Weekday/Weekend Differences in Concentrations of Air Toxics in New York, NY; Philadelphia, PA; and Houston, TX

Task 2 Report
CRC Project A-49

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Abstract

In this task of CRC Project A-49, weekday/weekend differences are analyzed using routine ambient data for three air toxics related to mobile source emissions, including elemental carbon, formaldehyde, and benzene. New York City, Philadelphia, and Houston are the three metropolitan areas studied. Of the three pollutants, elemental carbon shows the largest weekday/weekend differences, with the East Coast cities showing larger differences than Houston. The weekly cycle reflects the activity patterns in diesel emissions, especially heavy duty vehicles. Formaldehyde shows no discernable weekly cycles at moderate concentrations, but there is some indication of a weekend increase in the East Coast cities. Secondary production of formaldehyde may increase during weekends in photochemical reactions that are related to O_3, which shows a weekend effect at the same locations. The weaker cycle for formaldehyde in Houston may be related to a larger contribution of secondary formation from biogenic rather than anthropogenic VOC emissions. Weekday/weekend differences in 24-hour average benzene are insignificant at many locations, but the weekday/weekend differences in rush-hour concentrations are significant. These observations will be used in Task 3 to evaluate the accuracy of the temporal profiles of emission data used in models.

Acknowledgments

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Executive Summary

The goals of CRC Project A-49 are to (1) assess the current state of knowledge of air toxics related to mobile source emissions, (2) analyze the ambient concentrations of air toxics associated with mobile sources to tease out weekly signals, if any, that may be attributed to mobile source emissions, and (3) conduct modeling and compare modeling results against the observed weekly profiles to assess the accuracy of the temporal representation of emissions used in the current inventories. Under Task 1, recent air toxics modeling studies were reviewed and recommendations were made for areas of improvement, including an analysis of the weekday/weekend differences in air toxics concentrations and improvements in the emissions data and spatial and temporal allocation factors. This report summarizes the results of Task 2, the data analysis task. The results not only address a major gap identified in Task 1, but are also useful for comparison with the modeling results of Task 3 for the identification of limitations in the inventories and temporal allocation factors.

Routine ambient data were used to study the day-of-the-week differences of three air toxics emitted in part from mobile-sources, including elemental carbon (EC), formaldehyde (HCHO), and benzene. The metropolitan areas of New York City, NY; Philadelphia, PA; and Houston, TX were chosen for this study because they have abundant data for each of these pollutants.

Measurement data were obtained from EPA's Air Quality System (AQS) database. Processing steps were taken to remove invalid data or data associated with known extraordinary events. Sites were selected for analysis when they provided at least 30 data points per day of the week. Each data set was manipulated so that all months were represented equally in a data set that contained multiple years. For the analysis of 24-hour average concentrations, sub-daily samples were aggregated only when they satisfied a data completeness criterion of 75%.

Elemental carbon measurements started in 2000 as a result of the promulgation of the $PM_{2.5}$ National Ambient Air Quality Standards. The Speciation Trends Network (STN) sampling protocol calls for a 24-hour average sample to be collected every third day. Benzene and formaldehyde are both target species of the Photochemical Assessment Monitoring Stations (PAMS) network. This network started in 1993 and certain sites make higher frequency or shorter duration measurements during the ozone season. Sampling frequencies range from every twelfth day, sixth day, third day, to every day. Sampling durations include 1 hour, 3 hours and 24 hours. Frequencies and sampling durations may also change during different years.

As a default, annual averages were considered. A data record in a multiple of 12 months was used, because it is desirable to represent equally every month of the year in an annual average. Because monitoring sites came and went, a uniform set of dates was not picked for each site with the requisite amount of data. Typically, a period of at least 3 years was considered to "average out" meteorological effects. For sites with long-term records, no more than 10 years' worth of data was used because changes in emissions may render earlier data incompatible with current trends. Metrics used to characterize the concentrations on each day of the week include the average, median, and 75^{th} percentile concentrations for each day. For the two gaseous pollutants, the average concentration is sometimes skewed by high concentrations. The median concentration is considered a more robust statistical metric. The 75^{th} percentile concentration is used to compare high concentrations. Two types of plots are used throughout this analysis. Box plots present the average, median, 25^{th}, and 75^{th} percentiles for each day of the week. Quantile-quantile plots present the corresponding concentrations of two groups of days (weekdays vs. weekends) at corresponding percentiles.

Of the three pollutants studied in this work, elemental carbon and benzene are emitted species while formaldehyde is both emitted and formed in the atmosphere. There are some differences in the day-of-the-week behavior of these pollutants that are quite consistent with expectations due to their different sources.

Elemental carbon shows significant decreases in concentrations during weekends at most sites. The magnitude of weekday-weekend change is higher in New York City and Philadelphia than in Houston, perhaps in part due to overall lower concentrations in Houston. The Wednesday-Sunday differences in the median concentrations are 0.2 to 0.9 $\mu g/m^3$ in the two East Coast cities and 0.1 $\mu g/m^3$ in Houston. Figure ES-1 shows the average, median, 25^{th}, and 75^{th} percentile elemental carbon concentrations for each day of the week at the Queens, NY site, which shows a significant decrease of elemental carbon concentrations on weekends. Elemental carbon is emitted from combustion sources, including a significant contribution from heavy-duty diesel trucks. Previous studies have found that the activity of heavy-duty diesel trucks decreases by 40-80% on weekends compared to weekdays in the California South Coast Air Basin (Chinkin et al., 2003), contributing to a strong weekly cycle at all three urban areas studied.

At moderate concentrations, midweek day and weekend concentrations of formaldehyde are not different statistically. There is some indication that at high concentrations (e.g., 75^{th} percentile), weekend concentrations can be higher than weekday concentrations in New York City and Philadelphia, although the difference is statistically significant at only one site (Bronx, NY, shown in Figure ES-2). No other consistent difference is identified. Formaldehyde is directly emitted, as well as formed during the atmospheric oxidation of VOC, whose anthropogenic emissions may also be subject to a weekly cycle depending on the source types. The formation and destruction of formaldehyde depends on the availability of oxidants. The weekend increase in formaldehyde in the East Coast cities may be related to the ozone weekend effect (increase during weekends) that has been identified in that part of the country (Pun et al., 2003). Because formaldehyde is a universal photochemical product of anthropogenic and biogenic VOC, locations with significant biogenic emissions (e.g., Houston) may have a weaker day-of-the-week signal of formaldehyde compared with locations with large anthropogenic contributions.

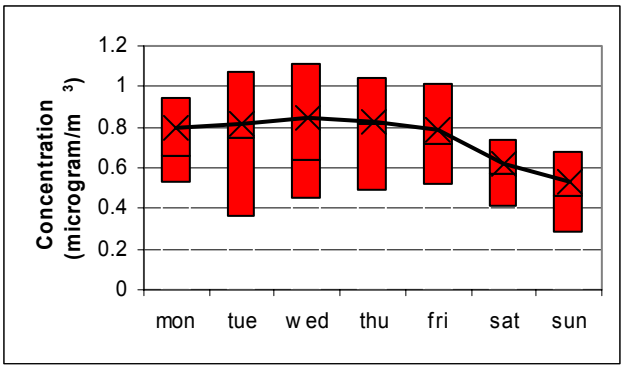


Figure ES-1. The mean, median, 25th percentile, and 75th percentile elemental carbon concentrations for each day of the week at the Queens, NY site. (Means are represented by lines and symbols, medians are represented by lines in the middle of box, 25th and 75th percentiles are shown as the edges of the box.)

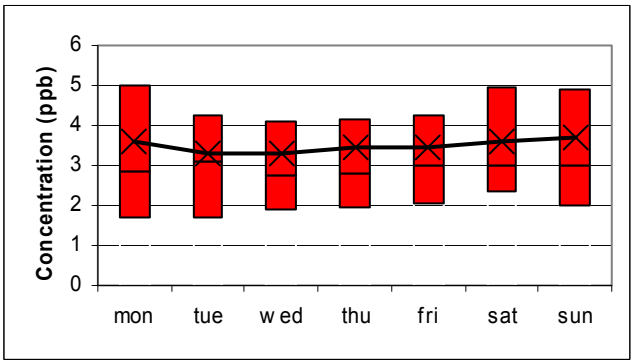


Figure ES-2. The mean, median, 25th percentile, and 75th percentile formaldehyde concentrations for each day of the week at the Bronx, NY site. (Means are represented by lines and symbols, medians are represented by lines in the middle of box, 25th and 75th percentiles are shown as the edges of the box.)

For benzene, the differences in the weekday vs. weekend 24-hour average concentrations are statistically significant at a few sites in the three urban areas studied but not at all sites. Statistically significant differences range from 0.03 to 0.08 ppb between midweek median concentrations and weekend concentrations. In New York City, the Wednesday-Sunday differences in median concentrations are 0.12, 0.09, -0.02, and 0.02 ppb at the four sites; the two largest differences, in Kings and Queens, are statistically significant. Sites in Philadelphia record statistically insignificant differences (0.02 to 0.05 ppb) of Wednesday vs. Sunday median concentrations. The Wednesday median concentrations are more than 0.1 ppb greater than the Sunday median at 3 sites in Houston. Those are the only statistical significant Wednesday-Sunday differences in Houston; statistically insignificant Wednesday-Sunday differences range from -0.04 to 0.09 ppb in Houston. Benzene is emitted from gasoline vehicles among other sources. Between weekdays and weekends, there is a large difference in the traffic patterns in terms of when activities take place, but the overall change in emissions may be quite small (of the order 10 to 15%) (Chinkin et al., 2003). This change is much smaller than the expected change in diesel activity, and, therefore, the weekly cycle of benzene can be expected to be much smaller than that of elemental carbon. At a few monitors where short-duration samples are taken during traffic rush hours, significant decreases on weekends are observed, lending confidence to the ability to see a stronger signal. Therefore, the weaker signal in the 24-hour concentrations is postulated to be due to a smaller change in the average daily emissions as well as to other factors whose variabilities do not depend on the day of the week, such as dilution and dispersion. Figure ES-3 shows a comparison of the day-of-the-week behavior of 24-hour vs. rush hour benzene concentrations.

The next task in A-49 is to conduct modeling and compare the modeled weekday/weekend differences of elemental carbon, formaldehyde, and benzene against observations of the weekday/weekend differences documented in this report. The comparison will be used to evaluate the accuracy of the temporal profile data used in models and recommendations will be made on areas of improvement for the model input data.

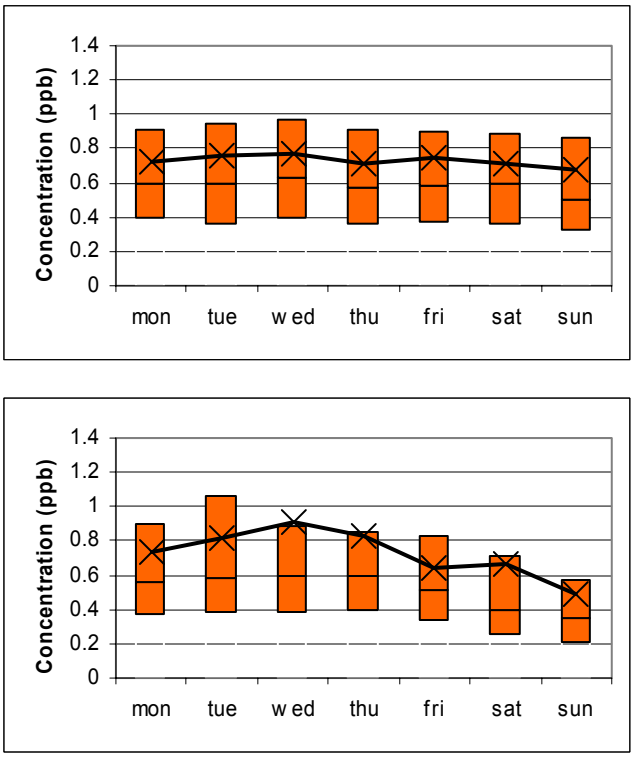


Figure ES-3. The mean, median, 25th percentile, and 75th percentile benzene concentrations for each day of the week at the Clinton Drive, Houston site: (top) 24-hour average concentrations and (bottom) rush hour concentrations.

Using ambient data to infer day-of-the-week behavior is subject to uncertainties, including, but not limited to, variations in emissions and meteorology. The uncertainties mentioned, however, should become inconsequential once the data sets are large enough, especially if statistical metrics that are insensitive to extreme values are used. There is also some evidence that certain sites are affected by short-term high concentrations (spikes) of formaldehyde or benzene. Although these high concentrations are not routine, they occur with enough frequency to skew the 24-hour data. Shorter duration data during rush hours have proven to provide a clearer picture for deciphering changes in benzene emissions – they may be less affected by concentration spikes because of their higher concentration levels, or they may simply focus on a period of time with the maximum change in emissions with the day of the week.

1. Introduction

Elemental carbon (EC), formaldehyde (HCHO) and benzene are examples of toxic air pollutants that are associated with mobile source emissions. Elemental carbon, which is a component of fine particulate matter with aerodynamic diameter less than or equal to 2.5 microns ($PM_{2.5}$), is typically associated with a variety of combustion activities, including diesel vehicle emissions. HCHO is a primary pollutant released from gasoline and diesel vehicles as well as other combustion sources. HCHO is also a product of photochemical reaction of virtually all classes of volatile organic compounds, including alkanes, alkenes, aromatic compounds, alcohols and other oxygenated compounds. The secondary HCHO can be formed from atmospheric reactions of anthropogenic and biogenic emissions. Benzene is a component of gasoline. Both evaporation and tail pipe emissions are sources of benzene in the urban atmosphere. Other anthropogenic sources of benzene include tobacco smoke and some industrial processes.

The goals of CRC Project A-49 are to (1) assess the current state of knowledge of air toxics relating to mobile source emissions, (2) analyze the ambient concentrations of air toxics associated with mobile sources to tease out weekly signals, if any, that may be attributed to mobile source emissions, and (3) conduct modeling and compare modeling results against the observed weekly profiles to assess the accuracy of the temporal representation of emissions used in the inventories. This report summarizes the results of Task 2, the data analysis task. The objective of this task is to compare and contrast the weekday/weekend signals of these three toxic air pollutants in three urban areas. The target areas of New York, NY; Philadelphia, PA, and Houston, TX were selected based on data availability.

2. Data Preparation

EC is associated with $PM_{2.5}$ and is measured at the $PM_{2.5}$ speciation trends network (STN) and supplemental sites. Monitoring of $PM_{2.5}$ composition started in 2000 as a result of the promulgation of the $PM_{2.5}$ National Ambient Air Quality Standards. The STN sampling protocol calls a 24-hour average sample to be collected every third day. Many supplemental sites also follow the same protocol.

Benzene and HCHO are both target species of the Photochemical Assessment Monitoring Stations (PAMS) network. This network started in 1993 with a goal of understanding photochemical ozone air pollution. Therefore, there is an emphasis on ozone-season measurements at many sites, either in terms of frequency (higher) or duration (shorter) of measurements. There is a lesser degree of standardization of protocols among different PAMS sites compared to the STN. Sampling frequencies range from every twelfth day, sixth day, third day, to every day. Sampling durations range from 1 hour, 3 hours to 24 hours. There are also instances where several frequencies and sampling durations were employed at a given site during different years.

The Air Quality System (AQS) database is the central repository of monitoring data taken by EPA and State and Local agencies. Raw AQS data were obtained from V. Ambrose, EPA on August 16, 2005. Data extraction criteria were specified as follows. Parameters of interest were benzene (AQS parameter code 45201), HCHO (parameter code 43502), and EC (parameter code 88307). A separate query for the parameter for BC (88313), an acronym for black carbon that is an alternative name for EC, resulted in no data for the three metropolitan statistical area of interest, which were: Houston (AQS MSA code 3360), New York City (NYC, MSA code 5600), Philadelphia (MSA code 6160). The resulting data file contained some data for 2005, the most recent data being from May 2005 at some sites, but such recent data were not available at all sites.

Data assurance steps were performed to remove null data and data associated with qualifier flags. The only exception was that data associated with a qualifier flag of "V"

(for validated) were retained. Other qualifying flags signal quality assurance (QA) issues and extraordinary events. QA issues, such are field or laboratory issues or operational deviation, could result in data of uncertain quality. Extraordinary events, such as fires or construction, could lead to outliers that skewed the statistics.

A complete list of sites was prepared for each species. For a site to be included in the weekday/weekend analysis, its sample record must be continuous and contain 30 or more data points of comparable sample duration (typically 24-hour average) for each day of the week. Thirty data points for each day of the week were needed for stable estimates of the average concentration for each day of the week. The criterion on the number of data points was satisfied at sites that had long data records (e.g., five years), that operated throughout the year (as opposed to only during summer months), or that sampled at a high frequency (e.g., every day instead of every third/sixth day)

As a default, annual averages were considered. A data record in a multiple of 12 months was used, because it is desirable to represent equally every month of the year in an annual average. Because monitoring sites came and went, a uniform set of dates was not picked for each site with the requisite amount of data. For the same period considered, the number of valid data points differed among sites due to differences in data capture. Typically, a period of at least 3 years was considered to "average out" meteorology effects. For sites with long-term records, no more than 10 years' worth of data was used because changes in emissions may render earlier data incompatible with current trends. Because Phase II reformulated gasoline entered the market in 2000, a post-2000 analysis was also performed for benzene and HCHO where sufficient data are available to test the consistency of the weekday/weekend differences.

Once a period was selected, the data from each site were inspected to identify any uneven frequencies of measurements. No change in collection frequency was identified for EC. For benzene and HCHO, at sites where summer data occurred at a higher frequency than during the remainder of the year, the higher frequency data were decimated based on the differences in sampling frequency to ensure that equal weights

were put on every month for an annual average analysis. For example, if measurements were taken everyday for the months of June, July and August, and only every third day for the other 9 months of the year, then for the months of June, July, and August, two out of every three samples were removed from the data set, forming a data stream that resembled one that would have been generated if the collection was performed with a frequency of one in three days throughout the year.

For some sites, summer data were available with shorter averaging time. For example, samples were taken every three hours during June, July and August, whereas 24-hour samples were taken during the remainder of the year. The shorter duration samples were aggregated to 24-hour averages when used with data with the longer duration. When aggregating, a 24-hour average was only deemed useable when a data completeness criterion of 75% was satisfied. Therefore, if only five 3-hour samples were available during a 24-hour period, a 24-hour average was not calculated for that period. If six 3-hour samples were available, the 18-hour average value is considered to be representative of the 24-hour period.

If co-located measurements were available for a pollutant, averages of valid co-located measurements (including 24-hour averages aggregated from shorter duration measurements) were calculated on any given day. No judgment was made as to whether certain types of measurements are more reliable than others.

Traffic rush hour analyses were possible for both benzene and HCHO using 3-hour samples. For HCHO, more than 30 rush-hour samples were available for each day of the week at three sites that took these short duration samples during rush hours of summer months. For benzene, rush-hour analysis can be conducted for the annual concentrations at sites that took 3-hour samples throughout the year and for the summer concentrations at a combination of sites (including sites in the annual group and sites that only took measurements during the summer).

For benzene, there were sufficient (30+ samples per day of week) data at a few sites for a summer-only analysis. For that analysis, the equal representation of June, July, and August data was also ensured.

Sites that have sufficient data for each day of the week, together with the dates considered, and some general information about the duration, frequency and method of measurements, are listed in Tables 2-1, 2-2 and 2-3, respectively for EC, HCHO, and benzene. The last column lists both the actual number of days with valid 24-hour concentrations and the number of data points used in the analysis (after intermittent high frequency data are decimated to equalize the number of data points from different months).

Table 2-1. Sites selected for analyses of weekday/weekend differences of EC.

Site [1]	Land use	Dates [1]	Measurement method [2]	Sampling frequency	Sampling duration	Number of days with valid 24-hour samples
New York City						
Bronx Botanical Garden 360050083	urban, commercial	May 2000-April 2005	MetOne [3]	1-in-3 days	24-hours	561
Bronx 6th Street 360050110	urban, residential	May 2001 – April 2005	R&P 2300	1-in-3 days	24-hours	414
New York 360610062	urban, commercial	May 2003 – April 2005	MetOne	1-in-3 days	24-hours	232
Queens 360810124	suburban, residential	May 2002-April 2005	R&P 2300	1-in-3 days	24-hours	309
Philadelphia						
Camden 340070003	suburban, residential	June 2001-May 2005 [1]	MetOne	1-in-3 days	24-hours	277
Philadelphia 421010004	urban, residential	May 2000-April 2005	MetOne [3]	1-in-3 days	24-hours	517
Houston						
Aldine Mail Road 482010024	suburban, residential	November 2001 – October 2004	R&P 2025	1-in-3 days,	24-hours	327
Sheldon Road 482010026	suburban, residential	November 2000 – October 2004	R&P 2025	1-in-3 days [4]	24-hours	391
Bissonnet Street 482011055	urban, residential	November 2000 – October 2004	R&P 2025	1-in-3 days [4,5]	24-hours	449
Durant Street 482011039	suburban, residential	May 2000-April 2005	URG [3]	1-in-3 days [6,7]	24-hours	528
Hwy 1484 483390078	urban, commercial	November 2001 – October 2004	R&P 2025	1-in-3 days	24-hours	309

(1) Longest and most recent 12-month period considered. Maximum length of records used up to 10 years. January of starting year to December of ending year unless otherwise specified. As of August 2005, data are available for some sites up to May 13. Therefore, May 2005 was excluded from the period of consideration except at 340070003 where a fourth year is completed in May 2005.
(2) All EC methods use thermal optical transmittance for detection.
(3) Alternative methods were used, either as co-located measurements or replacement measurements to the main method. Method listed corresponds to the largest number of valid data.
(4) During July 2001, daily samples taken – these were decimated back to 1-in-3 days to prevent giving undue weight to that month.
(5) Include at least one data point taken off the 1-in-3 day schedule (e.g., 16, **20**, 22 May 2001)
(6) During August and September 2000, daily samples were taken using a different instrument (during part of that period, no data records obtained with main instrument) – these were decimated back to 1-in-3 days to prevent giving undue weight to that month.
(7) 6 samples were designated 1-in-6 days. They were not treated separately.

Table 2-2. Sites selected for analyses of weekday/weekend differences of HCHO.

Site	Land use	Dates [1]	Measurement Method [2]	Sampling frequency[4]	Sampling duration [4]	Number of days with valid 24-hour samples (including aggregation of sub-daily measurements)
New York City						
Bronx 360050083	urban, commercial	October 1995-September 2004	(1) HPLC UV detection (2) heated O_3 denuder HPLC photodiode array (3) KI O_3 scrub HPLC UV absorption [3]	1-in-6 days everyday or 1-in-3 days	24-hour 3-hour	792
Queens 360810097	urban, residential	1998-2001	(1) HPLC UV detection (2) heated O_3 denuder HPLC photodiode array	1-in-6 days 1-in-3 days	24-hour; 3-hour	329
Philadelphia						
Camden 340070003	suburban, residential	April 1996-March 2005	KI O_3 scrub HPLC UV absorption	1-in-6 days everyday or 1-in-3 days	24-hour; 3-hour [5]	596
Philadelphia 421010004	urban, residential	1995-2004	HPLC UV absorption	1-in-6 days 1-in-3 days	24-hour; 3-hour [5]	863
Houston						
Clinton Dr. 482011035	suburban, industrial	October 1998 – September 2004	HPLC diode array detector	1-in-6 days	24-hour [6]	350
Durant St. 482010039	suburban, residential	1999-2004	HPLC diode array detector	1-in-6 days	24-hour [7]	358

(1) Maximum length of records used up to 10 years; multiples of 12 months considered for the data period; January of starting year to December of ending year unless otherwise specified.
(2) All methods involve collection on DNHP medium; multiple methods indicate either concurrent measurements or instrumentation changes over the time period.
(3). Not all are operational at any given year.
(4) Higher frequency and/or shorter duration data were available during summer months when multiple duration/frequency listed.
(5) Several co-located instruments with different parameter occurrence code (POC); no 3-hour average samples were taken during summer months in 2002; measurements for POC 4 not used because only 1 3-hour sample recorded per day with rotating start time.
(6) Three co-located instruments with different POC, 1-hour and 3-hour measurements were obtained during some years for several hours a day, there were no discernible patterns to the schedule.
(7) Two co-located instruments with different POC, 1-hour measurements were obtained during some years for several hours a day, there were no discernible patterns to the schedule.

Table 2-3. Sites selected for analyses of weekday/weekend differences of benzene.

Site	Land use	Dates [1]	Measurement Method [4]	Sampling frequency	Sampling duration	Number of days with valid 24-hour samples (including aggregation of sub-daily measurements)
New York City						
Bronx Botanical Garden 360050083	urban, commercial	1995-2004 [2]	(1) Preconcentration trap auto GC/FID (2) Pressurized canister, cryogenic precon. GC/MS	1-in-6 days everyday	24-hour 1-hour	847
Kings 360470118	suburban, residential	April 2000 – March 2005	Pressurized canister, cryogenic precon. GC/MS	1-in-6 days	24 hour	237
Queens 360810098	urban, residential	April 2000 – March 2005	Pressurized canister, cryogenic precon. GC/MS	1-in-6 days	24 hour	289
Richmond 360850055	urban, residential	1994-1998	Mixed sorbent cartridge GC/MS	1-in-6 days	24 hour	231
Philadelphia						
Camden 340070003	suburban, residential	1997-2004 [2]	(1) Preconcentration trap auto GC/FID (2) Canister subambient pressure; multidetector GC	1-in-6 days everyday [5]	24-hour 1-hour [5]	664
Philadelphia 421010004	urban, residential	1995-2004	(1) Canister subambient pressure; multidetector GC (2) Stainless steel canister pressurized cryogenic precon. GC/FID (3) Stainless steel canister pressurized capillary GC ITD MS (4) Sorbant tube carbosieve C trap GC/FID	Everyday 1-in-6 days [5]	3-hour 3- or 24-hour [5]	958
Philadelphia Amtrak 421010136	urban, residential	2001-2004	(1) Canister subambient pressure; multidetector GC (2) Stainless steel canister pressurized cryogenic precon. GC/FID (3) Stainless steel canister pressurized capillary GC ITD MS	1-in-6 days	24-hour	238

Table 2-3. Sites selected for analyses of weekday/weekend differences of benzene (continued).

Site	Land use	Dates [1]	Measurement Method [4]	Sampling frequency	Sampling duration	Number of days with valid 24-hour samples (including aggregation of sub-daily measurements)
Houston						
Aldine Mail Rd. 482010024	suburban, residential	1996-2004	(1) Preconcentration trap auto GC/FID (2) Subatmospheric canister; precon. GC/FID/MS (3) Passivated canister cryogenic precon. GC/MS	1-in-6 days everyday or uneven frequency [6]	3- or 24-hour 1-hour [6]	764
Sheldon Rd. 482010026	suburban, residential	May 1996-April 2005	(1) Preconcentration trap auto GC/FID (2) Pressurized canister; precon. GC/FTIR/MS (3) Subatmospheric canister; precon. GC/FID/MS (4) Passivated canister cryogenic precon. GC/MS	1-in-6 days everyday [6]	24-hour 1-hour [6]	1318
Kitman 482010029	urban, residential	1999-2004	(1) Subatmospheric canister; precon. GC/FID/MS (2) Passivated canister cryogenic precon. GC/MS	1-in-6 days uneven frequency [5]	24-hour 1-hour [5]	316
Bissonnet St. 482010055	urban, residential	1999-2004	(1) Preconcentration trap auto GC/FID (2) Subatmospheric canister; precon. GC/FID/MS (3) Passivated canister cryogenic precon. GC/MS	1-in-6 days everyday [6]	24-hour 1-hour [6]	771
Stewart St. 482100057	urban, residential	1998-2004	(1) Subatmospheric canister; precon. GC/FID/MS (2) Passivated canister cryogenic precon. GC/MS	1-in-6 days	24-hour	375
Bayway Dr. 482010058	urban, residential	1999-2004	(1) Subatmospheric canister; precon. GC/FID/MS (2) Passivated canister cryogenic precon. GC/MS	1-in-6 days	24-hour	320
Old Hwy 146 482010061	suburban, commercial	1999-2004	(1) Subatmospheric canister; precon. GC/FID/MS (2) Passivated canister cryogenic precon. GC/MS	1-in-6 days	24-hour	343
Old Galveston Rd. 482010064	suburban, industrial	April 1994-March 1999	(1) Pressurized canister; precon. GC/FID (2) Pressurized canister; precon. GC/FTIR/MS (3) Subatmospheric canister; precon. GC/FID/MS	1-in-6 days	24-hour	249

Table 2-3. Sites selected for analyses of weekday/weekend differences of benzene (continued).

Site	Land use	Dates [1]	Measurement Method [4]	Sampling frequency	Sampling duration	Number of days with valid 24-hour samples (including aggregation of sub-daily measurements)
Central St. 482010069	suburban, residential	2000-2004 [3]	(1) Subatmospheric canister; precon. GC/FID/MS (2) Passivated canister cryogenic precon. GC/MS	1-in-6 days	24-hour	249
Haden Rd. 482010803	suburban, industrial	1995-2004	(1) Preconcentration trap auto GC/FID (2) Pressurized canister; precon. GC/FTIR/MS (3) Subatmospheric canister; precon. GC/FID/MS (4) Passivated canister cryogenic precon. GC/MS	1-in-6 days everyday [5]	24-hour 1-hour [5]	594
Clinton Dr. 482011035	suburban, industrial	July 1996 – June 2005	(1) Preconcentration trap auto GC/FID (2) Subatmospheric canister; precon. GC/FID/MS (3) Passivated canister cryogenic precon. GC/MS	1-in-6 days everyday	24-hour 1-hour	2926
Durant St. 482010039	suburban, residential	1997-2004	(1) Preconcentration trap auto GC/FID (2) Subatmospheric canister; precon. GC/FID/MS (3) Passivated canister cryogenic precon. GC/MS	1-in-6 days everyday	24-hour 1-hour	2536

(1) Maximum length of records used up to 10 years; multiples of 12 months considered for the data period; January of starting year to December of ending year unless otherwise specified.
(2) Summer only; insufficient data for annual analysis; more limited number of samples during other months and not available for entire period.
(3) Data gap in January 2005; February to June 2005 data available at higher sampling frequency and shorter duration; therefore, not mixed with previous data.
(4) Multiple methods indicate concurrent measurements or instrumentation changes over the period.
(5) Higher frequency and/or shorter duration data were available during summer months when multiple duration/frequency listed.
(6) Some years, higher frequency and/or shorter duration data were available during summer months when multiple duration/frequency listed

3. Method

3.1 Groups of data

For each site and each species, concentrations are grouped by the individual days of the week. A group of weekdays, which consists of Tuesdays, Wednesdays, and Thursdays, (hereafter referred to as midweek) and a group of weekend days, which consists of Saturdays and Sundays, are also considered in the analysis.

3.2 Graphical displays

When comparing between groups of concentrations from weekdays and weekend days, displays of certain metrics of concentrations are used. An example of a box plot is presented in Figure 3-1. For each day of the week, the mean concentration is presented using a symbol (x) connected by a line. The 25^{th} percentile and 75^{th} percentile are represented as the bottom and top edges of the box, and the middle line represents the median concentrations.

A second type of plot that is useful for comparing two distributions is the quantile-quantile plot (QQ plot). The QQ plot is a scatter plot where the n-th percentiles of two datasets are plotted against one another. It gives an indication of whether the shapes of the distributions of two data sets are similar and if not, which concentration ranges show the most differences. Figure 3-2 is an example QQ plot of EC at the Bronx site in NY. The points represent the minimum value, the 10^{th}, 20^{th}, ...80^{th}, 90^{th} percentile values and the maximum values the weekday concentrations observed on Tuesdays, Wednesdays, and Thursdays, and the weekend concentrations observed on Saturdays and Sundays. In this particular example, except for 20% of the samples with the lowest concentrations, weekend concentrations are lower than weekday concentrations.

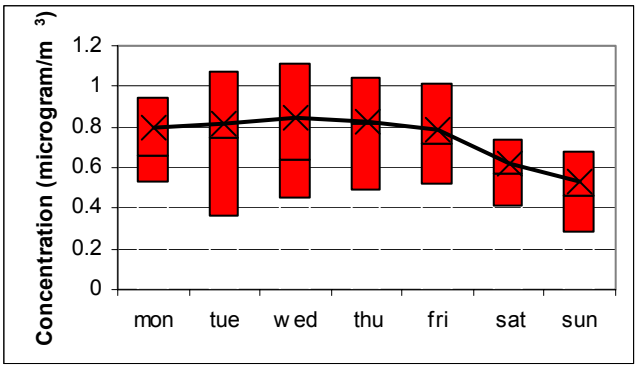


Figure 3-1. An example box plot illustrating the mean, median, 25th percentile, and 75th percentile EC concentrations in Queens, New York.

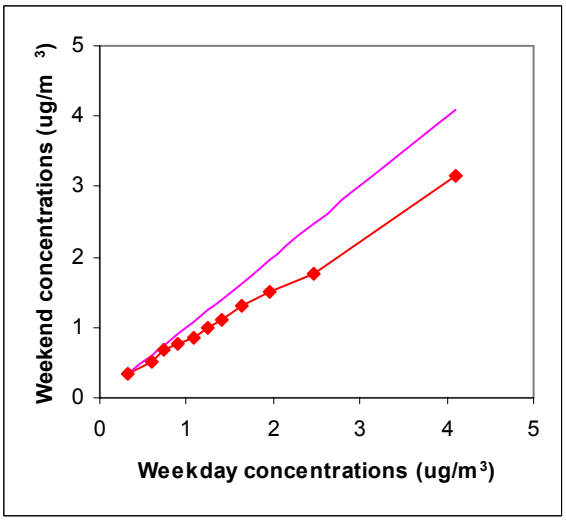


Figure 3-2. An example quantile-quantile plot illustrating the minimum values, 10th, 20th ... 80th, 90th percentile values and the maximum values of the weekend (y-axis) concentrations compared to the weekday concentrations (x-axis) of EC at the Bronx site, New York City. The line for perfect agreement is also shown for reference.

3.3 Statistical metrics

Concentrations on each day of the week or each group of weekdays or weekend days are characterized by statistical metrics. The mean and median concentrations are used in most cases. The average concentration is higher than the median in cases where the distribution of concentrations is skewed and has a tail towards high concentrations. To analyze the high values within each group, the 75^{th} percentile is calculated.

3.4 Statistical significance of weekday/weekend differences

Ambient concentrations are associated with significant variability. Even two samples drawn from the same underlying distribution of, say, Monday concentrations may by chance have different values for a given statistical quantity (mean, median, or 75^{th} percentile), especially if the sample sizes are limited. It is, therefore, important to test the statistical significance of any difference calculated between a weekday quantity and a weekend quantity.

Previously, a technique involving Bootstrap Resampling (Pun et al., 2003) was used to test the significance of weekday/weekend differences in ozone. The same technique is used here. Briefly, statistical significance is determined relative to a null hypothesis. In this case, the null hypothesis is that there is no difference between the weekday concentrations and of the weekend concentrations. The next step is to define a test metric that satisfies certain criteria. First, the test metric needs to be a single valued function of the data. Second, the larger the metric, the stronger is the evidence that reality deviates from the null hypothesis. Let's say we are comparing two median concentrations and the difference of the medians is Δ. The difference of the medians is a suitable test metric.

The statistical significance corresponds to the probability of the test statistic being greater than or equal to Δ if the null hypothesis was true. This is illustrated in Figure 3-3. On the left hand side, the test metric assumes a value equal to or greater than the

observed quantity (Δ) with a relatively high probability under the null hypothesis scenario, so an observed value of Δ is consistent with the null hypothesis. The null hypothesis cannot be rejected in this case, and the difference Δ is not significant. On the right hand side, a higher value of Δ occurs with only a very small probability (e.g., 5%) if the null hypothesis is true. In this case, the null hypothesis is rejected and the difference Δ is statistically significant (e.g., at the 5% level).

Generating the distribution of the test statistic under the null hypothesis is tricky, because we are typically unable to conduct enough measurements to generate a distribution in a world where the null hypothesis is true. Instead, this distribution is approximated as follows. The observed data set is assumed to be the best estimate of the underlying population in the real world. Bootstrap resampling is applied to generate alternative samples by resampling the observed data set with replacement. For each bootstrap sample, the test metric is calculated. This generates a distribution of the test metric that is consistent with the real data set. Assuming that the distribution of the test metric in the null hypothesis world has the same shape as the test metric in the real world, the distribution of the test metric under the null hypothesis is approximated by simply shifting the distribution so that it centers around the value of the metric under the null hypothesis (0 for the no difference case). Then, the value of the test metric in the real data can be compared to the approximated distribution under null hypothesis, as shown in Figure 3-3.

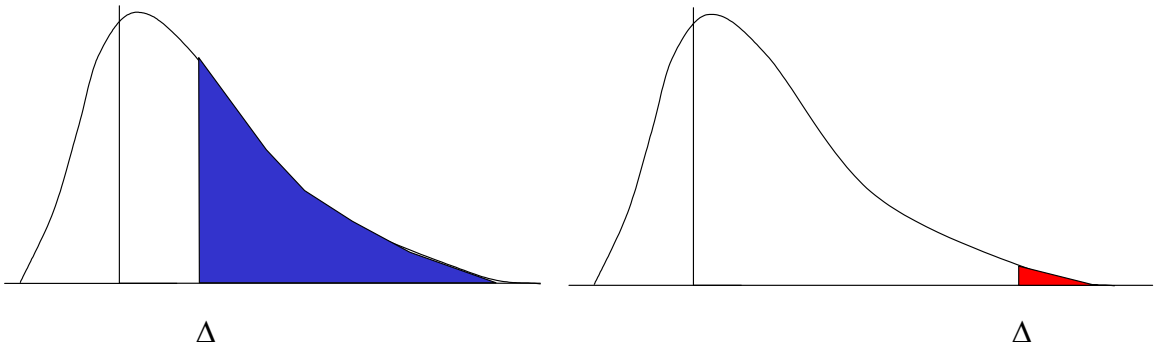


Figure 3-3. Distribution of the test metric under the null hypothesis and examples where the observed metric is not significant (left) and where it is significant (right).

4. EC Results

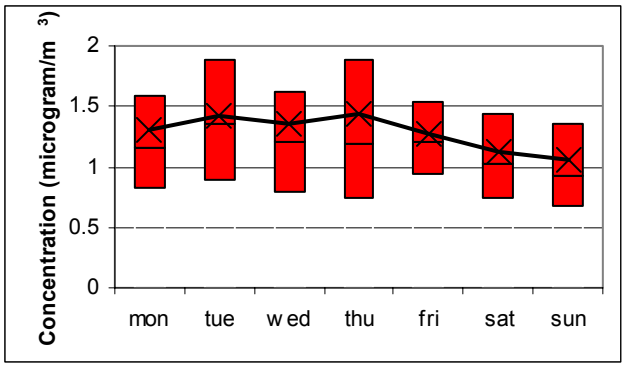
4.1 NYC

Box plots for EC concentrations on each day of the week are shown in Figure 4-1 for four sites in NYC.

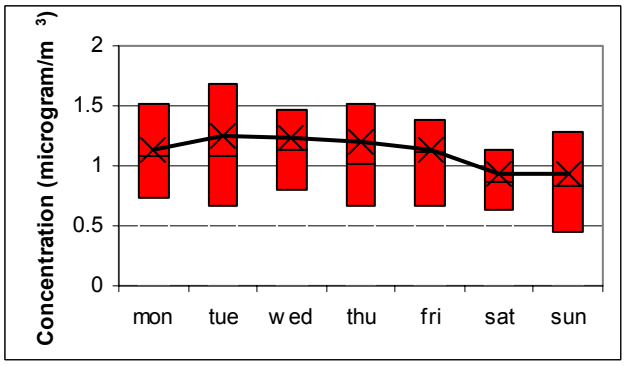
Of the urban (3) and suburban (1) sites in NYC, the suburban site in Queens shows lower EC concentrations than the urban sites. At all sites, the highest average concentrations are observed on Tuesdays, Wednesdays, or Thursdays. The lowest average concentrations are observed on Sundays and the second lowest average concentrations are observed on Saturdays, except the 6th Street site (360050110) in Bronx, which shows very similar average concentrations on Saturdays and Sundays. The same weekly trend observations apply to the median concentrations. For the median concentrations, the Saturday-Sunday difference at the 6th Street site is small, but not zero.

For the 75th percentile concentrations, weekday values are higher than weekend values at all sites. At the 6th Street site, Sundays' 75th percentile concentration is higher than Saturdays'. The 25th percentile concentrations on Sundays are lower than weekdays at all sites. However, at the Bronx Botanical Garden (360050083) and Queens (360810124) sites, Saturdays' 25th percentile concentrations are comparable to or higher than the 25th percentile concentration on a midweek day. Therefore, the day-of-week trends in EC seem to be stronger for the moderate to high concentrations compared to the low concentrations in NYC. This may be due in part to better signal-to-noise ratios in the measurements when overall ambient concentrations are higher.

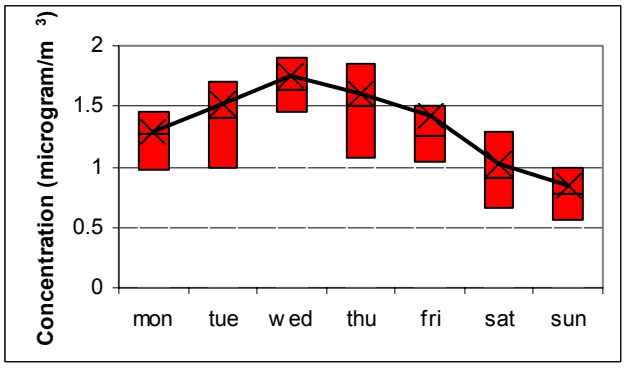
(a) Bronx Botanical Garden (360050083)



(b) Bronx 6th Street (360050110)



(c) New York (360610062)



(d) Queens (360810124)

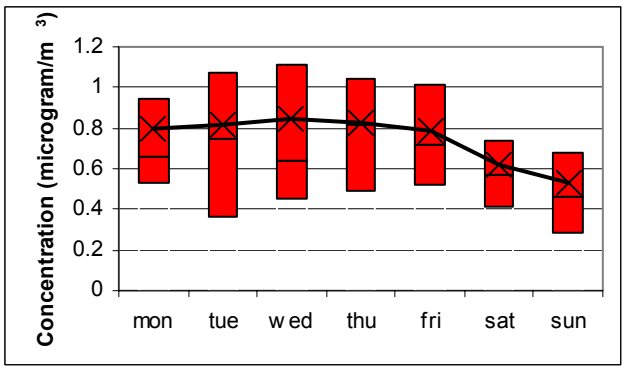


Figure 4-1. Box plots for EC concentrations at sites in New York City.

As shown in Figure 4-1, at all four sites, the average Wednesday concentrations are higher than the average Sunday concentrations. The differences in the average values are 0.3 $\mu g/m^3$ at the Bronx and Queens sites and 0.9 $\mu g/m^3$ at the NYC site (360610062). The Wednesday-Sunday difference in average concentrations is statistically significant at the 5% level at all sites. In fact, Sundays' average concentrations are lower than those on midweek days (Tuesdays and Thursdays) at all sites and the differences are statistically significant at the 5% level for all Tuesday-Sunday and Thursday-Sunday pairs as well.

Saturdays' average concentrations are also lower than average concentrations on Tuesdays, Wednesdays, or Thursdays at all sites. The Saturday-Wednesday differences range from 0.2 to 0.3 $\mu g/m^3$ at the Bronx and Queens sites to 0.7 $\mu g/m^3$ at the NYC site. These are also statistically significant at the 5% level. Table A-1 shows the differences in the average concentrations and statistical significance of the differences between each pair of days.

Table 4-1 shows the differences in the median concentrations between each pair of days. Sundays' median concentrations are lower than Wednesdays' median concentrations by 0.2 $\mu g/m^3$ at the Queens site, 0.3 $\mu g/m^3$ at the Bronx site, and 0.9 $\mu g/m^3$ at the NYC site. These differences are statistically significant at the 5% level. The differences in the Tuesday-Sunday and Thursday-Sunday medians are also statistically significant at the 5% level. At the NYC site, the differences in the medians are 0.6 $\mu g/m^3$ for the Tuesday-Sunday pair and 0.7 $\mu g/m^3$ for the Thursday-Sunday pair. The Tuesday-Sunday differences in medians are 0.4 $\mu g/m^3$ at the Bronx Botanical Garden and 0.3 $\mu g/m^3$ at the 6th Street and Queens sites. The Thursday-Sunday differences in median concentrations range from 0.2 $\mu g/m^3$ to 0.4 $\mu g/m^3$ at these sites.

Table 4-1. Differences in the median concentrations of EC between each pair of days for sites in New York City. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%)

(a) Bronx Botanical Garden (360050083)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.19					
Wed	-0.04	0.15				
Thu	-0.03	0.16	0.01			
Fri	-0.04	0.15	0.00	-0.01		
Sat	0.13	0.32	0.17	0.16	0.17	
Sun	0.24	0.43	0.28	0.27	0.28	0.11

(b) Bronx 6th Street (360050110)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.01					
Wed	-0.05	-0.04				
Thu	0.06	0.07	0.11			
Fri	-0.04	-0.03	0.01	-0.10		
Sat	0.21	0.22	0.26	0.15	0.25	
Sun	0.25	0.26	0.30	0.19	0.29	0.03

(c) New York (360610062)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.12					
Wed	-0.36	-0.24				
Thu	-0.23	-0.11	0.13			
Fri	0.03	0.15	0.39	0.26		
Sat	0.38	0.50	0.74	0.61	0.35	
Sun	0.51	0.63	0.87	0.74	0.48	0.13

(d) Queens (360810124)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.08					
Wed	0.02	0.10				
Thu	-0.16	-0.08	-0.18			
Fri	-0.05	0.03	-0.07	0.11		
Sat	0.10	0.18	0.08	0.26	0.15	
Sun	0.20	0.28	0.18	0.36	0.25	0.11

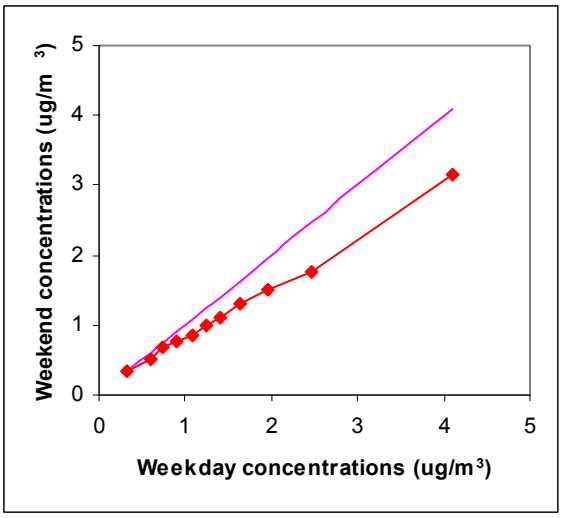
At the NYC site, the differences of medians between midweek days and Saturdays range from 0.5 $\mu g/m^3$ to 0.7 $\mu g/m^3$ and these differences are statistically significant at the 5% level. The differences between the median concentrations on midweek days and Saturdays range from 0.1 $\mu g/m^3$ to 0.3 $\mu g/m^3$ at the Bronx and Queens sites. The Thursday-Saturday difference (0.15 $\mu g/m^3$) in median concentrations is statistically insignificant at the 6th Street site, Bronx site, and the Wednesday-Saturday difference (0.1 $\mu g/m^3$) in medians is similarly insignificant at the Queen site. At each of these three sites, only one of the differences between the Tuesday/Wednesday/Thursday median and the Saturday median is statistically significant at the 5% level.

Figure 4-2 shows the QQ plots comparing the percentiles of concentrations on Tuesday/Wednesdays/Thursdays and the percentiles of concentrations on Saturdays/Sundays. All four sites show larger differences (weekdays > weekends) at the higher concentration percentiles.

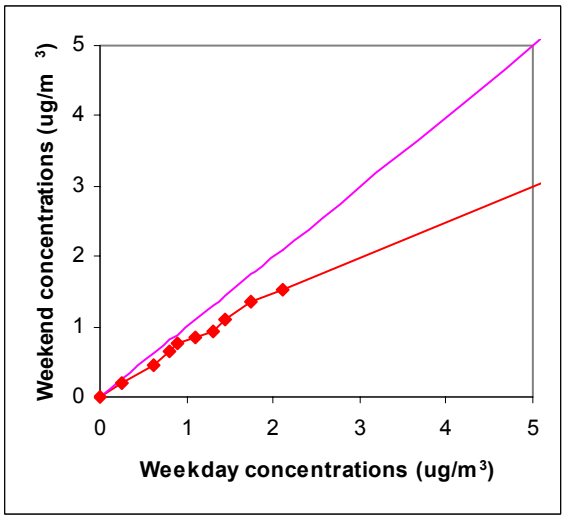
When considering midweek days as a group (Tuesday/Wednesdays/Thursdays) and weekend days (Saturdays and Sundays) as a group, the average concentration during midweek is higher than that during weekends at all sites. Differences of 0.3 $\mu g/m^3$ are observed at the Bronx and Queens sites, and the difference in the average concentrations is 0.8 $\mu g/m^3$ at the NYC site. All sites show statistically significant differences at the 5% level (See Table A-2 in Appendix).

Table 4-2 shows the differences in the median concentrations between midweek days (Tuesday/Wednesdays/Thursdays) and weekend days (Saturdays and Sundays). Differences in median concentrations are similar to or slightly smaller than differences in the average concentrations at the Bronx and Queens sites. They are, nonetheless statistically significant at the 5% level. At the NYC site, the difference between the median midweek concentration and the median weekend concentration is 0.75 $\mu g/m^3$, statistically significant at the 5% level.

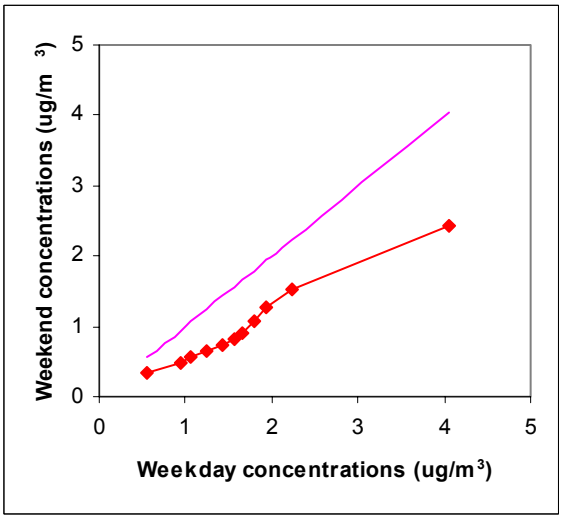
(a) Bronx Botanical Garden (360050083)



(b) Bronx 6th Street (360050110)



(c) New York (360610062)



(d) Queens (360810124)

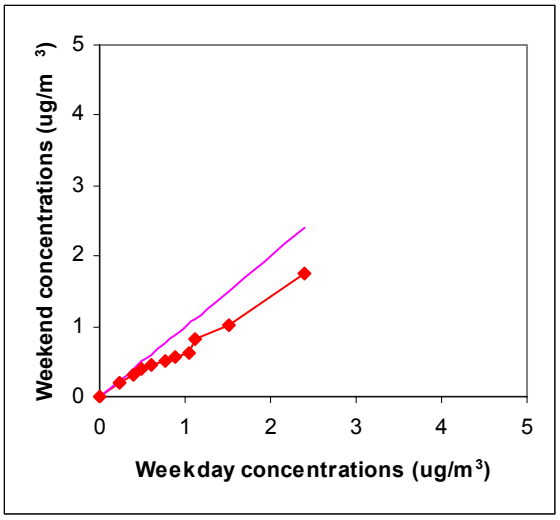


Figure 4-2. QQ plots for weekend vs. midweek EC concentrations at sites in New York City.

Table 4-2. Differences in the median concentrations of EC between midweek days and weekend days in New York City, Philadelphia, and Houston.

Site	Nwkd	Nwke	Cwkd	Cwke	ΔC	Significant?	
			($\mu g/m^3$)			10%	5%
Bronx Botanical Garden	244	159	1.25	1.00	0.26	Y	Y
Bronx 6th Street	179	110	1.09	0.86	0.23	Y	Y
New York, New York	102	64	1.56	0.81	0.75	Y	Y
Queens	133	88	0.76	0.50	0.26	Y	Y
Camden	143	93	0.69	0.47	0.22	Y	Y
Philadelphia	226	147	0.87	0.54	0.33	Y	Y
Aldine Mail Rd., Houston	134	98	0.59	0.51	0.08	Y	Y
Sheldon Rd., Houston	157	112	0.48	0.42	0.06	Y	Y
Bissonnet St., Houston	184	125	0.42	0.37	0.06	Y	N
Durant St., Houston	230	141	0.31	0.26	0.05	Y	Y
Hwy 1484, Houston	134	82	0.38	0.33	0.05	Y	Y

4.2 Philadelphia

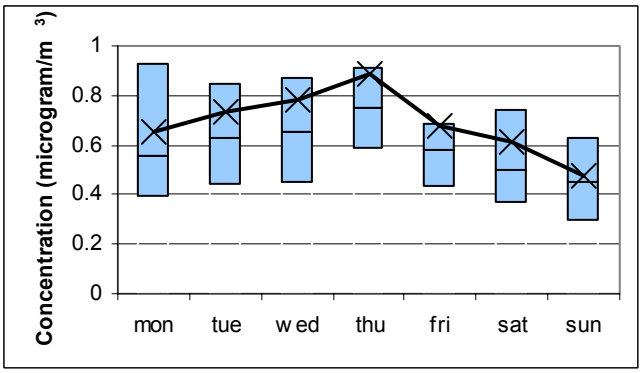
There are two sites in the Philadelphia metropolitan area. Box plots for these sites are shown in Figure 4-3. The residential site at Camden (340070003) shows lower concentrations than the urban site in Philadelphia (421010004). At both sites, Sundays have the lowest average concentration of the week, and Saturdays have the second lowest average concentration. The highest average concentrations are observed on Thursdays at both sites.

Median and 25th percentile EC concentrations are also lowest on Sundays, followed by Saturdays. Highest EC median and 25th percentile concentrations are observed on Thursdays. These observations are consistent with the day-of-week behavior of the mean concentrations.

For the 75th percentile concentrations, the Philadelphia site shows a maximum concentration on Thursdays and a minimum concentration on Sundays, consistent with behavior of the average, median, and 25th percentile metrics. At the Camden site, the 75th percentile concentration is the highest on Mondays, second highest on Thursdays, the lowest on Sundays, and second lowest on Fridays. Camden may be subject to more variability, especially at high concentration ranges.

(a) Camden

(340070003)



(b) Philadelphia

(421010004)

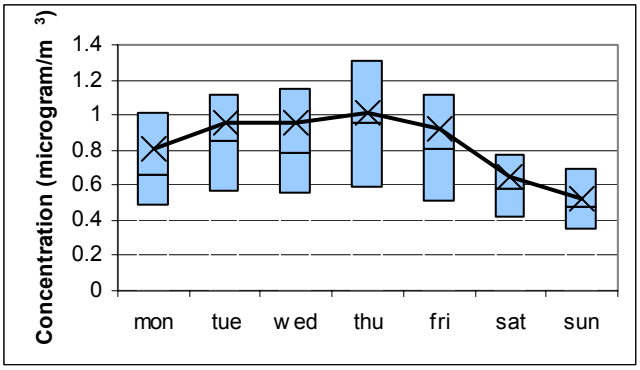


Figure 4-3. Box plots for EC concentrations at sites in Philadelphia

At both sites, Sundays' average concentrations are lower than the average concentrations on Tuesdays, Wednesdays, and Thursdays, and these differences are statistically significant at the 5% level. The Wednesday-Sunday differences are 0.3 $\mu g/m^3$ at the Camden site and 0.4 $\mu g/m^3$ at the Philadelphia site. The Thursday-Sunday differences in average concentrations are 0.1 $\mu g/m^3$ more than the Wednesday-Sunday differences. The average midweek-Saturday concentration differences are 0.1 to 0.3 $\mu g/m^3$ at the Camden site and 0.4 to 0.5 $\mu g/m^3$ at the Philadelphia site, smaller than the midweek-Sunday differences. Weekday-Saturday differences that are greater than or equal to 0.2 $\mu g/m^3$ in average concentrations are statistically significant at the 5% level. Differences in the average EC concentrations between each pair of days and the statistical significance of those differences are shown in Table A-3 in the Appendix for the Philadelphia area sites.

Table 4-3 shows the differences in the median EC concentrations between pairs of days. The Tuesday-Sunday, Wednesday-Sunday, and Thursday-Sunday differences range from 0.2 to 0.3 $\mu g/m^3$ in Camden and from 0.3 to 0.5 $\mu g/m^3$ in Philadelphia, all statistically significant at the 5% level. The largest differences in median EC concentrations are observed for Thursday vs. Sundays at these sites. The Tuesday-Saturday, Wednesday-Saturday, and Thursday-Saturday differences in median concentrations are 0.1 $\mu g/m^3$ less than the corresponding Sunday differences. The midweek-to-Saturday differences in median concentrations are also significant at the 5% level.

Figure 4-4 shows QQ plots at Camden and Philadelphia for weekend (Saturday and Sunday) vs. weekday (Tuesdays, Wednesdays, Thursdays) EC concentrations. At both sites, the corresponding concentrations are lower on weekends than on weekdays. At Camden, the 90^{th} percentile concentration on weekends is below the 90^{th} percentile concentration on weekdays, but the maximum concentration on weekends approach that on weekdays. In contrast, the gap between the same percentile concentrations on weekends vs. weekdays increases with increasing concentrations in Philadelphia.

Table 4-3. Differences in the median concentrations of EC between each pair of days for sites in Philadelphia. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%)

(a) Camden

(340070003)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.08					
Wed	-0.10	-0.03				
Thu	**-0.20**	**-0.12**	-0.09			
Fri	-0.03	0.05	0.07	**0.17**		
Sat	0.06	**0.13**	**0.16**	**0.25**	0.09	
Sun	0.10	**0.18**	**0.21**	**0.30**	**0.13**	0.05

(b) Philadelphia

(421010004)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	**-0.19**					
Wed	-0.12	0.08				
Thu	**-0.29**	-0.09	**-0.17**			
Fri	-0.14	0.05	-0.03	**0.14**		
Sat	0.09	**0.28**	**0.20**	**0.37**	**0.23**	
Sun	**0.19**	**0.38**	**0.30**	**0.47**	**0.33**	**0.10**

(a) Camden (b) Philadelphia

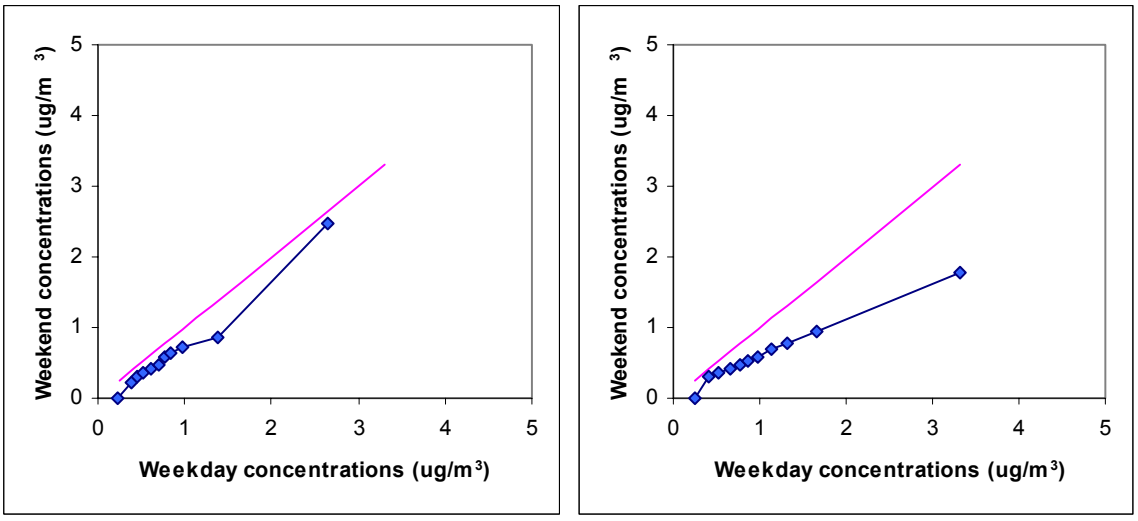


Figure 4-4. QQ plots for weekend vs. midweek EC concentrations at sites in Philadelphia

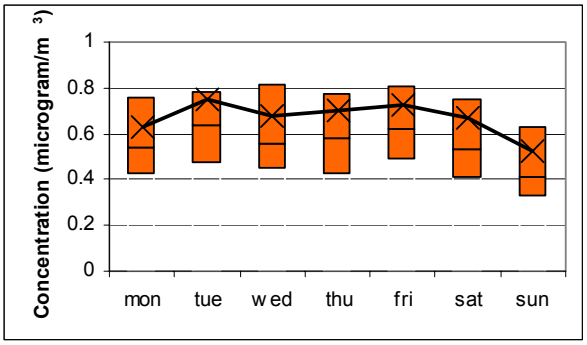
Differences in the median EC concentrations between midweek days (Tuesday/Wednesdays/Thursdays) and weekend days (Saturdays and Sundays) are calculated. Table 4-2 shows the differences in the median concentrations. A difference of 0.2 $\mu g/m^3$ is observed at the suburban Camden site for the median concentrations. The difference in the median concentrations is 0.3 $\mu g/m^3$ at the Philadelphia site. Both sites show statistically significant differences at the 5% level. The differences in the average concentrations between midweek and weekends are slightly higher at both sites compared to the differences of the medians (Table A-2) and are also statistically significant at the 5% level.

4.3 Houston

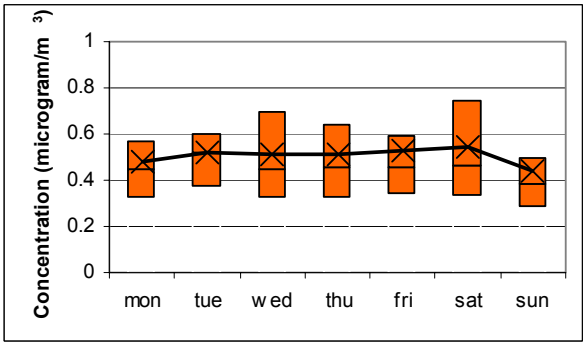
There are five EC monitors in Houston. Three are designated as suburban and residential, Aldine Mail Road (482010024), Sheldon Road (482010026) and Durant Street (482011039). Two are urban, on Bissonnet Street (482010055) and Hwy 1484 (483390078). Figure 4-5 shows that EC concentrations in Houston are generally lower than those in NYC and Philadelphia. Sites with urban designations do not necessarily show higher concentrations or stronger day-of-week signals than sites with suburban designations. The suburban site at Aldine Mail road shows the highest EC concentrations. The Durant Street site and Hwy 1484 site show the lowest EC concentrations. Of the two, the urban site at Hwy 1484 shows very little day-of-the-week variations.

At all five sites in Houston, the average EC concentrations are lower on Sundays than on the other days of the week. Decreases in the average concentrations on Saturdays, which are observed in NYC and Philadelphia, are non-existent or not prominent in the Houston data. Maximum 24-hour average concentrations are observed on different days at different sites. The Sheldon Road site shows maximum average concentrations on Saturdays, the Durant Street site shows maximum average

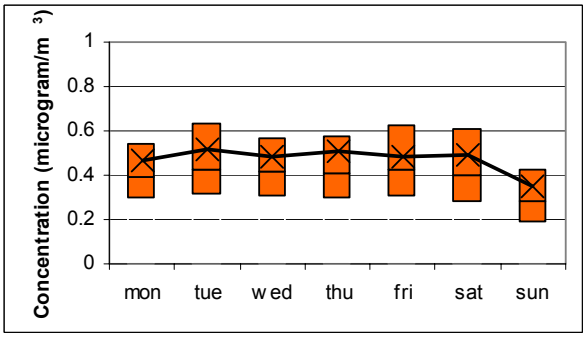
(a) Aldine Mail Road (482010024)



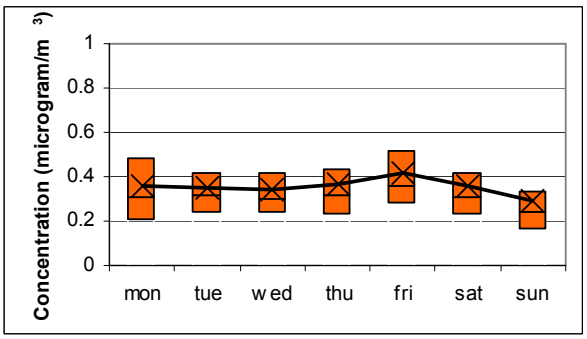
(b) Sheldon Road (482010026)



(c) Bissonnet Street (482010055)



(d) Durant Street (482011039)



(e) Hwy 1484 (483390078)

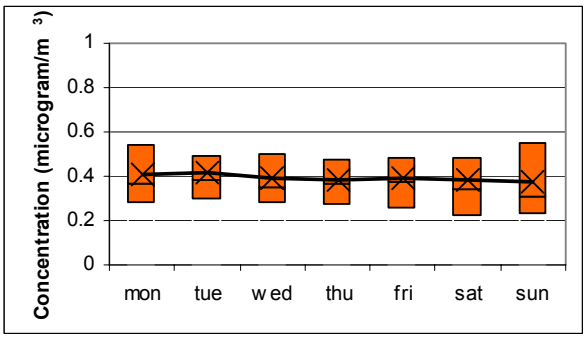


Figure 4-5. Box plots for EC concentrations at sites in Houston.

concentrations on Fridays and other sites record maximum average concentrations on Tuesdays.

Median concentrations of EC are lowest on Sundays at all sites. Median concentrations at 4 out of 5 sites are highest on Tuesdays, with the remaining site showing high median concentrations on Fridays.

At the site on Hwy 1484, neither the 25th nor 75th percentile concentration shows a minimum on Sundays. At the other sites, Sunday minimums are consistently observed for these two metrics. No consistent trend is observed for high 25th and 75th percentile concentrations, which occur on different days of the week at different sites. High 25th and 75th percentile concentrations do not always occur on the same day at a given site. In part because of lower concentrations, the Houston data set is subject to higher variability that may obscure any day-of-the-week signal compared to the NYC and Philadelphia data sets.

As shown in the box plots, the Wednesday-Sunday differences range from 0.02 to 0.2 $\mu g/m^3$ for the average concentrations. The smallest difference of 0.02 $\mu g/m^3$ at Hwy 1484 is statistically not different from a zero difference. In fact, at this site, no weekday-weekend pair shows meaningful differences (all less than 0.03 $\mu g/m^3$). At the other sites, differences are statistically significant at the 10% level (Sheldon Road) or at the 5% level (Aldine Mail Rd., Bissonnet St., Durant St.). Tuesday-Sunday and Thursday-Sunday differences in the average concentrations at these sites also range between 0.1 and 0.2 $\mu g/m^3$ and these are statistically significant at the 5% level except for the Thursday-Sunday difference at Sheldon Road, which is significant at the 10% level. Differences between the average concentrations on midweek days and Saturdays range from 0 to 0.1 $\mu g/m^3$ and are statistically insignificant. The differences of the average concentrations for pairs of days and the statistical significance of the differences are shown in Table A-4.

Table 4-4 shows the differences in the median concentrations at each Houston site for each pair of days. The majority of the Tuesday-Sunday, Wednesday-Sunday, and

Thursday-Sunday differences in the median concentrations are statistically significant at the 5% level, despite small differences of only 0.1 to 0.2 $\mu g/m^3$. Several small differences of 0.1 $\mu g/m^3$ between pairs of median concentrations are significant at the 10% level, including the Wednesday-Sunday difference at Sheldon Road and the Thursday-Sunday difference at Hwy 1484. The Wednesday-Sunday difference at Hwy 1484 is statistically insignificant. The Tuesday-Saturday, Wednesday-Saturday, and Thursday-Saturday differences in median concentrations are statistically significant, except the 0.1 $\mu g/m^3$ difference at Aldine Mail Road between Tuesdays and Saturdays.

Figure 4-6 shows the similarities of the concentrations on midweek days and on weekend days at sites in Houston. Many of the corresponding percentile concentrations lie on the 1:1 line. Despite some evidence that Sunday concentrations are lower than midweek concentrations, weekend days as a group do not show lower concentrations than midweek days as a group. This is in part due to a negligible to small reduction of EC concentrations on Saturdays compared to weekdays. The lack of a reduction of Saturdays is unique to Houston, compared to the day-of-the-week behavior of EC in NYC and Philadelphia.

Table 4-2 shows the corresponding differences in the median concentrations. The median EC concentrations for weekend days as a group are about 0.1 $\mu g/m^3$ lower than midweek days. These small differences, however, are statistically significant at the 5% level at 4 sites and at the 10% level at the remaining site. Table A-2 shows the differences in the average EC concentrations between midweek days (Tuesday/Wednesdays/Thursdays) and weekend days (Saturdays and Sundays). At the Houston sites, the differences in the average concentrations are also smaller than 0.1 $\mu g/m^3$. The differences of the averages are statistically significant only at the Aldine Mail Road and Bissonnet Street monitors.

Table 4-4. Differences in the median concentrations of EC between each pair of days for sites in Houston. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%)

(a) Aldine Mail Street (482010024)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.09					
Wed	-0.01	0.08				
Thu	-0.04	0.06	-0.03			
Fri	-0.08	0.02	-0.06	-0.04		
Sat	0.01	0.11	0.02	0.05	0.09	
Sun	**0.13**	**0.23**	**0.14**	**0.17**	**0.21**	**0.12**

(b) Sheldon Road (482010026)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	**-0.07**					
Wed	0.00	0.07				
Thu	-0.01	0.06	-0.01			
Fri	-0.01	0.06	-0.01	0.00		
Sat	-0.02	0.05	-0.02	-0.01	-0.01	
Sun	**0.07**	**0.14**	0.07	**0.08**	0.08	0.08

(c) Bissonnet Street (482010055)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.03					
Wed	-0.02	0.01				
Thu	-0.02	0.02	0.01			
Fri	-0.03	0.00	-0.01	-0.01		
Sat	-0.01	0.02	0.01	0.01	0.02	
Sun	**0.11**	**0.15**	**0.13**	**0.13**	**0.14**	**0.12**

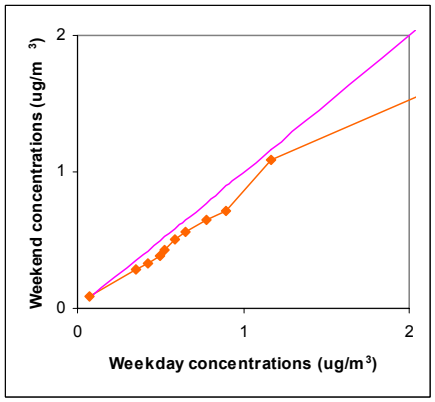
(d) Durant Street (482011039)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.01					
Wed	0.01	0.02				
Thu	-0.01	0.00	-0.02			
Fri	-0.05	-0.04	-0.06	-0.04		
Sat	0.00	0.01	-0.01	0.01	0.05	
Sun	0.07	**0.08**	**0.06**	**0.08**	**0.12**	**0.07**

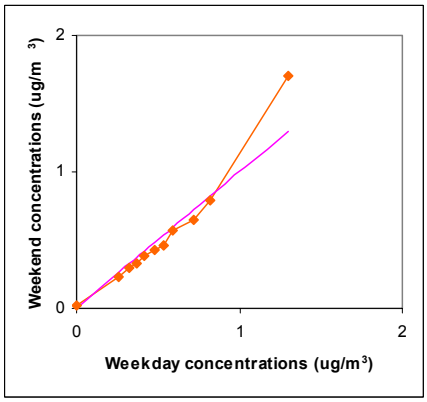
(e) Hwy 1484 (483390078)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.02					
Wed	0.01	0.03				
Thu	-0.01	0.01	-0.02			
Fri	-0.02	0.00	-0.03	-0.01		
Sat	0.02	0.04	0.01	0.03	0.04	
Sun	0.06	**0.08**	0.05	0.07	0.07	0.04

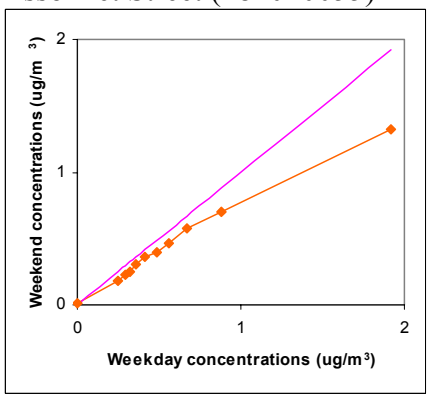
(a) Aldine Mail Road (482010024)



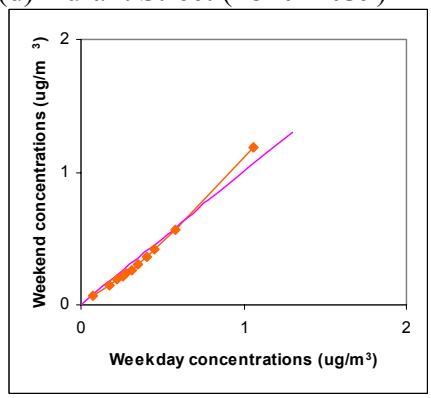
(b) Sheldon Road (482010026)



(c) Bissonnet Street (482010055)



(d) Durant Street (482011039)



(e) Hwy 1484 (483390078)

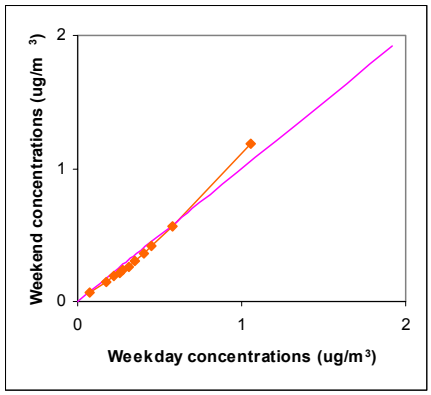


Figure 4-6. QQ plots for weekend vs. midweek EC concentrations at sites in Houston.

4.4 Discussion of the EC results

New York City and Philadelphia show consistent day-of-the-week signals for EC, where average and median concentrations decrease on Saturdays and Sundays compared to midweek days, with Sundays being the day with the lowest concentrations at all sites. The Wednesday-Sunday differences in the median concentrations are 0.2 to 0.9 $\mu g/m^3$ in the two East Coast cities. At a limited number of monitors, EC concentrations also tend to be higher at urban locations compared to suburban locations.

Sites in Houston record lower EC concentrations than NYC and Philadelphia throughout the week. The day-of-the-week signal is also weaker, with Wednesday-Sunday differences in the median concentrations of approximately 0.1 $\mu g/m^3$ in Houston. Urban sites in Houston do not always record higher EC concentrations or stronger day-of-week cycles than suburban sites. Sundays show slightly lower average and median concentrations compared to Tuesdays, Wednesdays, and Thursdays, but Saturdays show little or no significant decrease in EC concentrations compared to the weekdays.

5. Formaldehyde Results

5.1 NYC

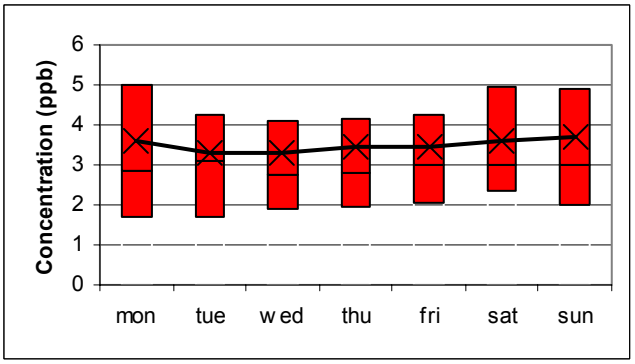
There are two monitors for HCHO in NYC that have sufficient data for each day of the week for analysis. No day-of-the-week trend is observed in the box plots in Figure 5-1. If any day-of-the-week signal exists, it is obscured by the variability in the concentrations at these sites. For example, at the Bronx site (360050083), the highest 75th percentile and the lowest 25th percentile HCHO concentrations both occur on Mondays. The highest average concentration is observed on Sundays at the Bronx site and on Saturdays at the Queens site. The lowest average concentration is observed on Wednesdays at Bronx and Fridays at Queens.

At the Bronx site, the highest median concentration is observed on Tuesdays. The lowest median concentrations occur on the same days (Wednesdays) as the lowest average concentrations. At the Bronx site, the lowest 25th percentile concentration is observed on Mondays, whereas the lowest average and median concentrations are observed on Wednesdays. The lowest 75th percentile concentration is also observed on Wednesdays. The highest 25th percentile, median, 75th percentile and average concentrations occur on different days at the Bronx site.

High median concentrations are observed on Wednesdays at the Queens site. The lowest median and average concentrations occur on Fridays. The lowest and highest 25th percentile concentrations occur on the same days as the lowest and highest average values, respectively, at the Queens site, but the lowest and highest 75th percentile concentrations occur on Thursdays and Sundays, respectively, which differ from the other metrics.

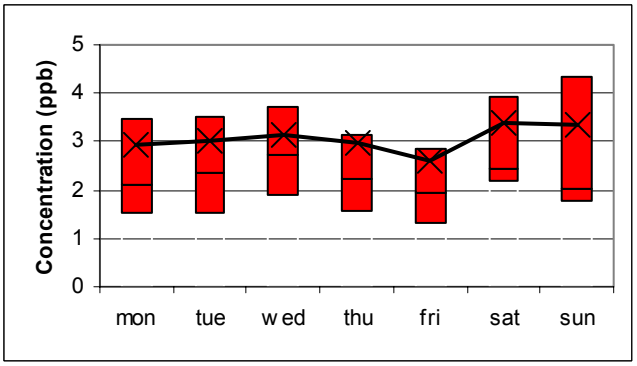
(a) Bronx

(360050083)

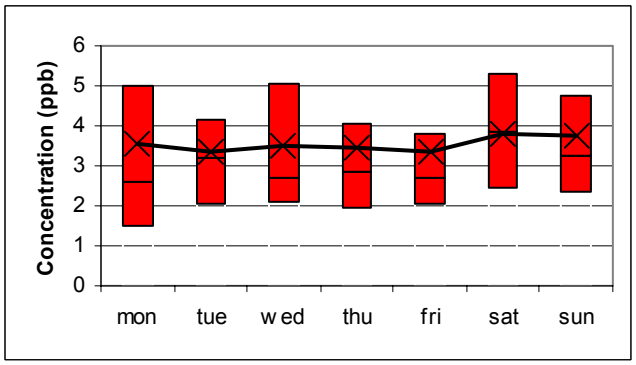


(b) Queens

(360810097)



(c) Bronx, post 2000 only



(d) Bronx: summer, rush hour

(360050083)

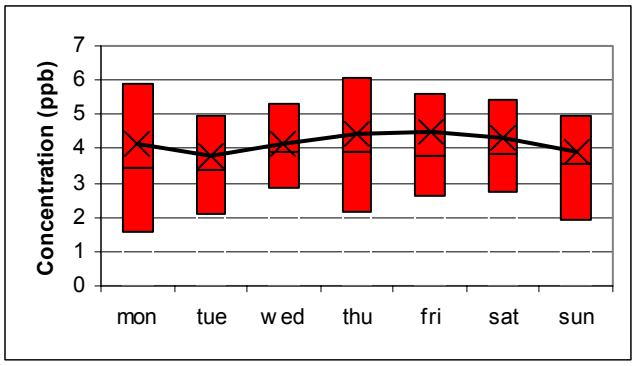


Figure 5-1. Box plots for HCHO concentrations at sites in New York City

To assess the variability due to the changes in fuel characteristics, a limited data set is used for the Bronx site, which contains only data from the post gasoline reformulation (Phase 2) era (see Figure 5-1c). The weekend increase seems more prominent compared to the full dataset (Figure 5-1a), especially for the mean, median, and 25th percentile metrics.

The Queens data set for HCHO shows some average concentrations that are closer in magnitude to the 75th percentile value than the median values (e.g., Thursdays and Fridays), indicating the presence of some high concentrations that have a strong effect on the average. The boxes for Saturdays, Sundays, and Mondays in Figure 5-1a, with a wider range between the median and 75th percentile value than between the 25th percentile and median, also indicate that the distributions of concentration data tends to be skewed with a tail on the high concentration side.

Due to the effect of high concentrations on the average concentration, the average metric is not used for numerical analyses regarding the day-of-the-week differences. Table 5-1 shows the differences of the median values for each pair of days at the Bronx and Queens monitors. At the Bronx site, the median concentrations on Saturdays and Sundays are higher than the median concentration on Wednesdays by 0.25 ppb. This difference is statistically insignificant at the 10% level. None of the weekday-weekend differences of the median concentrations is statistically significant; they range from -0.2 ppb (weekend > weekday) to + 0.1 ppb (weekday > weekend). At the Queens site, the only statistically significant difference between a midweek day median concentration and a weekend median concentration is the Wednesday-Sunday pair, with Sundays' median being 0.7 ppb lower than Wednesdays' median value. Other statistically different pairs at the 5% level are between Mondays and Wednesdays (Wednesdays' median higher by 0.6 ppb), and between Wednesdays and Fridays (Wednesdays higher by 0.8 ppb).

Table 5-1. Differences in the median concentrations of HCHO between each pair of days for sites in New York City. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%)

(a) Bronx

(360050083)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.24					
Wed	0.09	0.33				
Thu	0.07	0.31	-0.02			
Fri	-0.17	0.07	-0.26	-0.24		
Sat	-0.16	0.08	-0.25	-0.23	0.01	
Sun	-0.16	0.08	-0.25	-0.23	0.01	0.00

(b) Queens

(360810097)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.26					
Wed	**-0.62**	-0.35				
Thu	-0.15	0.11	0.47			
Fri	0.15	0.41	**0.77**	0.30		
Sat	-0.35	-0.08	0.27	-0.20	-0.50	
Sun	0.08	0.34	**0.69**	0.23	-0.07	0.42

At the Bronx site, the 75th percentile concentrations are higher on Saturdays and Sundays compared to Tuesdays, Wednesdays, and Thursdays by 0.7 to 0.9 ppb. Of these differences, the Saturday-Wednesday pair is statistically significant at the 5% level and the Saturday-Thursday pair is statistically different at the 10% level. The Sunday 75th percentile concentration is lower than Saturdays' and is not statistically different from the midweek values. At Queens, the 75th percentile concentrations are also higher on Saturdays and Sundays compared to midweek days. At this site, Sundays show higher concentrations than Saturdays. The maximum difference between 75th percentile concentrations of 1.5 ppb (5% significant) is between Sundays and Fridays. The second largest difference of 1.2 ppb (10% significant) is between Sundays and Thursdays. The Sunday-Tuesday and Sunday-Wednesday differences are 0.8 and 0.6 ppb, respectively, and are not statistically significant. Table B-1 shows the differences in the 75th percentile concentrations between pairs of days and their corresponding statistical significance.

Figure 5-2 shows the QQ plots of weekend concentrations vs. midweek concentrations. These plots show a tendency for the middle percentiles of weekend and midweek HCHO concentrations to be quite similar. There is some indication that at the high range of percentiles, concentrations on weekends may be higher than those on weekdays.

Grouping midweek days and weekend days, the differences in the median concentrations are shown in Table 5-2. The median concentration on midweek days is not statistically different from that on weekend days at the Bronx site. The midweek median concentration is higher than the weekend median concentration by 0.3 ppb at the Queens site, but this difference is not statistically significant. Differences in the 75th percentile concentrations are presented in Appendix B-2. At both the Bronx and Queens sites, the weekend 75th percentile concentrations are higher than the midweek 75th percentile concentrations. The difference of 0.81 ppb is statistically significant at the Bronx site at the 5% level. The smaller difference of 0.6 ppb in Queens is statistically insignificant at the 10% level due in part to larger variability in the Queens data.

(a) Bronx (360050083) (b) Queens (360810097)

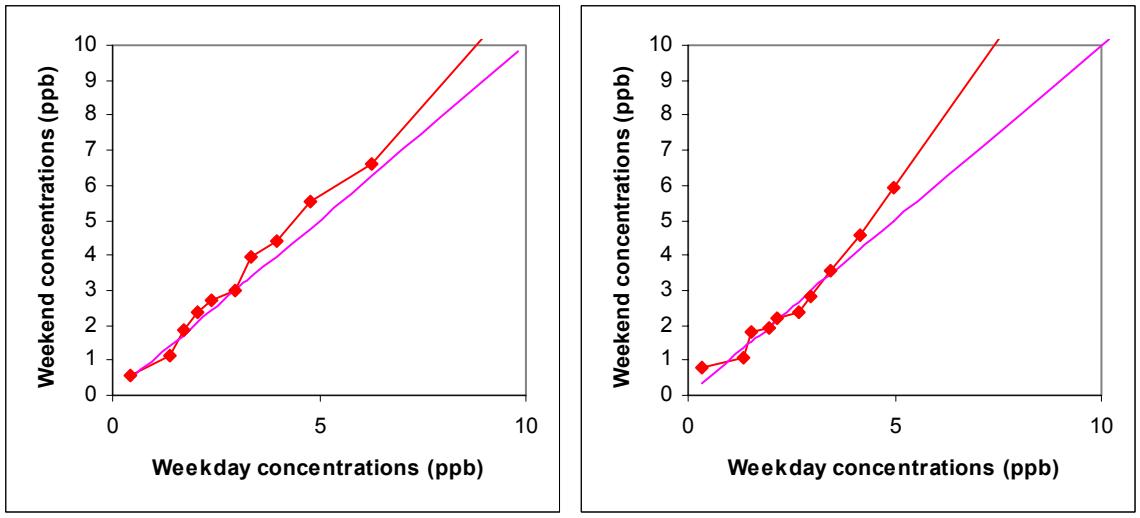


Figure 5-2. QQ plots for weekend vs. midweek HCHO concentrations at sites in New York City

Table 5-2. Differences in the median concentrations of HCHO between midweek days and weekend days in New York City, Philadelphia, and Houston

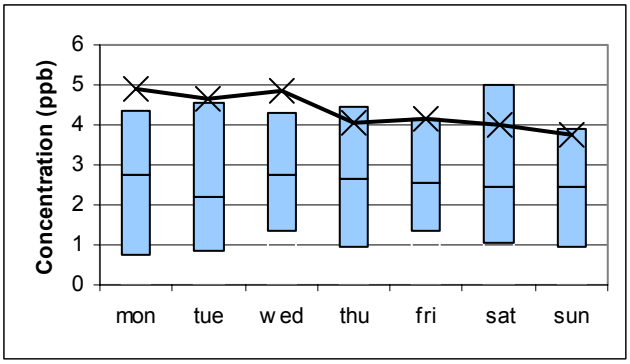
Site	Nwkd	Nwke	Cwkd	Cwke	ΔC	Significant?	
			(ppb)			10%	5%
Bronx	226	145	2.97	3.01	-0.05	N	N
Queens	106	72	2.66	2.38	0.27	N	N
Camden	183	113	2.66	2.46	0.20	N	N
Philadelphia	232	159	3.02	2.82	0.20	N	N
Clinton Drive, Houston	161	90	3.32	3.23	0.09	N	N
Durant Street, Houston	156	101	2.84	2.68	0.16	N	N

Short-duration samples are taken during rush hours (6-9 a.m. or 5-8 a.m.) at the Bronx site in NY (summer only). These data may provide some information for the day-of-the-week signal due to primary emissions or due to carry over from the previous day. At the Bronx site, the variability of early morning concentrations is typically larger than that of the 24-hour concentrations (see box plot in Figure 5-1c). The midweek day median concentrations cover a range of 3.3 to 3.9 ppb weekend, which are slightly higher than the 24-hour averages (2.8-3.1 ppb), but the range includes the median weekend morning concentrations (3.6-3.8 ppb). No weekend increase is observed with the 75th percentile concentrations in the rush-hour data. The weekday-weekend differences are statistically insignificant for the morning samples.

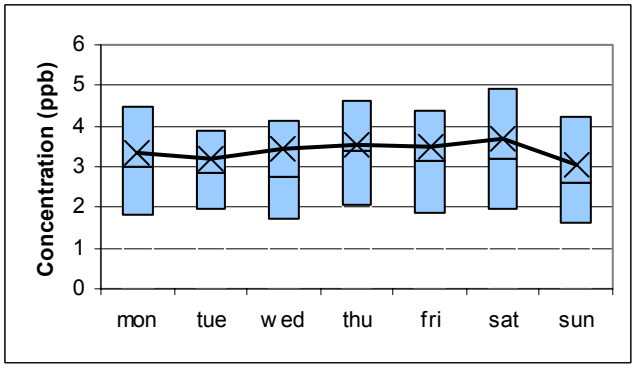
5.2 Philadelphia

Box plots for Camden and Philadelphia are shown in Figure 5-3. The average concentrations in Camden are at or above the 75th percentile for four days of the week, indicative of a very skewed distribution. An inspection of the time series (Figure 5-4) at this site shows that the time series contains a lot of structure, but has no discernible seasonal signal. Persistent high concentrations were recorded from March to August 2004. These data points are not flagged, nor are they associated with a different monitoring method or instrument that is inconsistent with the remainder of the data set. Therefore, the high values cannot be arbitrarily removed from the data set. To avoid undue influence of the high concentrations, the analysis focuses on median concentrations rather than average concentrations.

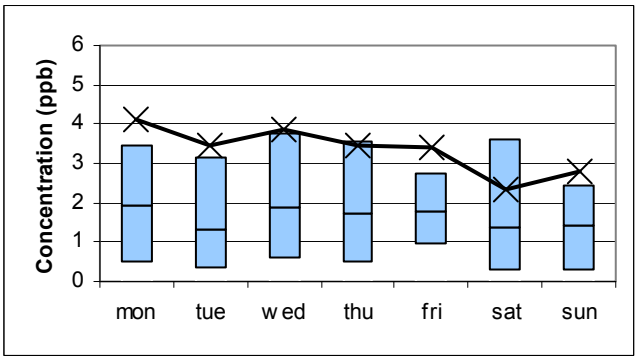
(a) Camden
(340070003)



(b) Philadelphia
(421010004)



(c) Camden (post 2000)
(340070003)



(d) Philadelphia (post 2000)
(421010004)

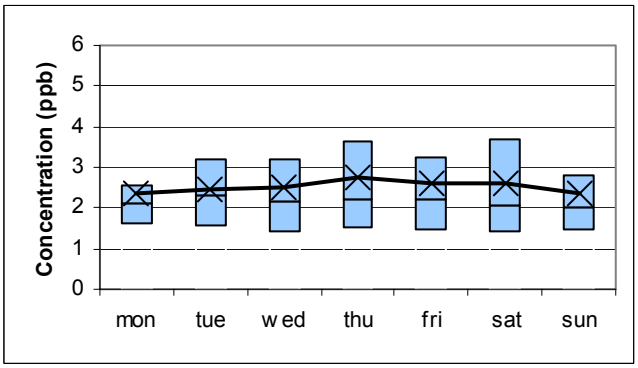
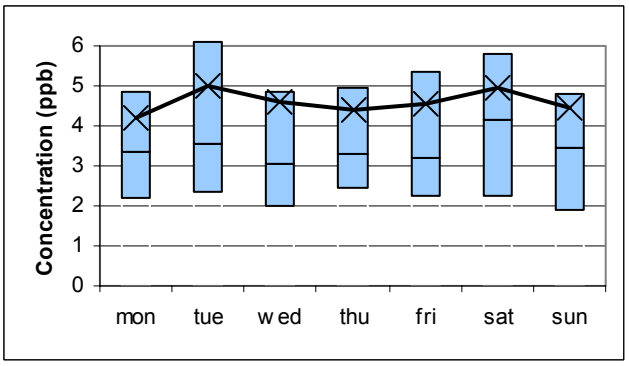


Figure 5-3. Box plots for HCHO concentrations at sites in Philadelphia.

(e) Camden, summer rush hour (340070003)



(f) Philadelphia, summer, rush hour (421010004)

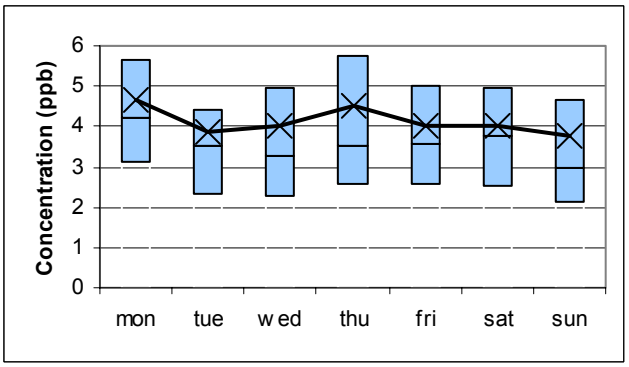


Figure 5-3. Box plots for HCHO concentrations at sites in Philadelphia (continued).

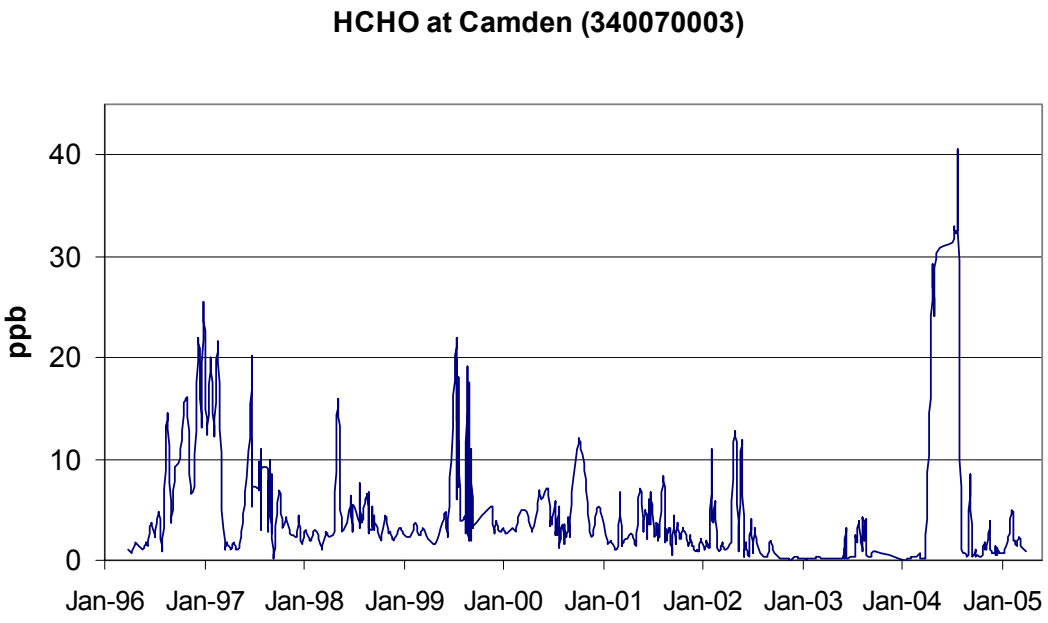


Figure 5-4. Time series of HCHO in Camden, NJ, near Philadelphia, PA.

The median, 25th percentile, and 75th percentile concentrations show no day-of-the-week patterns. At the Camden site, the median value is the highest on Mondays and the lowest on Tuesdays. In Philadelphia, the highest median is observed on Thursdays and the lowest median concentration is observed on Sundays. The 25th percentile concentration is the highest on Wednesdays at Camden and lowest on Mondays. The 25th percentile concentrations are high on Saturdays and Tuesdays and low on Sundays in Philadelphia. The 75th percentile concentration is the highest on Saturdays at each site. The lowest 75th percentile concentrations are observed on Sundays in Camden and on Tuesdays in Philadelphia.

Table 5-3 shows the differences in the median concentrations between pairs of days. In Camden, Sundays' median concentration is higher than Tuesdays (by 0.3 ppb), but lower than Wednesdays' and Thursdays' (by 0.2 to 0.3 ppb). Saturdays' median concentration is also higher than Tuesdays' but lower than Wednesdays' and Thursdays'. None of these differences is statistically significant at the 10% level. In Philadelphia, the median concentration on Sundays is lower than the median concentrations on Tuesdays (by 0.3 ppb), Wednesdays (by 0.1 ppb), and Thursdays (by 0.8 ppb). The larger Thursday-Sunday difference is statistically significant at the 5% level. The median concentration on Saturdays at this site is slightly above some of the midweek median concentrations (e.g., by 0.4 to 0.5 ppb for Tuesdays and Wednesdays). The Saturday-midweek differences are not statistically significant.

Table 5-3. Differences in the median concentrations of HCHO between each pair of days for sites in Philadelphia. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%)

(a) Camden

(340070003)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	0.58					
Wed	0.04	-0.54				
Thu	0.14	-0.44	0.10			
Fri	0.20	-0.38	0.16	0.06		
Sat	0.33	-0.25	0.29	0.19	0.13	
Sun	0.31	-0.27	0.27	0.17	0.11	-0.02

(b) Philadelphia

(421010004)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	0.13					
Wed	0.24	0.11				
Thu	-0.40	**-0.53**	**-0.64**			
Fri	-0.19	-0.32	-0.43	0.21		
Sat	-0.22	-0.35	-0.46	0.18	-0.03	
Sun	0.38	0.25	0.14	**0.78**	0.57	0.60

Differences in the 75th percentile concentrations for pairs of days are shown in Appendix B-3. In Camden, the 75th percentile concentration on Sundays tends to be lower than the corresponding concentrations on Tuesday, Wednesday, and Thursdays. The Wednesday-Sunday difference is 0.4 ppb, while the Tuesday-Sunday difference is 0.6 ppb. The Saturday 75th percentile concentration is higher than the 75th percentiles on Tuesdays (by 0.5 ppb), Wednesdays (by 0.7 ppb), and Thursdays (by 0.6 ppb). These differences are not statistically significant at the 10% level. In Philadelphia, the 75th percentile concentration on Sundays is slightly above those on Tuesdays (by 0.4 ppb) and Wednesdays (by 0.1 ppb), but below that on Thursdays (by 0.4 ppb). The Sunday-midweek differences in 75th percentile concentrations are not statistically significant at the 10% level. The 75th percentile concentration on Saturdays at the Philadelphia site is higher than those on midweek days by 0.3 to 1 ppb. The Tuesday-Saturday difference of 1 ppb is statistically significant at the 5% level and the Wednesday-Saturday difference of 0.8 ppb is statistically significant at the 10% level.

The QQ plots in Figure 5-5 show that as a group, weekend concentrations are quite similar to weekday concentrations. Concentrations corresponding to the same percentiles lie very close to the 1:1 line. Some differences are seen at the top (> 90th) percentile concentrations for Camden and Philadelphia, with weekend concentrations showing some tendency to be lower than the corresponding concentrations on midweek days.

Table 5-2 shows the comparison between the weekend days and the midweek days for median concentrations. The differences in the median values are 0.2 ppb at both sites. The differences are too small to be statistically significant. The corresponding comparison for the 75th percentile value is show in Table A-2. The 75th percentile concentrations on weekends tend to be slightly higher than the weekday values (by 0.4 ppb). Again the differences are statistically insignificant. The differences in the 90th percentile concentrations between midweek days and weekend days are tested in light of Figure 5-5. The differences in the 90th percentile concentrations are 2.6 ppb in Camden and 0.5 ppb in Philadelphia. The differences are statistically insignificant.

(a) Camden (b) Philadelphia

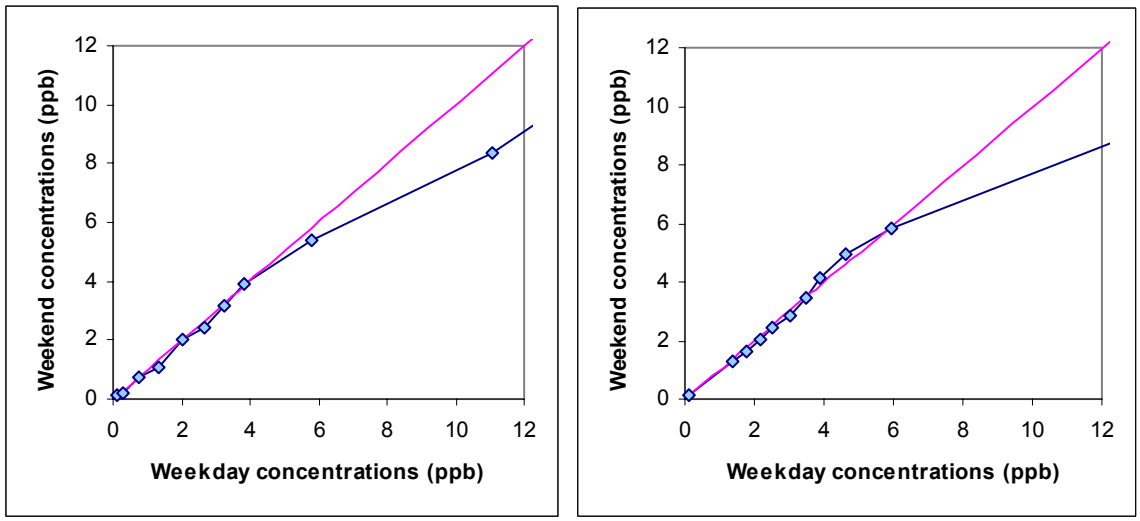


Figure 5-5. QQ plots for weekend vs. midweek HCHO concentrations at sites in Philadelphia

The lack of statistical significance of the differences is related to the variability of the HCHO data. Intrinsic variability, related to random measurement errors, or meteorological variability, cannot easily be reduced. It has been suggested that changes in the oxygen content of gasoline can introduce additional variability into the data set, since oxygenated fuels are associated with higher HCHO production. The chemistry effect in the ambient atmosphere, is expected to be non-linear, depending on the oxygenate and ambient conditions. Reformulated gasoline, which mandates an oxygen content of 2% by weight, was introduced in 1998. (Phase II implemented in 2000 requires no additional change in oxygen content.) Both sites in the vicinity of Philadelphia were operational during the gasoline change-over. The day-of-the-week analyses for HCHO are repeated restricting the data to post 2000 to investigate the effects of changing gasoline, if any, on the conclusions of the analyses. As shown in the bottom panels of Figure 5-3, HCHO concentrations are lower and the variability on all days at all sites is reduced when the restricted data set is used. The post 2000 data set in Camden shows high median concentrations on Mondays, high 25th percentile concentrations on Fridays and high 75th percentile concentrations on Wednesdays. Low median, 25th percentile and 75th percentile concentrations are observed on Tuesdays, Saturdays, and Sundays, respectively. In Philadelphia, high median, 25th, and 75th percentile concentrations are recorded on Tuesdays, Mondays, and Saturdays. Low concentrations are recorded on Sundays for the median and 75th percentile and on Wednesdays for the 25th percentile concentrations.

The differences in the median values on Wednesdays and Sundays range from 0.2 ppb in Philadelphia to 0.5 ppb in Camden for the post 2000 data set. The differences are larger than the longer data set but statistically insignificant. The Wednesday-Sunday differences in the 75th percentile concentrations are 0.3 ppb in Philadelphia and 1.3 ppb in Camden, the latter being statistically significant at the 5% level. At both sites, the Thursday-Sunday differences (0.8 – 1.1 ppb) in the 75th percentile values are statistically significant at the 10% level. The negative differences between the midweek 75th percentile concentration and Saturdays' 75th percentile concentration are less pronounced in the post 2000 data set than in the longer data set (shown in Table B-3).

Overall, the post 2000 weekday (Tuesday through Thursday)-weekend comparison shows larger differences in the median concentrations (0.3 to 0.4 ppb) compared with Table 5-2 for the larger data set. However these differences remain statistically insignificant at the 10% level. The differences in the 75th percentile concentrations change from negative (larger 75th percentile concentration on weekends) to zero or +0.4 ppb (larger 75th percentile concentration on weekdays). Statistically, the weekday-weekend differences of the 75th percentile concentrations are insignificant at 10%.

Camden and Philadelphia both have sufficient short-duration samples for an analysis of the day-of-the-week behavior during morning rush hours. Rush hour concentrations are higher than the corresponding 24-hour averages (see box plots in Figure 5-3). At Camden, the average concentration falls between the median and 75th percentile value, indicating that the short duration data are less affected by anomalous high concentrations. The median concentrations are the highest on Saturdays and Mondays, respectively, at Camden and Philadelphia. Due to high median concentrations on Saturdays in Camden, the group of weekend days shows higher median concentrations than midweek days by 0.8 ppb, a statistically significant difference at the 5% level. The 75th percentile concentration is also higher on weekends by 0.7 ppb (not significant). No such difference is seen at the Philadelphia site.

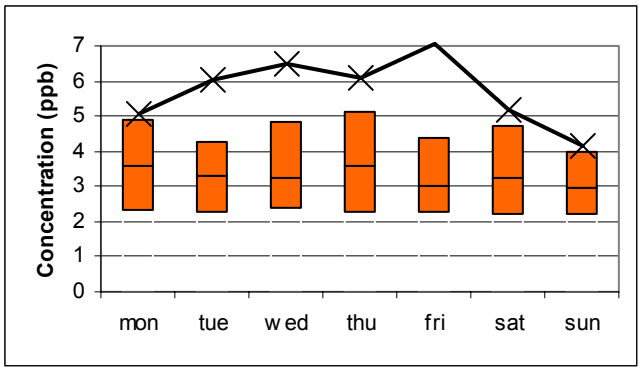
5.3 Houston

Box plots of HCHO concentrations for each day of the week are shown in Figure 5-6 for two suburban sites in Houston. The Clinton Drive site shows an average concentration for each day of the week that is substantially higher than the corresponding 75th percentile concentration, prompting an inspection of the time series, as shown in Figure 5-7. There was an increase in HCHO concentrations starting late May 2004. Aside from the magnitude of the sampling values, there is no change in the reported method, units, sampling duration, or frequency that may signify some transient changes. These data are not flagged as having quality issues or associated with extraordinary events. Possibilities such as changes in the emission patterns in the vicinity of the monitoring site cannot be investigated within the scope of the current project. Therefore, to avoid undue influence of the high concentrations, emphasis is placed on the median and percentile values rather than the average concentrations in the analysis of the day-of-the-week patterns.

At the Clinton Drive site, the median, 25th percentile, and 75th percentile concentrations are all lowest on Sundays. The highest median, 25th percentile, and 75th percentile concentrations are observed on Mondays, Wednesdays, and Thursdays, respectively. Higher variability is apparent at the Durant Street site. For example, Mondays show the highest 75th percentile concentration and the lowest 25th percentile concentration. The lowest median concentration is observed on Wednesdays; the highest median concentration is observed on Fridays. Sundays are associated with the lowest 75th percentile concentration and Mondays are associated with the highest. The 25th percentile concentration is the lowest on Mondays and the highest on Wednesdays. No consistent day-of-the-week pattern is observed.

(a) Clinton Drive

(482011035)



(b) Durant Street

(482011039)

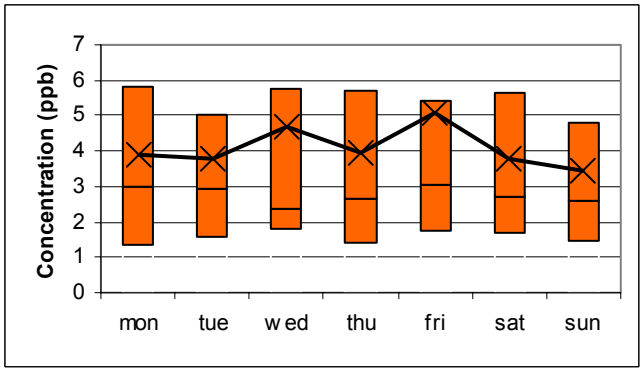


Figure 5-6. Box plots for HCHO concentrations at sites in Houston

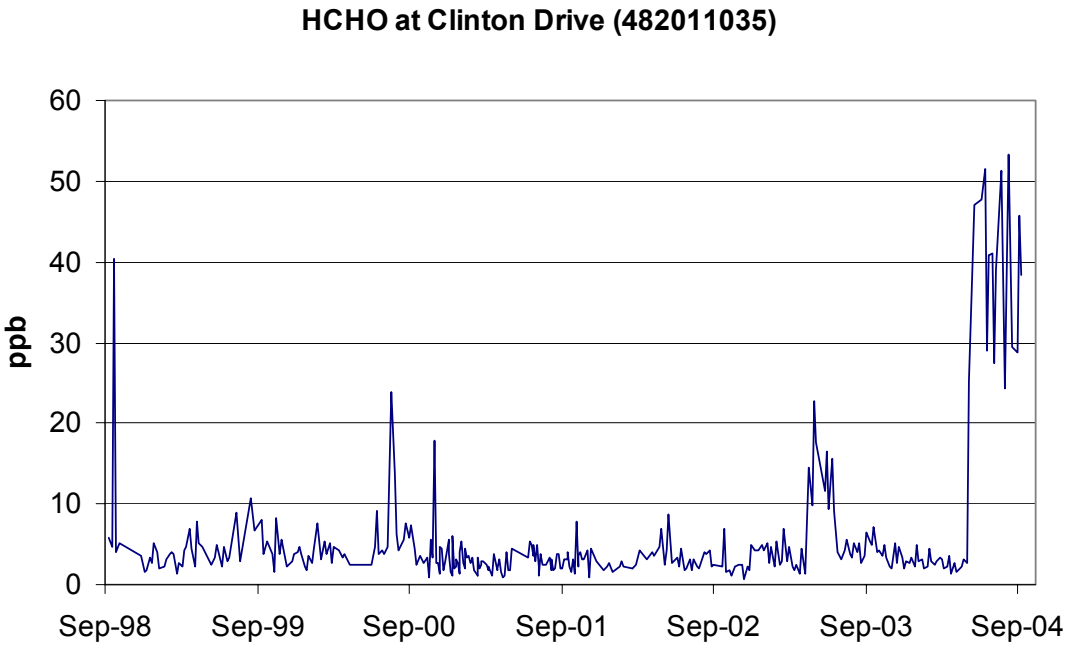


Figure 5-7. Time series of HCHO at Clinton Drive, Houston, TX.

Table 5-4 shows the differences in median concentrations between each pair of days. At the Clinton Drive site, the Tuesday-Sunday, Wednesday-Sunday, and Thursday-Sunday differences are 0.3, 0.3, and 0.6 ppb, respectively. The largest difference is statistically significant at the 10% level. Saturdays' median concentration is very similar to those on Tuesdays and Wednesdays. The Thursday-Saturday difference of 0.3 ppb is statistically insignificant. At Durant Street, Sunday-midweek differences in the median concentrations are smaller, ranging from -0.2 ppb (Sundays higher than Wednesdays) to 0.3 ppb (Tuesdays higher than Sundays). These differences are statistically insignificant. The Saturday-midweek differences in median concentrations span a range of -0.3 ppb (Wednesday minus Saturday) to 0.2 ppb (Tuesday minus Saturday); these differences have no statistical significance.

At Clinton Drive, the Wednesday-Sunday difference in the 75th percentile concentrations is 0.8 ppb, but it is not statistically significant at the 10% level. The Thursday-Sunday difference is 1.2 ppb, which is statistically significant at the 5% level. Interestingly, the Monday-Sunday and Saturday-Sunday differences (0.9 and 0.7 ppb, respectively) are statistically significant, but the Tuesday-Sunday difference (only 0.3 ppb) is not. Saturdays' 75th percentile value is higher than Tuesdays (by 0.5 ppb), but lower than Wednesdays' and Thursdays' (by 0.1 and 0.4 ppb, respectively). These weekday-Saturday differences are statistically insignificant. At Durant Drive, the Wednesday-Sunday difference in median concentrations is 1 ppb, but this value is statistically insignificant. The Tuesday-Sunday and Thursday-Sunday differences are 0.3 ppb and 0.9 ppb, respectively; they are also statistically insignificant. Saturdays' 75th percentile concentration at Durant Street is higher than Tuesdays' by 0.6 ppb but lower than Wednesdays' and Thursdays' (by 0.1 ppb). These differences are not significant. The differences and statistical significance of 75th percentile concentrations are tabulated in Appendix B-4.

Table 5-4. Differences in the median concentrations of HCHO between each pair of days for sites in Houston. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%)

(a) Clinton Drive

(482011035)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	0.31					
Wed	0.32	0.01				
Thu	0.01	-0.30	-0.31			
Fri	0.56	0.26	0.25	0.56		
Sat	0.32	0.01	0.00	0.31	-0.24	
Sun	0.60	0.29	0.28	0.59	0.04	0.28

(b) Durant Street

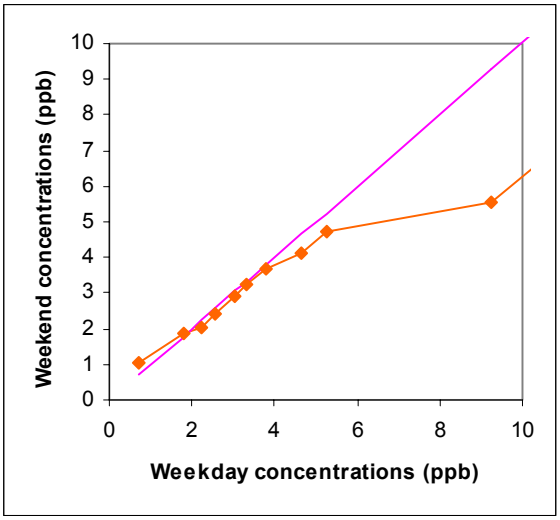
(482011039)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	0.04					
Wed	0.60	0.56				
Thu	0.30	0.26	-0.30			
Fri	-0.08	-0.12	-0.68	-0.38		
Sat	0.28	0.23	-0.33	-0.03	0.35	
Sun	0.37	0.33	-0.23	0.07	0.44	0.09

Figure 5-8 shows the QQ plots for the two Houston area sites comparing a group of weekend days and a group of midweek days. Weekend concentrations are quite similar to weekday concentrations at low percentiles. At high (> 90th) percentiles, there is some indication that weekend concentrations are lower than weekday concentrations at the highest percentiles, especially at the Clinton Drive site.

Differences in the median values between the weekend (Saturdays and Sundays as a group) and the midweek (Tuesdays, Wednesdays, and Thursdays as a group) are of the order of 0.1 to 0.2 ppb at the Houston sites (Table 5-2). These small differences are not statistically significant. The weekend 75th percentile concentration is lower by 0.4 ppb to 0.6 ppb at Clinton Drive and Durant Street, respectively. The smaller difference at Clinton Drive is statistically significant at the 10% level, whereas the Durant Street difference is not (Table B-2).

(a) Clinton Drive



(b) Durant Street

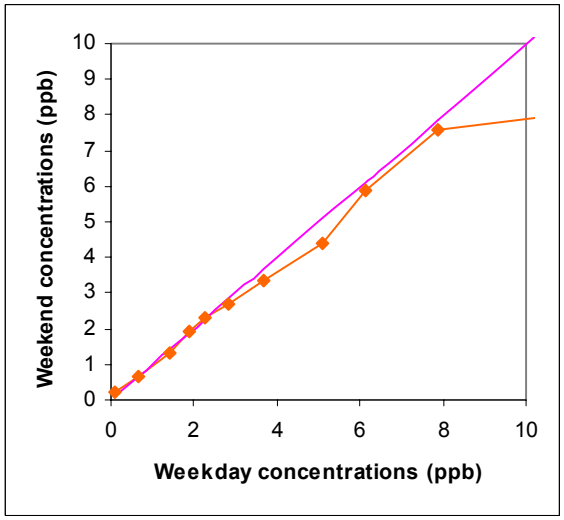


Figure 5-8 QQ plots for weekend vs. midweek HCHO concentrations at sites in Houston

5.4 Discussion of HCHO Results

Day-of-the-week patterns in HCHO concentrations can be obscured by variability due to the interplay of anthropogenic emissions, biogenic emissions, meteorology, and photochemistry. The analysis was undertaken to see if there were any discernable patterns in the HCHO data without attempting any adjustments.

At moderate HCHO concentrations, no consistent day-of-the-week pattern is observed at any of the metropolitan areas investigated. The Wednesday-Sunday differences in median concentrations range from -0.3 ppb to 0.7 ppb. The only statistically significant difference (0.7 ppb) is observed in Queens, NY. Weekend days as a group do not show statistically significant different median concentrations compared to midweek days as a group. The weekday-weekend differences in medians are 0 – 0.3 ppb in NY, 0.2 ppb in Philadelphia, and 0 – 0.2 ppb in Houston.

At the high end of HCHO concentrations, the 75th percentile concentrations show larger differences between weekdays and weekends than other metrics. The 75th percentile concentrations are higher on weekends in NY, with Wednesday-Sunday differences of -0.8 ppb and -0.6 ppb at Bronx and Queens, respectively. While these numbers are not statistically significant, other pairs of low weekday-high weekend differences are statistically significant at 10% or 5% level, including the Thursday-Sunday difference in Queens and the Wednesday-Saturday and Thursday-Saturday differences at the Bronx site. Overall the midweek vs. weekend comparison also shows that the 75th percentile concentration is higher on weekends in NY (by 0.6 to 0.8 ppb), with a statistically significant difference observed at the Bronx site.

The Wednesday-Sunday differences in 75th percentile are 0.4 ppb in Camden and -0.1 ppb in Philadelphia. However, Saturdays' 75th percentile concentrations are higher than Wednesdays' by 0.7 ppb (statistically insignificant) in Camden and by 0.8 ppb (statistically significant at the 10% level) in Philadelphia. As a result, the 75th percentile HCHO concentrations on weekends are about 0.4 ppb higher than the 75th percentile

concentrations on midweek days at the Philadelphia area sites. These differences are statistically insignificant.

There is limited evidence that the weekly behavior of HCHO is influenced by the reformulation of gasoline. When the Bronx, NY data are limited to post 2000, the weekend increase in HCHO becomes more pronounced. When the Philadelphia data sets are limited to post reformulation years, the Saturday increase in the 75th percentile concentration in Camden and Philadelphia is less pronounced. As a result, an overall decrease is observed in the 75th percentile concentration on weekends relative to weekdays. One property of the gasoline expected to affect direct HCHO emissions is the oxygen content. However, increasing the oxygen content in reformulated should increase HCHO emissions by the same relative amount every day of the week. Changes in the day-of-the-week behavior, if verified, imply differences in photochemical activities, which may be due to changes in oxygen content or other parameters affecting the reactivity of gasoline in the ambient atmosphere.

Short-duration samples are available during rush hours (6-9 a.m. or 5-8 a.m.) at several sites (summer only). Rush-hour concentrations are higher than 24-hour averages at the Bronx, Camden and Philadelphia sites, due most likely to less mixing and some carry-over or emissions. The weekday-weekend differences are statistically insignificant for the morning samples in NY. At Camden, the short duration rush-hour data are less affected by anomalous high concentrations. Due to high median concentrations on Saturdays in Camden, the group of weekend days shows higher median concentrations than midweek days by 0.8 ppb, a statistically significant difference at the 5% level. The 75th percentile concentrations are also higher on weekends by 0.7 ppb (not significant). No such difference is seen at the Philadelphia site.

The increase in HCHO concentrations on weekends, which seems to be more prominent after the introduction of reformulated gasoline in NY and before the introduction of reformulated gasoline in Philadelphia and for the 75th percentile concentration in NY, is particularly interesting. Previous studies have found definitive

weekly patterns for ozone. In Philadelphia, a Saturday peak on the weekly cycle of ozone was found (Pun et al., 2003). In other parts of the eastern U.S., weekend increases are also common (Huser, 1998). Carry-over and long range transport of pollutants may play a role in increased concentrations of HCHO and O_3. Because HCHO is both emitted and formed in the atmosphere, it may be speculated that the increase photochemical reactivity that leads to higher ozone on weekends contributes also to the production of HCHO on weekends at the east coast locations.

The 75th percentile concentrations of HCHO in Houston do not show any increase during weekends compared to weekdays. The midweek-weekend difference at Clinton Drive of 0.4 ppb is statistically significant at the 10% level, but not the 0.6 ppb difference at Durant Street. At locations with significant biogenic emissions, e.g., Houston, the anthropogenic day-of-the-week signal may be harder to detect. HCHO is a universal product of photochemical reactions of biogenic and anthropogenic VOC. The larger the contribution of biogenics to the total VOC budget, the weaker the day-of-the-week variability relative to the total concentrations.

6. Benzene Results

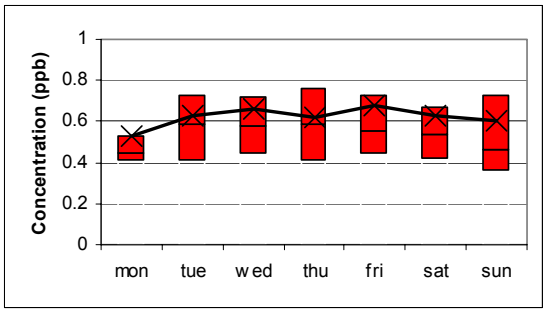
6.1 NYC

Day-of-the-week box plots for 3 sampling sites in NYC are provided in Figure 6-1. Richmond shows larger ranges of concentrations than the Kings and Queens sites. None shows an obvious day-of-the-week trend in benzene concentrations. The highest median concentrations are observed on Thursdays in Kings and Tuesdays in Queens and Richmond. Low median concentrations are observed on Mondays in Kings and Saturdays in Queens and Richmond. On average, median concentrations on Tuesdays, Wednesdays, and Thursdays are higher than median concentrations on Saturdays and Sundays. High 25^{th} and 75^{th} percentile concentrations also occur on weekdays at all three sites, although low 25^{th} and 75^{th} percentile concentrations can occur on Mondays, Sundays and midweek days.

The differences in median concentrations for pairs of days are shown in Table 6-1 for Kings, Queens, and Richmond, NY. The differences are quite small between weekdays and weekends. Wednesday-Sunday differences in the median concentrations are 0.1 ppb in Kings and Queens and 0.0 ppb in Richmond. The 0.1 ppb differences are nevertheless statistically significant at the 5% level. Tuesday-Sunday differences of the median values are 0.1 ppb in Kings and Queens and 0.2 ppb in Richmond. The difference in Queens is significant at the 5% level while the differences in Kings and Richmond are significant at the 10% level. A Thursday-Sunday difference of 0.1 ppb in Queens is also statistically significant at the 5% level, but smaller Thursday-Sunday differences are statistically insignificant at the other two sites. In Queens, Saturdays' median concentration is lower than those on Tuesdays through Thursdays by 0.1 ppb (significant at the 5% level). Interestingly, the median concentration is lower on Mondays than on the other weekdays in Kings and Queens. In Kings, Mondays' median is statistically significantly lower than Tuesdays' through Saturdays' median values.

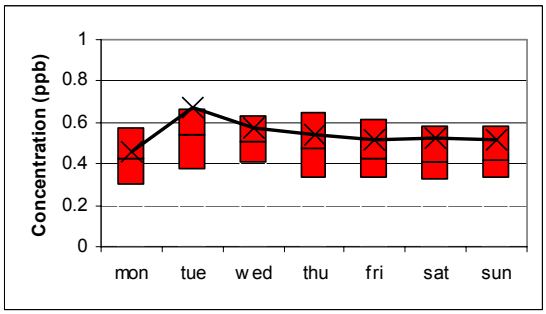
(a) Kings

(360470118)



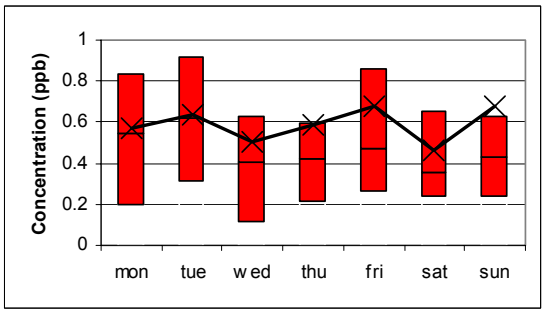
(b) Queens

(360810098)



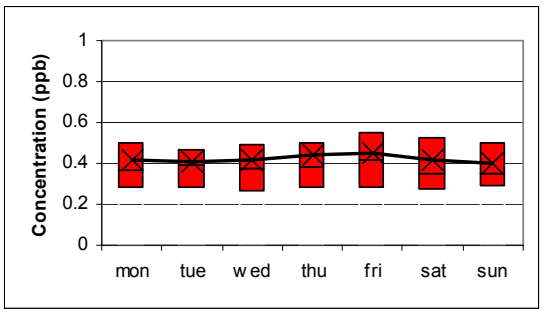
(c) Richmond

(360850055)



(d) Bronx, summer only

(360050083)



(e) Bronx, summer, rush hour

(360050083)

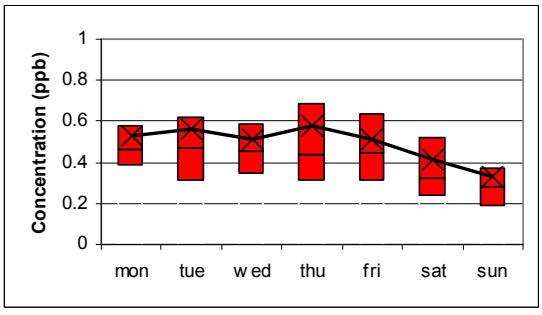


Figure 6-1. Box plots for benzene concentrations at sites in New York City

Table 6-1. Differences in the median concentrations of benzene between each pair of days for sites in New York City. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%)

(a) Kings

(360470118)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.14					
Wed	-0.13	0.01				
Thu	-0.13	0.01	0.00			
Fri	-0.11	0.04	0.03	0.03		
Sat	-0.09	0.05	0.04	0.04	0.02	
Sun	-0.01	0.13	0.12	0.12	0.10	0.08

(b) Queens

(360810098)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.12					
Wed	-0.09	0.03				
Thu	-0.06	0.07	0.03			
Fri	-0.01	0.12	0.08	0.05		
Sat	0.01	0.14	0.10	0.07	0.02	
Sun	0.00	0.12	0.09	0.06	0.01	-0.01

(c) Richmond

(360850055)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.08					
Wed	0.14	0.22				
Thu	0.13	0.20	-0.01			
Fri	0.07	0.15	-0.07	-0.06		
Sat	0.19	0.27	0.05	0.06	0.12	
Sun	0.11	0.19	-0.02	-0.01	0.04	-0.08

(d) Bronx (summer only)

(360050083)

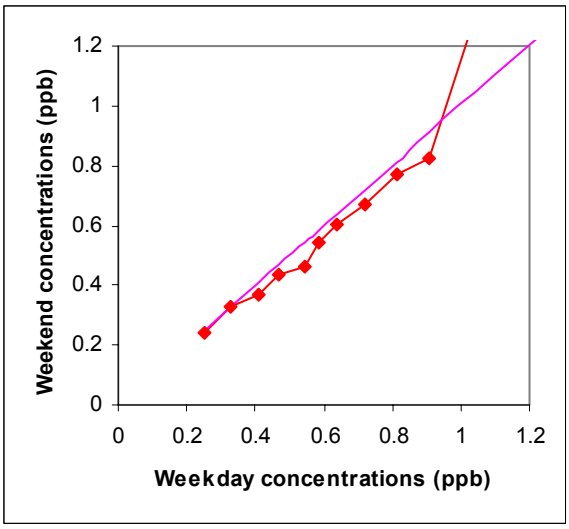
B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.02					
Wed	0.00	0.02				
Thu	-0.01	0.01	-0.01			
Fri	-0.05	-0.02	-0.04	-0.03		
Sat	0.02	0.04	0.02	0.03	0.06	
Sun	0.02	0.04	0.02	0.03	0.06	0.00

Differences in the 75th percentile concentrations between midweek days and Sundays tend to be smaller than the differences in the median concentrations. Therefore, statistically significant differences are not observed in Kings and Queens. The only pair of midweek vs. Sunday 75th percentile concentrations that give a significant difference is the Tuesday-Sunday pair from Richmond. Lower 75th percentile concentrations are observed on Mondays compared to the rest of the week in Kings and Queens, with statistically significant (5% or 10% level) differences of 0.1 ppb in Kings and smaller, statistically insignificant differences in Queens. Mondays' 75th percentile concentration is observed to be higher by 0.2 ppb than Wednesdays', Thursdays', Saturdays' and Sundays' in Richmond. Except for the Monday-Saturday pair, the differences in the 75th percentile concentrations are significant (10% level). Tuesdays' 75th percentile concentrations are also higher than Wednesdays', Thursdays', Saturdays' and Sundays' in Richmond. The significance of the Tuesdays differences are at the 5% level. Differences in the 75th percentile concentrations for pairs of days, as well as their statistical significance, are listed in Appendix C-1 for the sites in New York City.

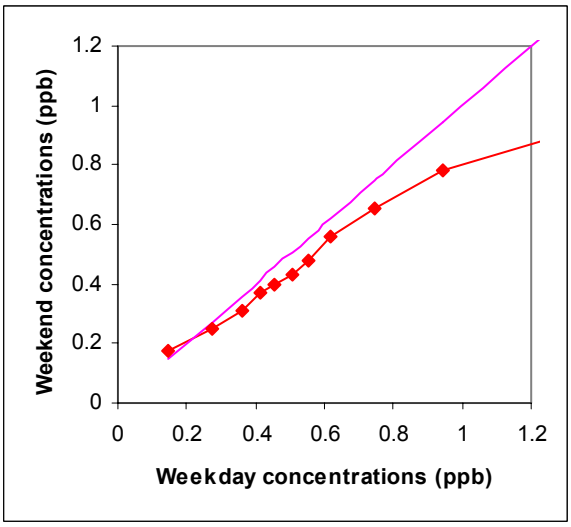
QQ plots are shown in Figure 6-2 to compare the distributions of the midweek day concentrations and the weekend contributions. Except at very high concentrations in Kings, the concentration at each percentile on weekends tend to be slightly lower than the corresponding percentile concentration on midweek days in Kings and Queens. At Richmond, weekend concentrations are higher than weekday concentrations at low percentiles and lower at high percentiles.

When a group of concentrations from midweek days is compared to a group from weekend days, the differences (Table 6-2) in median concentrations range from 0.01 ppb for Richmond to 0.04 ppb for Kings and 0.08 ppb for Queens. The difference in Queens is statistically significant at the 5% level, but the differences at the other sites are statistically insignificant.

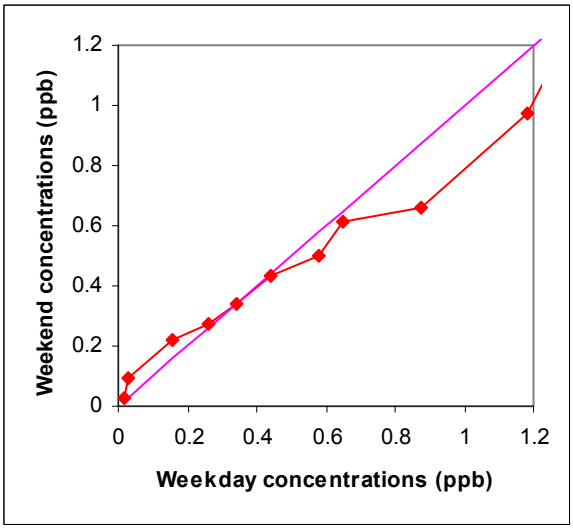
(a) Kings



(b) Queens



(c) Richmond



(d) Bronx – summer only

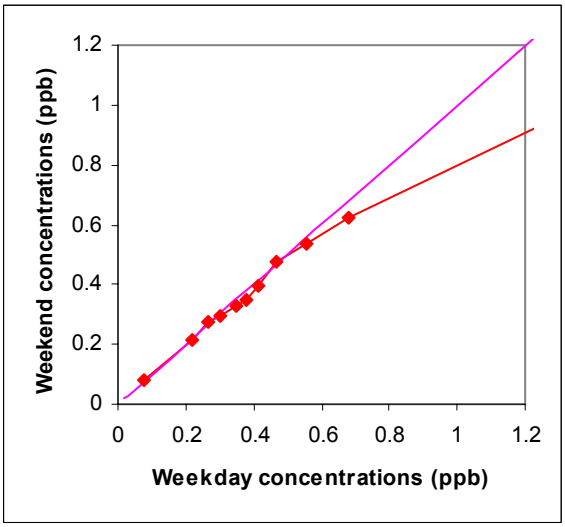


Figure 6-2. QQ plots for weekend vs. midweek benzene concentrations at sites in New York City

Table 6-2. Differences in the median concentrations of benzene between midweek days and weekend days in New York City, Philadelphia, and Houston

Site	Nwkd	Nwke	Cwkd	Cwke	ΔC	Significant?	
			(ppb)			10%	5%
Bronx (summer only)	232	163	0.38	0.35	0.03	Y	Y
Kings	103	66	0.58	0.54	0.04	N	N
Queens	125	84	0.51	0.43	0.08	Y	Y
Richmond	97	66	0.44	0.43	0.01	N	N
Camden (summer only)	279	191	0.31	0.30	0.01	N	N
Philadelphia	329	218	0.56	0.54	0.02	N	N
Philadelphia (Amtrak)	102	68	0.38	0.33	0.05	Y	N
Aldine Mail Rd., Houston	204	139	0.52	0.47	0.05	N	N
Sheldon Rd., Houston	229	160	0.80	0.75	0.05	N	N
Kizman, Houston	127	92	0.36	0.35	0.01	N	N
Bissonnet St., Houston	308	207	0.31	0.30	0.01	N	N
Stewart St., Houston	165	101	1.18	1.06	0.12	N	N
Bayway Dr., Houston	138	91	0.46	0.47	-0.01	N	N
Old Hwy 146, Houston	149	94	0.57	0.57	0.00	N	N
Old Galveston Rd., Houston	112	71	0.66	0.64	0.02	N	N
Central St., Houston	109	70	0.41	0.45	-0.04	N	N
Haden Rd., Houston	253	167	0.80	0.78	0.02	N	N
Clinton Drive, Houston	1078	771	0.59	0.55	0.04	Y	N
Durant Street, Houston	943	634	0.47	0.47	0.00	N	N

Differences between the 75th percentile concentrations (Table C-2) on weekdays vs. weekends tend to be larger than the differences in the median values. The largest weekday-weekend difference is 0.13 ppb at Richmond. The difference in the 75th percentile concentrations on midweek days vs. weekend days in Queens is 0.09 ppb. This difference is significant at the 5% level. The significance level is higher in Queens than in Richmond despite a smaller difference due to less scatter in the Queens data. A difference of 0.05 ppb in Kings is statistically insignificant.

A benzene monitor is operated at the Bronx site (360050083) only during summer. Short time duration data are taken at this site. At this site, the lowest median (24-hour average) concentration is observed on Sundays, and the highest median is observed on Fridays followed by Tuesdays (Figure 6-1). The Tuesday-Sunday (0.04 ppb) and Friday-Sunday (0.06 ppb) differences of median concentrations are statistically significant at the 5% level. The 75th percentile concentration on Sundays is quite comparable to those Wednesdays and Thursdays. The Sunday 75th percentile concentration is not statistically different from those on Tuesdays, Wednesdays, and Thursdays (maximum difference is 0.03 ppb) at the Bronx site for the summer season.

Sufficient data also exist for a summer-only analysis of the day-of-the-week behavior and an analysis that focuses on the morning rush-hour period. Box plots of these data are shown in Figure 6-1. A very strong day-of-the-week signal is observed for benzene during rush hours, indicating the influence of mobile sources at the Bronx site. The median concentration decreases from 0.46 ppb on midweek days to 0.32 ppb on Saturdays and 0.28 ppb on Sundays. Significant decreases are also observed in the 25th and 75th percentile concentrations.

The Wednesday-Sunday difference in median concentrations is 0.17 ppb at the Bronx site during morning rush hours (Table 6-1). This difference is statistically significant at the 5% level. Also significant are the Tuesday-Saturday, Wednesday-Saturday, Thursday-Saturday, Tuesday-Sunday and Thursday-Sunday differences of 0.15, 0.13, 0.11, 0.19 and 0.16 ppb, respectively. Differences in the 75th percentile

concentrations for midweek-Sunday pairs range from 0.22 ppb (Wednesday) to 0.32 ppb (Thursday). These differences are statistically significant at the 5% level. Tuesday-Saturday, Wednesday-Saturday, and Thursday-Saturday differences are 0.07 ppb (10% significant) to 0.17 ppb (5% significant).

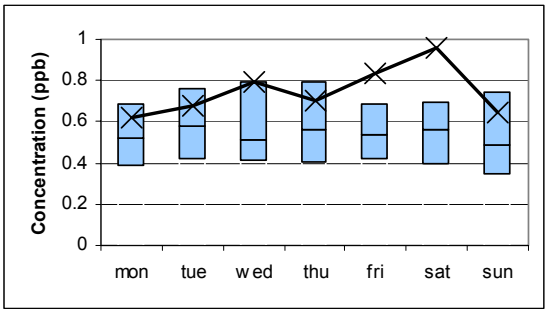
The weekday-weekend differences in rush-hour concentrations are statistically significant at the 5% level for the median concentrations (difference of 0.15 ppb) and 75th percentile concentrations (difference of 0.17 ppb).

Compared to the rush-hour signal, the weekly cycle of 24-hour concentrations is much weaker. Figure 6-1 compares the weekly cycle of the 24-hour concentrations and rush-hour concentrations at the Bronx site for the summer season. Rush-hour concentrations are very sensitive to weekly changes in traffic emissions, whereas 24-hour concentrations are less sensitive due to redistribution of passenger traffic from narrow windows of commute times on weekdays to a more spread-out pattern during the weekend and influence of other factors such as dilution and transport, which do not vary by the day of the week. Therefore, shorter time scale measurements are extremely useful for the purpose of inferring activity patterns.

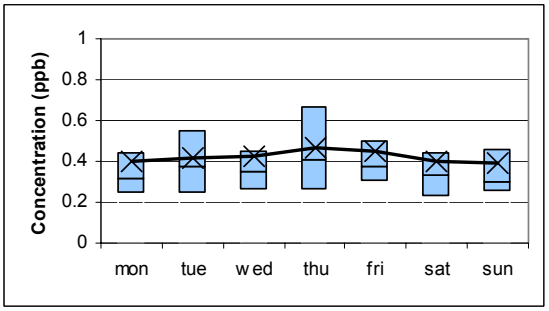
6.2 Philadelphia

Two benzene monitors in urban Philadelphia (421010004 and 421010136) operate throughout the year; one in Camden operates only during the summer. Box plots are shown in Figure 6-3 for these sites. Both sites in Philadelphia show strong variability, either in terms of high concentrations driving average concentrations to be larger than 75th percentile concentrations or in terms of large variability of some days compared to others. Median concentrations are the lowest on Sundays at both Philadelphia sites. High median concentrations are observed on Tuesdays and Thursdays. Low 25th percentile concentrations are observed on Saturdays and Sundays, and low 75th percentile concentrations are observed on Saturdays and Mondays. High 25th and 75th percentile concentrations are observed between Tuesdays and Fridays.

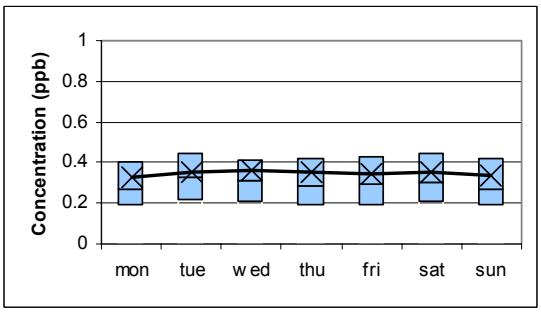
(a) Philadelphia
(421010047)



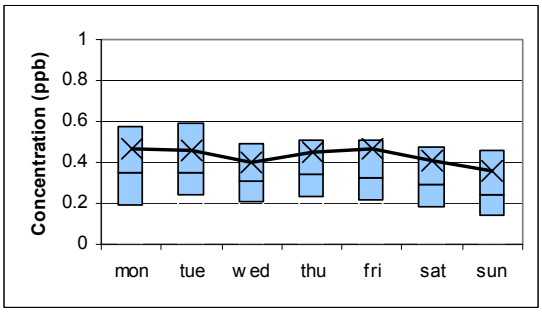
(b) Philadelphia Amtrak
(421010136)



(c) Camden, summer only
(340070003)



(d) Philadelphia, rush hour, summer only



(e) Philadelphia Amtrak, rush hour, summer only

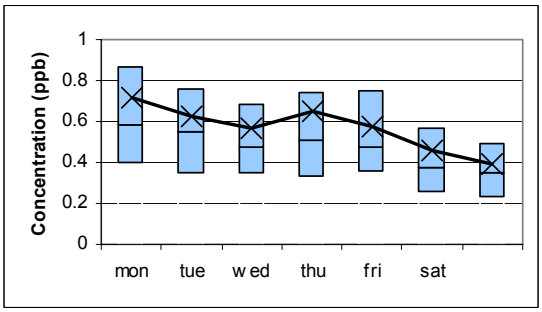


Figure 6-3. Box plots for benzene concentrations at sites in Philadelphia

During summer in Camden, Tuesdays show the highest median, 25th, and 75th percentile concentrations compared to the other days of the week. The lowest median concentration is observed on Sundays, but the lowest 25th and 75th percentile concentrations are observed on Mondays.

Differences in the median concentrations between all pairs of days are presented in Table 6-3 for the two Philadelphia sites. The maximum difference of 0.09 ppb at Site 421010004 is calculated between Tuesdays and Sundays, and this difference is statistically significant at the 5% level. The Wednesday-Sunday difference of 0.02 ppb is statistically insignificant, but the Thursday-Sunday difference of 0.07 ppb is significant at the 10% level. At the Amtrak (421010136) site, the Wednesday-Sunday difference in median concentrations of 0.05 ppb is statistically insignificant. However, the Tuesday-Sunday and Thursday-Sunday differences are larger (0.07 to 0.11 ppb) and are statistically significant at the 10% level.

Differences in the median concentrations during summer in Camden are neither larger nor more statistically significant compared to the annual counterparts in Philadelphia. The midweek-Sunday differences range from 0.02 to 0.06 ppb. The largest difference, between Tuesdays and Sundays, is the only one that is statistically significant at the 10% level.

At the Philadelphia site (421010004), none of the midweek-Sunday pairs shows a statistical significant difference (0.02 to 0.05 ppb) for the 75th percentile differences. The Thursday-Sunday difference at the Amtrak site (421010136) is 0.21 ppb and is statistically significant at the 5% level. However, the difference between Wednesdays' and Sundays' 75th percentile concentrations is negligible, and the Tuesday-Sunday difference of 0.09 is not statistically significant (see Table C-3 in the Appendix).

The QQ plots in Figure 6-4 show that taken as a group, the distribution of weekend concentrations have a tendency to be lower than the corresponding distribution

Table 6-3. Differences in the median concentrations of benzene between each pair of days for sites in Philadelphia. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%)

(a) Philadelphia

(421010004)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.06					
Wed	0.01	**0.07**				
Thu	-0.04	0.02	-0.05			
Fri	-0.02	0.04	-0.03	0.02		
Sat	-0.04	0.02	-0.05	0.00	-0.02	
Sun	0.03	**0.09**	0.02	0.07	0.05	**0.07**

(b) Philadelphia Amtrak

(421010136)

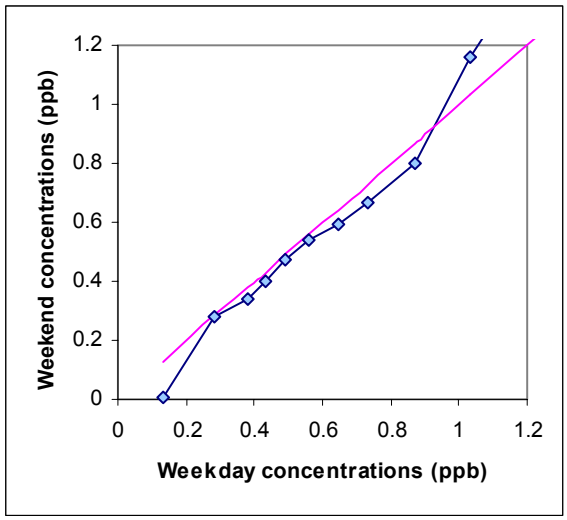
B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.05					
Wed	-0.03	0.02				
Thu	-0.09	-0.04	-0.06			
Fri	-0.06	0.00	-0.03	0.04		
Sat	-0.01	0.04	0.02	0.08	0.05	
Sun	0.02	0.07	0.05	0.11	**0.08**	0.03

(c) Camden, summer only

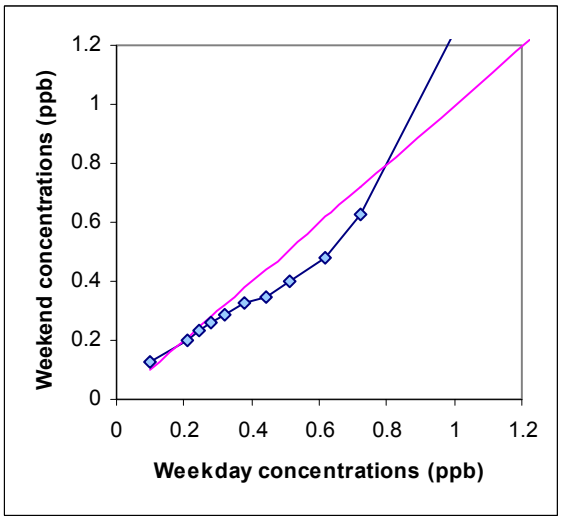
(340070003)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.05					
Wed	-0.04	0.01				
Thu	-0.01	0.04	0.02			
Fri	-0.02	0.03	0.01	-0.01		
Sat	-0.03	0.02	0.01	-0.02	-0.01	
Sun	0.01	0.06	0.04	0.02	0.03	0.04

(a) Philadelphia



(b) Philadelphia Amtrak



(c) Camden (summer only)

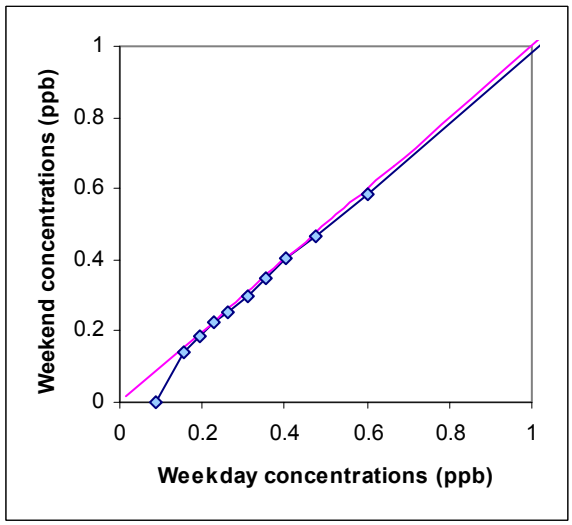


Figure 6-4. QQ plots for weekend vs. midweek benzene concentrations at sites in Philadelphia

of midweek concentrations except at very high concentrations at the Philadelphia Amtrak site. The Philadelphia (0004) site shows slightly lower concentrations on weekends at the moderate percentiles, but they are very close to the weekday concentrations. In Camden, where only summer data are available, the distribution of benzene on weekends and midweek days are very similar.

The weekday/weekend comparisons in Table 6-2 and Table C-2 for the median and 75th percentile concentrations, respectively, are consistent with the QQ plots. The difference in the median concentrations between midweek and weekend is 0.05 ppb at the Amtrak site, which is statistically significant at the 10% level. The corresponding difference is 0.02 ppb (statistically insignificant) at the Philadelphia site. The difference in the medians in Camden for the summer season is also statistically insignificant, at only 0.01 ppb. The difference in the 75th percentile concentrations are 0.09 ppb and 0.07 ppb at the two Philadelphia sites. These midweek-weekend differences are statistically significant at the 10% level. However, there is no difference in the 75th percentile concentrations between summer weekdays and summer weekends at the Camden site.

Short duration samples are available in Camden and Philadelphia (42101004) for analysis of the day-of-the week behavior during morning rush hours. As is the case for the Bronx site, the day-of-the-week signal for benzene is much stronger during rush hours compared to the 24-hour average concentrations (see Figure 6-3). Differences in the median concentrations for the Tuesday-Sunday, Wednesday-Sunday, and Thursday-Sunday pairs range from 0.07 to 0.2 ppb and are statistically significant at the 5% level for all pairs at both sites. Differences in the 75th percentile concentrations in Camden are less than the corresponding differences in Philadelphia. In Camden, the Tuesday-Sunday difference of 0.13 ppb is the only weekday-weekend difference in this metric that is statistically significant at the 10% level. The Wednesday-Sunday and Thursday-Sunday differences in 75th percentile concentrations are 0.03 and 0.05 ppb, respectively. In Philadelphia, however, the Tuesday-Sunday, Wednesday-Sunday, and Thursday-Sunday differences in the 75th percentile concentrations are 0.27, 0.19, and 0.25 ppb, respectively, and all are significant at the 5% level.

Considering weekend days as a group and Tuesdays/Wednesdays/Thursdays as a group, the distribution of the concentrations on weekends falls well below the same percentile concentrations on weekdays for both sites. In fact, the weekday/weekend differences in rush-hour benzene concentrations are 0.07 ppb and 0.15 ppb for the medians in Camden and Philadelphia, respectively. Both differences are statistically significant at the 5% level. The differences in the 75th percentile concentrations are 0.06 (not significant) in Camden and 0.21 ppb (significant at the 5% level) in Philadelphia.

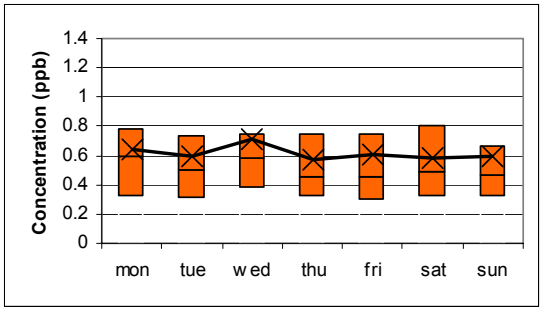
6.3 Houston

There are twelve benzene monitors in Houston. While the 24-hour average concentrations are typically 0.4 ppb to 0.6 ppb in NY and Philadelphia, a few sites in Houston show higher median concentrations, including Sheldon Road (482010026, 0.7 ppb), Stewart Street (482010057, ~ 1 ppb) and Haden Road (482010803, 0.8 ppb). Of these sites, Haden Road has an industrial land use characterization, but the other two sites are located in residential neighborhoods. As shown in Figure 6-5, half the sites show average concentrations that approach or exceed the 75th percentile concentration on at least one day of the week, indicating that the data set contains high concentrations that affect the robustness of the average statistic.

Figure 6-5 shows that the day-of-week cycles are small in magnitude at many sites compared to the variability observed for each day. At these 12 sites, low median concentrations occur on every day of the week except Wednesdays. The largest group, four sites, records the lowest median concentrations on Sundays. Highest median concentrations occur on every day except Sundays at these sites. Three sites record the highest medians on Wednesdays, three on Fridays. There is also a lack of a consistent weekly behavior for the 75th percentile concentrations. Low 75th percentile concentrations are observed on every day except Wednesdays. However, only two sites

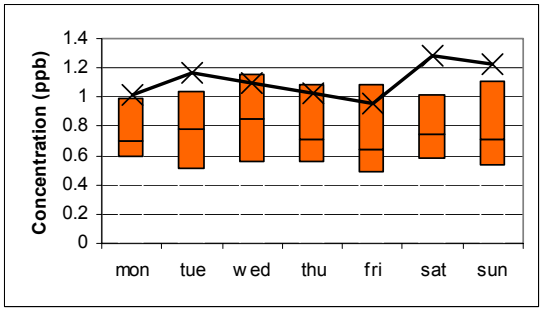
(a) Aldine Mail Road

(482010024)



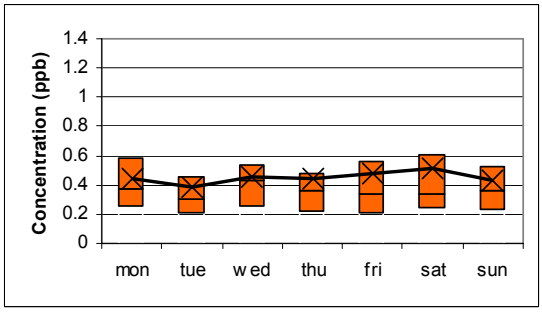
(b) Sheldon Road

(482010026)



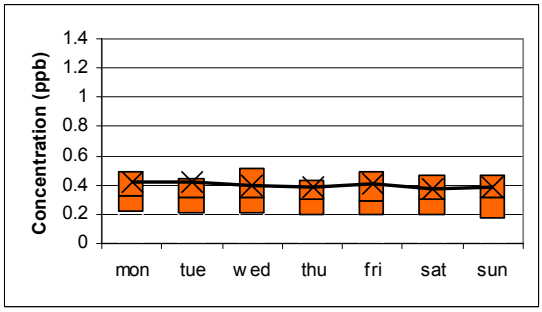
(c) Kizman

(482010029)



(d) Bissonnet Street

(482010055)



(e) Stewart Street

(482010057)

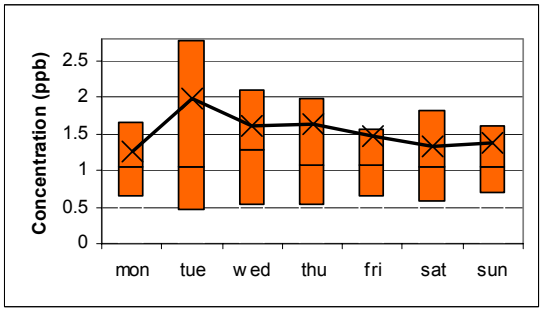
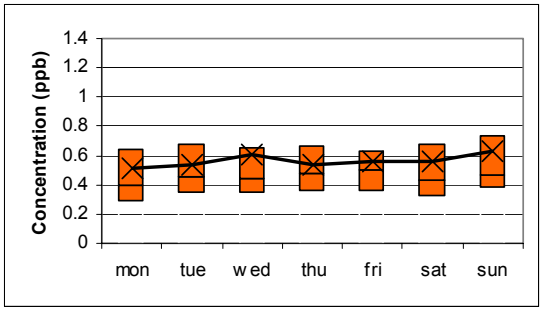
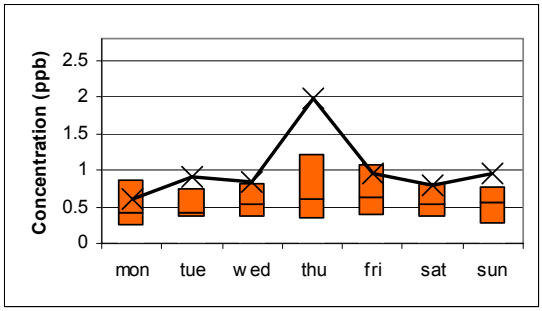


Figure 6-5. Box plots for benzene concentrations at sites in Houston

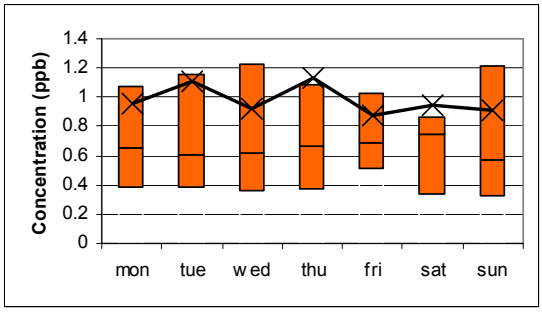
(f) Bayway Drive (482010058)



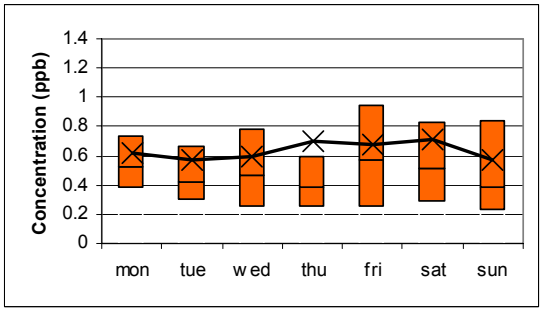
(g) Old Hwy 146 (482010061)



(h) Old Galveston Road (482010064)



(i) Central Street (482010069)



(j) Haden Road (482010803)

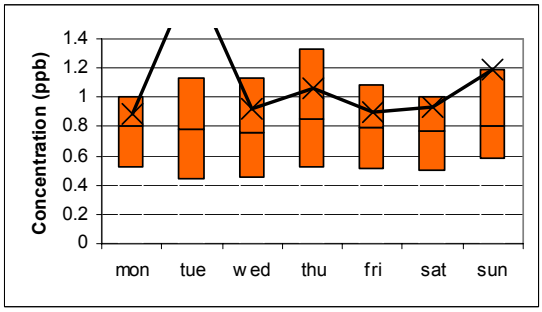
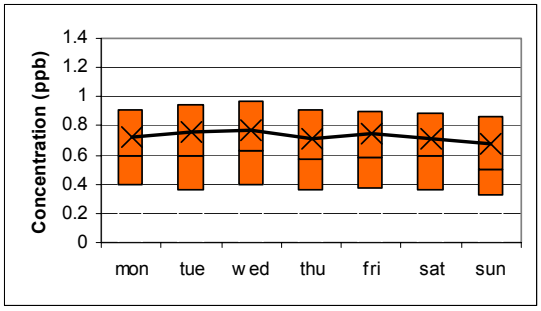
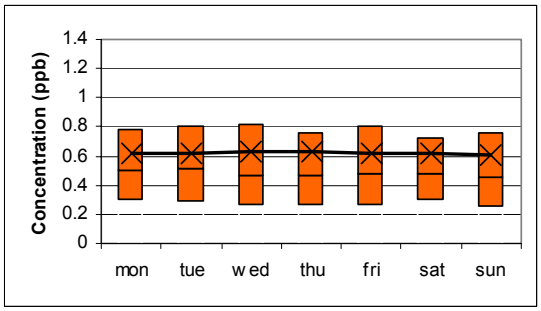


Figure 6-5. Box plots for benzene concentrations at sites in Houston (continued)

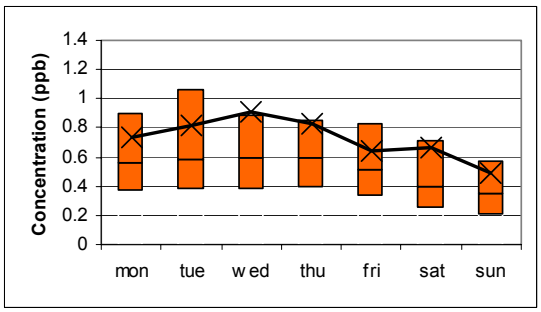
(k) Clinton Drive (482011035)



(l) Durant Street (482011039)



(m) Clinton Drive, rush hour summer only



(n) Durant Street, rush hour, summer only

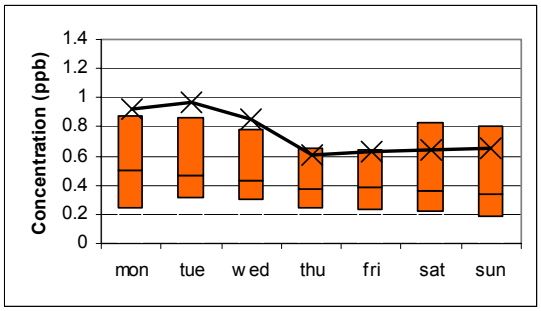


Figure 6-5. Box plots for benzene concentrations at sites in Houston (continued)

record the lowest 75th percentile concentrations on Sundays. Five sites, the largest group, show the highest 75th percentile benzene concentrations on Wednesdays. However, two also show high 75th percentile concentrations on Sundays.

As shown in Table 6-4, the Wednesday-Sunday differences in the median concentrations range from -0.03 ppb to 0.22 ppb. The differences are statistically significant at the 5% level at 3 sites: Aldine Mail Road (482011024), Sheldon Road (482011026), and Clinton Drive (482011035). The significant differences range from 0.12 ppb to 0.14 ppb. The only site showing statistically significant Tuesday-Sunday, Wednesday-Sunday and Thursday-Sunday differences in median concentrations is the Clinton Drive site, with Tuesday-Sunday and Thursday-Sunday differences of 0.1 and 0.08 ppb, respectively.

Differences in the 75th percentile concentrations, shown in the Appendix (Table C-4) for all pairs of days, are no more statistically significant than the differences in median concentrations. The Wednesday-Sunday differences in the 75th percentile benzene concentrations range from -0.08 ppb to 0.48 ppb. The largest value of 0.48 ppb is observed at Stewart Street (482010057) and is the only statistically significant (10%) difference of the Sunday-Wednesday pairs. At the same site, the Tuesday-Sunday difference is 1.15 ppb in the median values and this value is also statistically significant at the 10% level. None of the other Tuesday-Sunday, Wednesday-Sunday or Thursday-Sunday differences is statistically significant. The second largest Wednesday-Sunday difference is 0.08 at Aldine Mail Road.

Insignificant differences in the weekday (group of Tuesdays, Wednesdays, and Thursday) vs. weekend distributions of concentrations are also observed in the QQ plots (Figure 6-6). Most of the QQ plots lie very close to the 1:1 line, indicating that there is very little difference between the benzene concentrations at various percentiles for the two groups of days. The only exception is the Stewart Street site, which shows that at the higher percentile concentrations, weekend concentrations fall below weekday values.

Table 6-4. Differences in the median concentrations of benzene between each pair of days for sites in Houston. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%)

(a) Aldine Mail Road

(482010024)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	0.10					
Wed	0.01	-0.09				
Thu	**0.14**	0.04	**0.13**			
Fri	**0.14**	0.05	**0.13**	0.00		
Sat	0.11	0.01	0.10	-0.03	-0.03	
Sun	**0.13**	0.03	**0.12**	-0.01	-0.01	0.02

(b) Sheldon Road

(482010026)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.08					
Wed	**-0.15**	-0.07				
Thu	-0.01	0.08	**0.14**			
Fri	0.06	**0.14**	**0.21**	0.07		
Sat	-0.05	0.03	**0.10**	-0.04	**-0.11**	
Sun	-0.01	0.08	**0.14**	0.00	-0.07	0.04

(c) Kizman

(482010029)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	0.07					
Wed	-0.06	**-0.13**				
Thu	0.01	-0.06	0.07			
Fri	0.03	-0.04	0.09	0.02		
Sat	0.03	-0.04	0.09	0.02	0.00	
Sun	0.01	-0.06	0.07	0.00	-0.02	-0.02

(d) Bissonnet Street

(482010055)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	0.01					
Wed	0.01	0.00				
Thu	0.03	0.02	0.02			
Fri	0.03	0.02	0.02	0.00		
Sat	0.03	0.02	0.02	0.00	0.00	
Sun	0.02	0.01	0.01	-0.01	-0.01	-0.01

Table 6-4. Differences in the median concentrations of benzene between each pair of days for sites in Houston. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%) (continued).

(e) Stewart Street (482010057)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.01					
Wed	-0.23	-0.22				
Thu	-0.03	-0.02	0.20			
Fri	-0.03	-0.02	0.20	0.00		
Sat	0.00	0.01	0.23	0.03	0.03	
Sun	-0.01	0.00	0.22	0.02	0.02	-0.01

(f) Bayway Drive (482010058)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.05					
Wed	-0.04	0.01				
Thu	-0.08	-0.03	-0.04			
Fri	-0.10	-0.05	-0.06	-0.02		
Sat	-0.03	0.02	0.01	0.05	0.07	
Sun	-0.07	-0.02	-0.03	0.01	0.03	-0.04

(g) Old Hwy 148 (482010061)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.02					
Wed	-0.13	-0.11				
Thu	-0.19	-0.17	-0.06			
Fri	-0.22	-0.20	-0.09	-0.03		
Sat	-0.13	-0.11	0.00	0.06	0.09	
Sun	**-0.16**	**-0.14**	-0.03	0.03	0.06	-0.03

(h) Old Galveston Road (482010064)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	0.04					
Wed	0.03	-0.01				
Thu	-0.02	-0.06	-0.05			
Fri	-0.04	-0.08	-0.07	-0.02		
Sat	-0.10	-0.14	-0.13	-0.08	-0.06	
Sun	0.08	0.04	0.05	0.10	0.12	0.18

Table 6-4. Differences in the median concentrations of benzene between each pair of days for sites in Houston. Differences are presented as day A (column heading) minus day B (row heading). Statistically significant differences are colored in red (5%) or blue (10%) (continued).

(i) Central Street (482010069)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	0.11					
Wed	0.06	-0.05				
Thu	0.14	0.03	0.08			
Fri	-0.04	-0.15	-0.10	-0.18		
Sat	0.02	-0.09	-0.04	-0.12	0.06	
Sun	0.15	0.04	0.09	0.01	0.19	0.13

(j) Haden Road (482010803)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	0.03					
Wed	0.05	0.02				
Thu	-0.04	-0.07	-0.09			
Fri	0.02	-0.01	-0.03	0.06		
Sat	0.04	0.01	-0.01	0.08	0.02	
Sun	0.01	-0.02	-0.04	0.05	-0.01	-0.03

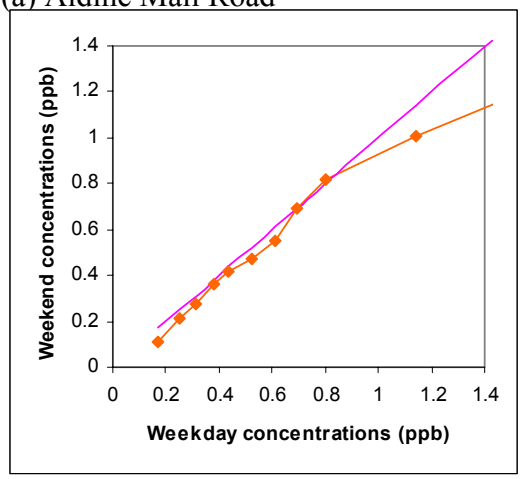
(k) Clinton Drive (482011035)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.01					
Wed	-0.04	-0.03				
Thu	0.02	0.03	0.06			
Fri	0.01	0.01	0.04	-0.02		
Sat	-0.01	0.00	0.03	-0.03	-0.01	
Sun	**0.09**	**0.10**	**0.12**	0.07	**0.08**	**0.09**

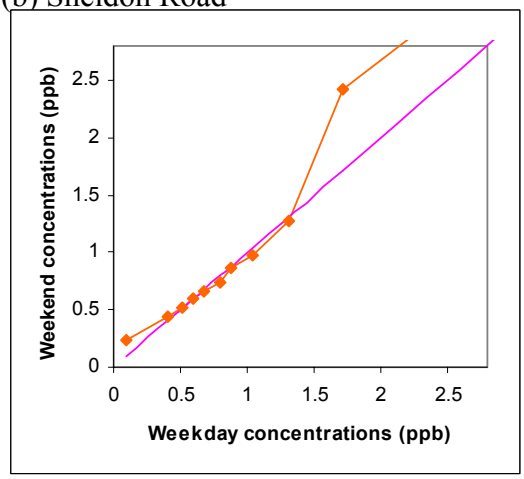
(l) Durant Street (482011039)

B \ A	Mon	Tue	Wed	Thu	Fri	Sat
Tue	-0.01					
Wed	0.04	0.04				
Thu	0.04	0.05	0.00			
Fri	0.02	0.03	-0.01	-0.01		
Sat	0.02	0.03	-0.01	-0.02	0.00	
Sun	0.05	0.06	0.02	0.02	0.03	0.03

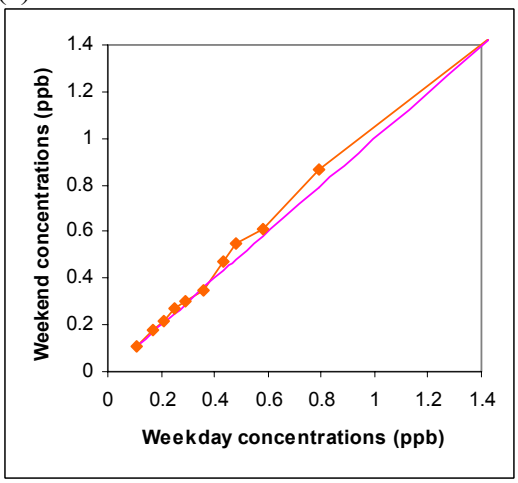
(a) Aldine Mail Road



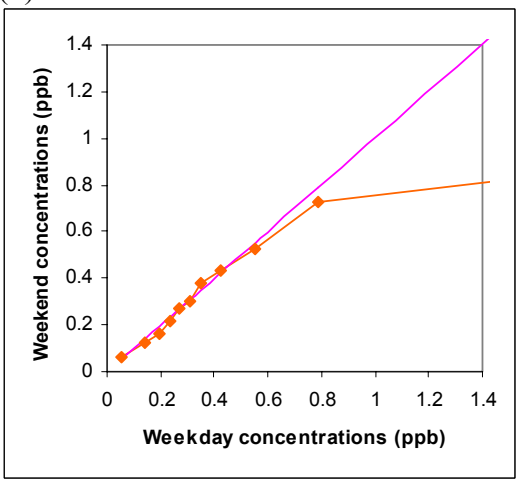
(b) Sheldon Road



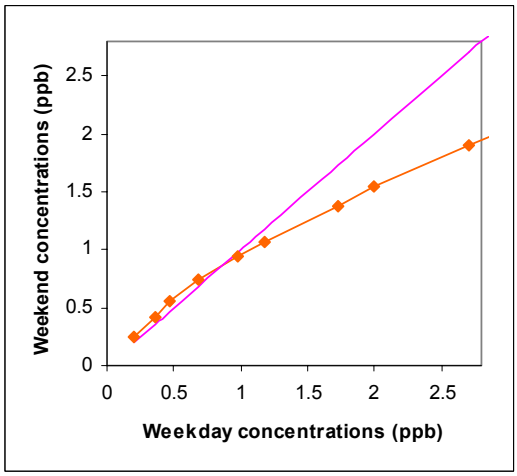
(c) Kizman



(d) Bissonnet Street



(e) Stewart Street



(f) Bayway Drive

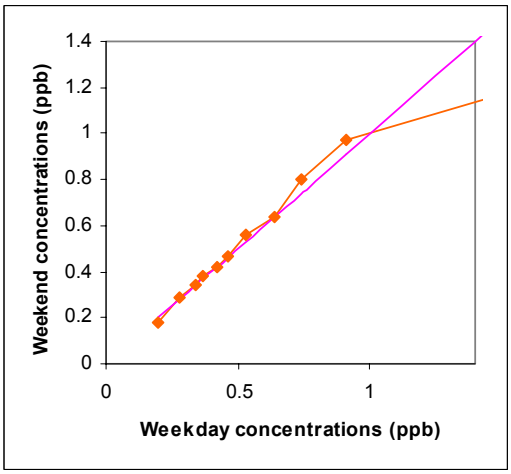
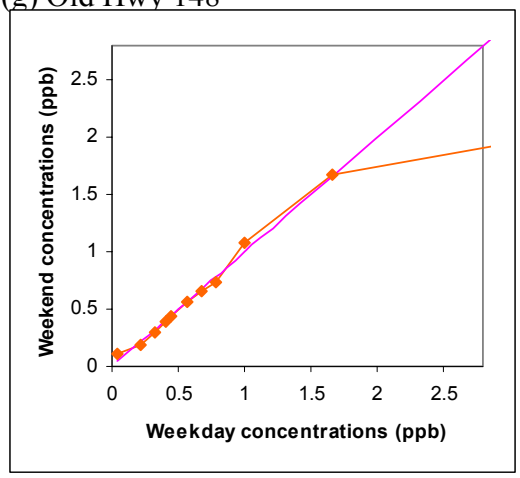
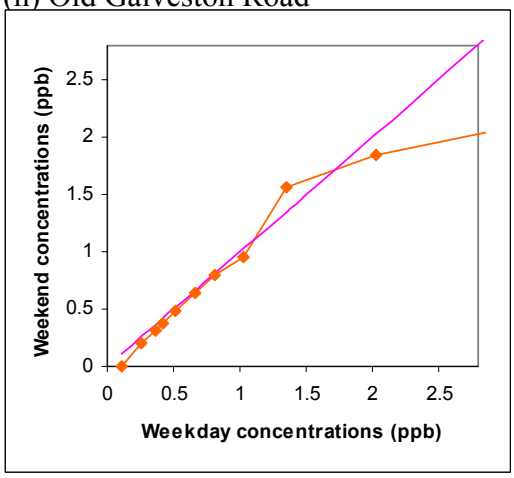


Figure 6-6. QQ plots for weekend vs. midweek benzene concentrations at sites in Houston

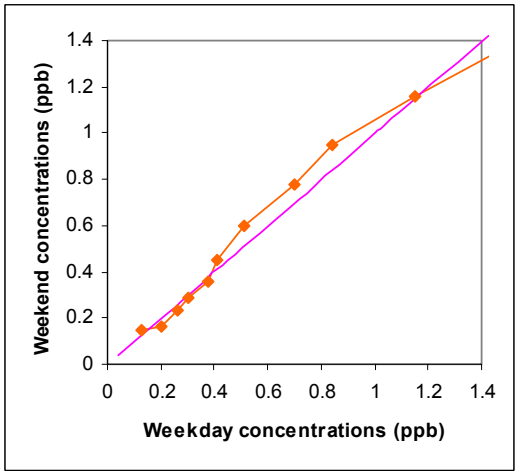
(g) Old Hwy 148



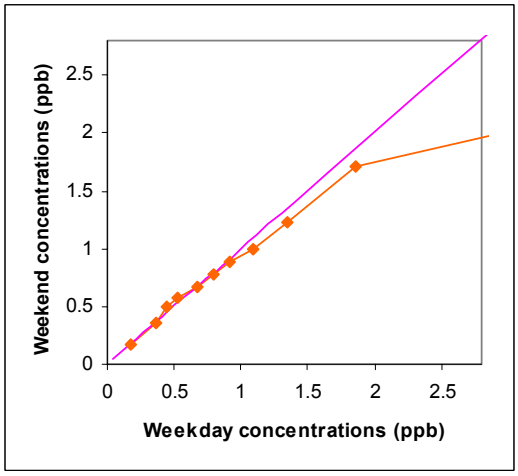
(h) Old Galveston Road



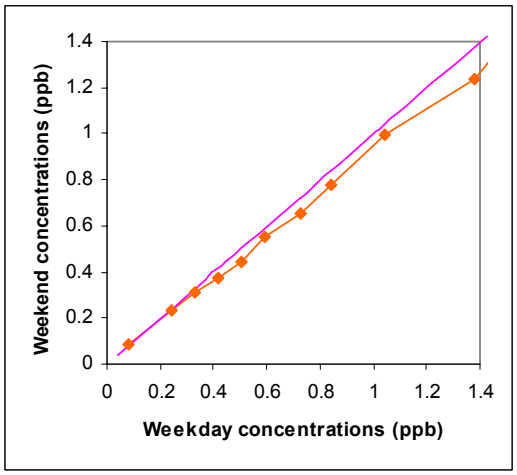
(i) Central Street



(j) Haden Road



(k) Clinton Drive



(l) Durant Street

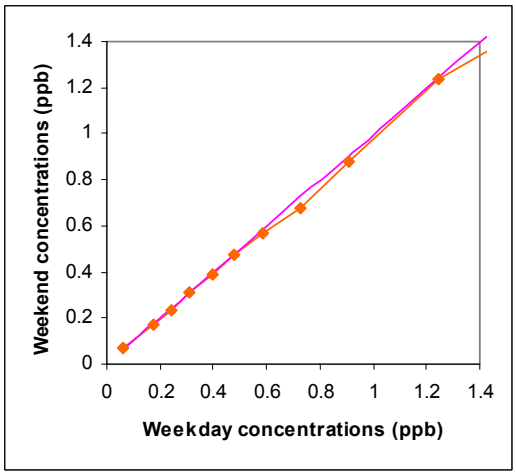


Figure 6-6. QQ plots for weekend vs. midweek benzene concentrations at sites in Houston (continued)

However, from Figure 6-5, it can be seen that among the midweek days, high concentrations tend to occur on Tuesdays at this site, which seems unusual.

Most of the Houston area sites do not show significant differences between weekday and weekend median concentrations (Table 6-2). The same is true for the 75th percentile concentration (Table C-2 in Appendix). Differences in median concentrations range from -0.04 ppb to 0.05 ppb. The only statistically significant (10%) difference of medians is observed at Clinton Drive (482011035), with a difference of 0.04 ppb. As for the 75th percentile concentrations, weekday-weekend differences range from -0.07 ppb to 0.08 ppb. Two sites show statistically significant differences besides Haden Road. These are Clinton Drive (difference of 0.06 ppb) and Durant Street (difference of 0.07 ppb).

The weak day-of-the-week signal at Houston sites occurs despite strong traffic-related day-of-the-week signals in the morning rush-hour data at two sites (Figure 6-5 for Clinton Drive and Durant Street). During rush hours, Sundays' concentrations are lower than those on the other days of the week at Clinton Drive for the median, 75th percentile, and 25th percentile values. Wednesdays show the highest median concentration at that site. At the Durant Street site, Sundays are also associated with the lowest median value, although the 75th percentile benzene concentration on Sundays is comparable to that on Wednesdays and higher than that on Thursdays due to considerable variability.

The Tuesday-Sunday, Wednesday-Sunday, and Thursday-Sunday median differences of 0.23-0.24 ppb at Clinton Drive are statistically significant at the 5% level for the morning rush-hour concentrations. The Wednesday-Sunday difference in median concentrations (0.09 ppb) at Durant Drive is also statistically significant at the 5% level. The Wednesday-Sunday difference in the 75th percentile concentrations at Clinton Drive (0.31 ppb) is statistically significant at the 10% level. In addition, the Tuesday-Sunday and Thursday-Sunday differences in the median concentrations (0.49 and 0.28 ppb, respectively) are statistically significant at the 5% level. At Durant Drive, the sometimes negative differences in the 75th percentile values between midweek days and Sundays are statistically insignificant.

A comparison of concentrations at corresponding percentiles shows definitively that weekday concentrations of benzene are lower than weekend concentrations during rush hours at both Clinton Drive and Durant Road. At Clinton Drive, the midweek day vs. weekend differences are 0.2 ppb for the median concentrations and 0.26 ppb for the 75th percentile concentrations. These differences are statistically significant at the 5% level (Tables 6-2 and C-2). The difference in the median concentrations at Durant Drive is 0.05 ppb, which is statistically significant at the 10% level. The difference in the 75th percentile concentrations is -0.03 ppb, which is statistically insignificant.

6.4 Discussion of the Benzene Results

Benzene is less reactive than HCHO, with an atmospheric lifetime of 8 to 12 days based on its reaction rate with hydroxyl radicals. Therefore, benzene is subject to regional transport. The impact of local emission changes between weekday and weekend were mostly only evident during the morning rush hours.

Benzene concentrations are statistically significantly different on weekends compared to weekdays at some sites within each city, but at not all sites. For 24-hour concentrations, the median and 75th percentile concentrations are in general more similar than different on Wednesdays vs. Sundays.

Benzene is a primary pollutant emitted from gasoline vehicles. It shows a very strong traffic signature in the day-of-the-week behavior of the morning rush hour concentrations. Blanchard and Tanenbaum (2004) also found significant decreases in the average daytime benzene concentrations from Wednesdays to Sundays at some sites in New York City and Houston. When 24-hour average concentrations are considered, the traffic signal is weak in many cases, and non-existent in some. This is partly because the change in overall activities of gasoline vehicles from weekdays to weekends is relatively small, e.g., only about 15% in Los Angeles (Chinkin et al., 2003). It is accompanied by a

temporal shift from rush hours to the middle part of the day. This signal may be hard to detect in the ambient 24-hour average concentrations given the variability in the data.

At several sites in Houston, benzene concentrations are high and these could be a result of the influence of local sources. In the Houston area, point sources account for 14% of the benzene emissions (NEI, 1999), whereas point sources account for only 0.4% and 2% of the benzene emissions, respectively, in New York City and Philadelphia. The on-road mobile source contribution is lowest in Houston (55%) as well. On-road mobile sources contribute 63 and 73% of the benzene emissions in New York City and Philadelphia, respectively. The difference in emissions may also lead to a weaker day-of-the-week cycle in Houston compared to the east coast cities, because the activities of point sources may not decrease in the same manner as on-road sources.

Reformulated gasoline has reduced aromatic content. Restricting the analysis to post reformulation years does not change the conclusions about the weekday-weekend differences of benzene concentrations in the three metropolitan areas. No statistically significant difference is observed at any site in the post 2000 data where the weekday-weekend difference is insignificant in the larger data set. Conversely, sites showing significant differences in the longer data set continue to show statistically significant weekly cycles in the post 2000 data. Since benzene is an emitted species, reducing the aromatic content of gasoline should result in a reduction in ambient concentrations on every day of the week, but should not affect the existence of a weekly cycle.

Other factors may also contribute to differences between the cities. On the east coast, pollutants build up due to transport along a densely populated corridor. In
H