



## Volatile organic compounds in some urban locations in United States

Mahmoud F. Mohamed<sup>a,b</sup>, Daiwen Kang<sup>a,c</sup>, Viney P. Aneja<sup>a,\*</sup>

<sup>a</sup> Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695-8208, USA

<sup>b</sup> Department of Occupational Health, High Institute of Public Health, Alexandria University, Alexandria, Egypt

<sup>c</sup> Air Modelling Division, U.S. EPA, Research Triangle Park, NC 27111, USA

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*Importance of this paper: Air pollution in urban locations contains many components that originate from a wide range of industrial, motor vehicle, and natural emissions sources. Some of these components include compounds known or suspected to be carcinogenic, and some of them play important roles in atmospheric chemistry such as tropospheric ozone pollution and stratospheric ozone depletion. Therefore, it is essential to characterize the composition, magnitude, and the distribution of urban air pollution through extensive ambient air monitoring and assess the impact of these components on human health and global atmospheric chemistry.*

### Abstract

Volatile organic compounds (VOCs) have been determined to be human risk factors in urban environments, as well as primary contributors to the formation of photochemical oxidants. Ambient air quality measurements of 54 VOCs including hydrocarbons, halogenated hydrocarbons and carbonyls were conducted in or near 13 urban locations in the United States during September 1996 to August 1997. Air samples were collected and analyzed in accordance with US Environmental Protection Agency-approved methods. The target compounds most commonly found were benzene, toluene, xylene and ethylbenzene. These aromatic compounds were highly correlated and proportionally related in a manner suggesting that the primary contributors were mobile sources in all the urban locations studied. Concentrations of total hydrocarbons ranged between 1.39 and 11.93 parts per billion, by volume (ppbv). Ambient air levels of halogenated hydrocarbons appeared to exhibit unique spatial variations, and no single factor seemed to explain trends for this group of compounds. The highest halogenated hydrocarbon concentrations ranged from 0.24 ppbv for methylene chloride to 1.22 ppbv for chloromethane. At participating urban locations for the year of data considered, levels of carbonyls were higher than the level of the other organic compound groups, suggesting that emissions from motor vehicles and photochemical reactions strongly influence ambient air concentrations of carbonyls. Of the most prevalent carbonyls, formaldehyde and acetaldehyde were the dominant compounds, ranging from 1.5–7.4 ppbv for formaldehyde, to 0.8–2.7 ppbv for acetaldehyde. © 2002 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction

During the past few years, an increased awareness of air pollutants and new potential sources of airborne toxic chemicals have raised a concern that the release of these materials may be a health hazard. Generally more localized in their impact than the criteria pollutants, air toxics or hazardous air pollutants (HAPs) may endanger

\* Corresponding author. Tel.: +1-919-515-7808; fax: +1-919-515-7802.

E-mail address: viney\_aneja@ncsu.edu (V.P. Aneja).

human health and welfare. The adverse effects on health from exposure to air toxics on HAPs can be as diverse as the substances themselves. Cancer is one health effect of wide concern; others include birth defects, damage to the immune and nervous systems, and other fatal diseases (Singh et al., 1982; Kao, 1994).

Recently, a number of volatile organic compounds (VOCs) have been identified as important cancer risk factors in the urban environment (Hagerman et al., 1997). These compounds (VOCs) are not routinely monitored in urban air, and no ambient air quality standards have yet been established for them. In addition, through complex photochemical reactions, VOCs contribute to the formation of toxic oxidants (World Meteorological Organization, 1985; Finlayson-Pitts and Pitts, 1986; Lioy and Daisey, 1986; Atkinson et al., 1988; Shah and Singh, 1988) such as tropospheric ozone, and peroxyacetyl nitrate (PAN), which are detrimental to health and are phytotoxic.

In urban and industrial areas, many hydrocarbons, including VOCs, are emitted from anthropogenic sources, such as transportation, fossil fuel-burning power plants, chemical plants, petroleum refineries, certain construction activities, solid waste disposal and slash burning (Arya, 1999; Davis and Otson, 1996). In addition to the anthropogenic sources, many VOCs are produced naturally by vegetation. Biogenic emissions of hydrocarbons are likely to exceed anthropogenic emissions in heavily vegetated and forested regions (Winer et al., 1992; Arya, 1999). The mechanisms and products of atmospheric reactions of biogenic organics are not well understood. A few quantitative studies (Kamens et al., 1982; Atkinson, 1990; Tuazon and Atkinson, 1990), have indicated that formaldehyde is the only HAP known to result from atmospheric transformations of biogenic hydrocarbons.

Data on airborne VOCs in urban and rural areas in the United States have been reviewed (Brodzinsky and Singh, 1983; Edgerton et al., 1989; Sweet and Vermette, 1992). Elevated levels of benzene and other aromatic hydrocarbons as well as a variety of chlorinated VOCs are found in the air of most urban areas. These air pollutants are emitted by a wide variety of area and point sources. The most recent comprehensive amendments to the Clean Air Act (CAA) in 1990 list 188 substances as HAPs. Eighty two of these HAPs have atmospheric lifetimes of less than one day. Seven others have conflicting data reporting atmospheric lifetimes both shorter and longer than one day (Spicer et al., 1993). These data imply that over 40% of the HAPs have low atmospheric persistence. For these air toxics, the transformation products, in addition to the actual emitted pollutants, should be monitored at ambient sites to determine the effectiveness of the control strategies.

The urban air toxics monitoring program (UATMP) is sponsored by the US Environmental Protection

Agency (EPA) and designed to characterize the composition and magnitude of urban air toxics through ambient air monitoring. Since the program's inception in 1987, many environmental and health agencies have voluntarily participated in the UATMP to determine the causes and access the effects of air pollution within their jurisdictions. In this paper, we (1) compare and characterize the C<sub>2</sub>–C<sub>10</sub> VOCs measured at 13 urban locations in the United States, (2) determine the significant sources of VOCs within any urban environment, and (3) examine the effect of seasonal changes on the levels of VOCs in urban areas.

## 2. Materials and methods

### 2.1. Monitoring locations

Thirteen air monitoring sites representing different urban communities in the United States are characterized (Fig. 1). To provide a first approximation of the respective contributions of motor vehicle emissions and industrial emissions on each monitoring site, Table 1 lists the 13 monitoring locations and the number of people living within 10 miles of each location and Table 2 is the text descriptions about the surrounding areas of each monitoring location. The number of industrial facilities that meet EPA's Toxic Release Inventory (TRI, 1995) reporting requirement within 10 miles of each location are also included in Table 1.

Although this spatial distribution of monitoring stations clearly is not a statistically significant sample of urban locations in the US, the monitoring data from these stations may indicate certain air quality trends that are common to all urban environments.

### 2.2. Sampling and analytical methods

At every monitoring location, the air sampling equipment was installed in a small enclosure—usually a

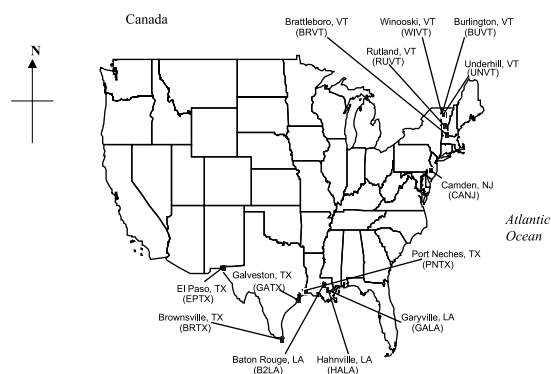


Fig. 1. Locations of the 1996 UATMP monitoring stations.

Table 1  
Site description for the 1996 UATMP monitoring stations

Location	Location code	Population residing (1996) within 10 miles of the monitoring system	Number of facilities located within 10 miles of the monitoring station
Baton Rouge, LA	B2LA	336 577	13
Brownsville, TX	BRTX	125 547	2
Brattleboro, VT	BRVT	27 862	2
Burlington, VT	BUVT	103 912	3
Camden, NJ	CANJ	2 021 082	38
El Paso, TX	EPTX	410 475	6
Garyville, LA	GALA	56 800	3
Galveston, TX	GATX	103 167	12
Hahnville, LA	HALA	107 033	8
Port Neches, TX	PNTX	146 467	19
Rutland, VT	RUVT	38 969	2
Underhill, VT	UNVT	18 997	0
Winooski, VT	WIVT	109 541	3

trailer or a shed—with the sampling inlet probe protruding through the roof. With this setup, each monitor sampled ambient air at heights approximately 5–20 feet above local ground level.

At each site, 24-h integrated samples were collected once every 12 days. Each sample collection began and ended at midnight, standard time. This sampling frequency ensures the collection of sufficient data for characterizing annual-average concentrations of toxic compounds. Further, the 12-day sampling frequency ensures the distribution of sampling days among the seven days of the week—a feature that enables comparison of air quality on weekdays to air quality on weekends. Also, as a part of the sampling schedule, duplicate samples were collected on roughly 10% of the sampling days. These samples were analyzed in replicate to gauge the precision of the sampling and analytical methods.

Fifty four organic compounds were selected for studying during the current program: 11 hydrocarbons, 27 halogenated hydrocarbons, and 16 carbonyls. Many of these compounds are toxic and many are ubiquitous to urban air pollution.

The capabilities and limitations of sampling and analytical methods are important considerations when interpreting ambient air monitoring data. During the present study, two EPA-approved methods were used to characterize urban air pollution: “Compendium Method TO-14A” was used to measure ambient air concentrations of the 38 VOCs (US EPA, 1984a; McClenny et al., 1991) and “Compendium Method TO-11/11A” was used to measure ambient air concentrations of the 16 carbonyl compounds (US EPA, 1984b).

### 2.2.1. Sampling and analytical method for VOCs

As the EPA method specifies, ambient air samples that were analyzed for VOCs were collected in passivated stainless steel canisters. The prepared (cleaned and evacuated) canisters were distributed to the monitoring stations where they were connected to the air sampling equipment prior to each sampling day. Before their use in the field, the passivated canisters are evacuated to much lower than atmospheric. Because of this pressure difference, ambient air naturally flows into the canisters once they are opened, and pumps are not needed to collect the canister samples for VOC analysis. An electronic mass flow controller on the sampling device ensures that ambient air enters the canister at a constant rate across the collection period. At the end of the 24-h sampling period, a solenoid valve automatically stops ambient air from flowing into the canister. Then, the canisters are returned to the laboratory for analysis.

By analyzing each sample with capillary gas chromatography (GC) and mass selective detection and flame ionization detection (GC/MSD–FID), the ambient air concentrations of 38 VOCs—11 hydrocarbons and 27 halogenated hydrocarbons—within the canister sample are determined. The detection limit reported by the analytical laboratory for every compound is lower than 0.5 parts per billion, by volume (ppbv), with many detection limits below 0.1 ppbv.

### 2.2.2. Sampling and analytical method for carbonyls

Following the specifications of EPA Compendium Method TO-11/11A, ambient air samples that were analyzed for carbonyls were collected by passing ambient air over silica gel cartridges coated with 2,4-dinitrophenylhydrazine (DNPH), a compound known to react selectively and reversibly with many aldehydes and ketones. Due to this reactivity, carbonyls in ambient air are derivatized remain within the sampling cartridge, while other compounds pass through the cartridge without reacting with the DNPH-coated matrix. Consistent with the VOC sampling, the silica gel cartridges were distributed to the monitoring locations where they were connected to the air sampling equipment including O<sub>3</sub> denuders and after the 24-h sampling period, they were returned to the laboratory for analysis.

To quantify concentrations of carbonyls in the sampled ambient air, the exposed silica gel cartridges were eluted with acetonitrile. This solvent elution liberated a solution of DNPH derivatives of the aldehydes and ketones collected from the ambient air. Analyzing this solution with high-performance liquid chromatography (HPLC) and ultraviolet detection determines the relative amounts of individual carbonyls present in the original air sample.

Like the VOC detection limits, the carbonyl limits were also evaluated by each analytical laboratory. Although the sensitivity of the analytical method varies

Table 2  
Text descriptions of the 1996 UATMP monitoring locations

Monitoring location	Description of the immediate surroundings
Baton Rouge, LA	Of the 1996 UATMP monitoring locations, Baton Rouge has the third highest population density within 10 miles of the monitoring station; located in downtown Baton Rouge, the monitoring site is in the back parking lot of an office building, directly across from the city motor pool; numerous industrial facilities, including refineries and chemical manufacturing plants, are located within a 10-mile radius; interstate highway 110 passes within two blocks of the monitoring station
Brownsville, TX	Located in the southernmost part of Texas, the Brownsville monitoring station is within viewing distance of Mexico and the Rio Grande River and is within 30 miles of the Gulf of Mexico. The monitoring station is located at the southern end of the Brownsville city limits, with no major roadways or industrial facilities adjacent to the site
Brattleboro, VT	Brattleboro, a small city in southern Vermont, has the second lowest population density of the 1996 UATMP monitoring locations. The monitoring station is located north of town in a vacant lot adjacent to a farm and garden center. The monitoring station is in a moderately industrial area, not immediately adjacent to heavily traveled roadways. Interstate highway 91 passes within 1 mile of the monitoring station
Burlington, VT	Burlington is Vermont's largest city, but it is moderately sized by national standards. The monitoring site is in the center of downtown Burlington, near several heavily traveled streets, two large parking lots, and two gas stations
Camden, NJ	A suburb of Philadelphia, Pennsylvania, Camden has the highest population density of the 1996 UATMP monitoring locations. Although the monitoring site is in a residential area, numerous industrial facilities and busy roadways are located within a 10-mile radius. The monitors are situated in a parking lot of a business complex
El Paso, TX	Located in western Texas, just across the border from Mexico and near the border of New Mexico, the region surrounding the El Paso monitoring station has the second highest population density of the 1996 UATMP monitoring locations. The monitoring site is located downtown, in a high-traffic area
Garyville, LA	Garyville is a small town located on the Mississippi River between the cities of Baton Rouge and New Orleans. The monitoring site is located on the property of the Garyville Elementary School. A large refinery and other industrial facilities are located nearby
Galveston, TX	Galveston is in eastern Texas, on the Gulf of Mexico. The monitoring site is on the grounds of a school in a residential neighborhood. Numerous industrial facilities are located within a 10-mile radius. Total TRI-reported emissions from these facilities were the third highest among TRI emissions associated with the 1996 UATMP monitoring locations
Hahnville, LA	Hahnville, another Mississippi River town, is located approximately 15 miles southeast of Garyville. A large refinery is located directly across the river from the monitoring station, and many other industrial facilities are located in close proximity. Total TRI-reported emissions from facilities near the Hahnville monitoring station were second highest among TRI emissions associated with the 1996 UATMP monitoring locations
Port Neches, TX	Port Neches is in eastern Texas, near the coast of the Gulf of Mexico and also near the Louisiana border. The site is located on the property of a high school, in a mixed residential–industrial neighborhood. There are many petrochemical plants and other industrial facilities within a 10-mile radius. Four of these facilities are within 2 miles of the monitoring station. Industrial emissions near the Port Neches monitoring station were higher than the emissions near any of the other 1996 UATMP monitoring locations
Rutland, VT	Rutland is a moderately sized city in central Vermont. The monitoring station is located in a parking lot in downtown Rutland. A heavily traveled state highway and several busy city streets run within 1 mile of the monitoring station
Underhill, VT	The Underhill monitoring site is located in a rural area, about 20 miles East of Burlington. The site is at the base of Mount Mansfield, in a remote field surrounded by forest. Not surprisingly, the area surrounding the Underhill monitoring station has the lowest population density and the lowest total emissions from industrial facilities of the 1996 UATMP monitoring locations
Winooski, VT	Located across the Winooski River from Burlington, Winooski is a small city in northern Vermont. The monitoring site is located on the grounds of a high school. The Burlington and Winooski monitoring stations are less than 5 miles apart

from compound to compound, the central laboratory for the 1996 UATMP was capable of quantifying each carbonyl at levels down to at least 0.03 ppbv.

### 2.2.3. Data quality

During the 1996 UATMP, duplicate samples were collected on approximately 10% of the scheduled sampling days, and most of these samples were analyzed in replicate. To calculate sampling and analytical precision, data analysts first averaged the results from each replicate analysis (if performed), then compared these average concentrations between the two samples in each duplicate.

Concentrations of VOCs measured in duplicate samples during the 1996 UATMP were in excellent agreement. On average, these concentrations differed by 0.10 ppbv or less for almost every compound detected during the program. For the most prevalent compounds, the relative percent difference (RPD) that expresses average concentration differences relative to the average concentrations detected during replicate analyses, for sampling and analytical precision ranged from 4% to 25%; for the least prevalent compounds, the RPDs ranged from 25% to 66%. This finding seems to confirm the notion that the UATMP monitoring data are least precise for compounds typically found at levels near their detection limits.

Like the duplicate sampling results for VOCs, the duplicate sampling results for carbonyls were highly precise. Data show that every carbonyl compound had an RPD for sampling and analytical precision lower than 40%. Consistent with the findings for VOCs, the poorest sampling and analytical precision results (i.e., the highest RPDs) were observed for compounds measured at levels near their detection limits. Random sampling errors most likely resulted from trace amounts of carbonyls contaminating the silica gel sampling cartridges before the scheduled sampling days. As the estimates of sampling and analytical precision show, however, such sources of contamination did not have significant impacts—not greater than 0.20 ppbv, on average—on the carbonyl monitoring results.

To summarize, duplicate sampling results indicate that the UATMP air quality measurements generally have precision better than 40%—well within the UATMP data quality objectives of 100% (US EPA, 1998). This excellent measurement precision suggests that the UATMP monitoring data offer a good account of air quality at the selected monitoring locations, especially for the most prevalent compounds.

## 3. Results and discussion

Table 3 summarizes the monitoring data from 13 stations that took part in the UATMP/SNMOC pro-

gram in 1996. Table 3 indicates the number of stations that listed compounds within certain ranges. These data show that peak concentrations varied significantly among compounds and monitoring stations. We note that ambient air concentration measured during this study for about half of the compounds identified by the analytical method never exceeded 1 ppbv.

The following is a discussion of the spatial variation for hydrocarbons, halogenated hydrocarbons and carbonyls, the correlations between individual compounds within each group, the correlations between VOCs and temperature, and the long-term trend (temporal variations) of the hydrocarbon compounds.

### 3.1. Spatial variations

#### 3.1.1. Hydrocarbons

As shown in Table 3, the concentrations of 11 hydrocarbons were measured during this study. All of the 11 hydrocarbons are VOCs because they have <10 carbon atoms and tend to be gases or volatile liquids under standard atmospheric conditions.

To provide a sense of how overall levels of hydrocarbons (HCs) varied among the 13 monitoring locations, Fig. 2 compares the sum of geometric mean concentrations for the 11 most prevalent hydrocarbons. The figure indicates that levels of hydrocarbons at El Paso, Texas (EPTX) were significantly higher than the levels measured at the other monitoring stations. It also indicates that levels of these compounds were lowest at Underhill, Vermont (UNVT).

To study the impact of motor vehicle and industrial emissions on the atmospheric hydrocarbon levels near the monitoring stations, Table 4 presents estimates of the number of cars owned by residents within 10 miles of each monitoring station (USDOT, 1990) and the hydrocarbon emissions reported to TRI in 1995 by facilities also within 10 miles of the monitoring stations (TRI, 1995). The table also shows the observed levels of total prevalent hydrocarbons in descending magnitude.

Although there is no good correlation between car ownership data and ambient air concentrations of hydrocarbons, different coincidences have been observed for some locations. For example, the monitoring station at the EPTX measured the highest concentrations of the total hydrocarbons and has the second highest car ownership data, while UNVT has the lowest ranks for both categories. Generally, the “magnitude” of emissions from motor vehicles depends on the volume of traffic in urban areas, but the “composition” of these emissions depends more on vehicle design. Because the distribution of vehicle design (i.e., the relative number of cars of different styles) is probably quite similar from one urban area to the next, the composition of air pollution resulting from motor vehicle emissions is not expected to exhibit significant spatial variations. In support

Table 3

Number of monitoring stations with highest concentrations of hydrocarbons, halogenated hydrocarbons and carbonyl compounds

Chemical	Number of stations			
	Concentration <1 ppbv	Concentration >1 but <5 ppbv	Concentration >5 but <10 ppbv	Concentration >10 ppbv
<i>Hydrocarbons</i>				
Acetylene	0	5	6	2
Benzene	0	13	0	0
1,3-Butadiene	9	2	1	1
Ethylbenzene	9	3	1	0
<i>n</i> -Octane	12	0	0	1
Propylene	0	9	3	1
Styrene	8	4	0	1
Toluene	0	12	1	0
<i>m,p</i> -Xylene <sup>a</sup>	1	12	0	0
<i>o</i> -Xylene	10	3	0	0
<i>Halogenated hydrocarbons</i>				
Bromochloromethane	13	0	0	0
Bromodichloromethane	13	0	0	0
Bromoform	13	0	0	0
Bromomethane	13	0	0	0
Carbontetrachloride	13	0	0	0
Chlorobenzene	13	0	0	0
Chloroethane	13	0	0	0
Chloroform	13	0	0	0
Chloromethane	5	7	1	0
Chloroprene	12	0	1	0
Dibromochloromethane	13	0	0	0
<i>m</i> -Dichlorobenzene	13	0	0	0
<i>o</i> -Dichlorobenzene	13	0	0	0
<i>p</i> -Dichlorobenzene	13	0	0	0
1,1-Dichloroethane	13	0	0	0
1,2-Dichloroethane	13	0	0	0
<i>trans</i> -1,2-Dichloroethylene	13	0	0	0
1,2-Dichloropropane	13	0	0	0
<i>cis</i> -1,3-Dichloropropylene	13	0	0	0
<i>trans</i> -1,3-Dichloropropylene	13	0	0	0
Methylene chloride	9	3	1	0
1,1,2,2-Tetrachloroethane	13	0	0	0
Tetrachloroethylene	11	2	0	0
1,1,1-Trichloroethane	11	2	0	0
1,1,2-Trichloroethane	13	0	0	0
Trichloroethylene	12	0	1	0
Vinyl chloride	13	0	0	0
<i>Carbonyls</i>				
Acetaldehyde	0	3	7	3
Acetone	0	10	3	0
Acroline	12	1	0	0
Benzaldehyde	12	1	0	0
Butyr/Isobutyraldehyde <sup>b</sup>	12	1	0	0
Crotonaldehyde	13	0	0	0
2,5-Dimethylbezaldehyde	13	0	0	0
Formaldehyde	0	2	4	7
Hexanaldehyde	11	2	0	0
Isovaleraldehyde	13	0	0	0
Propionaldehyde	11	2	0	0
Tolualdehyde <sup>c</sup>	13	0	0	0
Valeraldehyde	13	0	0	0

<sup>a</sup> Sum of *m*-xylene and *p*-xylene because they were eluted from the GC column at the same time.<sup>b</sup> Sum of butyraldehyde and isobutyraldehyde as they were eluted from the HPLC at the same time.<sup>c</sup> Sum of concentrations of the three tolualdehyde isomers for the same reason.

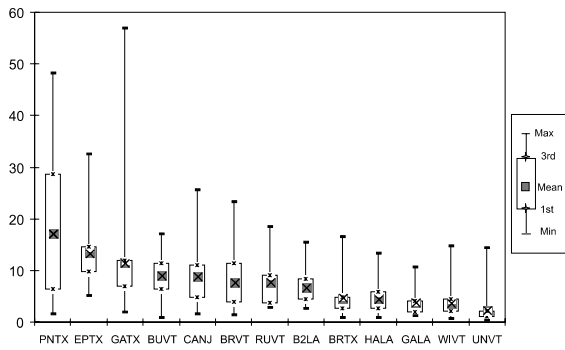


Fig. 2. Sum of the concentrations of the 11 most prevalent hydrocarbons, by monitoring locations.

of this hypothesis, previous air monitoring studies have observed relatively constant composition of ambient air samples collected along heavily traveled urban roadways (Evans et al., 1992; Conner et al., 1995). Roadside studies have found particularly consistent proportions of benzene, toluene, ethylbenzene and the xylene (BTEX)—both in motor vehicle exhaust and in ambient air near roadways. The comparison between the concentration ratio for the BTEX measured during any study and the ratio reported in the previous studies provides a qualitative depiction of how greatly motor vehicle emissions affect air quality at the monitoring station. The more similar the concentration ratios, the more likely that motor vehicle emissions impact ambient levels of hydrocarbons.

Fig. 3 compares concentration ratios of the BTEX compounds measured during the present study to the ratios reported in the roadside study (Conner et al., 1995). It is shown that the concentration ratios for BTEX compounds measured at every monitoring sta-

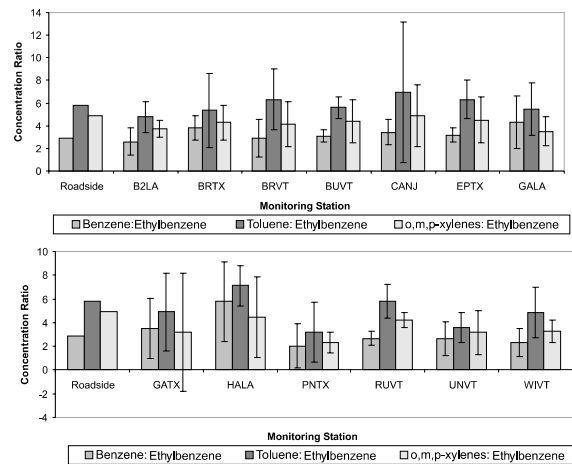


Fig. 3. Comparison of BTEX concentration profile to roadside study.

tion bear some resemblance to the ratios reported in the roadside study. The concentration ratios of the BTEX compounds—benzene/ethylbenzene (2.26–2.88), toluene/ethylbenzene (3.62–5.63), *o,m,p*-xylene/ethylbenzene (4.32–5.97)—reported by other roadside studies and dynamometer studies (Zweidinger et al., 1988; Westerholm et al., 1996; Zielinska et al., 1996; Staehelin et al., 1998) are also comparable with the values in Fig. 3. This observation suggests, though certainly does not prove, that emissions from motor vehicles significantly affect levels of hydrocarbons in urban ambient air.

On the other hand, BTEX concentration ratios for three stations, Port Neches (PNTX), Galveston (GATX), Hahnville (HALA), and Garyville (GATA) deviated significantly from the roadside study profile. This deviation indicates that emissions from sources

Table 4  
Ranking of monitoring stations by levels of total prevalent hydrocarbons

Monitoring location	Sum of geometric means of prevalent hydrocarbon concentrations (ppb)	Industrial emissions (pounds) of hydrocarbons within a 10-mile radius of the monitoring location	Total number of cars owned within a 10-mile radius of the monitoring location
EPTX	11.93	63 224	205 320
BUVT	7.38	15 990	65 972
PNTX	7.31	7 107 980	87 741
GATX	6.91	1 571 498	63 446
CANJ	6.11	884 910	1 128 734
RUVT	6.08	63 270	24 460
B2LA	5.76	1 256 132	204 821
BRVT	5.02	20 330	18 469
HALA	3.73	2 082 614	61 911
BRTX	3.64	20 450	51 236
GALA	3.02	75 377	29 728
WIVT	2.83	15 990	69 545
UNVT	1.39	0	12 061

other than motor vehicles in these locations may have a strong influence on local air quality. The importance of industrial emissions is confirmed by the highest emissions of the most prevalent hydrocarbons recorded near these three stations (Table 4). The above findings are consistent with the previous studies that were conducted in different urban areas in the United States (Fujita et al., 1994).

As Table 4 shows, each site's emission rank is not entirely consistent with the respective rank of the total ambient air concentration of the most prevalent hydrocarbons. For instance, some monitoring locations (e.g. Burlington) had relatively high concentrations of the most prevalent hydrocarbons, but had relatively low levels of industrial emissions reported through TRI; and other monitoring locations (e.g., Hahnville) had relatively low concentrations of hydrocarbons, but had relatively high levels of emissions in the study reported here.

### 3.1.2. Halogenated hydrocarbons

Halogenated hydrocarbons are organic compounds that contain carbon, hydrogen and halogen. Most of these compounds are used for industrial purposes and as solvent, though some are produced naturally (Campbell and McConnell, 1980; Godish, 1991). Because motor vehicles emit significantly greater quantities of hydrocarbons than they do halogenated hydrocarbons, motor vehicle emissions generally do not correlate well with airborne levels of halogenated hydrocarbons. Once emitted to the air, many volatile halogenated hydrocarbons resist photochemical breakdown and therefore persist in the atmosphere for relatively long period of time (Godish, 1991; Ramamoorthy and Ramamoorthy, 1997).

Like hydrocarbons, only the halogenated hydrocarbons with lower molecular weights are volatile, and the sampling and analytical methods used in this study measured a subset of these volatile compounds. Only five halogenated hydrocarbons were consistently detected in over 75% of the air samples collected at all monitoring locations (i.e., these compounds had a prevalence greater than 75% at most of the monitoring locations). These compounds are: carbon tetrachloride, chloromethane, methylene chloride, tetrachloroethylene, and 1,1,1-trichloroethane. Because these compounds were consistently present at detectable levels, the monitoring data during the present study characterize their ambient levels more accurately than the halogenated hydrocarbons with lower prevalence.

Unlike hydrocarbons, we do not know how the overall levels of the most prevalent five halogenated hydrocarbons vary among the 13 monitoring stations or compare the sum of their concentrations because the air monitoring data for each of these compounds exhibited unique trends and patterns. The following analysis focuses on their spatial variations separately. Table 5

represents the geometric mean concentration and the total air releases for each one of the most prevalent halogenated hydrocarbons at every monitoring station.

*3.1.2.1. Carbon tetrachloride.* Carbon tetrachloride is mainly produced by industrial solvent, dry cleaning, and fire extinguishers (Warneck, 1988).

The statistical analysis data for carbon tetrachloride indicated that the geometric mean concentrations at every monitoring location were nearly identical (0.72–0.90 ppbv) and the coefficients of variation were lower than those for the other prevalent compounds. These observations suggest that ambient air concentrations of carbon tetrachloride in urban locations are relatively constant, regardless of geographical location, time of year, and proximity to industrial or vehicle emissions sources.

The unique air quality trend is consistent with current knowledge of carbon tetrachloride. Although use and emissions of this compound have decreased dramatically (as a part of an international agreement attempting to phase out ozone-depleting chemicals) (ATSDR, 1997; Ramamoorthy and Ramamoorthy, 1997) ambient air concentration of the compound have not. This apparent contradiction results from the fact that carbon tetrachloride in air is extremely resistant to breakdown; estimates of its half-life in the troposphere range from tens to hundreds of years. As a result, once emitted to the atmosphere, where tetrachloride appears to gradually diffuse to regions of lower concentration rather than decompose or react with other air pollutants (ATSDR, 1997). Compared with the tropospheric background abundance of  $\text{CCl}_4$  ( $0.146 \pm 0.015$  ppbv) at 1990 level (Fabian et al., 1996) and the European mean  $\text{CCl}_4$  concentration range of 0.114–0.104 ppbv from 1987 to 1994 (Simmonds et al., 1996), the concentrations of  $\text{CCl}_4$  measured during this study are up to 50% lower.

*3.1.2.2. Chloromethane.* Concentrations of chloromethane were highest for monitoring stations located closest to large bodies of salt water (BRTX, GATX, and PNTX), and these concentrations appear to peak during the warm summer months. These trends in chloromethane concentrations are supported by recent air quality analysis (ATSDR, 1995). For example, some studies have estimated that over 90% of global air releases of chloromethane are from natural sources, such as biogenic production by marine phytoplankton (ATSDR, 1995). This observation suggests that emissions from marine environments may indeed have been the predominant factor affecting ambient levels of chloromethane at the monitoring station during the present study. The concentrations of chloromethane at other locations are close to the tropospheric abundance of  $0.602 \pm 0.015$  ppbv at the 1990 level (Fabian et al., 1996).



Table 5  
Comparison of geometric means of prevalent halogenated hydrocarbons with total air releases reported by facilities within a 10-mile radius of monitoring stations

Station code	Carbon Tetrachloride		Chloromethane		Methylene Chloride		Tetrachloroethylene		1,1,1-Trichloroethane	
	Geometric mean concentration (ppbv)	Total air releases (lbs)	Geometric mean concentration (ppbv)	Total air releases (lbs)	Geometric mean concentration (ppbv)	Total air releases (lbs)	Geometric mean concentration (ppbv)	Total air releases (lbs)	Geometric mean concentration (ppbv)	Total air releases (lbs)
PNTX	0.09	86117	1.093	3950	0.067	0	0.027	2021	0.12	7247
GATX	0.089	250	0.952	348334	0.098	204	0.049	250	0.109	1300
HALA	0.088	0	0.576	13375	0.049	0	0.035	0	0.122	0
B2LA	0.087	898	0.537	55459	0.08	12	0.048	6227	0.124	1055
CANJ	0.082	0	0.542	4	0.118	24192	0.063	696	0.13	22991
GALA	0.081	0	0.641	0	0.052	0	0.036	505	0.116	60
BUVT	0.079	0	0.495	0	0.069	0	0.024	0	0.094	343
BRVT	0.079	0	0.511	0	0.241	6044	0.034	0	0.097	0
RUVT	0.079	0	0.483	0	0.065	0	0.038	0	0.098	0
EPTX	0.078	0	0.676	0	0.084	0	0.038	0	0.097	0
BRTX	0.077	0	1.222	0	0.093	0	0.037	0	0.107	0
WIVT	0.075	0	0.526	0	0.158	0	0.047	0	0.101	343
UNVT	0.072	0	0.481	0	0.05	0	0.03	0	0.084	0

3.1.2.3. *Methylene chloride (dichloromethane)*. Air quality references indicate that many industries use methylene chloride as a solvent and some distribute it as a propellant in consumer products (ATSDR, 1993; Ramamoorthy and Ramamoorthy, 1997). During the current study, the three highest geometric mean concentrations were observed at Brattleboro, Winooski and Camden; and according to the 1995 TRI data, the highest total air releases of methylene chloride were recorded at Brattleboro and Camden. These findings suggest that industrial emissions sources may account for the relatively high concentrations of this compound in air.

On the other hand, the relatively high concentrations observed at Winooski, despite no local facilities reporting releases to TRI, may be explained that many industrial facilities that use and emit methylene chloride are not subject to the TRI reporting requirements.

3.1.2.4. *Tetrachloroethylene*. Ambient air concentrations of tetrachloroethylene had relatively weak spatial variations. Although some industrial emissions sources near selected monitoring locations emit this compound to the air, Table 5 suggests that the impact of these industrial sources is marginal. However, the mean concentrations are about 2–4 times greater than its background concentration of 0.014 ppbv at northern hemisphere (Wang et al., 1995). Not included in Table 5, however, are data from industries (such as dry cleaners) that are known to emit tetrachloroethylene but are not required to report these emissions to TRI. In fact, evaporative losses from the dry cleaning industry are suspected to represent a significant portion of releases of this compound to the air (ATSDR, 1997), which is supported by the data of the present study. For instance, the highest geometric mean concentration of tetrachloroethylene was observed at Camden—the monitoring location with the highest population density (Tables 1 and 2) and, therefore, presumably the highest density of dry-cleaning businesses.

3.1.2.5. *1,1,1-Trichloroethane*. Although monitoring stations located near industrial facilities that emit 1,1,1-trichloroethane have marginally higher geometric mean concentrations (Table 5), the difference in concentrations among the monitoring locations of this study is too small to conclude which factors most strongly affect ambient levels of this compound. The geometric mean concentrations measured in 13 distinctly different urban environments ranged only from 0.09 to 0.13 ppbv, and they are very close to the median mixing ratios of 0.124–0.127 ppbv measured over the Western Pacific Region (Blake et al., 1997), but lower than the tropospheric abundance of  $0.145 \pm 0.015$  ppbv (Fabian et al., 1996) and the European mean distribution range of

0.143–0.186 ppbv for the years 1987–1994 (Simmonds et al., 1996).

### 3.1.3. Carbonyls

Carbonyls are organic compounds characterized by their composition of carbon, hydrogen and oxygen, and by the presence of at least one carbon–oxygen double bond. During the present study, 16 carbonyl compounds were measured, 10 of which were detected in at least 75% of the sample collected. These compounds are acetaldehyde, acetone, acrolein, benzaldehyde, butyrl/isobutyraldehyde, formaldehyde, hexanaldehyde, propionaldehyde and valeraldehyde.

Following the same approach used to interpret variations of hydrocarbons, the following discussion compares spatial variations of the most prevalent carbonyls to indicators of industrial and motor vehicle emissions.

**3.1.3.1. Industrial emissions.** Fig. 4 indicates levels of the most prevalent carbonyls compared with total air releases reported by facilities within 10 miles of the monitoring locations for 6 of the 10 most prevalent carbonyls (Table 6). The figure does not present emissions data for the other four compounds because industries were not required to disclose releases of these compounds to TRI. Although the figure indicates that the TRI data seem to be uncorrelated with the spatial variations in concentrations of carbonyls, industrial emissions are still contributing to the airborne levels of carbonyls detected during the current study because industrial facilities were shown to emit significant quantities of hydrocarbons (Table 4) which may have reacted in the ambient air to form carbonyls (National Research Council,

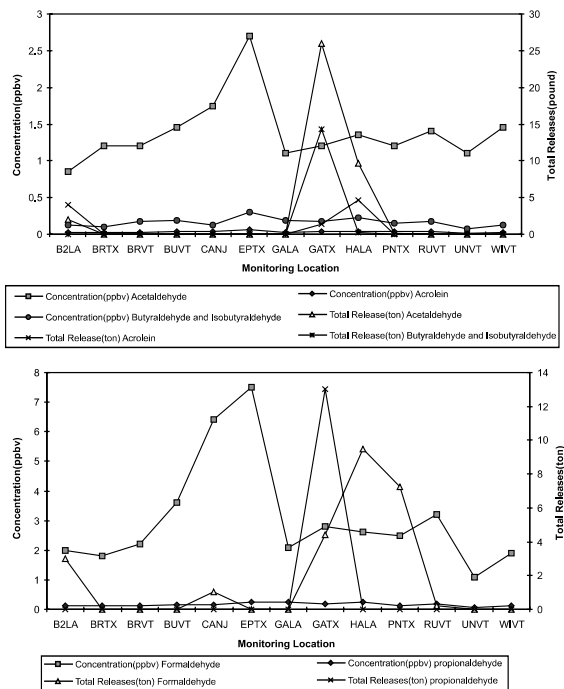


Fig. 4. Levels of the most prevalent carbonyls compared with total air releases reported by facilities within a 10-mile radius of monitoring station.

1991). Also, industrial facilities that were not subject to TRI reporting requirements may have emitted significant quantities of carbonyls, particularly those with combustion sources (e.g., electrical utilities and incinerators).

Table 6

Total air releases of the most prevalent carbonyls reported by facilities within a 10-mile radius of monitoring stations

Monitoring location	Pounds of air releases by facilities within 10 miles of the monitoring station				
	Acetaldehyde	Acrolein	Butyraldehyde and isobutyraldehyde	Formaldehyde	Propionaldehyde
B2LA	4412	4	0	6558	0
BRTX	0	0	0	0	0
BRVT	0	0	0	0	0
BUVT	0	0	0	0	0
CANJ	0	0	0	2319	0
EPTX	0	0	0	0	0
GALA	0	0	0	0	0
GATX	57 245	3046	31 516	9693	28 629
HALA	21 283	10 046	585	20 920	0
PNTX	153	0	0	16 000	0
RUVT	0	0	0	429	0
UNVT	0	0	0	0	0
WIVT	0	0	0	0	0

**3.1.3.2. Motor vehicle emissions.** The observed spatial variations for some of the most prevalent carbonyl compounds during this study were strikingly similar to those for the BTEX compounds. For example, it was found that concentrations of acrolein and benzaldehyde, like concentrations of the BTEX compounds, were relatively higher at El Paso, Burlington, and Rutland, and lowest at Underhill. Because the data analysis in Section 3.1.1 strongly suggested that the BTEX compounds measured during this study originated primarily from motor vehicles, it is likely that motor vehicle emissions also affect ambient air concentrations of the carbonyls that exhibit similar spatial variations, such as acrolein and benzaldehyde. However, the exact mechanism by which motor vehicle emissions affect airborne levels of carbonyls is not clear. Motor vehicles may emit carbonyls directly to the air, photochemical reactions involving motor vehicle emissions may form carbonyls in the air, or (most likely) some combination of these mechanisms occurs.

Analysis of concentration ratios of selected carbonyls provides further evidence that motor vehicle emissions strongly influence ambient levels of these compounds. More specifically, if motor vehicles indeed significantly affect ambient air concentrations of carbonyls, it would be expected that ratios of concentrations of carbonyls to concentrations of any BTEX compound would be consistent across monitoring locations. As a test of this hypothesis, Fig. 5 shows ratios between the concentrations of four carbonyls—acrolein, benzaldehyde, acetaldehyde and formaldehyde—and concentrations of *m,p*-xylene for the 13 monitoring stations. The roadside study cited earlier did not consider concentrations of carbonyls. In any case, the ratios shown in Fig. 5 are

quite similar for most stations, which strongly suggests that emissions from motor vehicles significantly affect airborne levels of these four carbonyl compounds.

On the other hand, although the concentration ratios were also similar across all sites for acetaldehyde and formaldehyde, the ratios for these carbonyls were not as consistently similar as those of the other compounds. This suggests that emissions from motor vehicles probably affect ambient levels of these compounds, and other factors also strongly influence ambient air of their concentrations. Grosjean et al. (1983) estimated that photochemical reactions can contribute as much as 85% of the ambient formaldehyde and 95% of the ambient acetaldehyde levels in Los Angeles.

### 3.2. Correlation analysis

Pearson correlation coefficients were used in this study to measure the degree of correlation between two variables. These coefficients always lie between  $-1$  and  $1$ . A correlation coefficient of  $-1$  indicates a perfectly “negative” relationship, which occurs when increases in the magnitude of one variable are associated with proportionate decreases in the magnitude of the other variable and vice versa. A correlation coefficient of  $1$  indicates a perfectly “positive” relationship, which occurs when the magnitudes of two variables both increase and both decrease proportionately.

For each monitoring location, a Pearson correlation coefficient was calculated for every possible pair of the most prevalent compounds to know the extent at which the 24-h average concentrations of one compound are related to 24-h average concentrations of other compounds measured at the same time at the same monitoring location. Also, the correlation between a compound’s measured ambient air concentration and the corresponding daily temperature was calculated to provide a measure of how ambient air concentrations vary with temperature and how they vary with seasons.

#### 3.2.1. Correlations between different compounds

Fig. 6 represents a summary of data correlations between different groups of compounds, including hydrocarbons with hydrocarbons, hydrocarbons with halogenated hydrocarbons, hydrocarbons with carbonyls, halogenated hydrocarbons with halogenated hydrocarbons, halogenated hydrocarbons with carbonyls and carbonyls with carbonyls.

The Pearson correlation coefficients that were calculated from the ambient air monitoring data for pairs of the most prevalent hydrocarbons, were generally positive and some pairs of these compounds had air concentrations that were very strongly correlated (i.e., they had Pearson correlation coefficients greater than 0.75). The strong correlations indicate that ambient air concentrations of the corresponding hydrocarbons generally

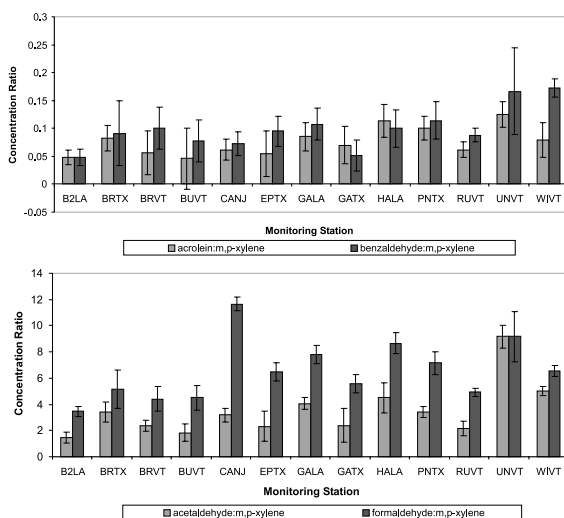


Fig. 5. Comparison of concentration ratios of selected carbonyls to *m,p*-xylene.

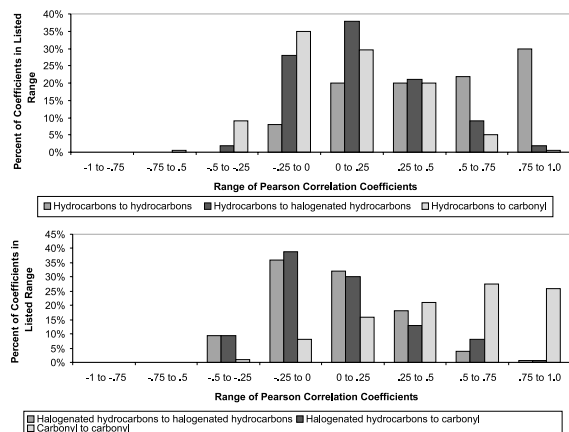


Fig. 6. Summary of data correlations between groups of compounds.

rose and fell in proportion during this study—an observation consistent with most hydrocarbon species originating primarily from one type of emissions source. The strong correlations also suggest that emissions from a source common to all urban environments (e.g., motor vehicles) might account for a large fraction of hydrocarbons commonly found in urban air pollution.

On the other hand, the ambient air concentrations of styrene were essentially uncorrelated with ambient air concentrations of the other prevalent hydrocarbons. This observation suggests that styrene in ambient air may have originated primarily from emissions sources other than motor vehicles (the predominant source affecting ambient levels of most hydrocarbons). However, the TRI data for styrene correlated fairly well with the corresponding geometric mean concentrations. The three monitoring stations with the highest concentrations of styrene also had the highest reported air emissions. Therefore, levels of styrene measured during the current study appear to originate largely from industrial emissions sources.

The ambient air concentrations of the most prevalent hydrocarbons were very weakly correlated with those of the most prevalent halogenated hydrocarbons and carbonyls. These weak correlations generally suggest that the factors that most strongly affect levels of hydrocarbons in ambient air are different from those that affect ambient air concentrations of halogenated hydrocarbons or carbonyls.

The majority of Pearson correlation coefficients calculated from air monitoring data for one halogenated hydrocarbon and those for another halogenated hydrocarbon fell between  $-0.25$  and  $0.25$ —a range indicating weakly correlated or uncorrelated data. Also, closer examination of the data found that the direction and strength of correlations between the different halogenated hydrocarbons varied from one monitoring lo-

cation to the next. This observation suggests that each of the five most prevalent halogenated hydrocarbons is released and transported in the atmosphere by unique mechanisms.

Like the distribution of correlations between individual halogenated hydrocarbons, the distribution of correlations between halogenated hydrocarbons and carbonyls is most heavily populated in the range from  $-0.25$  to  $0.25$ . This observation also suggests that the emissions sources and photochemical reactions that most significantly affect ambient air concentrations of halogenated hydrocarbons differ from those sources and reactions that tend to affect ambient levels of carbonyls.

Among the most prevalent carbonyl compounds, despite the strong correlations between concentrations of different compounds, no trends as strong as those observed among the hydrocarbon compounds were readily apparent (the pairs of carbonyl compounds having the most significant correlations varied from site to site). The absence of general trends among the carbonyl compounds suggests that no single factor determines how ambient air concentrations of carbonyls vary from one monitoring location to the next. A more likely explanation is that many different factors, such as motor vehicle emissions, industrial emissions and photochemical reactions, affect ambient air concentrations of carbonyls, with no single factor exhibiting a dominating effect.

### 3.2.2. Correlations between concentrations and temperature

Table 7 summarizes how temperature correlated with ambient air concentrations of the most prevalent compounds during this study. The daily average temperature data representative of each monitoring location were obtained from the National Climate Data Center (NCDC), an organization that oversees a network of meteorological stations across the country.

**3.2.2.1. Hydrocarbons.** Except for styrene, the most prevalent VOCs generally had negative correlations with temperature (their concentrations were high in winter and low in summer). Because total emissions from motor vehicles in an urban area do not vary significantly from day to day, factors other than emissions from motor vehicles contribute to the observed seasonal changes in urban air pollution. For instance, higher concentrations of hydrocarbons during the winter months are consistent with the effects of photochemical reactions, which are known to consume airborne hydrocarbons, especially in the summer (Hagerman et al., 1997). Further, the seasonal trends for hydrocarbons also can be explained by emissions from home heating sources (e.g., fireplaces, wood-burning stoves), which are notably higher during the winter months, especially for locations with cold temperatures (e.g., Vermont).

Table 7  
Correlations between ambient air monitoring data and temperatures

Compound group	Compound	Number of monitoring locations with positive correlations between the listed compound and temperature	Number of monitoring locations with negative correlations between the listed compound and temperature
Hydrocarbons	Acetylene	1	12
	Benzene	3	10
	1,3-Butadiene	2	11
	Ethylbenzene	7	6
	<i>n</i> -Octane	7	6
	Propylene	4	9
	Styrene	11	2
	Toluene	4	9
	<i>m,p</i> -Xylene	4	9
	<i>o</i> -Xylene	3	10
Halogenated hydrocarbons	Carbon tetrachloride	6	7
	Chloroform	13	0
	Methylene chloride	5	8
	Tetrachloroethylene	11	2
	1,1,1-Trichloroethane	4	9
Carbonyls	Acetaldehyde	10	3
	Acetone	2	11
	Acrolein	12	1
	Benzaldehyde	10	3
	Butyr/isobutyraldehyde	6	7
	Formaldehyde	9	4
	Hexanaldehyde	12	1
	Propionaldehyde	8	5
	Valeraldehyde	12	1

The ambient air concentrations of styrene had weak positive correlations with temperature at most of the monitoring locations. The unique correlations for styrene support the hypothesis that the major emissions sources of styrene in urban locations are not the same as the major emissions sources of the other most prevalent hydrocarbons.

**3.2.2.2. Halogenated hydrocarbons.** The ambient air concentrations of the most prevalent halogenated hydrocarbons during the present study were either positively or weakly correlated with temperature. The direction and strength of correlations for the individual halogenated hydrocarbons provides important insight into seasonal air quality trends.

Relatively strong concentration–temperature correlations for chloromethane and tetrachloroethylene suggest that, regardless of the monitoring location, temperature affects the mechanism by which these compounds are released to the air. As previously mentioned, the natural releases from oceans and evaporative losses from small industrial facilities likely explain the air quality trends for these compounds.

Although the correlations for methylene chloride alternated between positive and negative values, the correlations at Brattleboro and Winooski were quite strong

and positive. These two monitoring stations also had higher methylene chloride concentrations than the other monitoring locations. As stated before, the particularly strong correlations and relatively high concentrations at these sites are consistent with how evaporative losses of solvents are known to affect air quality.

Unlike the concentration–temperature correlations for the other halogenated hydrocarbons, the correlations for carbon tetrachloride and 1,1,1-trichloroethane do not exhibit any unique trends and patterns. Accordingly, ambient air concentrations of these compounds appear to be relatively unaffected by temperature and season.

**3.2.2.3. Carbonyls.** The ambient air concentrations of the most prevalent carbonyls, with the exception of acetone, were generally positively correlated with temperature. This correlation supports the hypothesis that carbonyls in ambient air originate, to a certain extent, as products of photochemical reactions.

On the other hand, at almost most every monitoring location, concentrations of acetone decreased as temperature increased because of the photochemical reactions that consume (not produce) acetone as was investigated by several studies (Cox et al., 1980; Grosjean et al., 1983; Seinfeld, 1986). This also was consistent with the relatively higher concentrations of acetone in

Vermont than other locations. Because photochemical reactivity in Vermont is much weaker than in Texas or Louisiana, airborne acetone in Vermont may persist for relatively longer periods of time before being consumed by photochemical reactions.

### 3.2.3. Temporal variations

Generally, changes in concentrations of an air pollutant over a two-year period may result simply from shifting prevailing winds and may not necessarily indicate increases or decreases in emissions. So, annual variations over longer time periods should be considered to evaluate the impacts of long-term changes in emissions. As an example, Table 8 indicates how the geometric mean concentrations of benzene, ethylbenzene and toluene in Camden have changed since 1989 U-ATMP. It is clear that the concentrations of all three compounds appear to have decreased by approximately a factor of three over the eight years shown in the table. Because BTEX compounds were shown to originate largely from motor vehicle emissions, as previously mentioned, the long-term decline in geometric mean concentrations of these compounds suggests that motor vehicle emissions in the Camden area have decreased steadily since 1989. However, more details are needed to confirm this consistent decline.

### 3.2.4. Seasonal variations

In addition to the correlation analysis between concentrations and temperatures that indirectly indicate seasonal variations, Table 9 summarizes the seasonal statistics of the sum of concentrations of each group at each monitoring location. For the year-round monitoring period, Summer includes samples collected from June to August, Fall from September to November, Winter from December to February, and Spring from

March to May. The statistics is calculated over each individual compound before it is summed up according to hydrocarbons, halogenated hydrocarbons, and carbonyls.

Hydrocarbons have the largest winter or Fall arithmetic mean and median concentrations at 12 of 13 monitoring locations; seven locations have the largest mean and median in winter, the rest have the largest values in the Fall. The only exception is at Port Neches (PNTX), where the values in summer are the largest, and in winter the least. However, when compared with halogenated hydrocarbons and carbonyls at PNTX, both have the least values during winter. This may indicate that the local emissions at PNTX were significantly reduced in winter. This result is in agreement with the previous concentration–temperature correlation analysis, and it is also in agreement with literature results (Hagerman et al., 1997).

Unlike hydrocarbons, halogenated hydrocarbons do not have significant seasonal trend. Except for Galveston, TX (GATX), PNTX, and Rutland, VT (RUVT) where significant seasonal difference exists in arithmetic mean and median concentrations, there are no significant difference at the other nine monitoring locations. This further verifies that ambient air concentrations of halogenated hydrocarbons are not affected by temperature and season.

Although there is no common seasonal trend for carbonyls at all locations, the seasonal variations are significant at most of the monitoring locations. At GATX, El Paso, TX (EPTX), Burlington, VT (BRVT), there are significant higher summer concentrations than in other seasons. However, the winter concentrations at Camden, NJ (CANJ) are the highest among all the four seasons. This signifies that carbonyl compounds have complex sources. Carbonyl compounds are the intermediate products of photochemical processes of hydrocarbons, and they can also be emitted by anthropogenic processes.

### 3.3. Distribution in urban environments and comparison with literatures

To study the distribution of ambient air organic compounds in urban environments, the sum of the most prevalent hydrocarbons, halogenated hydrocarbons and carbonyls was separately calculated for each monitoring station. Fig. 7 shows the concentration percents for the three groups at every monitoring location. It is evident that 8 of the 13 stations had over 50% of the carbonyl compounds, while only 3 stations had over 50% of the hydrocarbon compounds. The other two stations had approximately equal percents of both groups.

As previously mentioned, because of the positive correlation with temperature, the most prevalent carbonyls (except for acetone) in ambient air originate as

Table 8

Annual trends in geometric mean concentration observed at the Camden, New Jersey (CANJ) monitoring station

UATMP program year	Geometric mean concentration (ppbv)		
	Benzene	Ethylbenzene	Toluene
1989	1.46	0.36	3.25
1990	1.19	0.22	2.2
1991	0.79	0.32	2.45
1992	a	a	a
1993	a	a	a
1994	0.47	0.24	1.69
1995	0.46	0.14	1.04
1996	0.55	0.16	1.11

<sup>a</sup>In UATMP program years 1992 and 1993, ambient air monitoring was performed by a different contractor. For reference, the monitoring results for CANJ for these years are available from the Air Quality Subsystem (AQS) of AIRS.

Table 9  
 Statistics of season split sum of concentrations (ppbv) of hydrocarbons, halogenated hydrocarbons, and carbonyl compounds

	Summer			Fall			Winter			Spring		
	Mean	Median	Std <sup>a</sup>	Mean	Median	Std <sup>a</sup>	Mean	Median	Std <sup>a</sup>	Mean	Median	Std <sup>a</sup>
<i>B2LA</i>												
Hydrocarbons	2.43	1.77	1.14	3.48	3.70	1.74	5.14	4.51	4.18	2.79	2.14	2.47
Halogenated hydrocarbons	1.47	0.90	1.25	1.14	1.02	0.47	1.09	0.86	0.88	0.73	0.77	0.30
Carbonyl	4.51	3.75	3.66	4.92	4.41	3.53	4.84	4.03	2.51	6.28	5.82	3.33
<i>BRTX</i>												
Hydrocarbons	1.50	0.85	1.70	2.62	1.62	2.55	2.53	2.12	1.91	1.61	1.73	0.70
Halogenated hydrocarbons	5.39	4.05	3.81	3.80	3.19	2.13	5.21	3.25	5.83	3.84	3.69	1.97
Carbonyl	2.59	2.45	0.95	11.17	12.29	6.22	4.15	4.05	1.70	3.50	2.99	1.63
<i>BRVT</i>												
Hydrocarbons	3.53	3.13	2.06	8.11	7.98	3.93	11.08	9.60	7.60	3.70	3.03	2.29
Halogenated hydrocarbons	2.20	1.94	1.22	0.98	0.88	0.44	0.94	0.85	0.42	2.34	2.38	1.85
Carbonyl	10.83	9.76	4.46	3.81	3.55	0.97	5.24	5.13	1.34	5.04	5.18	2.08
<i>BUVT</i>												
Hydrocarbons	2.47	2.44	0.90	2.89	3.01	0.94	2.60	2.47	1.36	2.76	2.85	0.70
Halogenated hydrocarbons	3.48	3.66	1.40	3.23	3.32	1.25	3.40	3.40	1.85	4.06	4.20	1.28
Carbonyl	6.97	6.17	3.64	10.23	9.48	3.69	7.83	7.65	2.82	6.09	6.35	1.52
<i>CANJ</i>												
Hydrocarbons	4.82	4.00	3.21	12.08	9.52	7.50	10.88	8.22	6.93	5.68	5.40	3.49
Halogenated hydrocarbons	1.09	1.12	0.54	1.42	1.42	0.70	1.28	1.03	0.79	0.95	0.85	0.35
Carbonyl	10.34	10.75	3.87	15.61	13.55	9.07	23.90	24.89	6.13	4.67	3.92	2.70
<i>EPTX</i>												
Hydrocarbons	10.15	9.05	5.21	19.82	20.33	9.25	12.88	11.91	3.94	11.10	10.07	4.63
Halogenated hydrocarbons	1.08	0.93	0.47	1.45	1.05	0.82	1.48	0.88	2.19	0.89	0.83	0.20
Carbonyl	25.96	8.03	26.87	12.14	8.40	11.97	8.54	4.38	7.55	23.68	23.37	11.31
<i>GALA</i>												
Hydrocarbons	2.78	2.30	1.53	6.60	6.90	3.52	2.30	2.09	1.07	3.45	2.79	2.71
Halogenated hydrocarbons	1.19	1.02	0.61	1.87	1.10	2.12	0.78	0.75	0.24	1.59	0.81	1.92
Carbonyl	4.90	4.62	2.17	4.77	4.27	2.20	4.09	3.96	1.27	5.63	5.29	2.29
<i>GATX</i>												
Hydrocarbons	5.62	4.93	3.06	4.65	4.41	2.14	7.58	8.78	5.44	5.25	4.79	3.34
Halogenated hydrocarbons	3.67	3.14	1.81	9.90	3.23	16.45	5.44	4.13	4.17	3.77	3.62	2.08
Carbonyl	19.71	5.29	25.49	4.47	4.05	2.08	5.79	4.94	2.97	5.00	4.83	1.22
<i>HALA</i>												
Hydrocarbons	2.39	2.49	1.03	3.29	2.93	1.76	2.61	2.09	1.51	1.88	1.37	1.10
Halogenated hydrocarbons	2.61	1.77	1.48	2.90	2.63	1.69	1.86	1.52	1.35	2.33	1.10	3.61
Carbonyl	7.46	5.26	4.78	6.89	6.60	2.85	8.73	5.26	9.47	5.69	4.54	4.18
<i>PNTX</i>												
Hydrocarbons	5.02	4.81	2.87	4.24	3.14	2.95	2.14	1.34	2.08	2.84	2.91	1.19
Halogenated hydrocarbons	6.58	4.83	7.07	22.89	18.38	19.26	2.67	1.26	3.16	16.93	14.76	14.63
Carbonyl	5.87	4.54	5.54	8.17	5.84	7.14	2.27	2.37	1.32	4.72	3.43	3.59

(continued on next page)

Table 9 (continued)

	Summer			Fall			Winter			Spring		
	Mean	Median	Std <sup>a</sup>	Mean	Median	Std <sup>a</sup>	Mean	Median	Std <sup>a</sup>	Mean	Median	Std <sup>a</sup>
<i>RUVT</i>												
Hydrocarbons	1.63	1.50	0.50	1.84	1.79	0.60	3.58	3.24	1.67	2.13	1.95	0.99
Halogenated hydrocarbons	2.18	2.16	0.61	2.57	2.25	1.16	5.56	4.36	3.64	2.65	2.68	1.37
Carbonyl	8.59	5.92	5.31	10.49	10.92	6.23	9.82	8.89	3.42	3.81	4.06	2.99
<i>UNVT</i>												
Hydrocarbons	1.24	0.96	0.97	0.71	0.74	0.34	1.19	1.01	1.12	0.80	0.80	0.16
Halogenated hydrocarbons	0.93	0.40	1.51	0.68	0.60	0.53	1.44	1.02	1.37	0.51	0.49	0.16
Carbonyl	4.56	3.84	3.28	2.82	2.81	0.92	2.72	2.63	1.07	2.98	2.70	1.07
<i>WIVT</i>												
Hydrocarbons	1.37	1.33	0.63	1.28	1.31	0.43	1.99	1.35	1.91	1.13	1.03	0.63
Halogenated hydrocarbons	1.93	1.33	1.47	1.52	1.31	0.81	2.26	1.72	1.58	1.48	1.05	1.58
Carbonyl	4.80	3.83	3.03	7.58	6.65	2.65	6.14	5.86	2.44	3.21	3.21	1.05

<sup>a</sup> std =  $\pm 1$  standard deviation.

products of photochemical reactions. Supporting this hypothesis is the fact that the correlations between ambient air concentrations and temperature were particularly strong for the Vermont monitoring locations such as UNVT, WIVT and BRVT (as shown in Fig. 7), where seasonal differences in temperature and the number of daylight hours are more pronounced than in locations along the Gulf of Mexico such as PNTX and GATX. Also, this observation is supported by the fact that most of the prevalent VOCs generally had negative correlations with temperature (Cox et al., 1980).

On the other hand, locations of PNTX, GATX and B2LA mixed residential–industrial neighborhood areas. These sites are characterized by the high population density and industrial emissions. The industrial facilities near monitoring stations at these locations include many refineries, chemical manufacturing and petrochemical plants; and some of these facilities are within only 2 miles of the monitoring station (PNTX). The B2LA monitoring site was located in the back parking lot of an office building, directly across from the city motor pool. Also, all three sites are located in the south where seasonal changes in daily average temperature are much smaller than the locations in the North.

Generally, percents of halogenated hydrocarbons were very small at all stations compared with the percent of the hydrocarbons or carbonyls. It is evident from the figure that percent of the halogenated hydrocarbons varied from one monitoring location to the next. This observation confirms that local sources, such as evaporative losses from small industries and natural releases from oceans, are likely responsible for the air quality trends of these compounds. Unlike hydrocarbons and carbonyls, once emitted to the air, many volatile halo-

genated hydrocarbons resist photochemical breakdown and therefore persist in the atmosphere for relatively long periods of time.

Table 10 summarizes the arithmetic mean concentrations of the most prevalent hydrocarbons measured in this program and in other urban, semi-urban, or rural locations. The mean concentrations of all the hydrocarbons listed in Table 10 are much lower than the median or mean values in other US cities, but the values are very close to those at 24 urban monitoring locations in Canada. Even at three rural US Southeast National Parks the concentration levels of selected hydrocarbons are within the range of mean concentrations of the 13 UATMP monitoring locations.

It should be noted that the atmosphere is an open system, concentrations of any elements are not only dependent on the emissions strength and chemical/photochemical processes, they depend on meteorological conditions such as atmosphere stability, wind velocity and direction as well. Detailed discussion including meteorological conditions and other atmospheric parameters is beyond the scope of this paper.

#### 4. Conclusions and recommendations

Overall, levels of airborne hydrocarbons were highest at the El Paso monitoring location and were lowest at the Underhill monitoring location. At most stations, emissions from motor vehicles appeared to be the primary source of hydrocarbons in ambient air; however, industrial emissions sources in the vicinity of Galveston, Hahnville, and Port Neches seemed to affect local airborne levels of hydrocarbons significantly. The links



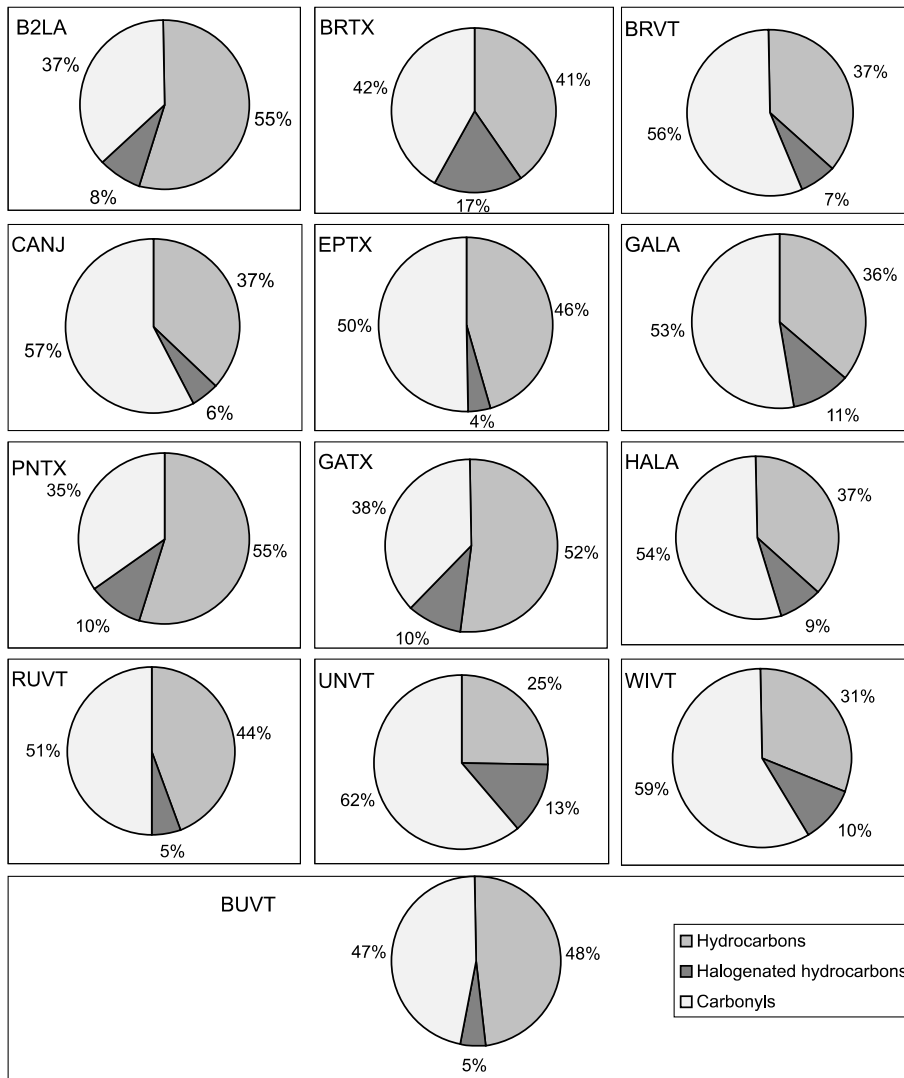


Fig. 7. Percent of hydrocarbons, halogenated hydrocarbons, and carbonyl levels at every monitoring station.

between motor vehicle emissions and ambient air concentrations of hydrocarbons were particularly strong for the BTEX compounds, and somewhat strong for acetylene and propylene. Industrial emissions data were consistent with observed spatial variations for 1,3-butadiene and for styrene: monitoring locations near facilities that emitted these chemicals tended to have relatively high geometric mean concentrations. There was some evidence that monitoring stations located in close proximity to petroleum refineries measured relatively high levels of *n*-octane.

Ambient air concentrations of each of the most prevalent halogenated hydrocarbons appeared to exhibit unique spatial variations, and no single factor seemed to explain air quality trends for this group of compounds.

Detailed analyses identified likely explanations for the measured levels of specific compounds: concentrations of carbon tetrachloride could be best explained as “global background” levels, chloromethane appeared to be influenced most by natural emissions from bodies of salt water, and concentrations of methylene chloride and tetrachloroethylene seemed to be linked in part to emissions from industrial sources. No notable trends in the concentrations of 1,1,1-trichloroethane were observed.

The monitoring data seem to suggest that emissions from motor vehicles and photochemical reactions most strongly influence ambient air concentrations of carbonyls. The fact that ambient air concentrations of most carbonyls were positively correlated with temperature at

Table 10  
Comparison of selected anthropogenic hydrocarbons measured at various urban and rural sites<sup>a</sup>

Compound	Range of mean (UATMP 1996)	Median <sup>b</sup> (39 US cities)	Range of mean <sup>c</sup> (seven US cities)	Median <sup>d</sup> (nine major US cities)	24 Canada cities <sup>e</sup>	Mammoth KY <sup>f</sup>	Cove Mtn TN <sup>f</sup>	Shenandoah VA <sup>f</sup>
Acetylene	0.85–5.49	13.9	5.4–16.2			0.65	0.77	1.15
Benzene	0.24–1.25	13.7	4.3–18.9	1.3–5.9	0.9	0.85	0.85	1.29
Ethylbenzene	0.08–0.41	6.5	3.3–16.5	0.3–2.3	0.3	0.38	0.29	0.87
<i>n</i> -Octane	0.05–1.94	3.1				0.06	0.08	0.14
Propylene	0.23–3.02	9.0	4.6–19.8		0.14	1.56	1.81	1.09
Styrene	0.06–3.10					1.92	1.23	1.97
Toluene	0.36–2.67	37.0	17.5–52.5	2.1–16.6	2.43	1.2	1.67	5.87
<i>m,p</i> -Xylene	0.21–1.29	20.0	8.8–41.9	0.7–8.6	1.17	0.47	0.44	2.13
<i>o</i> -Xylene	0.11–0.56	8.0	3.31–19.8	0.3–3.1	0.37	0.47	0.27	1.91

<sup>a</sup>Unit was transformed from ppbC or  $\mu\text{g m}^{-3}$  to ppbv from original publications.

<sup>b</sup>Parrish et al. (1998) (median concentrations from 39 US cities, data collected from 1984 to 1986).

<sup>c</sup>Sexton and Westberg (1984) (data collected between 6 and 9 a.m.).

<sup>d</sup>Edgerton et al. (1989).

<sup>e</sup>Davis and Olson (1996) (mean concentrations from 24 Canada urban sites in 1990–1991).

<sup>f</sup>Kang et al. (2001) (rural, surface, data collected from June to August 1996, 12:00–13:00 local time).

most monitoring locations supported the hypothesis that photochemical reactions form carbonyls in ambient air. Unique trends and patterns for concentrations of acetone, however, suggested photochemical reactions that consume the compound are an important mechanism affecting the measured ambient air concentrations. Although emissions data from facilities subject to the Toxic Release Inventory reporting requirements were quite inconsistent with the observed spatial variations in concentrations of carbonyls, emissions from other industrial emissions sources may have contributed to the levels of carbonyls detected during the present study.

Of the compounds identified by the sampling and analytical methods used in this program, nearly half were detected in less than 50% of the samples. This limited number of detections restricts the accurate estimates of air quality trends for these compounds. To avoid such limitations, research efforts should continue to focus on developing more sensitive sampling and analytical methodologies that can measure concentrations of urban air pollutants at trace levels.

The TRI emissions data often could not explain notable spatial variations in ambient air quality, presumably because its database does not characterize emissions from all industrial sources or from any mobile or natural sources. So, efforts to expand the scope of the TRI or to develop extensive local emissions inventories should be strongly encouraged.

Although the data analysis in this study provided compelling evidence that motor vehicle emissions significantly affect ambient air concentrations of several hydrocarbons, this study did not compare estimates of local traffic volume to the monitoring data. To understand the actual impacts of motor vehicle emissions, researchers are encouraged to derive estimates of motor vehicle flow near their respective monitoring locations and compare these estimates to the spatial variations in the measured levels of hydrocarbons.

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- Mohmoud F. Mohamed** was a Fulbright senior scholar visiting the Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC 27695-8208. He is currently a professor in Alexandria University, Egypt.
- Daiwen Kang** is a Canon National Park Science Scholar.
- Viney P. Aneja** is a research professor—Air Quality and professor—Environmental Technology in the Department of Marine, Earth, and Atmospheric Sciences, Raleigh, NC.