

**CHARACTERISTICS OF VOLATILE
ORGANIC COMPOUNDS IN THE
MID-ATLANTIC REGION**

**FINAL REPORT
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1. INTRODUCTION

1.1 BACKGROUND

In accordance with the 1990 Clean Air Act Amendments, the U.S. Environmental Protection Agency (EPA) initiated the Photochemical Assessment Monitoring Stations (PAMS) program for serious, severe, and extreme ozone nonattainment areas. The PAMS networks monitor for volatile organic compounds (VOCs), ozone, oxides of nitrogen (NO_x), and meteorological parameters. The PAMS networks were designed to provide data for the assessment of population exposure, ozone formation, and evaluation of ozone control strategies. The Mid-Atlantic Regional Air Management Association (MARAMA) is sponsoring research into the importance of mobile source emissions in the region. MARAMA is an interstate association of air quality control agencies in the Mid-Atlantic States. The member entities are comprised of the Allegheny County Health Department Air Quality Program, Delaware Air Quality Management Section, District of Columbia Air Resources Management Division, Maryland Air and Radiation Management Administration, New Jersey Office of Air Quality Management, North Carolina Division of Air Quality, Pennsylvania Bureau of Air Quality, Philadelphia Air Management Services, and Virginia Department of Environmental Air Quality Division. This report summarizes VOC data analyses performed on the behalf of MARAMA.

1.2 STUDY OBJECTIVES

This study had the following two objectives:

- Validate 1995-1997 PAMS data and provide feedback to reporting agencies. This task was documented separately by Main et al. (1999).
- Assess the importance of motor vehicle-related emissions in the region.

In order to assess the importance of motor vehicle-related emissions in the region, we first described and displayed the PAMS data. Next, we performed interpretative analyses that included assessment of ozone formation potential, the relative age of an air mass, and multivariate analysis of VOC sources. We performed the following tasks in this regard:

- Assessed general characteristics of VOCs
- Assessed spatial and temporal issues
- Investigated source identification (qualitative)
- Assessed air mass age (an investigation of transported vs. fresh emissions)
- Reviewed day of week distributions
- Assessed trends

1.3 GUIDE TO THIS REPORT

The remainder of this report provides a summary of the data used in the analyses and data quality (Section 2), a discussion of data analysis results (Section 3), and a summary of conclusions and recommendations for further work (Section 4). References are provided in Section 5, supporting information is provided in Appendix A, and revised lists of flagged samples for Corbin, Virginia and Philadelphia, Pennsylvania are provided in Appendix B.

2. AVAILABLE PAMS DATA

2.1 PAMS PROGRAM

This study focused on data collected at PAMS sites in the Mid-Atlantic region. There are up to four types of PAMS sites based on the site location relative to the emissions and transport pathways in an area, defined as follows:

- Type 1 - located to provide upwind and background characterization of ozone and precursors being transported into an area.
- Type 2 - located to document the maximum ozone precursor emissions impact. These sites are typically located downwind of the central business district and operate on the most intensive monitoring schedule of the PAMS sites.
- Type 3 - located to measure the maximum ozone concentration and typically situated further downwind than the Type 2 sites.
- Type 4 - located downwind of the nonattainment areas to assess the extreme downwind conditions. In some parts of the country, a Type 4 PAMS site may also be defined as a Type 1 site for another non-attainment area well downwind.

Some PAMS sites employ an automatic gas chromatography system (auto-GC) that reports hydrocarbon concentrations of 57 target hydrocarbon species and the total nonmethane hydrocarbon (NMHC). At other sites, canisters are collected for later laboratory analysis; at most of these sites, eight 3-hr samples are collected either every day or every third day. Carbonyl compounds are collected at the PAMS sites using commercially available dinitrophenylhydrazine (DNPH)-impregnated silica gel cartridges; however, results from most of the PAMS sites are reported only for formaldehyde, acetaldehyde, and acetone.

2.2 SITE LOCATIONS

The PAMS sites investigated in this report are listed in **Table 2-1** (from Main et al., 1999). The sites are also shown in **Figure 2-1**.

2.3 DATA USED IN THIS PROJECT

An extensive data validation effort was undertaken as a part of this project and summarized by Main et al. (1999) and MacDonald et al. (1998). Our validation efforts were reported to and discussed with the monitoring personnel for every site. The MARAMA member agencies made a concerted and commendable effort to address data quality issues, revise problem data, and resubmit the revised data to AIRS. As a result of these efforts, the data for the Mid-Atlantic region are of good quality. A summary of data completeness is provided in **Table 2-2**.

Because of several data quality issues, the Corbin, Virginia data were not used in analyses described in the first draft of this report. The reporting agency subsequently addressed reported zero concentrations of abundant species by changing key chromatographic

processing parameters and re-reported their data to AIRS. We obtained and re-evaluated the reprocessed data set. We inspected a time series plot of every species, prepared numerous scatter plots, and inspected a fingerprint plot of every sample. Concentrations at the Corbin site are generally low; thus, hydrocarbons were often below detection in many samples. The revised list of suspect samples at the Corbin site is provided in Appendix B.

Please note that in order to meet the time deadline and budget constraints of this report, we were only able to use the revised data for Corbin, Virginia. For all sites in the analyses, we have ignored the data we flagged. The practical implication of this is that later analysis results based on revised data may differ slightly from the results in this report. We do not believe, however, that conclusions will be significantly affected.

2.4 REGARDING FLAGGED DATA

During data validation, we flagged data as "suspect" that appeared odd based on one or more of several investigations. Essentially, data are flagged as suspect when the data do not fit the analysts' conceptual model of hydrocarbon emissions, formation, and removal. *Flagging these data points or samples does not necessarily mean that the data are invalid or that there has been a monitoring or analytical error.* The flags are placed on the data so that the monitoring staff can check their data to rule out possible monitoring or analytical errors and for future data analysts to note that the data appear odd. Data analysts can use the list of suspect or odd data to look for patterns, help select case studies for analysis, etc. Note that the data validation report is a snapshot in time. As the analyst understands more about the data, the list of suspect and invalid samples will probably be modified.

Since the publication of the validation report (Main et al., 1999), some issues regarding the Philadelphia, Pennsylvania data have been updated as follows:

- The 1994 samples with unusual concentrations of 3-methyl-1-butene have since been identified as invalid because of coelution problems with acetonitrile. These data have been invalidated in AIRS.
- No analytical causes were found for the 1994 and 1995 samples with relatively high concentrations of t-2-pentene, 2-methyl-2-butene, 1-pentene, and c-2-butene. These data were flagged because the concentrations were significantly different from the bulk of the data and stood out as odd in time series, scatter, and fingerprint plots. While the laboratory staff report that "there is no physical evidence that these high concentrations are not real and valid," we believe other analysts need to be aware of these samples. Therefore, we recommend that the suspect labels still apply to these data for the benefit of future data analysts; these hydrocarbons are quite important in ozone formation.
- The 1995 o-xylene data that we had obtained from the NARSTO-Northeast program were subsequently updated in AIRS; the detection limit is no longer an issue.
- The 1995 problems regarding TNMOC values have also been addressed since the original posting of the data and are no longer an issue.

A revised list of suspect samples for the Philadelphia, Pennsylvania data set is provided in Appendix B.

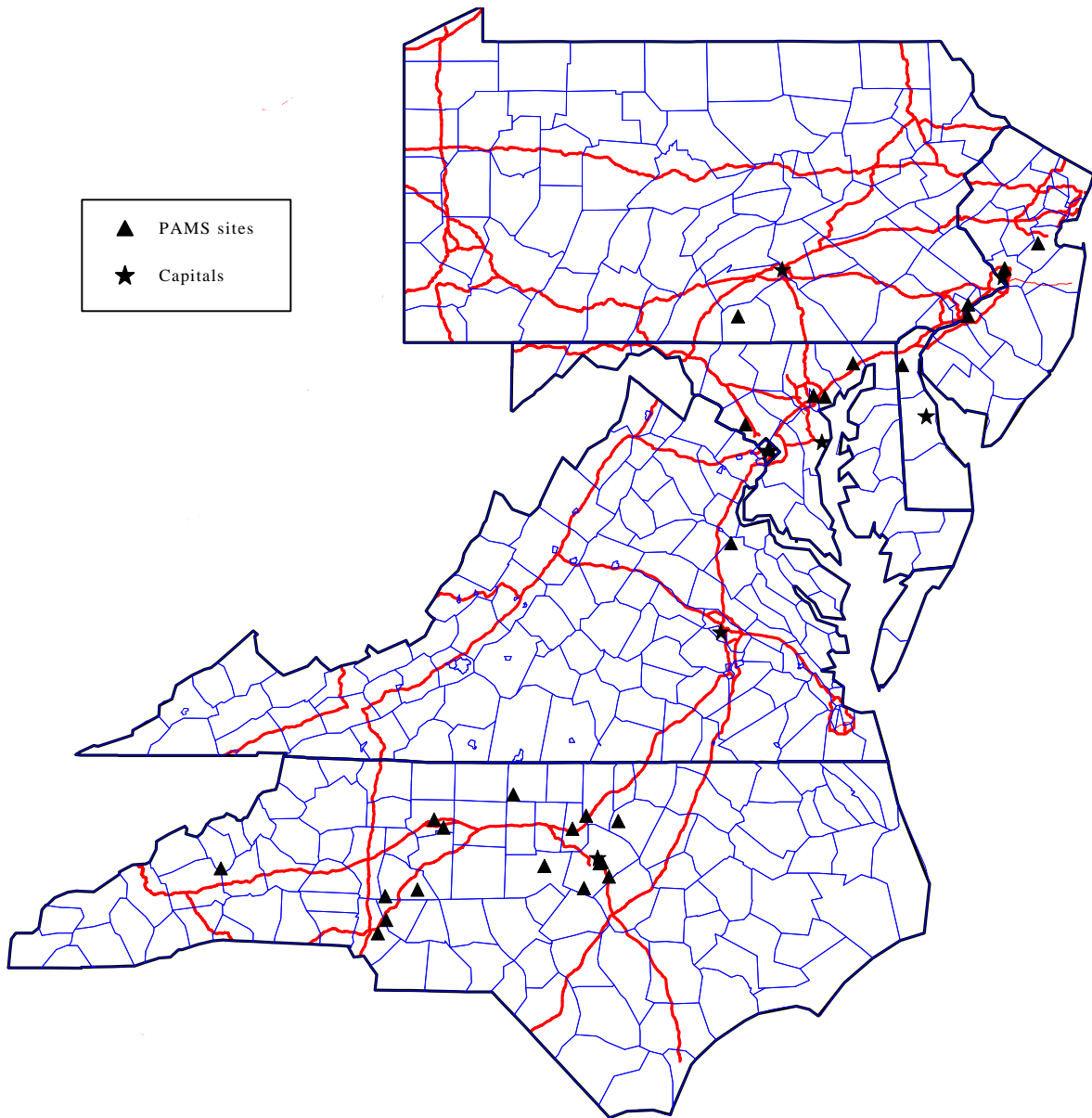


Figure 2-1. Location of PAMS sites in the Mid-Atlantic Region in 1997.
Major highways and state and county boundaries are shown.

Table 2-1. Available VOC data for PAMS and PAMS-like sites in the Mid-Atlantic Region (v=validated).

Site	AIRS Code	Dur.	1995	1996	1997
Rider College, NJ	340210005	1-hr	v ¹	v ⁴	v ⁴
New Brunswick, NJ	340230011	1-hr		v ⁴	v ⁴
Camden, NJ	340070003	1-hr			v ⁴
Philadelphia, PA	421010004	3-hr	v ^{1,2}	v ²	v ⁴
Arendtsville, PA	420010001	1-hr	v ¹	v ⁵	v ⁵
Lums Pond, DE	100031007	1-hr	v ¹	v ⁴	v ⁴
Essex, MD	240053001	3-hr		v ⁴	v ⁴
Baltimore (Lake Clifton), MD ⁶	245100050	1-hr	v ¹	v ⁴	No
Fort Meade, MD	240030019	3-hr	v ¹	v ⁴	v ⁴
Aldino, MD	240259001	3-hr	v ¹	v ⁴	v ⁴
Washington (McMillan Reservoir), DC	110010043	1-hr	v ^{1,2}	v ²	v ⁴
Corbin, VA	510330001	3-hr	v ⁴	v ⁴	v ⁴
North Carolina	various	3-hr	v ³	v ³	v ³

¹ = Obtained from the Coordinating Research Council data validation task (e.g., Main and Haste, 1997)

² = Obtained from EPA Office of Mobile Sources trend analysis (Main et al., 1998a)

³ = Obtained from the North Carolina Division of Air Quality analysis (MacDonald et al., 1998)

⁴ = Obtained from EPA Aerometric Information Retrieval System (AIRS)

⁵ = Obtained from reporting agency; data had not yet been submitted to AIRS

⁶ = The Lake Clifton site did not operate in 1997; the VOC measurements were moved to the Living Classroom site and data were reported beginning in 1998.

No = No VOC data collected.

Table 2-2. Summary of data completeness for the Mid-Atlantic Region (adapted from Main et al., 1999).

Site	Site Type	Data Completeness 1995-1997
Rider College, NJ	3	85-95%
New Brunswick, NJ	1/4	80-89%
Camden, NJ	2	78%
Philadelphia, PA	2	80-96%
Arendtsville, PA	Rural	53-69%
Lums Pond, DE	1/4	83-90%
Essex, MD	2	83-89%
Baltimore (Lake Clifton), MD	2	86-93%
Fort Meade, MD	1/3	68-92%
Aldino, MD	3	89-97%
Washington (McMillan Reservoir), DC	2	63-93%
Corbin, VA	1	80-96%
North Carolina (several sites)	Mix	82-99%

3. DATA ANALYSIS RESULTS

3.1 SPATIAL, TEMPORAL, AND STATISTICAL DISTRIBUTION OF THE PAMS MEASUREMENTS

A description and analysis of the validated PAMS data support control strategy and transport assessment. Control strategy assessment includes an investigation of NO_x versus hydrocarbon controls, hydrocarbon source identification, and identification of hydrocarbons that are specifically important to ozone formation. Further, our aim is to identify the importance of motor vehicle emissions in the region. To aid in these assessments, useful analyses include the statistical description of the data including the spatial and temporal variations, analysis of the age of the air mass using ratio techniques, and an evaluation of the ozone formation potential (photochemical reactivity) of the VOCs.

3.1.1 Overall Characteristics

The analyses should progress from the total nonmethane hydrocarbon (NMHC), to the species groups (i.e., aromatic and unidentified hydrocarbons, olefins, paraffins, carbonyl compounds), to the individual species. It is helpful to have an overall understanding of the database before proceeding to a more detailed analysis. VOC data used in this project are described in Section 2. We focused on 1997 data for most analyses since these data generally are the most complete (i.e., the most valid data) and are most recent (see Haus, 1998 for an analysis focusing on 1996 data). **Table 3-1** summarizes the median total NMHC concentration, unidentified percentage, isoprene percentage, and toluene to benzene ratio at each site (grouped by site type). Our observations follow (these topic areas are further discussed later in this chapter):

- Total NMHC values are an indicator of emission source strength impacting the site. In general, the concentrations were higher at the Type 2 sites than at the other site types. NMHC concentrations were higher at the Fort Meade and New Brunswick sites compared to sites with similar type classifications including Lums Pond, Aldino, and Rider College. Concentrations were lowest at Arendtsville, the most remote site.
- The percentage of "unidentified" species in the total reported NMHC varied across the sites. The unidentified values were computed by taking the difference between the reported NMHC and the sum of the reported identified hydrocarbons. Unidentified compounds can include polar (often oxygenated) species when drying of the samples is not performed, PAMS species that were missed or misidentified, or VOCs not on the target list such as higher molecular weight alkanes and aromatics. Through discussions with the states, we learned that some sites identify and quantify additional hydrocarbons, but do not report them to AIRS, thus the mass associated with these species ends up as "unidentified". Five sites have about 40 percent unidentified (or unreported) mass: Corbin, Fort Meade, Aldino, New Brunswick, and Philadelphia. Because we do not know the ozone formation potential of the unidentified hydrocarbon mass, some analyses are less certain for the sites with high unidentified.

- Isoprene is the only tracer for biogenic emissions that is reported in the PAMS program. We would expect the contribution of isoprene to the NMHC to be higher for more rural sites, even on a 24-hr basis. In general, the isoprene percentage was higher for the non-Type 2 sites, as expected. The highest overall isoprene contribution was at Corbin.
- The toluene/benzene ratio is an indicator of source strength and the proximity of fresh emissions. Toluene reacts away faster in the atmosphere than benzene and, thus, a lower ratio can be an indication of a more aged air mass. We would expect higher ratios for the Type 2 sites and lower ratios for the more rural sites. In general, the toluene-to-benzene ratio was lowest (< 2) at Lums Pond and Arendtsville indicating more aged air.

Another overview of the data is provided in **Table 3-2**. This table lists the median composition at each site by species groups. The paraffins were the most abundant species group at most sites except Corbin, Aldino, Philadelphia, New Brunswick, and Fort Meade, where the unidentified (or unclassified) totals were higher in most of the samples. The aromatic fraction typically exceeded the olefin fraction with the exceptions of Arendtsville, Fort Meade, and Corbin. This may be an indicator of the greater overall importance of isoprene (classified as an olefin) at these three sites.

Another way to compare sites and obtain an overall understanding of the data is to inspect various stratifications of selected hydrocarbons and species groups. The data may be stratified in many different ways: by site, year, month, day of week, weekday/weekend, and time of day. For these stratifications, various statistical descriptions of the PAMS data may be made using meaningful graphical depictions of the data including: box whisker plots; diurnal summary statistics (mean, median, 25th, 75th, 90th percentiles, minimum, maximum); and fingerprint (composition) plots. In box-whisker plots (an example is shown in **Figure 3-1**), the box shows the 25th, 50th (median), and 75th percentiles. The whiskers always end on a data point, so when the plots show no data points beyond the end of a whisker, the whisker shows the value of the highest or lowest data point. The whiskers have a maximum length equal to 1.5 times the length of the box (the interquartile range). If there are data outside this range, the points are shown on the plot and the whisker ends on the highest or lowest data point within the range of the whisker. The “outliers” are also further identified with asterisks representing the points that fall within three times the interquartile range from the end of the box and circles representing points beyond this. These plots are also useful for data validation.

For example, **Figures 3-2 and 3-3** show the diurnal variation of NMHC concentrations at all sites in 1997. Observations include the following:

- At all sites, the NMHC concentrations are higher at night than during the day. This is consistent with the difference in mixing heights between these two time periods (low at night, higher in the day allowing for more dilution of the emissions).
- The variation in the NMHC concentrations with time of day is less at Arendtsville, Lums Pond, Corbin, and Aldino than at the other sites. This may indicate that these sites are less affected by nearby VOC emissions.
- Most of the NMHC concentrations fall below 100 ppbC at the more rural sites of Lums Pond, Corbin, and Arendtsville, and at the Type 3 sites of Aldino and Rider College. This is also an indicator that these sites are less affected by nearby VOC emissions.

However, at Lums Pond, Aldino, and Rider College, air parcels with higher concentrations occasionally impact the sites.

- The majority of NMHC concentrations fall in the 100 to 500 ppbC range at all the Type 2 sites and at New Brunswick. The diurnal variation and concentration levels at New Brunswick are more similar to the Type 2 sites than to the other Type 4 sites.
- At Fort Meade, NMHC concentrations fall between the Type 2 and the data for other site types.

Figure 3-4 illustrates the diurnal variation of NMHC, isoprene, acetylene, and the xylenes at a Type 2 site (Lake Clifton). This plot shows the typical variation in isoprene with time of day. Isoprene emissions are a function of sunlight and temperature and, thus, we would expect higher concentrations during the daylight hours. Acetylene is a key component of motor vehicle exhaust. Acetylene exhibits higher concentrations during the morning and evening than at midday. This diurnal behavior is a function of both emission strength and meteorology. In the morning and at night, the mixing height is lower and higher concentrations can result. Also, emissions are higher during the morning and afternoon commute periods. Xylenes show similar behavior to acetylene.

In contrast to the Type 2 site, **Figure 3-5** illustrates the diurnal variation of the same species at a Type 1/4 site (Lums Pond). The isoprene concentrations are higher and the diurnal variation is more pronounced at this site. Isoprene concentrations peak in the late afternoon in response to a buildup of emissions (function of temperature and sunlight) midday and a decrease in both the photochemical destruction rate and the amount of atmospheric mixing in the early evening. Acetylene concentrations are lower than at the Type 2 sites and appear to be less influenced by nearby sources (i.e., less change with time of day). The xylene concentrations are low and show a more marked decrease at midday, probably indicative of more aged air mass impacting the site.

3.1.2 Abundant Hydrocarbons

There are approximately (depending upon the year and the number of coelutions, etc.) 57 PAMS target species. Many of these species may be at or below the detection limit in most samples. Therefore, individual species analyses should focus on the most abundant species based on concentration and on reactivity-weighted composition. The maximum incremental reactivity (MIR) scale developed by Carter (1994) was used to characterize the reactivity of the samples. The MIR scale provides an estimate of moles ozone formed per mole carbon of each hydrocarbon measured, where the ozone formation estimates are intended to be used in a relative rather than absolute manner. The reactivity of each species is estimated by multiplication of its weight percent or concentration by its MIR factor. Note that a new detailed isoprene-NO_x mechanism has recently been developed that indicates the incremental reactivity of isoprene in urban-like scenarios may be half that predicted by earlier mechanisms (Carter 1996; Carter and Atkinson, 1996). Note also that the unidentified mass can be a significant contributor to the total carbon and its potential reactivity is unknown.

Tables 3-3 and 3-4 list the ten most abundant hydrocarbons on a weight percent basis and on a reactivity-weighted basis, respectively. To determine these lists, the median values of each species over the data set are sorted. We focused on the most recent year of data (1997) for most sites as the most up-to-date assessment of ambient VOC conditions. We also inspected the ten most abundant hydrocarbons for other years and found similar results. Observations from these tables include the following:

- Many of the same species are abundant on a concentration basis at all sites in the tables including ethane, propane, toluene, n-butane, and i-pentane.
- All Type 2 sites also had n-pentane, ethene, and xylenes as abundant species. The Type 1 sites had isoprene in the top 10. Both these findings are consistent with the site characteristics.
- Benzene was less abundant than in the past (e.g., Stoeckenius et al., 1998); it was only present in the top 10 list at three sites. Benzene's decrease in importance probably reflects changes in fuel content (e.g., Main et al., 1998).
- On a concentration basis, the biogenic tracer isoprene is important at the non-Type 2 sites. This is consistent with the emission sources near the sites as we expect Type 2 sites to be dominated by motor vehicle and industrial emissions.
- When reactivity is considered, the increased importance of olefins and aromatic hydrocarbons is illustrated. Ethene, m- & p-xylenes, toluene, i-pentane, and isoprene were in the top ten at every site. At the Type 2 sites, propene and 1,2,4-trimethylbenzene were also abundant. At the Type 1 and 3 sites (except Corbin), 1,2,3-trimethylbenzene was abundant. Many sites added t-2-butene, c-2-butene, or 1-butene to the abundant reactive species list.

Some chemical species are uniquely (or nearly uniquely) associated with a particular source and may be viewed as a “tracer of opportunity”. If an indicator species can be identified for a major source within an urban area, information concerning source contributions may be obtained without the need for sophisticated approaches. Several examples of species which are identified in the PAMS measurements and may be useful in this regard include (Stoeckenius et al., 1994): butane for gasoline evaporative emissions; acetylene, benzene, or aromatic hydrocarbon ratios for motor vehicle exhaust; ethane and propane for natural gas; and isoprene for biogenic emissions (**Table 3-5**). The most abundant species identified at the MARAMA sites indicate that motor vehicle exhaust was very important.

3.1.3 Composition

Ultimately, the composition of the VOC samples are used to try and assess what hydrocarbons are most important in ozone formation and then to try and determine the likely sources of those hydrocarbons. Control strategies can then be developed to target these sources.

We investigated the composition of hydrocarbons (i.e., weight percent) at each site and how the composition varied with time of day. We computed the median weight percent of each species during each sampling period and then plotted these values. The compositions instead of

concentrations are used because it is easier to compare the relative differences among time periods and among sites. Observations from **Figures 3-6 through 3-17** include:

- The weight percent of isoprene was higher at midday and in the afternoon than in the morning at Corbin, Lums Pond, Arendtsville, New Brunswick, Aldino, and Rider College. This is consistent with biogenic emission patterns.
- Even Type 2 sites showed a significant change in isoprene (see McMillan and Essex, for example).
- The composition at Type 2 sites (Philadelphia, McMillan, Lake Clifton, and Essex) showed little change with time of day for anthropogenic hydrocarbons indicating fresh emissions impact the site all day long.
- Reactive species declined relative to less reactive species at midday and in the afternoon at most non-Type 2 sites including Corbin, Arendtsville, New Brunswick, Fort Meade, Aldino, and Rider College. Changes at Camden were more similar to this group than to the other Type 2 sites.
- The i-pentane and n-pentane fractions at Fort Meade were higher in the late afternoon sampling period than during other periods; this pattern was not observed at other sites. Main et al. (1999) noted that concentrations of these species were higher at this site relative to other hydrocarbons but a possible source was not identified.
- The downwind site of Lums Pond showed little change in the composition with time of day, but was generally more aged overall (as evidenced by relatively lower percentages of reactive xylenes and olefins).
- Ethane, propane, i-pentane, and isoprene dominated the composition at Corbin, Lums Pond, Arendtsville, and New Brunswick. This is consistent with the relatively low reactivity of these alkanes compared to most olefins or aromatic hydrocarbons and to the proximity of biogenic emissions.
- At the Camden, Philadelphia, and Essex Type 2 sites, higher fractions of the C6-C8 alkanes and C8+ aromatics were apparent. Also, i-pentane, toluene, and butanes became more prominent than the lighter alkanes (ethane, propane) compared to the other site types. These findings are all consistent with the sites' proximity to emissions sources. Farther downwind, the heavier alkanes and aromatic hydrocarbons would react away faster relative to the lighter alkanes.
- The compositions at Lake Clifton, Aldino, and Rider College appear to be a mixture of the Type 2 characteristics and the Lums Pond characteristics.
- At Essex, 1,2,4-trimethylbenzene was prominent indicating a possible source impacting the site.

3.2 RELATIONSHIPS AMONG SPECIES

We investigated the relationship among the abundant species. Scatter plots can help the analyst understand which species potentially come from the same source, and what the typical ratios are between species or species groups. Graphical depictions for both concentration and

weight percent data for selected species and species groups are necessary to determine the important differences among sites and at a site by time period. It is also instructive to compare the composition of species at source and receptor sites including the diurnal variation in composition, relative age of the air mass at each site, and total reactivity. Investigations of the relationships among important VOC species and species groups, and other pollutants (e.g., ozone, NO_x, wind direction, and temperature) can be made using scatter plot matrices, correlation matrices, and linear regressions.

3.2.1 Scatter Plot and Correlation Matrices

We prepared scatter plot matrices of the ten abundant hydrocarbons at each site (based on each site's reactivity-weighted list). To interpret a scatter plot matrix, locate the row variable (e.g., ispna in **Figure 3-18** near the top left) and the column variable (tolu) on the bottom. The intersection is the scatter plot of the row variable on the vertical axis against the column variable on the horizontal axis. Each column and row are scaled so that data points fill each frame. Scale information is omitted for clarity. The diagonal plots contain histograms of the data for each row variable.

Interesting relationships from the scatter plots included the following:

- In general, the hydrocarbons at Type 2 sites (e.g., McMillan Reservoir, Lake Clifton, Camden—**Figures 3-18 through 3-20**) have stronger correlations than the sites more downwind from sources (e.g., Aldino, Fort Meade, Arendtsville, Corbin —**Figures 3-21 through 3-24**).
- At Rider College (**Figure 3-25**), combustion-related hydrocarbons acetylene and ethene, xylenes, and i-pentane correlate relatively well indicating they are emitted from the same source. The i-pentane versus n-pentane scatter plot shows that while most of the data were from the same source type, there were other sources of i-pentane and/or n-pentane.
- At New Brunswick (**Figure 3-26**), the toluene concentrations showed little correlation with other abundant species indicating a separate, nearby source impacting the site.
- At Philadelphia (**Figure 3-27**), the toluene concentrations correlated relatively well with xylenes, acetylene, and other motor vehicle related hydrocarbons. The i-pentane, n-pentane, and 2-methylpentane concentrations showed a split in the relationships indicating either two unique sources of these hydrocarbons or an analytical issue.
- At Lums Pond (**Figure 3-28**), propane outliers were evident. High propane and propene concentrations were probably from an upwind industrial complex (Main et al., 1999).
- At Essex (**Figure 3-29**), there are strong relationships between many of the motor vehicle related hydrocarbons (such as ethene and 2-methylpentane) with many "outliers" indicating other sources of toluene, i-pentane, xylenes, 1,2,4-trimethylbenzene, etc. Main et al. (1999) noted high concentrations of n-butane and propane and an odd relationship between n-pentane and i-pentane at this site.

CO is emitted as a product of combustion and is widely monitored as a tracer for motor vehicle exhaust. CO measurements are not required as a part of PAMS, but CO data were

reported for a few sites. Unfortunately, most CO monitors in the United States report data in 500 ppb to 1 ppm increments reducing the usefulness of the data for the types of analyses in this report. In the Mid-Atlantic region, CO data from the Camden site were reported at sufficient detail for use in this analysis. **Figure 3-30** shows scatter plots of ethene, toluene, I-pentane, and NMHC concentrations versus CO. Ethene and toluene correlated relatively well ($r^2=0.6$) with CO indicating that exhaust was a significant contributor to ambient concentrations of these two hydrocarbons. On the other hand, i-pentane showed significant non-combustion sources as evidenced by the scatter in the plot and the poor correlation with CO. Correlations with CO for other hydrocarbons included isoprene (poor, $r^2=0.01$), benzene (moderate, $r^2=0.5$), acetylene (moderate, $r^2=0.6$), and the xylenes (good, $r^2=0.7$).

We also performed a Pearson correlation analysis on the morning rush hour(s) data (0500 to 0800 EST). We identified hydrocarbons that exhibited a correlation coefficient, r , of ≥ 0.707 (i.e., accounts for more than 50 percent of the variance). This analysis showed some interesting results:

- At all sites, hydrocarbons associated with exhaust (e.g., acetylene, benzene) and evaporative emissions (e.g., butanes, isopentane) generally showed significant correlations. From the emission-dominated Type 2 sites to the more downwind sites, many of the hydrocarbons appear to be from a common source: motor vehicles.
- At Philadelphia, good correlations between acetylene and benzene and benzene and other aromatic hydrocarbons indicated the importance of motor vehicle exhaust. Good correlations between decane and 1,2,4-trimethylbenzene, toluene, and the xylenes were probably indicative of an industrial signature.
- At Arendtsville and Corbin, many of the hydrocarbons showed significant correlations with each other even though the air masses reaching this site tend to be well aged. More scatter (and thus lower correlation coefficients) was observed in the relationships of more reactive species.
- At Essex, the good correlation between nonane and styrene may be indicative of an industrial source.
- At Aldino and Camden, hydrocarbons associated with industrial sources (e.g., toluene and 2,2,4-trimethylpentane) showed significant correlations.
- At Lums Pond, propane and propene correlated very highly ($r=0.99$) with one another indicating a common source.

3.2.2 Cluster and Factor Analyses

Cluster analysis is a multivariate procedure for detecting natural groupings in data. This analysis provides a graphical depiction of the relationships among data groupings, such as individual hydrocarbon species, samples collected at different sites or time of day, etc. Depending upon the complexity of the hydrocarbon mix at a site, one to several clusters or factors may be needed to account for a majority of the variability in the data. Multivariate analyses are useful for inferring the mix of hydrocarbon sources impacting a receptor location. As shown in Table 3-5, there are several key species (such as acetylene, ethene, ethane, i-butane,

isoprene, benzene, and xylenes) that are helpful tracers of sources. Some of these species may serve as “surrogates” for a broader group of hydrocarbons. Once these surrogates and strong correlations are identified, additional analyses can be simplified by focusing on these fewer parameters.

We ran cluster analyses on most sites including all data and morning only data. Example cluster analysis results for Philadelphia, Essex, and Rider College are shown in **Figures 3-31 through 3-33**. To interpret the figures, consider a vertical line drawn at an arbitrary distance of about 4 in Figure 3-31 (Philadelphia). Dissecting the figure at 4 appears to be a logical break in the number of clusters. (We could just as easily select 6 in this example to reduce the number of clusters to consider.) The species from n-pentane to 2,3-dimethylpentane (a key to species abbreviations is provided in Appendix A) on the figure are clustered together suggesting a common source. These species probably represent motor vehicle emissions, both exhaust (e.g., benzene, ethene, acetylene) and evaporative (e.g., n-pentane). The propane and ethane (natural gas), i-pentane and toluene (motor vehicle and solvent use), 2-methylpentane (motor vehicle and other sources), n-butane (evaporative and consumer products), and propene (exhaust and industrial emissions) concentrations do not cluster with the rest of the data indicating that the species did not behave similarly. Isoprene, a biogenic hydrocarbon, is expected to be in a different cluster from the anthropogenic hydrocarbons, however, its contribution to NMHC in the morning at this site is low. Later in the day, isoprene is in a separate cluster (not shown).

At Essex (Figure 3-32), we chose an arbitrary line at about 3. The hydrocarbons from m- & p-xylene to diethylbenzene form a cluster with motor vehicle exhaust components (e.g., acetylene, ethene) and evaporative emissions (butanes). Other groupings include propane and ethane (natural gas), 1,2,4-trimethylbenzene (unknown, possibly industrial source), and i-pentane and toluene (motor vehicle emissions and solvent use). Other Type 2 sites showed similar groupings.

At Rider College (Figure 3-33), we chose an arbitrary line at about 2.5. Clusters include n-butane through 1,2,3-trimethylbenzene (motor vehicle), isoprene (biogenic), ethane and propane (natural gas), and i-pentane and toluene (motor vehicle, solvents). The results at this site were similar to those at Essex.

3.2.3 Factor Analyses

Principal component analysis (PCA) has been applied as an objective method of removing the highly intercorrelated nature of variations in atmospheric concentrations. The PCA receptor model classifies variables into groups that can then be associated with factors that contribute to pollutant levels at receptors. These factors can be identified as emissions sources, chemical interactions, or meteorological phenomena, depending on the data sets that have been submitted to PCA. Many of these factors indicate more than one possible cause.

Factor analysis was performed on the same data set as the cluster analysis; and factor analysis results were similar to those for the cluster analysis. At Philadelphia (**Figure 3-34**), three factors accounted for about 61 percent of the variance in the data. The first factor contained benzene, toluene, butanes, pentanes, and acetylene (with more than 50 percent of the

variance in these species explained by the factor) and is probably representative of motor vehicle exhaust and evaporative emissions. The second factor contained o-xylene, 1,2,4-trimethylbenzene, undecane, ethyl toluenes, nonane, and other aromatic hydrocarbons and may be indicative of industrial emissions. Factor three contained isoprene and 1-butene indicative of biogenic emissions. These cluster and factor analyses can be repeated for different data sets including: data collected at different times of day rather than all data combined, data collected under selected wind directions or ozone concentrations, weight percent data rather than concentration data, using additional hydrocarbons, using additional air quality parameters such as NO_x or NO, and sample comparisons rather than species comparisons. Additional analyses were beyond the scope of this project.

3.3 ASSESSING THE AGE OF AN AIR MASS

Many of the hydrocarbon species are used as indicators of ozone formation potential and tracers of urban emissions. Assuming that the ratio of these species of interest in the emissions are relatively constant throughout the day, the relative abundance of the more-reactive species (olefins and more-reactive aromatic hydrocarbons such as xylenes) should decrease with time during the daylight hours, and the relative abundance of less-reactive species, such as paraffins and the less-reactive aromatic hydrocarbons, will appear to increase. The ratios of more-reactive species concentrations to less-reactive species concentrations are also useful as indicators of the relative changes in species composition and age. Scatter plots of more-reactive to less-reactive species, diurnal plots of pertinent ratios, and comparisons of nighttime and daytime ratios are useful for investigating mixture age. Comparisons of the ratios among sites can be made to estimate the relative age of air parcels and help provide evidence of transport. In addition, this analysis may present evidence of the presence of fresh emissions or the presence of unique regional sources for a species. Commonly used ratios include xylenes/benzene, toluene/benzene, and ethane/acetylene (Nelson and Quigley, 1983). In this type of analysis, we have found it important to assess several different species ratios and look for consensus among the results. Analytical problems, nearby emissions of selected species, and other factors make it risky to rely upon the results of a single ratio.

While we investigated several different ratios, we have summarized results from two of them: toluene to benzene (T/B) and total xylenes to benzene (X/B). To put these ratios in perspective, consider ratios of these species as measured in urban tunnels. For example, measurements in the Fort McHenry tunnel in Baltimore in 1992 yielded T/B = 1.0 and X/B = 3.1 (Sagebiel et al., 1996). Gertler et al. (1996) reported T/B = 2.5 and X/B = 1.4 for the Lincoln tunnel in New York in 1995. The higher T/B ratio in 1995 versus 1992 may be explained by the decrease in benzene observed in ambient air. The differences in the X/B ratios are probably a function of nearby sources of xylenes. **Table 3-6** lists the median morning ratios observed at the Type 2 sites in the Mid-Atlantic region. It is probably safe to assume that "fresh" emissions representative of the source mixes in these cities exhibit T/B ratios of 2.4 to 3.2 and X/B ratios of 1.2 to 1.6.

Figures 3-35 and 3-36 show the median T/B ratios at all the Mid-Atlantic sites in 1997 as a function of time of day. Observations from these figures include the following:

- At Type 2 sites (see Figure 3-35), there is generally little change with time of day in the ratio. However, the ratios at McMillan and Essex show more diurnal variation (i.e., ratios are higher at night than at the other sites). The ratios at Essex and McMillan are also higher, in general, than at the other sites. This indicates that either there was more toluene, less benzene, or some combination of these in the ambient air compared to the other sites. Note that at these sites, the median ratio never falls below 2.4. These observations are consistent with the site type.
- At the Type 3 sites of Aldino, Fort Meade, and Rider College (see Figure 3-36a), the ratios are similar in magnitude and how they vary with time. The ratios are lower during the daytime (i.e., drop below 2.4), probably due to aging of the air mass. These observations are consistent with the site type.
- At New Brunswick (see Figure 3-36b), the ratio shows relatively little change with time of day and is of a similar magnitude as the Type 2 sites (i.e., in the 2.5 to 3.5 ranges). This is not consistent with the site type. Note that earlier we found a toluene source impacting the New Brunswick site; this is the likely source of the "fresh" T/B ratio.
- At Corbin (see Figure 3-36b), the ratio is similar in behavior with the Fort Meade and other Type 3 sites rather than the more rural sites. The ratios are lower during the daytime (i.e., drop below 2.4), probably due to aging of the air mass. The ratios are higher during the nighttime than at Arendtsville. While these findings are not inconsistent with the site type, we might have expected lower overall ratios indicating more aging.
- At Arendtsville and Lums Pond sites (see Figure 3-36b), the ratios are generally lower overall (i.e., at or below about 2.0) reflecting the more aged air all day with some decline observed at midday due to additional aging. These observations are consistent with the site type.

Figure 3-37 shows the median X/B ratios at all the Mid-Atlantic sites in 1997. Observations from this plot includes the following:

- At the Type 2 sites, the ratios are similar, ranging from about 1 to 2. The ratios at these sites also show a slight decline midday as xylenes react away. Camden ratios show the largest midday decline. The X/B ratio appears to be more sensitive to aging than the T/B ratio. Xylenes are more reactive than toluene and there are fewer sources of xylenes other than motor vehicle emissions.
- Fort Meade, Aldino, and Lums Pond ratios were very similar and showed a pronounced decline midday ($X/B < 1.0$).
- New Brunswick and Rider College ratios are higher at night than Fort Meade, Aldino, and Lums Pond, but also show a marked decline midday.
- At Arendtsville, the xylene concentrations drop below detection in more than half the data midday. The air parcels impacting this site appear to be well aged.
- At Corbin, the magnitude and temporal variation of the X/B ratios seems inconsistent with site. The ratios change less with time of day than we might expect for a Type 1 site. We investigated other ratios including the ethylbenzene to toluene ratio and the propene to ethene ratio and found that these ratios indicated the air mass was relatively aged all

day. Given the results for the toluene to benzene ratio, the consensus view is that the air mass is well aged at Corbin consistent with the PAMS site type.

3.4 NMHC/NO_x

Emission control strategies are based on assessments of whether an area is “VOC-limited” or “NO_x-limited.” Ozone Transport Assessment Group (OTAG) studies concluded that regional NO_x controls are needed, with some local VOC and NO_x controls, in order to reduce ozone concentrations in the domain. Ozone is a secondary pollutant formed by the reaction of nitrogen oxides and hydrocarbons. In the presence of oxygen, and with the stimulus of solar radiation, nitrogen oxides react in the atmosphere to form ozone and nitric oxide (NO). Resultant ozone, however, is quickly reacted away to form nitrogen dioxide (NO₂). Ozone, therefore, cannot accumulate unless VOCs are present to consume or convert NO back to NO₂. The precursors to ozone (i.e., NO_x and VOCs) have both anthropogenic and biogenic origins.

There are several data analysis methods to evaluate the relative sensitivities of peak ozone concentrations to emissions of VOCs and NO_x. These methods all rely on the use of ambient measurements and have been deemed “observation-driven methods” (ODMs). ODMs are used in a diagnostic sense to assess the qualitative response of ozone concentrations to changes in VOC or NO_x concentrations. Specifically, the methods characterize expected responses of peak ozone concentrations at a given time and place to reductions in upwind VOC or NO_x emissions by determining if ozone formation is VOC- or NO_x-limited (Blanchard, 1997).

No single analysis should form the basis for emission control strategy decisions. Rather, several analyses of indicators, the results from previous data analysis tasks in this project, review of results from other projects, and modeling should provide concurrent evidence. Potential indicators include those listed in **Table 3-7**. Data to calculate several of these indicators are available in North Carolina (where NO_y measurements were made) but not in the rest of the region. Typically only morning hydrocarbon data and hourly ozone, NO, and NO_x data were available for investigation. In addition, there are other methods for assessing this issue that were investigated for North Carolina under separate contract (MacDonald et al., 1998), including the smog-production (SP) algorithm. Ambient ozone, NO, and NO_x (or NO_y) concentrations are used to compute the extent of reaction (Blanchard et al., 1994). This project focused only on the morning NMHC/NO_x (or NO_y) ratios.

The ratio of NMHC to NO_x in the morning is an important parameter for photochemical systems. The ratio characterizes the efficiency of ozone formation in NMHC-NO_x-air mixtures. At low ratios (less than 10), ozone formation is slow and inefficient (VOC-limited). Decreasing NO_x levels may result in increased ozone, due to less NO titration of ozone. At high ratios (greater than 15), ozone formation is limited by availability of NO_x rather than VOC. Under transitional regimes, both NO_x and VOC controls may be effective.

Figure 3-38 shows the morning NMHC/NO_y ratios at the North Carolina sites in 1996. In past studies, the data typically show more VOC-limited conditions at the urban influenced sites with the ratios showing more NO_x-limitations farther downwind at rural sites. Most of the

data appeared to fall in the VOC-limited regime with only the bulk of the data at Franklinton appearing in the transitional regime.

Figure 3-39 shows the NMHC/NO_x ratios for the sites in the other MARAMA states that sampled hydrocarbons on an hourly basis. Data were screened for 0600-0800 EST, NO_x concentrations greater than 10 ppb, and NMHC concentrations greater than 100 ppbC similar to analyses by Haus (1998). All the sites indicate that the bulk of the data are in the VOC-limited regime. These results are not surprising for the McMillan Reservoir, Essex, and Lake Clifton urban sites, based on previous studies. Only a few days at Lums Pond had data meeting the screening criteria (none met the criteria at Arendtsville); for those days, the ratio showed VOC-limitations. Similar results were observed for all sites when the data were not screened; even Arendtsville data showed VOC-limitations. The New Brunswick and Rider College data also showed VOC-limitations; however, data at these two sites indicate that a few days were transitional. Additional analyses using other indicator methods and the SP algorithm should be performed to obtain consensus on these results.

3.5 DAY OF WEEK ISSUES

Since we are finding that many of the hydrocarbons measured in the PAMS program are most likely associated with motor vehicle emissions, we would expect the concentrations to be a function of driving patterns. Since traffic patterns largely depend on the Monday-Friday workweek, we might expect to see large differences in hydrocarbon and CO concentrations as a function of day of the week.

Figure 3-40 shows the morning concentrations of CO, a convenient tracer for motor vehicle exhaust, at Camden in 1997 as a function of the day of the week. This figure shows that the morning CO concentrations are significantly lower on the weekend than on weekdays. The morning NMHC concentrations were lower on the weekend at McMillan, New Brunswick, and Lake Clifton (**Figure 3-41**). At Philadelphia, the NMHC concentrations were lower on Sunday and Monday. One explanation for the observations at these sites is that emission source strengths are strong at these sites and, thus, changes are more easily observed. As a contrast, we investigated isoprene concentrations by day of week and found no differences (as expected). At all other sites, no significant differences among the days were observed for morning NMHC concentrations. Additional analyses of individual hydrocarbons could be performed to further investigate this issue.

NMHC/NO_x ratios were higher on the weekend than on weekdays at Essex, McMillan, New Brunswick, and Rider College (**Figure 3-42**). However, ratios were all still in the VOC-limitation range.

3.6 OZONE EPISODE ANALYSIS

We investigated the NMHC concentrations and composition on days when maximum ozone concentrations at the site were greater than or equal to 100 ppb (an "ozone episode") versus days when the maximum ozone concentrations did not reach this level. **Figure 3-43** shows a box plot of the morning NMHC concentrations on "episode" and "non-episode" days at

New Brunswick. The NMHC concentrations were statistically higher on the mornings of high ozone days. We also compared the median compositions on episode versus non-episode days (**Figure 3-44**). The composition, including the species groups and unidentified totals were mostly similar with the exception of a few hydrocarbons including ethene, ethane, propane, n-butane, i-pentane, n-pentane, and isoprene. The higher concentrations of the less reactive paraffin species (i.e., ethane, propane, butanes) may indicate a build up of VOCs overnight. The higher isoprene concentrations in the morning may be a function of temperature, transport, or other physical processes. We also observed higher isoprene concentrations in the northeast on episode days (Dye et al., 1998). This investigation should be expanded to more sites and include a broad range of meteorological analyses (such as synoptic features, upper-air winds, etc.); such analyses were beyond the scope of this project.

3.7 TRENDS

One of the simplest ways to investigate trends in VOCs is to compare the summer morning concentrations of the VOCs from one year to the next. The morning concentrations are suggested because the morning rush hour is the period when ozone precursors accumulate in the atmosphere leading to the highest precursor concentrations and it is more likely that changes will be observed when concentrations are high than when concentrations are low. STI investigated the possible effects of reformulated gasoline (RFG) implementation on ambient VOC (Main et al., 1998). Since fuel benzene, for example, was reduced significantly in RFG (implemented in 1995), the ambient levels of benzene were investigated. There have been many documented changes of benzene levels in fuel, and decreases have been observed in the weight fractions of benzene and benzene ratios (Main et al., 1998). Statistical tests confirmed the differences between the annual means and medians at many PAMS sites in the United States. We expanded upon the trend analysis performed by Main et al. (1998) using the morning benzene concentrations, weight fraction, and ratios; results are provided in **Figures 3-45 and 3-46**.

- At McMillan, the benzene concentrations, weight percent, and ratios showed a significant decrease between 1994 and 1995. The weight percent of benzene and its ratios have stayed about the same since 1995.
- At Philadelphia, a significant decrease in ambient benzene concentrations was also noted between 1994 and 1995. The benzene weight percent shows a continued drop in 1997. Fuel composition data for 1997 should be inspected to corroborate the ambient benzene reductions.
- No trends were observed in benzene concentrations, weight fractions, or ratios at Fort Meade or Rider College for 1995-1997; however, no data were available prior to the change in fuel composition

3.8 PHYSICAL PROCESSES LEADING TO HIGH OZONE

High ozone concentrations in the Mid-Atlantic region and Northeast are the result of a complex interplay between precursor emissions and meteorological conditions. To better understand these factors, a major field study was undertaken in the northeastern United States under the auspices of NARSTO-Northeast. An extensive database of routine and supplemental

surface and upper-air meteorological and air quality observations was compiled as a result of this effort. Several data analysis projects have been performed using data from this field study (e.g., Roberts et al., 1999). Analyses of the field study data were used to prepare the following conclusions regarding important meteorological (physical) conditions in the Mid-Atlantic and Northeast regions:

- Surface air quality and meteorology measurements do not represent air quality and meteorological conditions aloft (above 200 m agl, for example), especially at night. In particular, ozone concentrations aloft at night can be 80-110 ppb when surface concentrations are close to zero, aloft winds can be significantly faster, and aloft wind directions can be different from the surface wind direction.
- Low-level jets generally form at night when a surface-based temperature inversion decouples the aloft air from the surface frictional forces and the air aloft accelerates, as discussed by Blackadar (1957). These jets are observed in the layer above the top of the nocturnal inversion up to about 900 m agl. During NARSTO-Northeast, Clark (1997) showed that the ozone concentrations within these jets can be higher than at the surface. Therefore, analysis of these low-level jets is important to better understand the transport of ozone and ozone precursors in the OTR. Low-level jets can also be caused by other weather phenomena, including approaching fronts, convergence, sloping terrain, lake effects, etc. However, these phenomena are typically not associated with the conditions that produce high ozone levels.
- Low-level jets were observed at one time or another at all of the upper-air monitoring sites throughout the northeastern United States during the summer of 1995. They were observed more frequently, had stronger winds, and lasted longer at the coastal plain sites located east of the Appalachians than at the sites located west of the Appalachians or in the Hudson River Valley. In addition, no evidence of transport across the Appalachians via a low-level jet was observed.
- Low-level jets were observed on most nights preceding a regional ozone episode day at one or more radar profiler sites. In addition, low-level jets were two to three times more likely to be observed on nights preceding an ozone episode day in the OTR than on other nights. This is not surprising, as the low-level jets were most likely to develop when the synoptic meteorological conditions were such that the entire OTR was under the influence of a large surface high-pressure system. Such systems typically produce high ozone concentrations in the region.
- Low-level jets in the OTR may be capable of transporting aloft ozone concentrations of 80-100 ppb or more long distances (up to 300 km or more) within the OTR overnight.
- Slower growing mixed layers can lead to higher afternoon ozone concentrations.
- The observed mixing height structure and evolution during ozone episodes showed significant day-to-day variations. The day-to-day evolution of the mixed layer showed similar diurnal changes, shallow at night, deep during the day, with one important difference: the growth of the mixed layer was slower on high ozone concentration days than on the other days. This slower-growing mixed layer was important because it confined emissions near the surface for a longer time; thus, photochemistry occurred in the presence of higher precursor concentrations. Slower growth rates were one key factor

that produced higher ozone concentrations on the exceedance days. High ozone concentrations during the July 13-15, 1995 episode in the Mid-Atlantic states can also be attributed to the lowering of the subsidence inversion and reduced dilution.

- The photochemical box model base case runs and subsequent sensitivity runs showed higher ozone concentrations on days with slow mixing growth rates and lower ozone concentrations on days with fast mixing growth rates. The model results also showed that when the aloft ozone concentrations are high, ozone concentrations at the surface initially rise more rapidly on fast mixing growth rate days compared to the slow mixing growth rate days. This faster ozone rise at the surface is due to entrainment of higher concentrations of ozone aloft down into the mixed layer.
- Warming and stabilization of the aloft air caused the mixed layer to grow more slowly on exceedance days. Aloft temperature data and weather maps showed that this warming and stabilization was produced mostly by warm-air advection on the backside of the high-pressure system. The theoretical estimates of the mixed layer growth showed a trend similar to the observations (i.e., slower growth on high ozone days) and suggested that the growth rates are primarily controlled by the aloft stability and not by differences in surface heat flux.
- To successfully model ozone, both the meteorological and air quality models must simulate these aloft processes and the resulting mixed-layer evolution.

Section 3

Figures 3-1 to 3-46

Please see the following electronic files:

Section 3 Portrait Figures.PDF

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Table 3-1. Median values based on 1997 valid data collected during all time periods. Exceptions are: Lake Clifton data were collected in 1996, no data were collected in 1997, and North Carolina data were collected only in the morning at most sites.

Site	Site Type	NMHC (ppbC)	Unidentified %	Isoprene %	Toluene/Benzene
Corbin, VA	1	59	41	13	2.2
Lums Pond, DE	1/4	30	15	3.7	1.7
Arendtsville, PA	Rural	23	18	4.1	1.9
Fort Meade, MD	1/3	98	39	3.2	2.4
New Brunswick, NJ	1/4	102	41	2.9	2.9
N. Carolina	Mix	112	21	3.3	3.4
Camden, NJ	2	109	25	0.65	2.8
Essex, MD	2	89	19	1.9	3.3
Lake Clifton, MD	2	115	31	0.55	2.5
McMillan Reservoir, DC	2	173	11	1.4	2.9
Philadelphia, PA	2	210	42	0.93	2.8
Aldino, MD	3	73	43	1.0	2.6
Rider College, NJ	3	45	17	3.4	2.6

Table 3-2. Median values based on 1997 valid data collected during all time periods. Exceptions are: Lake Clifton data were collected in 1996 and no data were collected in 1997.

Site	Site Type	NMHC (ppbC)	Paraffins %	Olefins %	Aromatics %	Unidentified %
Corbin, VA	1	59	24.3	17.3	12.5	41
Lums Pond, DE	1/4	30	52.0	10.7	17.6	15
Arendtsville, PA	Rural	23	44.1	20.0	10.7	18
Fort Meade, MD	1/3	98	34.5	12.2	10.6	39
New Brunswick, NJ	1/4	102	33.4	11.6	11.9	41
Camden, NJ	2	109	50.3	8.3	14.3	25
Essex, MD	2	89	44.5	11.4	22.9	19
Lake Clifton, MD	2	115	40.3	10.3	17.4	31
McMillan Reservoir, DC	2	173	53.7	14.8	19.9	11
Philadelphia, PA	2	210	34.0	8.4	13.6	42
Aldino, MD	3	73	34.9	9.4	11.5	43
Rider College, NJ	3	45	49.4	13.6	17.2	17

Table 3-3. Ten most abundant hydrocarbons (weight percent) at the Mid-Atlantic region PAMS sites in 1997^a. Major sources of these hydrocarbons are provided in Table 3-5.

VOC	Corbin	Lums Pond	Arendts-ville	Fort Meade	New Brunswick	Camden	Philadelphia	McMillan Reservoir	Lake Clifton	Essex	Aldino	Rider College
Site Type	1	1/4	Rural	1/3	1/4	2	2	2	2	2	3	3
Ethane	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Toluene	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
i-Pentane	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Propane	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
n-Butane	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
n-Pentane		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Ethylene			✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
m&p-xylenes		✓			✓	✓	✓	✓	✓	✓		✓
Acetylene	✓			✓			✓		✓		✓	✓
Benzene	✓	✓	✓						✓			
Other	Isoprene 2-m-pentane styrene	isoprene i-butane	isoprene t-2-butene	isoprene 2-m-1-pentene	i-butane isoprene	i-butane	2-m-pentane	2-m-pentane i-butane		2-m-pentane 124-TMB	2-m-1-pentene 224-tm-pentane	isoprene

^a The North Carolina data (morning only, 1997) had the same top ten list as Rider College.

Table 3-4. Ten most abundant hydrocarbons on a reactivity weighted basis at the Mid-Atlantic region PAMS sites in 1997. Major sources of these hydrocarbons are provided in Table 3-5.

VOC	Corbin	Lums Pond	Arendts -ville	New Brunswick	Fort Meade	Camden	Philadelphia	McMillan Reservoir	Lake Clifton	Essex	Aldino	Rider College
Site Type	1	1/4	Rural	1/3	1/4	2	2	2	2	2	3	3
Ethylene	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
m&p-xylenes	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Propene		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Toluene	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
i-Pentane	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Isoprene	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
124-TMB	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓	✓
o-Xylene		✓				✓		✓	✓	✓		✓
123-TMB		✓	✓	✓	✓		✓		✓		✓	✓
Other	Styrene 2-m-pentane propane n-butane	m-ethyl-toluene	t-2-butene c-2-butene 1-butene	t-2-butene c-2-butene	2-m-1-pentene 1-butene	n-butane n-pentane	1-butene 2-m-pentane	t-2-butene 3-m-butene	1-pentene	t-2-butene	2-m-1-pentene 1-butene	n-butane

Table 3-5. Key species and their major sources (from Stoeckenius et al., 1994).

Species	Major Sources	Comments
acetylene, benzene	MV exhaust, combustion	Tracer for vehicle exhaust
ethene	MV exhaust, petrochemical industry	Tracer for vehicle exhaust
ethane	natural gas use	non-reactive
propane	LPG/natural gas use, oil and gas production	Relatively non-reactive, often underestimated in E.I.
i-butane	consumer products, gasoline evap. emissions, refining	Used as replacement of CFCs in consumer products
butane	gasoline evap. emissions	Tracer of gasoline use
isoprene	biogenics	Tracer of biogenics, highly reactive
benzene	MV exhaust, combustion processes, refining	Tracer for vehicle exhaust
toluene	solvent use, refining, mobile sources	one of most abundant species in urban air
olefins	gasoline evap., plastics	reactive
xylenes	solvent use, refining, mobile sources	reactive

Table 3-6. Summary of median ratios (ppbC/ppbC) observed at Type 2 sites in the Mid-Atlantic region on summer mornings in 1997.

Type 2 Site	Toluene/ Benzene	Xylenes/ Benzene
Lake Clifton (1996)	2.4	1.2
Essex	3.1	1.6
Philadelphia	2.7	1.6
Camden	2.9	1.5
McMillan	3.2	1.6

Table 3-7. Threshold values of VOC- or NO_x-limited indicators (afternoon concentrations or ratios).

Indicator	Threshold for NO _x - Limitation	Reference
NO _y	< 10 to 25 ppb	Milford et al., 1994
NO _z	< 5 to 20 ppb	Milford et al., 1994
Ozone/NO _y	> 5 to 10	Sillman, 1995; Jacob et al., 1995
Ozone/NO _z	> 6 to 11	Sillman, 1995; Jacob et al., 1995
(Ozone - 40 ppb)/NO _y	> 4	Sillman, 1995; Jacob et al., 1995
Formaldehyde/NO _y	> 0.2 to 0.4	Sillman, 1995; Jacob et al., 1995
Hydrogen Peroxide/Nitric Acid	> 0.3 to 0.5	Sillman, 1995; Jacob et al., 1995
Hydrogen Peroxide/NO _y	> 0.2 to 0.4	Sillman, 1995; Jacob et al., 1995
Hydrogen Peroxide/NO _z	> 0.2	Sillman, 1995; Jacob et al., 1995
Morning NMOC/NO _x	> 10 to 15	National Research Council (1991)
Afternoon NMOC/NO _x	> 15 to 20	National Research Council (1991)

NO_x = NO + NO₂ + poorly defined fraction of other NO_y species (given conventional analyzers)

NO_y = NO_x + HNO₃ + organic nitrates + inorganic nitrates = NO_x + NO_z

NO_z = Oxidation products of NO_x = NO_y * (1 - NO_x/NO_y)

NMOC = nonmethane organic compounds

4. CONCLUSIONS

VOCs are important contributors to the production of ozone. The PAMS VOC data in the Mid-Atlantic region are of good quality and have proven useful to assess many aspects of air quality in the region. This section summarizes the findings of an analysis of the PAMS VOC data.

4.1 GENERAL CONCLUSIONS

We focused on the 1997 data for most analyses since these data are generally the most complete (i.e., the most valid data) and are most recent (see Haus, 1998 for an analysis focusing on the 1996 data). Our principal conclusions from this analysis were:

- Motor vehicle emissions are the dominant source of VOC at the PAMS sites in the region as evidenced by the relationships among the abundant hydrocarbons, sample compositions, and spatial and temporal analyses.
- Morning NMHC/NO_x ratios for all sites in the Mid-Atlantic region in 1997 generally were VOC-limited indicating that VOC controls may be effective in reducing ozone levels. Decreasing NO_x levels under these conditions may result in increased ozone, due to less NO titration of ozone.
- The data indicate that at some sites, nearby non-motor vehicle related sources significantly impacted the site including possible industrial sources of toluene, pentanes, decane, xylenes, 1,2,4-trimethylbenzene, propane, propene, nonane, and styrene.
- The 1997 data at New Brunswick indicate in several analyses that the site has many more characteristics of a Type 2 or 3 site than a Type 1 or 4 site. Arendtsville appears representative of a Type 1/4 site. All other site classifications appear consistent with the data.

4.1.1 Assess General Characteristics of VOCs

We investigated the general characteristics of the hydrocarbons, progressing from the total NMHC, to the species groups (i.e., aromatic and unidentified hydrocarbons, olefins, and paraffins), to the individual species. Overall, we found the following:

- Total NMHC values are an indicator of emission source strength impacting the site. In general, the concentrations were higher at the Type 2 PAMS sites than at the other site types, as expected. Concentrations were lowest at Arendtsville, the most remote site.
- Benzene was less abundant than in the past; it was only present in the top 10 list at three sites. Benzene's decrease in importance probably reflects changes in fuel content. Benzene concentrations are starting to drop below detection more often and it has dropped off the top ten list at many sites.

4.1.2 Assess Spatial and Temporal Issues

To gain a better understanding of the spatial and temporal variations in the VOC data, we performed many analyses, prepared numerous plots, and investigated statistical summaries of various subsets of the data. We found the following:

- At all sites, the NMHC concentrations are higher at night than during the day. This is consistent with the difference in mixing heights between these two time periods (low at night, higher in the day allowing for more dilution of the emissions).
- The variation in the NMHC concentrations with time of day is less at Corbin, Arendtsville, Lums Pond, and Aldino than at the other sites. In addition, most of the NMHC concentrations fall below 100 ppbC at Corbin, Lums Pond, Arendtsville, Aldino, and Rider College. These findings are indicators that these sites are less affected by nearby VOC emissions. However, at Lums Pond, Aldino, and Rider College, air parcels with higher concentrations occasionally impact the sites showing that transport of ozone precursors can be important.
- On a concentration basis, the biogenic tracer isoprene is important at all sites except the Type 2 sites. This is consistent with the emission sources near the sites as we expect Type 2 sites to be dominated by motor vehicle and industrial emissions.
- The most abundant hydrocarbons identified at the MARAMA sites (e.g., toluene, i-pentane, ethene, xylenes) indicate that motor vehicle exhaust was very important. We need to keep in mind, however, that the PAMS target species list focuses on hydrocarbons that are commonly found in gasoline and gasoline combustion and thus may "skew" our interpretation of the data. For example, diesel combustion products include semi-volatile hydrocarbons that may be important to ozone formation but that are not measurable with the current PAMS sampling and analysis methodology. Oxygenated hydrocarbons, including C4+ carbonyl compounds, also may play a significant role in ozone formation; these species are also not currently quantified.
- The VOC composition at Type 2 sites (e.g., McMillan, Lake Clifton, Essex, and Philadelphia) showed little change with time of day for anthropogenic hydrocarbons, indicating fresh emissions impact the sites all day long.
- The downwind site of Lums Pond showed little change in composition with time of day, but was generally more aged overall (as evidenced by relatively lower percentages of reactive xylenes and olefins).
- Ethane, propane, i-pentane, and isoprene dominated the composition at Corbin, Lums Pond, Arendtsville, and New Brunswick. This is consistent with the relatively low reactivity of these paraffins compared to most olefins or aromatic hydrocarbons and to the proximity of biogenic emissions.
- At the Camden, Philadelphia, and Essex Type 2 sites, higher fractions of the C6-C8 alkanes and C8+ aromatic hydrocarbons were apparent. Also, i-pentane, toluene, and butanes became more prominent than the lighter paraffins (ethane, propane), compared to the other site types. These findings are all consistent with the sites' proximity to emission sources. Farther downwind, the heavier paraffins and aromatic hydrocarbons would react away faster relative to the lighter paraffins.

4.1.3 Investigate Source Identification

Qualitative investigations of the relationships among important VOC species and species groups were made using scatter plot matrices, correlation matrices, and cluster and factor analyses. Our findings include the following:

- At all sites, hydrocarbons associated with exhaust (e.g., acetylene, benzene) and evaporative emissions (e.g., butanes, isopentane) generally showed significant correlations. From the emission-dominated Type 2 sites to the more downwind sites, many of the hydrocarbons appear to be from a common source: motor vehicles.
- Acetylene did not show as strong a relationship with other exhaust species as we have seen in the past. There have been data quality issues in the PAMS network regarding this troublesome hydrocarbon. Ethene may be a better exhaust tracer to use in source apportionment studies when industrial emissions of ethene are not significant. CO may also be a suitable tracer for motor vehicle exhaust when it is reported at sufficient resolution.
- In general, the hydrocarbons at Type 2 sites have stronger correlations with other hydrocarbons (e.g., McMillan Reservoir, Lake Clifton, Camden) than the sites more distant from sources (e.g., Corbin, Aldino, Fort Meade, Arendtsville). Downwind (or far upwind), the hydrocarbons have had more time to react away at different rates and be diluted, thus introducing more scatter in the relationships.
- Sources other than motor vehicle emissions were qualitatively identified at the following sites: a nearby source of toluene impacts the New Brunswick site; there were other sources of i-pentane and n-pentane at Rider College; at Philadelphia, the i-pentane, n-pentane, and 2-methylpentane concentrations showed a split in the relationships, indicating either two unique sources of these hydrocarbons or an analytical issue; also at Philadelphia, good correlations between decane and toluene, the xylenes, and 1,2,4-trimethylbenzene were probably indicative of an industrial signature; at Lums Pond, high propane and propene concentrations were probably from an upwind industrial complex (Main et al., 1999); at Essex, the good correlation between nonane and styrene may be indicative of an industrial source of these species; and at Aldino and Camden, hydrocarbons associated with industrial sources (e.g., toluene and 2,2,4-trimethylpentane) showed significant correlations.

4.1.4 Assess Air Mass Age

The ratios of more reactive species concentrations to less reactive species concentrations are useful as indicators of the relative changes in species composition and age. We found the following from an investigation of toluene/benzene (T/B) and total xylenes/benzene (X/B) ratios:

- At Type 2 sites, there is generally little change with time of day in the ratio of toluene or xylenes (more reactive) to benzene (less reactive). This behavior is consistent with the site type. The T/B ratios at Essex and McMillan sites are higher, in general, than at the other sites. This indicates that either there was more toluene, less benzene, or some combination in nearby emissions and, thus, in the ambient air compared to the other sites.

- At the Aldino, Fort Meade, and Rider College Type 3 sites, the ratios are similar in magnitude and how they vary with time. The ratios are lower during the daytime, probably due to aging of the air mass. These observations are consistent with the site type.
- At New Brunswick, the T/B ratio showed relatively little change with time of day and is of a similar magnitude as the Type 2 sites (i.e., in the 2.5 to 3.5 range). This is not consistent with the site type; we would expect to observe more aging of the air mass at midday.
- At Arendtsville and Lums Pond, both ratios were generally lower overall (i.e., at or below about 2.0) reflecting the more aged air all day with some decline observed at midday due to additional aging. These observations are consistent with the site type.
- At Corbin, the consensus view from a review of several ratios is that the air mass is well aged consistent with the PAMS site type.
- The X/B ratio appears to be more sensitive to aging than the T/B ratio. Xylenes are more reactive than toluene and there are fewer sources of xylenes other than motor vehicle emissions.
- We did not estimate the age of air parcels since these calculations rely upon the use of a T/B or X/B ratio representing fresh emissions. Typically, these ratios are derived from tunnel studies in the region. Due to the apparent differences among cities in the Mid-Atlantic region in these ratios, and the changes from year to year, we did not attempt these estimates using the existing pre-1997 tunnel data.
- The Type 3 sites of Aldino, Fort Meade, and Rider College show evidence of transported VOC emissions (i.e., aged air) during the daytime consistent with their siting criteria. The Type 3 site at New Brunswick, in contrast, shows evidence of fresh emissions all day that mask any transported emissions. The Arendtsville and Lums Pond VOC data show that the air mass is more aged all day indicating transported VOC emissions dominate the sites. At the sites with aged, rather than fresh, VOC, it is reasonable to assume that ozone is likely transported rather than locally generated.

4.1.5 Day Of Week Distributions

Since traffic patterns largely depend on the Monday to Friday workweek, we might expect to see large differences in hydrocarbon concentrations as a function of day of the week. We found the following from an investigation of this issue:

- Morning CO concentrations, another tracer of motor vehicle exhaust, were significantly lower on the weekend than on weekdays at Camden. Data were not available or were insufficiently resolved at other sites.
- The morning NMHC concentrations were lower on the weekend at McMillan, New Brunswick, and Lake Clifton. At Philadelphia, the NMHC concentrations were lower on Sunday and Monday. At all other sites, no significant differences among the days were observed for morning NMHC concentrations. One explanation for the observations at the Type 2 sites is that emission source strengths are strong at these sites and, thus, changes

are more easily observed. As a contrast, we also investigated isoprene concentrations by day of week and found no differences (as expected).

4.1.6 Ozone Episode Distributions

We investigated the possible difference in NMHC concentrations and composition on days with high ozone concentrations versus days that did not experience high ozone at New Brunswick. We found the following:

- The NMHC concentrations were statistically higher on the mornings of high ozone (>100 ppb) days.
- On a species-by-species comparison, we found higher concentrations of the less reactive paraffin species (i.e., ethane, propane, butanes) and isoprene in the morning. The higher concentrations of the paraffins may indicate a build up of VOCs overnight. The higher isoprene concentrations in the morning may be a function of temperature, transport, or other physical processes.

4.1.7 Assess Trends

We expanded upon the trend analysis performed by Main et al. (1998) using the morning benzene concentrations, weight fraction, and ratios. We found the following:

- At McMillan, the benzene concentrations, weight percent, and ratios showed a significant decrease between 1994 and 1995. The weight percent of benzene and its ratios have stayed about the same since 1995.
- At Philadelphia, a significant decrease in ambient benzene concentrations was noted between 1994 and 1995. The benzene weight percent shows an additional drop in 1997. Fuel composition data for 1997 should be inspected to corroborate the ambient benzene reductions.
- No trends were observed in benzene concentrations, weight fractions, or ratios at Fort Meade or Rider College from 1995 to 1997; however, no data were available prior to the change in fuel composition.

4.1.8 Assess NMHC/NO_x Ratios

Emission control strategies are based on assessments of whether an area is “VOC-limited” or “NO_x-limited.” One method for assessing these limitations is to investigate the morning NMHC/NO_x ratios. We found the following:

- Morning NMHC/NO_x ratios for all sites in the Mid-Atlantic region in 1997 generally were VOC-limited.
- NMHC/NO_x ratios were higher on weekends than on weekdays at Essex, McMillan, New Brunswick, and Rider College. However, ratios were all still in the VOC-limitation range.

4.2 MONITORING ISSUES

In the course of performing the analyses discussed in this report, we noted the following issues of interest to the monitoring personnel:

- The 1997 data at New Brunswick indicated in several analyses that the site has many more characteristics of a Type 2 or 3 site than a Type 1 or 4 site. Arendtsville appears representative of a Type 1/4 site. All other site classifications appear consistent with the data.
- CO is a convenient tracer for motor vehicle emissions. From a data analysis standpoint, CO should be measured, with ppb level accuracy and precision, at all PAMS sites.
- Through discussions with the states, we learned that some sites identify and quantify additional hydrocarbons, but do not report them to AIRS, thus, the mass associated with these species ends up as "unidentified". We recommend that the monitoring agencies report all identified species. As noted at a recent MARAMA-sponsored meeting, the PAMS list is intended to provide guidance as to a minimal list of species to monitor; the list of species to be reported to AIRS is not "set in stone".
- The unidentified (or unreported) concentrations were highest overnight at Philadelphia. Speciation of these data should be attempted to help identify likely sources of these hydrocarbons.
- Likely sources for the hydrocarbons noted as non-motor vehicle should be investigated (e.g., 1,2,4-trimethylbenzene at Essex).
- The monitoring agencies should continue their excellent work in improving laboratory analysis and data validation.

4.3 FUTURE ANALYSES

As in any data analysis project, there are other analyses, or more in-depth analyses that could not be performed due to budget, time, or data constraints. We recommend that the following analyses be considered in the future with the Mid-Atlantic data:

- Repeat cluster and factor analyses for different data sets including: data collected at different times of day rather than all data combined; data collected under selected wind directions or ozone concentrations; weight percent data rather than concentration data; those using additional hydrocarbons; those using additional air quality parameters such as NO_x or NO; and sample comparisons rather than species comparisons.
- Perform additional analyses regarding VOC- and NO_x-limitations using other indicator methods and the SP algorithm to obtain consensus on the results. Data for input to the SP algorithm (ozone, NO_x) are available for a broader geographic range than the PAMS data alone.
- Perform additional analyses regarding VOC concentrations and composition on episode versus non-episode days including more sites and the use of a broad range of meteorological analyses (such as synoptic features, upper-air winds, etc.).

- Assess the spatial and temporal variations in carbonyl compounds including their relative abundance, contribution to total carbon, and possible sources.
- Perform more quantitative source identification including source apportionment using the chemical mass balance model. Up-to-date and city-specific source profiles will be important to the success of this analysis.
- Expand the day of week distribution analysis to include a broader range of hydrocarbons and ratios.

Note that some of these recommended analyses were performed using the 1995 data in a project sponsored by the Coordinating Research Council (see Stoeckenius et al., 1998; Fujita and Liu, 1998; and Blanchard, 1997).

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APPENDIX A

HYDROCARBON ABBREVIATIONS USED IN THIS REPORT

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Table A-1. AIRS code, abbreviation, hydrocarbon name, and species group (O=olefin, P=paraffin, A=aromatic).

AIRS code	Abbreviation	Hydrocarbon	Species Group
43206	acety	Acetylene	O
43203	ethyl	Ethylene	O
43202	ethan	Ethane	P
43205	prpyl	Propylene	O
43204	propa	Propane	P
43214	isbta	Isobutane	P
43280	1bute	1-Butene	O
43212	nbuta	n-Butane	P
43216	t2bte	trans-2-Butene	O
43217	c2bte	cis-2-Butene	O
43282	3mlbe	3-Methyl-1-Butene	O
43221	ispna	Isopentane	P
43224	1pnte	1-Pentene	O
43220	npnta	n-Pentane	P
43243	ispre	Isoprene	O
43226	t2pne	trans-2-Pentene	O
43227	c2pne	cis-2-Pentene	O
43228	2m2be	2-Methyl-2-Butene	O
43244	22dmb	2,2-Dimethylbutane	P
43283	cypne	Cyclopentene	O
43234	4mlpe	4-Methyl-1-Pentene	O
43242	cypna	Cyclopentane	P
43284	23dmb	2,3-Dimethylbutane	P
43285	2mpna	2-Methylpentane	P
43230	3mpna	3-Methylpentane	P
43246	2m1pe	2-Methyl-1-Pentene	O
43231	nhexa	n-Hexane	P
43289	t2hex	trans-2-Hexene	O
43290	c2hex	cis-2-Hexene	O
43262	mcpna	Methylcyclopentane	P
43247	24dmp	2,4-Dimethylpentane	P
45201	benz	Benzene	A
43248	cyhxa	Cyclohexane	P
43263	2mhxa	2-Methylhexane	P
43291	23dmp	2,3-Dimethylpentane	P
43249	3mhxa	3-Methylhexane	P
43250	224tmp	2,2,4-Trimethylpentane	P
43232	nhept	n-Heptane	P
43261	mcyhx	Methylcyclohexane	P
43252	234tmp	2,3,4-Trimethylpentane	P

Table A-1. AIRS code, abbreviation, hydrocarbon name, and species group (O=olefin, P=paraffin, A=aromatic).

AIRS code	Abbreviation	Hydrocarbon	Species Group
45202	tolu	Toluene	A
43960	2mhpe	2-Methylheptane	P
43253	3mhpe	3-Methylheptane	P
43233	noct	n-Octane	P
45203	ebenz	Ethylbenzene	A
45109	m/pxy	m/p-Xylene	A
45205	mxyl	m-Xylene	A
45206	pxyl	p-Xylene	A
45220	styr	Styrene	A
45204	oxyl	o-Xylene	A
43235	nnon	n-Nonane	P
45210	ispbz	Isopropylbenzene	A
45209	npbz	n-Propylbenzene	A
43256	apine	alpha-Pinene	O
45207	135tmb	1,3,5-Trimethylbenzene	A
45208	124tmb	1,2,4-Trimethylbenzene	A
43257	bpine	beta-Pinene	O
45211	oetol	o-Ethyltoluene	A
45212	metol	m-Ethyltoluene	A
45213	petol	p-Ethyltoluene	A
45218	mdeben	m-diethylbenzene	A
45219	pdeben	p-diethylbenzene	A
45225	123tmb	1,2,3-trimethylbenzene	A
43238	ndec	n-Decane	P
43954	nundc	n-Undecane	P
43102	tnmoc	Total Non-Methane Organic Compounds	
43502	form	Formaldehyde	C
43503	aceta	Acetaldehyde	C
43551	acet	Acetone	C
43218	13buta	1,3-butadiene	O
43225	2m1bte	2-methyl-1-butene	O
43295	3ethex	3-ethylhexane	P
43955	25mhex	2,5-dimethylhexane	P
43293	hex24m	2,4-dimethylhexane	P
43294	hex23m	2,3-dimethylhexane	P
43222	propa22m	2,2-dimethylpropane	P
43270	ibute	Isobutene	O
43240	mcpne	Methylcyclopentene	O
43395	4mhpte	4-Methylheptane	P
43000	pamshc	Sum PAMS Target Species	

APPENDIX B

REVISED LIST OF FLAGGED SAMPLES FOR CORBIN, VIRGINIA AND PHILADELPHIA, PENNSYLVANIA 1995-1997

This appendix contains tables that list the samples and individual hydrocarbons that were flagged as suspect (S) or invalid (I). Data validation, when done well, is labor-intensive. To assess the validity of the data, we inspected a time series plot of every species, prepared numerous scatter plots and scatter plot matrices, including a plot of every species and species group versus the total NMHC, and inspected the fingerprint plot of every sample. Our strategy is to flag entire samples when we identify a problem with two or more of the most abundant species (e.g., toluene, i-pentane, n-pentane, i-butane, n-butane, benzene, acetylene, ethane, xylenes, ethene). We also flag samples when only one hydrocarbon has been identified as problematic if that hydrocarbon represents a significant portion of the total NMHC (e.g., more than 20 percent). Individual species are flagged as suspect when there are problems noted, but the concentration of the hydrocarbon is low compared to other species in the sample. *Data are flagged that do not fit our conceptual model of ambient VOC concentrations and relationships.* In some cases, the samples may have an analytical error that needs to be corrected, may have a sampling problem that was inadvertently missed, or may just appear odd. Upon review of the data by the reporting agencies, some suspect data may be deemed invalid, some data may be reprocessed and re-reported by the agency, and other data may remain suspect (cause unknown). *These latter samples remain flagged in our working database and in this report for the attention of data analysts.*

The tables in this appendix are set up as follows:

- Date/time = Date and hour (ST) of sample(s) flagged
- QC = the quality control code of S (suspect) or I (invalid). Invalid flags were typically only applied by the reporting agencies. For a sample or individual hydrocarbon to be flagged as invalid, a documented reason needed to be provided (e.g., instrument failure, known contamination, data not representative of ambient air such as calibration gas, etc.).

- Record/HC = A designation of the individual hydrocarbon (HC) or the entire sample record (record) to which the flag applies.
- No. = The number of samples flagged with the same code and reason (generally for the same date and used to shorten the list).
- Comments regarding why samples were flagged.
- Also included at the bottom of the files are comments for future data analysts that discuss additional observations of the data that may have a bearing on planned analyses or conclusions from the data.

We have provided two tables for the sites for which we have information. One table lists the samples that we originally flagged but that have subsequently been revised and resubmitted to AIRS. This table is provided as a check for data analysts who obtain their data from AIRS to ensure that they have the most up-to-date data file available. The second table lists the samples that we flagged for which no changes were made by the monitoring laboratory but that from a data analyst's point of view, do not fit our conceptual model of ambient hydrocarbon data. We typically recommend that these flagged data not be used in "over-arching" analyses (such as summary statistics) but be considered on a case study basis.

Table B-1. List of samples flagged as suspect by STI for Corbin, Virginia in 1995.

Date	Hour (ST)	QC	Record/HC	No.	Comments
5/3/95	17:00	S	ispna	1	low concentration
5/3/95	23:00	S	npnta	1	low concentration
5/6/95	2-23	S	Record	8	zero paraffins, several samples with same concentration isoprene
5/15/95	2, 5	S	Record	2	zero paraffins, several samples with same concentration isoprene
5/15/95	8:00	S	ethyl, prpyl	1	low concentration
5/15/95	11:00	S	isbta, ethyl, prpyl	1	zero or low concentration
5/15/95	14:00	S	Record	1	high concentration several species
5/15/95	17:00	S	Record	1	zero aromatics
5/15/95	23:00	S	Record	1	zero or low concentration several abundant species
5/18/95	11:00	S	2m1pe	1	high concentration
5/18/95	14:00	S	2m1pe	1	high concentration
5/21/95	14:00	S	ispna	1	low concentration
5/24/95	2:00	S	npnta	1	low concentration
6/8/95	14:00	S	Record	1	Odd low most species, higher prope
6/8/95	17:00	S	npnta	1	low concentration
6/14/95	2:00	S	npnta	1	zero
6/14/95	14:00	S	prpyl	1	low concentration
6/20/95	14:00	S	ispna, npnta	1	zero
7/5/95	23:00	S	t2bte	1	high concentration
7/17/95	5:00	S	Record	1	odd low most species high isbta
8/1/95	17:00	S	1bute	1	low concentration
8/1/95	20:00	S	ethan, 1bute	1	low concentration
				30	
					30 samples flagged
					136 samples total

Table B-2. List of samples flagged as suspect by STI for Corbin, Virginia in 1996.

Date/Hour (ST)	QC	Record/HC	No.	Comments
5/21/96 2:00	S	isbta	1	Low concentration
5/24/96 2:00	S	isbta	1	Low concentration
6/5/96 17:00	S	isbta	1	Low concentration
6/8/96 17:00	S	isbta, npnta	1	Low concentration
6/8/96 20:00	S	isbta, npnta	1	Low concentration
6/11/96 17:00	S	isbta, npnta	1	Low concentration
6/14/96 2:00	S	oxyl	1	Low concentration
6/17/96 5:00	S	isbta	1	Low concentration
6/17/96 8:00	S	isbta	1	Low concentration
6/17/96 17:00	S	isbta	1	Low concentration
6/17/96 20:00	S	isbta	1	Low concentration
6/17/96 23:00	S	isbta	1	Low concentration
6/20/96 8:00	S	isbta	1	Low concentration
6/20/96 14:00	S	isbta	1	Low concentration
6/20/96 17:00	S	isbta	1	Low concentration
6/20/96 20:00	S	isbta	1	Low concentration
7/5/96 20:00	S	npnta	1	Low concentration
7/11/96 11:00	S	nundc	1	High concentration
8/4/96 2:00	S	tolu	1	Low concentration
8/22/96 20:00	S	acety	1	Low concentration
9/3/96 2:00	S	tolu	1	Low concentration
9/3/96 14:00	S	npnta, tolu	1	Low concentration
9/12/96 23:00	S	Record	1	Missing several species
Also noted several samples with high concentrations of n-propylbenzene - possible source?				
Several samples with low concentrations of abundant species may just be low sample concentration.				

Table B-3. List of samples flagged as suspect by STI for Corbin, Virginia in 1997.

Date/Hour (ST)	QC	Record/HC	No.	Comments
06/21/1997 2:00	S	Record	1	Missing most species
06/21/1997 17:00	S	isbta	1	Low concentration
06/24/1997 2:00	S	isbta	1	Low concentration
06/24/1997 20:00	S	isbta	1	Low concentration
07/06/1997 14:00	S	benz	1	High relative to toluene
07/09/1997 14:00	S	benz	1	Low concentration
07/09/1997 17:00	S	isbta, benz	1	Low concentration
07/15/1997 14:00	S	isbta	1	Low concentration
07/15/1997 20:00	S	isbta	1	Low concentration
07/15/1997 23:00	S	isbta	1	Low concentration
07/27/1997 17:00	S	oxyl	1	Low concentration
08/08/1997 20:00	S	npnta	1	Low concentration
08/26/1997 23:00	S	benz	1	High relative to toluene
09/16/1997 17:00	S	benz	1	High relative to toluene
09/25/1997 17:00	S	npnta	1	Low concentration
09/25/1997 20:00	S	npnta	1	Low concentration
09/28/1997 5:00	S	benz	1	High relative to toluene
			17	
Flagged 17 of 294 samples				

Table B-4. Revised list of suspect and invalid samples for 1994-1997 Philadelphia, PA hydrocarbon data.

Date	Hour (ST)	QC	Record/HC	No.	Comments	
940607	20	S	sample	1	High concentration	
940729	8	S	c2hex	1	High concentration	
940811	17	S	prpyl	1	High concentration	
940823	8	S	c2pne	1	High concentration	
950620	5	S	mcpnta	1	high concentration of this species compared to rest of data	
950624	8-14	S	sample	3	possible cold trap failure based on low ethane concentrations	
950626	14	S	n-hexane	1	High concentration	
950707	2	S	propene	1	high concentration	
950708	2	S	propene	1	high concentration	
950804	2	S	propene	1	High concentration	
950814	23	S	sample	1	Possible cold trap failure based on low ethane concentration	
950828	5	S	aceta	1	High concentration	
960616	17	S	1pnte	1	High concentration	
960617	02, 20	S	1pnte	2	High concentration	
960619	8	S	1pnte	1	High concentration	
960708	5	S	c2bte	4	High concentration	
960712	2	S	1pnte	1	High concentration	
960713	8	S	1pnte	1	High concentration	
960714	5	S	c2bte	1	High concentration	
960726	5	S	c2bte	1	High concentration	
960808	17	S	sample	1	ispnta concentration = 0	
960809	14	S	sample	1	High concentration	
960820	14	S	sample	1	High concentration	
960821	14, 20	S	sample	2	High concentration	
960822	20	S	sample	1	High concentration	
960823	17, 23	S	sample	2	High concentration	
960824	17	S	sample	1	High concentration	
960827	14-20	S	sample	3	High concentration	
960829	11	S	sample	3	High concentration	
970625	23:00	S	mcpna	1	Low concentration	
970707	20,23	S	2mpna	2	Low concentration	
970723	14:00	S	m/pxy	1	Low concentration	
970810	5:00	S	ispna	1	Low concentration	
970816	20:00	S	oxyl	1	Low concentration	
970816	23:00	S	ispna	1	Low concentration	
970816	2,8	S	ispna	2	Low concentration	
The following data have been revised and resubmitted to AIRS						
Date	Hour (ST)	QC	Record/HC	No.	Comments	Revised QC
940606	14, 17	S	3m1be	2	Coelutes with acetonitrile	I
940618	11-20	S	3m1be	4	Coelutes with acetonitrile	I
940624	11-23	S	3m1be	5	Coelutes with acetonitrile	I
940625	2-23	S	3m1be	8	Coelutes with acetonitrile	I
940706	11-20	S	3m1be	4	Coelutes with acetonitrile	I
940712	11-20	S	3m1be	4	Coelutes with acetonitrile	I
940730	11-20	S	3m1be	4	Coelutes with acetonitrile	I
940805	11-20	S	3m1be	4	Coelutes with acetonitrile	I
940817	08, 14-23	S	3m1be	5	Coelutes with acetonitrile	I
940823	14-23	S	3m1be	4	Coelutes with acetonitrile	I
940829	08, 14- 20	S	3m1be	4	Coelutes with acetonitrile	I
1994 (52 of 630 samples flagged)						
1. Other problems noted include t-2-pentene apparent detection limit of about 1 ppbC; 2-m-2-butene high concentrations were high when t-2ptene was high.						
1995 (9 of 735 samples flagged)						
1996 (27 of 730 samples flagged)						
1. Odd high concentrations of olefins flagged.						
1997 (9 of 445 samples flagged)						
1. Some species were flagged low concentrations.						