.cert.ucr.edu/~carter/SAPRC/>). These MIR are comparable with those for such highly reactive species like isoprene or formaldehyde (MIR = 10.48 and 9.59 gmO₃/gm VOC, respectively) and in contrast to those for such abundant, but non-reactive species as ethane and propane (0.26 and 0.46 gmO₃/gmVOC, respectively).

1.3 Study Objectives

The overall goal of this study was to determine the relationships between wildfire emissions and ambient O₃ level. Specific objectives include:

1. Establish the relationship between pollutant levels and molecular markers for combustion.
2. Evaluate the potential for using combustion markers to estimate the impact of wildfire events on ambient O₃ level.

1.4 Study Description

The study consisted of two parts:

1. In the first part, the subset of ambient PM_{2.5} samples collected by the Clark County Department of Air Quality & Environmental Management (DAQEM) personnel in June – July 2005 during major fire events were analyzed for wildland fire emission's tracers.
2. In the second part, a field study was conducted in the summer of 2008 to collect VOC and PM_{2.5} samples during forecasted wild fire connected smoke events in the Las Vegas area.

2. EXPERIMENTAL

2.1 2005 Sample Collection.

Ambient PM_{2.5} samples were collected by the Clark County Department of Air Quality & Environmental Management personnel at the six monitoring stations located in the Las Vegas area. The monitoring stations were as follows (see Figures 1 and 2): Jean (JN), Apex (AP), Sunrise Acres (SA), JD Smith (JD), Green Valey (GV), and CL (?). The samples were collected over 24 hr using 37 mm Teflon filters and 1 m³/hr sampling rate. After

gravimetric mass measurements, all filters were archived and kept in the freezer in air tight containers. Filter samples collected from June 21, 2005 to July 03, 2005 were sent to DRI Organic Analytical Laboratory by overnight mail in a cooler filled with blue ice.

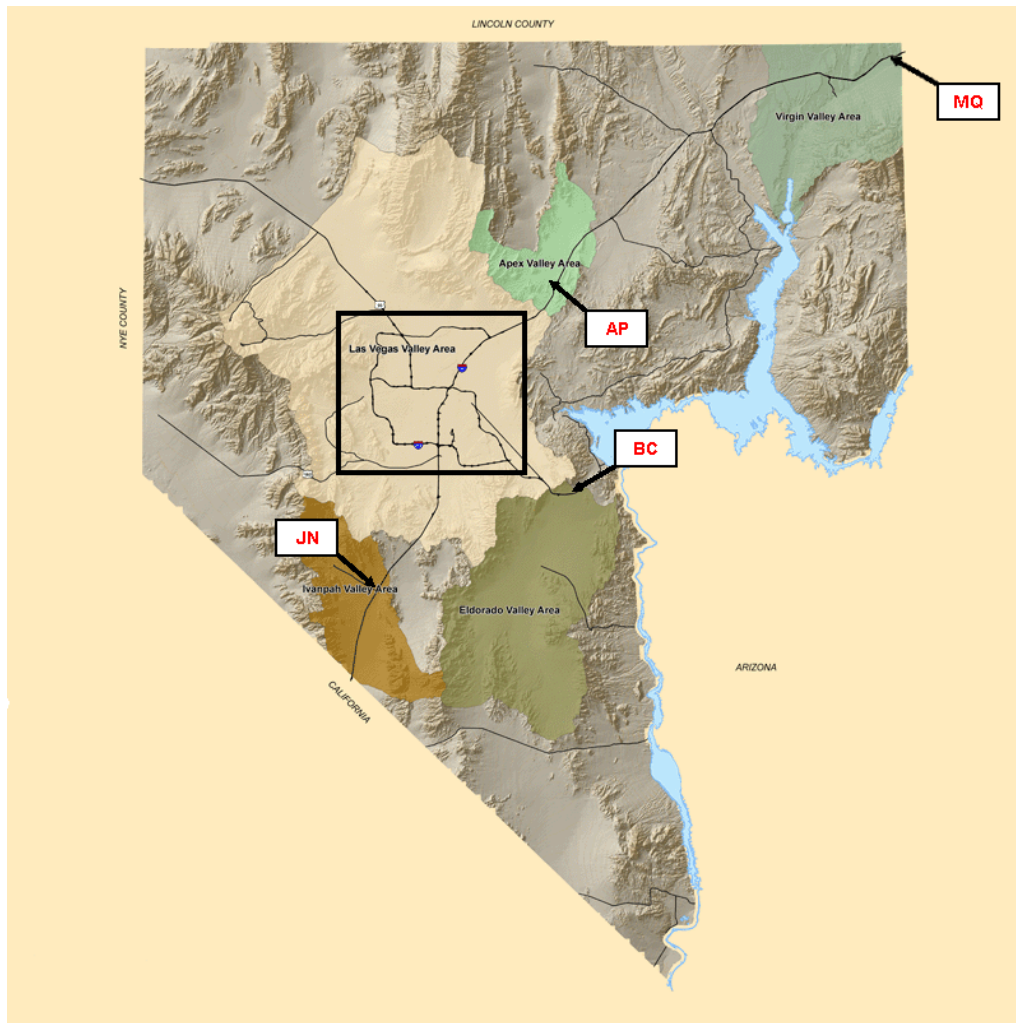


Figure 2.1. Clark County monitoring stations: JN: Jean, AP: Apex, BC: Boulder City and MQ: Mesquite.

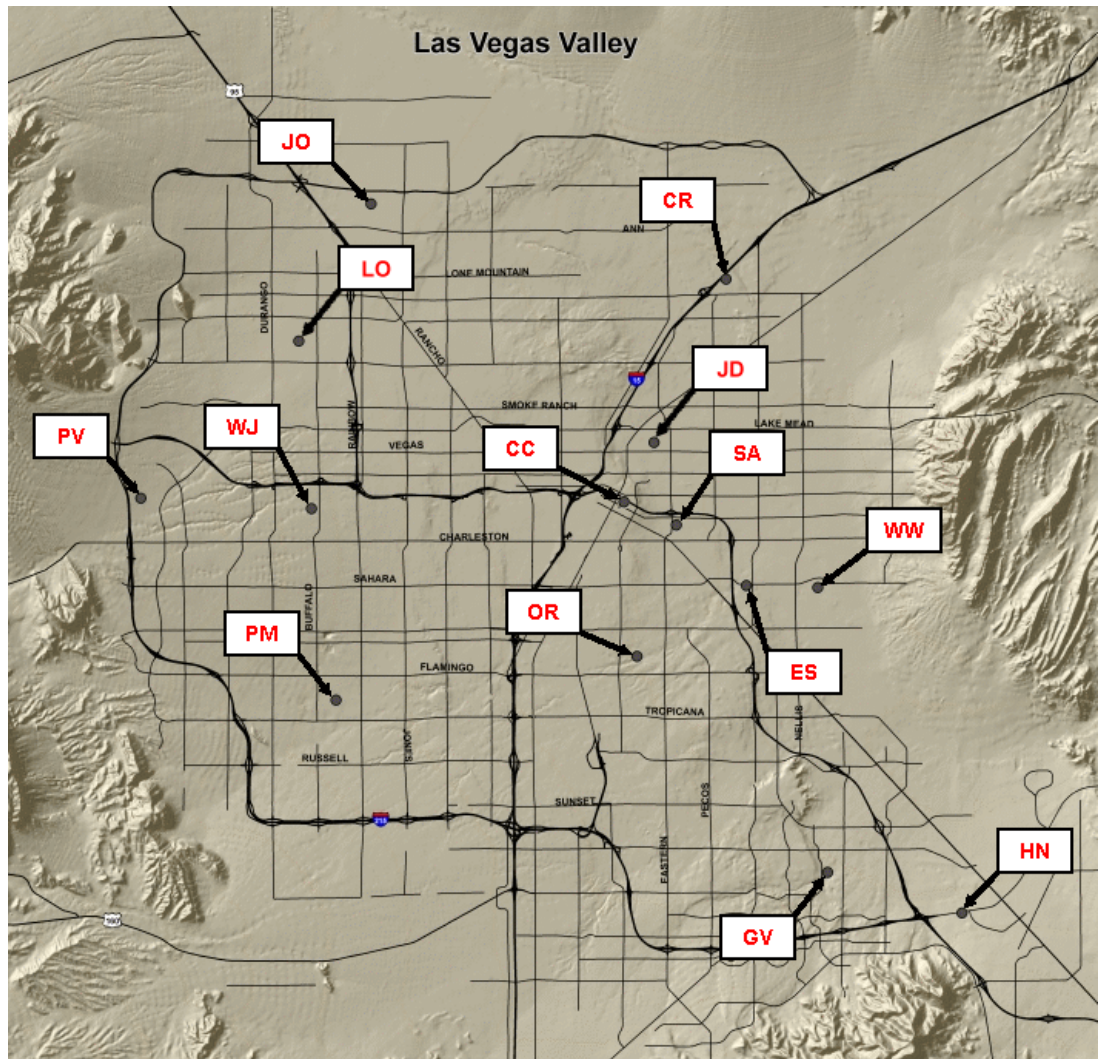


Figure 2.2. Las Vegas area monitoring stations. JO: Joe Neal, LO: Lone Mountain, CR: E. Craig Road, PV: Palo Verde, WJ: Walter Johnson, CC: City Center, JD: JD Smith, SA: Sunrise Acres, PM: Paul Mayer, OR: Orr, WW: Winterwood, ES: East Sahara, GV: Green Valley and HN: Handerson

2.2 2008 Field Study

2.2.1 Sampling Sites and Sampling Periods

The following five sites were selected for 2008 sample collections (see Figure 1 and 2): Jean (JN), Apex (AP), Joe Neal (JO), Walter Johnson (WJ), and JD Smith (JD). On May

27-28, 2008 the sampling equipment that included canister samplers and medium volume sequential filter samplers (MedVol) was deployed at each site. In addition carbonyl compound samplers were deployed at WJ and JO sites. JO site, for which collocated canister and MedVol samplers were deployed, served also as a QA site. The DRI personnel conducted two-days training session for the DAQEM site operators, who were designated to operate the sampling equipment at each site. In addition to canister, MedVol and carbonyl samplers, each site was equipped with continuous ozone analyzer, AP, JD and JN sites measured PM_{2.5} and AP, JO and JD measured oxides of nitrogen.

The samples were collected from 11 AM local time (PDT) over 24 hr time periods during the following three intensive operational periods (IOPs):

IOP 1. From June 3, 11 AM to June 4, 11 AM. This was the training/background sampling, since no major wildfires were registered in the area during this time period.

IOP 2. From June 23, 11 AM to June 27, 11 AM. Four 24-samples were collected during a moderate smog episode that affected the area in connection with Southern California wild fires. This fire, known as Clover fire, is shown on a satellite image below (Figure 2.3). The plume from this fire moved into the Clark County area during the late evening on June 23 and remained there for the next three days until June 26. This time period was characterized by relatively stagnant conditions with very low winds.

IOP 3. From July 9, 11 AM to July 11, 11 AM. Although no major fire in the vicinity of Clark County was reported during that time, it is possible that the long range transport from the Northern California wildfires was affecting the area.

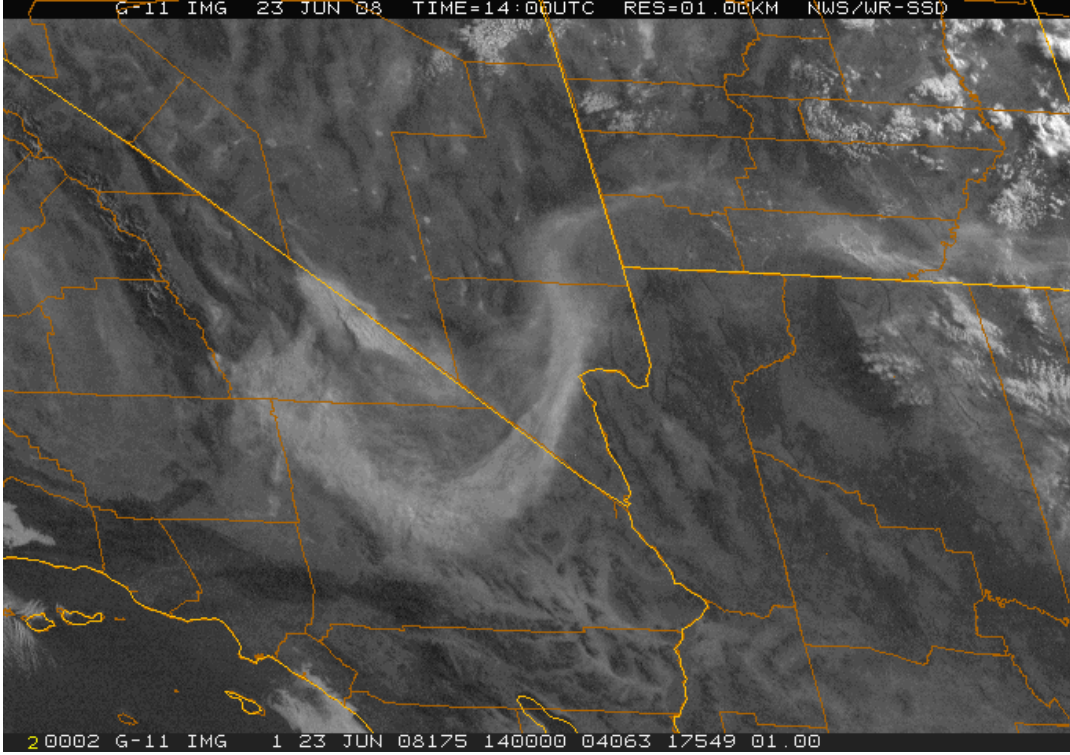


Figure 2.3. Satellite image of the Clower fire, affecting the Clark County area on June 23-26.

2.2.2 Sampling Procedures

Canister Sampling. Whole air samples were collected in pressurized stainless steel 6 L SUMMA canisters over 24 hr periods, using DRI sequential canister samplers. Up to six canister samples could be sequentially collected with this sampler. The DRI canister sampler takes air from the sample inlet and injects it into a canister at a constant flow rate for a preset time. The excess air is released through the bypass exhaust. The constant flow rate and elapsed time allow the operator to compute the volume of the integrated air sample. The sample is pumped through a 12 V.D.C. pump which develops sufficient pressure to control the flow with an electronic flow regulator. The pump also samples the air at a flow rate sufficient to keep any long sampling lines flushed. The sampler is automatically purged for five minutes at the beginning of each run. The timer turns on the pump for five minutes before the canister solenoid is turned on. Following sampling, the solenoid is shut off to seal the canister until an operator can shut off the canister valve.

Sampler components are disassembled and cleaned before the sampler is assembled. The cleanliness of the sampling system is determined by testing the sampler with humid zero air, using GC/MS analysis. The analytical system should not detect more than 0.2 ppbv of targeted VOC in order for the sampling system to pass the humid zero air certification tests. The DRI SOPs describing sampling and certification processes are available upon request

Carbonyl Compound Sampling. Carbonyl compounds were collected by drawing air through a cartridge impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH), available commercially from Waters. The resulting products (hydrazones) in the cartridge are measured in the laboratory using high performance liquid chromatography (see Section 2.3). The multi-event sampling systems were used for sample collection. This sampler consists of the check valves, solenoid valves and pump. The two-port manifold and flow control device allows two cartridges to be attached at once. Flow can be individually adjusted and measured for each cartridge. Each solenoid is controlled separately by the timer and can sample independently. There is one check valve for each individual solenoid valve, to protect the cartridge from any contamination when it is not being used for sampling.

Timers that allow unattended operation (activation and deactivation) of the two independent solenoids in the collection system are located in the unit. A 120 V.A.C. vacuum pump is capable of drawing air through the cartridges at up to 5 liters per minute.

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. To prevent this, the samplers are equipped with potassium iodide (KI) denuder, as recommended by the EPA Method TO-11A (US EPA, 1999).

When the exposed cartridges were removed, they were immediately plugged, put into the vials, and stored in a containers designated for exposed cartridges. The exposed cartridges were stored inside a refrigerator and returned to the laboratory in a cooler. The DRI SOP describing sampling process is available upon request.

Filter Sampling. DRI's medium volume sequential filter samplers (MedVol) were used in this study for 24-hour ambient samples on Teflon filters for PM_{2.5} mass and elements and on pre-fired quartz filters for OC/EC and chemical speciation analyses. The MedVol consists of an aluminum plenum to which a PM_{2.5} inlet is attached. Up to 12 sampling ports within the plenum are controlled by solenoid valves that divert flow from one channel to the next by means of a programmable timer. These ports accept filters that have been pre-loaded into open-faced 47 mm Nuclepore filter holders. The flow rate through each filter pack is adjusted accordingly to provide adequate sample loadings for analysis. Flow rates are set with a calibrated rotameter and are monitored with the same rotameter at each sample changeout. Teflon-membrane filter are used for mass, elements and ion analysis while quartz filters are used for carbon analysis (OC/EC) and for detailed chemical speciation for wood smoke tracer.

After sampling, filters were removed from the sampler and stored in their original containers in a refrigerator. They were returned to the laboratory in a cooler with a blue ice via overnight shipment. The DRI SOP describing sampling process is available upon request.

2.2.3 Continuous Gas Chromatography

Hourly concentrations of volatile organic compounds (from benzene to 1,2,4-trimethylbenzene) were continuously measured in Las Vegas valley from June 2-June 10 and from July 3 to August 28, 2008. A compact gas chromatography system (SRI Instruments) equipped with an automated sampling and calibration system was used at the Phase 1 building of Desert Research Institute (DRI) in Las Vegas. The Southern Nevada Science Center (SNSC) Phase 1 building of DRI is adjacent to the Atomic Testing Museum at the intersection of E. Flamingo Road and Swenson Street (177 ft southwest of the intersection), on the northwest corner of UNLV campus. The site is 188 ft west of Swenson St, 50 ft south of E. Flamingo Rd and 0.28 miles east of the Paradise Rd and E. Flamingo Rd. intersection (Figure 2.4). Both Flamingo Rd and Swenson St are characterized by high traffic density. There is also a parking lot 206 ft west of the sampling site. The Las Vegas Strip is about 1.45 miles to the west, while the McCarran International Airport runway is approximately 1.13 miles southwest of the site.

Figure 2.5 shows the gas chromatograph (GC) system and the individual components. It is composed of: (i) a complete sampling system (dryer, trap, mass flow meter, vacuum pump); (ii) a fully automated calibration system (clean air, calibration standard, regulators, dilution chamber); (iii) an analysis system composed of a temperature-controlled oven (capillary column) and three in-series detectors (flame ionization (FID) (for hydrocarbons), photo-ionization (PID) (for aromatic hydrocarbons) and dry-electrolytic conductivity (DELCD) for halogen-hydrocarbons). All components of the GC are controlled through a series of switch on/off relays and a laptop computer.

The GC system runs in either a monitoring mode or a calibration mode. During the monitoring mode, VOC concentrations in ambient air are measured. In the calibration mode, known VOCs mixtures are analyzed by the GC for identification and calibration of the compounds. For this study, a calibration standard was provided by DRI's Organic Analysis Laboratory in a pressurized canister (74 component mixture).



Figure 2.4. Location of the monitoring site at Desert Research Institute (DRI-SNSC) (Google Earth).

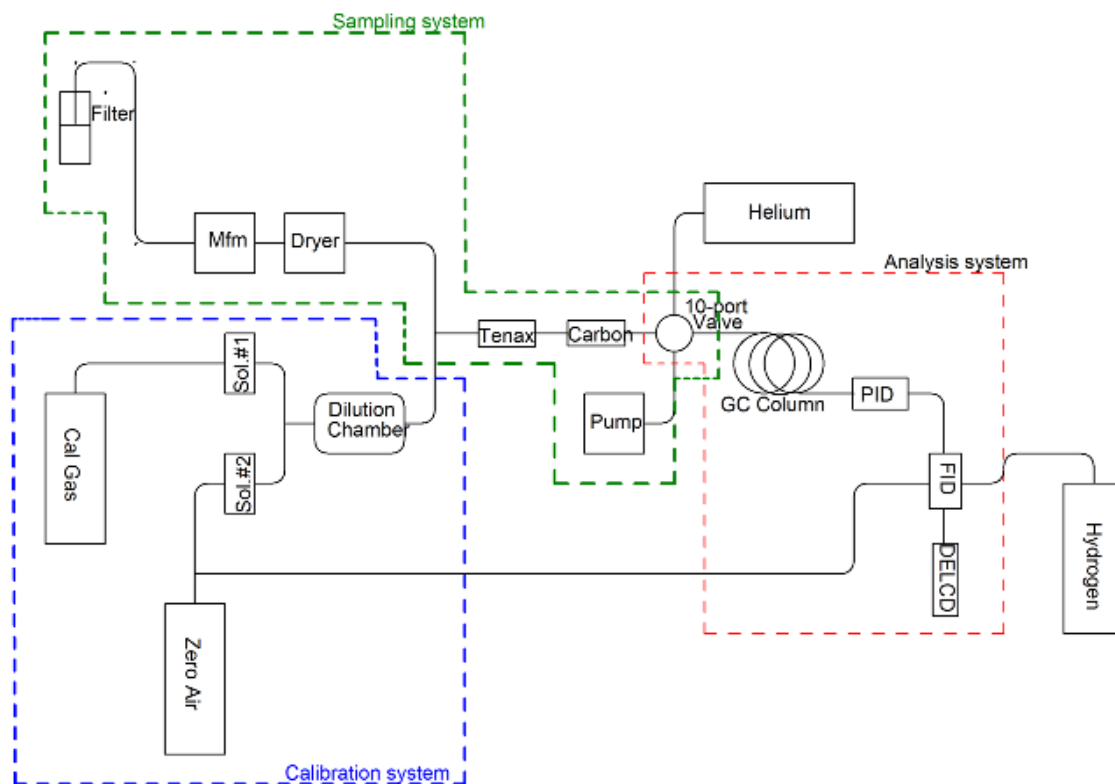


Figure 2.5. Schematic of the online continuous gas chromatography system

In the measurement mode the air sample is drawn through the filter (to remove particles), the mass flowmeter (to measure the flowrate: Mfm) and the dryer prior to the collection of VOCs by the Tenax and Carbon traps (Figure 2.5). After the desired volume of air is collected, the vacuum pump is switched off and the two traps are heated to 190°C. Concentrated VOCs are thermally desorbed and injected into the capillary column. The oven temperature is increased as a function of time and VOCs are eluted from the capillary column at different times depending on the temperature in the oven and the interaction of the VOC with the solid phase of the capillary column. The VOCs are then detected by the FID and PID detectors.

An air sample was collected during the last 45 minutes of the first run and then analyzed during the second run using a 1-hour temperature program. During the last 45 minutes of the second run, another sample of air was drawn and then analyzed during the third run. The sequence of these three consecutive runs is presented in Figure 2.6.

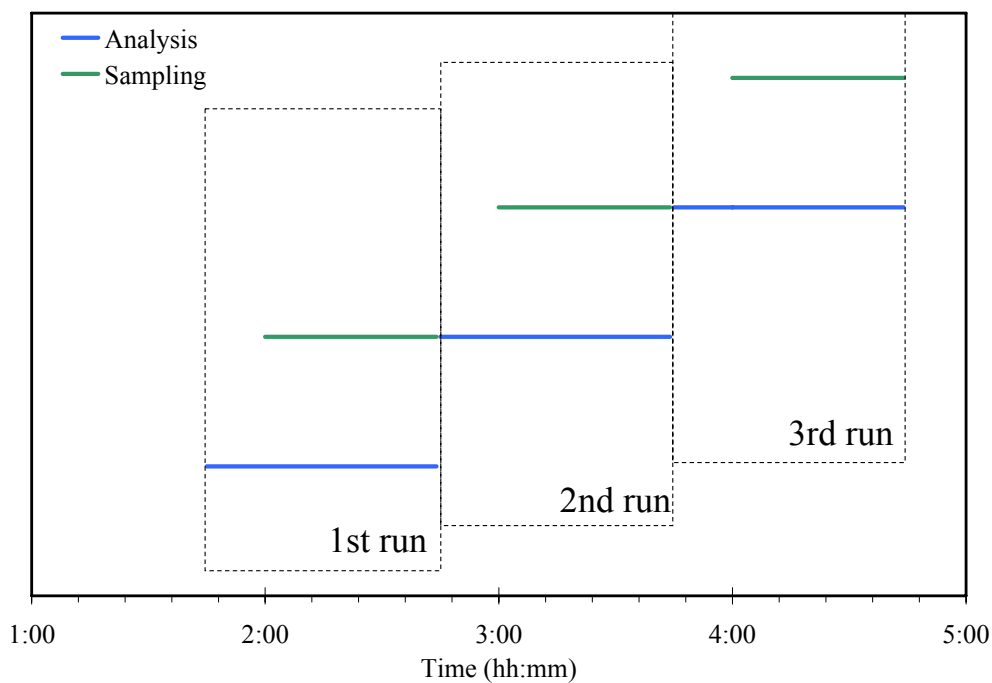


Figure 2.6. Sequence of sampling and analysis of ambient samples.

2.2.4 Aircraft Sampling

Ozone, fine particulate loading, temperature, and VOC sampling were measured using a single-engine airplane chartered from West Air Aviation at North Las Vegas Airport. The primary goal of the aircraft sampling was to document the existence and characteristics of the wildfire plume(s) upwind of Clark County. A secondary goal was to document the vertical extent of the smoke plume (i.e., was the plume mixing to the ground?). The VOC sampling is a key to uniquely characterizing the chemistry of the plume the airplane measured that can then be compared to the samples exposed in the surface network (see T&B draft report, Bush et al., 2008).

For VOC Sampling, a DRI Canister Sampler takes air from the sample inlet and injects it into a 3-liter canister at a constant flow rate for a preset time. The excess air is released through the bypass exhaust. The sample is pumped through a 12 V.D.C. pump which develops sufficient pressure to control the flow with a Variflo regulator. The pump also samples the air at a flow rate sufficient to keep any long sampling lines flushed. A small, constant flow of sampled air is pumped into the sample container. The sampler is automatically purged for 1-

minute at the beginning of each run. The timer turns on the pump for one minute before the solenoid is turned on. The sampler runs for 1-minute after shut-off to make up for this 1-minute loss of sample. Following sampling, the solenoid is shut off to seal the canister until an operator can shut off the canister valve. The canister is sealed with a Swagelok cap.

The carbonyl sampler consists of an adjustable valve, pump, and flowmeter. Cartridges installed in the sampler are installed upstream of the pump, followed by a Teflon sample line leading to the sample inlet. The cartridges are only exposed to the air stream during the period of sampling, at which point the pump is turned on. A flow rate in the range of 4 lpm is maintained for approximately 20-minutes, collected a total sample volume of at least 75 liters. When the exposed cartridges are removed, they are immediately plugged, put into the vials, and stored in sample envelopes designated for exposed cartridges. After the flight, the exposed cartridges are moved to an ice-chilled cooler, transferred for storage inside a refrigerator, and returned to the laboratory in a cooler.

A total of three flights were conducted during 2008 IOPs. June 3, 2008 was the checkout flight conducted at the beginning of the study, with the goal of verifying the operation of the equipment and refining procedures for collecting VOC and carbonyl samples.

The original goal of June 24 flight was to record regional background conditions upwind of Las Vegas on what was anticipated to be a relatively clean day. However, observations during the flight, as well as analysis after the flight, revealed the likelihood that the region was being impacted by smoke from the numerous fires that were burning in California at the time. Initially, the flight path was developed to concentrate on conditions along the I-15 corridor to southern California. On-board observations while over Jean showed the visibility to be notably worse towards the Sandy Valley, and the flight path was altered accordingly to investigate. Significantly higher $PM_{2.5}$ concentrations were noted in this region, possibly supporting smoke impact from California wildfires. This area of higher $PM_{2.5}$ concentrations was consequently chosen as the location of the VOC and carbonyl samples.

The goal of July 9 flight was to record conditions during a day with relatively high ozone concentrations that was clearly not impacted by wildfire smoke, which in turn could be

compared with days when high ozone was associated with smoke. Again, it was assumed that the I-15 corridor southwest of Las Vegas would provide the most representative conditions of this scenario, and VOC/carbonyl samples were collected during a spiral over Jean. Unfortunately, ozone concentrations in this layer remained low. During the initial sampling from North Las Vegas to Jean, however, significantly higher ozone concentrations were noted in Red Rock Park as evidenced in the plots (90-95 ppb). Thus, it was decided to return to this area to obtain a second set of VOC/carbonyl samples. All sampling equipment operated properly and no problems were encountered. It should be noted that overall ozone concentrations reached only moderate levels in Clark County this day.

2.3 Sample Analysis

2.3.1 Canister Sample Analysis

Canister samples were analyzed according to the EPA Method TO-15 (US EPA, 1999) using a Varian 3800 gas chromatograph interfaced to a Varian Saturn 2000 ion trap mass spectrometer (MS) and flame ionization detector (FID). Canister samples were preconcentrated using a Lotus Ultra Trace Toxics System-MS-TO15 preconcentrator before injection onto a Varian CP fused silica 60m widebore column with MS detection for C4-C11 VOC and an Agilent Alumina 30m megabore column with FID detection for C2-C4 VOC. Calibration of the system was conducted with a VOC mixture (purchased from AiR Environmental) that contained 74 most commonly found hydrocarbons 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 individual compounds is more than 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.

2.3.2 Carbonyl Sample Analysis

C₁ through C₇ carbonyl compounds were collected with Sep-Pak cartridges, which have been impregnated with an acidified 2,4-dinitrophenylhydrazine (DNPH) reagent (Waters, Inc). When ambient air was drawn through the cartridge, carbonyls in the air sample are captured by reacting with DNPH to form hydrazones, which are separated and

quantified using HPLC in the laboratory, according to the EPA Method TO-11A (US EPA, 1999).

After sampling, the cartridges were eluted with acetonitrile. An aliquot of the eluent was transferred into a 2-ml septum vial and injected with an autosampler into a high performance liquid chromatograph (Waters 2690 Alliance System with 996 Photodiode Array Detector) for separation and quantitation of the hydrazones. The samples were analyzed for the carbonyl compounds listed in Table 3.3 below. Identifications were made based on matching the HPLC retention times and the UV spectrum with those of authentic standards. A three-level calibration curve (plus blank) is constructed for each quantified hydrazone and the calibration check is run every 10 samples. If the response of individual compounds is more than 10% off, the system is recalibrated.

2.3.3 Filter Sample Analysis

2.3.3.1 Analysis of quartz filters for organic and elemental carbon (OC/EC)

Prior to use, quartz fiber filters were baked for several hours in a muffle furnace at 900°C. After sampling, a 0.56 cm² punch from each quartz filter sample was analyzed for organic and elemental carbon (OC/EC) by the Thermal – Optical Reflectance (TOR) method for OC/EC, using the IMPROVE (Interagency Monitoring of Protected Visual Environments) temperature/oxygen cycle (Chow et al, 1999; 2001). A 0.56 cm² 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

or transmittance. EC and OC are thus distinguished based upon the refractory properties of EC using a thermal evolution carbon analyzer with optical (reflectance or transmittance) correction to compensate for the pyrolysis (charring) of OC. Carbon fractions in the IMPROVE method correspond to temperature steps of 120°C (OC1), 250°C (OC2), 450°C (OC3), and 550°C (OC4) in a nonoxidizing helium atmosphere, and at 550°C (EC1), 700°C (EC2), and 850°C (EC3) in an oxidizing atmosphere.

The minimum detection limit (MDL) for this method is 0.8 and 6.2 µg of EC and OC, respectively, per 47 mm filter.

2.3.3.2 Analysis of quartz filters for wood smoke tracers

After taking a punch from each quartz filter sample for OC/EC analysis, several deuterated internal standards were added to each filter prior to extraction. The deuterated standards used include: hexanoic-d₁₁ acid, benzoic-d₅ acid, succinic-d₄ acid, decanoic-d₁₉ acid, adipic-d₁₀ acid, suberic-d₁₂ acid, levoglucosan-u-¹³C₆, homovanillic-2,2-d₂ acid, myristic-d₂₇ acid, heptadecanoic-d₃₃ acid, oleic-9,10-d₂ acid, tetradecanedioic-d₂₄ acid. Samples were extracted using the Dionex Accelerated Solvent Extraction (ASE) apparatus with acetone. These extracts were then concentrated by rotary evaporation followed by moisture filtered ultra high purity (UHP) nitrogen blow down to 100 microliters and transferred to 300µl silanized glass inserts (National Scientific Company, Inc.). Samples were further evaporated to 50µl, and 25µl of pyridine, 25µl of the internal standards, and 150µl of BSTFA with 1% TMCS [N, O-bis (trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane (Pierce)] were added. These derivatizing reagents convert the polar compounds into their trimethylsilyl derivatives for analysis of organic acids, methoxyphenols, and levoglucosan. The glass insert containing the sample was put into a 2 ml vial and sealed. The sample was then placed into a thermal plate (custom made) containing individual vial wells at 70°C for 2 hours. All samples were analyzed by GC/MS within 18 hours to avoid degradation. The samples were analyzed by electron impact ionization GC/MS technique using a Varian CP-3400 gas chromatograph with a model CP-8400 Auto-sampler and interfaced to a Varian 4000 Ion Trap Mass Spectrometer. Injections are 1µl in size in the splitless mode at 280 °C onto a 30 m long 5% phenylmethylsilicone

fused silica capillary column (CP-Sil 8 MS with 1 m deactivated guard column or Factor Four VF-5ms with an integrated 10 m of deactivated guard column). Initial column oven temperature was 50 °C held for 8 min then ramped to 320 °C at 8 °C per min and held for 5 min, for a total of 47 minutes. Identification and quantification of the analytes were made by monitoring the base peak ions of each analyte and each internal standard. Calibration of GC/MS instrument was performed with six levels of calibration solutions that were freshly prepared and derivatized identically as samples for each analytical set. Calibration curves were made for the base ion peaks of the compounds of interest using the deuterated species most closely matched in volatility and retention characteristics as internal standards and the authentic standards of quantified polar compounds. The calibration check (using median calibration standards) was run every 10 samples to check for accuracy of analyses. If the relative accuracy of measurement (defined as a percent difference from the standard value) was less than 20%, the instrument was recalibrated.

The measurement uncertainties associated with each individual compound were reported as the combined root mean square of the replicate precision for analytical uncertainty, which is defined by the following equation:

$$\text{Analyte uncertainty} = \sqrt{(\text{precision} * \text{concentration})^2 + (\text{MDL})^2}$$

where MDL = method detection limit.

This equation incorporates the analyte detection limit for each compound so when concentrations approach zero the error is reported as the analyte detection limit. Analytical precision was measured directly by replicate analysis of 4 duplicate analyses as part of the whole database.

2.3.3.3 Analysis of Teflon filters for PM mass

Weighing was performed on a Cahn 31 electro microbalance with ±0.001 mg sensitivity. Unexposed and exposed Teflon-membrane filters were equilibrated at a temperature of 20 ±5 °C and a relative humidity of 30±5% for a minimum of 24 hours prior to weighing. 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 200 mg Class 1 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 $\pm 5 \mu\text{g}$, the balance is recalibrated. If the difference exceeds $\pm 15 \mu\text{g}$, the balance is recalibrated and the previous 10 samples are re-weighed. 100% of the initial weights and 30% of the final weights are checked by an independent technician and samples are re-weighed if these check-weights do not agree with the original weights within $\pm 0.010 \text{ mg}$. 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.

2.3.3.4 Analysis of Teflon filters for elements

Energy Dispersive X-ray Fluorescence (EDXRF) analysis was performed on Teflon-membrane filters using a PANalytical Epsilon 5 EDXRF analyzer. Ten separate XRF analyses are conducted by the PANalytical instrument on each sample to optimize the detection limits for the specified elements Calibration against the same standards and regular cross-checks between excitation conditions assures comparability of the results.

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. The vacuum in the x-ray chamber and the heat induced by the absorption of x-rays may evaporate some materials, such as ammonium nitrate. A QC standard and a replicate from a previous analysis will be analyzed with each set of 10 filters. When a QC value differs from specifications by $\pm 10\%$ or more, or when a replicate value differs from the original value (where values exceed 10 times the detection limits) by $\pm 10\%$ or more, the previous 10 filters are reanalyzed. If further tests of standards show that the system calibration has changed by more than $\pm 5\%$, the instrument is recalibrated. In addition, DRI maintains a set of laboratory blanks that are analyzed periodically (~1 blank for every 20 filters analyzed) to test for baseline shifts in blank values. Also, as part of Level II data validation, field blank

values for each shipment are plotted by element as time series to check for potential shifts in baselines and potential contamination.

After EDXRF analysis, the Teflon-membrane filters are returned to their Petri slides and stored under refrigeration until the XRF data validation is completed and indicates that the runs were acceptable.

2.3.3.5 Analysis of Teflon filters for ions

Chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}) ions were measured with the Dionex 2020i (Sunnyvale, CA) ion chromatograph (IC). The Dionex system contains a guard column (AG4a column, Cat. No. #37042) and an anion separator column (AS4a column, Cat. No. #37041) with a strong basic anion exchange resin, and an anion micro membrane suppressor column (250' 6 mm ID) with a strong acid ion exchange resin. The anion eluent consists of sodium carbonate (Na_2CO_3) and sodium bicarbonate (NaHCO_3) prepared in distilled, deionized water. The eluent passes through a self regenerating suppressor and then to the conductivity detector. The resulting peaks are integrated and the integrals are converted to concentrations using calibration curves derived from solution standards.

The working calibration standards are prepared from an NIST traceable solution purchased from Dionex. They are prepared in concentrations that are compatible in range with the expected concentrations of the samples, ordinarily from 0.05 to 5.0 micrograms per mL. A calibration curve is generated at the beginning of each run using these prepared standards, which are also run as check standards after every 10th sample. Secondary NIST traceable check standards from Environmental Research Associates (ERA) are used in each run as quality assurance standards. Working standards are prepared as needed, but at least once a month. Replicate samples of the extracts are run every ten samples.

After analysis the resulting chromatograms are reviewed on screen for the following: proper operational settings, peak shapes, peak overlaps, and quality control comparisons. When the values of the standards or the replicate samples vary by more than a percentage based on their concentration, the previous 10 samples are rerun. Dilutions are prepared and run if the extracts are outside of the calibration range.

2.3.3.6 Analysis of Teflon filters for soluble potassium

The analysis of soluble cations is performed on a Varian (Varian Instruments, Sugarland, TX) SpectrAA 880 Atomic Absorption Spectrometer. Atomic absorption spectroscopy methods rely on the principle that free, uncombined atoms will absorb light at specific wavelengths corresponding to the energy requirements of the specific atom. Atoms in the ground state absorb light and are excited into a higher energy state. Each transition between energy states is characterized by a different energy, and therefore a different wavelength of light. The atomic spectrum of each element comprises a number of discrete lines arising from both the ground and excited states. The lines which originate in the ground state atoms, called resonance lines, are the most often of interest in atomic absorption spectrometry, as ground state atoms are most prevalent in practical atomization methods. The amount of light absorbed is proportional to the concentration of the atoms over a given absorption path length and wavelength. Standards of known concentration are prepared, matched to the sample matrix, and measured. The unknown sample absorbencies are compared to the absorbencies of the standards. Since the measured absorbance is directly proportional to the concentration of analyte this gives a simple and accurate method of determining the unknown concentration. Teflon filters, after performing XRF analysis will be extracted in 5 ml of water. A standard curve will be generated for each run using NIST traceable primary standards. The calibration will be verified with NIST traceable secondary standards. A replicate sample, blank, and check standard are run every ten samples.

2.3.4 Synoptic Meteorology during Sampling Events in 2008

The synoptic scale weather pattern affecting the Southwest US and the Clark County DAQEM project area during the initial two days of the IOP#2 (June 23 and 24) produced light flow conditions and somewhat limited mixing conditions in the project area that were conducive to moderate ozone development and weak transport from the west to southwest. This flow pattern would indicate that light transport conditions from the west to northwest were operating during the early morning of the 23rd, shifting to westerly to southwesterly transport by the afternoon. The “mixing” layer depth remained consistent during the

remainder of the field sampling operational period while wind flow became stronger southwesterly during the 24th and 25th. (see T&B draft report, Bush et al., 2008).

The outbreak of numerous wildfires in the northern half of California on June 21 did not affect the smoke situation in the southern half of the state and the field sampling operational period. However, the “Clover” fire in Tulare County in the South Sierra Wilderness did produce a substantial smoke cloud by the afternoon of June 22. The descriptive narrative for smoke observed in satellite imagery issued by the National Forest Service (NFS) stated that: “The Clover fire in eastern Tulare county has continued producing moderately dense to dense smoke which is fanning out to the east and reaching into southwestern Nye county, NV.” By 6/23, the NFS statement read: “Another wildfire (the Clover fire) on the Tulare and Inyo county border is emitting moderately dense smoke moving east across Inyo County.” With the light westerly flow indicated by the synoptic weather pattern and the DRA rawinsondes, it appears likely that the smoke that affected southern Nevada and Clark County on 6/23 came from the Clover fire in the southern Sierra.

Smoke continued in Clark County during June 24 and 25, but it is not clear if that smoke was left over from the Clover fire, or if it had origins from the other numerous fires in California. The MODIS satellite images for that period provide no visual information as to a definitive origin of the diffuse smoke cloud in southern Nevada.

The objective of the sampling operations on July 9 -10 (IOP#3) was to document particulate and air chemistry signatures associated with high ozone levels when regional background was not significantly influenced by wildfire smoke or other significant ozone transport from adjacent air basins.

A broad area of high-pressure dominated the synoptic weather pattern over the Southwest US by July 7. In addition, a large eastern Pacific ridge was circulating off the northern California coast. As a result, gradient flow in the southern Great Basin, including southern Nevada, was characterized by light easterly to southeasterly flow, and atmospheric dispersion conditions were typical of mid-summer in the desert. Strong surface heating during the daylight hours produced mixing layers that extended to above 10,000 ft msl. With the very light and somewhat variable flow pattern, and the generally stable subsiding nature

of the air mass associated with the high pressure, hot dry stagnant conditions prevailed in the region.

This broad area of high pressure continued to dominate the synoptic weather pattern over the Southwest US on July 8. Another prominent feature was a large eastern Pacific ridge positioned off the northern California coast. Gradient flow in the southern Great Basin, and southern Nevada remained light easterly to southeasterly. Hot dry stagnant conditions continued in the entire region.

This basic synoptic weather pattern continued to dominate over the Southwest US on July 9. The large eastern Pacific ridge located off the northern California coast had extended inland and joined with the interior high. Again the gradient flow in the southern Great Basin and southern Nevada was generally light and easterly. Local diurnal flow patterns were therefore dominant in the region. Associated with the broad high-pressure ridge was a stable sinking air mass in the region resulting in stagnant air dispersion conditions.

The high-pressure dominated weather pattern continued to be the main synoptic feature over the Southwest US for one more day on July 10. The primary center of the ridge now extended out over the Pacific Ocean off northern California, but pressure gradients remained very flat over the southern Great Basin and southern Nevada. A weak, closed cyclonic circulation off the southern Baja coast started to pump moisture into the southern portions of the ridge, triggering thunderstorm activity in Arizona beginning on the 9th. As the interior high weakened during the next few days, the monsoonal moisture spread into the region by the 11th, resulting in a breakdown of the weather conditions that had prevailed. However, the light gradient flow and stagnant dispersion conditions still continued through July 10, resulting in a lack of definitive transport flow, and air mass recirculation in the local diurnal flow patterns.

3. RESULTS AND DISCUSSION

This section presents the selected, the most important data from the 2005 and 2008 study. The full data set is submitted in the electronic format with this report.

3.1 Results from the 2005 Filter Analysis

3.1.1 Chemical Analyses

Table 3.1 lists the samples submitted to DRI Organic Analytical Laboratory for analysis. There were 24 samples, including 5 field blanks, collected at 6 different sites abbreviated as AP, CL, GV, JD, JN, and SA. All samples were collected between June 21 and July 3, 2005, but only selected samples from each site were submitted for analysis. Table 3.1 also lists concentrations of fine particulate matter (PM_{2.5}) recorded for these dates.

Table 3.1. List of filter samples analyzed for biomass smoke tracers

Site	Date	Filter No	PM_{2.5} (µg/m³)
AP	6/27/2005	T4184909	3.71
	7/3/2005	T4184936	8.29
CL	6/27/2005	T4184899	4.58
GV	6/30/2005	T4184920	17.00
JD	6/27/2005	T4184908	5.00
	6/30/2005	T4184918	32.08
	7/3/2005	T4184932	10.33
JN	6/21/2005	T4184884	6.87
	6/27/2005	T4184911	3.04
	6/30/2005	T4184919	11.38
SA	6/21/2005	T4184891	12.97
	6/22/2005	T4184892	11.91
	6/23/2005	T4184895	14.68
	6/27/2005	T4184914	4.42
	6/28/2005	T4184915	6.74
	6/29/2005	T4184916	31.65
	6/30/2005	T4184917	33.61
	7/1/2005	T4184921	13.09
	7/2/2005	T4184922	8.30
CL	7/3/2005	T4184927_FB	Field Blank
JD	7/3/2005	T4184933_FB	Field Blank
JN	6/21/2005	T4184885_FB	Field Blank
SA	6/22/2005	T4184893_FB1	Field Blank
	7/2/2005	T4184923_FB2	Field Blank

As shown in Table 3.1, the highest PM_{2.5} concentrations were observed on 6/30/05 at each site (if a sample was collected on this date). In addition, a very high PM concentration was recorded on 6/29/05 at SA site. Relatively high concentrations were also observed on 6/21-23 and 7/1 at this site.

Figure 3.1 shows the concentrations (in ng/m³) of the main biomass smoke tracers for all samples listed in Table 3.1. As Figure 3.1 shows, the highest concentrations of levoglucosan, the main biomass burning marker, are observed on 6/30/05 at all sites. In addition, very high concentrations of this marker are also observed on 6/30/05 and 6/23/05 at SA site. The sample collected on 6/23/05 contains also a high concentration of dehydroabietic acid, which is one of the resin acids typically found in the emissions from coniferous woods, pine needles and other foliar fuel (Hays et al., 2002). Figure 3.2 shows the concentrations of resin acids in the samples. Clearly, the sample collected on 6/23/05 at SA is different from the other samples with high levoglucosan concentrations, as far as the concentration of resin acids is concerned, which indicates different type of biomass burning.

To further gain insight into the type of the biomass burning that affected the Las Vegas area, we examined methoxyphenol concentrations. Figure 3.3 shows the syringol (2,5-dimethoxy-phenol) and guaiacol (2-methoxy-phenol) derivative concentrations. Although the concentrations of these species are rather low, the most abundant are vanillic acid (guaiacol derivative), syringic acid and syringaldehyde (both syringol derivatives). As mentioned above, both syringols and guaiacols are formed during pyrolysis of deciduous lignin (hardwood) but during pyrolysis of coniferous lignin (softwood), syringols are generally not formed (McDonald, 2000). Sagebrush, foliar fuel and grasses emit both guaiacols and syringols, but pine needles (especially white pine needles) have a high PM fraction of

guaiacols with very little syringols, similar to softwoods (Mazzoleni et al, 2007, Hays et al., 2002). Samples collected on 6/29/05 and 6/30/05 contain vanillic acid, syringic acid and syringaldehyde, whereas sample collected on 6/23/05 contains 4-formyl-guaiacol and homovanillic acid in addition to vanillic and syringic acid.

These data taken together indicate that the biomass burned during the fire that impacted the Clark County area on 6/29/05 and 6/30/05 was primary a mixture of sagebrush, grasses and/or some foliar fuel, whereas the biomass burned on or before 6/23/05 had a higher component of coniferous wood and pine needles. Thus, both these wild fires originated most probably in different areas.

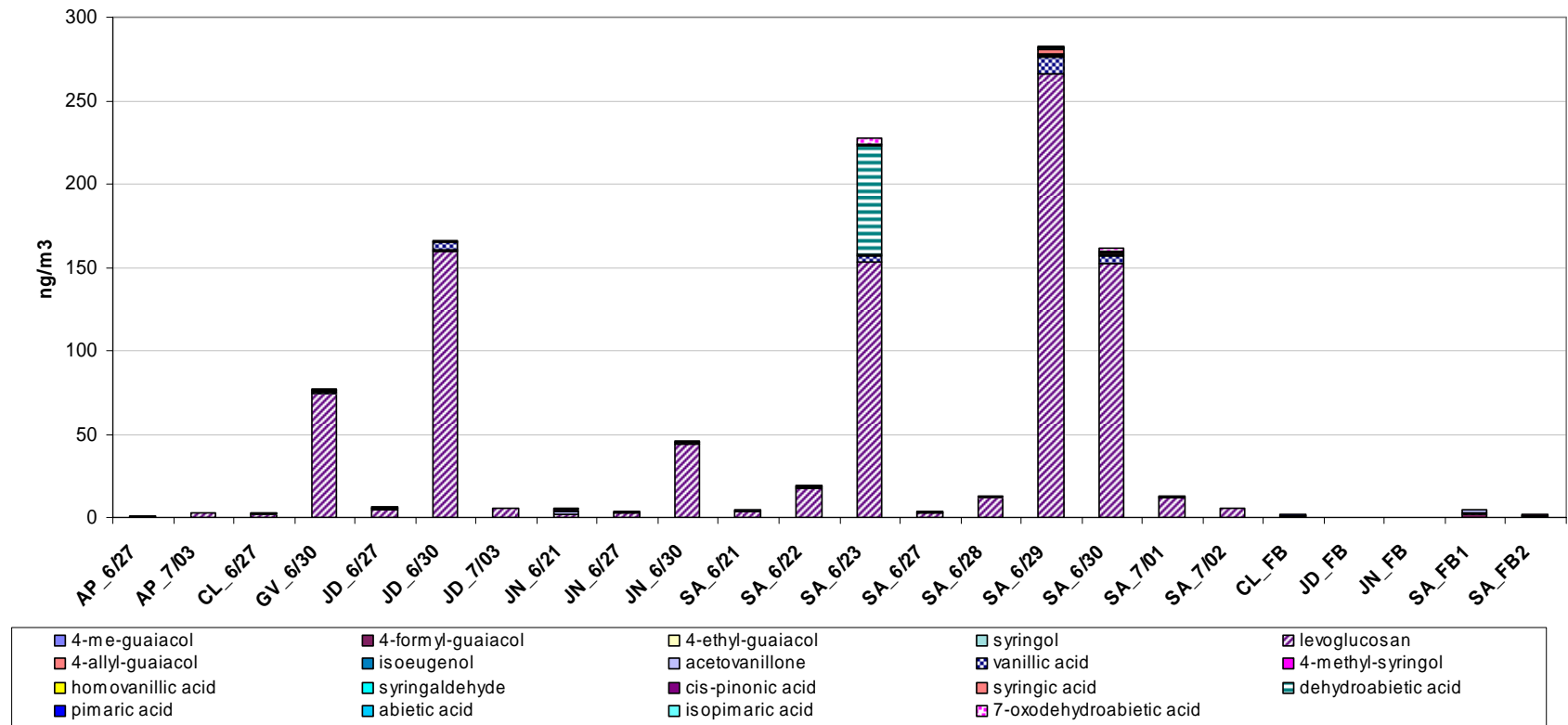


Figure 3.1. Biomass burning tracers for all analyzed Clark County samples.

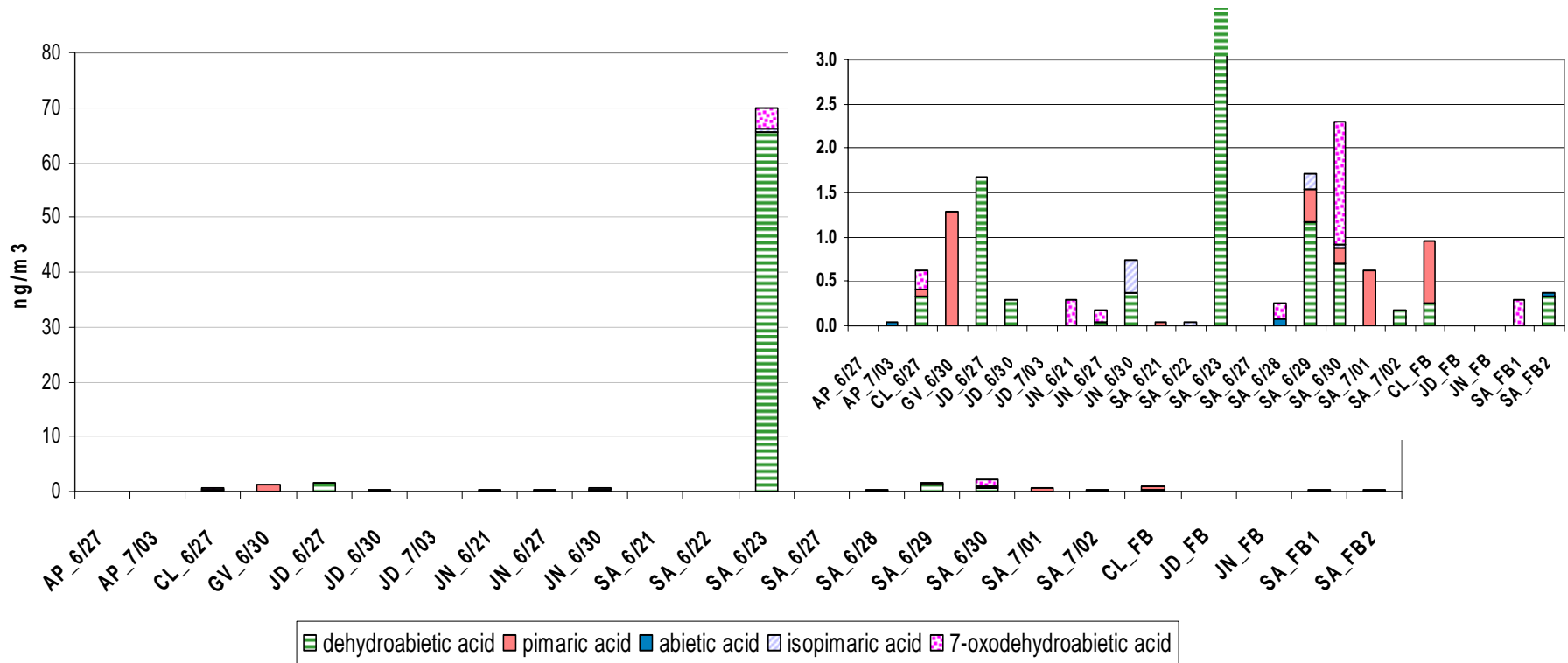


Figure 3.2. Resin acid concentrations in the Clark County samples analyzed for biomass burning tracers. The inset shows samples with very low abundance of resin acids.

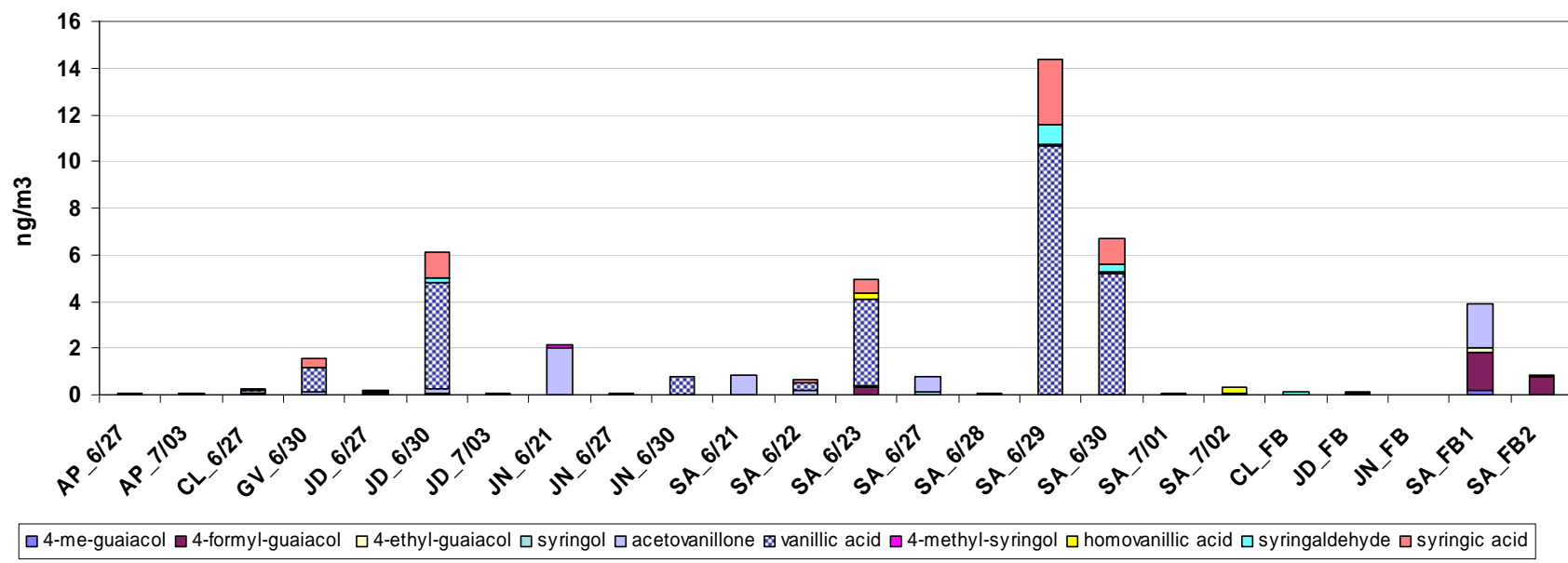


Figure 3.3. Methoxy-phenol concentrations in the Clark County samples.

3.1.2 Satellite Images

Figures 3.4, 3.5 and 3.6 show the satellite images of the area that was impacted by the wild fires on 6/23/05, 6/29/05 and 6/30/05, respectively. The red dots indicate the fire location and its size. The direction of the plume from each fire is also visible. As Figure 3.4 shows, on 6/23/05 the Las Vegas area was impacted by the smoke from the fires located east and south-east of the area, in a southern Nevada and in California. Figures 3.5 and 3.6 show that the main smoke impact on 6/29 and 6/30/05 was from the wild fires located west and south of Las Vegas, mostly in Arizona and southern tip of Nevada. Although the exact mix of vegetation burned during these fires is not known, it is likely that coniferous woods, pine needles and foliar fuel were the main contributors to fires recorded on 6/23/05, whereas a desert type of vegetation was more prominent in the wild fires on 6/29 and 6/30, 2005.

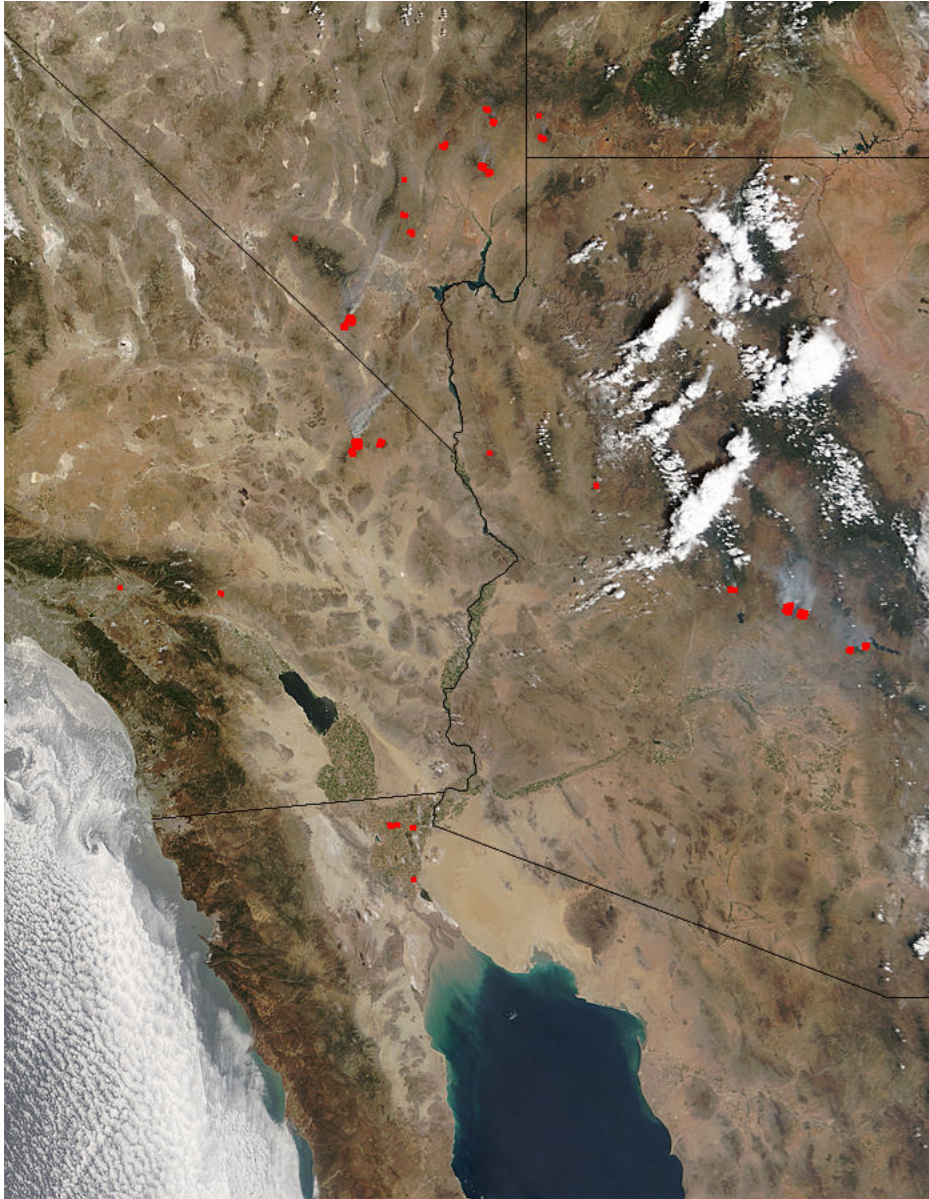


Figure 3.4. Wild fire locations on June 23, 2005.

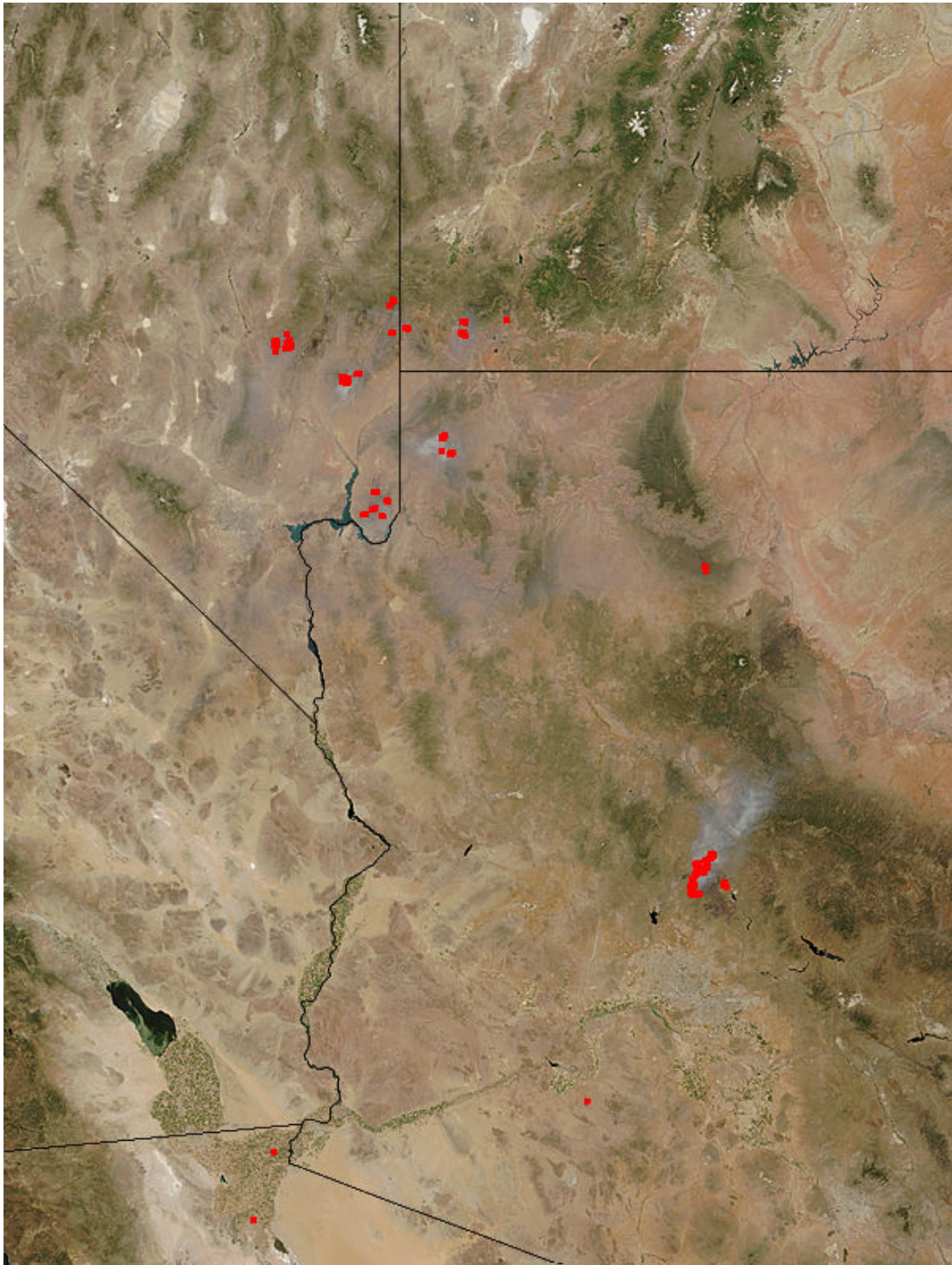


Figure 3.5. Wild fire locations on June 29, 2005.

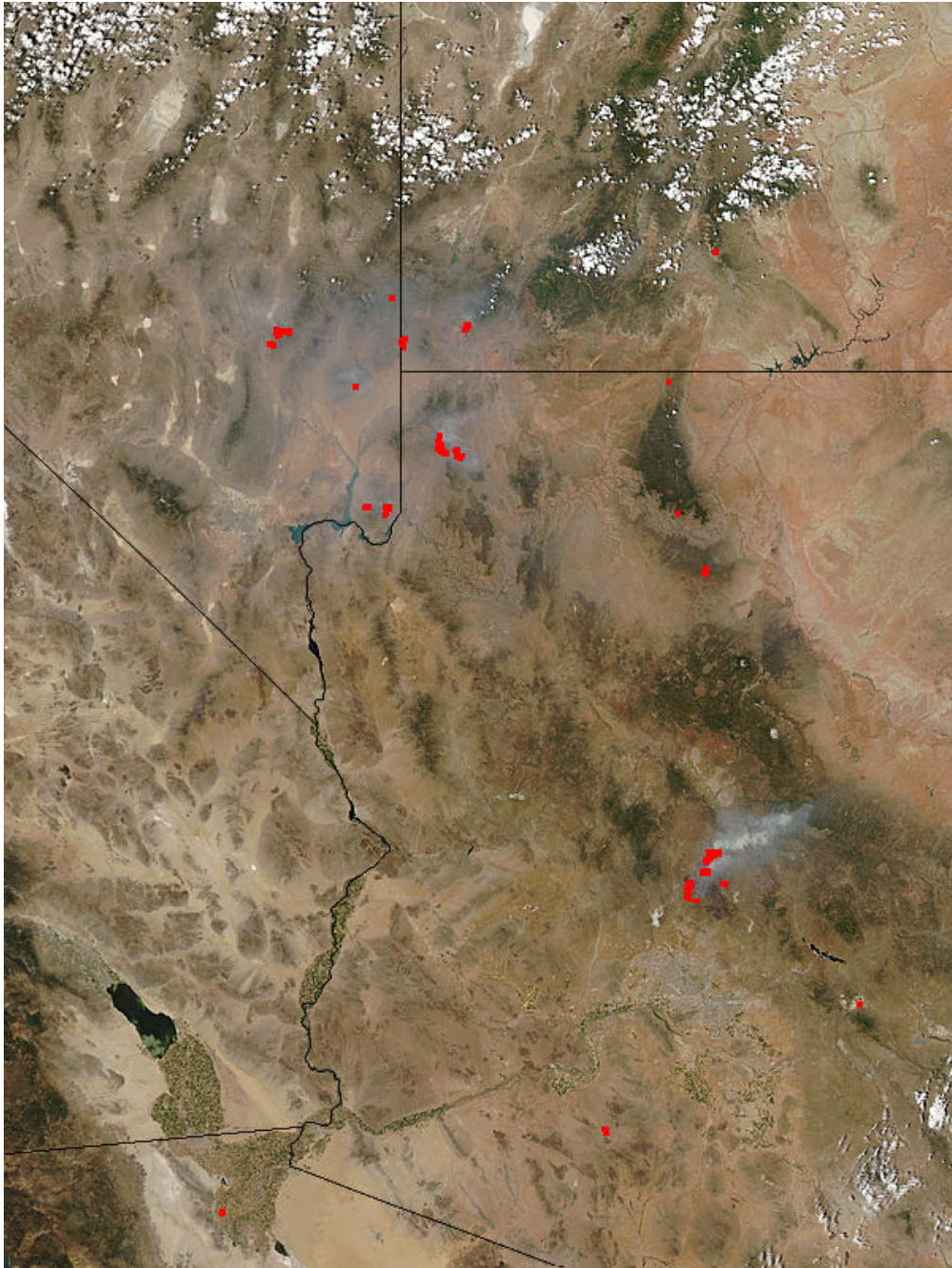


Figure 3.6. Wild fire locations on June 30, 2005

3.1.3 Ozone and Levoglucosan Correlations in 2005 Study

Since levoglucosan is the most abundant, stable and universal biomass emission marker, it was interesting to examine the correlations between ozone and levoglucosan concentrations for the 2005 samples. The ozone data were obtained from the DAQEM web page, at http://www.ccairquality.org/cgi-bin/daily_average.pl. The average and maximum daily O₃ concentrations during the days the PM samples were collected were corrected for O₃ concentrations when there was no influence of wildfire emissions. The ozone concentrations from the days before and after the event were averaged and subtracted from the ozone concentrations during the event. Only Sunrise Acres (SA) levoglucosan data were used for these correlations, since only this site has a sufficient number of samples analyzed (see Table 3.1). Figures 3.7 and 3.8 show the average and maximum ozone concentration correlations with levoglucosan, respectively.

As it can be seen from these figures, 24-hr levoglucosan and corrected ozone concentrations track each other very good (Fig 3.7A) with the exception of the last day of collected data, 7/2/05. If this one point is excluded from the correlation between the concentrations of these two species, the correlation coefficient (R^2) improves from 0.27 to 0.68. Since the levoglucosan concentration for this day is low, the increase in ozone is most probably due to other than wildfire sources. For 1-hr maximum ozone concentrations (Figure 3.8 B) the correlation is slightly worse, $R^2 = 0.64$. This can be expected, as we compare here 1-hr ozone with 24-hr levoglucosan concentrations.

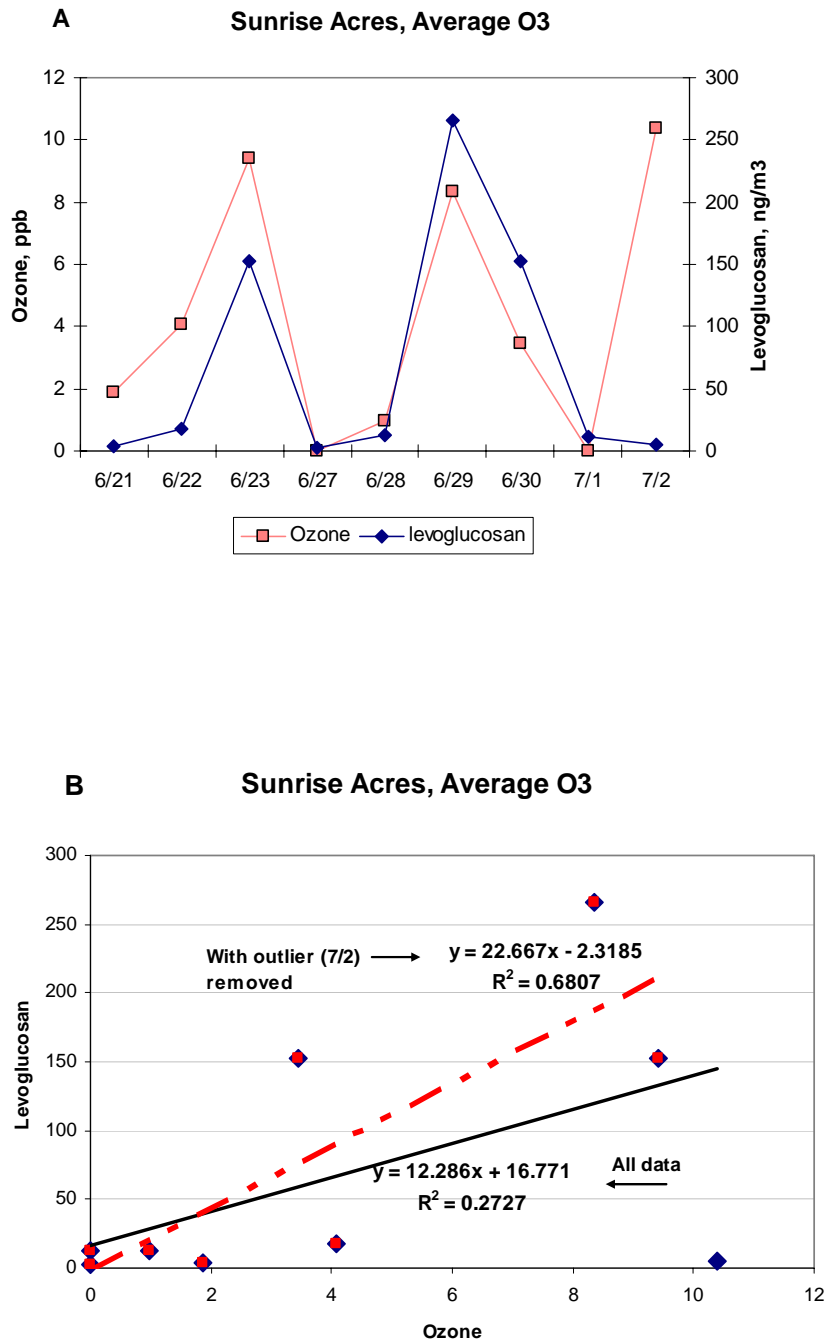


Figure 3.7. Corrected average (24 hr) ozone and levoglucosan concentrations at the SA site (A); and correlation between these concentrations (B). Red dotted trend line shows the correlation with the outlier (7/2) removed

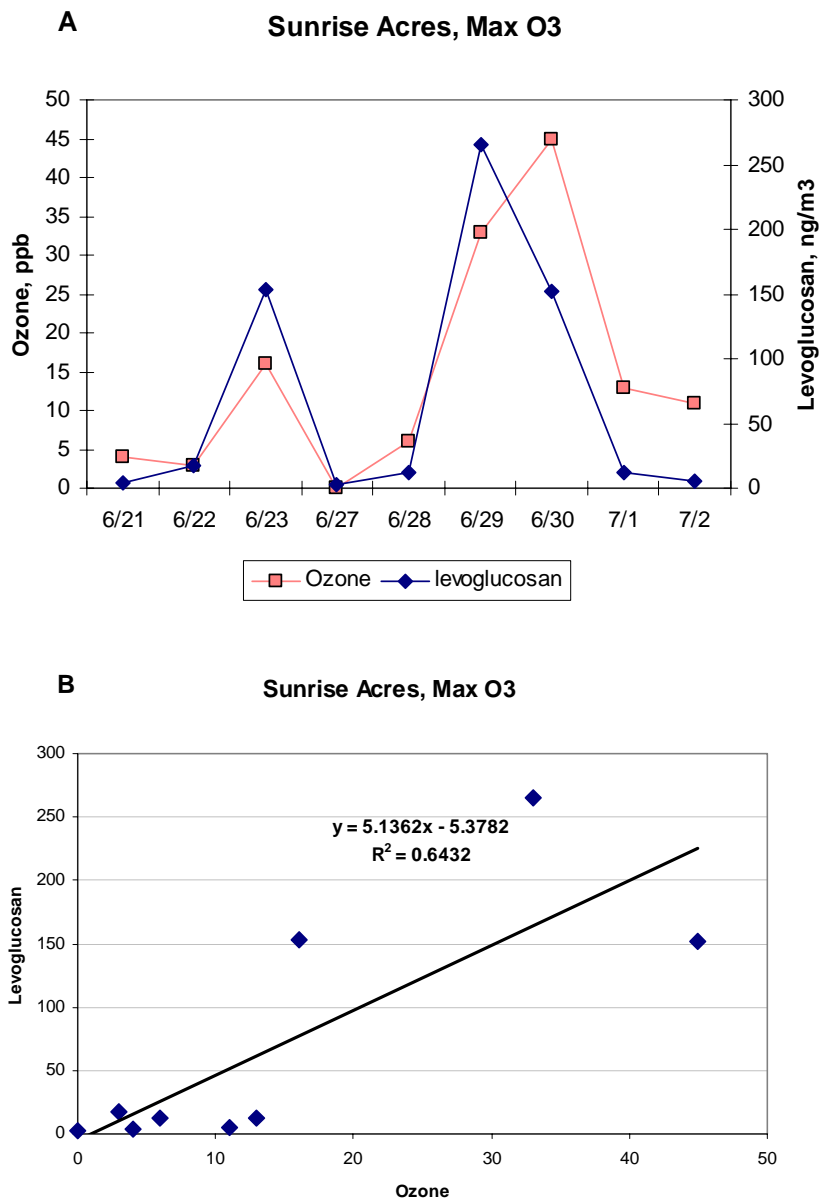


Figure 3.8. Corrected maximum (1 hr) ozone and 24- hr levoglucosan concentrations at the SA site (A); and correlation between these concentrations (B).

3.2 Results from the 2008 Study

3.2.1 Canister Samples

Table 3.2 lists the VOC analyzed for this study. Compounds that are marked with the asterisk are the most abundant and are shown in Figure 3.9.

Table 3.2 List of VOC (with their mnemonics) analyzed from canisters.

Mnemonic	Compound	Mnemonic	Compound
ETHANE	Ethane*	CYHEXE	Cyclohexene
ETHENE	Ethane*	HEXA3M	3-Methylhexane
ACETYL	Acetylene*	CPA13M	1,3-Dimethylcyclopentane (cis)
PROPA	Propane*	N_HEPT	n-Heptane*
PROPE	Propene*	HEP1E	1-Heptene
IBUTA	iso-Butane*	P2E23M	2,3-Dimethyl-2-Pentene
BUTAN	n-Butane*	MECYHX	Methylcyclohexane
T2BUT	t-2-Butene	PA234M	2,3,4-Trimethylpentane
C2BUT	c-2-Butene	TOLUE	Toluene*
BUT1E	1-Butene	HEP2ME	2-Methylheptane
IBUTE	Iso-Butene	HEP4ME	4-Methylheptane
BUD13	1,3-Butadiene	HEP3ME	3-Methylheptane
BUD12	1,2-Butadiene	N_OCT	n-Octane*
N_PENT	n-Pentane*	ETBZ	Ethylbenzene*
IPENT	iso-Pentane*	MP_XYL	m&p-Xylene*
PENTE1	1-Pentene	STYR	Styrene*
B1E2M	2-Methyl-1-Butene	O_XYL	o-Xylene*
I_PREN	Isoprene	N_NON	n-Nonane*
T2PENE	t-2-Pentene	IPRBZ	Isopropylbenzene
C2PENE	c-2-Pentene	N_PRBZ	n-Propylbenzene
B2E2M	2-Methyl-2-Butene	A_PINE	Alpha-Pinene
BU22DM	2,2-Dimethylbutane	M_ETOL	m-Ethyltoluene*
CPENTE	Cyclopentene	P_ETOL	p-Ethyltoluene*
CPENTA	Cyclopentane	BZ135M	1,3,5-Trimethylbenzene*
BU23DM	2,3-Dimethylbutane	O_ETOL	o-Ethyltoluene*
PENA2M	2-Methylpentane*	BZ124M	1,2,4-Trimethylbenzene*
PENA3M	3-Methylpentane*	N_DEC	n-Decane*
P1E2ME	2-Methyl-1-Pentene	BZ123M	1,2,3-Trimethylbenzene*
N_HEX	n-Hexane*	INDAN	Indan
T2HEXE	t-2-Hexene	DETBZ13	1,3-Diethylbenzene
C2HEXE	c-2-Hexene	DETBZ14	1,4-Diethylbenzene
HXDI13	1,3-Hexadiene (trans)	N_BUBZ	n-Butylbenzene
MCYPNA	Methylcyclopentane	N_UNDE	n-Undecane*

Mnemonic	Compound	Mnemonic	Compound
PA224M	2,2,4-Trimethylpentane	MECL	Chloromethane*
PEN24M	2,4-Dimethylpentane	FURAN	Furan*
BENZE	Benzene*	FU2ME	2-Methyl-Furan*
CYHEXA	Cyclohexane	FU25DM	2,5-Dimethyl-Furan*
HEXA2M	2-Methylhexane	FUFAL2	2-Furfural*
PEN23M	2,3-Dimethylpentane*	FUFAL3	3-Furfural*
		FU2ET	2-Ethyl-Furan*

Figure 3.9A shows the hydrocarbons in the range of C2-C6 (light VOC), Figure 3.9B – hydrocarbons from C6 to C11 (heavier VOC, including aromatic hydrocarbons) and Figure 3.9C shows furan derivatives and chloromethane that are considered wood smoke tracers. The five monitoring sites are shown in the order from north to south (See Figure 1 and 2), i.e. Apex (AP), Joe Neal (JO), JD Smith (JD), Walter Johnson (WJ) and Jean (JN).

As explained in the Experimental section, there were no wildfires registered on June 3, 2008, and this IOP was considered as a practice run. Since most of the samples were collected successfully, this run could also serve as a baseline run. IOP#2, from June 23 to June 26, was influenced by the Clover wild fire, as discussed in Section 2.2. For IOP#3, July 9 and 10, no direct wildfire impact was recorder. However, it is not clear if the smoke from the Clover wildfire was still in the area or there was some impact from the Northern California wildfires.

As Figure 3.9 shows, light hydrocarbons (A, C2-C6) are the most abundant with ethane, ethane, acetylene, propane and iso-pentane dominating this group of compounds. Among heavier hydrocarbons (B), BTEX compounds (i.e. benzene, toluene, ethylbenzene, xylenes) predominate. Furans and chloromethane show very low abundance (below 1 ppbv total), very close or below method detection limit that is between 0.05 – 0.1 ppbv. Chloromethane concentrations are nearly constant, indicating uniform background level in the area. The highest VOC concentrations are recorded for JD Smith site (JD), followed by Joe Neal (JO) and Walter Johnson (WJ) sites, that are located in the metropolitan Las Vegas area. Jean (JN) site, that is located south of Las Vegas shows the lowest VOC values, followed by Apex (AP), located north of Las Vegas (see Figure 2.1). Three urban sites (JD, JO, WJ) shows increase in VOC concentrations for IOP#2 and #3, as compared with IOP#1. This may indicate some impact of wildfires or increased motor vehicle activity.

Some light VOC, for example n-pentane or iso-pentane are usually attributed to evaporative gasoline emissions whereas ethene or acetylene - to motor vehicle combustion emissions. However, alkenes, such as ethene or propene are also emitted by wildland fires (see Table 1.1). Similarly, BTEX may be emitted by motor vehicles and/or wildfires. Figure 3.10 shows the correlations between pentane and iso-pentane (A), ethene and propene (B) and ethene and acetylene (C).

As Figure 3.10 shows, the correlation between pentane and iso-pentane is excellent for all IOPs ($R^2=0.97$) indicating single source of these species (most likely gasoline evaporative emissions). However, the correlation between ethene and propene (B) improves when only IOP#2 is included (from $R^2=0.8$ to $R^2=0.94$). The correlation between ethene and acetylene does not change significantly (from $R^2=0.37$ to $R^2=0.45$) and remain rather low. Since only IOP #2 was influenced by the wildfires, this may indicate that the concentrations of ethene and propene during this IOP are influenced mostly by wildland fire emissions, but acetylene originates mostly from motor vehicle emissions. However, these differences in correlations may also indicate the differences in photochemical reactivity of these compounds.

Similarly, the correlations between benzene and toluene and toluene and m/p-xylenes are very different for these IOPs. Figure 3.11A shows the correlations between benzene and toluene for all days, including IOP#1, 2 and 3. As it can be seen, this correlation is low ($R^2 = 0.31$). However, this correlation is very good for IOP #2 (Figure 3.11 B, $R^2 = 0.93$) and for IOP#3, if one outlier in Apex (high concentration of toluene is probably due to a local source) is removed (Figure 3.11C, $R^2= 0.98$). Figure 3.10D shows the correlations between toluene and m/p-xylene for IOP #2 ($R^2 = 0.96$) and #3 ($R^2 = 0.99$). Again, this may indicate different predominant sources during IOP#2 and #3, but it also may indicate differences in photochemical activity between IOP #2 and #3.

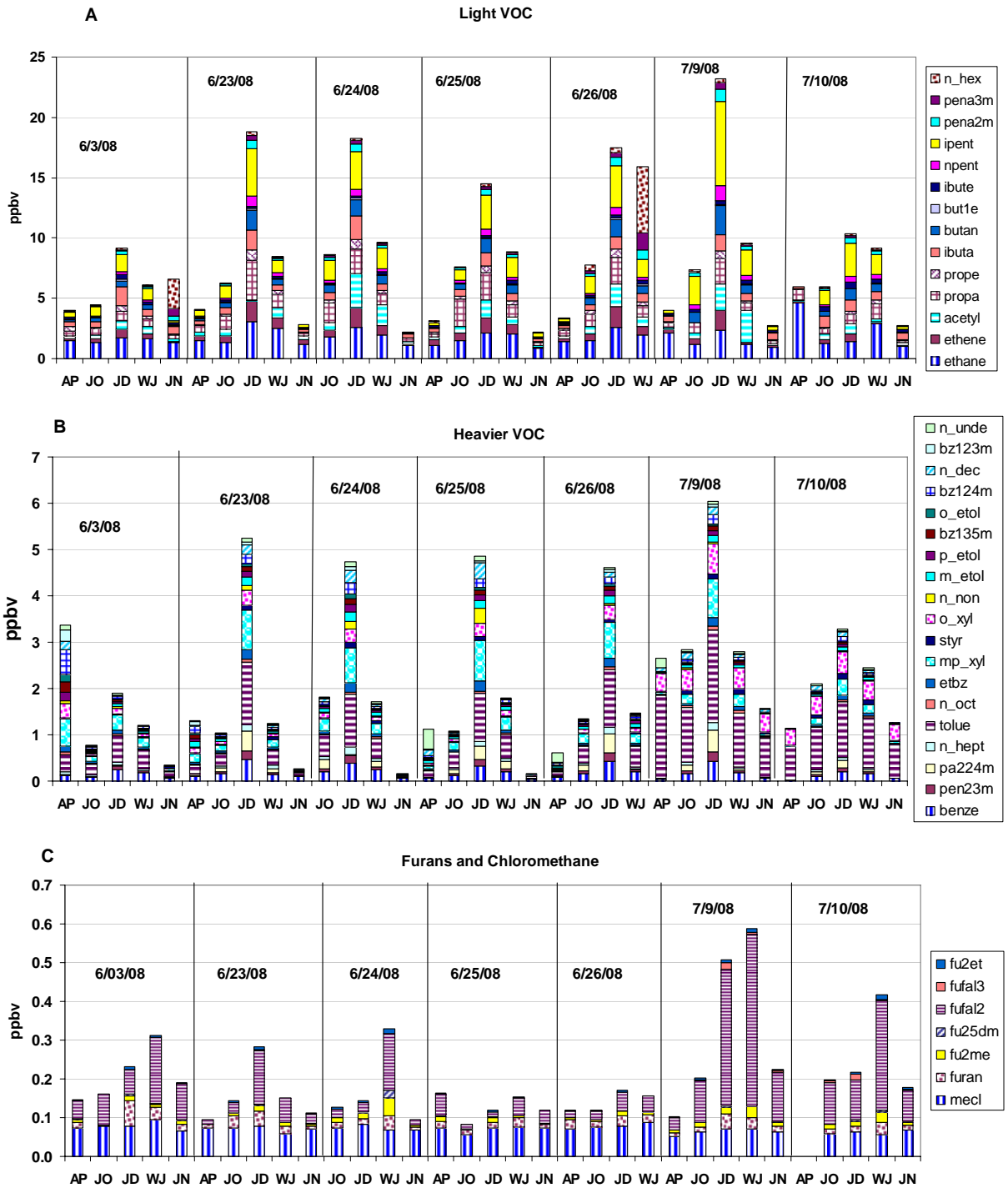
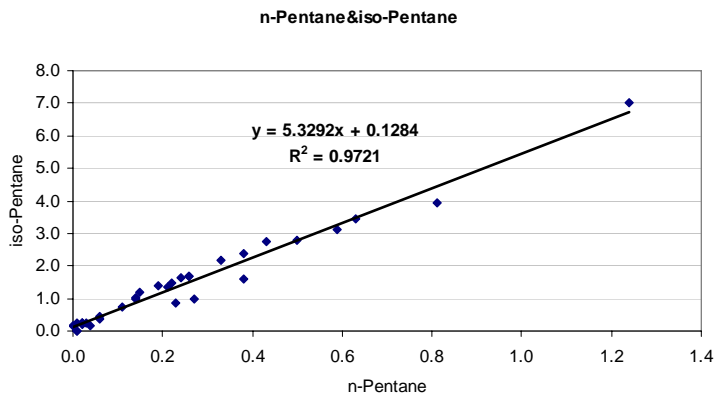
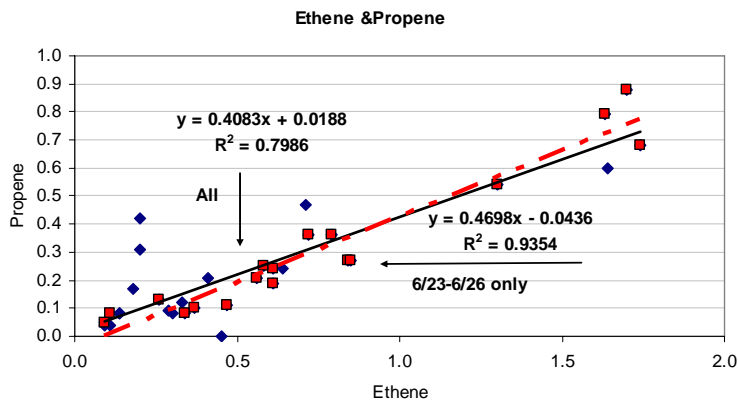


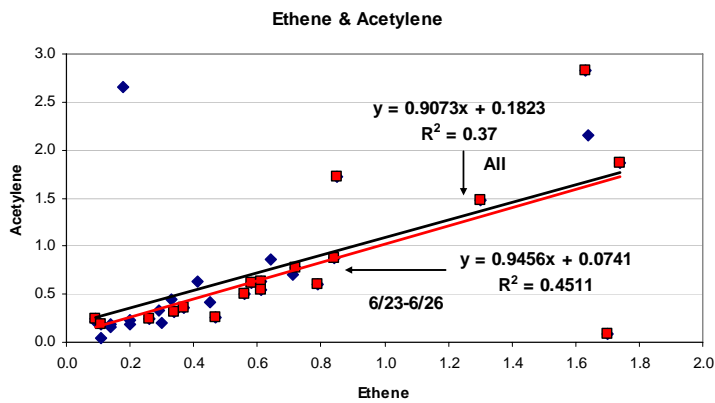
Figure 3.9. The most abundant VOC from canister samples collected during three IOP events (6/3/08, 6/23 – 6/26/08 and 7/9 – 7/10/08). A: light VOC, C2-C6; B: heavier VOC, C6-C12; C: furan derivatives and chloromethane. See Table 3.3. for compound mnemonics.



A



B



C

Figure 3.10. Correlations between pentane and iso-pentane (A); ethane and propene (B); and ethane and acetylene (C). Black trend line includes all data for IOP #1,2, and 3 and red trend line - data for IOP#2 (6/23-6/24/08) only

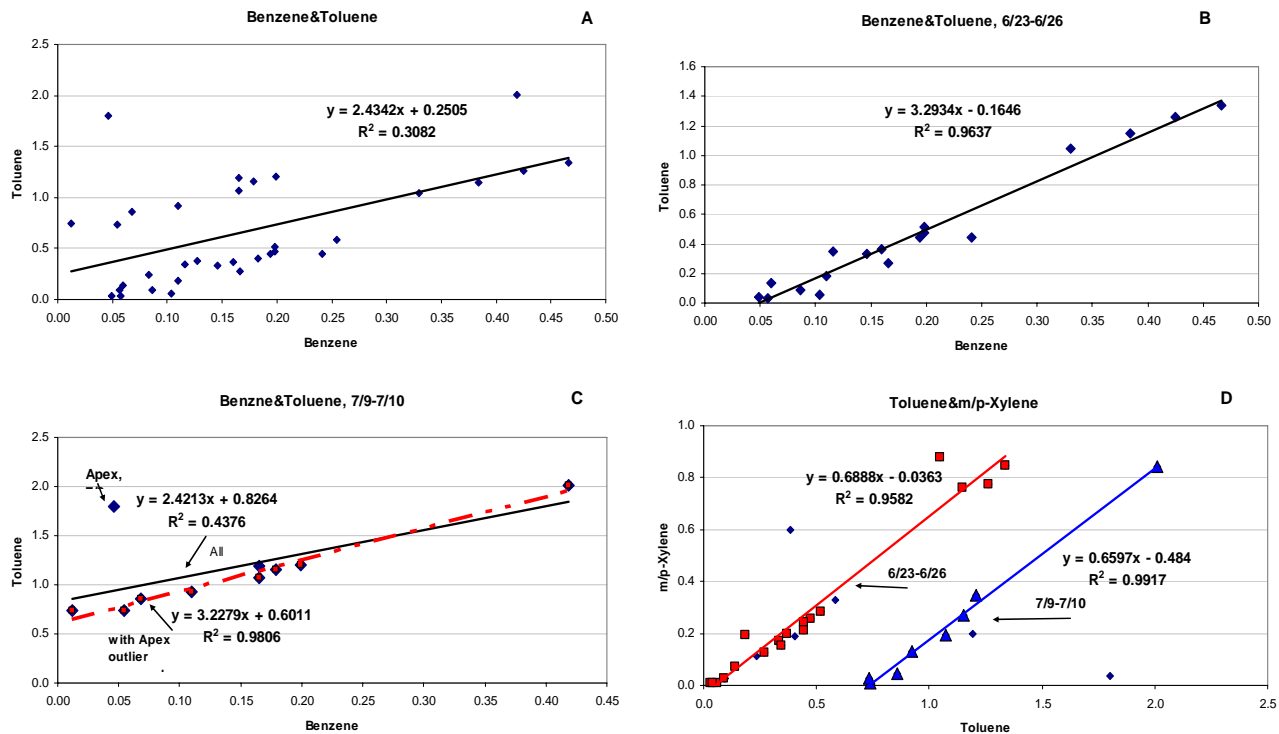


Figure 3.11. Correlations between benzene and toluene for all IOPs (A); for IOP#2 (B) and for IOP#3 (C). D: correlations between toluene and m/p-xylenes.

3.2.2 Carbonyl Samples

Carbonyl samples were collected only at two sites: Walter Johnson (WJ) and Joe Neal (JO). Table 3.3 shows the list of carbonyl compounds analyzed for this study. Figure 3.12 shows the concentrations of these species measured during three IOPs. To check for the breakthrough during sampling, each primary DNPH cartridge was equipped with a back-up cartridge and each pair of front-back-up cartridge was analyzed separately. As can be seen from Figure 3.12, breakthrough was generally negligible for all compounds (below 10%) with exception of acetone, for which the breakthrough up to 100% was observed for the IOP#3. This may be due to the higher relative humidity (RH) during the last period of sampling; it is known that acetone is more susceptible to the RH effect during a DNPH cartridge sampling. However, acetone is not photochemically active, thus it is of lesser interest for this study.

Table 3.3 List of carbonyl compounds analyzed for this study

Mnemonic	Compound
Formal	Formaldehyde
Acetal	Acetaldehyde
Aceto	Acetone
Acroln	Acrolein
Proal	Propionaldehyde
Croton	Crotonaldehyde
Mek	Methyl ethyl ketone
Macrol	Methacrolein
Butal	Butyraldehyde
Benzal	Benzaldehyde
Glyoxl	Glyoxal
Valal	Valeraldehyde
Tolual	m-Tolualdehyde
Hexal	Hexanaldehyde

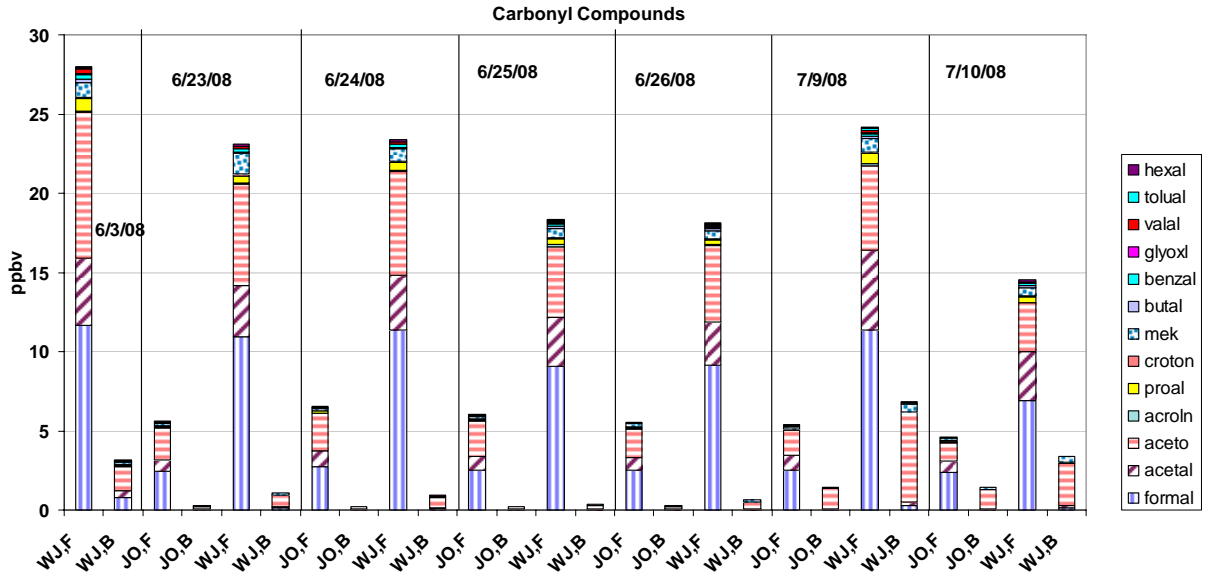


Figure 3.12 Carbonyl compound concentrations in Walter Johnson (WJ) and Joe Neal (JO) sites. F = front cartridge, B = back-up cartridge

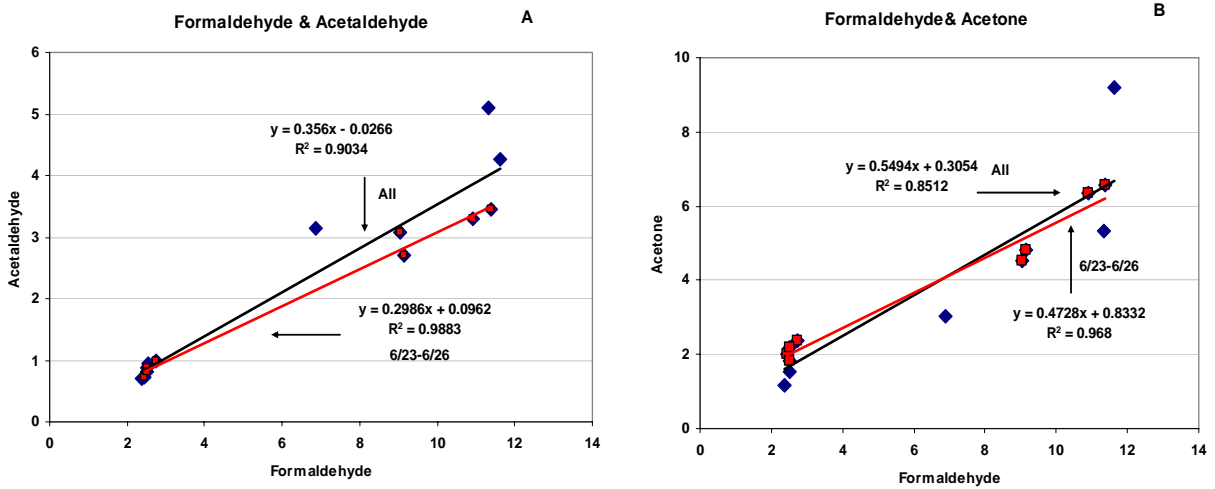


Figure 3.13. Correlations between formaldehyde, acetaldehyde (A) and acetone (B); black trend line includes all data for IOP #1,2, and 3 and red trend line - data for IOP#2 (6/23-6/24/08) only

As Figure 3.12 shows, the most abundant carbonyl compounds are formaldehyde, acetaldehyde and acetone and their concentrations are much higher at the WJ than JO site. These carbonyls can be directly emitted from motor vehicle or wildfires and/or can be produced in the atmosphere from photochemical transformation processes of VOC (predominantly from VOC and OH radical reactions). Figure 3.13 shows the correlations between formaldehyde and acetaldehyde (A) and formaldehyde and acetone (B). Although these correlations are good for all data ($R^2 = 0.90$ and 0.85 for A and B, respectively), the correlation coefficients improves significantly if the data from IOP #2 (6/23-6/26) are only included ($R^2 = 0.99$ and 0.97 , respectively). Since only IOP #2 was influenced by the wildfires, this may indicate that the concentrations of these carbonyls for this time period were dominated by the one common source, i.e. biomass burning emissions. As can be seen from Table 1.1, emissions of carbonyl compounds from the wildland fire events are significant.

3.2.3 Aircraft VOC and Carbonyl Samples

A total of four VOC canister samples and four carbonyl cartridges were collected. The sampling dates and times, airplane position and elevation are given in Table 3-4. Comments pertinent to each sample are provided as well.

Table 3.4. Aircraft sampling dates and times

Date	Time (PDT)	Latitude	Longitude	Altitude (m msl)	Comments
6/3/08	1757 – 1817	36.52	-115.53	2550	Aircraft practice area NW of airport
6/24/08	1231 – 1251	35.93	-115.73	1100 - 1300	Traverse over Sandy Valley, following terrain
7/9/08	1624 – 1644	35.65	-115.38	900 - 2950	Climbing spiral SW of Jean
7/9/08	1713 – 1733	36.15	-115.44	2950 - 2100	Descending spiral over Red Rock area

Canister VOC samples collected during these flights are shown in Figure 3.14 for light (A, C2-C6), heavier (B, C6-C11) hydrocarbons and for furans and chloromethane (C). As this figure shows, VOC concentrations measured during aircraft practice run on 6/3/08 are extremely low. In contrast, these concentrations on 6/24/08 and 7/9/08 are higher and similar to those measured at the ground sites. The highest VOC concentrations were observed on 7/9/08, which is in agreement with the ground monitoring sites in Las Vegas area (Figure 3.9)

Figure 3.15 shows the carbonyl compound concentrations collected during aircraft flights. Each primary cartridge was equipped with the back-up cartridge, to check for the breakthrough. Since the sampling rate was quite high (4 -5 L/min), much more breakthrough was observed for these samples as compared with ground sites samples where sampling rate was generally below 1 L/min. Unfortunately, the back-up cartridge from 6/24/08 was lost, but a similar breakthrough should be expected for this sample as for the remaining samples.

In contrast to VOC samples, significant concentration of carbonyl compounds was observed on 6/3/08, which makes the canister sample from this day somewhat suspicious. It is rather unlikely that there is such a big difference in VOC and carbonyl concentrations for the same sampling time and place. One of these samples (either the canister or carbonyl sample) is not correct.

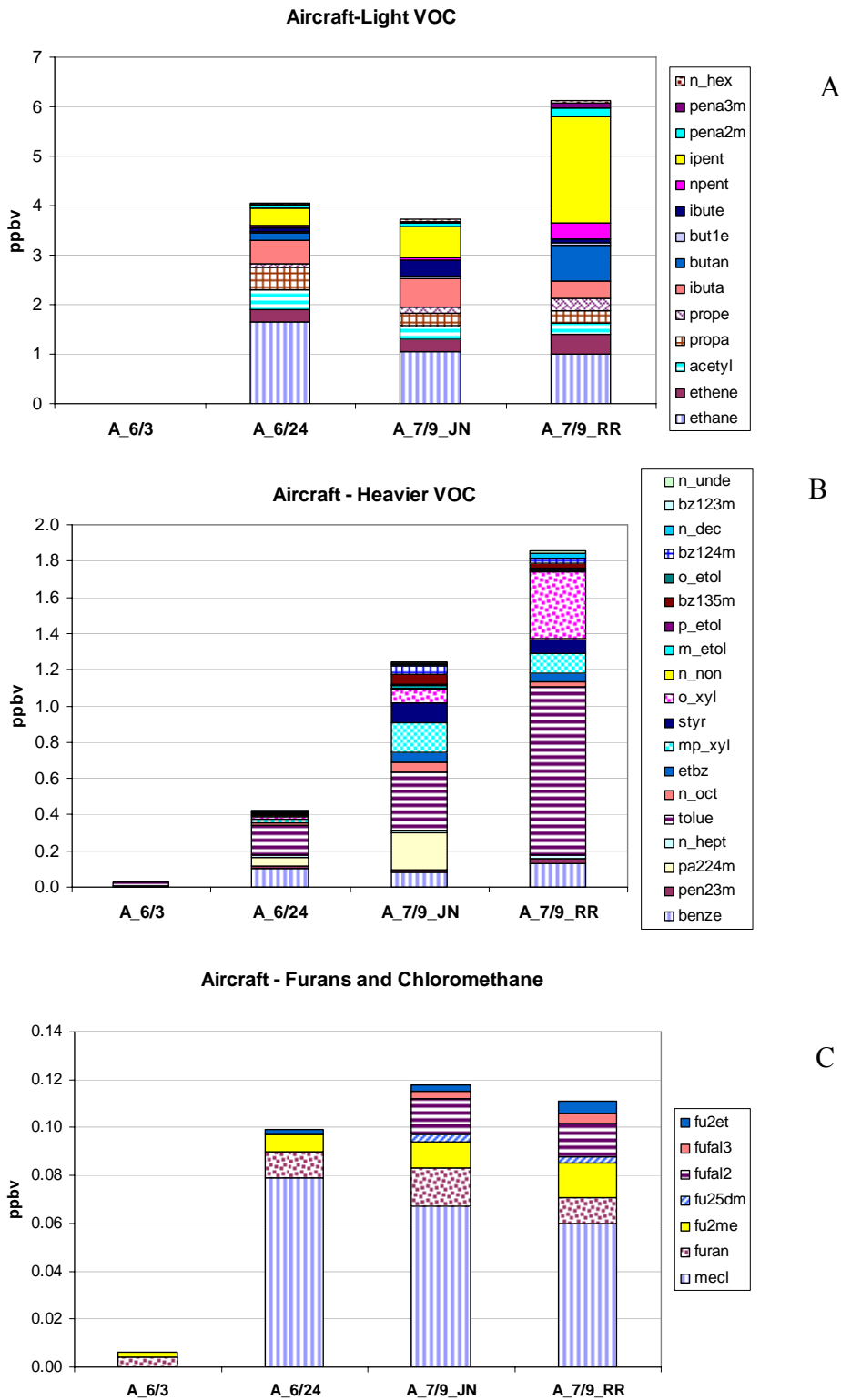


Figure 3.14. The most abundant VOC from canister samples collected during two aircraft flights (6/3/08, 6/24 and 7/9/08). A: light VOC, C2-C6; B: heavier VOC, C6-C12; C: furan derivatives and chloromethane. See Table 3.3 for compound mnemonics

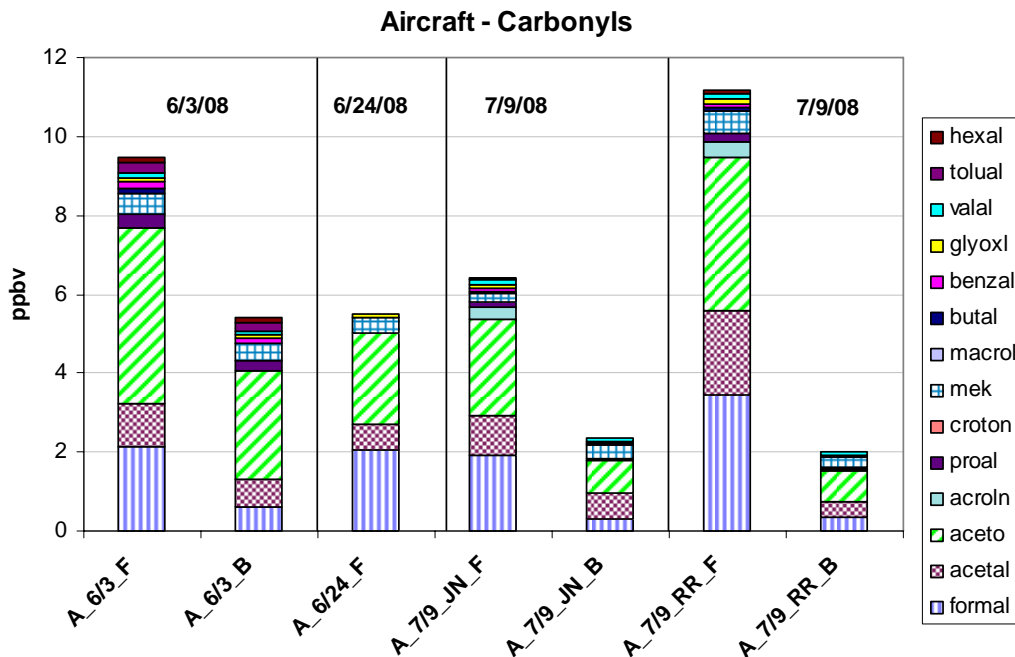


Figure 3.15 Carbonyl compound concentrations from the aircraft samples. F = front cartridge, B = back-up cartridge

3.2.4 Filter Samples

3.2.4.1 PM_{2.5} mass and organic/elemental carbon (OC/EC)

Gravimetric and OC/EC measurements were made from the Teflon and quartz filters, respectively, as described in Experimental section. Figure 3.16A shows the PM_{2.5} mass, organic and elemental carbon concentrations at the five measurement sites. As this figure shows, high PM mass was observed on 6/3/08, but the contribution of carbonaceous aerosol mass was rather low for this day in all sites. This indicates windy conditions and the contribution of crustal material to PM_{2.5} mass (as shown in Section 3.2.4.2 and 3.2.4.3). The concentrations of total carbon (TC, OC+ EC) in the PM increase in the next IOPs, as shown in Figure 3.16B. This may indicate the contribution from the wildland fires, since emissions from these fires is mostly organic in nature, with a little contribution of elemental carbon (see

Table 1.1). The highest TC increase is observed in Jean (JN), which is consistent with the impact of Clover fire plum, approaching from the southwest.

3.2.4.2 Water soluble ions

Sulfates ($\text{SO}_4^{=}$), nitrates (NO_3^-) chlorine (Cl^-), ammonium (NH_4^+) and soluble potassium (K^+) ions were measured for all sites. Figure 3.17 shows the concentrations of these species for all three IOPs. This figure shows that sulfates are the most abundant followed by nitrates and ammonium. Soluble potassium concentrations increase for the IOP#2, which indicates influence of the biomass burning emissions. Chlorine and K^+ are not correlated, thus suggesting different than biomass burning sources of chlorine. There is a deficit of ammonium to account for both sulfates and nitrates ions, which indicate that the sulfates are probably in different form than ammonium sulfates.

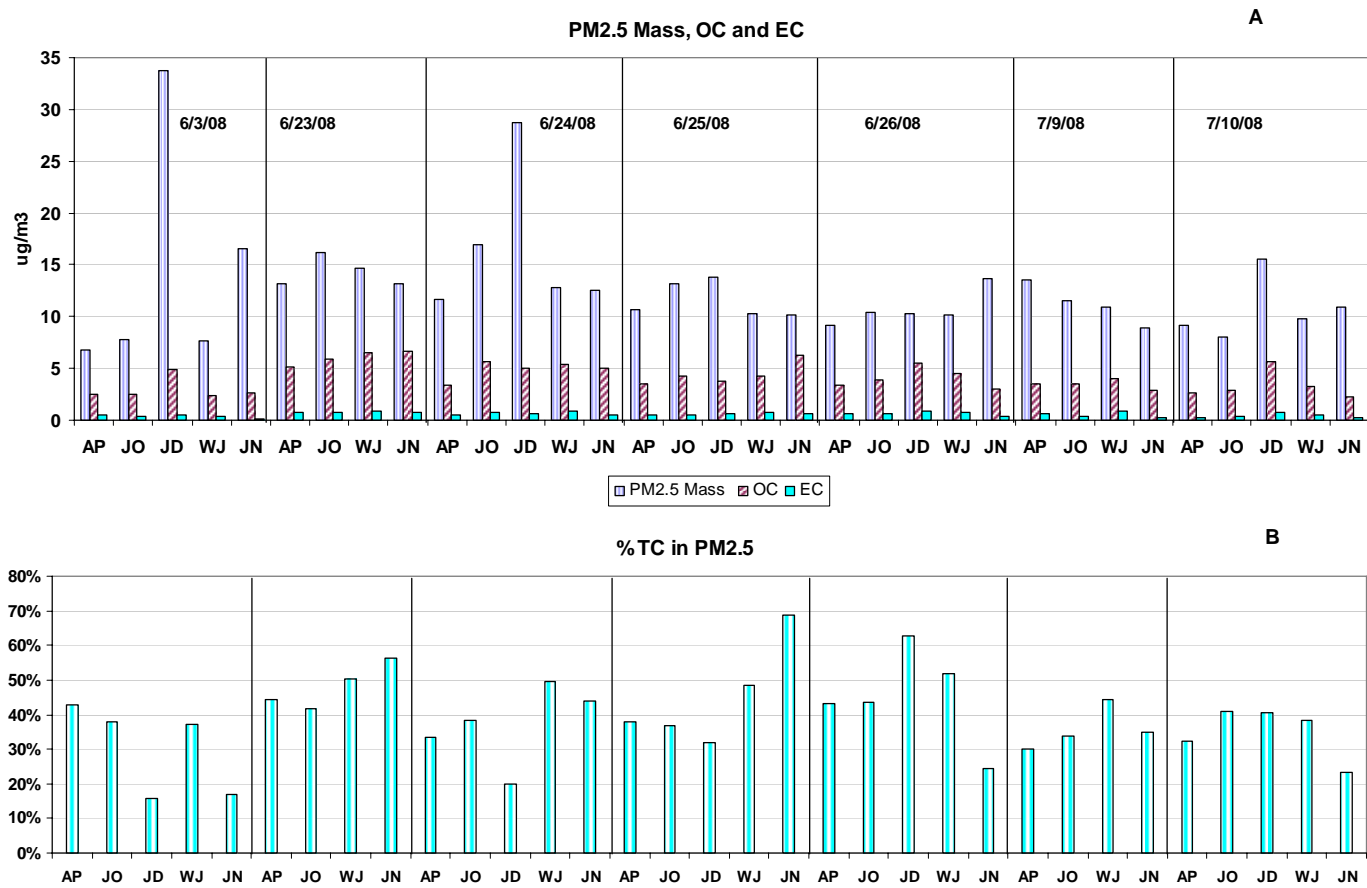


Figure 3.16. Concentrations of PM_{2.5}, OC and EC (A) and contribution of TC to PM_{2.5} (B)

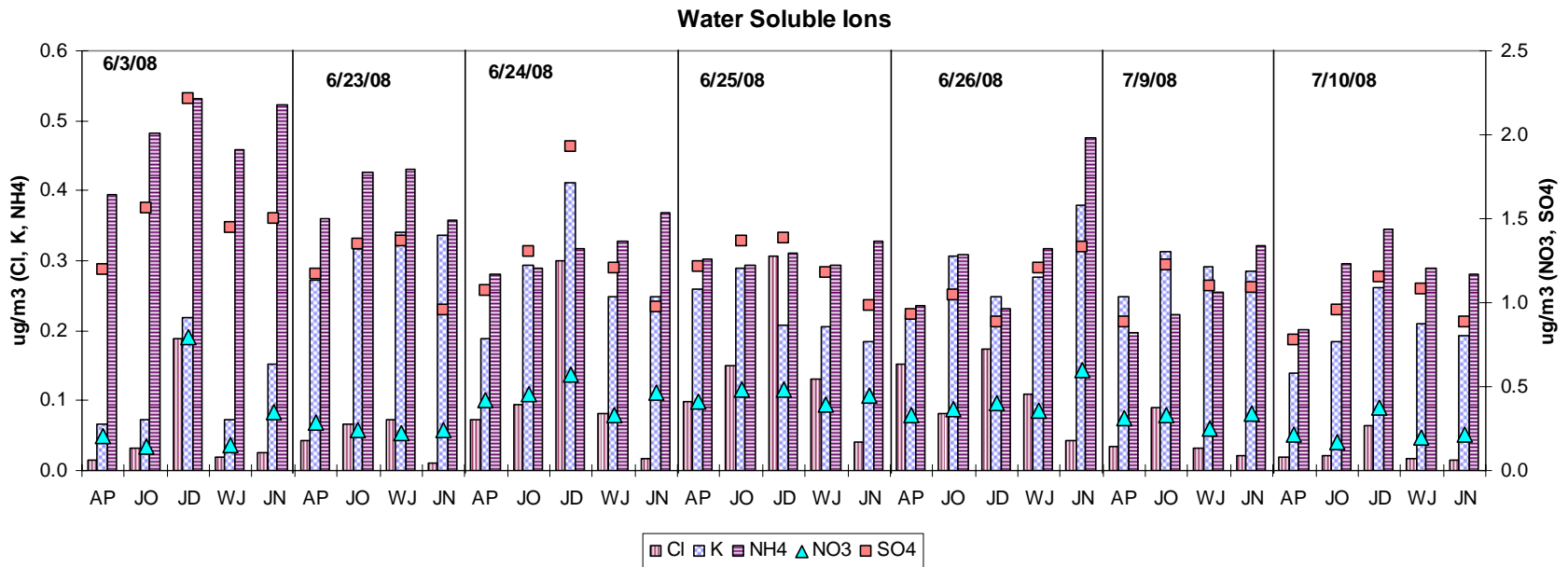


Figure 3.17. Concentrations of sulfates (SO4), nitrates (NO3) chlorine (Cl), ammonium (NH4) and soluble potassium (K)

3.2.4.3 Elements

Fifty one elements were measured by EDXRF, as described in the Experimental section. Figure 3.18 shows that the most abundant elements in all samples are calcium, silicon, iron and sulfur. Total potassium, sodium, magnesium, aluminum and chlorine are present in lower, more variable concentrations. Lower concentrations of vanadium are also observed in some samples.

3.2.4.4 Organic biomass burning tracers

Table 3.5 shows the wood smoke tracers quantified from the quartz fiber filters collected during three IOPs.

Table 3.5 List of wood smoke tracers with their mnemonics, quantified for 2008 study.

Mnemonic	Compound
guac	Guaicol
megua4	4-Me-guaiacol
etgua4	4-Ethyl-guaiacol
syri	Syringol
levg	Levogluconan
iseug	Isoeugenol
acvan	Acetovanillone
vanil	Vanillic acid
homov	Homovanillic acid
syrald	Syringaldehyde
cpinac	cis-Pinonic acid
syrgac	Syringic acid
dhabac	Dehydroabietic acid
pimara	Pimaric acid
abac	Abietic acid
isopim	Isopimaric acid
oxodeh7	7-Oxodehydroabietic acid

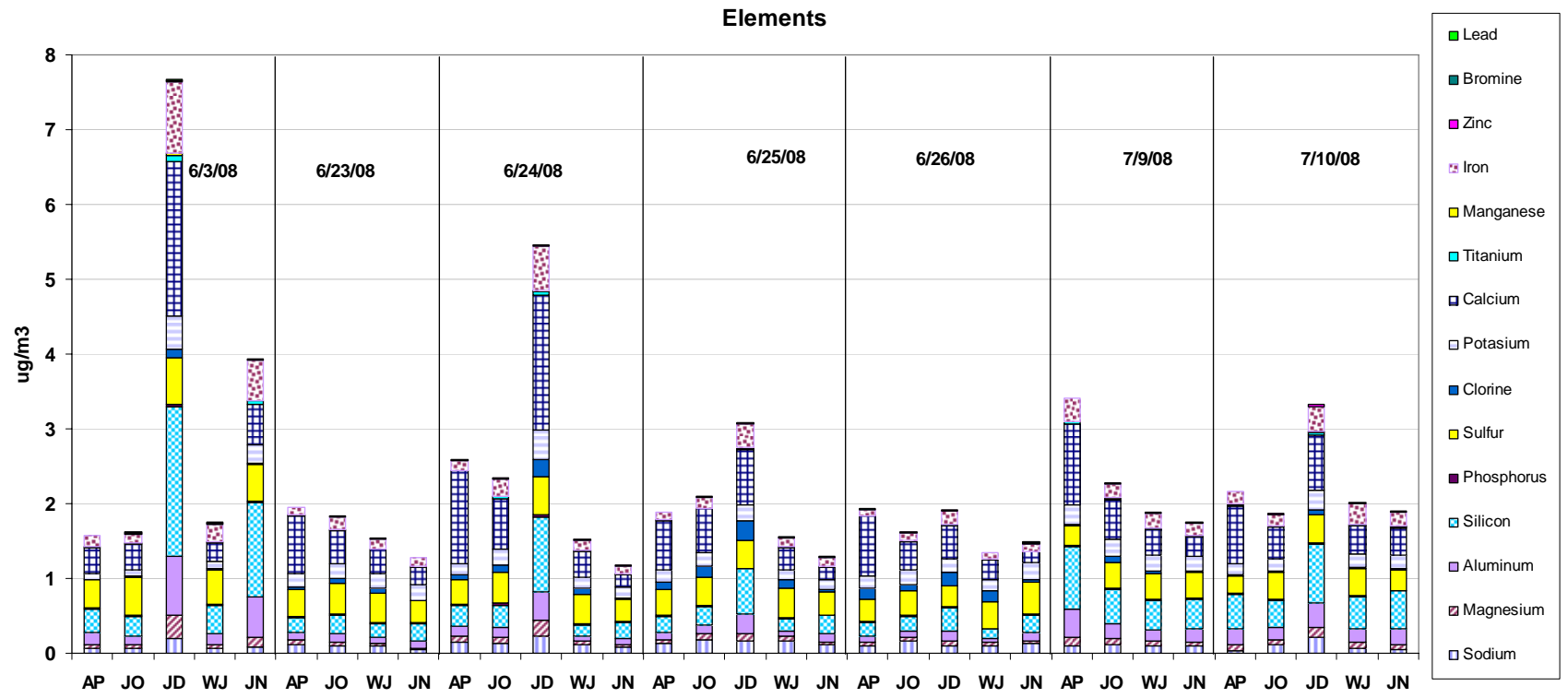


Figure 3.18. Concentrations of the major elements in filter samples

Figure 3.19A shows the concentrations of all wood smoke tracers measured for this study in the samples collected during three IOP events. Figure 3.19B shows the levoglucosan concentrations only. As discussed in the Introduction, levoglucosan is considered the most abundant and stable organic wood smoke tracer, although its relative concentration depends on the type of biomass burned. The concentrations of levoglucosan were very high on 6/23/08, the first day of IOP #2. These concentrations are consistently higher at the Jean (JN) site, which is the closest to the Clover wildfire that impacted the area during IOP# 2.

Figure 3.20A shows the concentrations of resin acids, and Figure 3.20B – methoxy-phenols in the filter samples collected during three IOP events. It is not clear why the concentration of one of the resin acids, dehydroabietic acid, is so high in JD and JO samples from 6/25/08 . Possibly some local sources (like a barbecue using mesquite wood) can contribute to this high concentration. Methoxy-phenols (Figure 3.20B) follow the levoglucosan pattern – the highest concentrations are observed during the beginning of IOP#2. There is a moderate correlation between guaiacol and levoglucosan ($R^2 = 0.66$) and vanilic acid and levoglucosan ($R^2 = 0.88$). Guaiacol, the most volatile of the methoxy-phenols, is observed in highest concentrations in all samples. This was not the case in the 2005 study. However, since this compound is volatile, it might evaporate from the filters that were stored over 2 years before analysis.

The correlation between levoglucosan and soluble potassium that is considered as an inorganic wood smoke marker is not very good ($R^2 = 0.31$). This is not surprising, since soluble K is not a good marker of wildland fires and it has been observed previously that its correlations with levoglucosan are very low (Mazzoleni et al., 2007).

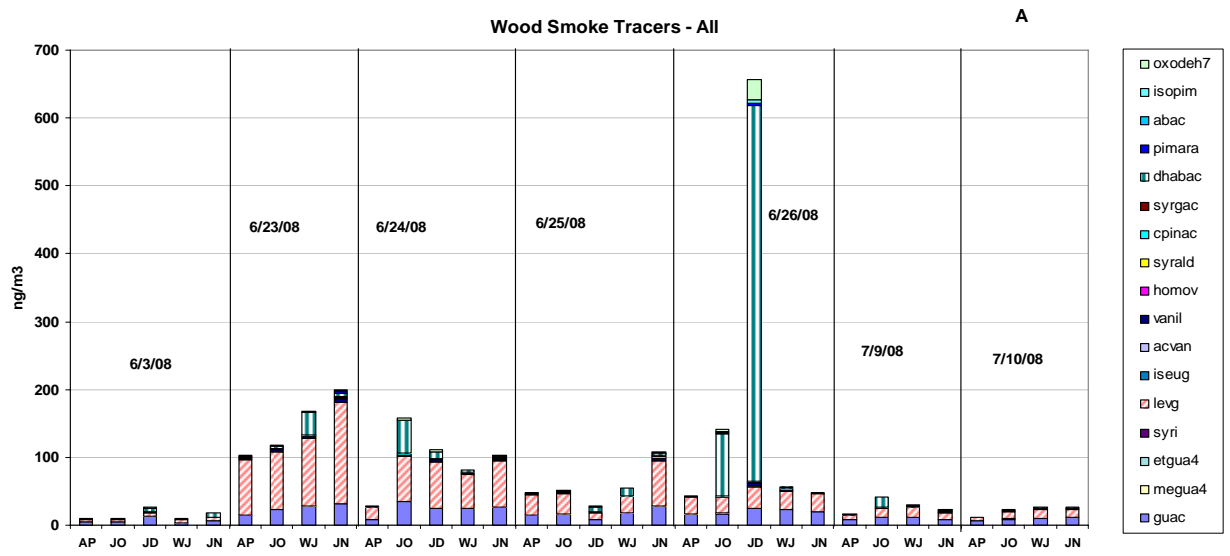


Figure 3.19. Wood smoke tracers (A) and levoglucosan (B) in filter samples

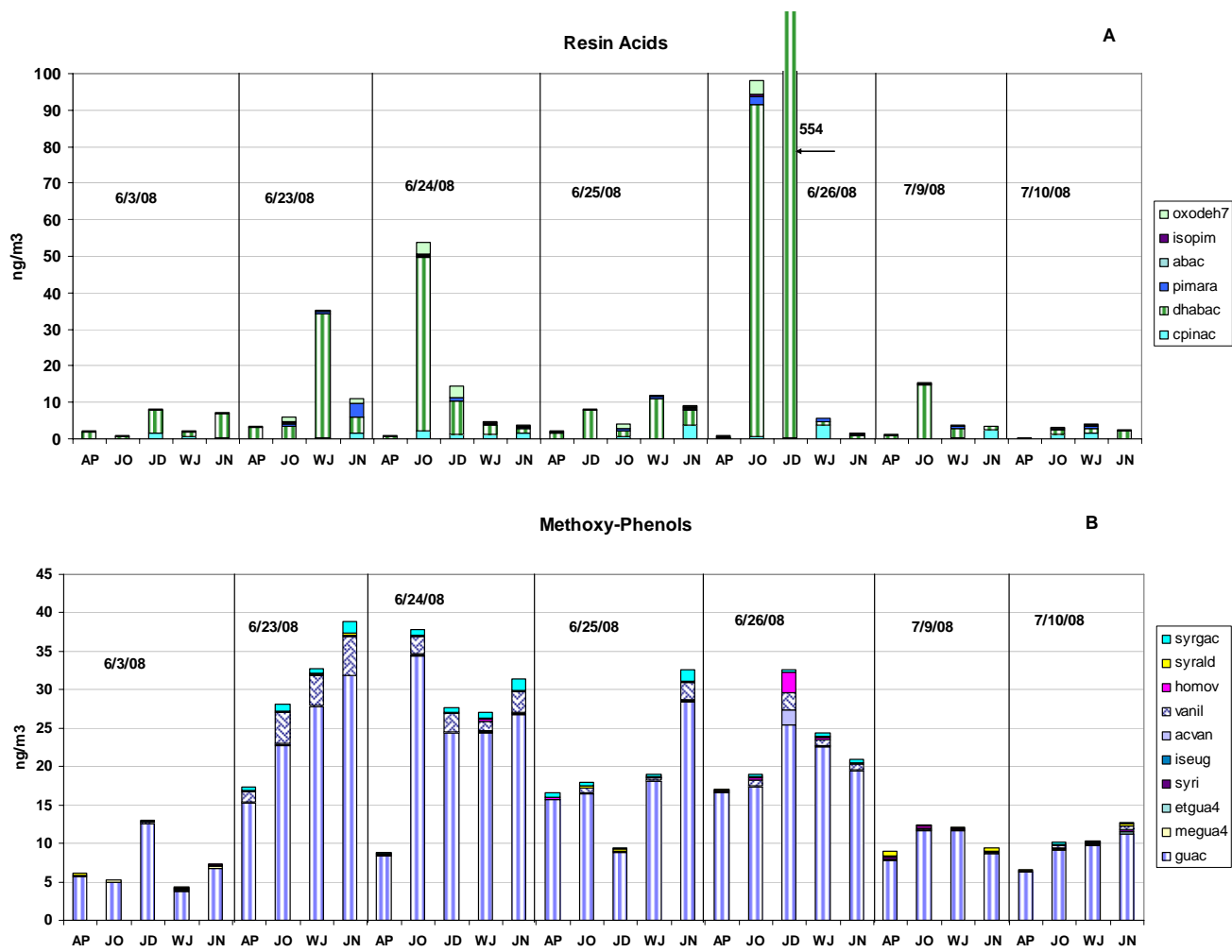


Figure 3.20. Resin acids (A) and methoxy-phenols (B) in the filter samples

3.2.5 Ozone and Levoglucosan Correlations in 2008 Study

Similarly to 2005 study, we examined the correlations between ozone and levoglucosan in 2008 study. The 24-hr average, 24-hr sum and maximum daily 1-hr O₃ concentrations during the days and times the PM samples were collected (i.e. 24 hrs starting from 11 AM local time), were corrected for O₃ concentrations when there was no influence of wildfire emissions. The ozone concentrations from the days before and after the events were averaged and subtracted from the ozone concentrations during the events.

Figure 3.21 shows the relations between 24-hr sum of 1-hr ozone concentrations and corresponding levoglucosan concentrations for all sites and all IOPs. The relations for 24-hr average ozone concentrations look basically identical, thus they are not shown here. There is more scatter in the levoglucosan relations with max ozone concentrations, as could be expected.

As Figure 3.21 shows, there was a high levoglucosan concentration observed on the first day of IOP#2, 6/23/08 which was not accompanied by a proportional increase in ozone concentration. However, the examination of the hourly PM_{2.5} mass data collected by DAQEM (http://www.ccairquality.org/cgi-bin/daily_average.pl.) revealed that the maximum impact of the Clover fire smoke occurred at the late afternoon on June 23 and continued throughout the night. Thus, although the levoglucosan concentrations were the highest for this first 24-hr time period, it wasn't until the next day, 6/24/08, that the ozone was mostly produced through the photochemical reactions of VOC transported with the smoke cloud. If this first day of the IOP#2 is excluded, correlations coefficients (R²) between 24-hr ozone sum and levoglucosan concentrations are 0.3; 0.83; 0.5; and 0.98 for AP, JN, WJ and JD, respectively. No correlation is observed for Joe Neal (JO) site. Also, for JD Smith (JD) site, no valid filter sample was collected for 6/23/08, 7/9/08 and 7/10/08. The IOP #3, 7/9-7-10/08 was not influenced significantly by the wildland fires and the increases in ozone concentrations were probably due to VOC emissions by other sources, most probably motor vehicles.

Figure 3.22 A and B shows the relations between 24-hr ozone sum and levoglucosan concentrations averaged over all sites during IOP# 2 only. If the first day of IOP# 2 is

excluded, the correlation coefficient R^2 between ozone sum and levoglucosan is 0.99 (Figure 3.22 B).

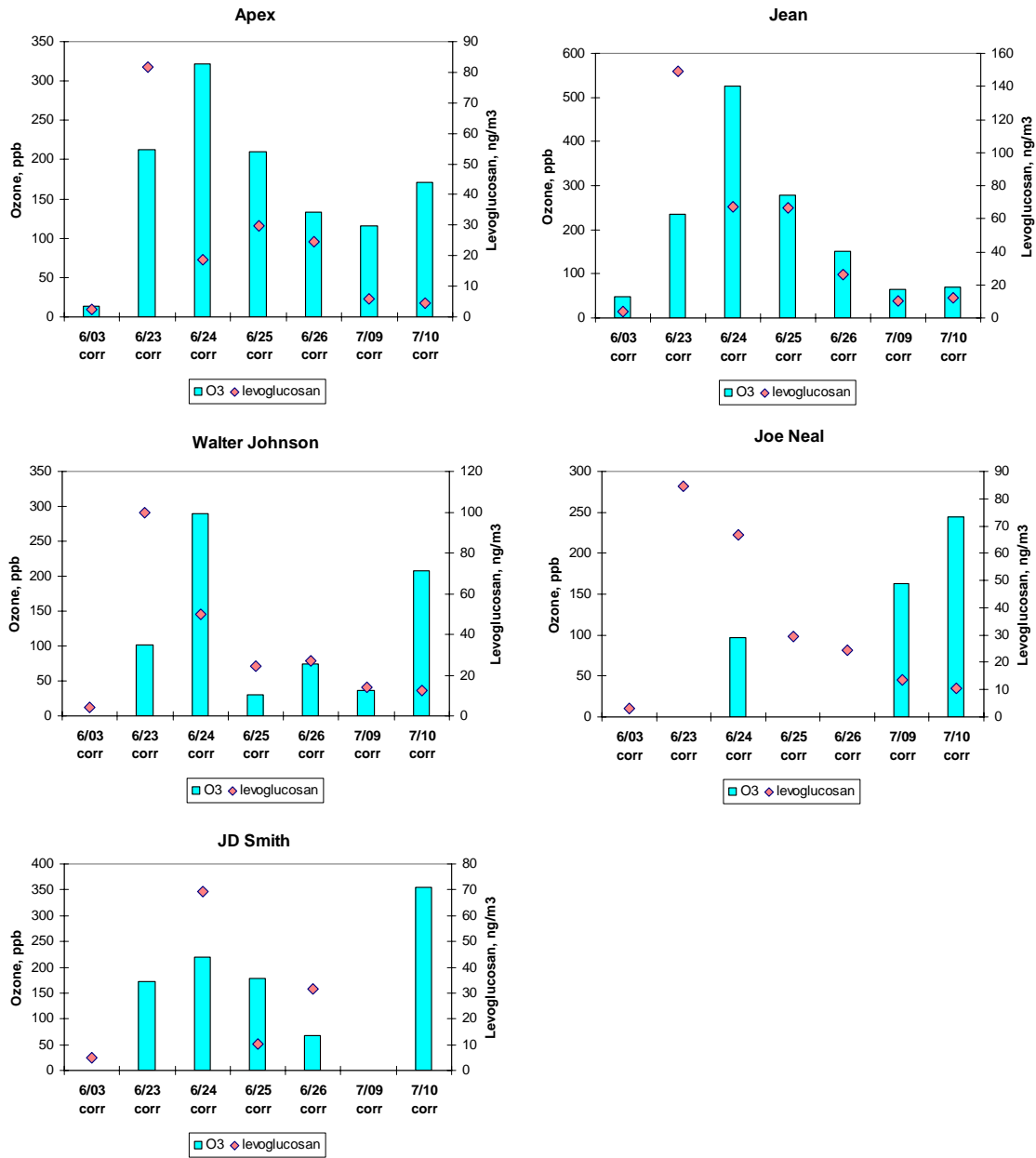


Figure 3.21 Relations between 24-hr sum of 1-hr ozone concentrations and corresponding levoglucosan concentrations for all sites and all IOPs.

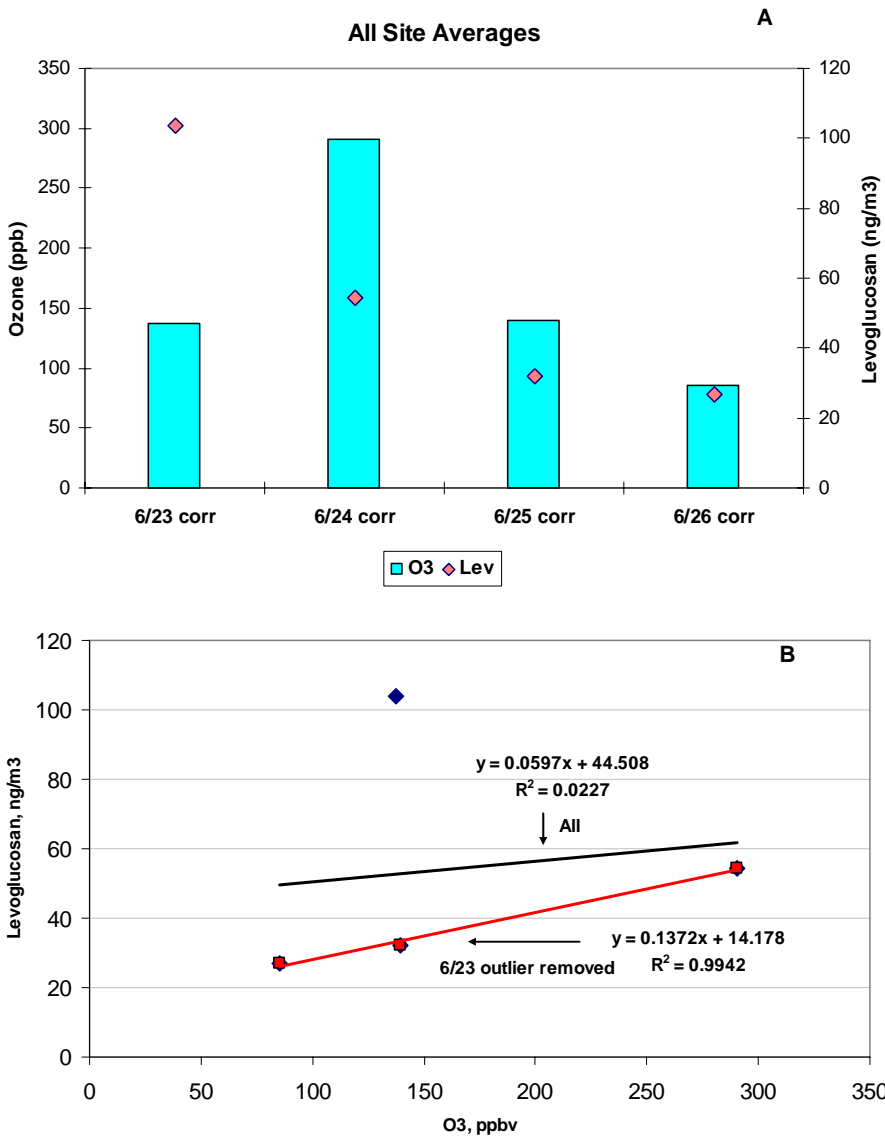


Figure 3.22. Relations between average 24-hr ozone sum and levoglucosan concentrations for all measured sites during IOP# 2

3.2.6 Continuous GC VOC Data

3.2.6.1 Mean, median concentrations and comparison with canister data

Table 3.6 presents the mean, median and 1-hour maximum concentrations of hydrocarbons measured at the DRI site in Las Vegas. The highest 1-hour concentrations were measured for benzene (4.792 ppbv) and ethylbenzene (4.705 ppbv). Higher mean concentrations were measured for benzene (0.134 ($\sigma=0.105$) ppbv), toluene (0.678 ($\sigma=0.601$) ppbv), ethylbenzene (0.126 ($\sigma=0.373$)) and *n*-octane (0.117 ($\sigma=0.158$)) as compared to the other detected organic compounds. This is most likely the combined outcome of different emission rates from sources and atmospheric reactivities with OH radicals and other atmospheric oxidants. In fact, the reaction rate constant of benzene, toluene and ethylbenzene with OH radicals (from 1.2 to 7.1 10^{-12} cm³/(mol s)) are two to three times lower than the rate constants for xylenes and methyl-toluenes (from 12.3 to 57.5 10^{-12} cm³/(mol s)). VOCs concentrations followed a log-normal distribution (as it is diagnosed by the difference between mean and median) that was influenced by the high-end outliers.

Table 3.6. Mean, median and maximum concentrations (in ppbv) of VOCs during the monitoring period

Compound	Mean	Median	Maximum	St.dev
Benzene	0.134	0.101	0.905	0.105
Toluene	0.678	0.483	4.792	0.601
2-methyl-Heptane	0.011	0.000	0.788	0.062
3-methyl-Heptane	0.018	0.002	0.468	0.048
4-methyl-Heptane	0.012	0.011	0.147	0.010
<i>n</i> -Octane	0.117	0.050	1.205	0.158
Ethylbenzene	0.126	0.026	4.705	0.373
<i>m/p</i> -Xylene	0.079	0.048	0.895	0.100
Styrene	0.008	0.005	0.158	0.011
<i>n</i> -Nonane	0.018	0.013	0.579	0.026
<i>o</i> -Xylene	0.044	0.027	0.865	0.057
<i>i</i> -propyl-Benzene	0.005	0.001	0.931	0.045
<i>n</i> -propyl-benzene	0.001	0.000	0.101	0.005
α -Pinene	0.015	0.003	0.307	0.032
<i>m</i> -ethyl-Toluene	0.024	0.010	0.475	0.042
<i>p</i> -ethyl-Toluene	0.012	0.003	0.221	0.023
1,3,5-trimethyl-Benzene	0.012	0.004	0.273	0.022
<i>o</i> -ethyl-Toluene	0.020	0.019	0.170	0.014
1,2,4-trimethyl-Benzene	0.007	0.003	0.122	0.012

Table 3.7 shows the 24-hour concentrations of VOCs measured at five locations (AP, JO, JD, WJ and JN) during IOP # 1, and 3 using canisters and the mean and range of VOCs concentrations measured at the DRI SNSC site using a continuous analyzer (the continuous GC analyzed was not available during IOP#2). Figures 3.23 through 3.26 present the comparison of benzene, ethylbenzene, o-xylene and o-ethyltoluene concentrations at DRI-SNSC and the other five sites. Overall, for the majority of organic compounds, mean VOC concentrations at the DRI SNSC site were comparable to those measured at the other sites. A noticeable exception was observed in early June, in which concentrations of ethylbenzene were substantially higher than those measured at the other sites or for the remaining of the monitoring period (July 3, 2008 – August 28, 2008).

Table 3.7. Daily concentrations of VOC measured in Apex (AP), JD Smith (JD), Jean (JN), Joe Neal (JO, primary and collocated) and Walter Johnson (WJ) sites of the Clark County Air Quality monitoring sites and 24-hour average, min, and max concentrations measured at DRI Southern Nevada Science Center

Site	AP	JD	JN	JO	JO col	WJ	DRI SNSC		
							Mean	Min	Max
June 03, 2008									
Benzene	0.127	0.255	0.056	0.083	0.133	0.183	0.091	0.06	0.125
Toluene	0.382	0.582	0.096	0.237	0.251	0.402	0.284	0.176	0.503
2-methyl-Heptane	0.009	0.013	0.015	0.007	0.005	0.009	0.011	0.002	0.023
4-methyl-Heptane	0.016	0.047	0.013	0.008	0.015	0.016	0.002	0.001	0.007
3-methyl-Heptane	0.013	0.113	0.098	0.188	0.240	0.080	0.022	0.003	0.080
n-Octane	0.044	0.028	0.018	0.022	0.026	0.028	0.023	0.005	0.040
Ethylbenzene	0.126	0.082	0.009	0.027	0.029	0.048	0.519	0.014	1.017
m/p-Xylene	0.597	0.328	0.026	0.112	0.115	0.190	0.242	0.047	0.510
Styrene	0.020	0.028	0.007	0.010	0.011	0.018	0.012	0.002	0.049
o-Xylene	0.299	0.122	0.013	0.047	0.052	0.076	0.115	0.057	0.230
n-Nonane	0.060	0.031	0.010	0.014	0.013	0.018	0.029	0.013	0.068
i-propyl-Benzene	0.011	0.033	0.000	0.000	0.009	0.010	0.004	0.001	0.013
n-propyl-Benzene	0.071	0.016	0.002	0.008	0.009	0.010	0.003	0.001	0.007
α-Pinene	0.000	0.054	0.008	0.029	0.036	0.037	0.010	0.003	0.020
m-ethyl-Toluene	0.000	0.076	0.009	0.036	0.044	0.043	0.137	0.103	0.164
p-ethyl-Toluene	0.186	0.031	0.004	0.015	0.016	0.018	0.026	0.000	0.062
1,3,5-trimethyl-Benzene	0.240	0.041	0.006	0.021	0.024	0.018	0.065	0.028	0.123
o-ethyl-Toluene	0.155	0.024	0.004	0.016	0.020	0.015	0.025	0.018	0.032
1,2,4-trimethyl-Benzene	0.528	0.062	0.010	0.044	0.054	0.037	0.026	0.015	0.038

Site	AP	JD	JN	JO	JO col	WJ	DRI SNSC		
July 09, 2008									
Benzene	0.046	0.419	0.068	0.165	0.160	0.179	0.189	0.054	0.744
Toluene	1.799	2.010	0.858	1.194	1.120	1.155	1.473	0.000	3.582
2-methyl-Heptane	0.014	0.062	0.014	0.012	0.010	0.011	0.012	0.000	0.049
4-methyl-Heptane	0.011	0.034	0.011	0.016	0.016	0.032	0.094	0.000	0.304
3-methyl-Heptane	0.000	0.055	0.000	0.013	0.012	0.009	0.016	0.001	0.056
n-Octane	0.010	0.067	0.016	0.030	0.020	0.062	0.218	0.005	0.756
Ethylbenzene	0.011	0.195	0.016	0.058	0.044	0.079	0.112	0.066	0.291
m/p-Xylene	0.036	0.842	0.046	0.200	0.174	0.271	0.191	0.047	0.584
Styrene	0.027	0.094	0.048	0.077	0.034	0.127	0.022	0.004	0.069
<i>o</i> -Xylene	0.386	0.649	0.381	0.458	0.449	0.442	0.134	0.013	0.406
<i>n</i> -Nonane	0.005	0.040	0.005	0.023	0.014	0.016	0.030	0.000	0.084
<i>i</i> -propyl-Benzene	0.003	0.009	0.001	0.005	0.002	0.005	0.003	0.000	0.015
<i>n</i> -propyl-Benzene	0.004	0.049	0.003	0.020	0.013	0.018	0.005	0.000	0.021
α -Pinene	0.007	0.079	0.006	0.032	0.021	0.030	0.078	0.010	0.307
<i>m</i> -ethyl-Toluene	0.015	0.159	0.010	0.063	0.049	0.059	0.026	0.011	0.059
<i>p</i> -ethyl-Toluene	0.006	0.100	0.004	0.032	0.023	0.029	0.068	0.016	0.216
1,3,5-trimethyl-Benzene	0.006	0.088	0.011	0.025	0.017	0.044	0.034	0.005	0.110
<i>o</i> -ethyl-Toluene	0.003	0.056	0.002	0.016	0.012	0.015	0.018	0.000	0.120
1,2,4-trimethyl-Benzene	0.012	0.189	0.015	0.055	0.037	0.061	0.024	0.003	0.087
July 10, 2008									
Benzene	0.012	0.199	0.054	0.110	0.209	0.165	0.203	0.080	0.428
Toluene	0.741	1.208	0.735	0.923	0.962	1.072	1.524	0.713	3.182
2-methyl-Heptane	0.000	0.016	0.000	0.006	0.085	0.068	0.007	0.000	0.031
4-methyl-Heptane	0.000	0.034	0.011	0.018	0.070	0.057	0.171	0.007	0.193
3-methyl-Heptane	0.000	0.017	0.000	0.005	0.006	0.014	0.023	0.000	0.033
n-Octane	0.000	0.042	0.011	0.030	0.070	0.041	0.474	0.002	0.790
Ethylbenzene	0.004	0.088	0.010	0.039	0.084	0.055	0.085	0.002	0.231
m/p-Xylene	0.010	0.348	0.028	0.132	0.259	0.192	0.210	0.133	0.341
Styrene	0.007	0.135	0.033	0.066	0.133	0.094	0.025	0.014	0.042
<i>o</i> -Xylene	0.342	0.475	0.346	0.399	0.464	0.425	0.152	0.000	0.236
<i>n</i> -Nonane	0.000	0.016	0.003	0.012	0.011	0.018	0.032	0.021	0.045
<i>i</i> -propyl-Benzene	0.000	0.009	0.001	0.002	0.002	0.004	0.004	0.000	0.008
<i>n</i> -propyl-Benzene	0.000	0.030	0.002	0.010	0.009	0.017	0.001	0.000	0.007
α -Pinene	0.000	0.049	0.000	0.017	0.013	0.027	0.058	0.003	0.186
<i>m</i> -ethyl-Toluene	0.000	0.085	0.006	0.039	0.034	0.053	0.037	0.026	0.061
<i>p</i> -ethyl-Toluene	0.000	0.045	0.002	0.017	0.014	0.026	0.074	0.034	0.120
1,3,5-trimethyl-Benzene	0.000	0.056	0.006	0.024	0.083	0.019	0.048	0.000	0.079
<i>o</i> -ethyl-Toluene	0.000	0.022	0.001	0.009	0.008	0.013	0.020	0.006	0.064
1,2,4-trimethyl-Benzene	0.001	0.090	0.009	0.039	0.065	0.040	0.025	0.000	0.044

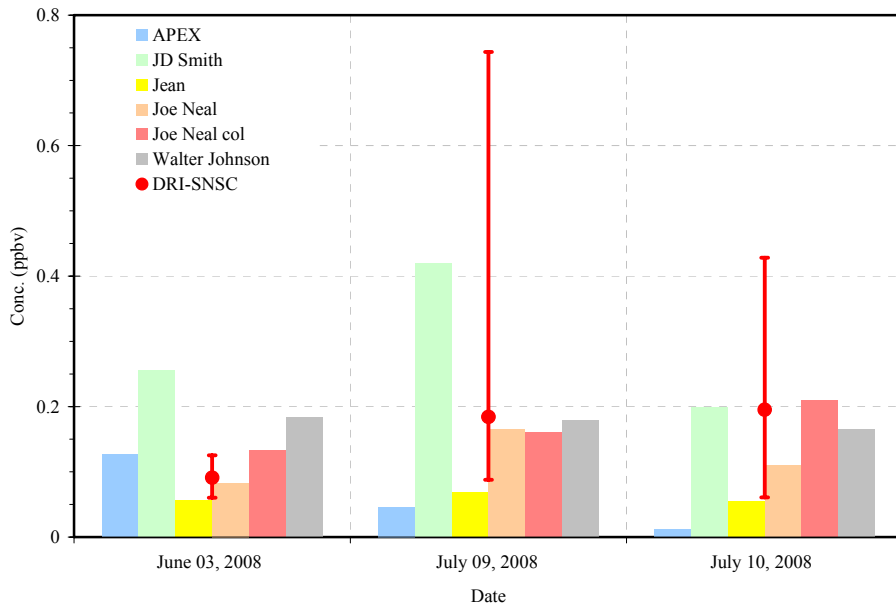


Figure 3.23. Hourly mean, minimum and maximum concentrations of benzene (in ppbv) measured at DRI-SNSC and daily benzene concentrations (in ppbv) at the five DAQEM sites

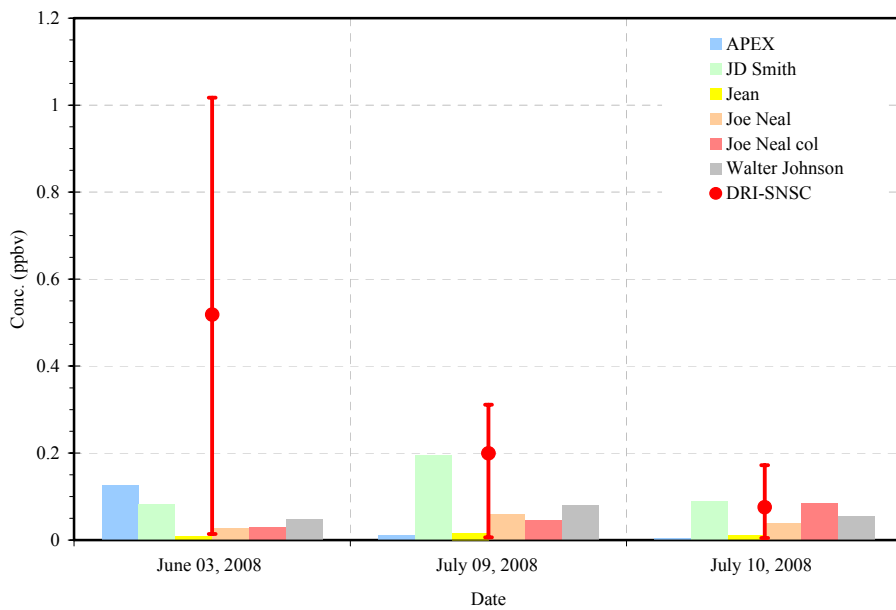


Figure 3.24. Hourly mean, minimum and maximum concentrations of ethylbenzene (in ppbv) measured at DRI-SNSC and daily o-xylene concentrations (in ppbv) at the five DAQEM sites

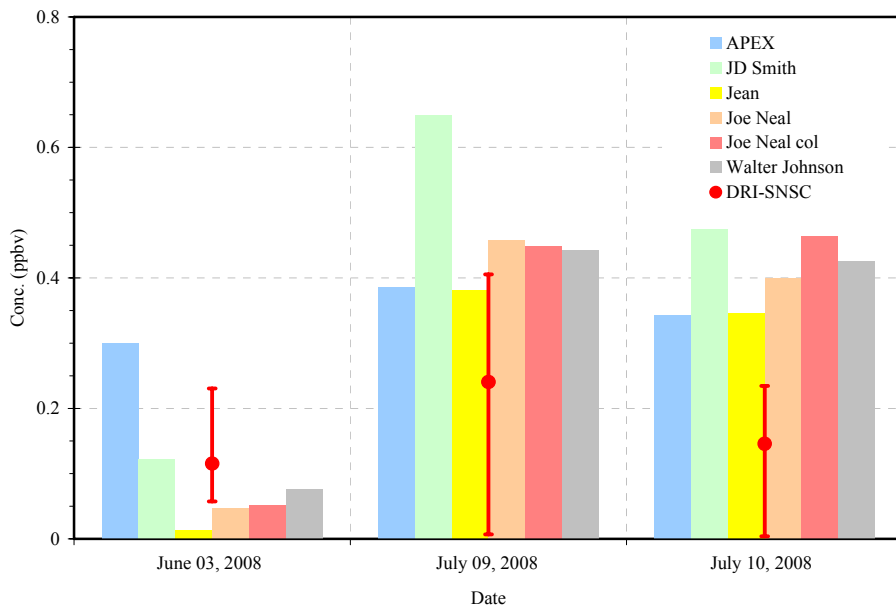


Figure 3.25. Hourly mean, minimum and maximum concentrations of o-xylene (in ppbv) measured at DRI-SNSC and daily o-xylene concentrations (in ppbv) at the five DAQEM sites

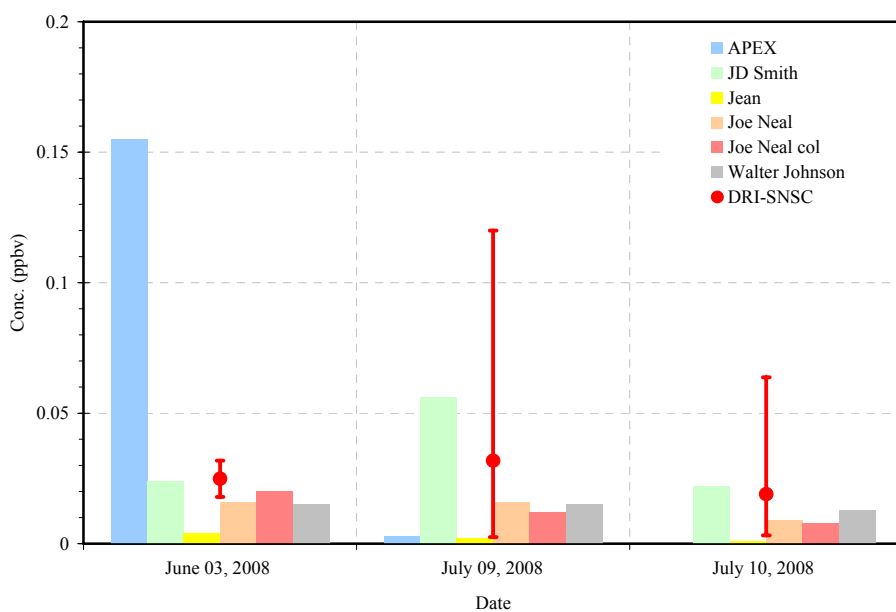


Figure 3.26. Hourly mean, minimum and maximum concentrations of o-ethyl-toluene (in ppbv) measured at DRI-SNSC and daily o-ethyl-toluene concentrations (in ppbv) at the five DAQEM sites

3.2.6.2 Temporal and diurnal variations

Figures 3.27 through 3.31 show the 24-h mean concentrations of measured VOCs for the entire monitoring period. Analysis of patterns showed that most of the organic compounds followed a clear temporal cycle of a rapid increase followed by elevated levels for 2-4 days, then a fast decrease followed by relatively low concentrations for 1-2 days. This was more pronounced for benzene, toluene, xylenes, ethylbenzene, and to a lesser extent, n-octane and styrene. The intensity and duration of these events varied for different compounds; however, higher concentrations were measured in early July (July 4, 2008; July 9-10, 2008, July 16-17, 2008). An increase was also observed in late August, which may be due to increased traffic volume around UNLV (beginning of the fall semester) and school buses. Concentrations of alkanes and heavier aromatic hydrocarbons in early June and from July 3 to July 16 were two to ten times higher than those measured for the remaining period.

The day-to-day variation of aromatic VOCs may be indicative of the importance of regional meteorology on local air quality. For example, stagnant conditions favored by high-pressure systems result in the accumulation of pollutant levels, whereas passages of weather fronts can trigger faster dilution and lower concentrations. Further comparison of these measurements with prevailing meteorological conditions and weather patterns may provide additional information.

Figure 3.32 shows the variation of selected VOCs for each day of the week. Levels of VOCs increased during the week reaching their maxima on Thursdays, followed by a rapid decrease on Friday and during the weekend, with the lowest concentrations measured on Sundays.

Figure 3.33 shows the diurnal variation of average benzene, toluene, m/p-xylene and o-xylene concentrations. Concentration levels of these aromatic hydrocarbons followed a trend similar to traffic intensity, with higher concentrations being measured in early morning (between 6:00 and 9:00) and decreasing progressively during the day. The lowest levels were measured in the late afternoon (15:00-16:00). A second, less pronounced increase was observed in early evening (17:00-20:00), probably associated with the evening commute.

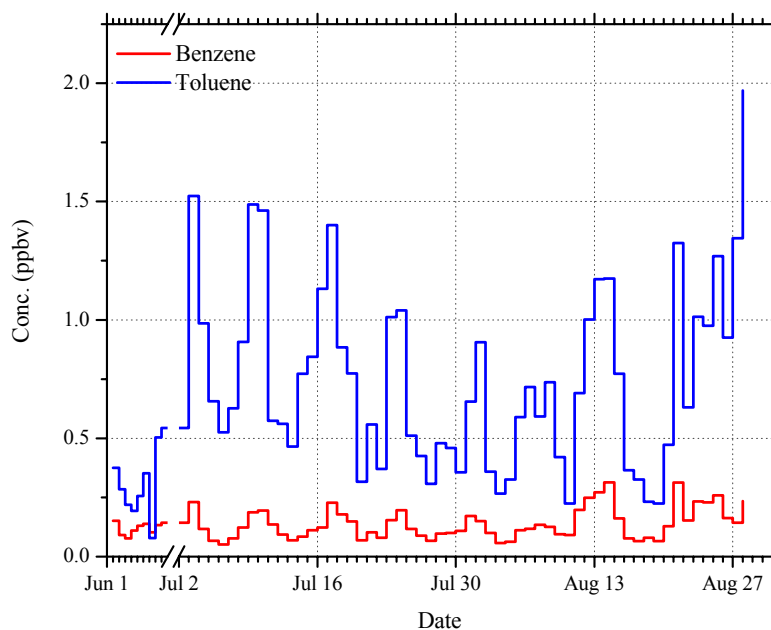


Figure 3.27 Daily variation of benzene and toluene concentrations (in ppbv)

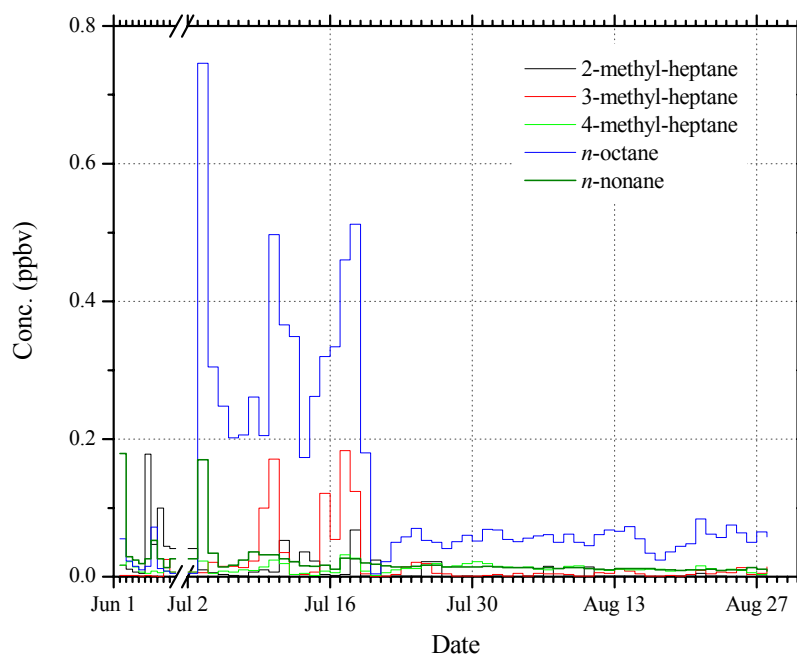


Figure 3.28 Daily variation of 2-,3- and 4-methyl-heptane, *n*-octane and *n*-nonane concentrations (in ppbv)

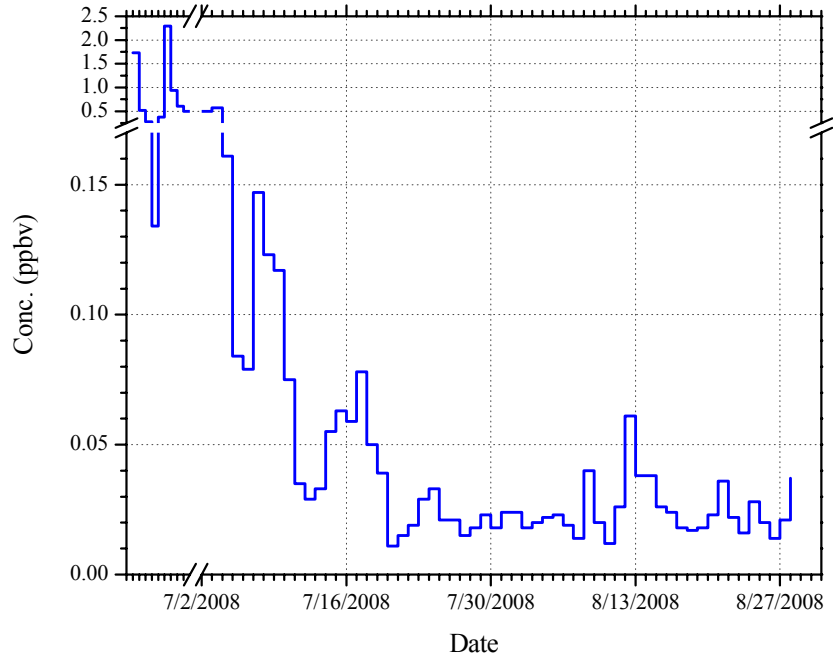


Figure 3.29 Daily variation of ethylbenzene concentrations (in ppbv)

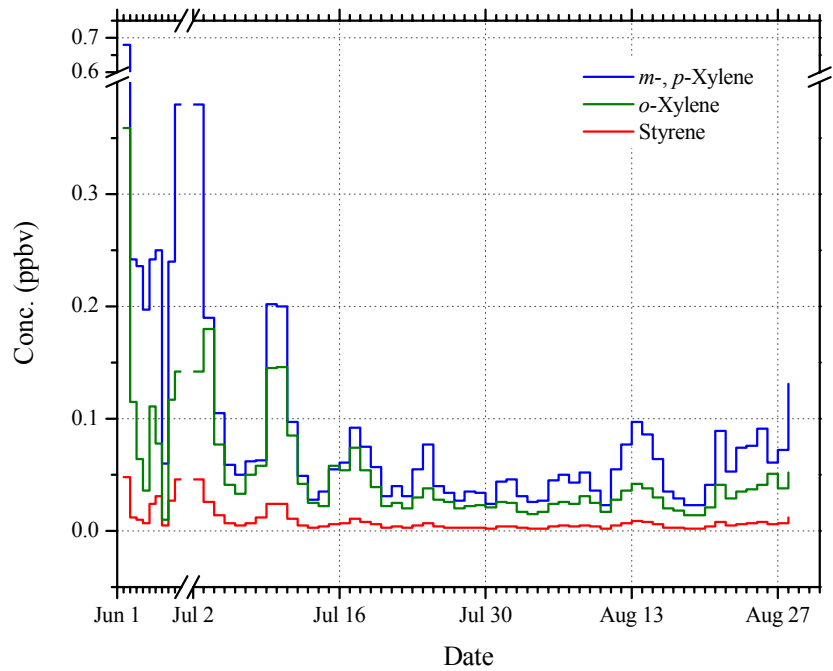


Figure 3.30 Daily variation of m-, p- and o-xylene and styrene concentrations (in ppbv)

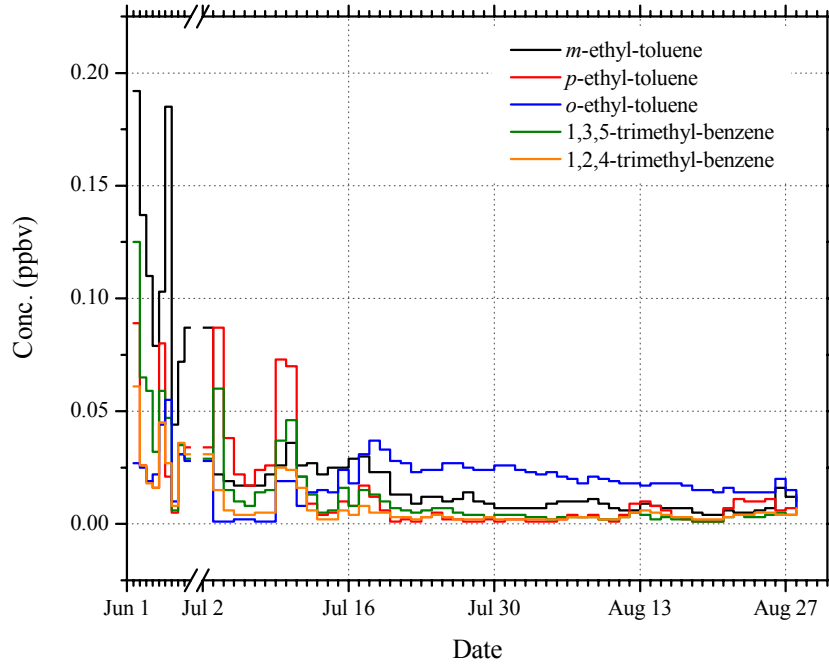


Figure 3.31 Daily variation of m-, p- and o-methyl-toluenes and, 1,2,4- and 1,3,5-trimethyl-benzenes concentrations (in ppbv)

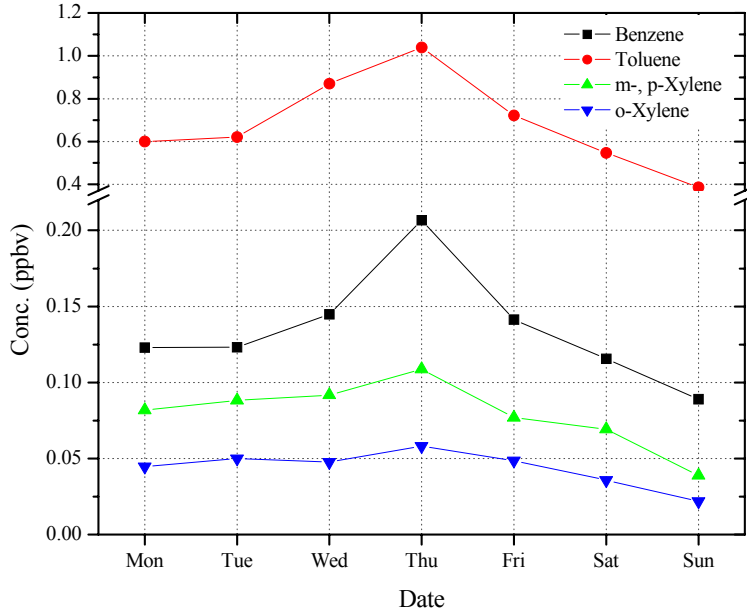


Figure 3.32 Day of the week variation of selected VOCs

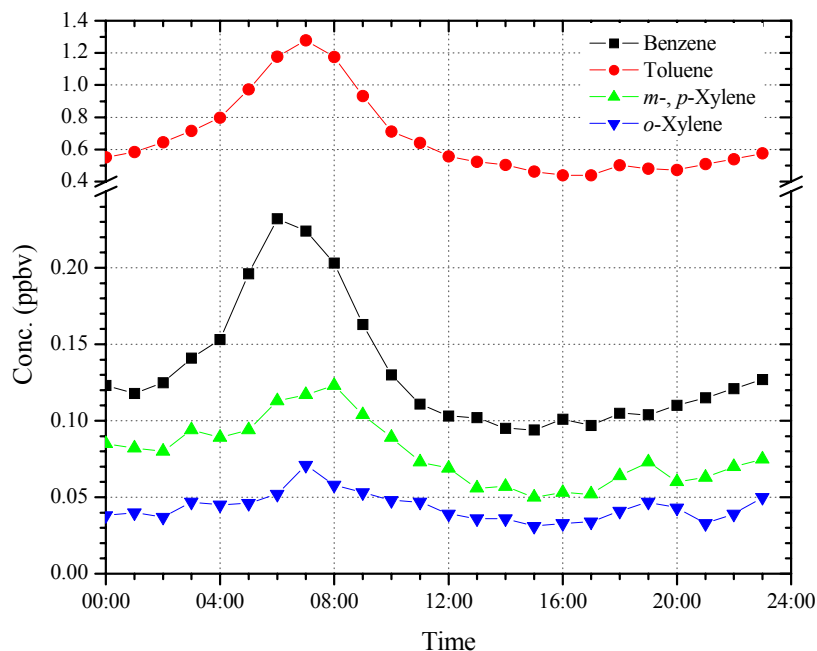


Figure 3.33 Diurnal variations of average benzene, toluene, m-/p-xylene and o-xylene

The concentrations of these aromatic compounds also increased moderately throughout the nighttime because of (a) the extremely slow reactions of alkanes and aromatic hydrocarbons with NO_3 radicals; (b) the descent of the boundary layer; and/or; (c) elevated mobile emissions on the Las Vegas Strip.

3.2.6.3 IOP #3

As mentioned above, the continuous GC was not available during the IOP#2, when the main impact of wildfires was observed. The continuous GC measurements were made during IOP#3, for which some impact of the Northern California fires was possible. In this section, the VOCs measurements on July 9-10, 2008 are compared against measurements before and after the IOP#3 event. Figure 3.34 shows the day-to-day variation of benzene and toluene before, during and after the event. Levels of both benzene and toluene on July 9 and July 10, 2008 were two to three times higher than those measured just before (July 7-8, 2008) and after (July 11-12, 2008) the event. While this indicates increased emissions of VOCs, it is noteworthy that these levels were also comparable to those measured on July 4, 2008 and on July 16-18, 2008.

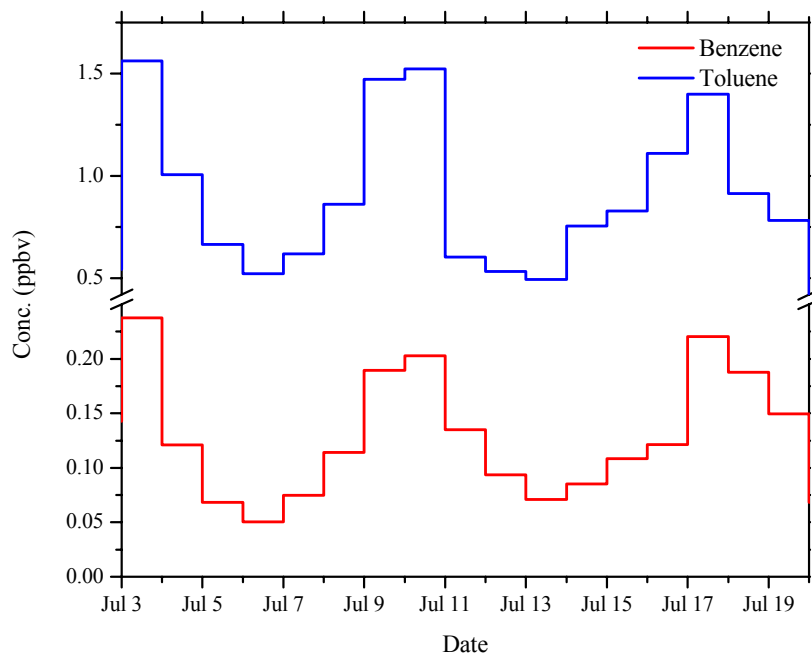


Figure 3.34 Mean 24-h concentrations of benzene and toluene from July 3, 2008 to July 19, 2008

To further examine the impact of wildfire smoke on VOC levels as compared to the impact of more regular emissions from vehicles, the hourly variation was analyzed. In Figures 3.35 to 3.37, benzene and toluene hourly trends from July 8, 2008 (Event 1, Day1) to July 11 (Event 1, Day 4) are compared against the hourly concentrations measured from July 15, 2008 (Event 2, Day 1) to July 18 (Event 2, Day 4) and from August 11, 2008 (Event 3, Day 1) to August 14 (Event 3, Day 4). For most cases, the diurnal profile of benzene and toluene was typical of vehicle emissions, with a maximum in the early morning and occasional increase in the late evening. On the other hand, both benzene and toluene concentrations increased rapidly in the late afternoon on July 9, 2008, and remained relatively high during the night, followed by a gradual decrease on July 10. It is noteworthy that levels of benzene and toluene increased in the late evening for most of the days of Event 2, but did not increase during Event 3 in August. The variation of the toluene/benzene ratio indicated a strong fossil fuel combustion signature for all three events, especially for Event #3, whereas the higher toluene/benzene ratios for the other two events suggested a mixed origin.

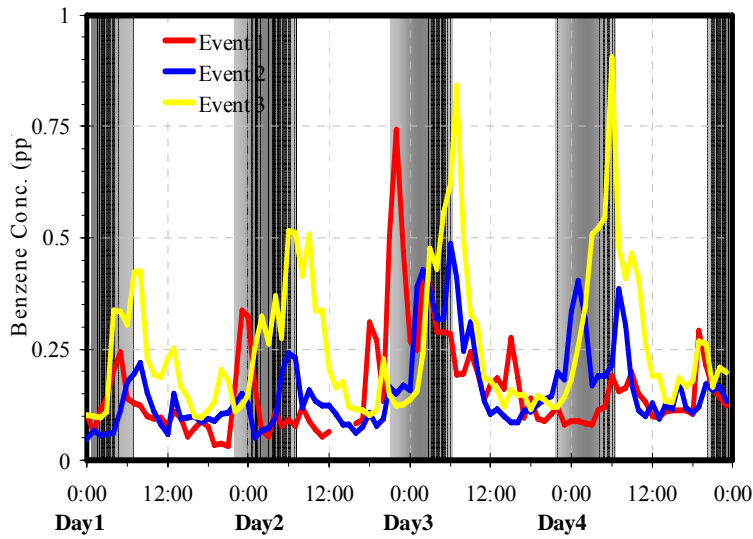


Figure 3.35 Hourly variation of benzene during July 8-11, 2008 (Event 1), July 11-15, 2008 (Event 2) and August 11-15, 2008 (Event 3)

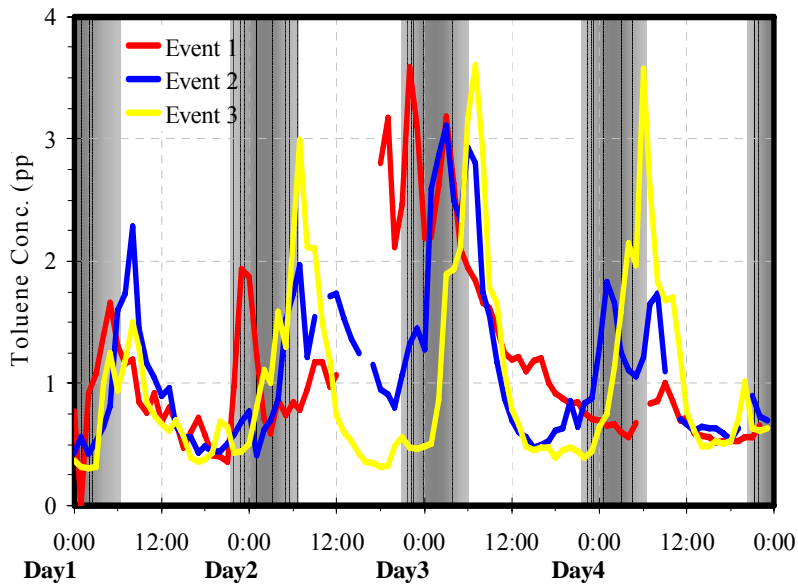


Figure 3.36 Hourly variation of toluene during July 8-11, 2008 (Event 1), July 11-15, 2008 (Event 2) and August 11-15, 2008 (Event 3)

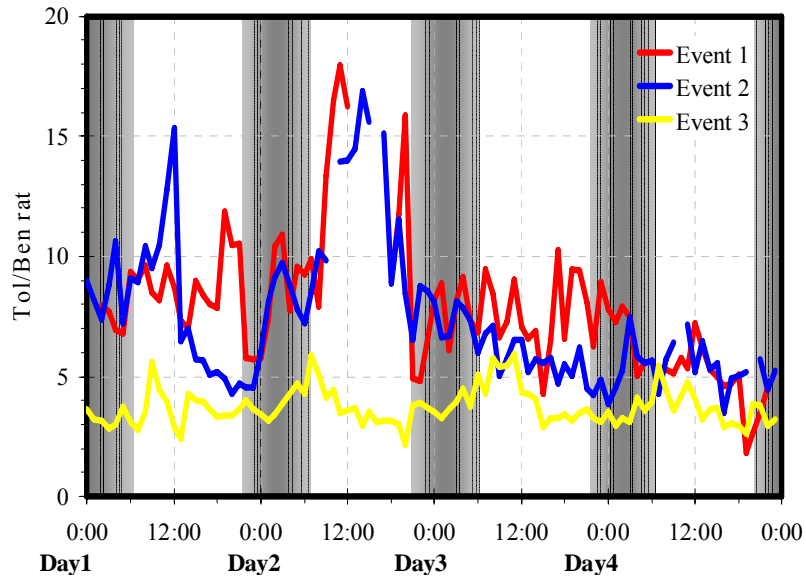


Figure 3.37 Variation of toluene/benzene ratio during July 8-11, 2008 (Event 1), July 11-15, 2008 (Event 2) and August 11-15, 2008 (Event 3)

3.2.7 Data Quality

For quality assurance, collocated MedVol filter and canister samples were collected at Joe Neal site. Table 3.7 shows the total number of samples collected at all six ground sites (including one collocated) and one aircraft site.

Table 3.8 Total number of samples collected during three IOP events

Sample type	Total number of samples	Total valid samples	Percentage of invalid samples	Notes
Canisters	46	43	6.5%	One collocated sample invalid
DNPH	18	17	5.5%	One sample from JO site
Quartz filters	42	39	7.5%	3 samples from JD site
Teflon filters	42	39	7.5%	As above

Figure 3.38A shows the collocated light VOC (C2 – C6) and Figure 3.38B – heavier VOC (C6-C11) canister samples (see Table 3.2 for compound mnemonics) collected at the Joe Neal site. There is generally a very good agreement between the collocated canister samples.

Figure 3.39 shows the collocated filter samples collected at the Joe Neal analyzed for the biomass burning tracers and Figure 3.40 - for PM_{2.5} OC and EC. Although the agreement between collocated samples is good, there is some small difference observed for 6/23 and 6/24 sampling dates. This difference is due to the changing flow rates for one of the MedVol sampler that was caused by the collapsing hose between the pump and the filter holder in the high ambient temperatures recorded for these days.

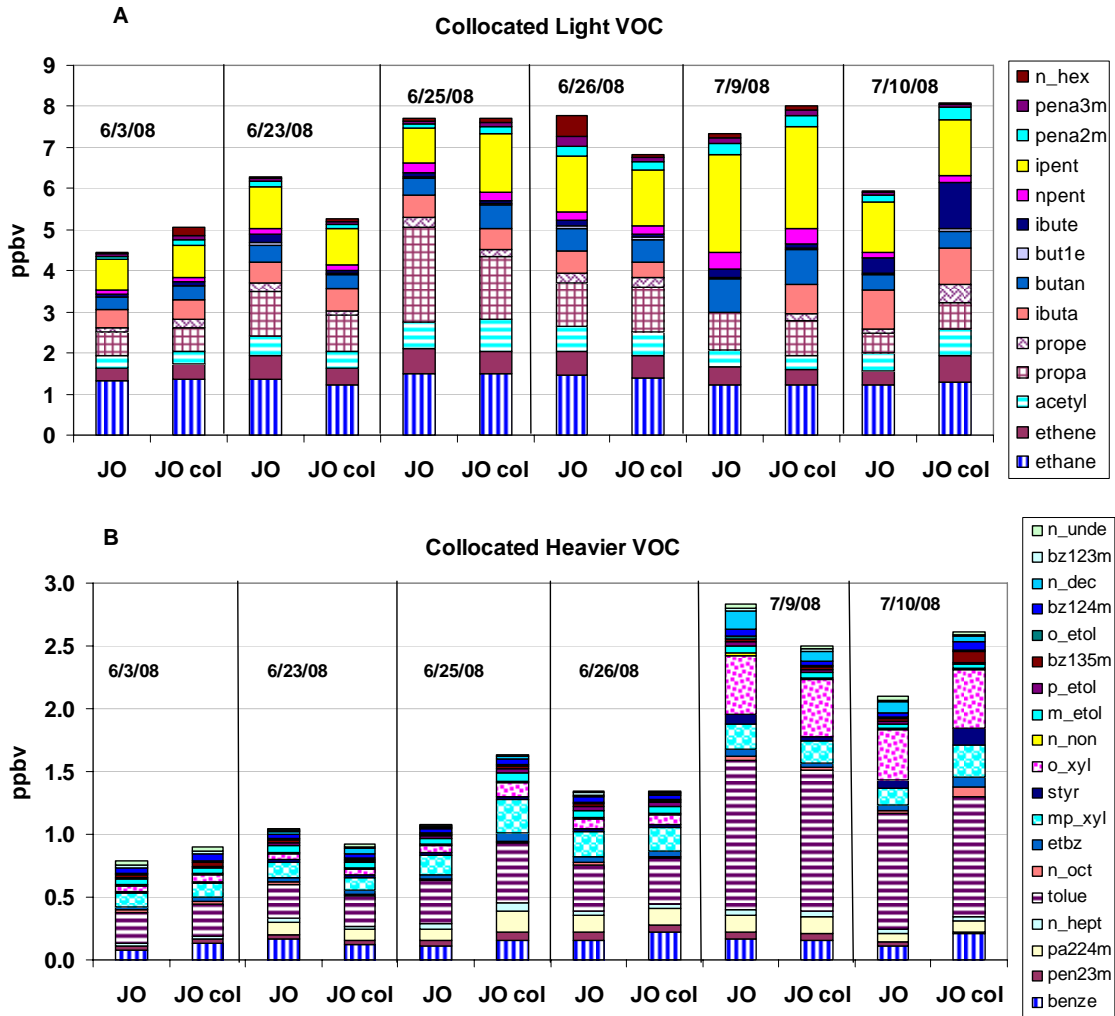


Figure 3.38. A: Collocated light VOC (C2 – C6) and B: heavier VOC (C6-C11) canister samples (see Table 3.2 for compound mnemonics) collected at the Joe Neal site.

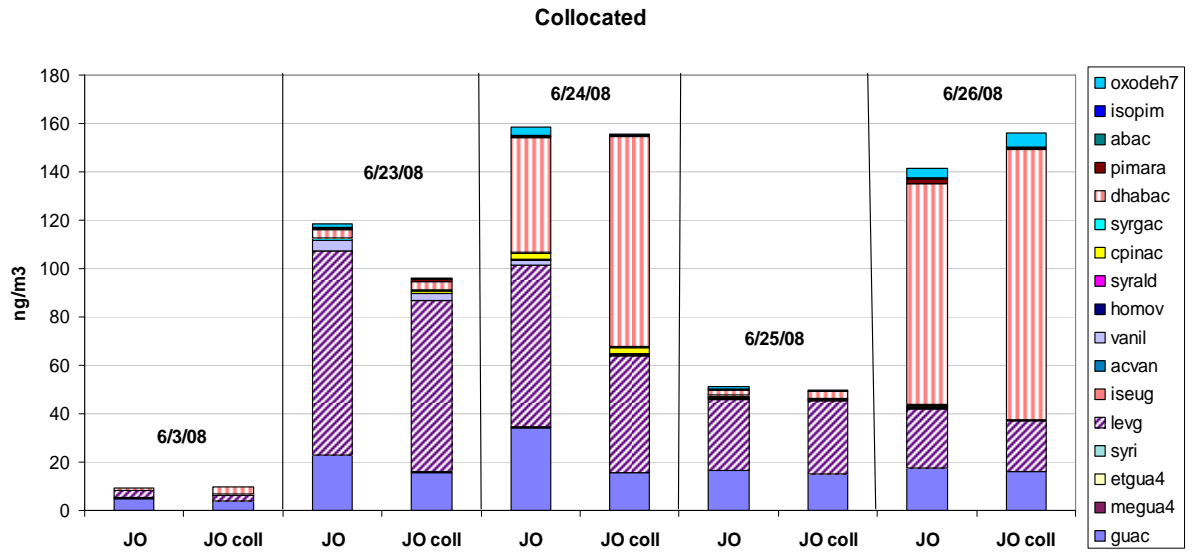


Figure 3.39. Collocated filter samples analyzed for the biomass tracers

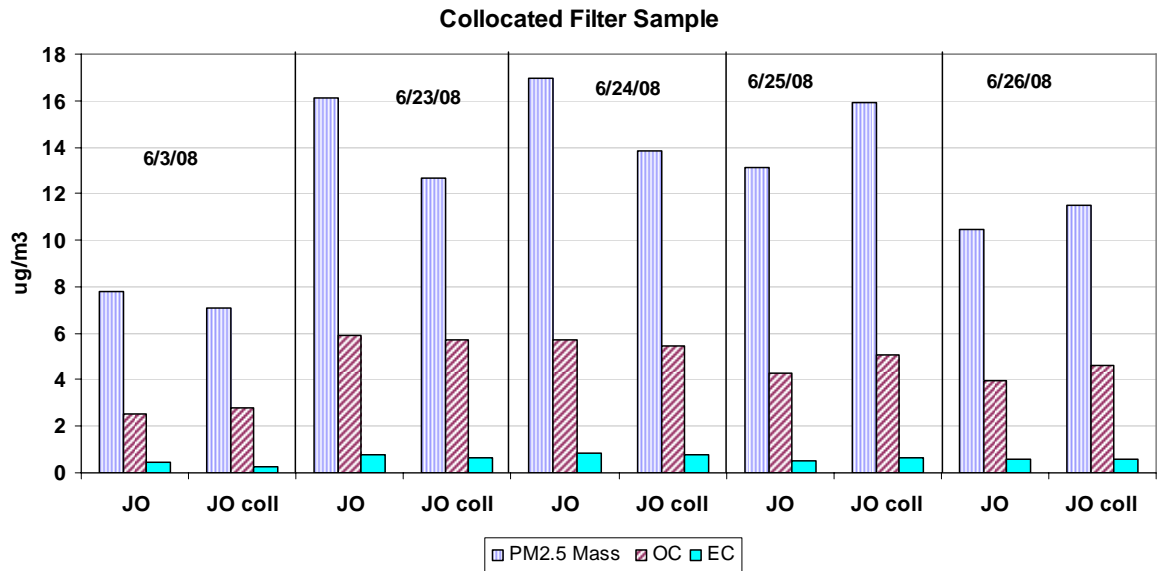


Figure 3.40. Collocated filter samples analyzed for PM mass, OC and EC

4. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Although the summer of 2008 was not impacted significantly by the wildland fire emissions, the limited data collected during the 2005 and 2008 study allows for the assessment of the relationships between wildfire emissions and ambient O₃ level and the importance of biomass burning on the ambient pollutants level. Specifically, we can draw the following conclusions:

- Levoglucosan, the most stable biomass burning marker, showed very good correlations ($R^2 = 0.7$) with the excess of 24-hr ozone concentrations in the 2005 study that were impacted significantly by the wildland fires.
- For the 2008 study, slightly worse correlations were observed, especially for the urban sites where the impact of motor vehicle emissions was predominant. However, there were no significant wildland fires recorded during this study.
- There is an excellent correlation ($R^2 = 0.99$) between 24-hr excess ozone sum and levoglucosan concentrations averaged over the whole study area. However, care has to be taken when interpreting the levoglucosan concentration data; meteorological conditions in the area and the smoke cloud transport time have to be taken into account.
- The correlation between soluble potassium and levoglucosan was rather low; this specie is not a good marker of wildland fires.
- Alkenes and aromatic VOCs that are emitted in larger quantities from wildland fires show good correlations during IOP#2 that was affected by the Clover fires. This may indicate that their concentrations during this monitoring period were influenced by wildland fire emissions. However, this may also indicate the differences in these compounds photochemical reactions during different IOPs.
- The most abundant carbonyl compounds observed during 2008 study were formaldehyde, acetaldehyde and acetone. These species showed excellent correlation during IOP#2 ($R^2 > 0.9$) Since only IOP #2 was influenced by the

wildfires, this may indicate that the concentrations of these species for this monitoring period were dominated by one common source, for example biomass burning that is a significant source of carbonyl compounds.

To formulate more definitive conclusions regarding the quantitative relationships between biomass burning tracers and ozone, more wildland fire events would need to be analyzed. Therefore, it is recommended that a similar field study will be conducted in the 2009 summer season. The incorporation of at least one continuous GC/FID instrument for 1-hr VOC measurements would be greatly beneficial for the future study.

5. REFERENCES

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