

1996 Paso del Norte Ozone Study VOC Measurements

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ABSTRACT

Ambient air VOC samples were collected at surface air quality monitoring sites near sources of interest, and aloft on the US and Mexican side of the border during a six week period of the 1996 Paso del Norte Ozone Study. On nine intensive operations (IOP) days, when high ozone concentrations were forecast, five 2-hr samples were collected at five IOP sites, three on the US side and two on the Mexican side. Six special survey sites on the US side and two on the Mexican side were sampled to characterize up-wind, down-wind and other emissions. In Ciudad Juárez, rush hour traffic, propane-powered bus exhaust, automobile paint shop emissions, propane and butane fuels, and an industrial manufacturing site were sampled. Carbonyl samples were collected at three surface sites. Carbonyl and canister grab samples were also collected during aircraft and hot air balloon flights. Most of the hydrocarbon samples were collected in electro-polished stainless steel canisters which were returned to laboratories for determination of C-2 to C-10+ hydrocarbons by cryogenic preconcentration GC-FID. The carbonyl samples were collected on DNPH impregnated C-18 Sep-Pak cartridges and analyzed by HPLC to quantify 13, C-1 to C-8 species. This paper presents the spatial and temporal characteristics of VOC species concentrations and compositions to examine the differences and similarities of the various locations and time periods. Overall surface TNMOC values ranged from 0.1 to 3.4 ppmC with the highest concentrations being recorded in the morning at three vehicle-dominated sites, two in Ciudad Juárez and one in downtown El Paso. Toluene in El Paso samples and propane, which is used as a cooking and transportation fuel in Ciudad Juárez, were the most abundant hydrocarbons. The most abundant carbonyls were acetaldehyde and acetone.

INTRODUCTION

The measurement of atmospheric volatile organic compound (VOC) concentrations is an important component of any large scale field study designed to characterize the air quality and meteorological processes that influence the formation and transport of ozone and ozone precursors in a large airshed such as the El Paso, Ciudad Juárez, Sunland Park area. Some of the objectives of the Paso del Norte Ozone Study required the measurement of speciated VOCs both at the surface and aloft at several locations in the airshed to determine VOC concentration levels, VOC composition and its relation to reactivity, and VOC concentration and composition variation over differing diurnal and meteorological conditions. A more complete examination of the Study's scope, objectives, and background is presented by Roberts *et al.*^{1,2}

For the Paso del Norte Study four types of VOC samples were collected. On nine intensive operations (IOP) days, when high ozone concentrations were forecast, five, 2-hr integrated samples were collected at five IOP sites, three on the US side and two on the Mexican side. Carbonyl samples were also collected at three of the IOP sites. VOC and carbonyl samples were collected aloft from balloon and aircraft platforms on some of the IOP days. Supplemental or source-specific survey sites, six on the US side and two on the Mexican side, were sampled on a twice daily, 2-hr integrated sample schedule unrelated to IOP events to determine up-wind, down-wind and other emissions characteristics. Several transportation and other source specific grab samples were taken mostly in Ciudad Juárez (Table 2). With the exception of one site, the samples were collected in electro-polished stainless steel canisters which were returned to laboratories for determination of C-2 to C-10+ hydrocarbons by cryogenic preconcentration gas chromatography-flame ionization detection (GC-FID). A continuous, automated gas chromatograph (auto-GC) was operated at one El Paso site.

EXPERIMENTAL METHODS

Surface ambient air samples were collected by microprocessor controlled samplers pumping air into passivated stainless steel spheres at sites in El Paso, Sunland Park and Ciudad Juárez. IOP samples were collected over 2-hr periods beginning at 06:00, 08:00, 10:00, 12:00, and 16:00 MDT on the nine IOP days. The El Paso survey site samples were taken over two, 2-hr periods on five week days in the first week of the study. The Ciudad Juárez survey sites, also two, 2-hr periods, and all source sites were sampled during the second week of the study. Carbonyl samples were collected on dinitrophenylhydrazine (DNPH) impregnated C-18 Sep-Pak cartridges at three surface sites. Carbonyl and canister samples were also collected during aircraft and hot air balloon flights. Table 1 shows sampling information by site. Further sampling details are available elsewhere.³

The canister samples were analyzed by GC-FID using two different columns. The C-2 to C-10+ hydrocarbons were separated on a 60-m, 0.32-mm i.d. fused silica capillary column with a 1- μ m thick film of a non-polar, cross-linked liquid phase (DB 1, J&W Scientific, Rancho Cordova, CA). Ethylene, acetylene, and ethane required separation on a 30-m, 0.53 mm i.d. GS-Q porous polymer open-tubular fused silica column (J&W Scientific), because they could not consistently be resolved on the 60-m non-polar column. The C-2 to C-10+ hydrocarbons were cryogenically preconcentrated in a 11-in x 1/8-in o.d. U-shaped trap filled with 60-80

mesh glass beads cooled by liquid argon in a Dewar flask. Injection was accomplished by switching a 6-port gas sampling valve and heating the trap with ~98°C water. In the case of the C-2 and C-3 hydrocarbons the trap was heated by room temperature water. A calibration/identification table of over 300 entries was used to identify peaks by retention times adjusted to prominent reference peaks. Some are labeled by compound name and others by a retention index identification number. The details of these analyses are published elsewhere.³ Selected samples were analyzed by GC-MSD (mass selective detection) to confirm peak identifications. One-hr samples were obtained from the auto-GC at the Chamizal site. The carbonyl samples were analyzed by high performance liquid chromatography (HPLC) to quantify 13, C-1 to C-8 species.⁴

RESULTS AND DISCUSSION

This paper reports the analysis results of 330 canister samples collected at surface sites between August 11 and September 21, 1996. We also include results of auto-gc measurements at the Chamizal site. Table 1 gives the site identification, number of samples, sampling regime, and brief description of the site characteristics for the IOP and survey samples. The site locations and other sampling details are given elsewhere.^{1, 2}

The total non-methane organic compounds (TNMOC) concentration was determined by summing all of the chromatographic peaks. It does not include the DNPH carbonyl results. This summation is not referred to as VOC or NMVOC, because not all of the VOC mass is recoverable and quantifiable from canister sampling and gc analysis. "VOC" is a more inclusive term that will refer to all volatile organic species including carbonyls. However, since no dryer was used prior to analysis, the TNMOC will contain some oxygenated hydrocarbon mass. The TNMOC distributions are presented in Figure 1 as scatter plots of concentration versus time for the surface monitoring sites.

Although the highest concentration sample was a 10:00 to midnight sample at the Ciudad Juárez Police Station (the only site where night time samples were taken), generally TNMOC was highest at the traffic dominated Ciudad Juárez sites of 20/30 Club, Advance Transformer, Police Station, and the El Paso Campbell site during the morning sampling periods. Four of the Ciudad Juárez samples were over 3 ppmC and 23% were over 1 ppmC. In El Paso the highest concentration was 1.2 ppmC at the Campbell site, which is in the downtown area near the interstate highway that bisects El Paso on an east-west axis. Only 6% of the El Paso measurements were over 1 ppmC. At the El Paso Chamizal site, maximum TNMOC was 2 ppmC; however, most of the concentrations were below 300 ppbC. With the exception of 06:00-08:00 at Winn Road, morning TNMOC at Sunland Park and the El Paso suburban sites (Dyer Road, Winn Road, and Turf Road) was much lower, ranging from 124 to 266 ppbC, than the four high concentration sites. Local traffic conditions at the Winn Road site were the likely cause of high TNMOC concentrations there (683 ppmC median; range from 233 to 974 ppbC).

The paraffins, olefins, aromatics, biogenics, and unidentified species groups were determined by summing the compounds in these groups. The group percentages were calculated for each sample by dividing the group sums by TNMOC. Plots of percent of TNMOC versus TNMOC for each group are shown in Figure 2. These plots show that compositions vary widely, especially at lower

concentrations. This is to be expected, since the distribution is over all sites and time periods and analytical precision and accuracy deteriorate with decreasing concentration. Variability is also increased by the mathematical certainty that a percentage change in one group must be compensated by changes in one or more other groups. The plots also show that paraffin and aromatic portions, from 10% to 72% and 4% to 67% respectively, vary more widely than the olefins and biogenics. As one might expect in a desert environment, the biogenic species concentrations (i.e., isoprene and α and β -pinenes) were low.

While the concentrations of unidentified species was relatively high overall, 50 to 200 ppbC, the median unidentified fraction of 21% is typical of urban results from other studies^{5,6}. The median unidentified portion of TNMOC was greater than 40% at Ascarate Park, Dyer Road and Franklin Mountain. Other studies have shown that the unidentified portion is typically higher in afternoon and background air samples.⁷ This was the case at the Ascarate Park, Dyer Road, and Franklin Mountain sites, possibly due to aging of the air mass.

Summations of the carbonyl compound concentrations, shown in Figure 3 as a function of time of day, were relatively low, typically less than 15 ppbC total. However a few measurements reached ~30 ppbC at Winn Road and Turf Road, but only 16 ppbC at 20/30 Club. Highest concentrations were observed at Winn Road and Turf Road during midday when TNMOC concentrations were lowest and accounted for a significant portion of the total carbon, up to 32%. At 20/30 Club the maximum percentage is only 4.4%. Acrolein, crotonaldehyde, and tolualdehyde were below detection in all samples. At 20/30 Club, the most abundant species were in order of abundance acetaldehyde, formaldehyde, acetone, and methylethylketone. Concentrations were typically highest during midday and changed the most with time of day for formaldehyde, acetaldehyde, and acetone. At Turf Road, the most abundant species was acetone. Significant concentrations of benzaldehyde were also observed at this site, while formaldehyde concentrations were low. At Winn Road the most abundant species was acetone. This site also showed relatively high concentrations of benzaldehyde compared to 20/30 Club. Formaldehyde concentrations were low at Winn Road.

The hydrocarbon species were ranked by median concentration. The 25 most abundant species accounted for 70 to 80% of the TNMOC and consisted of 15 paraffins, 6 aromatics, 3 olefins, and acetylene. The 12 most abundant compounds are plotted in Figures 4a and b as concentration versus site. Except for propane and ethane the abundant compounds are associated with vehicular emissions and gasoline.⁸

In Ciudad Juárez, as in Mexico City, the most abundant compound was propane.⁹ Concentrations over 1 ppmC at Advance Transformer and Police Station sites and 0.9 ppmC at 20/30 Club suggest local sources of propane. This is not surprising since propane is used for cooking and fuels buses in Ciudad Juárez. The Police Station in particular was dominated by propane powered bus traffic, which is consistent with its median propane proportion of 21% of TNMOC. The portion of propane at the Zenco and the Sunland Park sites were also over 10%, indicative of local sources. In contrast propane accounted for a median of ~5% in Baltimore in 1996.¹⁰

Toluene, a major industrial solvent and a principal component of automobile exhaust and gasoline,⁸ was the second most abundant compound in Ciudad Juárez and the most abundant compound on the El Paso side. Concentrations up to 221 ppbC were observed at the Police

Station and 108 at the El Paso Campbell site. The median toluene concentration in Ciudad Juárez was 37 ppbC compared to 25 ppbC at Campbell and 4.3 ppbC at Franklin Mountain. The median toluene percentage of TNMOC ranged between 5.3% and 6.8% for sites dominated by morning traffic. The highest median, 13.5% was at the Zenco industrial site.

Median concentration and weight percent composition plots for all sites and time periods (not shown here, see ref. 2) showed little change with time of day in species composition, indicating that most sites experienced fresh emissions during all sampling periods. This is to be expected, since of the five IOP sites with sufficient time of day resolution, three of them, 20/30 Club, Advance Transformer, and Campbell, were near major roadways and/or industrial sources. Matrix scatter plots of concentration of the 20 most abundant compounds (not shown here, see ref. 2) were prepared to look at relationships between compounds. Observations from these plots by site follow:

Chamizal: The composition was representative of other sites that are influenced by fresh motor vehicle emissions all day, with toluene, xylenes, benzene, C4-C8 paraffins, and propane dominating the profile. The dominance of gasoline vehicle exhaust was confirmed from source apportionment analyses of measurements at this site.¹¹

20/30 Club: The most abundant species was propane. Ethene was also a significant species at this site. The motor vehicle exhaust signature is observed by relatively good correlations among benzene, acetylene, ethene, propene, and several of the paraffins. The following species pairs also appear to be from common sources: xylenes and ethylbenzene, 2,2,4-trimethylpentane and several species associated with motor vehicle exhaust, and the butanes and pentanes (evaporative emission species). Many plots at this site show outliers, indicating that there may be more than one source type influencing this site.

Advance Transformer: The composition was very similar to 20/30 Club with the exception of the C2 species; there was little ethane and ethene at Advanced Transformer. Also at this site, isopentane was more abundant than toluene. Few species show strong relationships, indicating a mixture of sources impacting the site, consistent with the industrial setting of the site. The following species pairs appear to be from common sources: propane and the butanes, the xylenes and ethylbenzene. Many motor vehicle exhaust species correlate relatively well (e.g., benzene, acetylene, ethene, methylpentanes, hexane, etc.). Most of the relationships with toluene show a substantial amount of scatter, possibly indicating a separate source of toluene (such as solvent use). There is an interesting "split" in the scatter plots of many of the aromatic species versus paraffins, also suggesting the influence of different sources. Several samples show high concentrations of propane and ethene.

Campbell: Toluene was the most abundant species. The C2 species were important at this site (similar to 20/30 Club) as was isopentane (similar to Advanced Transformer). At Campbell the correlations among the species are very similar to that observed at Winn Road; most of the species associated with motor vehicle exhaust correlate well. Ethane and propane do not correlate with these species, however, indicating a separate source such as natural gas emissions. Some of the scatter in the n-butane concentrations may also be attributable to natural gas emissions. The 2,2,4-trimethylpentane concentrations correlate well with the other species in exhaust.

Sunland Park: Propane and ethane were the two most abundant species followed by toluene. The composition of the C3+ TNMOC at this site is similar to the Police Station, although the concentrations were much lower.

Ascarate Park: The dominant species were the xylenes. The contribution of the xylenes increased from the 1000-1200 to the 1200-1400 sampling period, suggesting a local source. Typically, ambient data show a decrease in the xylene composition with time of day, because these species are relatively more reactive than other species in the fingerprint. Also at this site, ethene concentrations were relatively low.

Dyer Road: TNMOC concentrations were low and the 1000-1200 and 1200-1400 sample compositions differed significantly. The afternoon composition showed some evidence of aging (i.e., the decrease of more-reactive species relative to less-reactive species). The composition at this site also differed from other sites with the higher relative abundance of styrene, cyclohexene, c-2-butene, and 1,3,5-trimethylbenzene. Ethene concentrations were low compared to ethane.

Turf Road: The composition was dominated by C2-C5 paraffins, toluene, and 1,2,4-trimethylbenzene. The composition changes somewhat with time of day; however, there is no clear indication of aging in the composition on a median basis. The source of 1,2,4-trimethylbenzene should be investigated. At Turf Road, the scatter plots show much weaker correlations than observed at Winn Road, the poorer correlations (e.g., benzene versus acetylene) are indicative of more-aged air. One exception is that the butanes and pentanes correlate very well, indicating a common source (probably evaporative emissions).

Winn Road: As observed at Turf Road, the 1,2,4-trimethylbenzene contribution to TNMOC was high. Also as observed at Turf Road, the composition changes somewhat with time of day; however, there is no clear indication of aging in the composition on a median basis. Many of the species typically associated with motor vehicle exhaust correlate well (e.g., toluene, isopentane, ethene, acetylene, benzene, methylpentanes, n-pentane, the xylenes, and propene). A strong correlation is found between n-butane and isobutane probably related to an evaporative emission source; these species also show a reasonable correlation with the exhaust species. The 1,2,4-trimethylbenzene concentrations do not correlate very well with other aromatic species or with the exhaust species indicating a separate source of this compound.

Franklin Mountain: Propane was the most abundant species. Styrene concentrations were generally greater than o-xylene at this site, similar to Dyer Road. Since the site was at a television tower facility, there may be a local source of styrene and other hydrocarbons.

CONCLUSIONS

In the El Paso-Sunland Park area TNMOC concentrations ranged from quite low in the afternoon at the out lying sites of Winn Road (36 ppbC) and Turf Road (39 ppbC) to over 1 ppmC in the morning at the traffic dominated Campbell site. TNMOC concentrations at the four Ciudad Juárez sites were much higher, ranging from 159 ppbC at Advance Transformer to over 3 ppmC at 20/30 Club, Advance Transformer and Police Station. The higher population, higher traffic abundance and density, greater vehicle age,^{12, 13} and the widespread use of propane for cooking and as fuel for buses probably account for much of the higher TNMOC concentrations in Ciudad

Juárez.

Propane was one of the most abundant hydrocarbons; this was expected due to the use of propane fuel. Toluene, also an abundant hydrocarbon, was likely mostly of vehicular origin. Other abundant hydrocarbons representative of vehicular related sources were pentanes, xylenes, butanes, benzene, ethylene, and acetylene. Some sites in El Paso and Ciudad Juárez showed evidence of other VOC sources such as industrial solvents(e.g., xylenes at Ascarate park, styrene at Franklin Mountain, and 1,2,4-trimethylbenzene at Turf Road).

Carbonyl compounds at the suburban sites were relatively low, ranging from 0.2 to 32 ppbC with highest concentrations midday. Since carbonyl compounds are both directly emitted and formed as photochemical products of reaction, the higher concentrations midday suggest the probable importance of photochemistry as a source of carbonyls at these sites. Concentrations were lower, ranging from 4 to 16 ppbC and did not vary much at the 20/30 Club, a high VOC, direct emissions source site.

The range of TNMOC at the background site on Franklin Mountain were relatively high for a downwind site, ranging from 128 to 250 ppbC. The concentrations and composition of VOC at this site, although much lower than the downtown Campbell site, showed the impact of urban emissions.

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DISCLAIMER

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TABLES

Table1. Paso del Norte VOC sampling locations.

Site	N ^a	Sampling Period ^b	Description
Delmex	2	5-min grab samples	Ciudad Juárez industrial area
Zenco	3	2-hr samples taken on 2 days during second week of study	Ciudad Juárez survey site: manufacturing area near airport
Police Station	10	6-8, 10-12 on 5 days during second week of study	Ciudad Juárez survey site: near downtown, high traffic area
Advance Transformer	50	2-hr samples beginning at 6, 8, 10, 12, 16 on IOP days	Ciudad Juárez IOP site: industrial manufacturing area with morning & evening traffic
20/30 Club	51	2-hr samples beginning at 6, 8, 10, 12, 16 on IOP days	Ciudad Juárez IOP site: commercial, suburban, near major thoroughfare
Campbell	48	2-hr samples beginning at 6, 8, 10, 12, 16 on IOP days	El Paso IOP site: downtown very near interstate highway
Franklin Mts	9	6-8, 8-10 on 5 days during first week of study	El Paso survey, boundary site on mountain north of El Paso
Sunland Park	10	6-8, 8-10 on 5 days during first week of study	Sunland Park, NM survey site: at city offices downtown area
Ascarate Park	10	10-12, 12-14 on 5 days during first week of study	El Paso survey site: park & golf course
Dyer Road	10	10-12, 12-14 on 5 days during first week of study	El Paso survey site, suburban location
Turf Road	51	2-hr samples beginning at 6, 8, 10, 12, 16 on IOP days	El Paso IOP site, suburban location
Winn Road	47	2-hr samples beginning at 6, 8, 10, 12, 16 on IOP days	El Paso IOP site, suburban location
Chevron refinery	10	2-hr samples, 2 per day over 5 days during second week	El Paso source site, oil refinery

^a N=number of samples. ^b Times are 24-hr, Mountain Daylight Time (MDT). IOP=Intensive Operating Period.

Table 2. Paso del Norte VOC special source samples.

Site	Number of Samples	Sampling Period	Description
Ciudad Juárez traffic	2	~5-min samples taken from car in moving traffic	samples taken near downtown Ciudad Juárez
Ciudad Juárez propane buses	2	~5-min samples taken from car in bus traffic. 1 grab sample taken from bus tailpipe	samples taken downtown Ciudad Juárez near bus station
Ciudad Juárez paint shop	4	~5-min samples	samples from small auto body paint shop
Ciudad Juárez propane and natural gas	7	canister grab samples	1 natural gas and 2 propane distributors
El Paso propane	2	canister grab samples	2 propane distributors

FIGURES

Figure 1. Distribution of TNMOC as a function of time of day by site.

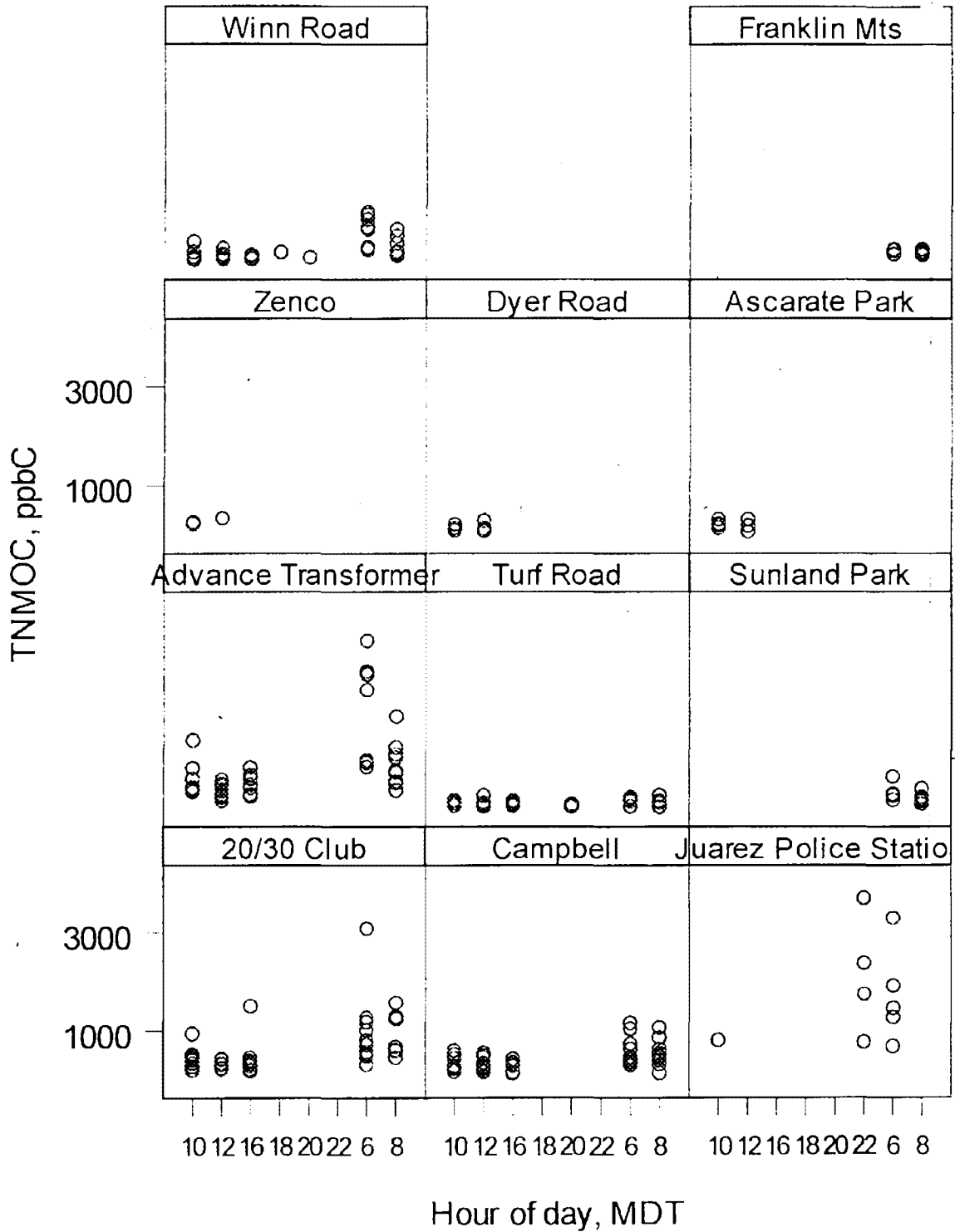


Figure 2. Distribution of compound groups versus concentration.

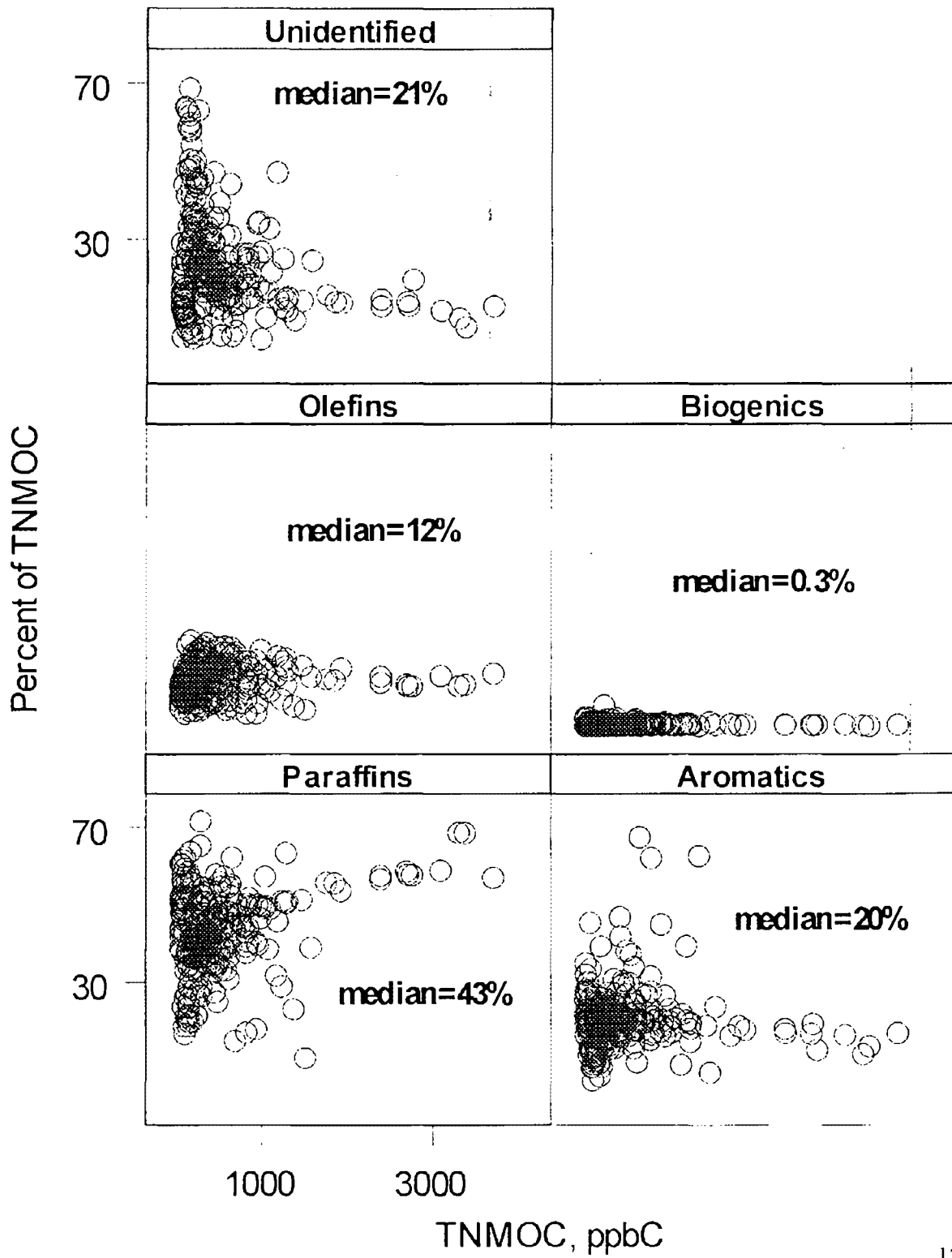


Figure 3. Distribution of total carbonyls by time of day

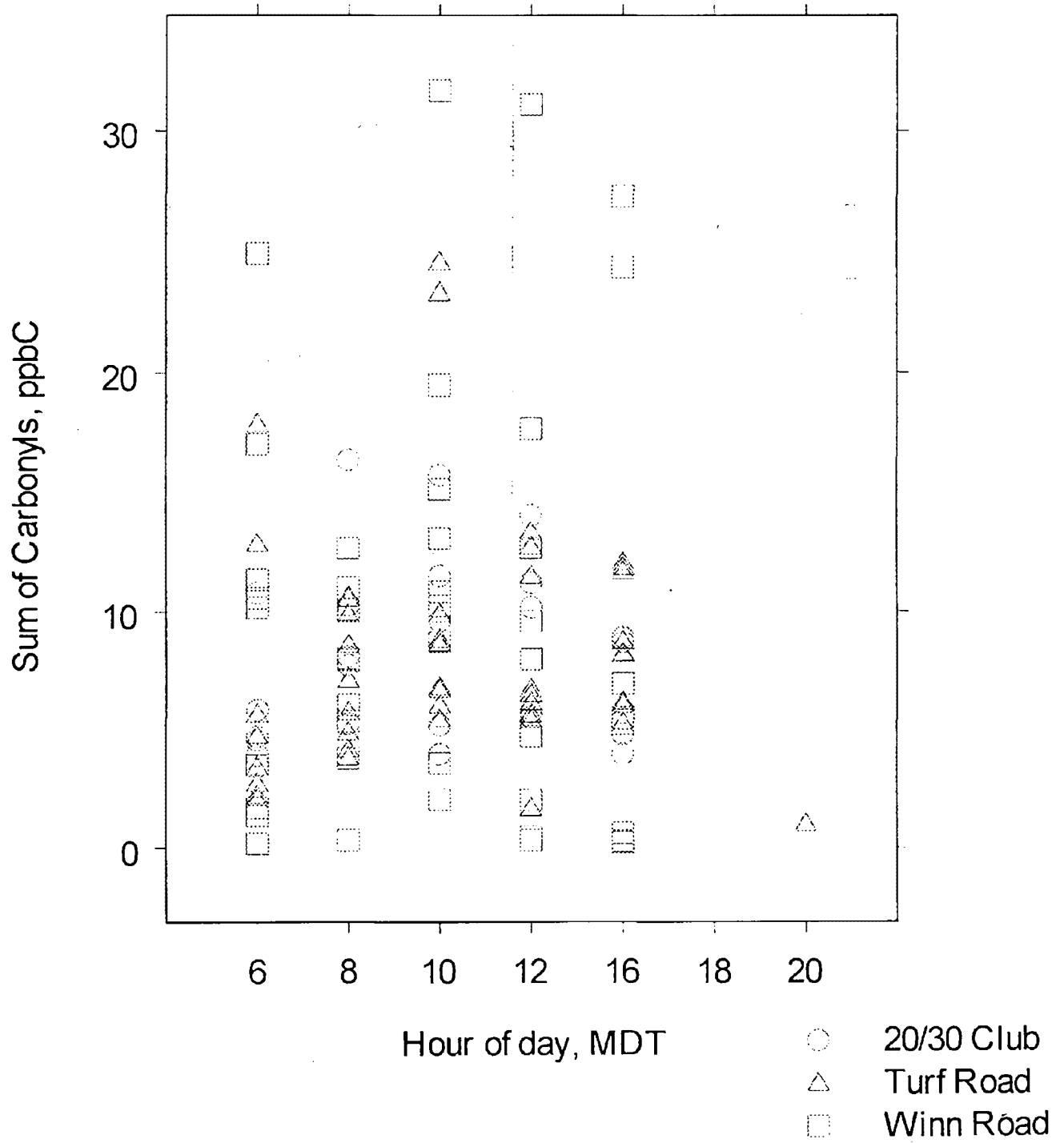


Figure 4a. Distribution of the six most abundant hydrocarbons by site. The x-axis range is not large enough to show all of the point for propane (see text).

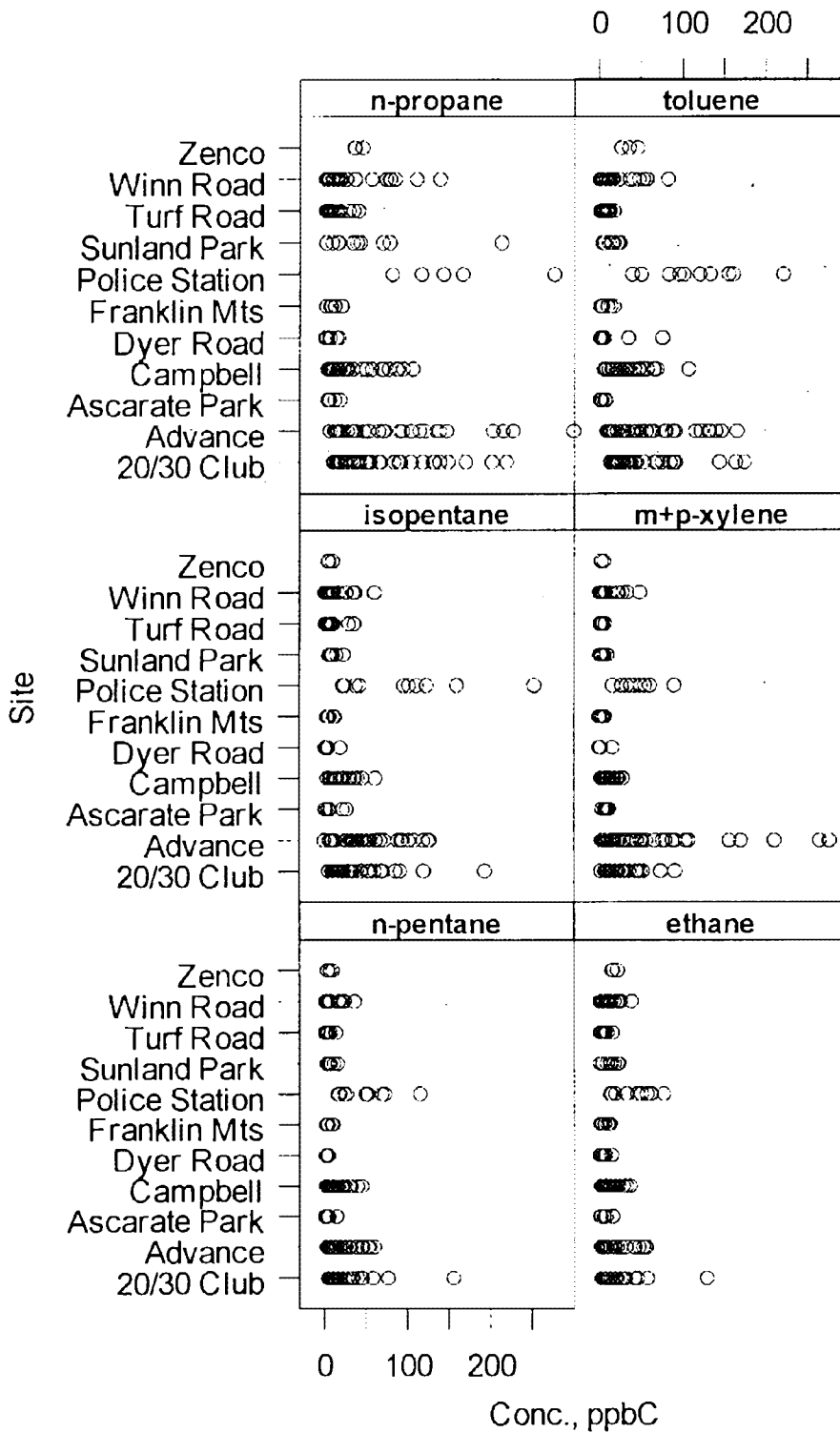
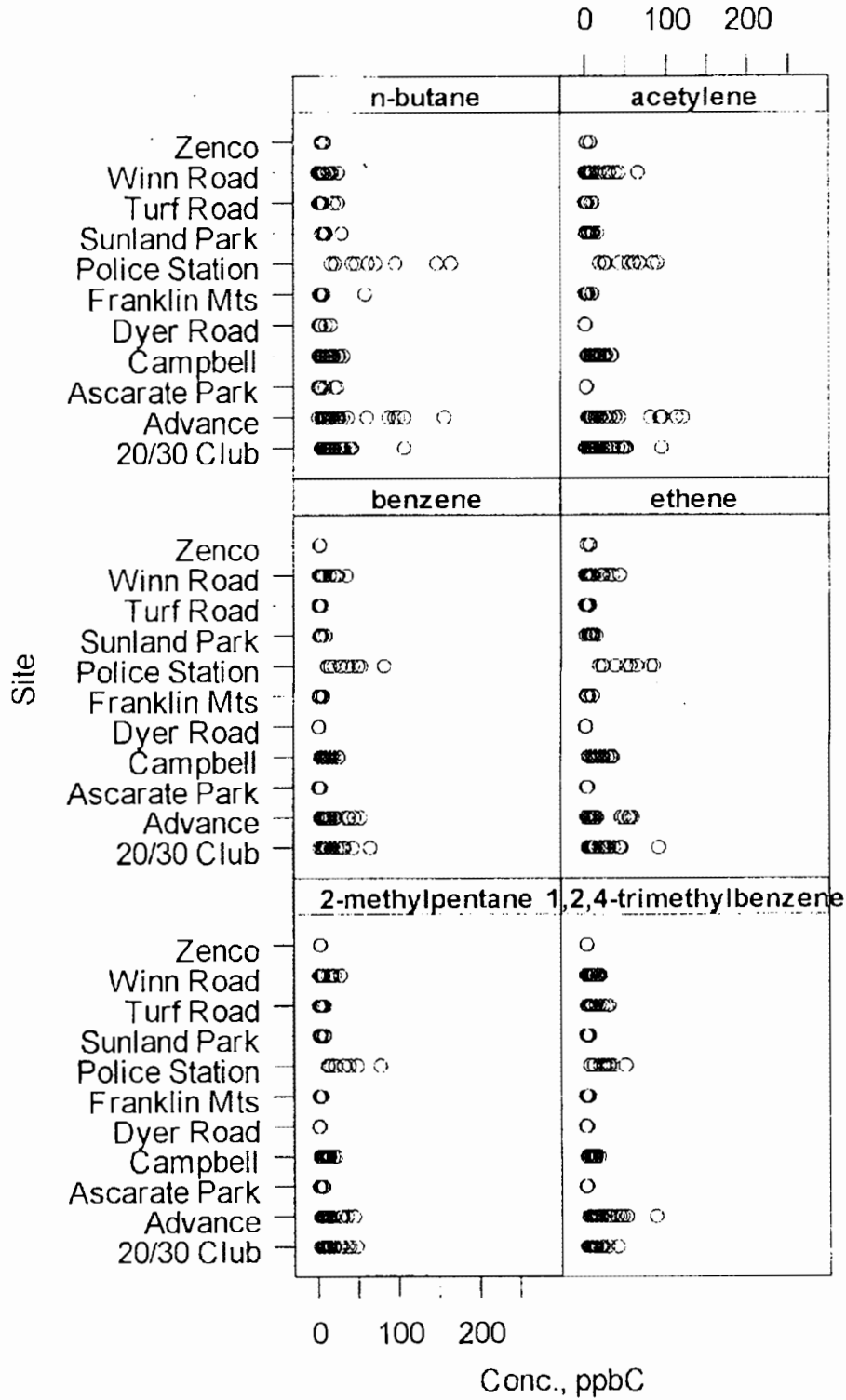


Figure 4b. Distribution of the second six most abundant hydrocarbons by site.



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