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SOUTHEASTERN AIR TOXICS DATA ANALYSIS

FINAL REPORT
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EXECUTIVE SUMMARY

This report summarizes the methodology and preliminary results for analyses of ambient air toxics concentrations in the Southeast. Analyses included preparing visual and statistical data displays of the variability of air toxics concentrations in the southeastern states over time and between sites, as well as performing trends analysis, geographic comparisons, and comparison of ambient data to the 1999 National Air Toxics Assessment (NATA99) model predictions. Overall, several findings are considered most significant:

- *Comparison of Southeastern Concentrations to National Concentration Ranges*
  - The concentration ranges of most pollutants in the Southeast were very similar to those observed in other parts of the country.
- *Risk and Hazard Screening*
  - Some key risk drivers identified in NATA99 are not measured well enough at many sites in the southeast to determine risk using ambient monitoring data. These key pollutants include 1,3-butadiene, cadmium (all particle size fractions), tetrachloroethylene, ethylene dibromide, ethylene dichloride, 1,1,2,2-tetrachloroethane, and 1,4-dichlorobenzene.
- *Trends in Air Toxics Concentrations in the Southeast*
  - Aromatic hydrocarbon mobile source air toxics (MSATs) concentrations are decreasing at most sites.
  - Trends in trace metal concentrations are correlated with changes in method detection limit (MDL) and methodology that are network-specific. These trends are unlikely to reflect actual trends in ambient concentrations. Sophisticated trends analysis that can account for changes in the MDL over time may be needed to determine how concentrations are changing for these pollutants.
- *Spatial Variability*
  - Large differences in sampling and analysis methodology and MDLs between reporting agencies and networks confound the spatial variability analysis. These differences confound quantitative comparisons of spatial variability.
    - Volatile organic compound (VOC) methods and MDLs vary among jurisdictions.
    - $PM_{2.5}$ metals methods and MDLs are monitoring network-dependent (e.g., Interagency Monitoring of Protected Visual Environments [IMPROVE] versus Speciation Trends Network [STN]); the sites in different networks are selected differently and represent different areas (urban vs. rural).
- *Comparison of Ambient Data to Model-Predicted Concentrations From NATA99*
  - Some pollutants were predicted well in NATA99 for the southeastern states, including acetaldehyde, benzene, dichloromethane, ethylbenzene, n-hexane, toluene, and nickel $PM_{2.5}$. Other pollutants were either underpredicted by the model or are not measured well enough to make a comparison.

- *MDL Comparison*
  - The MDLs of many key pollutants were higher in the Southeast than in other areas of the country. Steps need to be taken to lower MDLs for these air toxics.

A key recommendation from this work is that interlaboratory comparisons or regionally (or nationally) consistent sampling and analysis standards need to be implemented to promote consistency of data reported by different networks and agencies.

The specific task objectives and key findings from each task are summarized below in Sections ES.1 through ES.6.

ES.1 COMPARISON OF SOUTHEASTERN CONCENTRATIONS TO NATIONAL CONCENTRATION RANGES

Air toxics concentration ranges in the Southeast were compared to concentrations in the entire United States. Key questions addressed included "Are there unique pollutant issues in the Southeast?"; "Are concentrations typically higher, lower, or the same as the rest of the country?"

- The concentration ranges of most pollutants in the Southeast were very similar to those observed in other parts of the country.
- Variation in pollutant concentration ranges in the Southeast was often comparable to variations observed across the country as a whole. For most air toxics, concentrations varied by a factor of 3 to 10 across the Southeast.
- Concentrations of a few pollutants in the Southeast appeared to be significantly lower relative to those on a national scale; these pollutants included manganese PM_{10}, acetone, and propylene. The reason for these differences was not investigated.

ES.2 RISK AND HAZARD SCREENING

Air toxics were identified that had concentrations exceeding U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS) chronic human health benchmarks throughout the Southeast. Pollutants that were characterized as national or regional risk drivers or contributors in the NATA99 were compared to the air toxics in the Southeast that contribute to risk.

- Concentrations of some key risk drivers identified in NATA99 are not measured well enough, as reflected in the ambient monitoring data, to determine risk at most sites. These pollutants include 1,3-butadiene, cadmium (all particle size fractions), tetrachloroethylene, ethylene dibromide, ethylene dichloride, 1,1,2,2-tetrachloroethane, and 1,4-dichlorobenzene.
- Among pollutants that are characterized well, many pollutants were in reasonable agreement with model predicted risk from NATA99. For example, benzene, arsenic $PM_{2.5}$, carbon tetrachloride, and acetaldehyde were above the cancer benchmark at every site where they were monitored well enough to make a characterization. However, some pollutants considered likely risk drivers at a national level by NATA99 had concentrations that did not exceed cancer benchmark values at most sites in the

Southeast, for example, chromium VI, most of the particulate organic matter (POM), Bis(2-ethylhexyl)phthalate, dichloromethane, and trichloroethylene.

- Additional pollutants not mentioned in NATA99 as risk drivers or contributors that may contribute to risk in the Southeast include 1,2-dichloropropane, 1,1,2-trichloroethane, hexachlorobutadiene, benzyl chloride, and bromoform. However, these pollutants are all poorly characterized. Better sampling and analytical methodologies are needed to characterize the risk associated with these pollutants (i.e., MDLs need to be lower than health benchmarks).
- Most species did not exceed noncancer reference concentrations at sites in the Southeast. Only a few pollutants exceeded noncancer reference concentrations at any site. Noncancer hazard appears to be a local issue.
- Two species were uncharacterizable for noncancer hazard screening: acrolein and 1,2-dibromo-3-chloropropane. Acrolein is the primary noncancer hazard driver nationwide. Better sampling and analytical methods must be employed to estimate the hazard from this key pollutant.

ES.3 TRENDS IN AIR TOXICS CONCENTRATIONS IN THE SOUTHEAST

The task was to investigate concentration trends in air toxics at individual sites and in aggregate across the Southeast. It was important in this analysis to identify pollutants and sites showing trends that were highly variable and "suspect", often due to changes in methods or MDLs, rather than trends that reflect real changes in ambient concentrations.

- Aromatic MSAT concentrations appear to be decreasing at most sites; this decrease is consistent with predominant trends in MSATs observed at urban sites across the United States.
- Trends in trace metal concentrations in particulate matter less than 2.5 microns ($PM_{2.5}$) are correlated with changes in MDLs and methodology that are network-specific. These trends are unlikely to reflect actual trends in ambient concentrations. Sophisticated trends analysis that can account for changes in the MDL over time may be needed to determine how concentrations are changing for these pollutants.
- These trends should be considered a preliminary compilation of trend values only. Individual site trends need to be verified as reflective of true ambient concentrations at the state or local level.

ES.4 SPATIAL VARIABILITY

The task was to characterize spatial variability in air toxics concentrations across sites using visual inspection of maps and statistical metrics.

- Large differences in sampling and analytical methodology and MDLs between reporting agencies and networks confound this analysis.
  - Volatile organic compound (VOC) methods and MDLs vary among jurisdictions (e.g., between states and/or agencies).

- $PM_{2.5}$ metals methods and MDLS are monitoring network-dependent (e.g., Interagency Monitoring of Protected Visual Environments [IMPROVE] vs. Speciation Trends Network [STN]).

- VOCs appear to have a wider range of spatial variability across pollutants compared to metals and carbonyl compounds. It is unclear if this is due to real spatial differences or due to sampling and analytical differences across reporting agencies.
- A key recommendation from this work is that interlaboratory comparisons or regionally (nationally) consistent sampling and analysis standards need to be implemented to promote consistency of data reported by different networks or agencies.

ES.5 COMPARISON OF AMBIENT DATA TO MODEL-PREDICTED CONCENTRATIONS FROM NATA99

Ambient monitored concentrations in the Southeast were compared to NATA99 model-predicted concentrations at the Census tract level.

- Some pollutant concentrations were predicted well in NATA99 for the southeastern states, including acetaldehyde, benzene, dichloromethane, ethylbenzene, n-hexane, toluene, and nickel $PM_{2.5}$.
- No pollutants were monitored that were systematically overpredicted (model-to-monitor ratio > 2) by NATA99.
- Other pollutant concentrations were usually underpredicted (model-to-monitor ratio <0.5) by NATA99, including arsenic $PM_{2.5}$, chloroform, chromium $PM_{2.5}$, hexachlorobutadiene, lead ($PM_{2.5}$ and TSP), manganese $PM_{2.5}$, and selenium $PM_{2.5}$. Lead TSP may be underpredicted because it is often monitored close to a source and model resolution is not sufficient to characterize these near-source gradients.

ES.6 MDL COMPARISON

MDL values in the Southeast were assessed to determine if the southeastern MDLs were lower, the same, or higher than MDL values in the rest of the nation. The analyses focused on pollutants for which risk screening indicated a large fraction of sites had MDLs that were too high relative to health benchmarks to characterize risk at the one-in-a-million level.

- The MDLs of many pollutants identified as uncharacterizable in the Southeast were higher than those in other parts of the country.
- Some sampling and analytical methods were identified with MDLs below the relevant EPA OAQPS health benchmark. These alternative methods may be a reasonable way to achieve monitoring objectives for air toxics.
- Some pollutants had no reported sampling or analytical methods with MDLs lower than the health benchmark. These pollutants include key risk or hazard drivers such as acrolein, 1,1,2,2-tetrachloroethane, and ethylene dibromide. Better methods for measuring these pollutants may need to be developed (or are in development) to characterize risk.

1. INTRODUCTION

This project involved acquiring, processing, and analyzing air toxics data gathered from 1990 through 2005 in the states of Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, and Tennessee, the states that constitute the Southeastern States Air Resources Managers, Inc. (SESARM) region (see **Figure 1-1**). Sonoma Technology, Inc. (STI) performed a series of related tasks during the project.

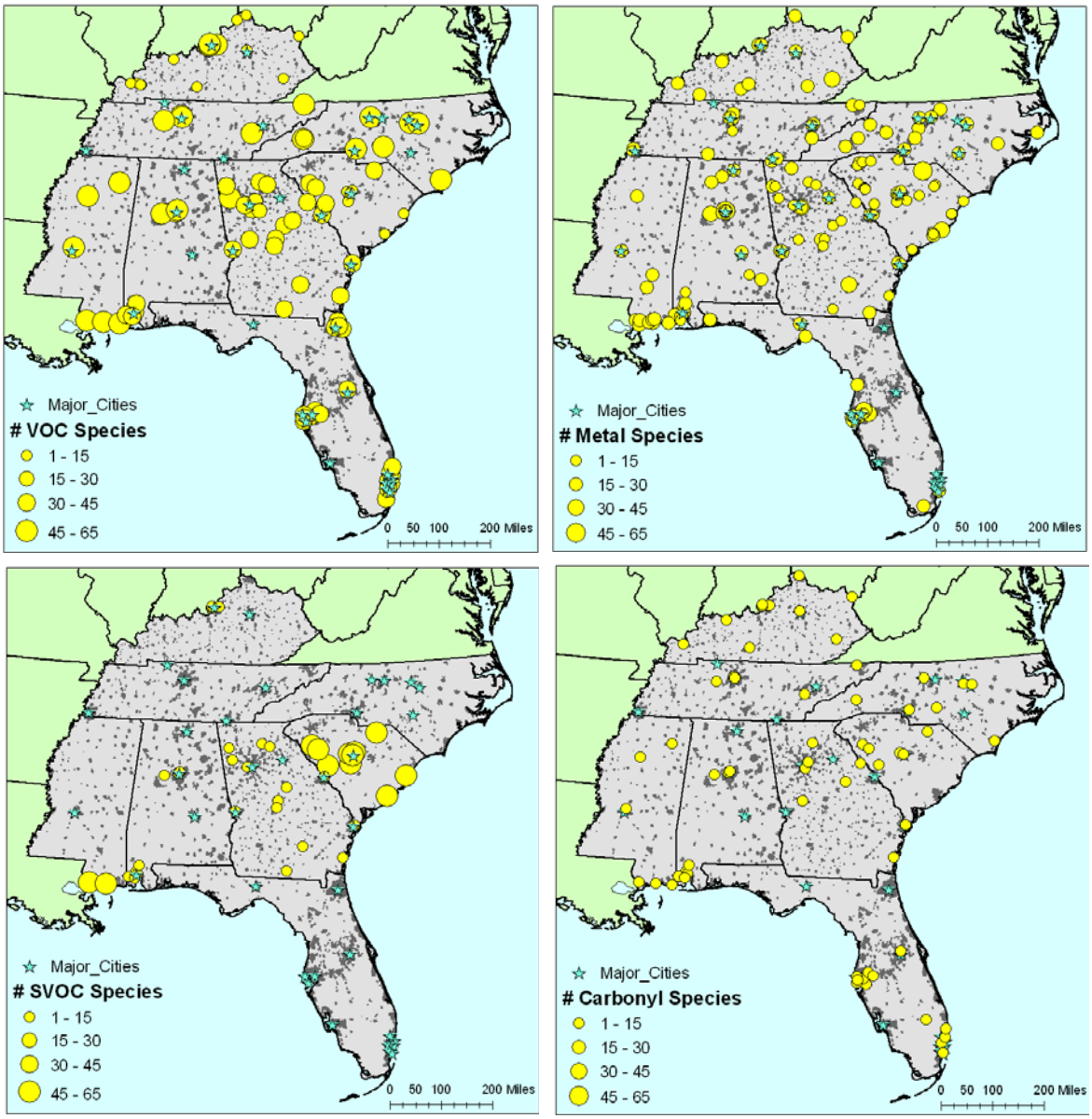

Figure 1-1. Major cities (population > 100,000), city boundaries, and monitoring sites with the number of air toxics species organized by broad parameter groups (e.g., volatile organic compounds [VOCs], particulate matter metals, semivolatile organic compounds [SVOCs], and carbonyl compounds) in the SESARM region.

These tasks included creating a project plan, acquiring and validating air toxics data, analyzing air toxics data, and attending and presenting results at an air toxics summit conference. This report summarizes the methodology and preliminary results of the analysis task and does not include the results of the acquisition and validation tasks. The analysis task included preparing visual and statistical data displays of the temporal and spatial variability of air toxics concentrations in the southeastern states, as well as performing trends analysis, geographic comparisons, and comparison of ambient data to the 1999 National Air Toxics Assessment (NATA99) model predictions. The specific tasks are outlined in Section 1.1, and an overview of the results is presented in Section 3.

In previous tasks, STI created a unified database of ambient air toxics in the Southeast for all available data from multiple data archives in the 1990-2005 time period. This database was auto-screened using checks described in a data evaluation technical memorandum (McCarthy, 2007). Sufficient data were found to be available for analysis although data below detection limits were found to constitute a large (59%) fraction of the total database. An evaluation of the effective bias of multiple substitution techniques was used to determine that substitution of half the method detection limit (MDL/2) when calculating annual means was no more biased than more sophisticated techniques. MDL/2 substitution for data below detection was recommended for use in later analysis tasks and is described in more detail in Section 2.

1.1 OVERVIEW OF ANALYSIS TASKS

A series of analysis tasks were included in the statement of work and are listed below, followed by a general description of the work that STI completed for each task.

- *Use validated data to generate statistical summaries of air toxics data based on a number of sorting criteria.* The statistical summaries included the number of samples, minimum, mean, median, standard deviation, coefficient of variation (CV), 95th percentile confidence intervals, and the 25th and 75th percentile concentrations for a given data set. Statistical summaries were generated for each pollutant meeting minimum sample criteria for all data by year, season, and hour; all data by state; and all data by urban area. Statistical summaries are reported in MS Excel spreadsheets.
- *Compare air toxics concentrations in the Southeast to national urban concentration ranges.* This spatial analysis provided a qualitative inspection of the typical ranges of concentrations in the SESARM region and in the rest of the country.
- *Compare concentration ranges of the most important southeastern air toxics against health benchmarks recommended by the EPA and the SESARM technical committee.* The committee decided to use the U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS) chronic health benchmarks (i.e., one-in-a-million cancer benchmarks and noncancer reference concentrations) (U.S. Environmental Protection Agency, 2004). These comparisons were used to show which pollutants frequently exceeded health benchmarks in the Southeast, which ones were usually below health benchmarks, and which pollutants were not measured adequately to determine if the concentration was above or below the relevant health benchmark.

- *Generate linear regressions for all pollutants at all sites with at least five valid annual or seasonal averages (e.g., five consecutive summer averages for hydrocarbons monitored only in the summer).* Linear regressions over the 2000-2005 time period were aggregated to create region-wide trend comparisons. In addition, trend plots by state were generated for each pollutant, showing the average trend in concentrations across all sites with at least five complete years of monitoring data. The primary goal of this analysis is to identify pollutants and sites with clear trends in the Southeast. However, this goal was at least partially compromised by changes in MDLs and/or sampling and analytical methodologies over time.
- *Perform visual and statistical analyses of the spatial variability of air toxics concentrations across geographical and political boundaries.* STI analysts qualitatively examined differences in concentrations. Statistical analyses such as coefficients of variations (CVs) and ratios of 75th:25th percentile concentrations were used to quantify spatial variability between sites.
- *Acquire the NATA99 model data from the EPA and compare it to mean annual average concentrations for 1998-2000 at each monitoring site at the census tract level.* Notched box plots showing the differences between ambient and modeled concentrations at all sites in the Southeast were generated and compared to national box plots. Statistical summaries detailing model biases relative to ambient concentration data were generated for each pollutant. Spatial biases were identified that may be caused by jurisdictional boundaries (e.g., differences in emission inventories resulting in large concentration differences across state lines). Depending on the availability of rural air toxics concentration data, analysis efforts were to focus on characterizing these differences in rural areas.
- *Compare MDL concentration ranges from sampling and analytical methodologies in the SESARM region to those at the national level to determine if the MDLs in the SESARM region are comparable to those typically used.* Pollutants were identified in the risk and hazard screening task that are inadequately characterized using current sampling and analytical methodologies. Alternate sampling and analytical methodologies available to adequately measure these pollutants were identified. Specifically, this analysis focused on those pollutants for which health risks cannot be adequately quantified using ambient data due to MDLs greater than typical concentrations and health benchmarks.

Additionally, STI is performing two tasks not reported directly in this document; we are providing a data display web site and case study analyses. These tasks are listed below for completeness.

- Make maps, figures, and tables generated from these analyses available to the SESARM and Metro 4 agencies on a web site. A web site will be available at http://staging.sonomatech.net/sesarm/ for one year. A username and password can be obtained from John Hornback at Metro-4/SESARM for authorized users.
- Leverage the resources from an EPA-sponsored case study analysis to assess how local, regional, and federal control programs are affecting ambient air quality. Two case studies were performed. The first case study was to investigate trends in particulate matter with aerodynamic diameter less than 2.5 micrometers ($PM_{2.5}$) metals that varied

wildly from state-to-state based on initial analysis. The hypothesis was that the trends in these metals were due to network specific changes in methods or MDLs, and do not reflect ambient air quality changes over time. The second case study was to investigate trends in ambient VOCs associated with mobile sources to determine if control measures such as reformulated gasoline, Reid Vapor Pressure alterations of fuels, or tier 1 vehicle emissions controls were responsible for the declining concentrations.

1.2 OVERVIEW OF THIS REPORT

Section 2 of this report describes the methodology used to prepare and aggregate data for the analysis tasks. Section 3 reports the results of each analysis task. Section 4 summarizes key findings from the results and lists recommendations. Appendices A and B show examples of accountability analyses. Additional supplementary information is available in MS Excel spreadsheets and images and in the STI File Transfer Protocol (FTP) site.

2. METHODS

This section briefly describes the methods used to prepare and aggregate data for the analyses used in later sections.

2.1 DATA ACQUISITION AND WORKING DATABASE STRUCTURE

The unified SESARM air toxics database currently holds EPA Air Quality System (AQS) AMP501 data from 1990 through part of 2006. Data from the Interagency Monitoring of Protected Visual Environments (IMPROVE), Southeastern Aerosol Research Characterization Experiment (SEARCH), Air Toxics Archive (ATA), and state and local air toxics data from the Southeast assembled as part of this project are all included in the project database. The general structure of the database is shown in Appendix A. We provided the database in flat files to facilitate finding information associated with a given record. Key data acquisition points for each of these resources are listed below:

- The full 1990-1994 AQS data set was acquired from EPA in October 2005.
- The 1995-2005 AQS data were downloaded from AQS using a statewide selection criterion in August and September 2006.
- IMPROVE metals data were acquired in September 2006 from the Visibility Information Exchange Web System (VIEWS) web site, <http://vista.cira.colostate.edu/views/>.
- SEARCH metals data were acquired in September 2006 from the Atmospheric Research Analysis web site, <http://www.atmospheric-research.com/public/index.html>.
- The ATA, a product of the 2004 Phase III national air toxics analysis project, was available in-house at STI (Hafner and McCarthy, 2004).
- Data from local and state air quality agencies not in the AQS were acquired from the May-October 2006 time period. These data were transformed into AQS format and imported into the database.
- A data transformation tool to take data from non-AQS format and convert it into AQS AMP501 data report format was developed to aid in this project. This tool enables a user to transform data from a non-AQS format to the AQS format with user-selected crosswalk tables. After this initial setup, any additional files in non-AQS can be automatically transformed by using the saved configuration files for that format. This tool is available to interested agencies via FTP with minimal documentation and no support.

2.2 DATA VALIDATION AND SCREENING

As part of the database unification and creation process, certain individual records were considered invalid for use in any analyses. Records that were considered invalid for use in analyses met one of the following criteria:

- the record was flagged as invalid or missing by the reporting agency
- the record had a value below −99 (any units).

Data that met one of these two criteria were flagged as invalid or missing and were not used in any of the analyses in this report, nor were they used in later data aggregation.

2.3 DATA AGGREGATION

For many analyses performed in this project, raw data needed to be aggregated temporally to efficiently conduct an analysis. For example, many comparisons were performed on valid annual averages, which were required to meet certain completeness criteria. Section 2.2.1 describes the rules used to temporally aggregate data.

2.3.1 Data Aggregate Tables

Four types of data aggregation were compiled for use in later analyses. The first three tables were provided to end-users of the database; site averages were generated for each individual task as necessary. The four temporally aggregated tables are 24-hr averages, calendar quarter averages, annual averages, and site averages. In each table, only valid data (i.e., not missing or invalid) were used.

Table 1 – 24-hr Averages

The 24-hr averages table contains two types of records. Raw 24-hr samples are records that were transferred directly from the full data table. These samples originally had 24-hr durations and are included in the data_derived table for completeness. Composite 24-hr averages refer to records calculated from subdaily measurements. These aggregates are calculated by averaging all records from the same monitor (site, parameter, pollutant occurrence code [POC], method) on a given day while requiring 75% completeness—at least eighteen 1-hr samples would be required, or at least six 3-hr samples, or five 4-hr samples, etc. If a daily derived value is not complete, the incomplete field is marked with a value of 1 to indicate that it is incomplete. Incomplete daily averages were not used in later analysis.

Each individual 24-hr average record can be identified as a raw or composite value using the raw_duration_id field. Each record also includes fields documenting the number of valid data records used to create the daily metric, the number of records used that were at or below the MDL, and the number of records considered suspect that are included in the daily average.

Table 2 – Calendar Quarter Averages

The calendar quarter averages table contains calendar quarterly averages consisting of 24-hr samples from the 24-hr averages table. Calendar quarters are January, February, March—the first quarter; April, May, and June—the second quarter; and so forth. Quarterly averages are calculated using a 75% sample completeness collection based on observed sampling frequency for a given monitor. If 90 samples are expected for a monitor sampling daily, then at least 68

24-hr samples would be required. Similarly, if 8 samples are expected for a 1-in-12-day frequency of collection, then only 6 samples would be required. Four sampling frequencies are allowed for a given monitor: daily, 1-in-3-day, 1-in-6-day, or 1-in-12-day. If a given monitor could not be assigned a specific frequency (based on 85% of months falling under a given category), the minimum completeness criteria was used (i.e., 1-in-12-day). In addition, all valid quarterly averages were required to have at least fifty-nine day duration between the first and last monitored sample to ensure that sampling represented the entire quarter for the less frequent sampling categories.

Table 3 – Yearly Averages

The yearly averages table contains the valid annual averages at each monitor for each pollutant. Annual means are calculated using valid calendar quarterly averages for a calendar year. At least three of the four quarters are required for an annual average to be considered valid (75%). The number of quarters used to create the annual average is provided, as is the number of individual samples making up the total annual average across all quarters and the number of individual samples below detection limits.

Table 4 – Site Averages

Site averages were generated for two three-year periods. Site averages are composed of the mean concentration of yearly averages from a three-year window. All tasks relied on the three-year window, 2003-2005, except the NATA99 comparison task for which the 1998-2000 time period was used. A site average was considered valid if any of the three years was available. Site averages were used to increase the number of available sites for all analysis tasks, rather than selecting a single year for comparison.

2.3.2 MDL Substitution

Concentrations of a large fraction of all data were reported at or below MDL levels. Individual agencies used a variety of options to report data at or below MDL. Some agencies reported the values as read by the analytical instrument, others reported zeroes, some reported MDL values, and others reported MDL/2. Data reporting was inconsistent across agencies and years. The magnitude of the toxics data available in the Southeast precludes checking by site, state, or agency to determine which method might be used; an automated method must be employed to deal with these inconsistencies.

At individually reported measurement levels, each record reported at or below the MDL was flagged. No substitution or alteration of the value was made, thus leaving the value intact. However, if the record was then used in an aggregate record (e.g., quarterly averages), a value equal to the MDL/2 was substituted for that value when calculating the average. This process was performed for both the yearly average and quarterly average tables. A tally of the number of records at or below the MDL for each aggregate record was kept, along with a count of the total number of records contributing to that aggregate.

In the data analysis phase, the percentage of data below MDL for any given aggregate record was examined as an indication of the reliability of the calculated mean value. Results

were typically color-coded to indicate the reliability of results for a given pollutant, site, or year. In general, two or three cutoff levels were used as bounds for confidence:

1. Records with more than 85% of data below the MDL (i.e., less than 15% of data above the MDL) were considered unreliable. These data are indicated in pink in some tables and figures to reflect poor confidence.
2. Records with less than 50% of data below the MDL (i.e., more than 50% of data above the MDL) were considered reliable. These data are indicated in green for good confidence.
3. Records with 50-85% of data below MDL were considered somewhat reliable. These data are indicated in yellow for moderate confidence.

Note that this treatment of the data did not result in excluding any data from the analysis because it was below detection limits. However, results using MDL/2 substituted data cannot necessarily be used to ascertain quantitative results, nor are qualitative results necessarily as reliable. Depending on the type of analysis being performed, the resulting data may not provide reliable information. Discussion of approach or results from the different analyses will include any rationale behind interpretations that may be influenced by MDL/2 substituted data.

3. ANALYSIS RESULTS

This section includes the results from each of the analysis tasks described in the introduction.

3.1 SUMMARY STATISTICS

3.1.1 Objective and Approach

The objective of this task was to calculate statistical summaries of air toxics data from the Southeast. Our approach was to calculate summary statistics across a wide variety of organizing categories. Summary statistics include the minimum, maximum, mean, standard deviation, 25^{th,} and 75th percentiles, coefficient of variation (CV), and the upper and lower 95th percent confidence intervals. In addition, the average MDL, percent of data below MDL, and number of records were reported. Individual statistics were calculated using MDL/2 substitution for any record reported at or below MDL. Categories of organization define the parameters by which the summary statistics were grouped. For example, summary statistics were calculated for each pollutant by year (i.e., aggregating data across all sites in the Southeast by pollutant and year). The full list of the categories for which summary statistics were calculated follows:

- Parameter, Year
- Parameter, Year, State
- Parameter, Year, Metropolitan Area
- Parameter, Year, Site
- Parameter, Calendar Quarter, Site (2003-2005 only)
- Parameter, Site, Hour (1-hr, 3-hr, and 4-hr sample durations; 2003-2005 only)

For each set of summary statistics, some statistical results were censored because the data were below MDL. For example, if 55% of data was below MDL for a given parameter and year combination, the minimum, 25th percentile, and median would not be provided. Other summary statistics such as the mean, 75th percentile, and maximum concentration would be provided. The rationale for this decision is to avoid reporting MDL/2 values for these statistics. While MDL/2 substitution will not bias a mean concentration significantly until approximately 85% of data is below detection, the substitution will skew percentiles and minimum values as soon as the percent of data below MDL exceeds that percentile. Finally, when more than 85% of data was below detection, no summary statistics are reported beyond number of records collected, the percent below detection, and the average MDL value. Summary statistics such as mean and median are completely unreliable when the fraction of data below MDL approaches 85%.

3.1.2 Results

A large (34 MB) spreadsheet containing the summary statistics is available at the STI FTP site. Instructions for accessing this spreadsheet and other figures were provided in a separate e-mail.

Table 3-1 lists the fields typically used in the summary worksheets using the parameter-year combination. Fields colored yellow provide grouping metadata (i.e., parameter and year). Uncolored fields provide the summary statistics. Fields colored green provide the data quantity and quality information.

3.2 COMPARISON TO NATIONAL CONCENTRATION RANGES

3.2.1 Objective and Approach

The objective of this task was to compare air toxics concentration ranges in the Southeast to concentrations in the entire United States. Two key questions were addressed: "Are there unique pollutant issues in the Southeast?" "Are concentrations typically higher, lower, or the same as those in the rest of the country?"

Site averages from 2003 to 2005 at all sites in the country were used to generate statistical summaries of the typical concentration ranges for each pollutant. For each pollutant, 5th, 25th, median, 75th, and 95th percentile concentrations were calculated at both the national and southeastern regional level of aggregation. For national data, southeastern sites were included in the statistical summaries. Box plots displaying this information were then created for all pollutants for which at least five monitoring sites are located in the Southeast. Summary statistics were calculated for pollutants monitored at fewer than five sites; however, these statistics cannot be considered regionally representative. Summary statistics of pollutants monitored at fewer than 10 monitoring sites were displayed, but pollutant concentrations in the 5th and 95th percentiles could not be included because of the number of sites is insufficient.

Pollutants were then grouped into categories of similar chemical compounds (e.g., VOCs or metals) and categories of similar reliability. To assess reliability, the percentage of records below detection limits across all sites in the Southeast was used to group pollutants. Pollutants with less than 50% of data below the MDL were considered high quality, those with 50-85% of data below the MDL were considered medium quality, and those with more than 85% of data below the MDL were considered poor quality. Concentrations of poor quality pollutants can be considered unreliable; ranges of the MDL concentrations across sites were plotted instead. We can only infer that concentrations of these pollutants are typically below the majority of their MDL values.

Table 3-1. Example of summary statistics for all sites in the southeast grouped by parameter and year combination. This example shows results for 1,3-butadiene.

Parameter name	Parameter AQS Code	Year	Minimum	25th Percentile	50th Percentile	75th Percentile	Maximum	Mean	Standard Deviation	Coefficient of Variation	Upper 95th Confidence Interval	Lower 95th Confidence Interval	Average MDL	# Records	# Records Below Detection	% Records Below Detection	Data Quality
1,3-Butadiene	43218	1990	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	1.3E-01	77	66	85.7	> 85% below detection
1,3-Butadiene	43218	1995	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.1E-01	29	26	89.7	> 85% below detection
1,3-Butadiene	43218	2000	2.6E-01	5.0E-01	5.9E-01	1.9E+00	5.7E+01	2.5E+00	7.2E+00	2.9E+00	4.1E+00	9.2E-01	6.6E-02	81	0	0.0	< 50% below detection
1,3-Butadiene	43218	2001	BD	BD	BD	1.1E-01	1.1E+00	1.3E-01	1.3E-01	1.1E+00	1.4E-01	1.1E-01	1.5E-01	413	303	73.4	50 - 85% below detection
1,3-Butadiene	43218	2002	BD	BD	BD	BD	1.4E+01	5.0E-01	9.8E-01	2.0E+00	5.7E-01	4.4E-01	6.0E-01	906	712	78.6	50 - 85% below detection
1,3-Butadiene	43218	2003	BD	BD	BD	5.5E-01	1.6E+01	4.9E-01	1.2E+00	2.4E+00	5.4E-01	4.3E-01	4.1E-01	1561	963	61.7	50 - 85% below detection
1,3-Butadiene	43218	2004	BD	BD	BD	5.5E-01	8.3E+00	5.0E-01	7.1E-01	1.4E+00	5.4E-01	4.7E-01	3.5E-01	1507	987	65.5	50 - 85% below detection
1,3-Butadiene	43218	2005	BD	BD	BD	1.8E-01	2.1E+01	3.5E-01	1.1E+00	3.0E+00	4.0E-01	3.0E-01	1.2E-01	1680	1175	69.9	50 - 85% below detection

Note: E-01 = 10^{-1}
E+00 = 10^{0}
BD = below detection limit, not reported
NA = not available; <15% of data above MDL so statistics were not calculated.

3.2.2 Results

Figures 3-1 through 3-6 show concentration ranges in the SESARM region compared to those at sites within the United States. Each box shows the 5th, 25th, 50th, 75th, and 95th percentile concentration within either the SESARM region (gray box) or nation (white box). Concentrations in a logarithmic scale are displayed on the x-axis in units of $\mu g/m^3$. For pollutants measured at fewer than 10 sites, only the 25th, 50th, and 75th percentile concentrations are shown. In addition, the median MDL in the geographical region is displayed as a diamond for each pollutant. Finally, the number of sites available over the time period is shown on the right side of the figure. Note that the southeastern sites are included in the national values. All plots were visually inspected by STI analysts to check for any systematic discrepancies between pollutants. The plots displayed are a subset of all of the figures prepared; additional figures are available on the STI FTP site. The particular plots were chosen to illustrate points raised later in the discussion and in the key findings and are representative of the other figures that are not shown in this report.

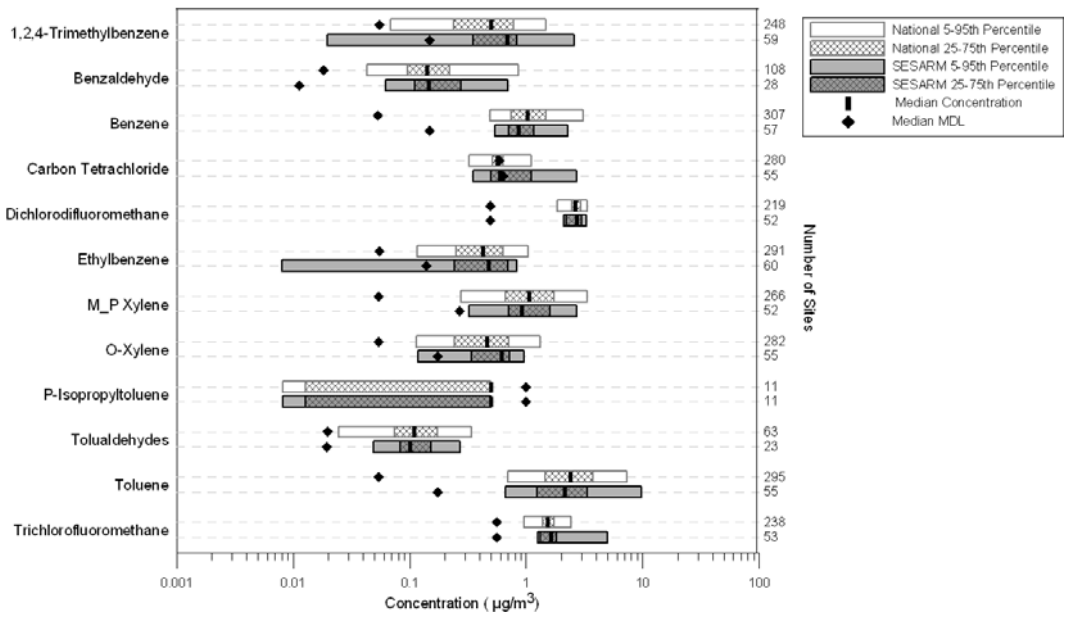

Figure 3-1. Concentration ranges in the SESARM region compared to those at the national level for selected VOCs with more than 50% of data above MDL. Note that acetonitrile concentrations in the Southeast and the nation have known sampling contamination issues leading to very high concentrations.

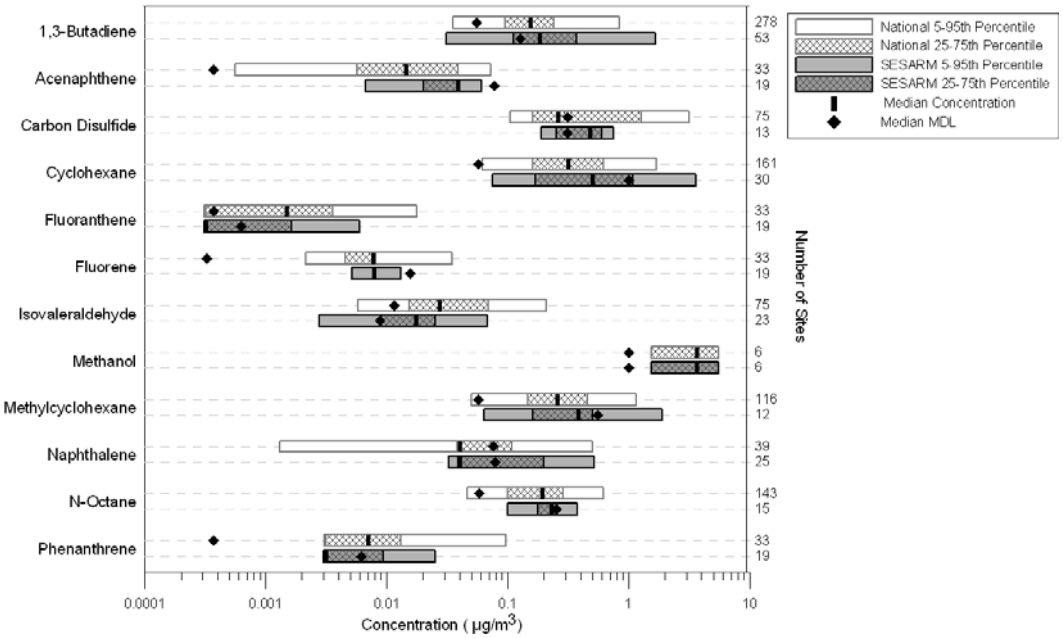

Figure 3-2. Concentration ranges in the SESARM region compared to those at the national level for selected VOCs and SVOCs with between 15 and 50% of data above MDL.

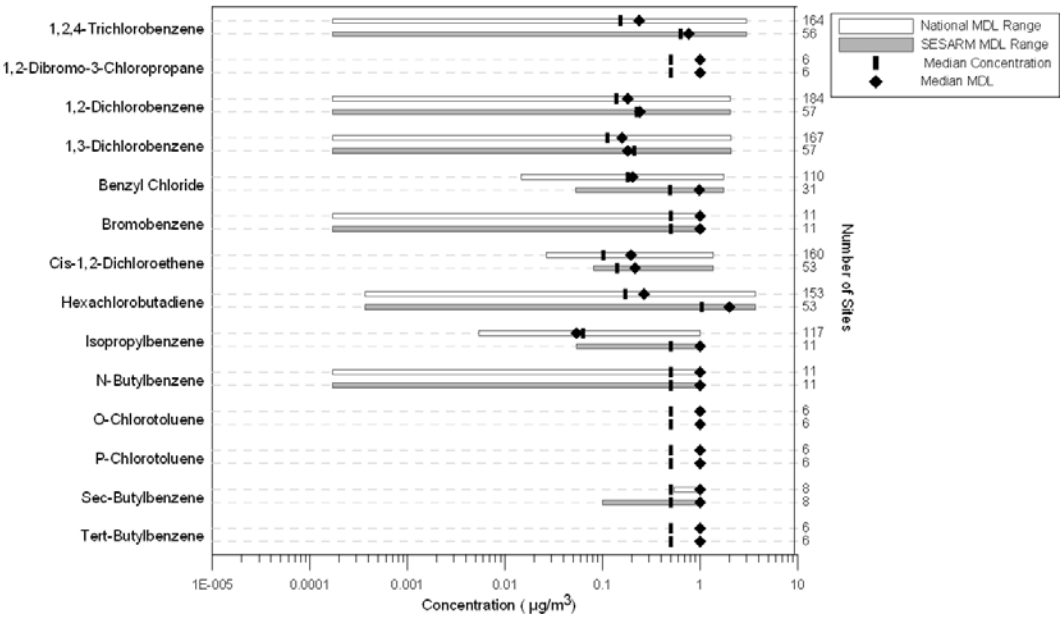

Figure 3-3. Concentration ranges of MDLs in the SESARM region compared to those at the national level for selected VOCs and SVOCs with less than 15% of data above the MDL.

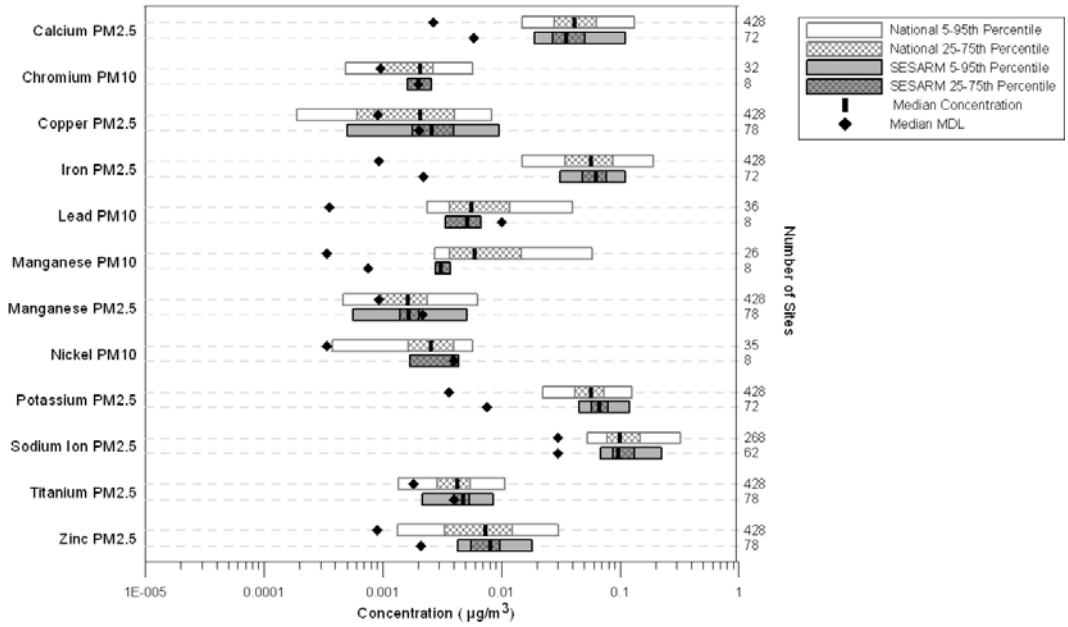

Figure 3-4. Concentration ranges in the SESARM region compared to those at the national level for selected metals with more than 50% of data above MDL.

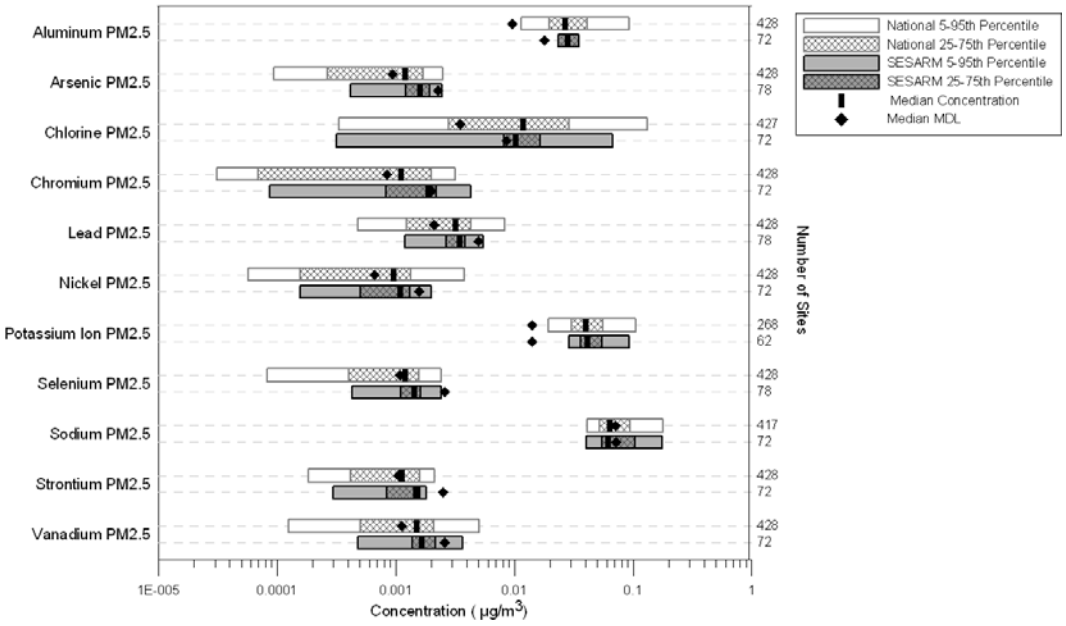

Figure 3-5. Concentration ranges in the SESARM region compared to those at the national level for selected metals with between 15% and 50% of data above MDL.

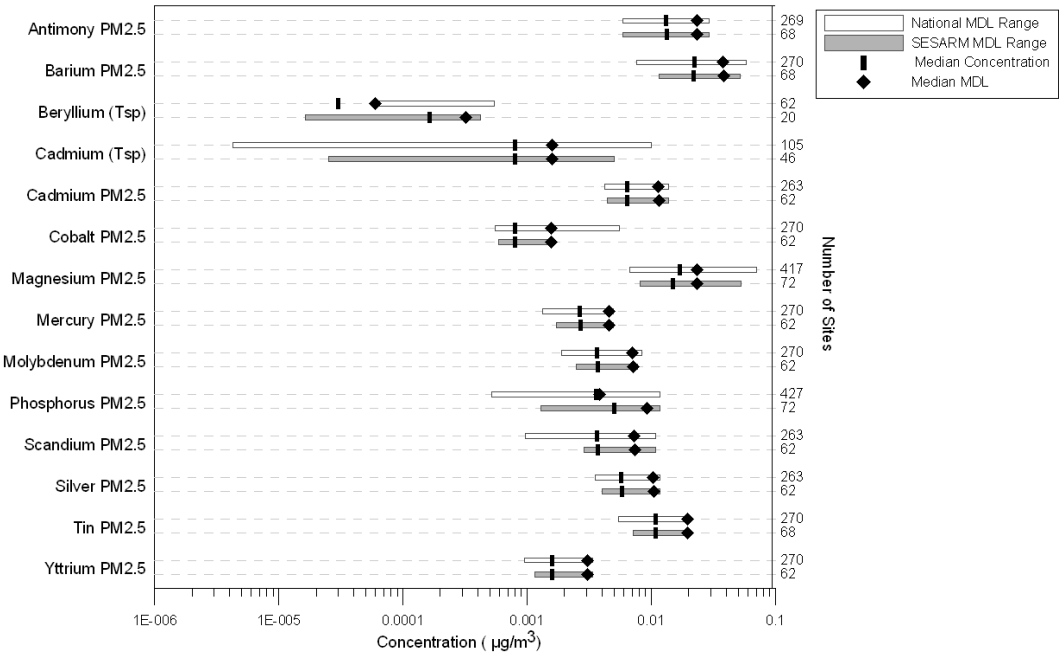

Figure 3-6. MDL ranges in the SESARM region compared to those at the national level for selected metals with less than 15% of data above MDL. Concentrations of these pollutants are typically below the MDL levels shown here.

SESARM region and national concentration ranges are similar across most pollutants, as seen in the figures. Although there are differences, one should not overinterpret them. Some variability between national and SESARM region ranges may be attributable to the large difference in the number of sites in the comparison leading to less robust statistics for the Southeast. Differences were not statistically quantified because typical pollutant concentrations varied by a factor of 3 to 10 across the region. Given this large spatial variability in concentrations within the SESARM region and the nation, average concentrations are likely to be skewed. STI analysts visually inspected the distributions to assess if the Southeast distribution appeared significantly higher or lower for all percentiles than the national distribution. Parameters that met this criterion can be found in **Table 3-2**. None of these pollutants are considered high risk or hazard drivers, as explained in the next section. In addition, STI analysts judged that the distribution of some pollutants with a large fraction of measurements below MDL was likely skewed by MDL/2 substitution. For example, cyclohexane concentrations in Figure 3-2 appear to be higher in the Southeast, but the median MDL concentration was more than an order of magnitude higher in the Southeast. Differences in MDLs between the SESARM region and the entire nation make direct comparisons substantially more difficult for lower quality pollutants.

Additionally, one can see odd distributions for pollutants such as ethylbenzene and p−isopropyltoluene in Figure 3-1. For ethylbenzene, the concentration distribution in the SESARM region is skewed lower because of a set of very low MDL measurements made in South Carolina which are not made anywhere else in the country. For p-isopropyltoluene, the

uniquely low MDL South Carolina measurements lead to a large range of concentrations up to the median site. However, higher MDL measurements of the species in Kentucky were all below detection limits, leading to the phenomenon of the median, 75th, and 95th percentile sites all having a concentration equal to a value of MDL/2. These examples illustrate that differences in detection limits across agencies can result in unreliable distributions.

Table 3-2. Pollutants with some of the largest differences between the SESARM region and national concentration ranges.

Parameter	# of SESARM Sites	# of National Sites	SESARM Concentrations are
Manganese PM_{10}	8	26	Lower
Acetone	37	176	Lower
Propylene	15	169	Lower

3.2.3 Key Findings

- The concentration ranges of most pollutants in the Southeast were very similar to those observed in other parts of the country.
- Variation in pollutant concentration ranges in the Southeast was often comparable to variations observed across the country as a whole. For most air toxics, concentrations varied by a factor of 3 to 10 across the Southeast.
- Concentrations of a few pollutants in the Southeast appeared to be significantly lower relative to those on a national scale; these pollutants included manganese PM_{10}, acetone, and propylene. The reason for these differences was not investigated.

3.3 RISK AND HAZARD SCREENING

3.3.1 Objective and Approach

Air toxics were identified that had concentrations exceeding EPA OAQPS chronic human health benchmarks in the Southeast. Results from this screening analysis were compared to the characterization of national or regional risk or hazard drivers or contributors in the NATA99.

Site averages from 2003 to 2005 at all sites in the southeastern region were used to compare mean concentrations for each pollutant and site to health benchmarks. STI, directed by the SESARM technical committee, used the chronic health benchmarks from OAQPS (U.S. Environmental Protection Agency, 2004). These screening values may not be those recommended by state or local agencies within the Southeast; however, for uniformity, only one set of health benchmarks for chronic risk and noncancer hazard were chosen. The one-in-a-million cancer benchmarks and reference concentrations in units of $\mu g/m^3$ were calculated for each pollutant monitored in the Southeast using the EPA OAQPS values.

Three categories were established and each site-pollutant combination was placed in one of the following categories:

1. Site average concentration is above the health benchmark.
2. Site average concentration is below the health benchmark.
3. Site average concentration relation to the health benchmark is uncharacterizable because both are below the MDL.

Three criteria were used to determine into which category a given site and pollutant was placed. **Figure 3-7** shows the decision tree used to categorize site-pollutant combinations. First, the percentage of data below detection was used to determine if the site-average concentration should be considered reliable. If the site-average concentration was below the MDL but not quantifiable (>85% of data below MDL), the MDL was compared to the health benchmark. If the MDL was below the health benchmark, the site-average concentration was assumed to be below the health benchmark as well. If the MDL was above the health benchmark, the comparison could not be made. For site-pollutant combinations with quantifiable concentrations, a direct comparison of site average concentration to health benchmark was made. Results from the categorization were then aggregated at the regional level to ascertain which monitored pollutants were of most concern in the Southeast.

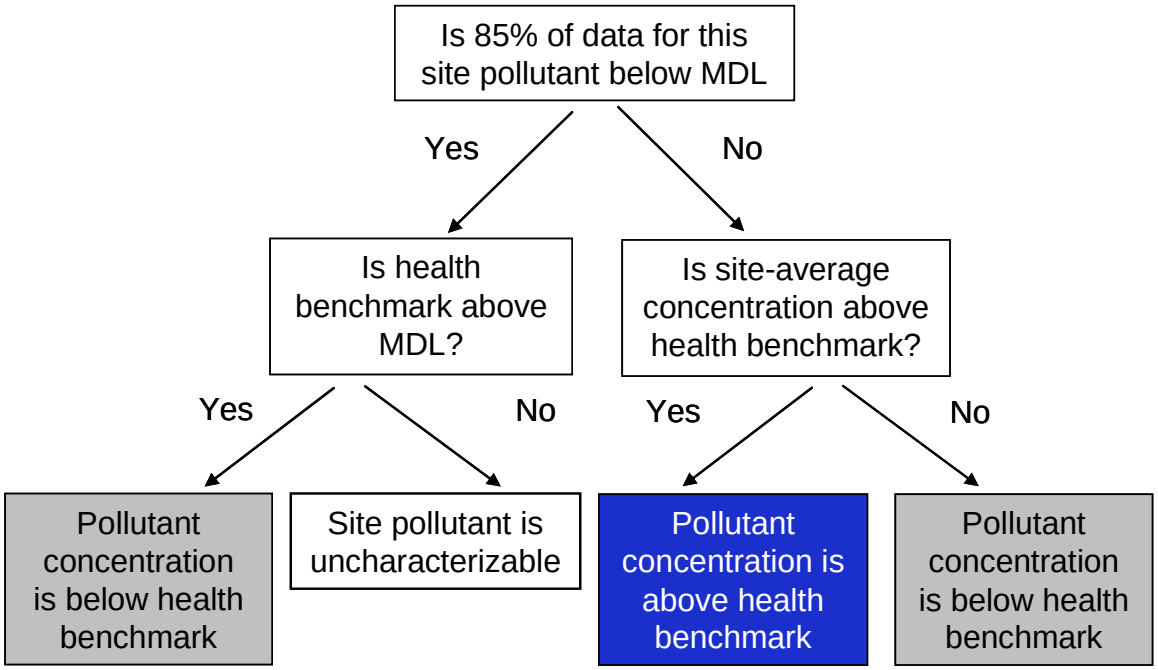

Figure 3-7. Decision tree for characterizing individual site-pollutant combinations.

3.3.2 Results

Results of the one-in-a-million cancer risk screen are shown in **Figure 3-8**. All pollutants with more than 10 site-averages are shown. The bar chart displays the number of sites above the one-in-a-million cancer risk for each pollutant as a pink bar, the number of sites below the one-in-a-million cancer risk level as a green bar, and the uncharacterizable sites as an orange bar. Most pollutants largely fell into only one or two of the three categories. **Table 3-3** shows the results of the risk-screen analysis for pollutants according to their risk categorized in the NATA99 model assessment for the entire nation.

Similarly, results were generated for the noncancer hazard across the Southeast using reference concentrations. Results from the hazard screen are shown in **Table 3-4**. Most pollutants do not exceed their hazard reference concentrations. Those few that exceeded did so at only one or two sites. Results indicate that the sampling and analytical methods of acrolein and 1,2-dibromo-3-chloropropane should be improved to better characterize possible hazard.

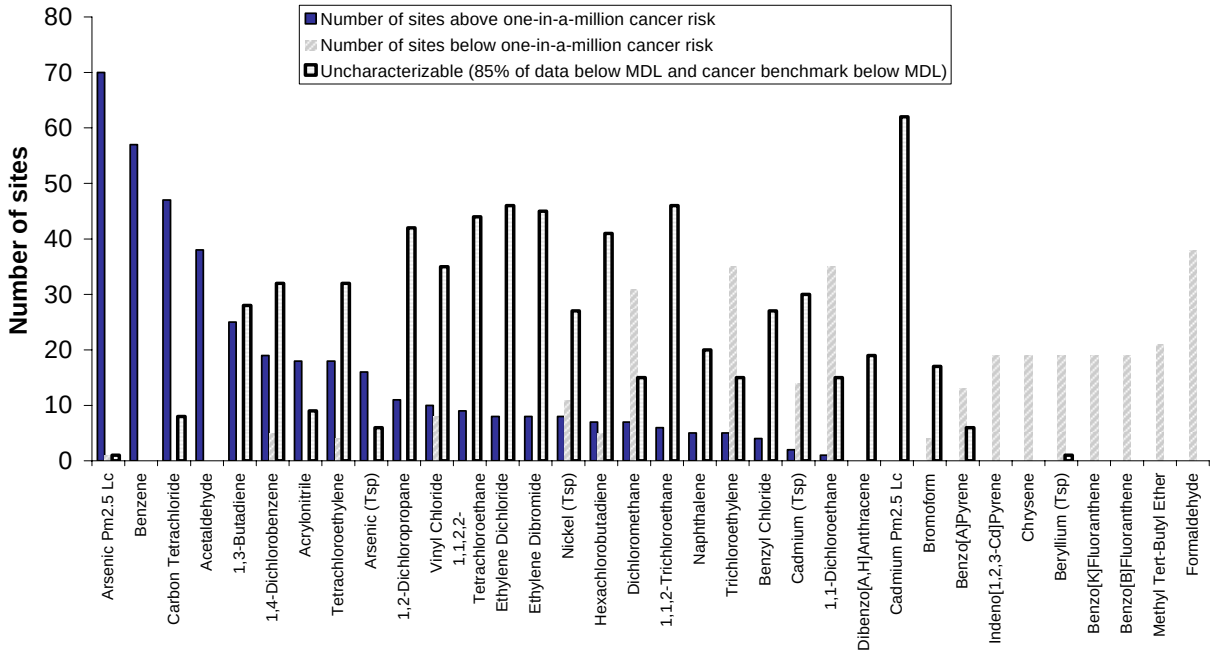

Figure 3-8. Number of sites classified in three risk categories in the southeastern region from 2003 to 2005 by pollutant. Pollutants with less 10 site averages from 2003 to 2005 are not shown.

Table 3-3. Risk screen results for key air toxics categorized using NATA99. All results are for 2003-2005 site averages. EPA OAQPS unit risk values were used to calculate one-in-a-million cancer risk values. Colors in the last column indicate the reliability of monitoring data for this risk screen; green meant more than 75% of sites were reliable, yellow indicates between 25-50% of sites were unreliable, and pink indicates more than 50% of sites were unreliable.

Pollutant	Number of Sites	Number of Sites with Mean Above One-in-a-Million Cancer Risk	Number of Sites with Mean Below One-in-a-Million Cancer Risk	Number of Uncharacterizable Sites (85% of Data Below MDL and Cancer Benchmark Below MDL)	Percent of Uncharacterizable Sites
National Risk Drivers (Risk exceeds 10-in-a-million for more than 25 million people)					
Benzene	57	57	0	0	0
Regional Risk Drivers (Risk exceeds 10-in-a-million for more than 10 thousand people)					
Arsenic $PM_{2.5}$	72	70	1	1	1
Arsenic TSP	22	16	0	6	27
Arsenic PM_{10}	7	3	0	4	57
1,3-Butadiene	53	25	0	28	53
Chromium VI TSP	4	0	4	0	0
Carbon Tetrachloride	55	47	0	8	15
Cadmium $PM_{2.5}$	62	0	0	62	100
Cadmium PM_{10}	7	0	3	4	57
Cadmium TSP	46	2	14	30	65
Tetrachloroethylene	54	18	4	32	59
Dibenzo[A,H]Anthracene	19	0	0	19	100
Benzo[A]Pyrene	19	0	13	6	32
Benzo[A]Anthracene	19	0	19	0	0
Benzo[B]Fluoranthene	19	0	19	0	0
Benzo[K]Fluoranthene	19	0	19	0	0
Chrysene	19	0	19	0	0
Indeno[1,2,3-Cd]Pyrene	19	0	19	0	0
Naphthalene	25	5	0	20	80
Heptachlor	5	0	0	5	100
Carbazole	5	0	5	0	0
Benzidine	Not Monitored				
Ethylene Oxide					
Hydrazine					
Coke Oven Emissions					

Table 3-3. **Continuation of** risk screen results for key air toxics categorized using NATA99. All results are for 2003-2005 site averages. EPA OAQPS unit risk values were used to calculate one-in-a-million cancer risk values. Colors in the last column indicate the reliability of monitoring data for this risk screen; green meant more than 75% of sites were reliable, yellow indicates between 25-50% of sites were unreliable, and pink indicates more than 50% of sites were unreliable.

Pollutant	Number of Sites	Number of Sites with Mean Above One-in-a-Million Cancer Risk	Number of Sites with Mean Below One-in-a-Million Cancer Risk	Number of Uncharacterizable Sites (85% of Data Below MDL and Cancer Benchmark Below MDL)	Percent of Uncharacterizable Sites
National Risk Contributors (Risk exceeds 1-in-a-million for more than 25 million people)					
Acetaldehyde	38	38	0	0	0
Ethylene Dibromide	53	8	0	45	85
Ethylene Dichloride	54	8	0	46	85
1,1,2,2-Tetrachloroethane	53	9	0	44	83
1,4-Dichlorobenzene	56	19	5	32	57
Bis(2-Ethylhexyl)Phthalate	5	0	5	0	0
Acrylonitrile	27	18	0	9	33
Dichloromethane	53	7	31	15	28
Trichloroethylene	55	5	35	15	27
Vinyl Chloride	53	10	8	35	66
Beryllium TSP	20	0	19	1	5
Beryllium PM10	7	1	2	4	57
Nickel PM10	7	4	3	0	0
Nickel TSP	46	8	11	27	59
Nickel PM2.5	72	3	69	0	0
1,3-Dichloropropene(Total)	3	3	0	0	0
Quinoline	Not Monitored				
Not mentioned in NATA99 results, but possible risk issues identified by this risk screen analysis (mostly uncharacterized)					
1,2-Dichloropropane	53	11	0	42	79
1,1,2-Trichloroethane	52	6	0	46	88
Hexachlorobutadiene	53	7	5	41	77
Benzyl Chloride	31	4	0	27	87
Bromoform	21	0	4	17	81

Table 3-4. Hazard screen results for key air toxics categorized using NATA99. All results are for 2003-2005 site averages. EPA OAQPS reference concentrations were used. Colors in the last column indicate the reliability of monitoring data for this hazard screen; green meant less than 25% of sites were unreliable, yellow indicates between 25-50% of sites were unreliable, and pink indicates more than 50% of sites were unreliable.

Pollutant	Number of Sites	Number of Sites with Mean Above Reference Concentration	Number of Sites with Mean Below Reference Concentration	Number of Uncharacterizable Sites (85% of Data Below MDL and Reference Concentration Below MDL)	Percent of Uncharacterizable Sites
National Noncancer Hazard Drivers (Hazard Quotient exceeds 1.0 for more than 25 million people)					
Acrolein	5	0	0	5	100
Regional Noncancer Hazard Drivers (Hazard Quotient exceeds 1.0 for more than 10 thousand people)					
Arsenic PM_{10}	7	0	7	0	0
Arsenic TSP	22	0	22	0	0
Arsenic $PM_{2.5}$	72	0	72	0	0
1,3-Butadiene	53	1	52	0	0
Cadmium PM_{10}	7	0	7	0	0
Cadmium TSP	46	0	46	0	0
Cadmium $PM_{2.5}$	62	0	62	0	0
Chlorine TSP	2	2	0	0	0
Chlorine $PM_{2.5}$	72	1	71	0	0
Chromium VI TSP	4	0	4	0	0
Formaldehyde	38	2	36	0	0
Manganese PM_{10}	7	0	7	0	0
Manganese TSP	46	2	44	0	0
Manganese $PM_{2.5}$	72	1	71	0	0
Nickel PM_{10}	7	0	7	0	0
Nickel Tsp)	46	0	46	0	0
Nickel $PM_{2.5}$	72	0	72	0	0
diesel PM	Not monitored				
hexamethylene 1-6 diisocyanate					
hydrazine					
hydrochloric acid					
maleic anhydride					
2,4-toluene diisocyanate					
triethylamine					
Not mentioned in NATA99, but may be important for the SESARM Region based on ambient data					
1,2-Dibromo-3-Chloropropane	6	0	0	6	100
Acetonitrile (known sampling issues)	9	1	8	0	0
Chloromethane	48	1	47	0	0

3.3.3 Key Findings

- Concentrations of some key risk drivers identified in NATA99 are not measured well enough, as reflected in the ambient monitoring data, to determine risk. These pollutants include 1,3-butadiene, cadmium (all particle size fractions), tetrachloroethylene, ethylene dibromide, ethylene dichloride, 1,1,2,2-tetrachloroethane, and 1,4-dichlorobenzene.
- Among pollutants that are characterized well, many pollutants were in reasonable agreement with model predicted risk from NATA99. For example, benzene, arsenic $PM_{2.5}$, carbon tetrachloride, and acetaldehyde were above the cancer benchmark at every site where they were monitored well enough to make a characterization. However, some pollutants considered likely risk drivers at a national level by NATA99 had concentrations that did not exceed cancer benchmark values at most sites, for example, chromium VI, most of the particulate organic matter (POM), Bis(2-ethylhexyl)phthalate, dichloromethane, and trichloroethylene.
- Additional pollutants not mentioned in NATA99 as risk drivers or contributors that may contribute to risk in the Southeast include 1,2-dichloropropane, 1,1,2-trichloroethane, hexachlorobutadiene, benzyl chloride, and bromoform. However, these pollutants are all poorly characterized. Better sampling and analytical methodologies are needed to characterize the risk associated with these pollutants (i.e., MDLs need to be lower than health benchmarks).
- Most species did not exceed noncancer reference concentrations at sites in the Southeast. Only a few pollutants exceeded noncancer reference concentrations at any site. Noncancer hazard appears to be a local issue.
- Two species were uncharacterizable for noncancer hazard screening: acrolein and 1,2-dibromo-3-chloropropane. Acrolein is the primary noncancer hazard driver nationwide identified by NATA99. Better sampling and analytical methods must be employed to estimate the hazard from this key pollutant.

3.4 TRENDS IN AIR TOXICS CONCENTRATIONS IN THE SOUTHEAST

3.4.1 Objective and Approach

This task was to characterize temporal trends in air toxics at individual sites and in aggregate across the Southeast. It was important in this analysis to identify pollutants and sites with trends that are highly variable and “suspect”, often due to changes in methods or MDLs, rather than reflecting real changes in ambient concentrations.

Trends in air toxics concentrations were calculated at all sites in the southeast where a pollutant had at least five valid years of monitoring data. Data were run through a statistical program to calculate the trend coefficients (slope and intercept). Statistical F-tests were used to determine if the slope was significantly different from zero (Wikipedia®, 2007). Data for individual sites and pollutants are provided on the STI FTP site.

Trends were also calculated for individual pollutants and states for the 2000-2005 trend period. All sites with at least five valid annual averages of monitoring data from 2000-2005 were used. A second criterion was that at least three of the years of available data needed more than 15% of data above MDL. Pollutant concentrations were averaged at the state level for all sites within a state. A regression was then calculated across the state for each pollutant.

Each pollutant at each site with at least five years of monitoring data from 1990 to 2005 was also used to create a graphical representation of the range of trends seen in the southeast. Individual linear regression trends at each site were calculated using SYSTAT statistical software. The percentage change in the concentration at each site was calculated using the *trend line*, rather than the start- and end-year actual concentrations. For example, Site A measuring benzene showed a starting concentration of 2 $\mu g/m^3$ and an end-year concentration of 1 $\mu g/m^3$. The percentage change using these two values alone would yield a percentage change of −50%. However, the trend line has a slope of −0.15 $\mu g/m^3$*year, which results in a percentage change of −38%. We chose the trend line value because it uses all available annual averages and is a more robust metric of actual change over time.[1] In addition, the count of individual sites with trends that were statistically significantly different from zero using the F-test was also tabulated. After calculating the percentage change over the trend period, each site was normalized by dividing the percentage change by the number of years of monitoring data at the site to calculate a mean percentage change per year. Results from all sites for each pollutant were used to display the minimum, maximum, and median percentage change per year for each pollutant.

Individual trends for each pollutant and state were plotted for the years 2000 to 2005. Examples for a few pollutants are shown in **Figures 3-9 through 3-16**. Red lines connect annual average concentrations, black lines show linear regressions, the number at the bottom is the calculated percentage change in the linear regression between 2000 and 2005, and the number on the top of each plot is the number of sites contributing to that trend. Finally, the scales of each plot are the same across states. For example, Figure 3-9 shows 1,3-butadiene concentration trends in Kentucky and Florida, both states have one site (i.e., N=1), Kentucky 1,3-butadiene concentrations decreased by 96%, but started at a much higher value than at the site in Florida.

Results from this analysis indicate very different trends among pollutants. One apparent success story is the VOC MSATs - benzene, 1,3-butadiene, toluene, and xylenes. Where measured, the annual averages of these pollutants consistently decreased (e.g., Figures 3-9, 3-11, and 3-12). These decreases could be due to a number of vehicle or gasoline control measures. In contrast, the toxic metals concentrations measured in the PM monitoring networks show wildly varying trends depending primarily on the network performing the measurements. For examples, Figures 3-14, 3-15, and 3-16 show trends in arsenic, chromium, and manganese $PM_{2.5}$ respectively at Interagency Monitoring of Protected Visual Environments (IMPROVE) and Speciation Trends Network (STN) sites. Figures 3-15 and 3-16 show the very consistent trends going on within networks that are completely different across networks. Chromium $PM_{2.5}$ and manganese $PM_{2.5}$ concentrations change drastically in 2002 as a result of a methodology change in the IMPROVE network, causing a dramatic drop in reported concentrations at all sites. In contrast, the STN network shows an increasing trend at all sites over the same time period.

[1] Note, a linear regression may not be an appropriate measure of a trend for some pollutants and sites and can result in non-physical values. To avoid this result, changes could not be smaller than −100%.

While it is theoretically possible that these trends are reflective of ambient concentrations, the extreme consistency within a network compared to the huge discrepancies between networks and sites certainly cast a suspicious light on these trends. An additional case study of metals trends will be attached as an appendix to this report.

Figure 3-9. Trends in 1,3-butadiene concentrations ($\mu g/m^3$) from 2000 to 2005.

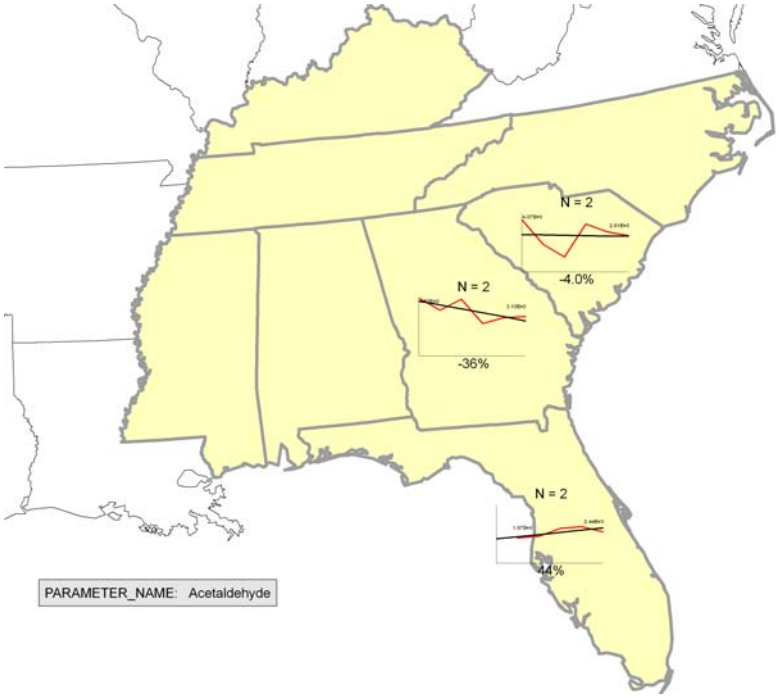

Figure 3-10. Trends in acetaldehyde concentrations (μg/m^3) from 2000 to 2005.

Figure 3-11. Trends in toluene concentrations (μg/m^3) from 2000 to 2005.

Figure 3-12. Trends in o-xylene concentrations (μg/m^3) from 2000 to 2005.

Figure 3-13. Trends in tetrachloroethylene concentrations (μg/m^3) from 2000 to 2005.

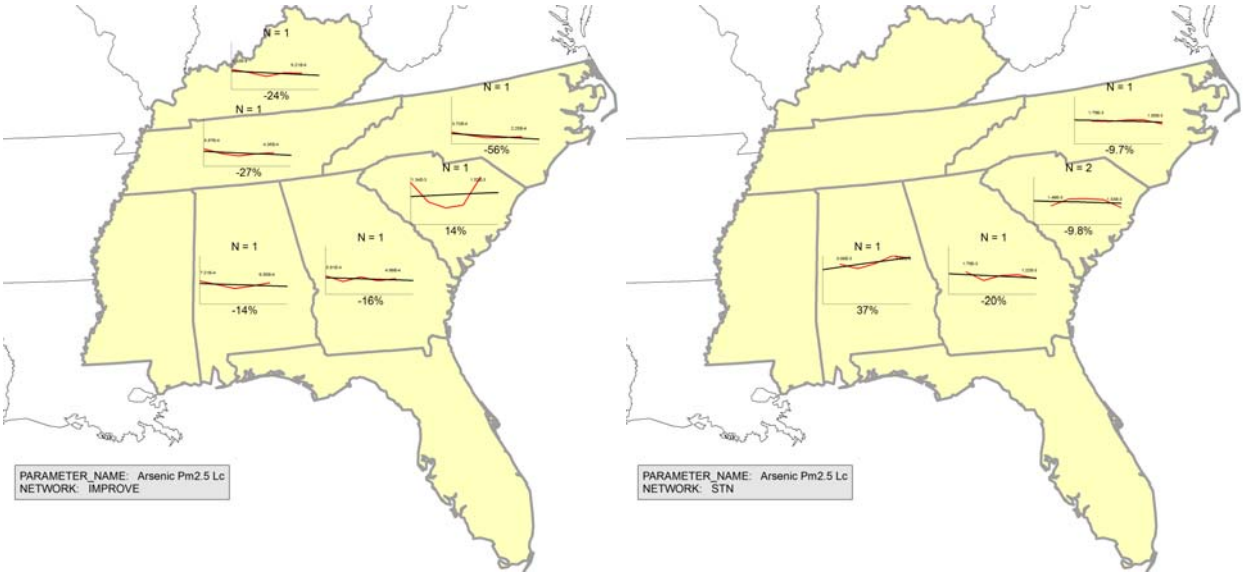

Figure 3-14. Trends in arsenic $PM_{2.5}$ concentrations ($\mu g/m^3$) from 2000 to 2005 at the IMPROVE (left) and STN (right) network sites.

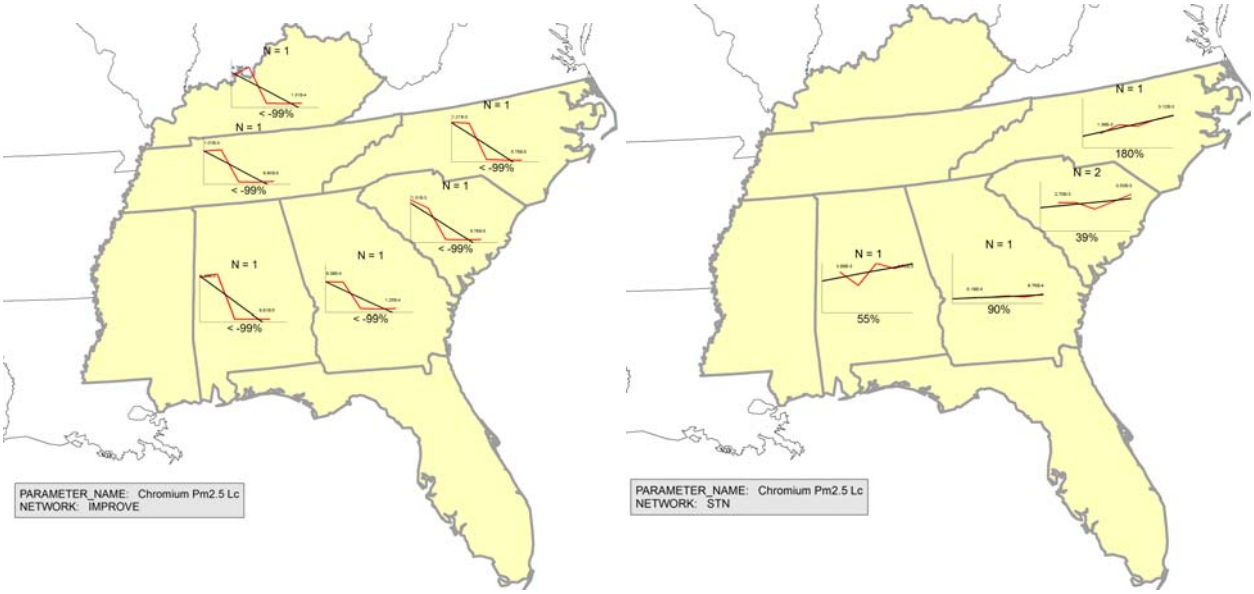

Figure 3-15. Trends[2] in chromium $PM_{2.5}$ concentrations ($\mu g/m^3$) from 2000 to 2005 at the IMPROVE (left) and STN (right) network sites.

[2] Note that large changes in concentrations may be due to changes in sampling or analytical methodology or changes in MDLs and may not reflect changes in ambient concentrations.

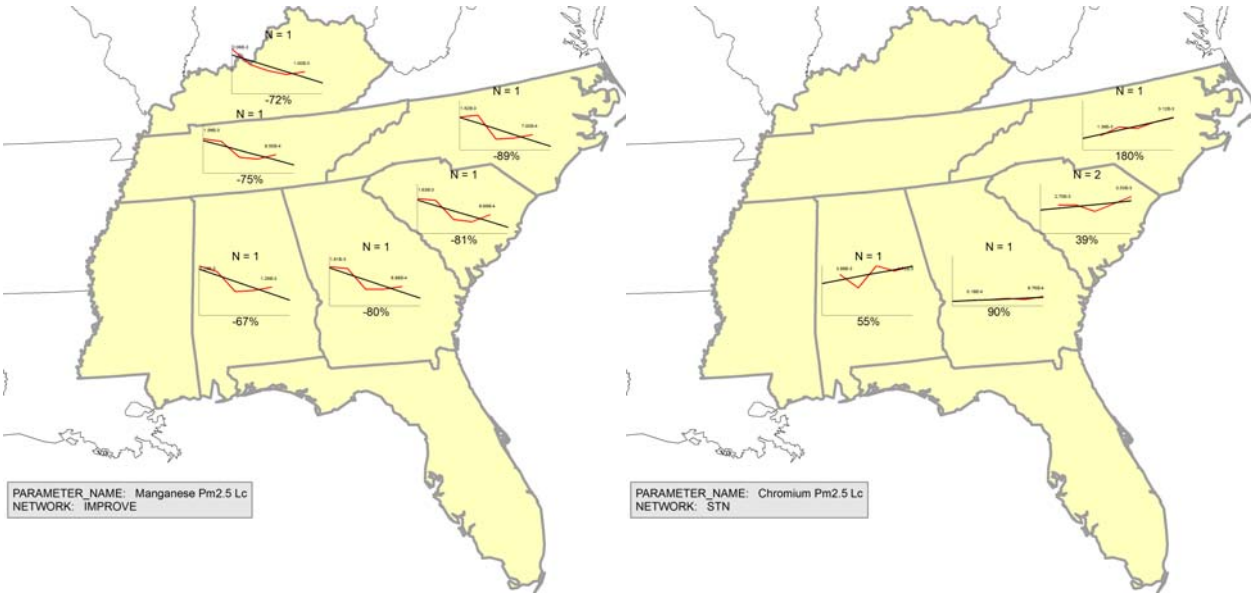

Figure 3-16. Trends in manganese $PM_{2.5}$ concentrations ($\mu g/m^3$) from 2000 to 2005 at the IMPROVE (left) and STN (right) network sites.

Given the possible changes in methods or MDLs at sites that may affect trends analysis, it should be noted that the trends described in this discussion are preliminary. Validation that an observed change in reported concentrations at a site reflects changes in ambient concentrations requires additional investigation including local knowledge of emissions changes near the monitoring site. Generating a trend is a first step to identify likely pollutants that may be good candidates for further investigation.

Despite the limitations of this large-scale analysis, we aggregated trends at all sites in **Table 3-5**. This table shows the median percentage change for each pollutant in the Southeast from 2000 to 2005 and the number of individual sites with statistically significant trends (increasing or decreasing), and the total number of sites available that met the trend criteria.

Two figures showing the minimum, median, and maximum percentage change per year in concentrations at all sites in the southeast with at least five years of monitoring data are shown in **Figures 3-17 and 3-18.** Note that this analysis does not provide the information necessary to identify method changes or MDL changes that will impact the observed trends in concentrations at individual sites. The floating bars in Figures 3-17 and 3-18 show the range of percentage change per year at all sites, and the bar in the middle shows the median percentage change per year. Pollutants with consistent changes from site-to-site will have a tighter range, while those with large variability from site-to-site will have a large range. A few pollutants are decreasing across the Southeast, including most of the aromatics (e.g., ethylbenzene, trimethylbenzene, xylenes, styrene, and benzene). Most other VOCs were statistically indistinguishable from no trend. Note that Figure 3-18 provides the range of trends for a number of pollutants even though many of the trends may not be reflective of actual changes in ambient concentrations, but are more likely a result of changes in methodology or MDL over the monitoring period.

Table 3-5. Aggregate trends in air toxics in the Southeast from 2000 through 2005. The table provides the median concentration in 2000, the mean percent change between 2000 and 2005, the 95% confidence interval about that change, the number of sites, and the number of sites with statistically significant changes.

Pollutant	Median First Year Concentration (µg/m^3)	Median % Change	# Sites (# Significantly Decreasing, # Significantly Increasing)
Formaldehyde	6.6	22	6 (1, 0)
Dichlorodifluoromethane	3.4	-26	3 (0, 0)
Toluene	3.3	-28	7 (2, 0)
Acetaldehyde	3.0	4	6 (0, 1)
M-&P-Xylene	2.5	-70	5 (3, 0)
Acetylene	2.1	-45	3 (1, 0)
Acetone	2.0	-35	4 (1, 0)
Trichlorofluoromethane	1.8	-14	3 (0, 0)
Chloromethane	1.4	0	3 (0, 0)
Benzene	1.2	-24	7 (1, 0)
O-Xylene	1.0	-62	7 (3, 0)
Propylene	0.97	-33	3 (0, 0)
2,2,4-Trimethylpentane	0.85	-38	4 (1, 0)
N-Hexane	0.83	-26	4 (0, 0)
1,2,4-Trimethylbenzene	0.74	-21	11 (2, 0)
Carbon Tetrachloride	0.61	-20	3 (0, 0)
Sodium Ion $PM_{2.5}$	0.35	-89	3 (3, 0)
Ethylbenzene	0.33	-15	12 (2, 2)
Methylcyclohexane	0.26	-50	3 (1, 0)
N-Octane	0.25	-46	3 (1, 0)
Cyclohexane	0.23	27	3 (0, 0)
Styrene	0.11	53	11 (2, 3)
Sodium $PM_{2.5}$	0.100	-24	10 (2, 0)
1,3,5-Trimethylbenzene	0.080	-3	10 (1, 0)
Isopropylbenzene	0.075	-16	3 (0, 0)
Naphthalene	0.072	-31	5 (1, 0)
Potassium $PM_{2.5}$	0.058	-13	10 (0, 0)
Iron $PM_{2.5}$	0.044	-15	10 (0, 0)
Barium $PM_{2.5}$	0.043	-42	3 (1, 0)
Potassium Ion $PM_{2.5}$	0.042	-12	3 (0, 0)
Calcium $PM_{2.5}$	0.037	-28	10 (2, 0)
Aluminum $PM_{2.5}$	0.031	5	10 (1, 0)
Chlorine $PM_{2.5}$	0.027	14	4 (0, 0)
Bis(2-Ethylhexyl)Phthalate	0.023	511	3 (0, 0)
Magnesium $PM_{2.5}$	0.017	10	3 (0, 0)
Phenanthrene	0.016	1	5 (0, 0)
Lead (Tsp)	0.011	-67	16 (7, 0)

Table 3-5. **Continuation of** aggregate trends in air toxics in the Southeast from 2000 through 2005. The table provides the median concentration in 2000, the mean percent change between 2000 and 2005, the 95% confidence interval about that change, the number of sites, and the number of sites with statistically significant changes.

Pollutant	Median First Year Concentration (µg/m^3)	Median % Change	# Sites (# Significantly Decreasing, # Significantly Increasing)
Acenaphthene	0.011	-19	5 (0, 0)
Zinc $PM_{2.5}$	0.0083	-15	16 (1, 1)
Titanium $PM_{2.5}$	0.0082	-69	11 (1, 0)
Fluorene	0.0067	-6	5 (0, 0)
Dibenzofuran	0.0039	263	5 (0, 0)
Biphenyl	0.0039	356	5 (0, 0)
Di-N-Butyl Phthalate	0.0035	247	5 (0, 0)
Fluoranthene	0.0026	73	5 (0, 0)
Manganese $PM_{2.5}$	0.0024	-37	11 (0, 0)
Lead $PM_{2.5}$	0.0023	-17	12 (0, 0)
Vanadium $PM_{2.5}$	0.0020	-22	10 (0, 1)
Copper $PM_{2.5}$	0.0020	-6	11 (0, 1)
P-Isopropyltoluene	0.0015	887	5 (0, 3)
Chromium $PM_{2.5}$	0.0014	-19	10 (0, 1)
Selenium $PM_{2.5}$	0.0013	9	9 (0, 1)
1,4-Dichlorobenzene	0.0013	391	7 (0, 1)
Arsenic $PM_{2.5}$	0.00061	-20	10 (0, 0)
Nickel $PM_{2.5}$	0.00042	4	9 (0, 0)
Strontium $PM_{2.5}$	0.00028	18	8 (0, 0)

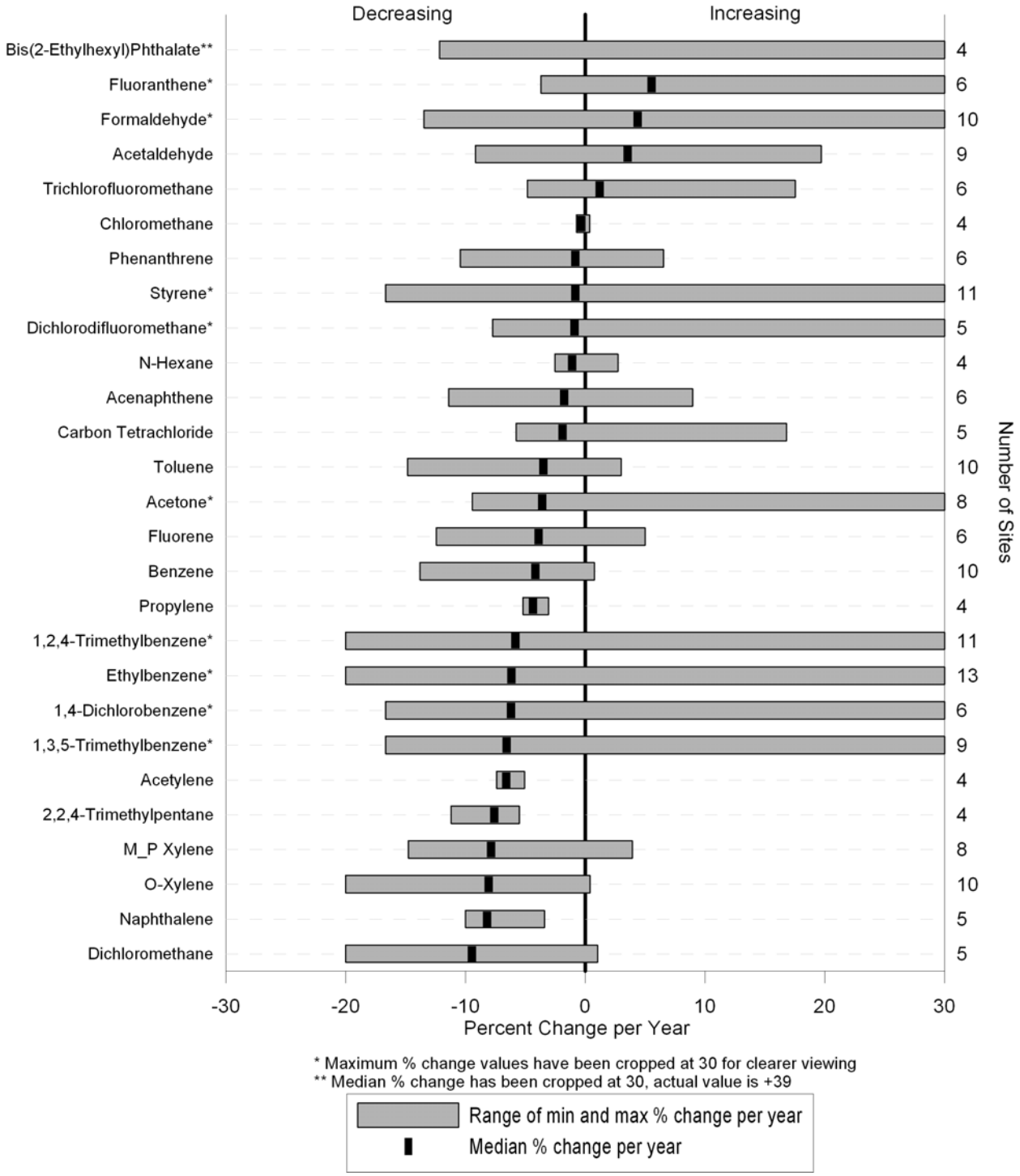

Figure 3-17. Minimum, median, and maximum percentage change per year in concentrations of VOCs and SVOCs at all sites with at least five years of monitoring data in the southeast. Note that some of the individual sites trends may not be reflective of actual concentration changes, but may be a result of changes in MDL or methodology.

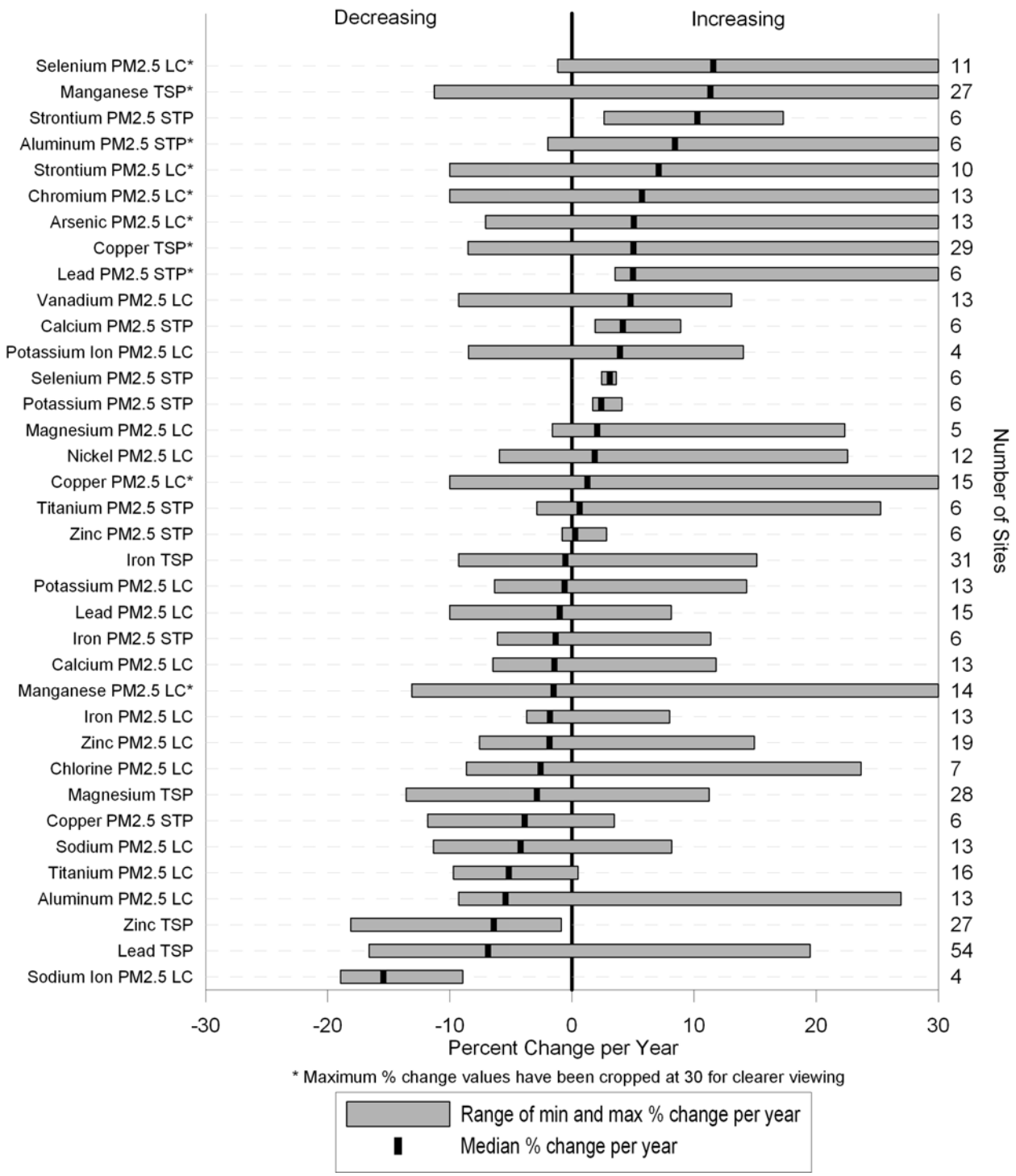

Figure 3-18. Minimum, median, and maximum percentage change per year in concentrations of particulate metals at all sites with at least five years of monitoring data in the southeast. Note that many of the individual sites trends may not be reflective of actual concentration changes, but may be a result of changes in MDL or methodology.

3.4.2 Key Findings

- Aromatic MSAT concentrations appear to be decreasing at most sites; this decrease is consistent with predominant trends in MSATs observed at urban sites across the United States.
- Trends in trace metal concentrations in particulate matter less than 2.5 microns ($PM_{2.5}$) are correlated with changes in MDLs and methodology that are network-specific. These trends are unlikely to reflect actual trends in ambient concentrations. Sophisticated trends analysis that can account for changes in the MDL over time may be needed to determine how concentrations are changing for these pollutants.
- These trends should be considered a preliminary compilation of trend values only. Individual site trends need to be verified as reflective of true ambient concentrations at the state or local level.

3.5 SPATIAL VARIABILITY

3.5.1 Objective and Approach

This task was to characterize spatial variability in air toxics using visual inspection of maps and statistical metrics. Site averages from 2003-2005 were used to generate maps of pollutant concentrations in the Southeast. Maps show proportional circles for each site average—the circle area is proportional to the concentration measured at that site. Larger circles indicate higher concentrations. In addition, the proportional circles are colored to indicate the percentage of data reported below the MDL (and therefore substituted with MDL/2) at each site. Green circles indicate sites with less than 50% of data below MDL, yellow circles indicate 50-85% of data was below MDL, and red circles indicate that more than 85% of data was below MDL. STI analysts then examined these maps to identify spatial variability and outlier sites for each pollutant. The maps are a useful qualitative tool.

STI analysts also used the site average concentrations to calculate metrics for quantifying differences in spatial variability between sites. Only pollutants monitored at at least eight sites with less than 85% of data below MDL were used. One metric used was the coefficient of variation (CV), which is simply the standard deviation divided by the mean. In this situation, the CV indicates the variance in concentrations across sites and can be used to compare the spatial variability of pollutants with very different concentrations. A difficulty of this metric is that it is based on a normal distribution of data. Unfortunately, ambient monitoring data are usually log-normally distributed. A second metric to assess spatial variability that is not as sensitive to the distribution is the 75th-to-25th percentile ratio. Higher ratios indicate higher variability.

3.5.2 Results

Figures 3-19 through 3-28 show concentrations of multiple pollutants that are key risk drivers and contributors in the Southeast as determined by the risk screen analysis. Maps were generated for all pollutants, but only a small fraction of them are shown in this report; all maps

will be available on a completed web site. Note that on a given map, all circles are drawn to the same scale. However, different maps may have different concentration scales; these scales are different because pollutant concentrations vary over many orders of magnitude, and a single scale cannot be applied to all. Maps in this section are organized in order of decreasing concentration scale (e.g., the scale for benzene is much greater than the scale for nickel $PM_{2.5}$); all concentrations are in $\mu g/m^3$.

Figure 3-19 displays concentrations of benzene, which is a national risk driver. Overall, relatively similar concentrations of benzene occur at most sites. Concentrations at the site in Jacksonville, Florida, are higher than at other sites. Otherwise, benzene concentrations across the Southeast are within the spatial variability expected at the national scale (roughly a factor of 3). Figure 3-20 shows acetaldehyde concentrations. Concentrations again appear relatively consistent across sites, although concentrations at a single site in South Carolina are somewhat higher than at other sites. Acetaldehyde appears to be reliably measured at all sites.

Figure 3-21 shows concentrations of dichloromethane. This figure illustrates some problems across different monitoring agencies that confound a spatial analysis. Note that some agencies have very different detection limits, as shown by the large red circles in some areas compared to the smaller green and yellow circles in another. This interagency difference confounds quantitative comparisons, since we are end up comparing differences in MDL/2 values with measured concentrations.

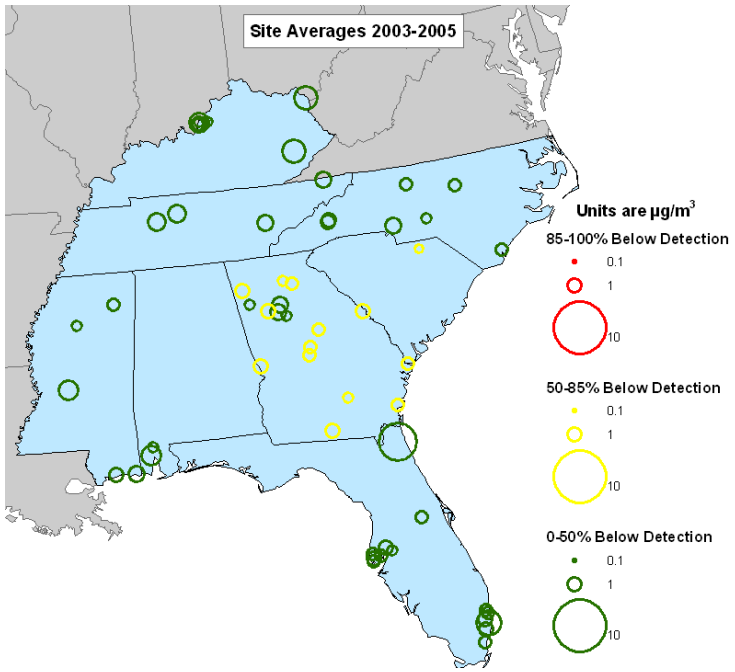

Figure 3-19. Site average concentrations ($\mu g/m^3$) of benzene from 2003-2005. Symbols are color coded by percent of data below MDL. Red =>85% below MDL, yellow = 50-85% below MDL, green =<50% below MDL.

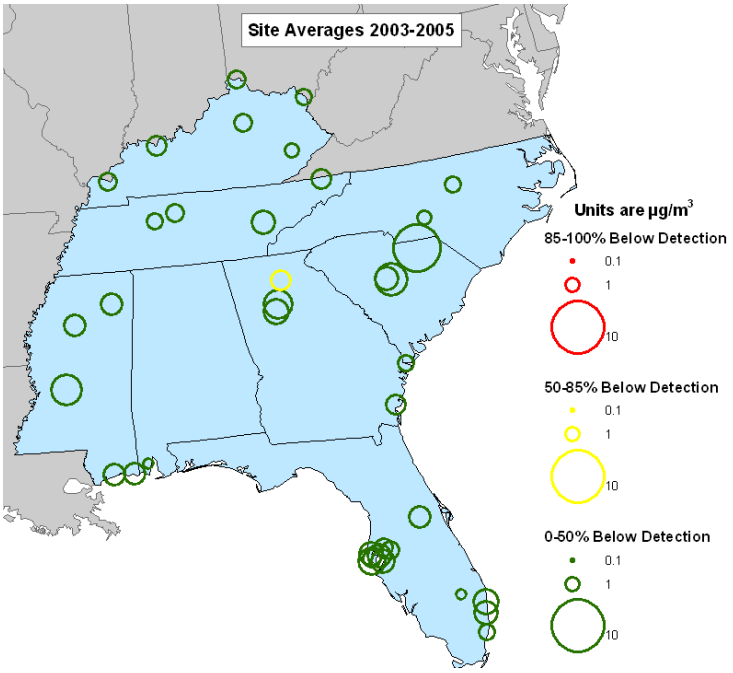

Figure 3-20. Site average concentrations (µg/m^3) of acetaldehyde from 2003-2005. Symbols are color coded by percent of data below MDL. Red =>85% below MDL, yellow = 50-85% below MDL, green =<50% below MDL.

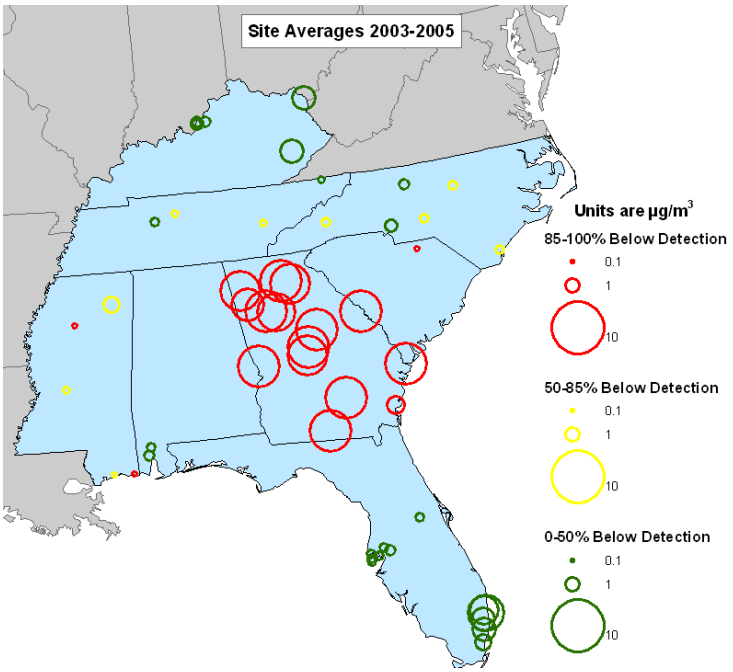

Figure 3-21. Site average concentrations (µg/m^3) of dichloromethane from 2003-2005. Symbols are color coded by percent of data below MDL. Red =>85% below MDL, yellow = 50-85% below MDL, green =<50% below MDL.

Figures 3-22 through 3-26 show concentrations of 1,3-butadiene, carbon tetrachloride, tetrachloroethene, ethylene dibromide, and 1,2-dichloropropane, respectively. Each pollutant was identified as a risk contributor or driver by NATA99. In each figure, interagency monitoring differences across the Southeast confound a quantitative spatial analysis. In Figure 3-22, 1,3-butadiene concentrations are higher in Kentucky and lower in Florida than concentrations in other southeastern states in which almost all concentrations are below MDL. Clearly, differences in sampling and analytical methodologies between agencies are responsible for at least some of the very different results across jurisdictional borders. Spatial variability within local or state jurisdictions are likely real and comparable, but differences among reporting agencies are suspect.

Note that the two sites in Eastern Kentucky that appear to have high concentrations for each of these figures relative to other sites in the Southeast are not real concentrations. A February contact with a representative from the Kentucky Department of Environmental Protection revealed that data reported to AQS used a qualifier code to indicate records below the lowest calibration level. These sites reported practical quantitation limits (PQL) or reporting limit (RL) values, rather than actual measured values. This unique reporting resulted in high concentrations that appear higher than MDL when they should, in fact, be considered below MDL values. Therefore, concentrations at these sites for most of the pollutants displayed are about a factor of 20 higher than they should be. Concentrations of VOCs displayed on these maps for the two eastern Kentucky sites should be considered invalid for the purpose of comparison with other sites.

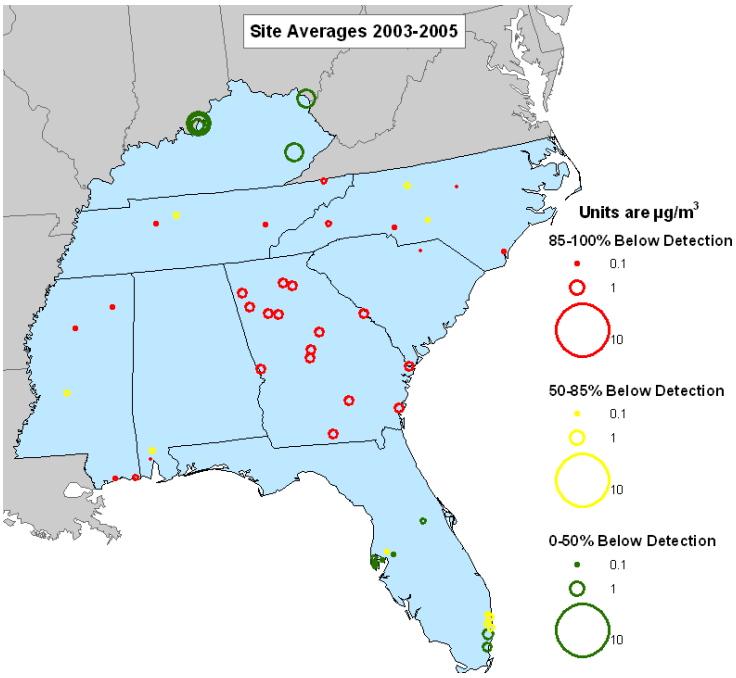

Figure 3-22. Site average concentrations (µg/m^3) of 1,3-butadiene from 2003-2005. Symbols are color coded by percent of data below MDL. Red =>85% below MDL, yellow = 50-85% below MDL, green =<50% below MDL.

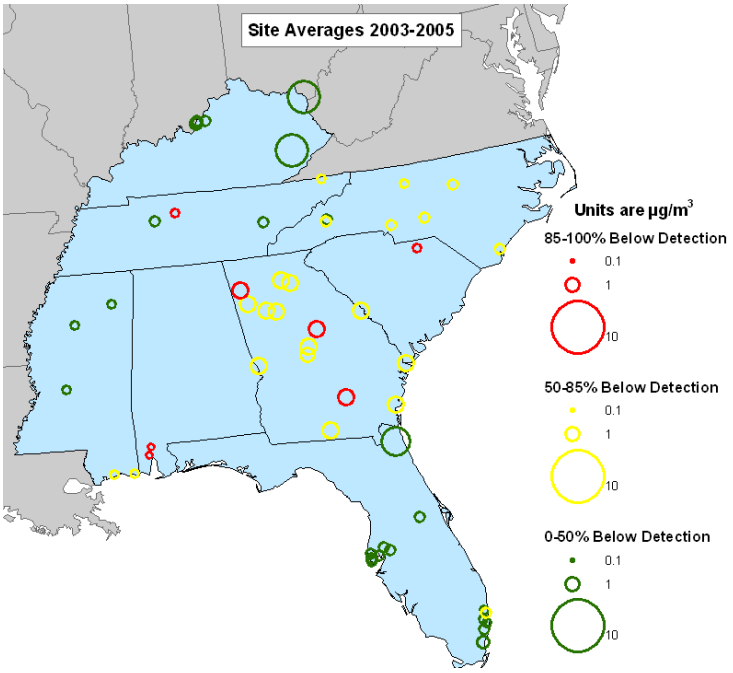

Figure 3-23. Site average concentrations (µg/m^3) of carbon tetrachloride from 2003-2005. Symbols are color coded by percent of data below MDL. Red =>85% below MDL, yellow = 50-85% below MDL, green =<50% below MDL.

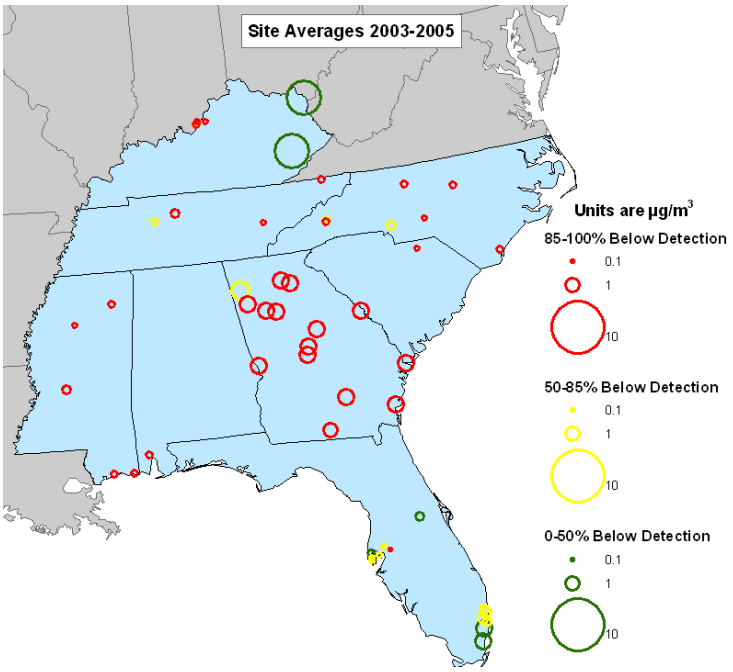

Figure 3-24. Site average concentrations (µg/m^3) of tetrachloroethene from 2003-2005. Symbols are color coded by percent of data below MDL. Red =>85% below MDL, yellow = 50-85% below MDL, green =<50% below MDL.

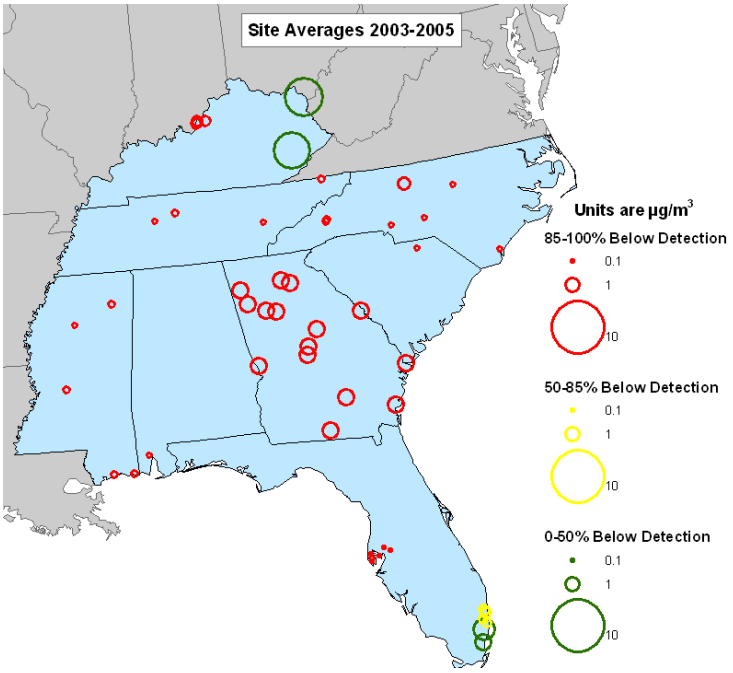

Figure 3-25. Site average concentrations (µg/m^3) of ethylene dibromide from 2003-2005. Symbols are color coded by percent of data below MDL. Red =>85% below MDL, yellow = 50-85% below MDL, green =<50% below MDL.

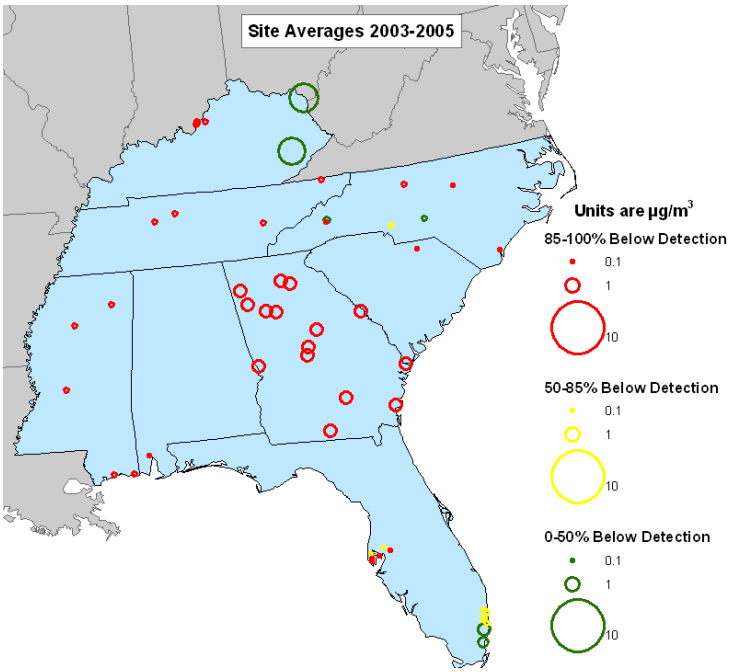

Figure 3-26. Site average concentrations (µg/m^3) of 1,2-dichloropropane from 2003-2005. Symbols are color coded by percent of data below MDL. Red =>85% below MDL, yellow = 50-85% below MDL, green =<50% below MDL.

Given the differences among VOC concentrations reported by different agencies, it is not surprising that large differences also appear to exist between trace metal concentrations in particulate matter (PM) monitored by networks. Figures 3-27 and 3-28 show concentrations of arsenic and nickel in PM of size fraction smaller than 2.5 micrometers ($PM_{2.5}$). In these two maps, the sites with the lowest concentrations are invariably monitored above MDL a higher fraction of the time. Previous analysis by STI has shown that IMPROVE rural sites have much lower MDLs than those in the STN network (Hafner et al., 2006). Network differences in MDLs are likely responsible for at least some of the differences in reported concentrations seen in these two figures.

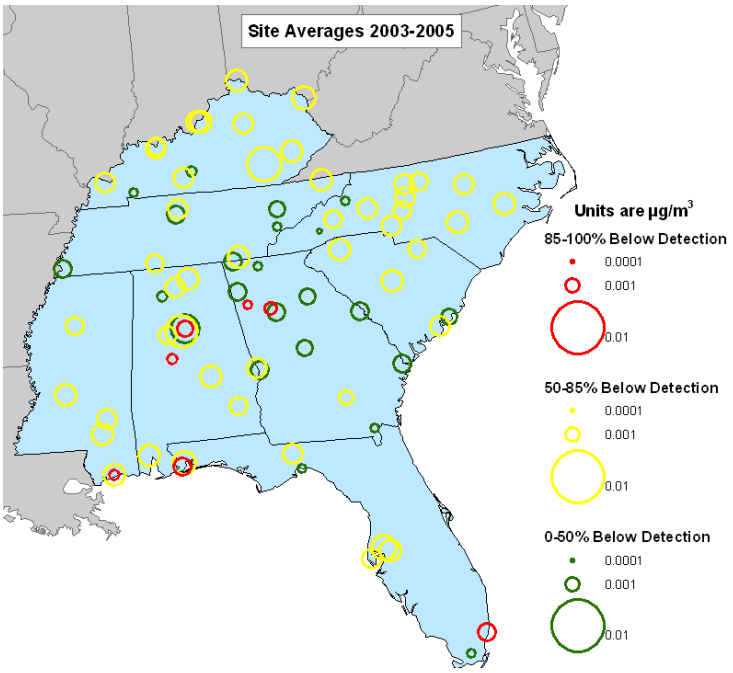

Figure 3-27. Site average concentrations ($\mu g/m^3$) of arsenic $PM_{2.5}$ from 2003-2005. Symbols are color coded by percent of data below MDL. Red =>85% below MDL, yellow = 50-85% below MDL, green =<50% below MDL.

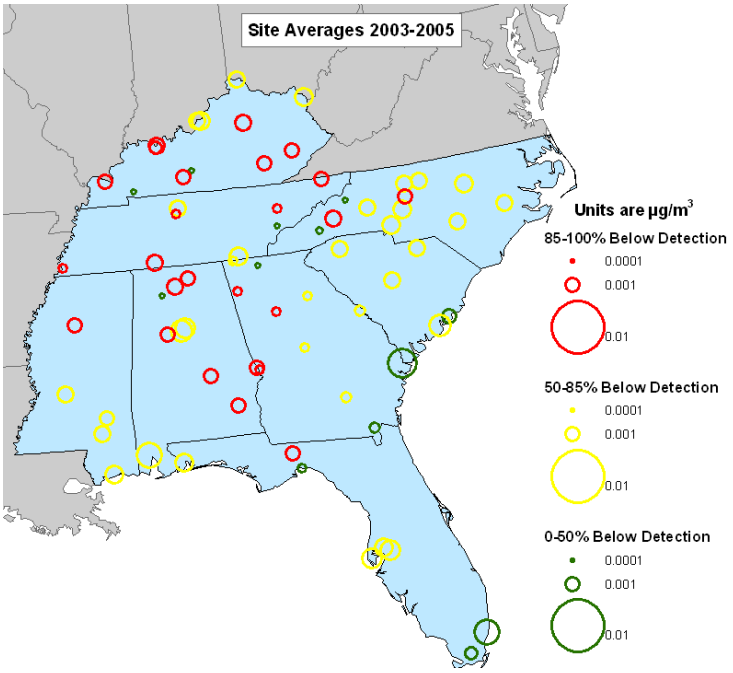

Figure 3-28. Site average concentrations ($\mu g/m^3$) of nickel $PM_{2.5}$ from 2003-2005. Symbols are color coded by percent of data below MDL. Red =>85% below MDL, yellow = 50-85% below MDL, green =<50% below MDL

Given the systematic differences between data reported by different monitoring agencies and networks, quantitative comparison of spatial variability is extremely difficult. However, it is possible to qualitatively compare within groups of pollutants that are monitored at similar sites. For this analysis, the relative variability of pollutants within a similar monitoring group can be inspected and systematic biases can be assumed to be similar across networks or reporting agencies. **Figure 3-29** shows the CV and 75th:25th percentile ratio metrics for assessing spatial variability. The largest range in spatial variability is seen across the VOCs. Some pollutants such as the chlorofluorocarbons have very little spatial variability (low CVs and 75th:25th ratios) while others have very high spatial variability. Concentrations of metals are the least variable. **Table 3-6** provides the same information in tabular format, along with the total number of monitoring sites and the number of monitoring sites with more than 85% of data below MDL. This table also provides an indication of the level of confidence that STI analysts assigned to the spatial variation based on visual inspection of the maps associated with the data. These judgments are subjective.

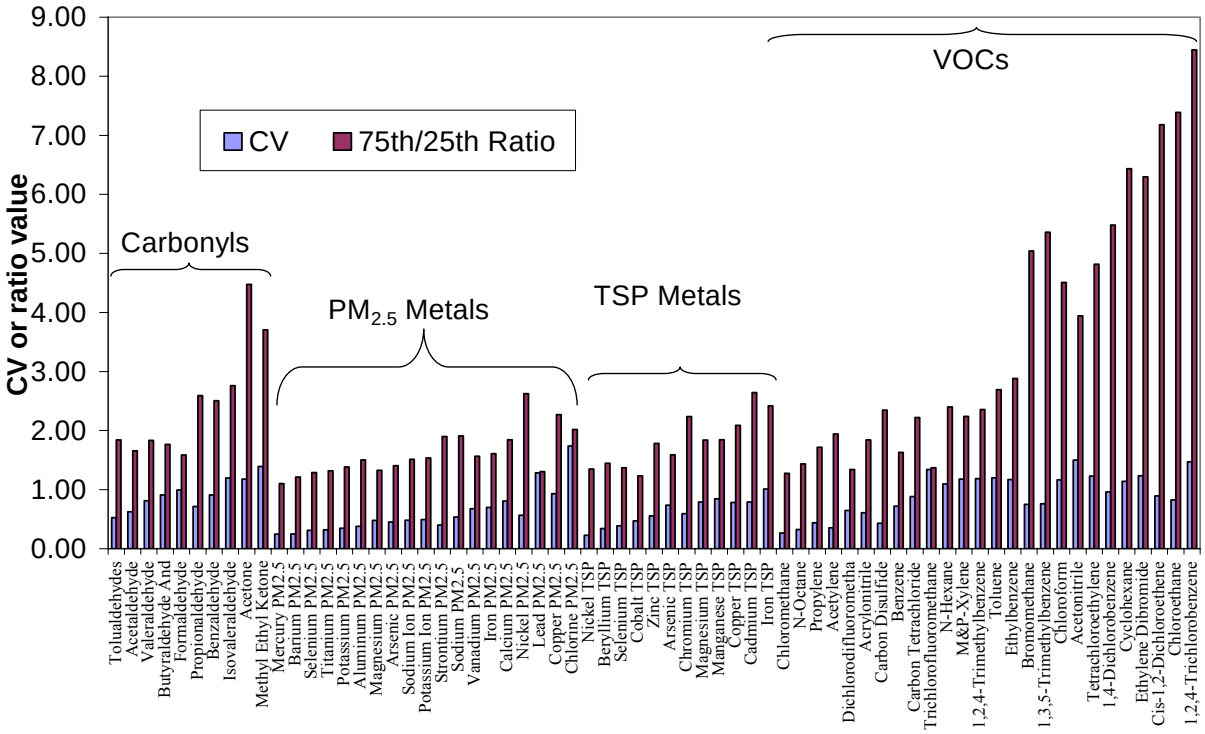

Figure 3-29. Spatial variability metrics for pollutants in the Southeast grouped by pollutant monitoring category. The largest range of spatial variability is seen in the VOCs.

Table 3-6. Metrics of spatial variability for air toxics ordered by pollutant category.

Pollutant	Grouping	Total Site Count	# Sites < 85% BD	CV	75th : 25th Ratio	Confidence
Tolualdehydes	Carbonyl	23	23	0.53	1.84	Confident
Acetaldehyde	Carbonyl	38	38	0.63	1.66	Confident
Valeraldehyde	Carbonyl	23	23	0.81	1.83	Confident
Butyraldehyde and Isobutyraldehyde	Carbonyl	23	23	0.91	1.77	Confident
Formaldehyde	Carbonyl	38	38	1.00	1.59	Confident
Propionaldehyde	Carbonyl	28	25	0.71	2.59	Confident
Benzaldehyde	Carbonyl	28	25	0.91	2.50	Less confidence
Isovaleraldehyde	Carbonyl	23	16	1.20	2.76	Not confident
Acetone	Carbonyl	37	37	1.18	4.48	Confident
Methyl Ethyl Ketone	Carbonyl	20	17	1.39	3.71	Less confidence
Mercury $PM_{2.5}$	$PM_{2.5}$	62	20	0.25	1.10	Not confident
Barium $PM_{2.5}$	$PM_{2.5}$	62	34	0.25	1.21	Not confident
Selenium $PM_{2.5}$	$PM_{2.5}$	72	43	0.31	1.29	Less confidence
Titanium $PM_{2.5}$	$PM_{2.5}$	72	72	0.32	1.32	Less confidence
Potassium $PM_{2.5}$	$PM_{2.5}$	72	72	0.35	1.38	Confident
Aluminum $PM_{2.5}$	$PM_{2.5}$	72	72	0.38	1.50	Less confidence
Magnesium $PM_{2.5}$	$PM_{2.5}$	72	22	0.48	1.33	Not confident
Arsenic $PM_{2.5}$	$PM_{2.5}$	72	71	0.45	1.41	Less confidence
Sodium Ion $PM_{2.5}$	$PM_{2.5}$	62	62	0.48	1.51	Confident
Potassium Ion $PM_{2.5}$	$PM_{2.5}$	62	62	0.49	1.54	Less confidence
Strontium $PM_{2.5}$	$PM_{2.5}$	72	36	0.40	1.90	Not confident
Sodium $PM_{2.5}$	$PM_{2.5}$	72	63	0.54	1.91	Not confident
Vanadium $PM_{2.5}$	$PM_{2.5}$	72	55	0.68	1.57	Not confident
Iron $PM_{2.5}$	$PM_{2.5}$	72	72	0.70	1.61	Confident
Calcium $PM_{2.5}$	$PM_{2.5}$	72	72	0.81	1.84	Confident
Nickel $PM_{2.5}$	$PM_{2.5}$	72	47	0.56	2.62	Not confident
Lead $PM_{2.5}$	$PM_{2.5}$	72	71	1.28	1.31	Confident
Copper $PM_{2.5}$	$PM_{2.5}$	72	71	0.93	2.27	Less confidence
Chlorine $PM_{2.5}$	$PM_{2.5}$	72	63	1.74	2.02	Not confident
Nickel TSP	TSP	46	19	0.23	1.35	Not confident
Beryllium TSP	TSP	20	8	0.34	1.45	Not confident
Selenium TSP	TSP	22	18	0.39	1.37	Not confident
Cobalt TSP	TSP	20	14	0.47	1.23	Not confident
Zinc TSP	TSP	40	40	0.55	1.78	Less confidence
Arsenic TSP	TSP	22	16	0.74	1.59	Not confident
Chromium TSP	TSP	46	26	0.60	2.24	Not confident
Magnesium TSP	TSP	26	24	0.79	1.84	Less confidence
Manganese TSP	TSP	46	42	0.85	1.85	Less confidence
Copper TSP	TSP	26	26	0.78	2.09	Less confidence
Cadmium TSP	TSP	46	17	0.79	2.64	Not confident
Iron TSP	TSP	26	26	1.01	2.42	Less confidence

Table 3-6. Metrics of spatial variability for air toxics ordered by pollutant category.

Pollutant	Grouping	Total Site Count	# Sites < 85% BD	CV	75th : 25th Ratio	Confidence
Chloromethane	VOC	48	48	0.26	1.28	Confident
N-Octane	VOC	15	10	0.33	1.44	Not confident
Propylene	VOC	15	15	0.44	1.72	Not confident
Acetylene	VOC	15	15	0.35	1.94	Less confidence
Dichlorodifluoromethane	VOC	52	52	0.65	1.34	Confident
Acrylonitrile	VOC	28	19	0.61	1.84	Not confident
Carbon Disulfide	VOC	13	8	0.43	2.34	Not confident
Benzene	VOC	57	57	0.72	1.63	Confident
Carbon Tetrachloride	VOC	55	51	0.89	2.22	Less confidence
Trichlorofluoromethane	VOC	53	53	1.34	1.37	Confident
N-Hexane	VOC	17	15	1.10	2.40	Not confident
M_P Xylene	VOC	52	45	1.18	2.24	Confident
1,2,4-Trimethylbenzene	VOC	59	47	1.19	2.36	Confident
Toluene	VOC	55	55	1.20	2.69	Confident
Ethylbenzene	VOC	60	50	1.17	2.88	Less confidence
Bromomethane	VOC	53	14	0.75	5.04	Not confident
1,3,5-Trimethylbenzene	VOC	53	33	0.76	5.36	Less confidence
Chloroform	VOC	53	22	1.16	4.51	Not confident
Acetonitrile	VOC	9	8	1.50	3.94	Less confidence
Tetrachloroethylene	VOC	54	26	1.23	4.81	Less confidence
1,4-Dichlorobenzene	VOC	57	24	0.96	5.48	Not confident
Cyclohexane	VOC	30	18	1.14	6.43	Not confident
Ethylene Dibromide	VOC	55	13	1.24	6.29	Not confident
Cis-1,2-Dichloroethene	VOC	53	10	0.90	7.18	Not confident
Chloroethane	VOC	49	17	0.83	7.39	Not confident
1,2,4-Trichlorobenzene	VOC	57	11	1.47	8.45	Not confident

3.5.3 Key Findings

- Large differences in sampling and analytical methodology and MDLs between reporting agencies and networks confound this analysis.
  - Volatile organic compound (VOC) methods and MDLs vary among jurisdictional boundaries (e.g., between states and/or agencies).
  - $PM_{2.5}$ metals methods and MDLS are monitoring network-dependent (e.g., Interagency Monitoring of Protected Visual Environments [IMPROVE] vs. Speciation Trends Network [STN]).
- VOCs appear to have a wider range of spatial variability across pollutants compared to metals and carbonyl compounds. It is unclear if this is due to real spatial differences or due to sampling and analytical differences across reporting agencies.

- A key recommendation from this work is that interlaboratory comparisons or regionally (nationally) consistent sampling and analysis standards need to be implemented to promote consistency of data reported by different networks or agencies.

3.6 COMPARISON OF AMBIENT MONITORING DATA TO PREDICTED MODEL CONCENTRATIONS FROM NATA99

3.6.1 Objective and Approach

This task was to compare ambient monitored concentrations in the Southeast to NATA99 model-predicted concentrations at the census tract level; site average concentrations from 1998-2000 were used. NATA Census tract level data was obtained from the NATA web site (U.S. Environmental Protection Agency, 2006a). Concentrations at each site were mapped to 1999 census tracts using latitude and longitude. Ratios of model-predicted concentrations to ambient concentrations (model-to-monitor) were generated for each site. Pollutants were then classified into high confidence and low confidence pollutants based on the fraction of sites with more than 85% of monitoring data below the MDL.

Ratios of predicted-to-monitored concentrations were then used to generate box plots for all pollutants with sufficient data for the analysis. Pollutant data monitored at at least five sites were considered somewhat representative of the Southeast. Pollutants for which a large fraction of the results had model-to-monitor ratios between 0.5 and 2 (i.e., within a factor of 2) were considered to have good agreement as defined in the NATA99 documentation. Scatter plots of the model-to-monitor agreement for all pollutants were also generated.

Finally, STI attempted to determine which sites met rural monitoring site criteria. Two criteria were used. First, the distance between the monitoring site and the nearest metropolitan city boundary (i.e., core-based statistical area or CBSA) was calculated. Cities within a CBSA were not considered rural. Second, the population density of each site was calculated by dividing the countywide population by the area of the county. For the United States as a whole, the median urban population county density was about 200 people per square mile. In the Southeast, no monitoring sites were located in counties with fewer than 800 people per square mile during the 1998-2000 time period. Therefore, this analysis was not performed.

3.6.2 Results

Figure 3-30 shows a box plot of the ratio of model-to-monitor concentrations in the Southeast for pollutants with reliable concentration estimates. Box plots show the 25th to 75th percentile range as the box, the mean as the dash within the box, 1.5 times the interquartile range as the whiskers, and outliers as asterisks. Pollutants showing good model-to-monitor agreement include acetaldehyde, benzene, dichloromethane, ethylbenzene, n-hexane, toluene, and nickel $PM_{2.5}$. No pollutants were systematically overpredicted (model-to-monitor ratio > 2). Other pollutants were systematically underpredicted (i.e., model-to-monitor ratio < 0.5) , including arsenic $PM_{2.5}$, chloroform, chromium $PM_{2.5}$, hexachlorobutadiene, lead ($PM_{2.5}$ and TSP), manganese $PM_{2.5}$, and selenium $PM_{2.5}$. These results are similar to results at the national level.

Figure 3-31 shows a box plot of the ratio of model-to-monitor concentrations taken from the NATA web site. Pollutants are underpredicted nationally, although not quite to the extent that they are underpredicted in the Southeast. At least some of the discrepancy between the two sets of results may be due to the few sites available for this comparison.

Table 3-7 shows the number of monitoring sites available for this analysis, along with the breakdown of the number of sites with data above and below the 85% below MDL threshold. This table also includes the median ratio of model-to-monitor concentrations and a standard deviation of this ratio across sites in the Southeast.

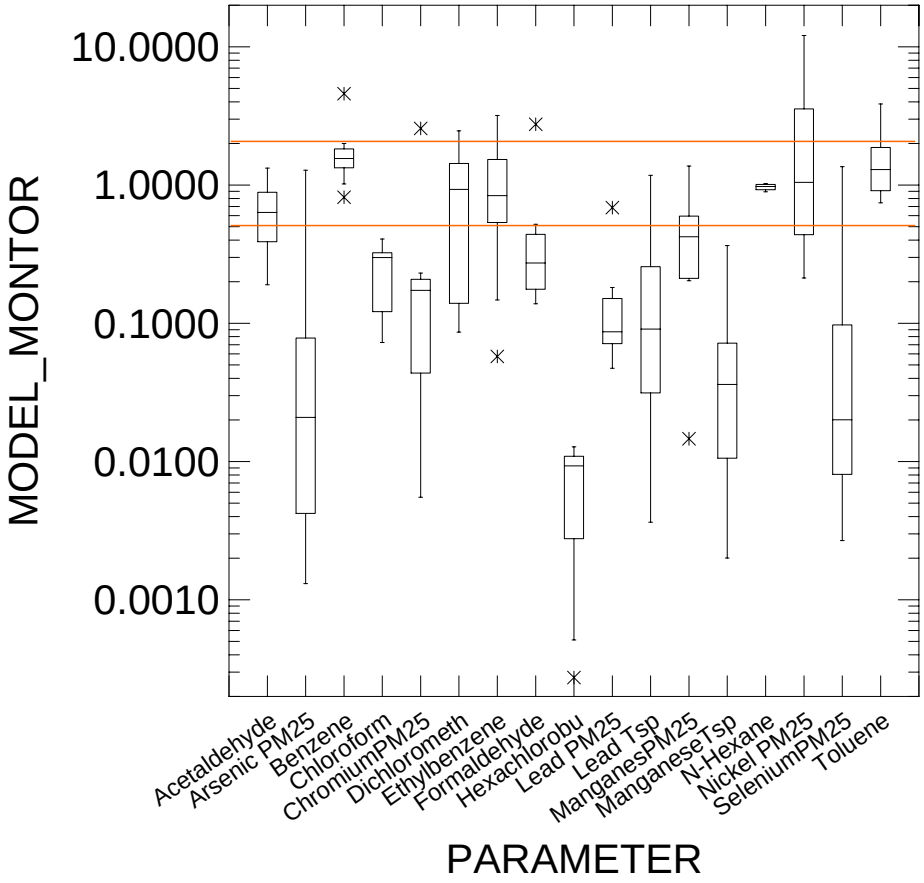

Figure 3-30. Box plots of model:monitor ratios across pollutants with relatively well measured concentrations (i.e., most sites have data above the MDL). Pollutants for which most of the ratios are between 0.5 and 2.0 are considered well monitored.

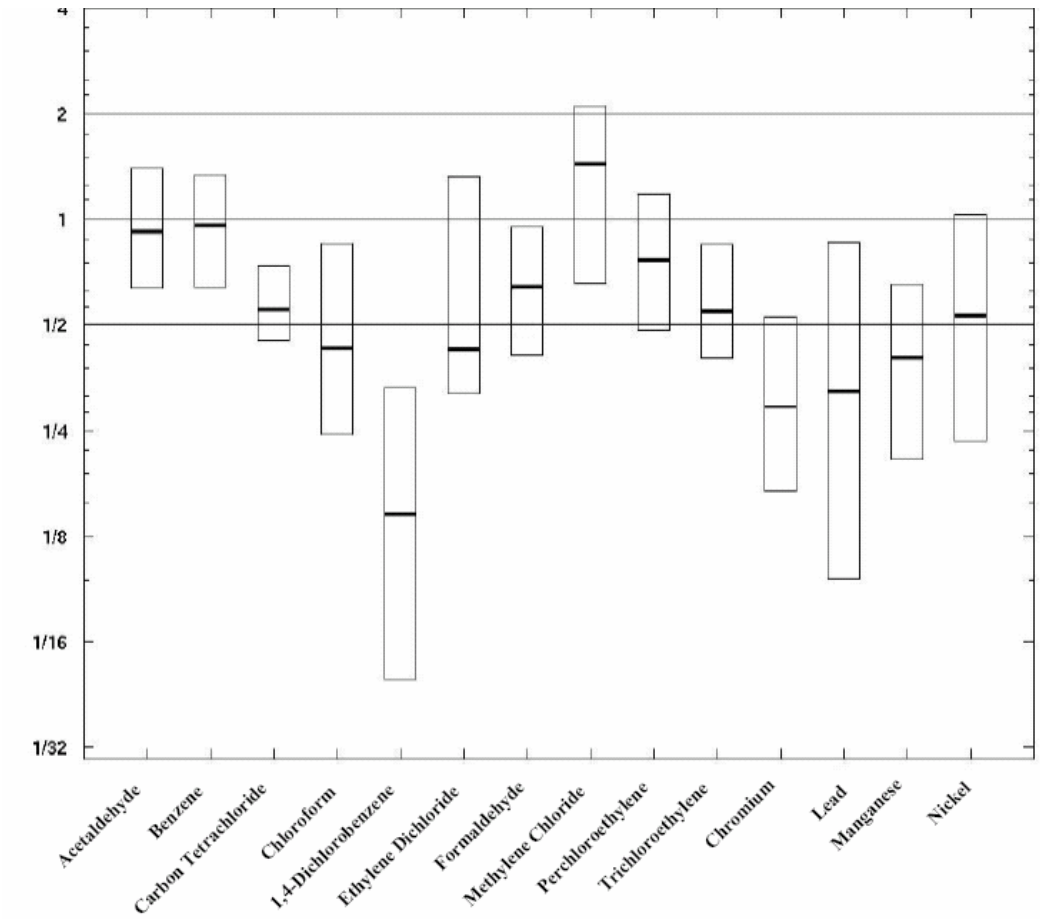

Figure 3-31. Box plots of model:monitor ratios across pollutants for the United States. Pollutants for which most of the ratios are between 0.5 and 2.0 are considered well monitored.
Source: http://www.epa.gov/ttn/atw/nata1999/99compare.html.

Table 3-7. Counts of available monitoring sites, median model-to-monitor ratio, and standard deviation of the model-to-monitor ratio across sites. Ratios between 0.5 to 2 are shown in boldface. Pink values indicate unreliable ratios.

Pollutant	Total # of Sites	Sites With Less Than 85% of Data Below MDL	Sites With More Than 85% of Data Below MDL	Median Model: Monitor Ratio	Standard Deviation of Model:Monitor Ratio Across Sites
1,1,2,2-Tetrachloroethane	5	0	5	0.232	0.104
1,1,2-Trichloroethane	5	2	3	0.000008	0.000004
1,1-Dichloroethane	5	0	5	0.0005	0.0017
1,1-Dichloroethylene	5	2	3	0.0012	0.0005
1,4-Dichlorobenzene	12	3	9	0.024	0.029
Acetaldehyde	7	7	0	**0.634**	0.416
Arsenic PM2.5	7	7	0	0.021	0.472
Benzene	9	9	0	1.56	1.11
Cadmium (TSP)	31	1	30	0.024	0.025
Carbon Tetrachloride	5	2	3	0.497	0.176
Chlorine ($PM_{2.5}$)	8	1	7	0.257	0.607
Chlorobenzene	5	2	3	0.139	0.020
Chloroform	5	3	2	0.299	0.142
Dichloromethane	5	5	0	**0.929**	0.991
Ethylbenzene	17	10	7	**0.839**	0.889
Ethylene Dibromide	5	0	5	0.069	0.027
Ethylene Dichloride	5	2	3	0.100	0.008
Formaldehyde	7	7	0	0.273	0.946
Hexachlorobutadiene	13	9	4	0.009	0.005
Lead (TSP)	48	43	5	0.091	0.234
Lead $PM_{2.5}$	7	7	0	0.087	0.227
Manganese TSP	31	31	0	0.036	0.076
Manganese $PM_{2.5}$	7	7	0	0.422	0.462
N-Hexane	4	4	0	**0.977**	0.056
Nickel (TSP)	31	1	30	0.058	0.453
Nickel $PM_{2.5}$	8	5	3	**1.06**	4.08
Selenium $PM_{2.5}$	7	7	0	0.020	0.501
Styrene	16	7	9	0.101	0.244
Tetrachloroethylenes	5	2	3	**0.564**	0.459
Toluene	9	9	0	**1.30**	0.975
Trichloroethylene	5	2	3	0.147	0.622
Vinyl Chloride	5	0	5	**0.594**	0.082

Individual scatter plots comparing model-to-monitor concentrations by pollutants at all sites in the Southeast were also created (e.g., **Figure 3-32** for benzene and **Figure 3-33** for lead TSP). Both figures show the 1:2 line and 2:1 line, between which data points are considered in reasonable agreement. Modeled benzene concentrations are in relatively good agreement with monitored concentrations, but lead (TSP) concentrations are greatly underpredicted by the model. Some of this discrepancy may be attributed to Census tract level concentrations reported lower than site-specific concentrations, especially for source-oriented monitors such as lead TSP.

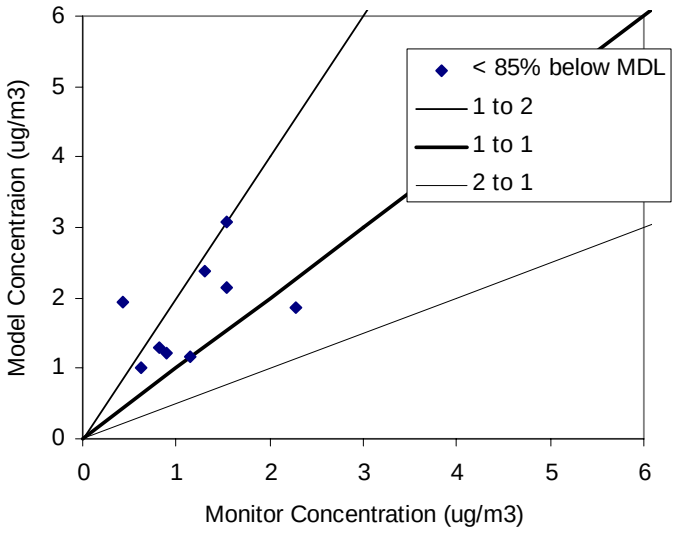

Figure 3-32. Scatter plot of modeled and monitored concentrations for benzene.

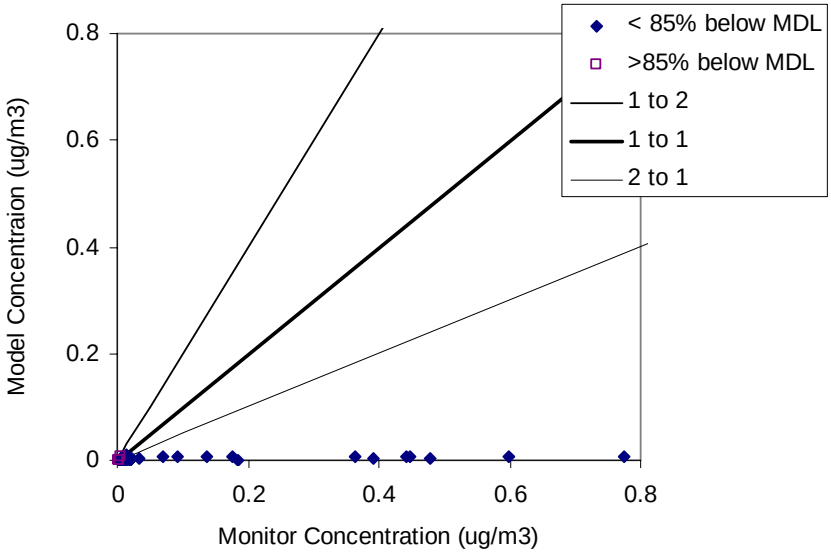

Figure 3-33. Scatter plot of modeled and monitored concentrations for lead (TSP). Most model-predicted concentrations were well below ambient concentrations.

3.6.3 Key Findings

- Some pollutant concentrations were predicted well in NATA99 for the southeastern states, including acetaldehyde, benzene, dichloromethane, ethylbenzene, n-hexane, toluene, and nickel $PM_{2.5}$.
- No pollutants were monitored that were systematically overpredicted (model-to-monitor ratio > 2) by NATA99.
- Other pollutant concentrations were usually underpredicted (model-to-monitor ratio <0.5) by NATA99, including arsenic $PM_{2.5}$, chloroform, chromium $PM_{2.5}$, hexachlorobutadiene, lead ($PM_{2.5}$ and TSP), manganese $PM_{2.5}$, and selenium $PM_{2.5}$. Lead TSP may be underpredicted because it is often monitored close to a source and model resolution is not sufficient to characterize these near-source gradients.

3.7 MDL COMPARISON

3.7.1 Objective and Approach

In this task, MDL values were assessed in the Southeast to determine if the Southeast MDLs were lower, the same, or higher than MDL values in the rest of the nation. Site average MDLs were calculated using the same methodology as that described for pollutant concentrations. One difference between reported concentrations and MDLs in the database is the availability of two possible sources for an MDL value. Some records in the database have an MDL value specifically reported with them. These MDLs are used whenever available. When no specific MDL was assigned to a given record, the default MDL associated with the sampling and analysis method code is used. For a site average MDL value, MDL values are averaged using the same criteria as those described for site average concentrations in Section 2.1. Site averages were calculated for sites within the SESARM region and nationwide.

After calculating site average MDLs, summary statistics including the minimum, maximum, 5th, 25th, 50th, 75th, and 95th percentile MDL concentrations were calculated for the SESARM region sites and for all sites in the United States outside the SESARM region. Data were plotted for comparison for all species with more than 25% of sites considered uncharacterizable by the risk screen as shown in Tables 3-3 and 3-4.

Pollutants with a significant discrepancy in typical MDL concentrations between the SESARM and national sites were noted. Sampling and analytical methodologies with particularly low MDLs were identified as candidates to replace current methods in the SESARM region. Analysis to fully determine acceptable sampling and analytical methodology would need to consider additional issues beyond a simple comparison of MDL values such as cost, sample size, duration requirements, availability of instrumentation, etc.

3.7.2 Results

Figures 3-34 through 3-36 show key pollutant MDL ranges in the Southeast compared to those in the rest of the country. Each figure shows the range of MDL concentrations, the number of sites from which the range was obtained, and a comparison to the EPA OAQPS one-in-a-million cancer benchmark (or reference concentration for acrolein). For most of these pollutants, MDL concentrations are typically higher than the cancer benchmark levels in both the Southeast and the rest of the country. For example, ethylene dibromide MDL concentrations are approximately a factor of 100 higher than the cancer benchmark (Figure 3-32). Characterizing the risk associated with this species at sites where concentrations are below the MDL requires a lower MDL.

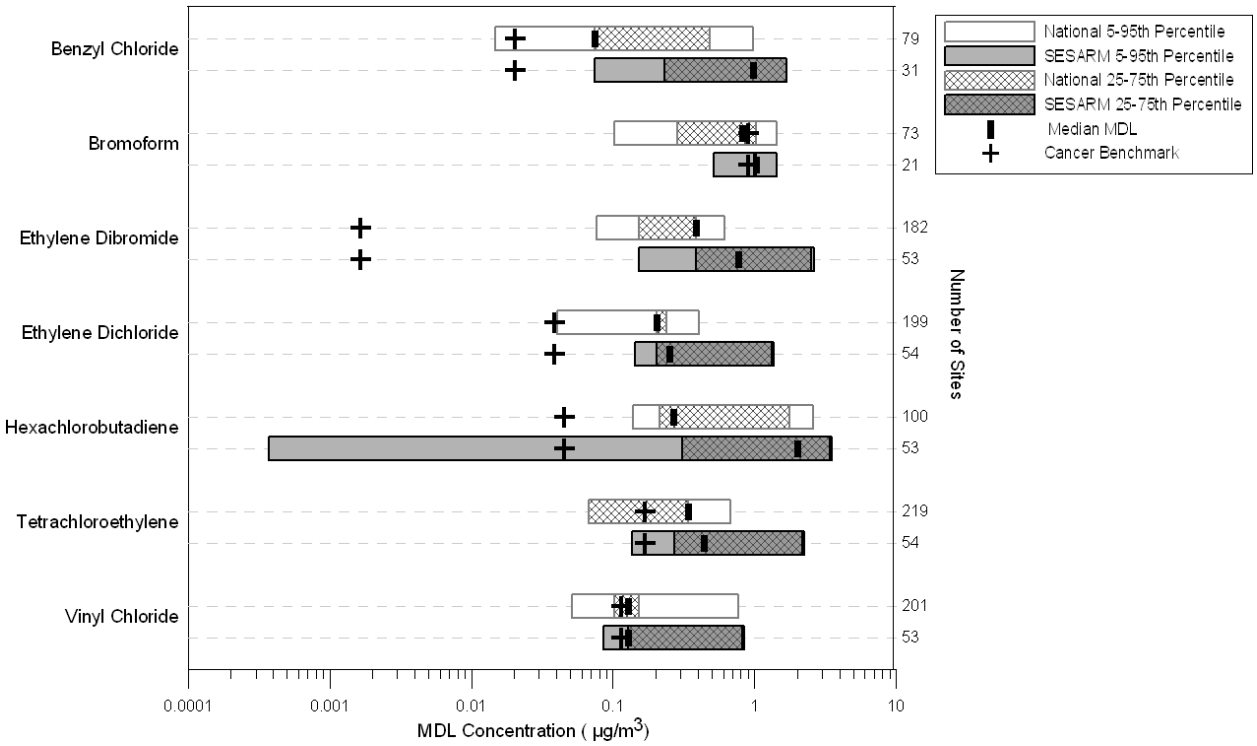

Figure 3-34. Comparison of MDL concentrations in the Southeast to the rest of the United States and to one-in-a-million cancer benchmarks from EPA OAQPS.

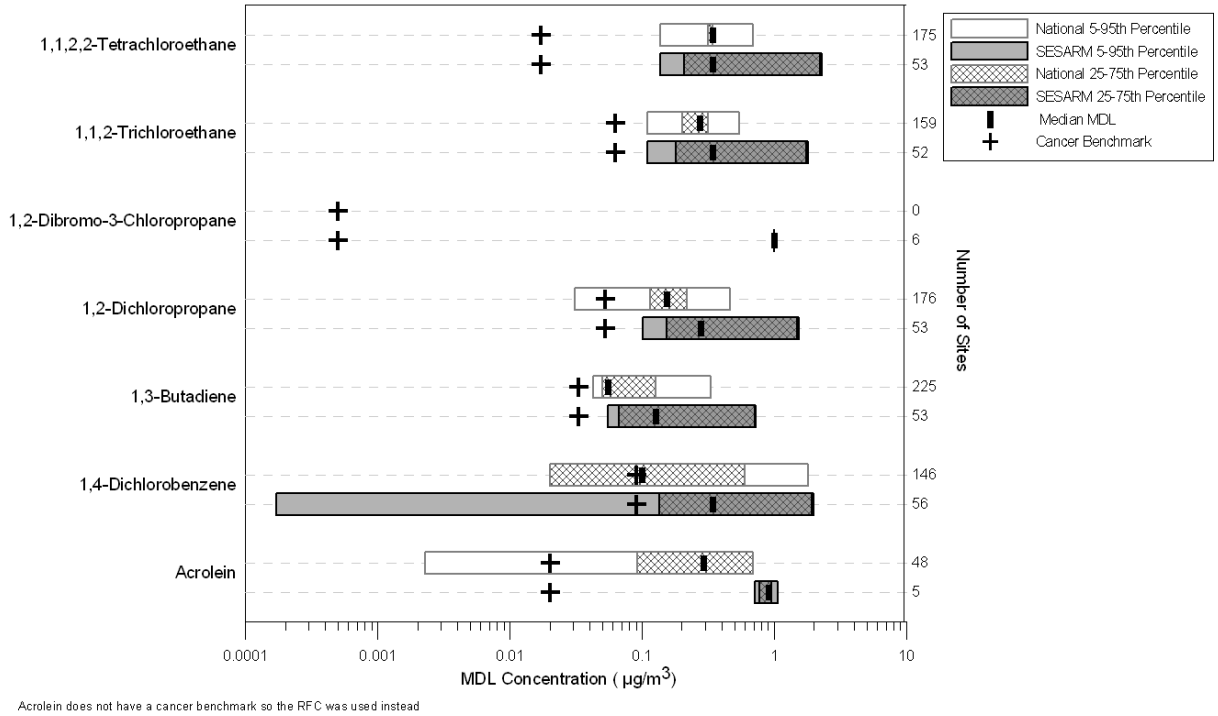

Figure 3-35. Comparison of MDL concentrations in the Southeast to the rest of the United States and to one-in-a-million cancer benchmarks from EPA OAQPS.

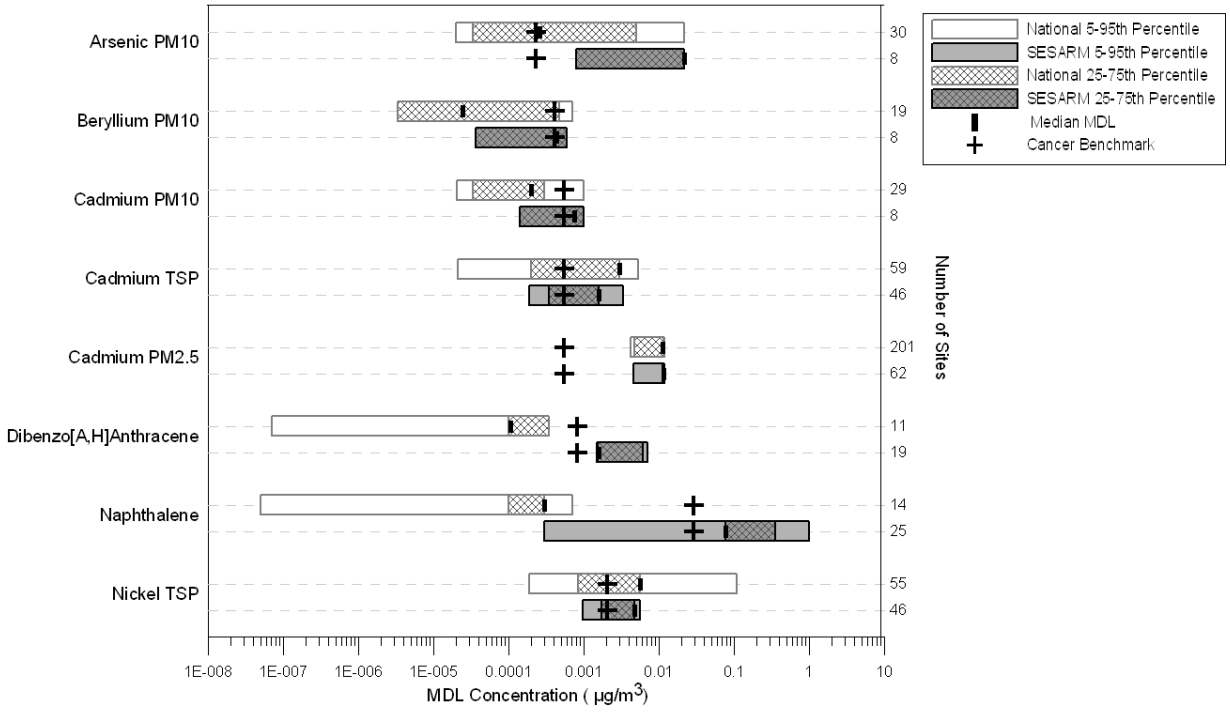

Figure 3-36. Comparison of MDL concentrations in the Southeast to the rest of the United States and to one-in-a-million cancer benchmarks from EPA OAQPS.

Typically, MDL ranges in the Southeast overlap significantly with MDL ranges for the rest of the nation. Overall, the distribution of MDL ranges is typically higher in the Southeast than in the rest of the country. This finding indicates that there is room for improvement in MDL levels for at least some of the sites in the southeastern region. A summary of results by pollutant is provided in **Table 3-8.**

Table 3-8. Summary of comparisons shown in Figures 3-32 through 3-34.

Pollutant	Compared to National MDL, SESARM MDL Is
Dibenzo[A,H]Anthracene	Higher
Naphthalene	Higher
Acrolein	Higher
1,1,2,2-Tetrachloroethane	Somewhat Higher
1,1,2-Trichloroethane	Somewhat Higher
1,2-Dichloropropane	Somewhat Higher
1,3-Butadiene	Somewhat Higher
1,4-Dichlorobenzene	Somewhat Higher
Arsenic PM_{10}	Somewhat Higher
Benzyl Chloride	Somewhat Higher
Bromoform	Somewhat Higher
Cadmium PM_{10}	Somewhat Higher
Ethylene Dibromide	Somewhat Higher
Ethylene Dichloride	Somewhat Higher
Hexachlorobutadiene	Somewhat Higher
Tetrachloroethylene	Somewhat Higher
Vinyl Chloride	Somewhat Higher
Beryllium PM_{10}	Similar
Cadmium TSP	Similar
Cadmium $PM_{2.5}$	Similar
Nickel TSP	Similar
1,2-Dibromo-3-Chloropropane	Not monitored elsewhere
Benzo[A]Pyrene	Higher
Dichloromethane	Somewhat Higher
Trichloroethylene	Somewhat Higher
Acrylonitrile	Similar
Arsenic TSP	Similar

A comparison of typical MDL values reported indicates which EPA sampling and analytical method codes for each pollutant are above or below the relevant health benchmark. **Table 3-9** lists the pollutants of interest and the analytical method codes with default MDLs below the relevant health benchmark. Identification of the specific analytical method

descriptions is available on a supplemental spreadsheet and on the AQS web site (U.S. Environmental Protection Agency, 2006b).

Table 3-9. List of method codes by pollutant with MDLs below the EPA OAQPS health benchmark.

Pollutant	Pollutant AQS Code	Sampling and Analytical Method Codes Below the EPA OAQPS Cancer Benchmark or Reference Concentration
Dibenzo[A,H]Anthracene	17231	101, 104
Naphthalene	17141	101, 106, 110, 117, 150
Acrolein	43505	165[a]
1,1,2,2-Tetrachloroethane	43818	None available
1,1,2-Trichloroethane	43820	None available
1,2-Dichloropropane	43829	113, 126
1,3-Butadiene	43218	123
1,4-Dichlorobenzene	45807	113
Arsenic PM_{10}	82103	113, 112, 202
Benzyl Chloride	45809	113
Bromoform	43806	129
Cadmium PM_{10}	82110	103, 109, 110, 113, 201, 202
Ethylene Dibromide	43843	None available
Ethylene Dichloride	43815	None available
Hexachlorobutadiene	43844	116
Tetrachloroethylene	43817	113
Vinyl Chloride	43860	113, 126
Beryllium PM_{10}	82105	110, 109, 113, 201, 202
Cadmium (TSP)	12110	108
Cadmium $PM_{2.5}$	88110	903, 905
Nickel (TSP)	12136	108, 114, 304
1,2-Dibromo-3-Chloropropane	51623	None available
Benzo[A]Pyrene	17242	101, 102, 104, 117
Dichloromethane	43802	101, 109, 110, 113, 126, 136, 153, 171, 175, 176, 211
Trichloroethylene	43824	101, 109, 113, 136, 151, 171, 175, 176, 211
Acrylonitrile	43704	113
Arsenic (TSP)	12103	108

[a] Note that known sampling issues result in loss of sample using the dinitrophenylhydrazine (DNPH) cartridges. EPA is developing a new canister sampling method.

3.7.3 Key Findings

- The MDLs of many pollutants identified as uncharacterizable in the Southeast were higher than those in other parts of the country.

- Some sampling and analytical methods were identified with MDLs below the relevant EPA OAQPS health benchmark. These alternative methods may be a reasonable way to achieve monitoring objectives for air toxics.
- Some pollutants had no reported sampling or analytical methods with MDLs lower than the health benchmark. These pollutants include key risk or hazard drivers such as acrolein, 1,1,2,2-tetrachloroethane, and ethylene dibromide. Better methods for measuring these pollutants may need to be developed (or are in development) to characterize risk.

4. CONCLUSIONS

This project encompassed an array of efforts including acquiring data from state and local air quality staff that had not previously been placed in the EPA's central data repository (AQS). After a comprehensive database was compiled and validated, a wide range of analyses were performed to obtain a first look at the region's air toxics concentrations. This first look will help state and local agencies assess which next steps should be taken. For example, most of the analyses in this report (e.g., Southeast-to-national MDL trends) could be performed at a local scale (e.g., at site vs. nation). This section reiterates the key findings from this report and lists some recommendations for agencies in the southeastern states to consider for additional analysis and improvements to air toxics monitoring.

A clear message from these analyses is that many of the findings from this study that are relevant for the state and local agencies in this region are also relevant at a national scale. For example, problems with data collection and chemical analysis, the need for lower MDLs for some pollutants, differences among reported values that are a direct result of inconsistent methods and MDLs, and monitoring data that are otherwise insufficient to meet monitoring objectives are issues at all scales of the air toxics monitoring program. Therefore, while these findings are specifically oriented to local, state, and southeastern region agencies, at least some of these problems may benefit from national level guidance or research. Key findings and recommendations are listed next.

How do air toxics concentrations in the Southeast compare to the rest of the country?

Concentrations of most air toxics in the Southeast are very similar to those in the rest of the country. Overall, the southeastern air toxics situation does not appear "exceptional".

Can air toxics data be used to assess risk in the Southeast? Which species were identified as the most important contributors to risk?

Sufficient monitoring data were available to perform a risk and hazard screen for most of the key pollutants identified as drivers or contributors in NATA99.

- Some pollutants were above cancer risk benchmarks at most sites with data sufficient for characterizing risk including benzene, arsenic, 1,3-butadiene, carbon tetrachloride, naphthalene, acetaldehyde, ethylene dibromide, ethylene dichloride, 1,1,2,2-tetrachloroethane, acrylonitrile, 1,2-dichloropropane, 1,1,2-trichloroethane, and benzyl chloride. In addition, many of these key risk driving pollutants are not characterized well at most sites
- Many pollutants could not be risk-evaluated because MDL values were too high. Key pollutants that need improved measurements include cadmium, tetrachloroethylene, dibenzo[a,h]anthracene, naphthalene, ethylene dibromide, ethylene dichloride, 1,1,2,2-tetrachloroethane, 1,4-dichlorobenzene, vinyl chloride, 1,2-dichloropropane, 1,1,2-trichloroethane, hexachlorobutadiene, benzyl chloride, and bromoform.
- Almost all pollutants were below hazard benchmarks at almost all sites. Only acrolein and 1,2-dibromo-3-chloropropane were uncharacterizable with respect to hazard.

How have air toxics concentrations changed over time?

An analysis of trends in air toxics concentrations indicated that

- Mobile source air toxics such as benzene, 1,3-butadiene, xylenes, toluene, and other aromatic hydrocarbons show decreasing concentrations at most sites. This is likely due to federal fuel or vehicle control measures that have targeted reductions in air toxics emissions.
- Changes in methods and MDLs over time appear to be confounding analysis of trends for trace metals and SVOCs in the Southeast.

Are air toxics concentrations similar among the southeastern states?

Large differences in agency and network methods and MDLs confounded the spatial variability analysis within the Southeast.

- Consistent regional/national monitoring standards (i.e., requiring MDL values below health benchmarks for key risk and hazard drivers) and interlaboratory comparisons would help reduce the significance of different methods and MDLs between reporting agencies (regional, state, local, and national).
- Improved monitoring methods are needed for some key pollutants, such as 1,1,2,2-tetrachloroethane and ethylene dibromide.

How did monitored concentrations compare to NATA99 modeled concentrations?

Concentration data from relatively few monitoring sites were available to compare with model-predicted concentrations from NATA99.

- For the sites and pollutants that were available, pollutants were either predicted relatively well (i.e., within a factor of two) or grossly underpredicted. This result is comparable to the analyses performed at the national level.

How did MDLs in the Southeast compare to MDLs at the national level?

Pollutants with MDLs too high to be characterized during the risk and hazard screen typically had higher MDL values in the Southeast than those monitored in the rest of the country.

- Sampling and analytical methods with MDL values sufficient to characterize risk were identified, if available. However, changing sampling and analytical methods should be part of an integrated effort to analyze other variables such as cost, number of pollutants monitored, monitoring objectives, and local health benchmark values.

5. REFERENCES

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Hafner H.R., McCarthy M.C., and Chinkin L.R. (2006) National, regional, between-city, and within-city spatial variability in air toxics. Presented at the *Air & Waste Management Association Symposium on Air Quality Measurement Methods and Technology, Durham, NC, May 9,* by Sonoma Technology, Inc., Petaluma, CA (STI-2884).

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Appendix A

Accountability Case Study: Understanding Differences in SESARM States $PM_{2.5}$ Metal Toxics Trends from 2000 through 2005

Objectives

- Identify cause of major discrepancy in $PM_{2.5}$ metal trends among states
- Determine whether trends in concentrations reflect ambient concentrations or were caused by other factors
- Identify systematic biases that may inhibit trends analysis for these pollutants

Approach

- Analyzed trends by network
- Analyzed trends in MDL by network
- Analyzed trends in method code
- Analyzed key toxics species at the site level (arsenic, chromium, lead, manganese, nickel)

MDL=method detection limit

Original Plots

Concentrations in certain states increased dramatically while concentrations in other states decreased.

What was the cause?

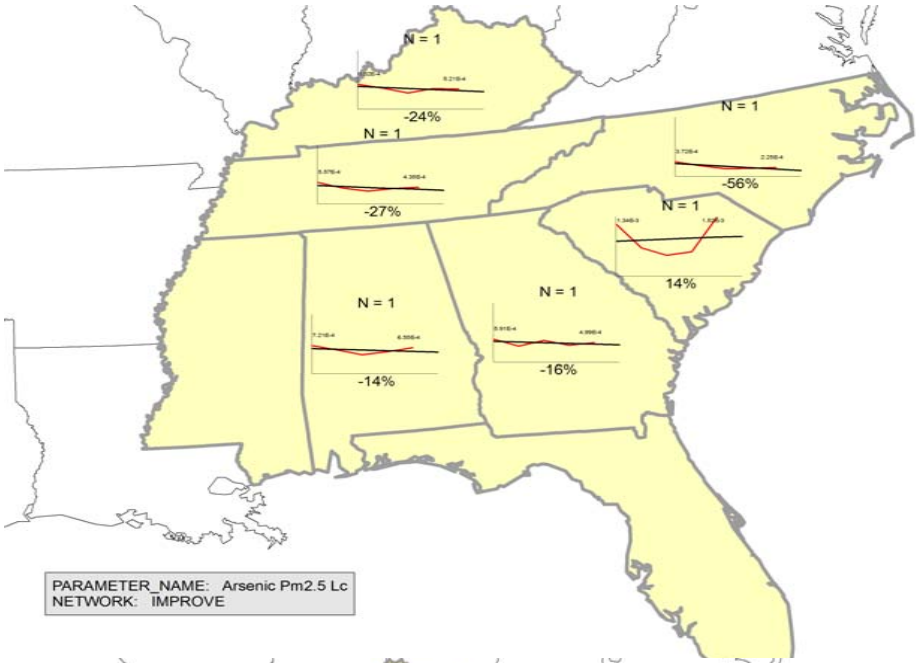
Results

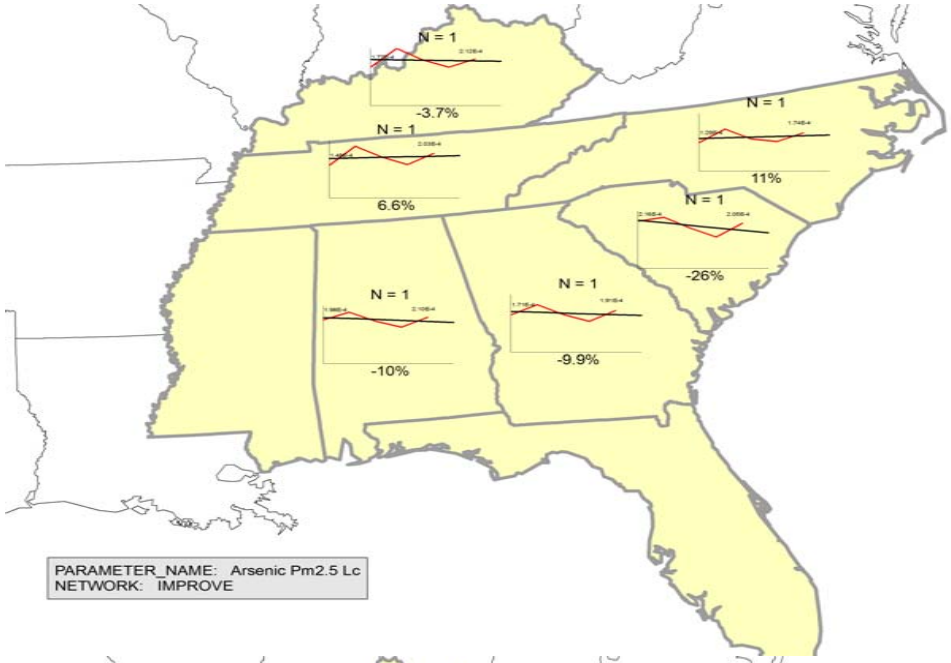
Each of the following plots shows IMPROVE and STN monitoring network trends in concentrations and MDLs by state for a given toxic metal from 2000 to 2005.

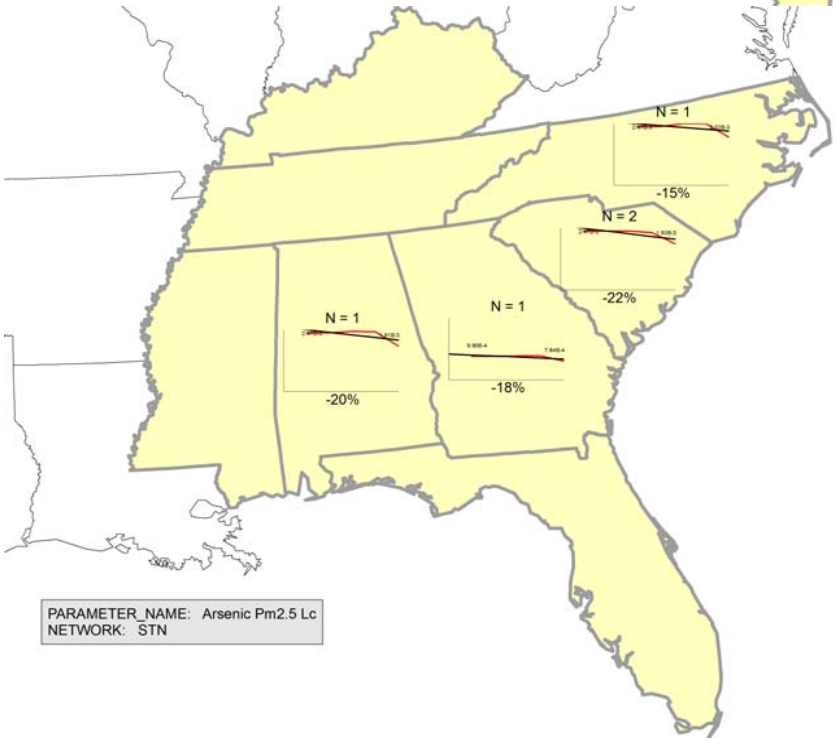
IMPROVE = Interagency Monitoring of Protected Visual Environments (rural)

STN = Speciation Trends Network (urban)

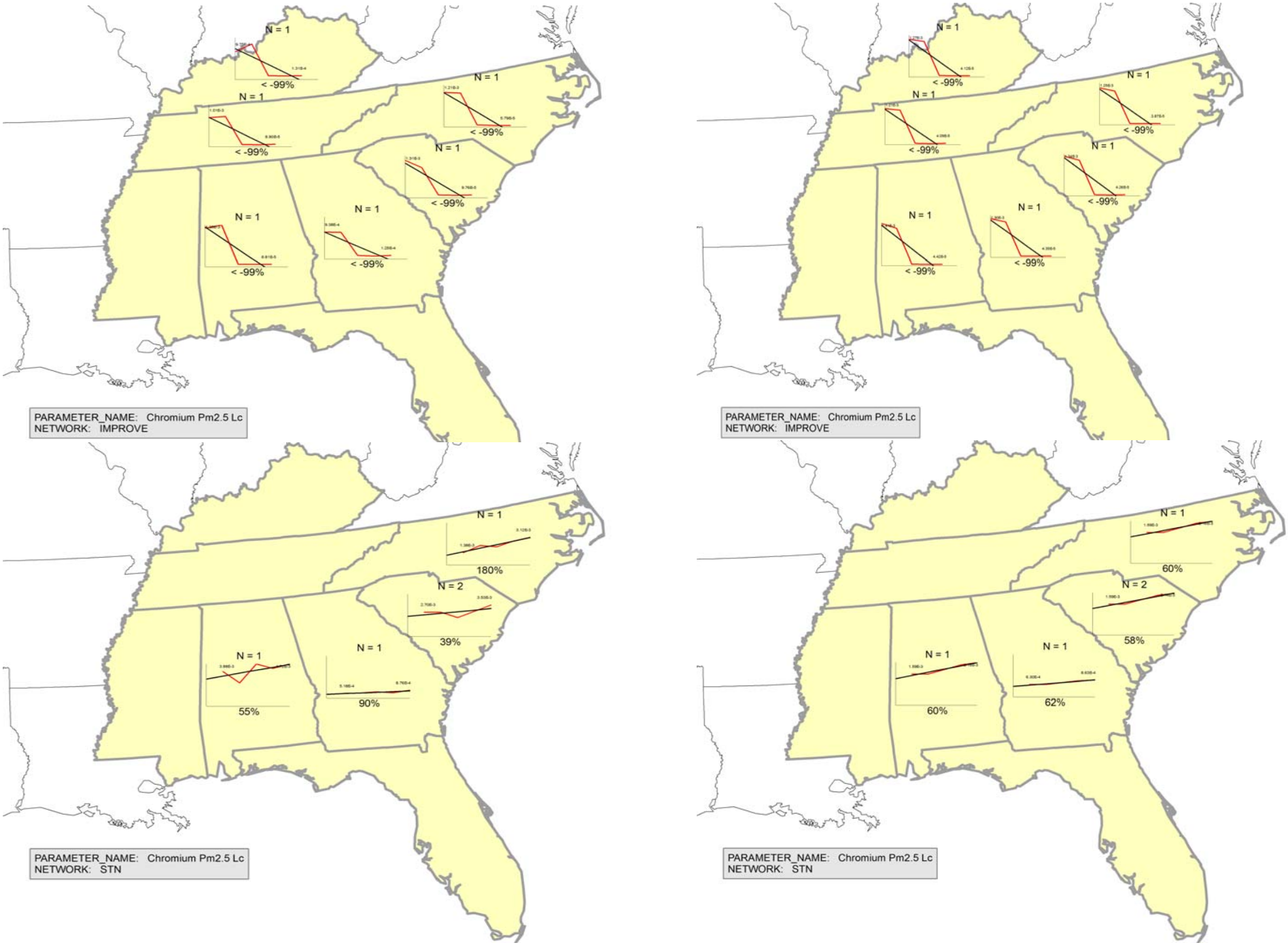
Arsenic $PM_{2.5}$ average concentration trends (left) and average MDL (right) by network from 2000-2005. IMPROVE on top, STN on bottom.



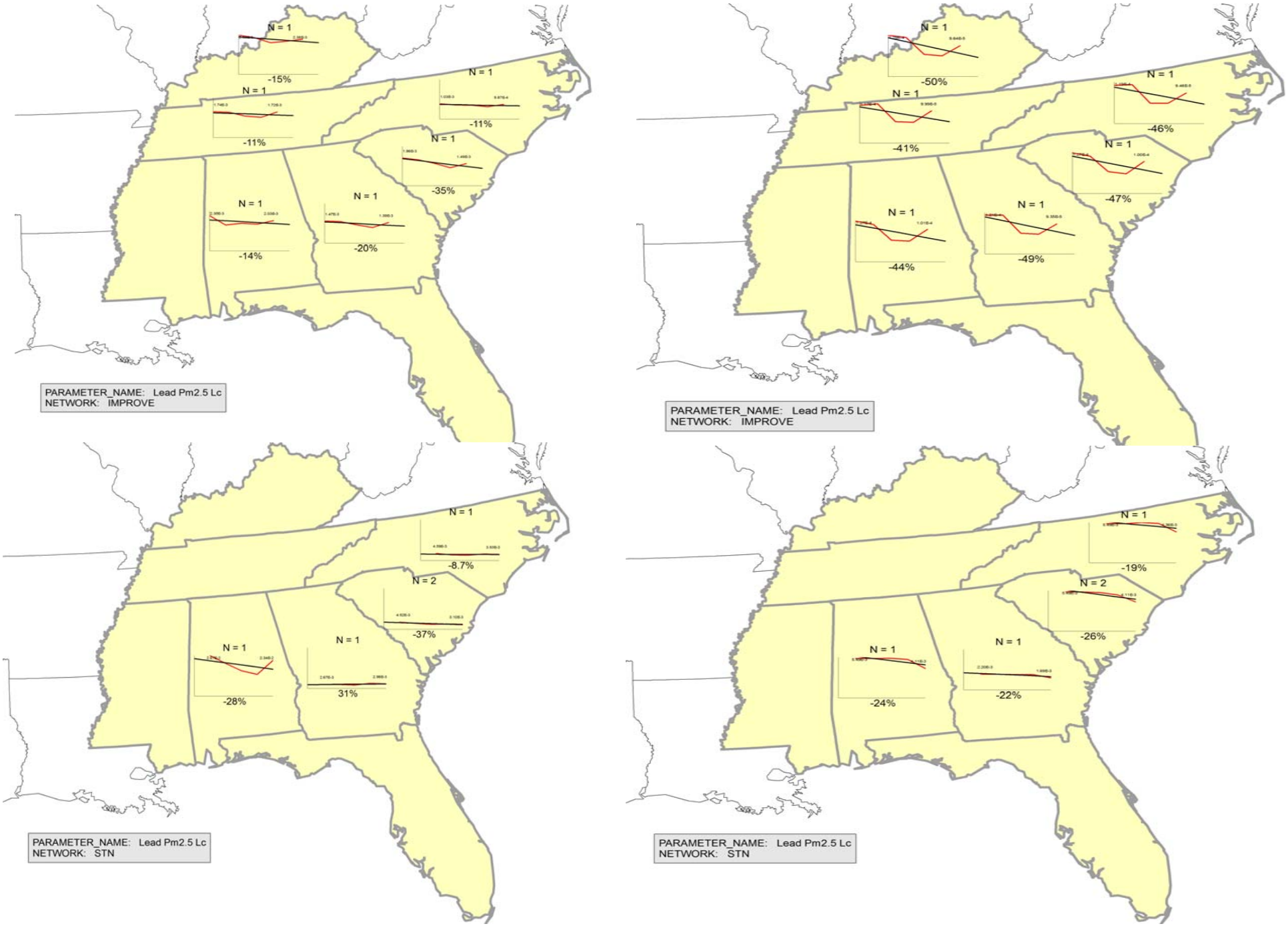




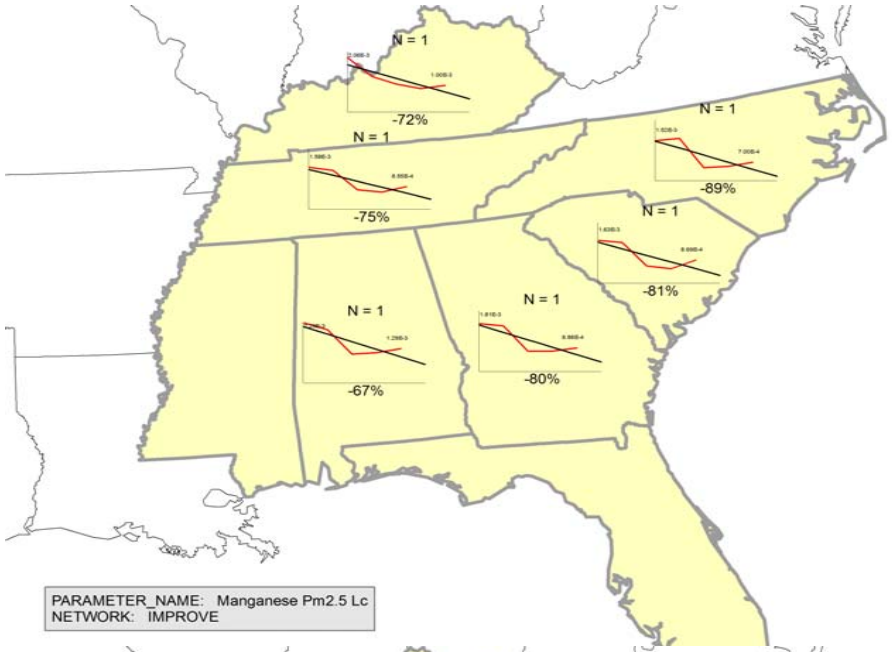
Chromium $PM_{2.5}$ average concentration trends (left) and average MDL (right) by network from 2000-2005. IMPROVE on top, STN on bottom.



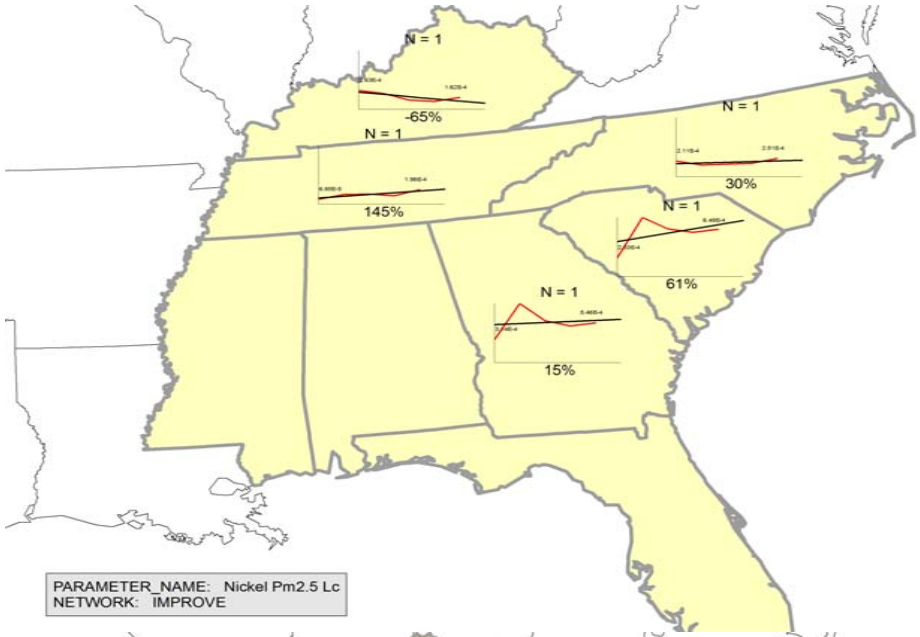
Lead $PM_{2.5}$ average concentration trends (left) and average MDL (right) by network from 2000-2005. IMPROVE on top, STN on bottom.

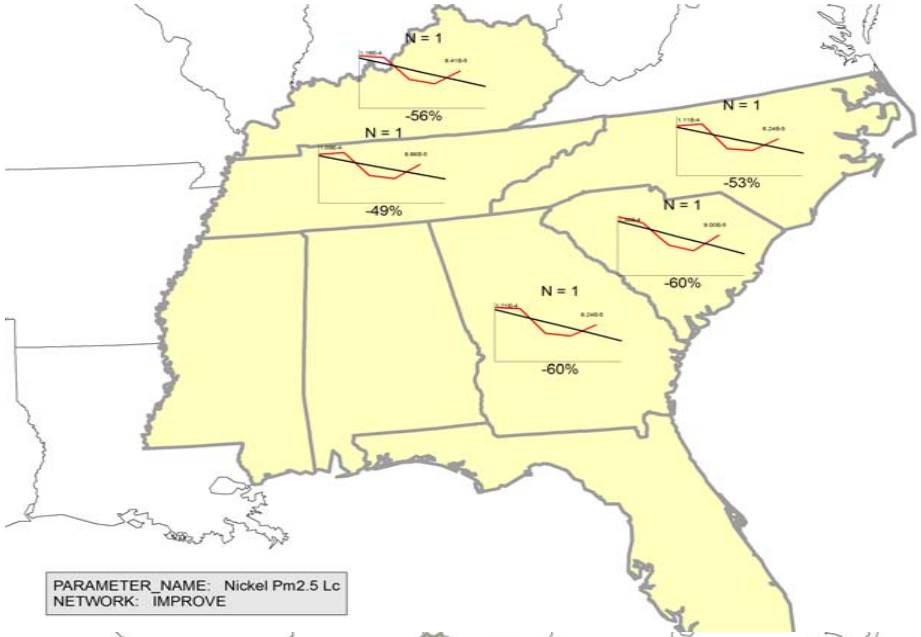


Manganese $PM_{2.5}$ average concentration trends (left) and average MDL (right) by network from 2000-2005. IMPROVE on top, STN on bottom.



Nickel $PM_{2.5}$ average concentration trends (left) and average MDL (right) by network from 2000-2005. IMPROVE on top, STN on bottom.





Discussion of Results (1 of 2)

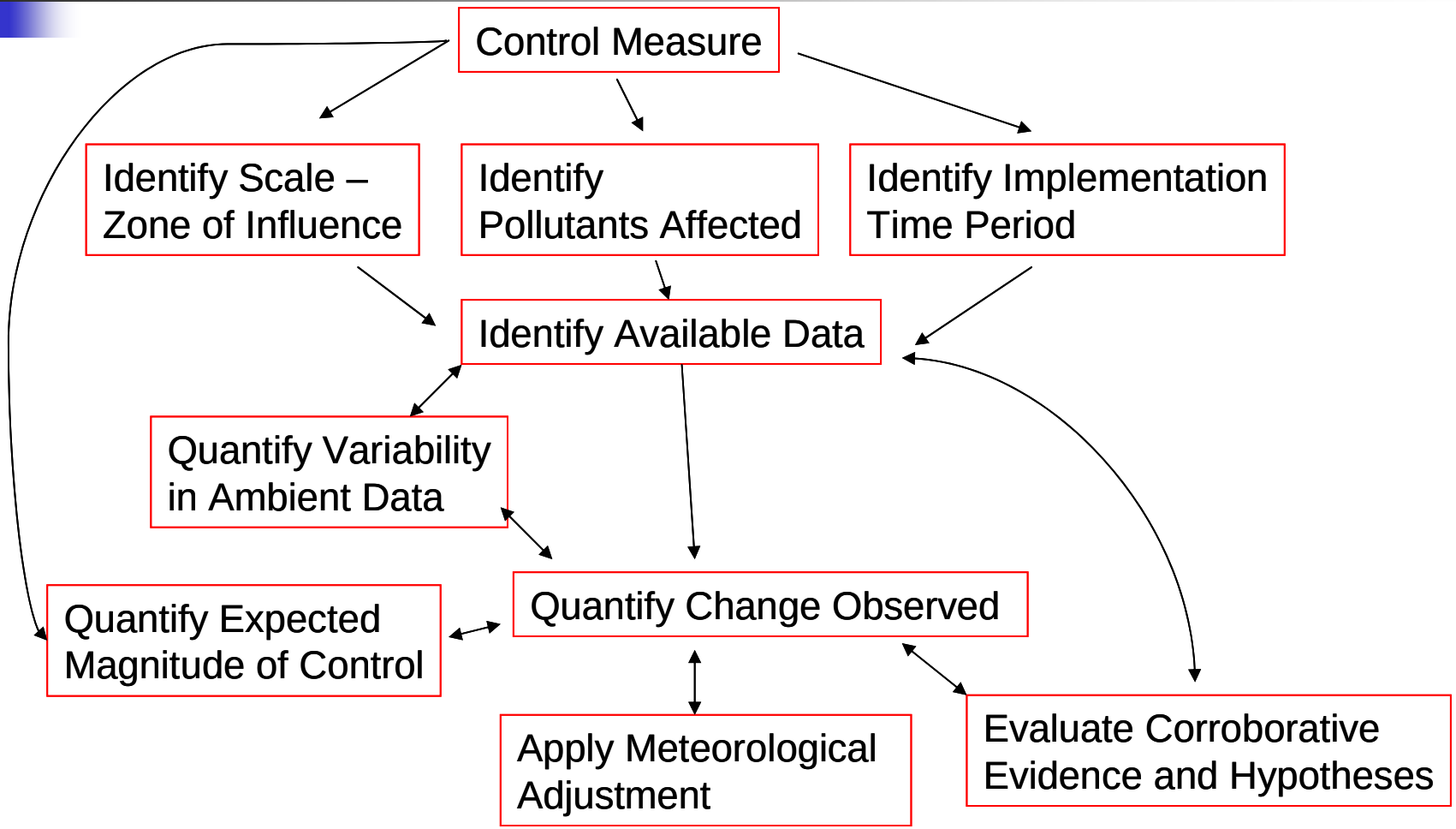
- The large increasing trends in original plots were artifacts of the averaging and plotting technique when a state had both IMPROVE and STN sites.
  - IMPROVE data were available from 2000 to 2004, and STN data were available from 2001 to 2005. Combining them led to very low 2000 averages (IMPROVE) and very high 2005 averages (STN) due to differences in location and monitoring methods.

Straight averaging of concentrations across sites can lead to large problems when data are not continuous. Averaging the trend lines across sites would be a better technique.

Discussion of Results (2 of 2)

- Changes in MDLs related to methodology changes were closely correlated with changing concentrations for chromium and manganese at IMPROVE sites.
  - Correlations between MDLs and concentrations were apparent at STN sites, but the relationship was weaker.
- Changes in MDLs for other toxics metals do not appear to directly correlate, but are still at least weakly correlated to changes in concentrations.
  - Trends for these pollutants may be useful in relative terms (site A showed increases while trends at other sites all decreased) within a given network.
  - Concentrations and trends are not comparable across networks.
- Trends in toxics metals should be examined with care before determining that changes are real, rather than due to changes in methodology or MDL over time.

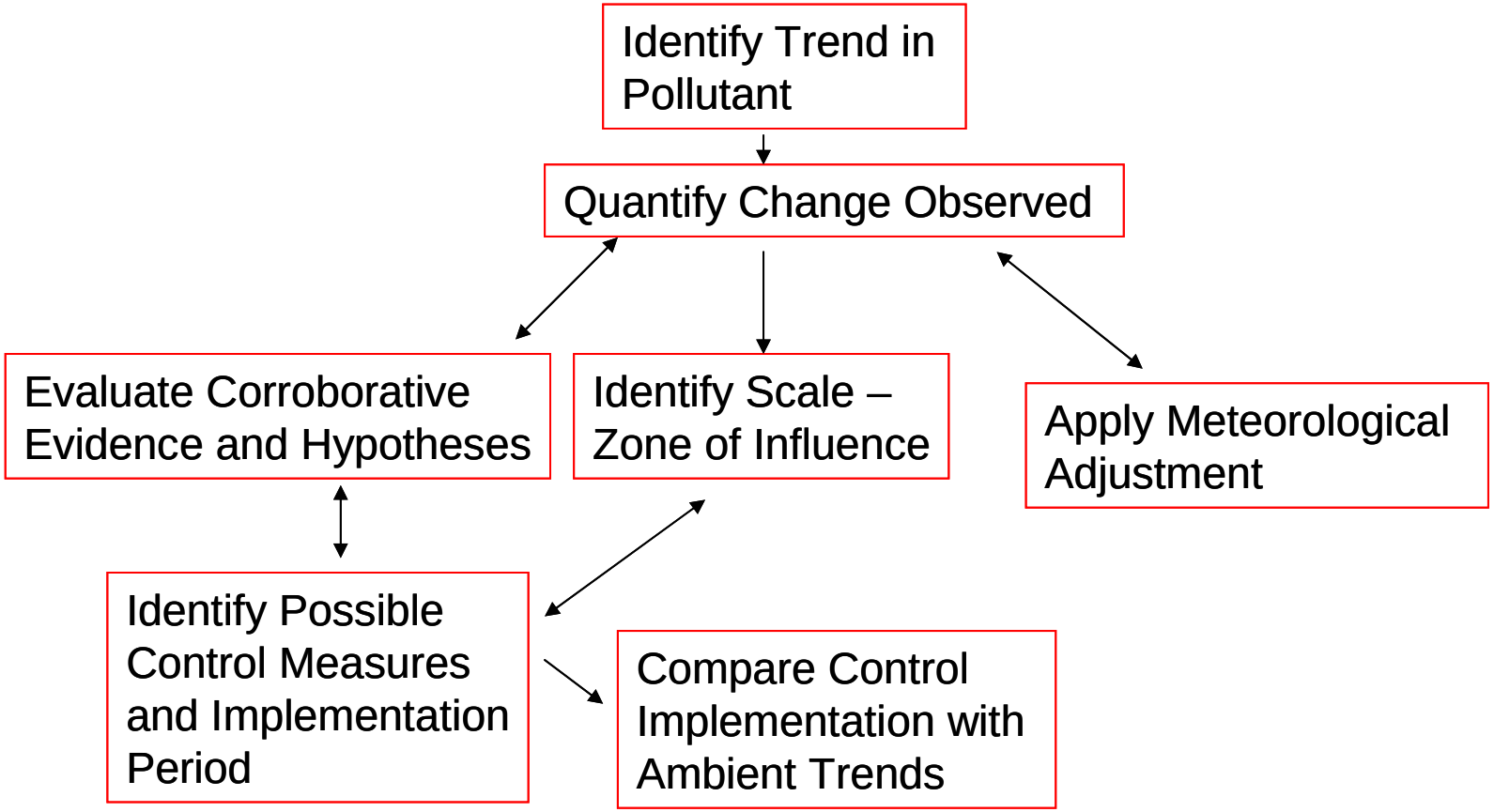
Guidance for Assessing Trends (1 of 4)



Decision tree for assessing trends starting with known emission changes or control strategy implementation

Hafner H.R. and Roberts P.T. (2006) A technical approach using ambient data to track and evaluate air quality programs. Draft final report prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC, by Sonoma Technology, Inc., Petaluma, CA, STI-905213.02-2918-DFR, March.

Guidance for Assessing Trends (2 of 4)



Decision tree for assessing trends starting with an observed trend in an ambient pollutant concentration over time

Hafner H.R. and Roberts P.T. (2006) A technical approach using ambient data to track and evaluate air quality programs. Draft final report prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC, by Sonoma Technology, Inc., Petaluma, CA, STI-905213.02-2918-DFR, March.

Guidance for Assessing Trends (3 of 4)

- Quantify the change observed in the ambient data. This approach could also be applied to a pollutant in which a change was not observed but expected.
- Identify and assess other data sets and sites that may have also been affected by a similar control measure or emission change to understand the spatial scale of the ambient change. If the control was applied across a broad area, changes at additional sites might be expected.
- Identify potential emissions changes or control measures that could have contributed to the ambient trends.
- Compare the control measure implementation schedule with the ambient trends. Do the timing of the control implementation and the change in ambient concentrations coincide?

Guidance for Assessing Trends (4 of 4)

- Investigate corroborative evidence of the change and test for changes in pollutants in which a change was not expected. It is important not to over-interpret changes in ambient data.
- Investigate whether changes in method detection limits (MDLs) or sampling/analysis methods correspond to abrupt changes in reported concentrations. Does the timing of any changes in MDLs or methodology correspond with changes in reported concentrations? If so, teasing out the underlying trend in concentrations is more complicated.
- Apply meteorological adjustments to the pollutant trend. The goal is to reduce the effect of meteorology on ambient concentrations so that the underlying trend in emissions can be more readily observed.

Appendix B

Regulation Effects on Mobile Source Air Toxics – A Case Study

Overview (1 of 2)

- Objective
  - Tie changes in concentrations of mobile source air toxics (MSATs) to control measures such as reformulated gasoline (RFG), Reid Vapor Pressure (RVP, fuel volatility) changes, fleet turnover, etc. *How effective have mobile source controls been in reducing air toxics (and other pollutant) concentrations?*
- Approach
  - Investigate decreases in concentrations of MSATs such as benzene, toluene, ethylbenzene, and 1,3-butadiene at sites in the Southeast
  - Determine whether any specific control measure(s) can be tied to significant changes in ambient concentrations over relatively recent time periods at locations for which applicable monitoring data are available

Overview (2 of 2)

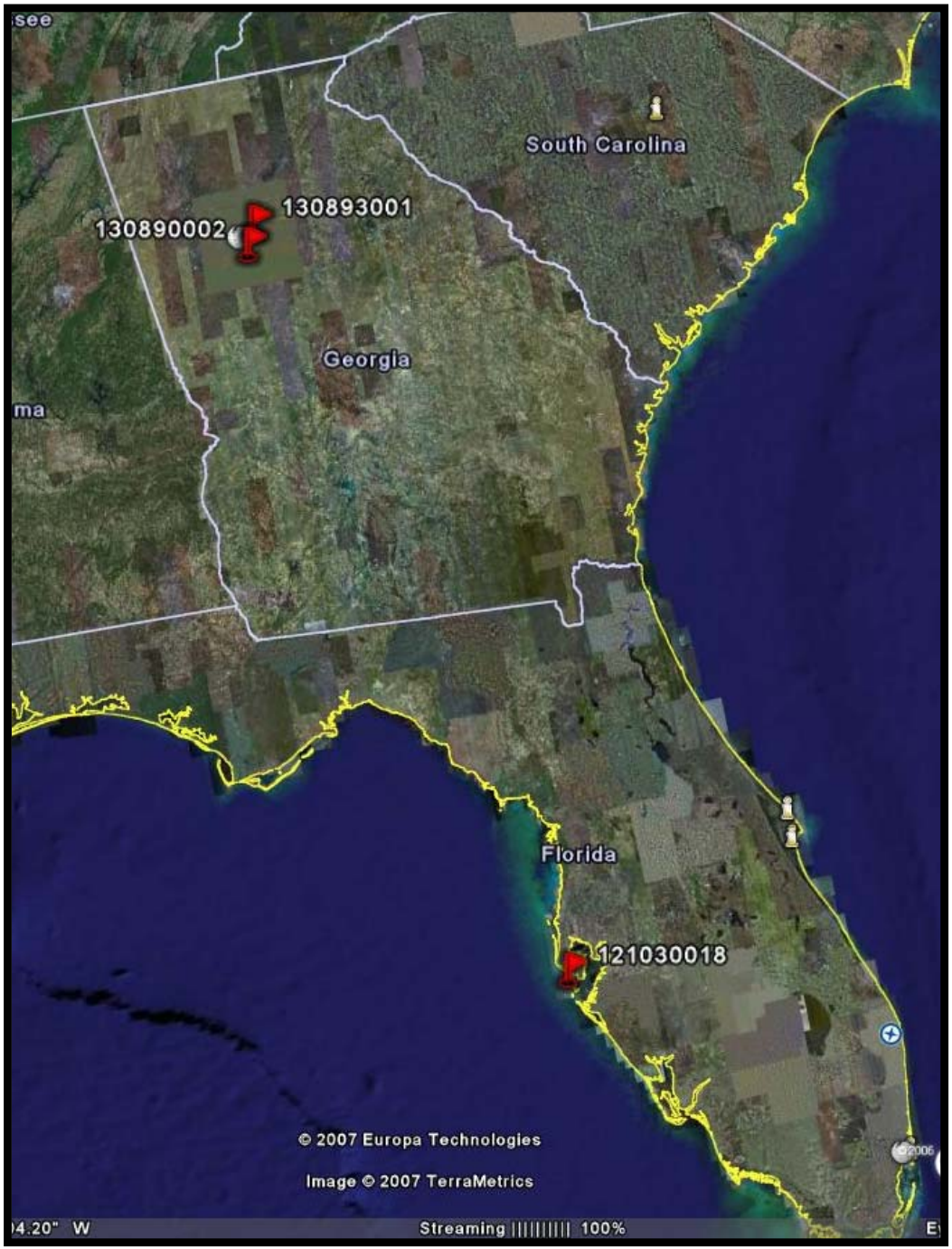
- Findings: Fleet turnover is the most likely explanation for the decreasing concentrations in MSATs such as benzene, 1,3-butadiene, and toluene
  - Concentrations of these species have decreased about 4% per year
  - Decreased concentrations of m-&p-xylene in Georgia may not be mobile source-related. Was a nearby emitter shut down?

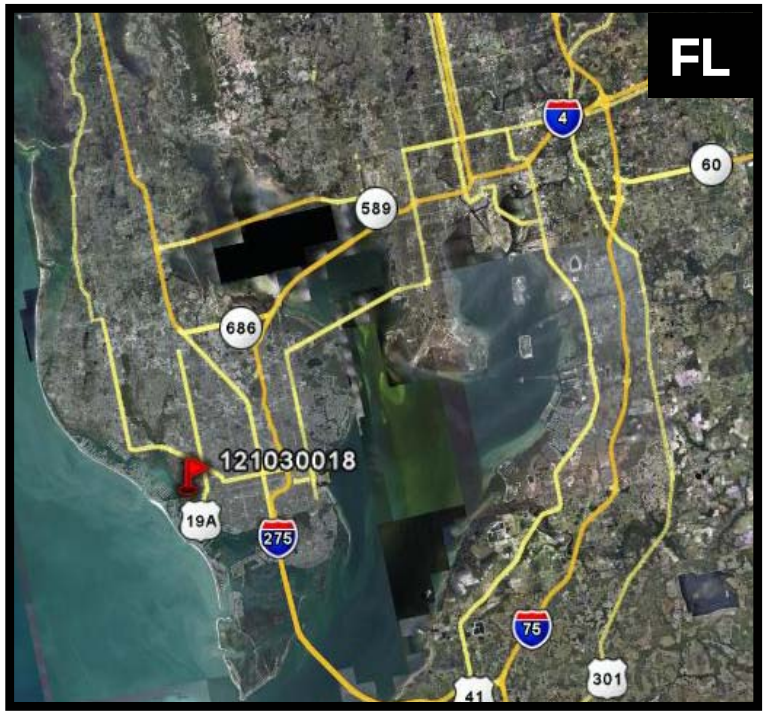
Site Selection

- Site selection was based on the following criteria:
  - Location near MSAT source (major freeway etc.) to ensure strong motor vehicle signature
  - Compounds measured with sufficient data above detection present in gasoline evaporative and exhaust emissions
    - Benzene
    - Toluene
    - Ethylbenzene
    - 1,3-Butadiene*
    - Formaldehyde
    - Acetaldehyde
    - Butanes, pentanes, and other mobile source related compounds if available
  - Length of monitoring
    - Historical data are necessary to assess trends

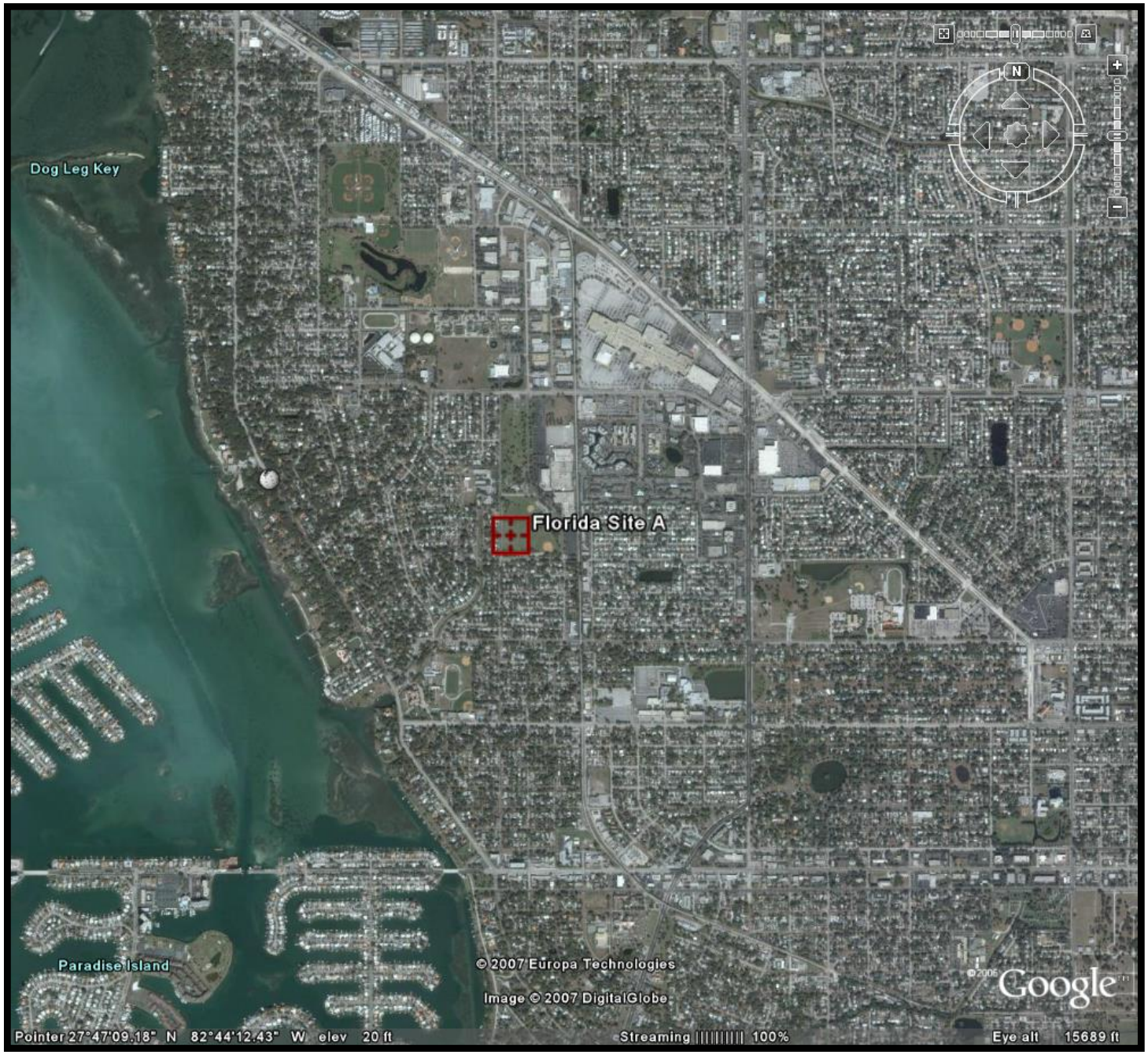
Three sites best met our selection criteria

Site Locations





Florida Site Location (121030018)



Georgia Site Locations

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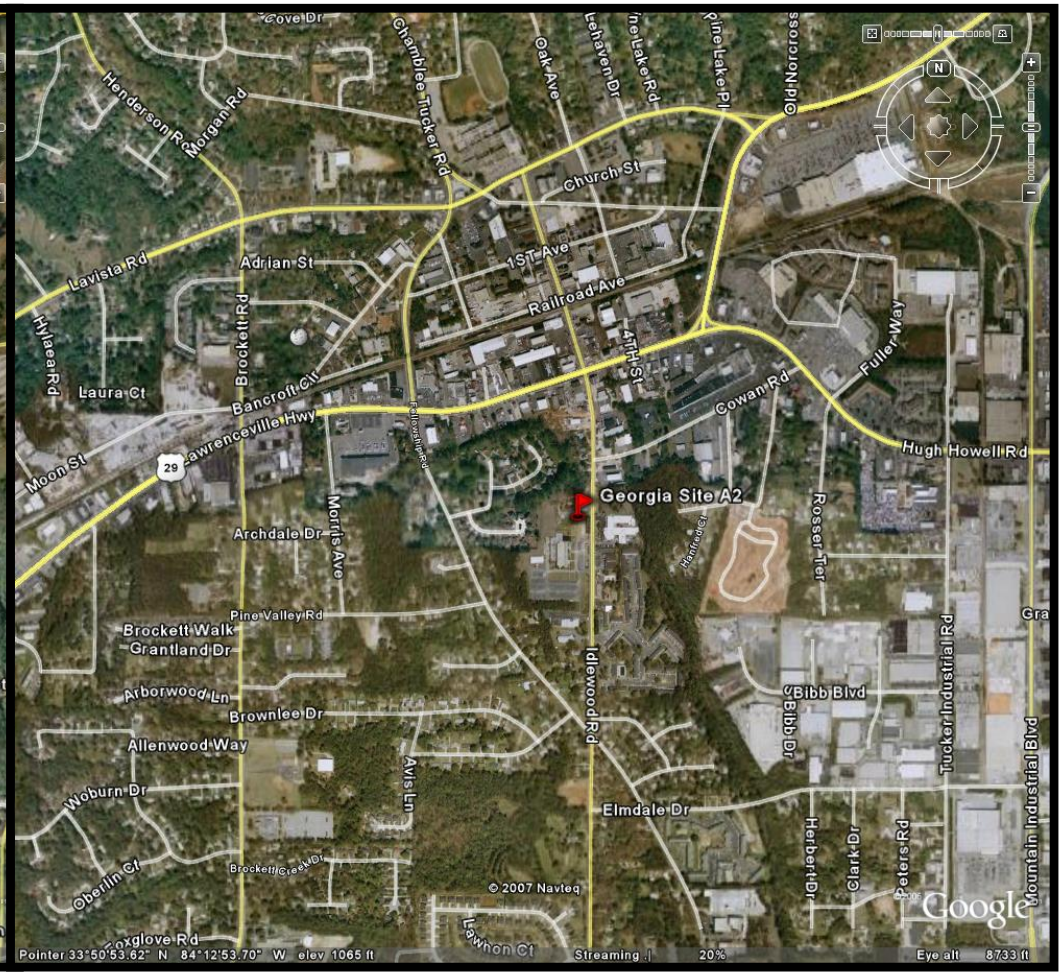
130893001



Mobile Source Emissions Regulations

- Reformulated Gasoline (RFG)[1]
  - Reductions in fuel benzene content are targeted
  - *GA and FL did not implement RFG*
- Reid Vapor Pressure (RVP) Requirements[2]
  - Measure of fuel volatility
  - Effective 1999

	May	June	July	August	Sept (1-15)
Florida (Pinellas)	9	7.8	7.8	7.8	7.8
Georgia (DeKalb)	9	7	7	7	7

Units = pounds per square inch (PSI)

  - Georgia receives a 1 PSI waiver for ethanol blending

[1]U.S. EPA (2005a)

[2]U.S. EPA (2005b)

Ambient Monitoring Data

- 24-hr averaged data were obtained from STI's database (1990-2005)
- Measurements below detection were substituted with the method detection limit (MDL)/2
- Data were excluded if > 85% of measurements were below detection for a given site, parameter, and year

Generally, 115 samples were available per year.

Site Examination – Scatter Plots (1 of 9)

Are pollutants predominantly from mobile source emissions?

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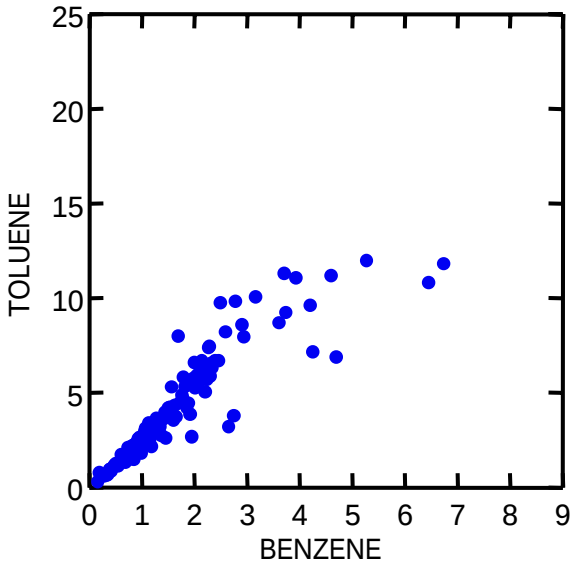

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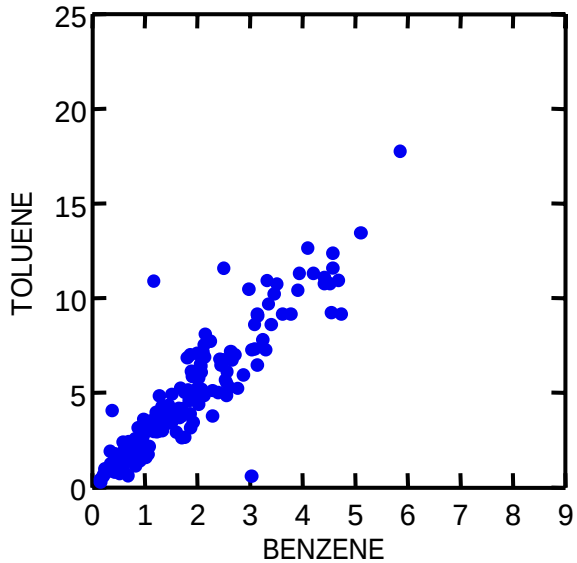

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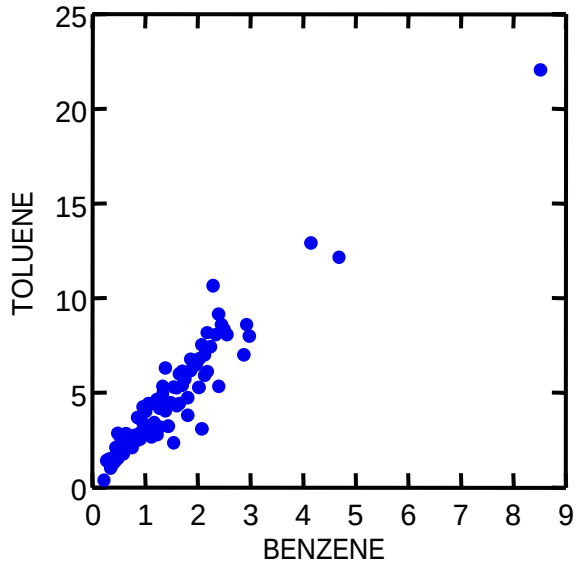
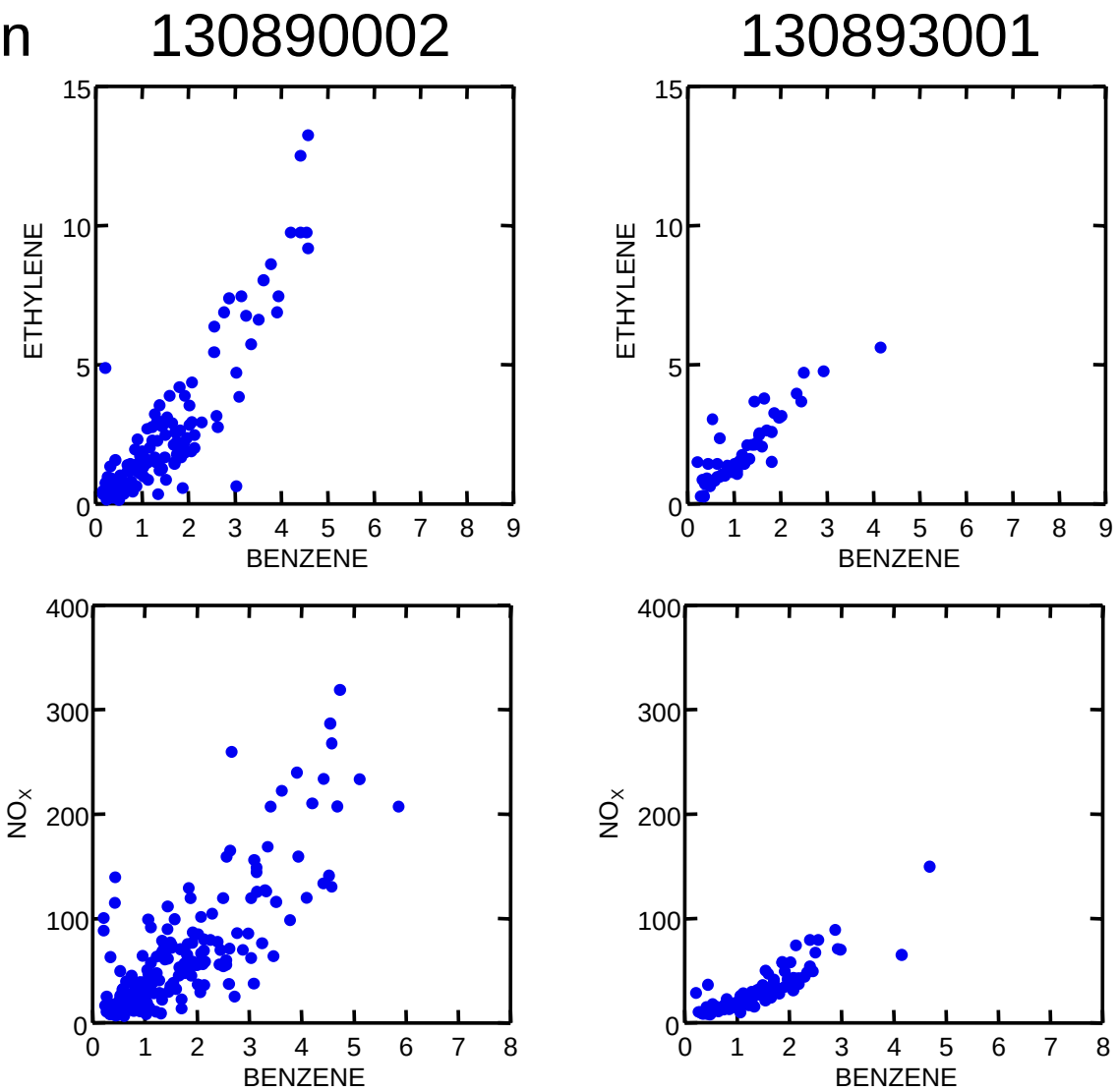


Good correlation between key aromatic hydrocarbons is seen as expected for motor vehicle exhaust.

Units are $\mu g/m^3$

Site Examination – Scatter Plots (2 of 9)

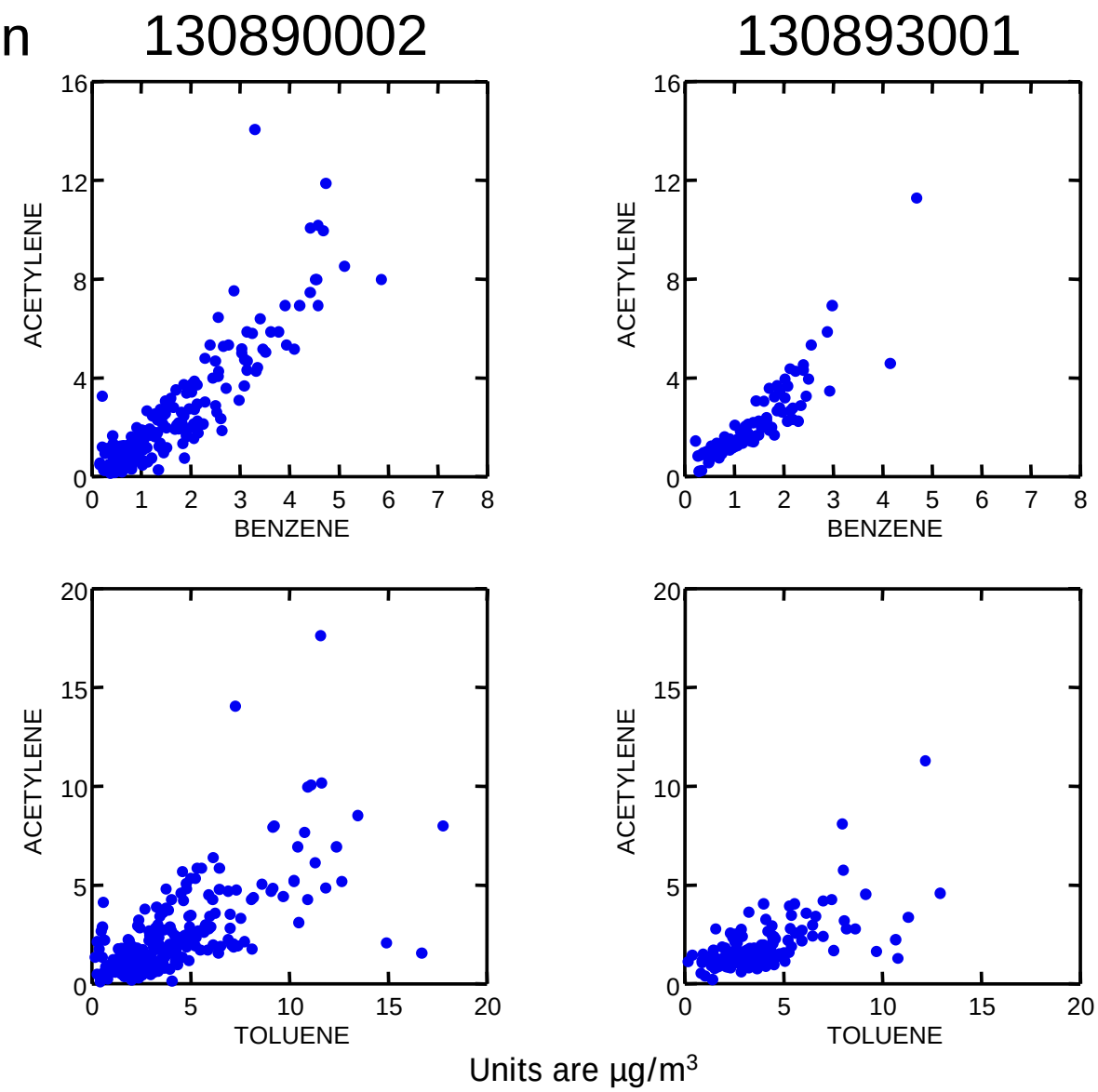
Generally good correlation of pollutants (only sites with data are shown).



Units are µg/m^3

Site Examination – Scatter Plots (3 of 9)

Generally good correlation of pollutants (only sites with data are shown).



Units are µg/m^3

Site Examination – Scatter Plots (4 of 9)

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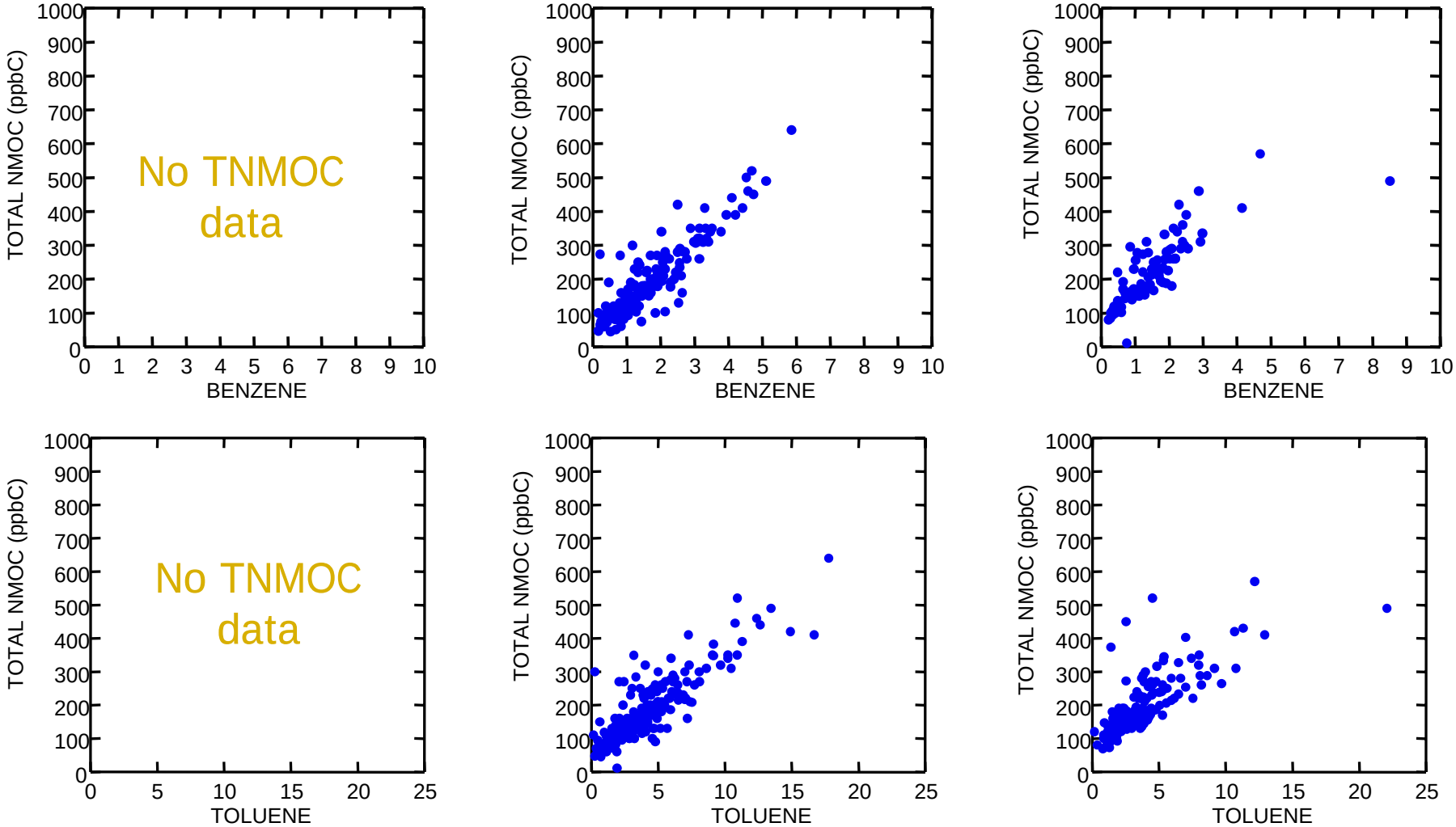
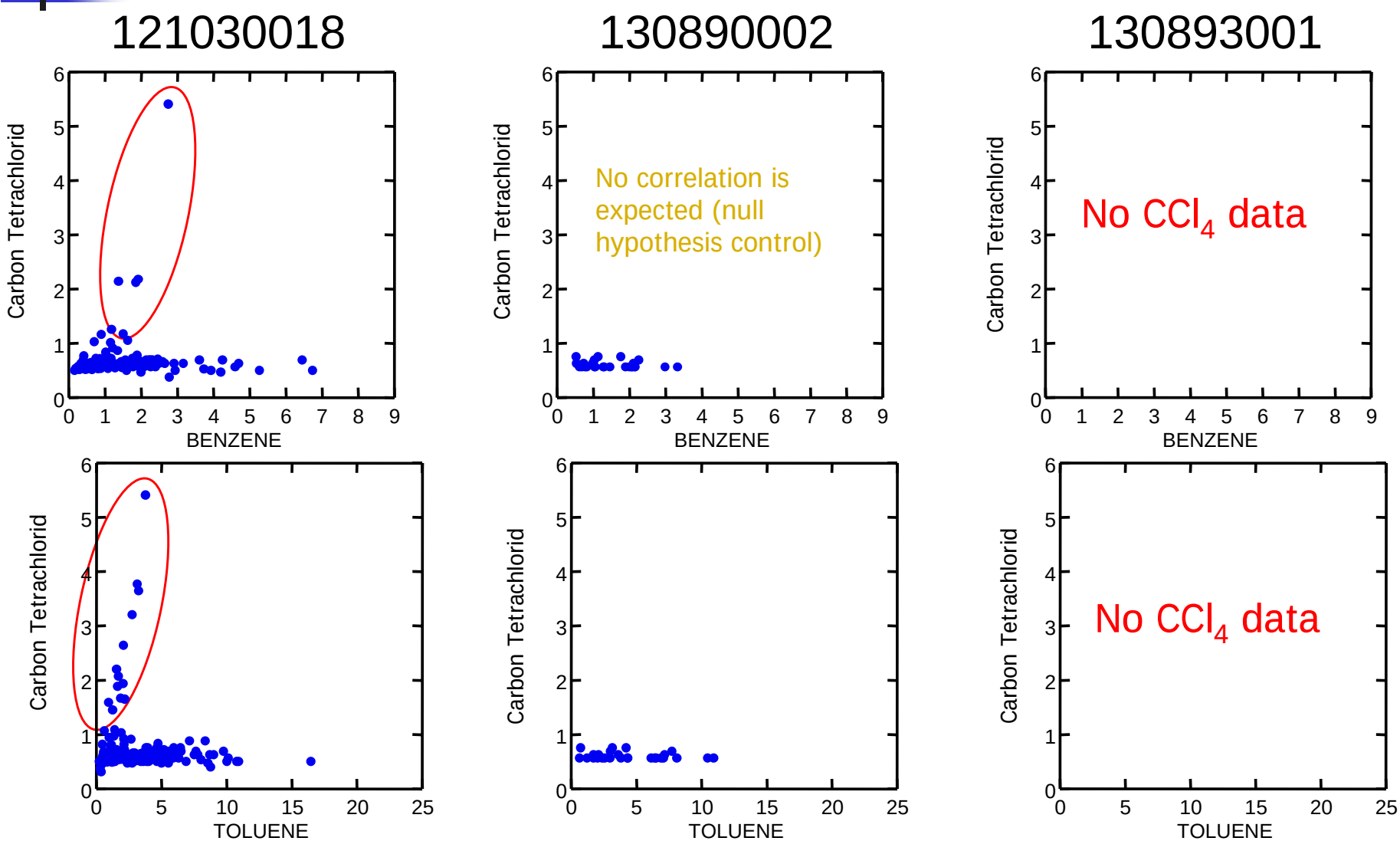


Units are µg/m^3

Site Examination – Scatter Plots (5 of 9)

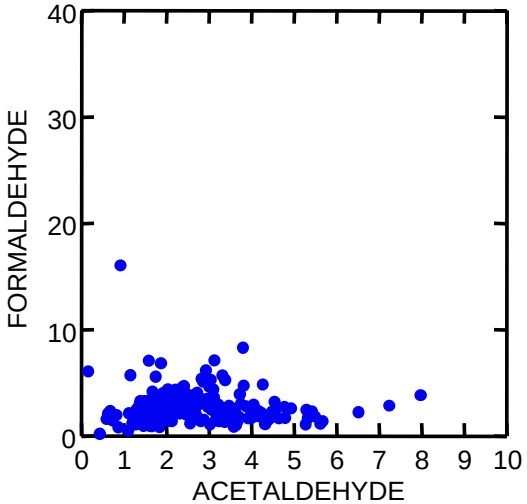


Circled data points are suspect and are probably not accurate representations of ambient data

Units are µg/m^3

Site Examination – Scatter Plots (6 of 9)

121030018



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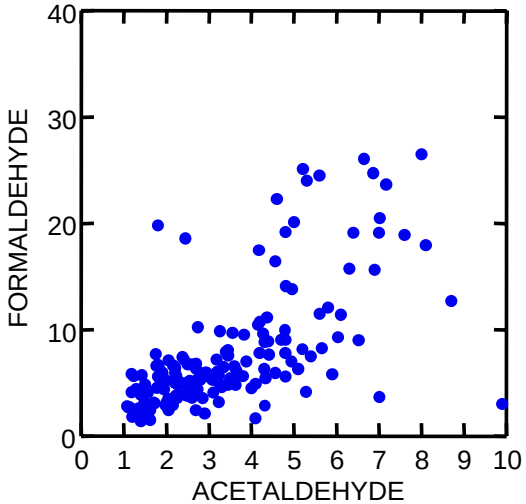

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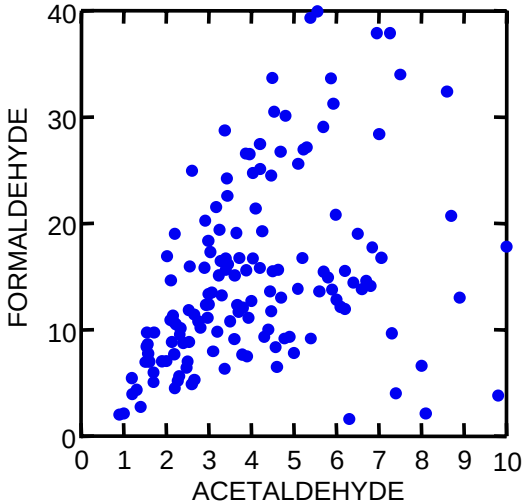
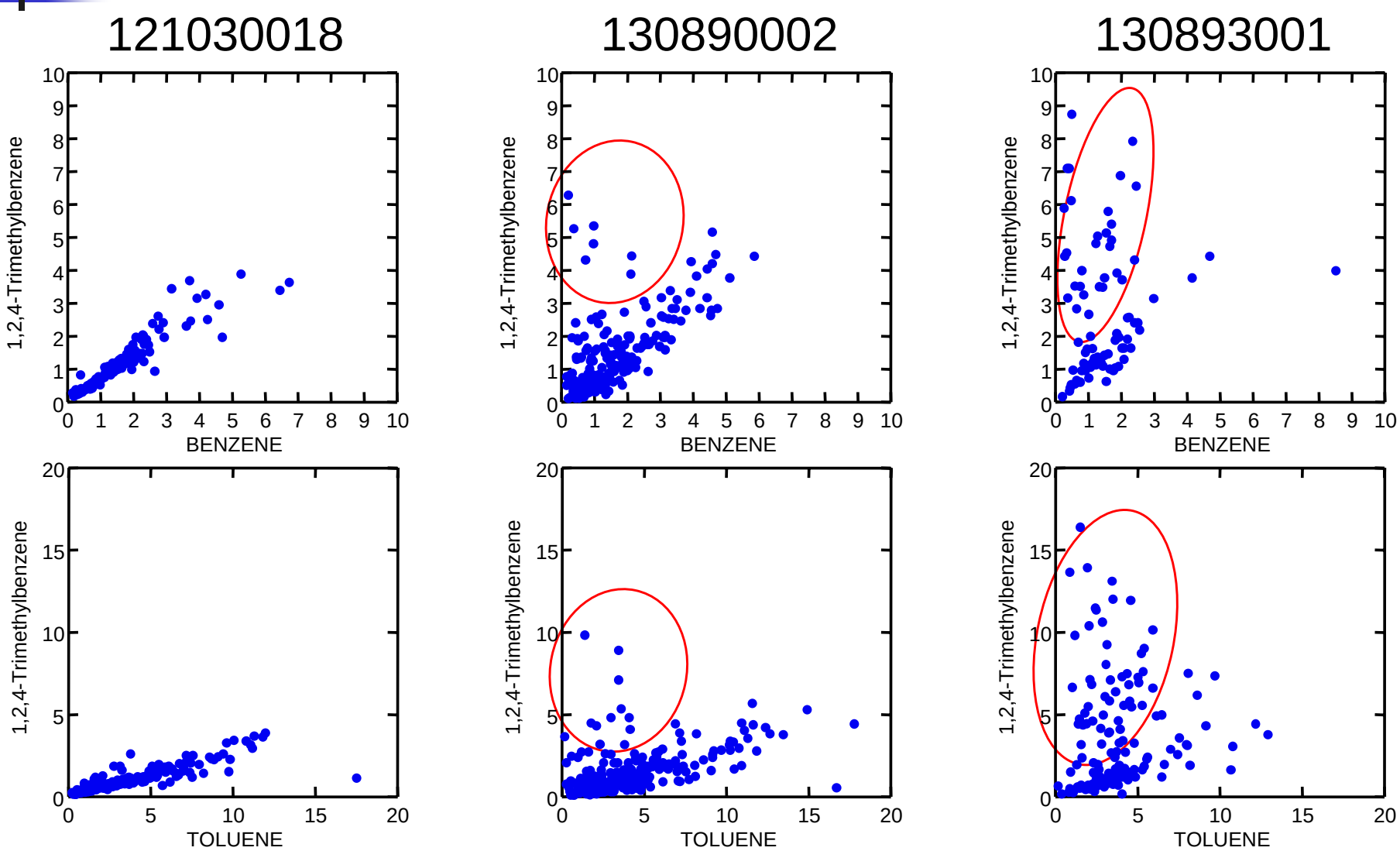


Expected “messy” relationship for these pollutants which have significant contributions from secondary formation

Units are µg/m^3

Site Examination – Scatter Plots (7 of 9)

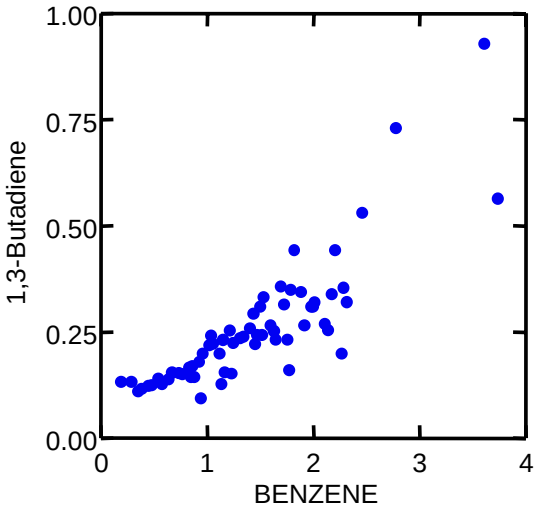


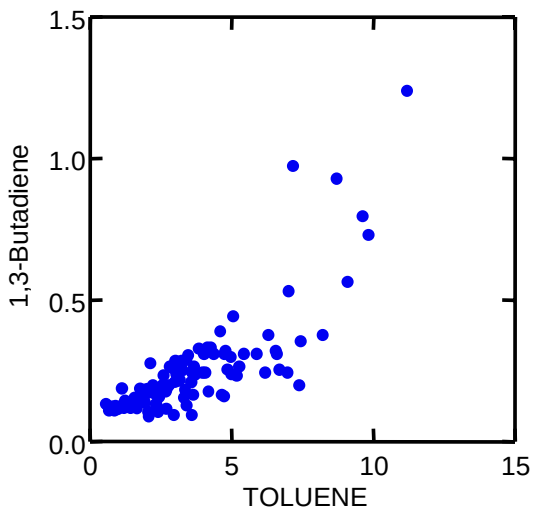
Circled data points indicate a non-motor-vehicle source for 1,2,4-Trimethylbenzene

Units are µg/m^3

Site Examination – Scatter Plots (8 of 9)

121030018





- 1,3-butadiene is very reactive and quickly falls to low concentrations as distance from roadway increases.
- These data, like 1,2,4-trimethylbenzene and toluene, show a strong motor vehicle signature.

Units are $\mu g/m^3$

Site Examination – Scatter Plots (9 of 9)

These pollutants are more likely from evaporative emissions than exhaust. Correlations are still quite good.

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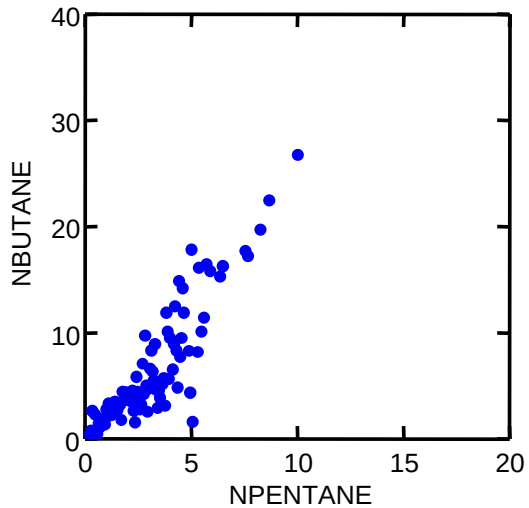

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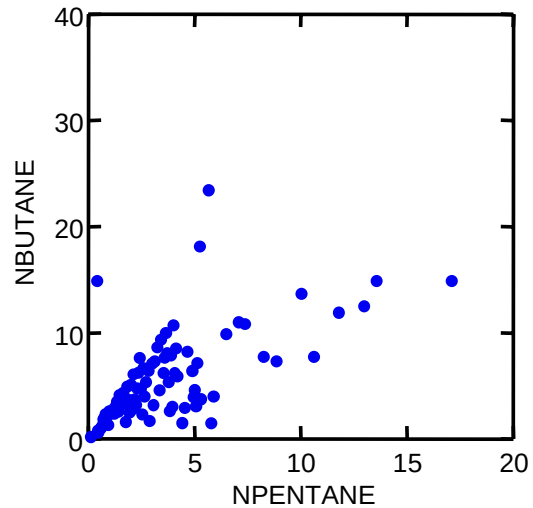
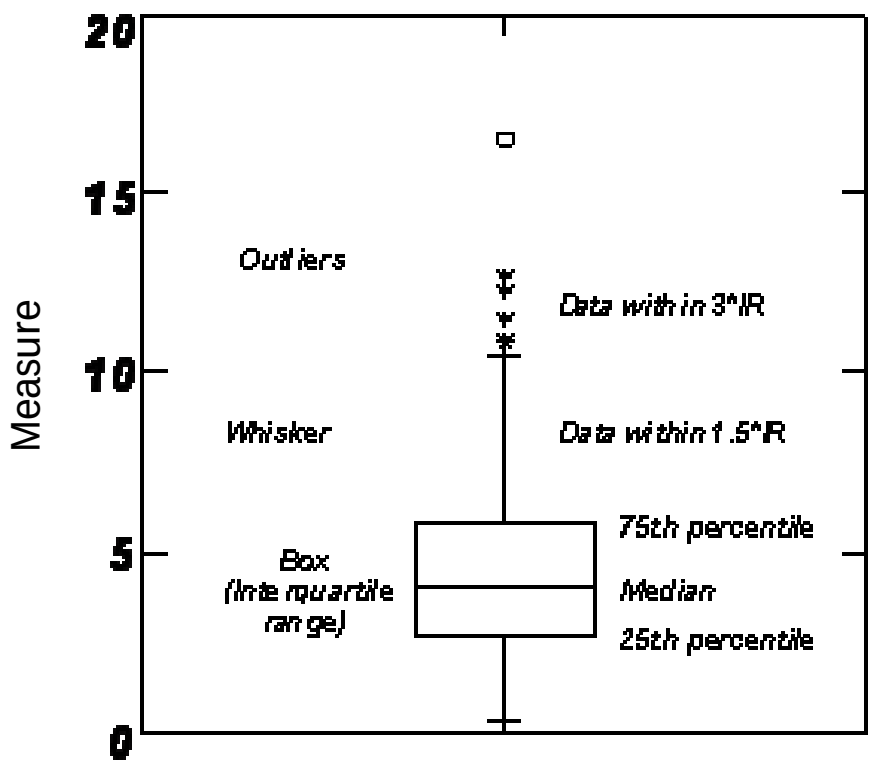


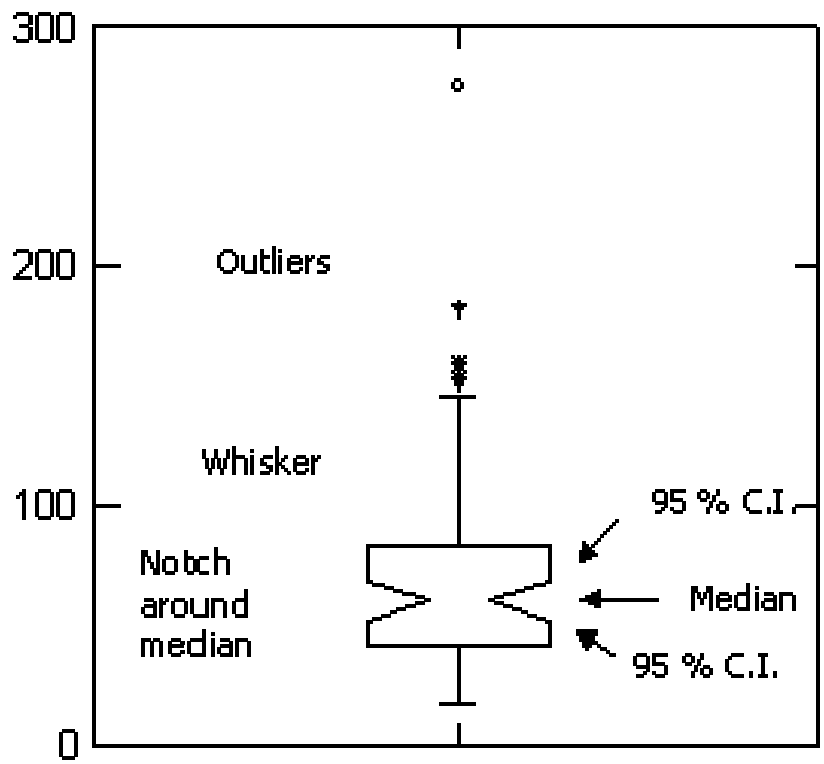
Units are µg/m^3

Scatter Plot Implications

- Strong correlation between MSAT parameters indicate that these sites are influenced by mobile sources.
- 1,2,4-trimethylbenzene may have a non-motor-vehicle source at the Georgia sites, though correlation with benzene is still apparent.
- Florida carbon tetrachloride data have a few suspect outliers that should be investigated. Concentrations should all be about the same in every sample.
- Examining site level data exposes trends and data sampling issues which can be lost at the regional level.

Showing Trends





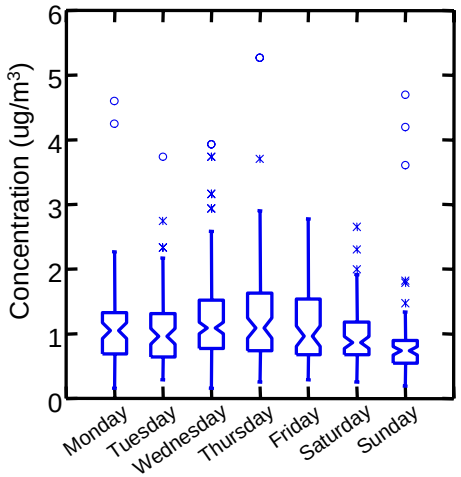
Notched box-whisker plots from SYSTAT statistical software

Day of Week Trends (1 of 6)

Benzene

For motor vehicles, lower concentrations on weekends than on weekdays may be expected as was observed at 121030018.

121030018



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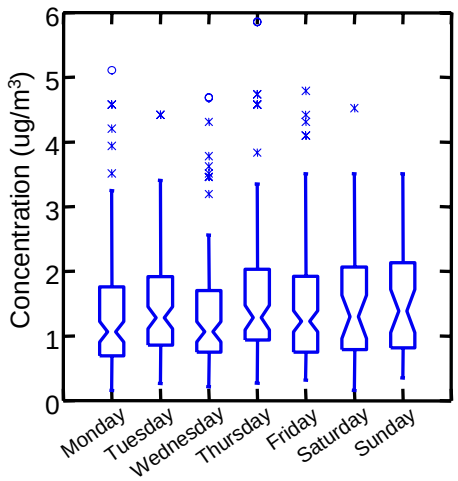

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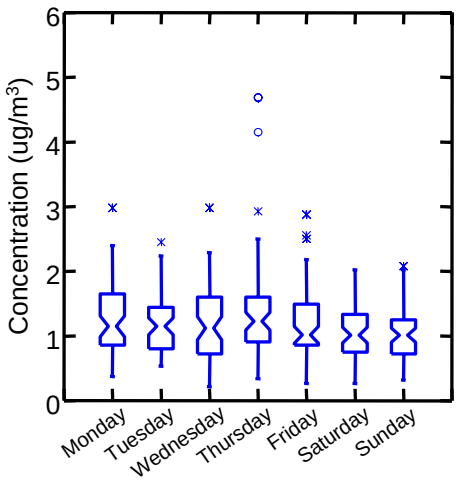

Acetylene

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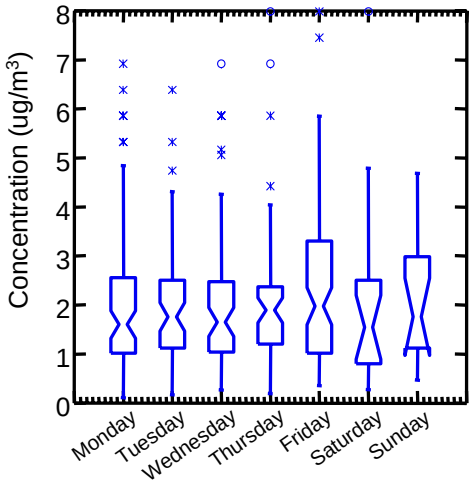

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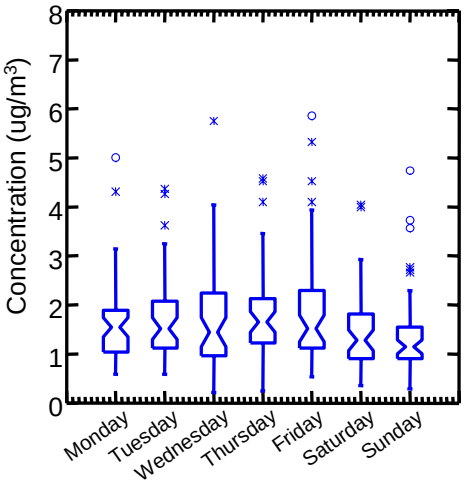

Day of Week Trends (2 of 6)

Toluene

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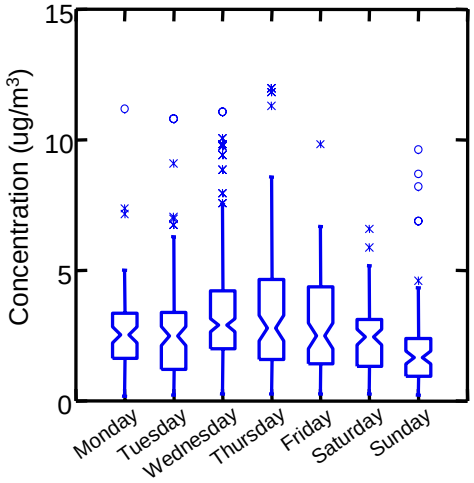

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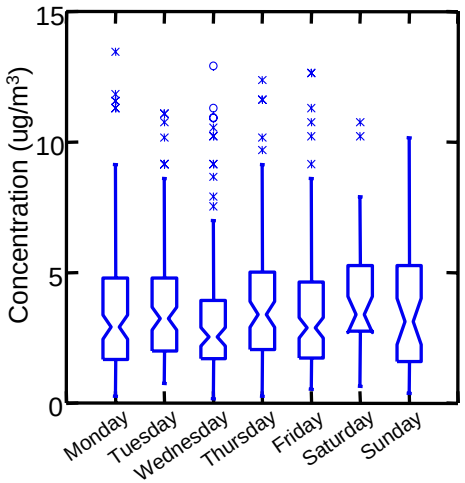

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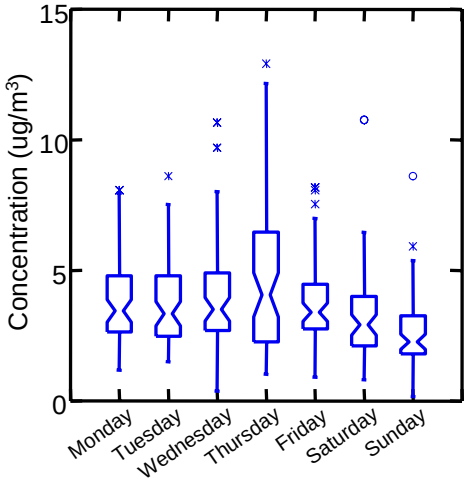
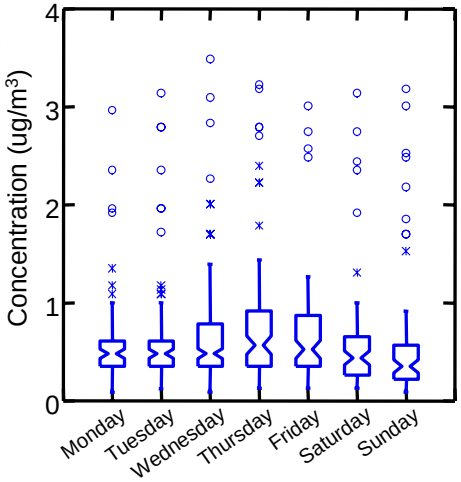


Ethylbenzene

121030018



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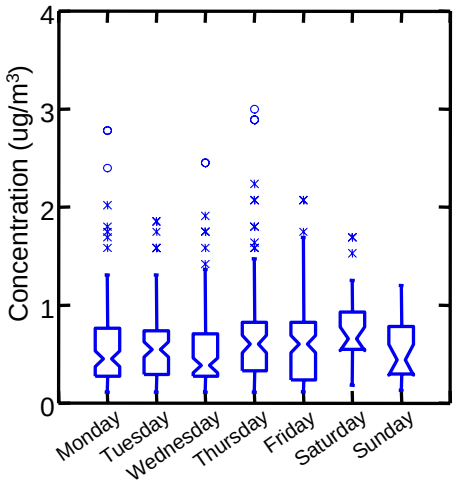

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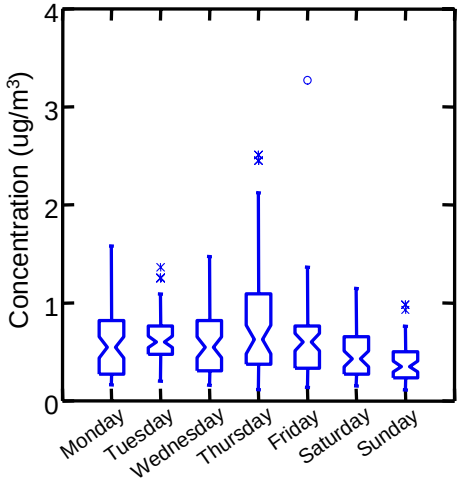
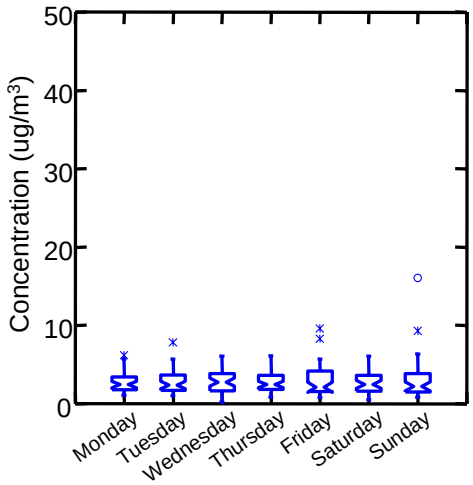


Day of Week Trends (3 of 6)

Formaldehyde

121030018



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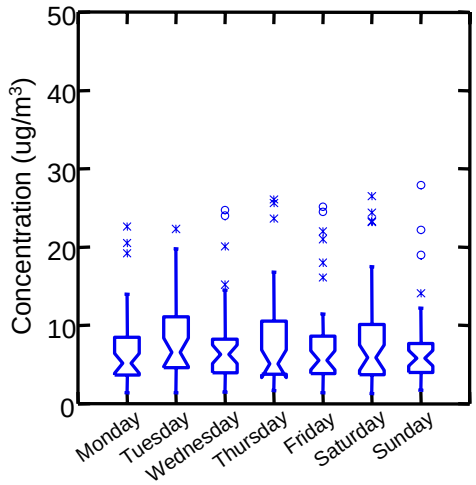

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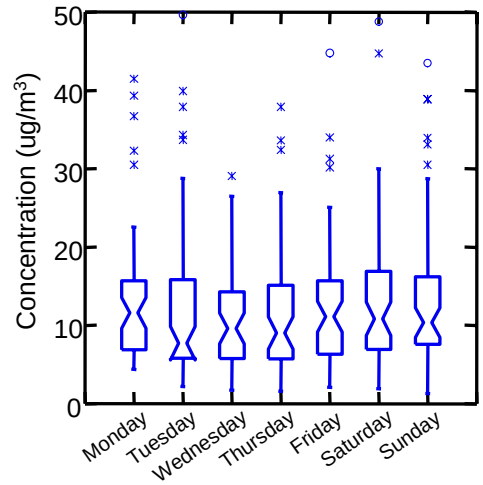
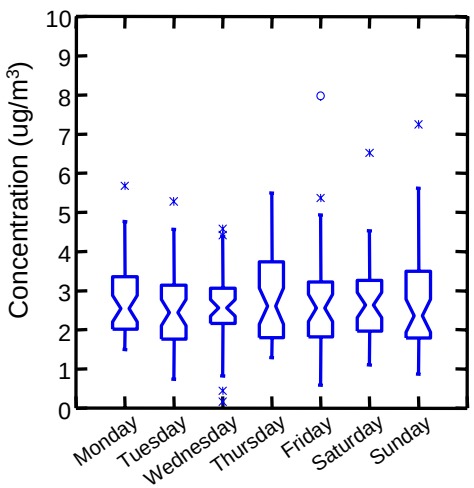


Acetaldehyde

121030018



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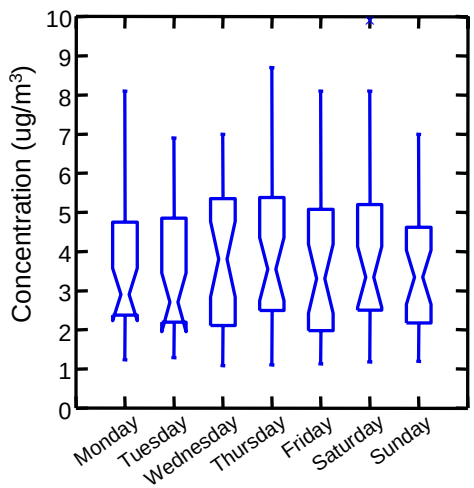

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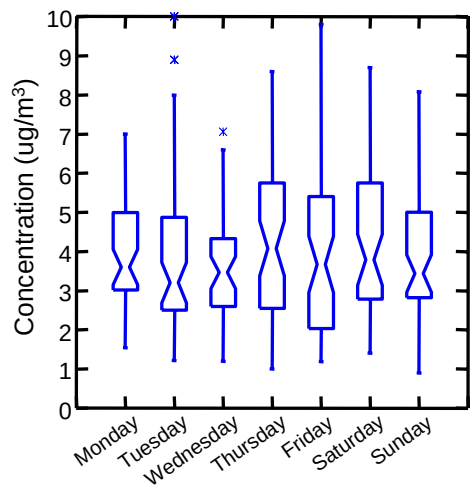
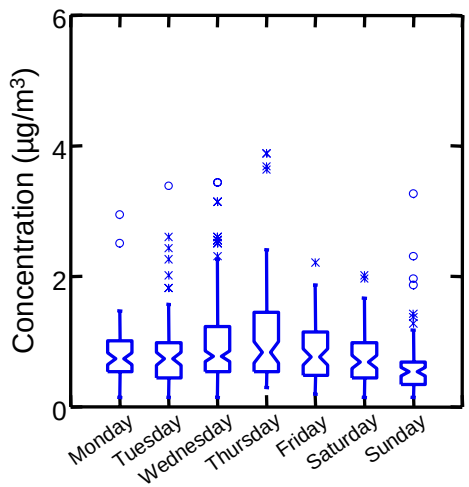


Day of Week Trends (4 of 6)

1,2,4-Trimethylbenzene

121030018



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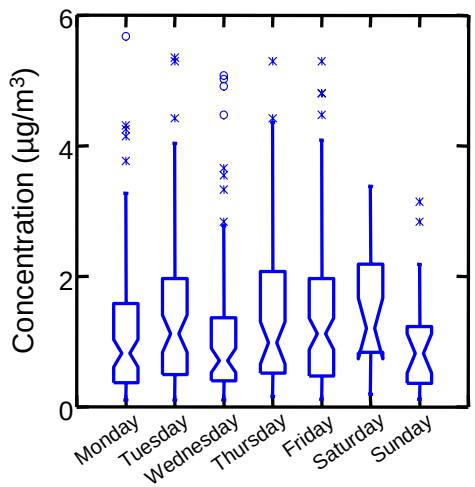

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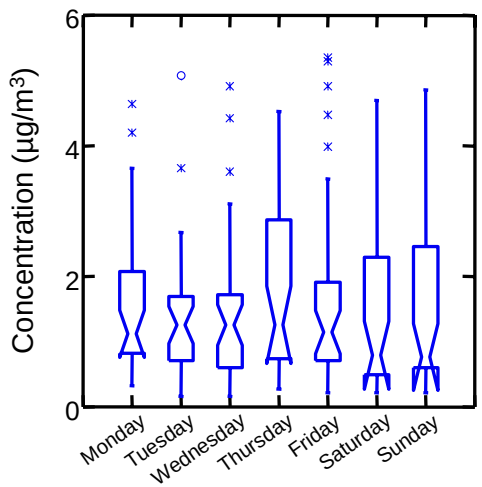
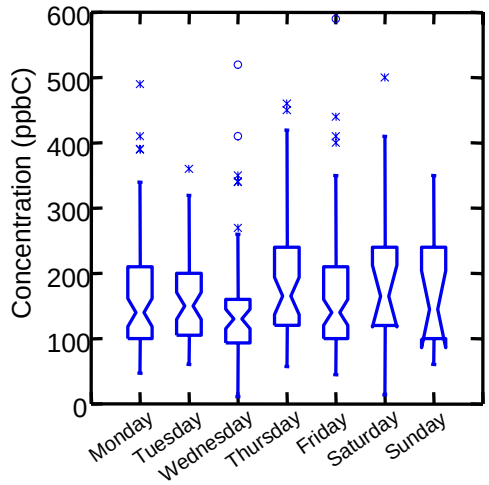


Total NMOC

130890002



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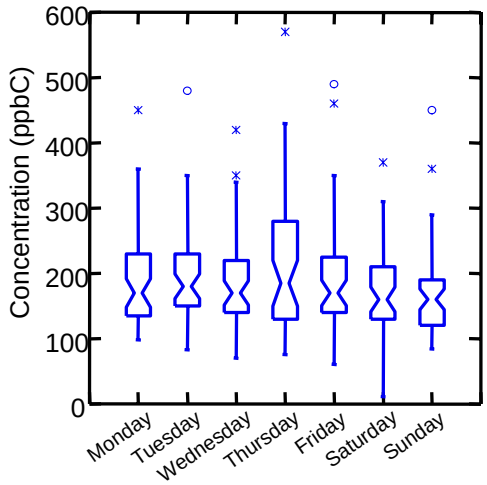
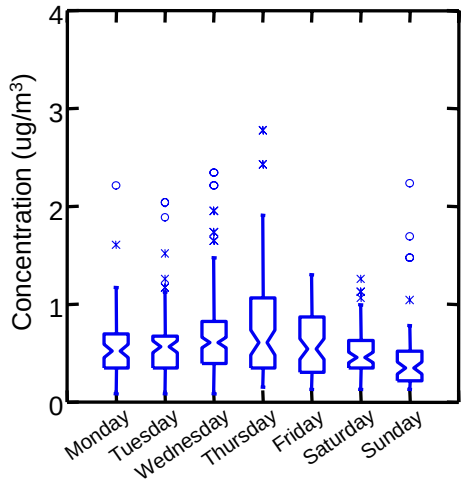


TNMOC = total nonmethane organic compounds

Day of Week Trends (5 of 6)

o-Xylene

121030018



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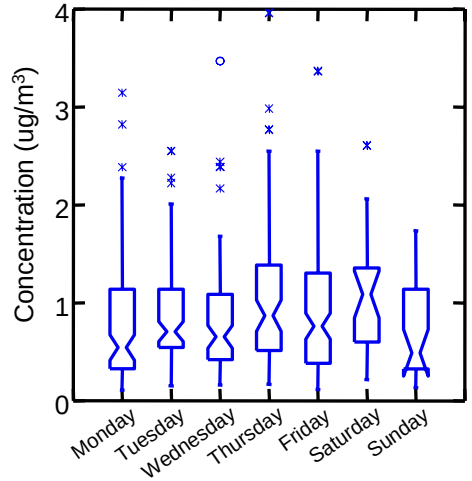

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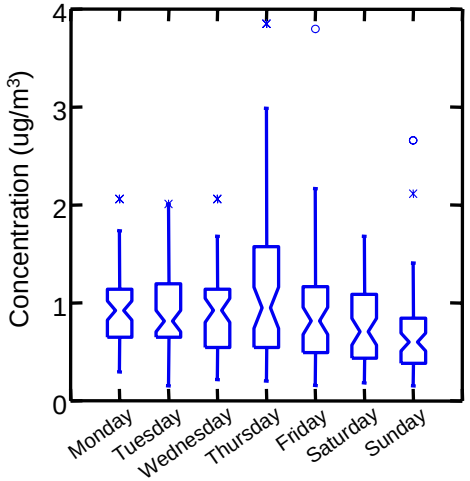
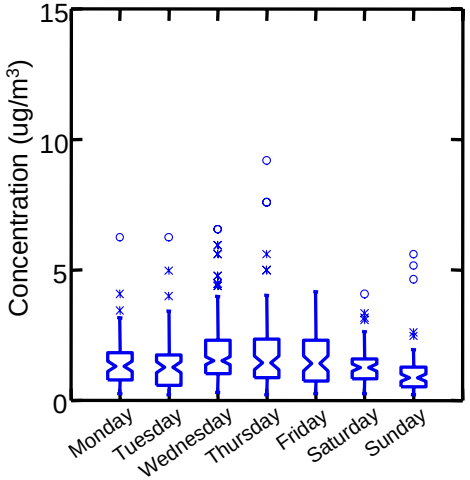


m-&p-Xylene

121030018



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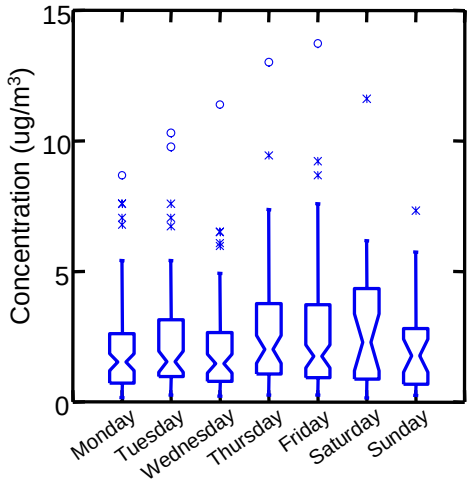

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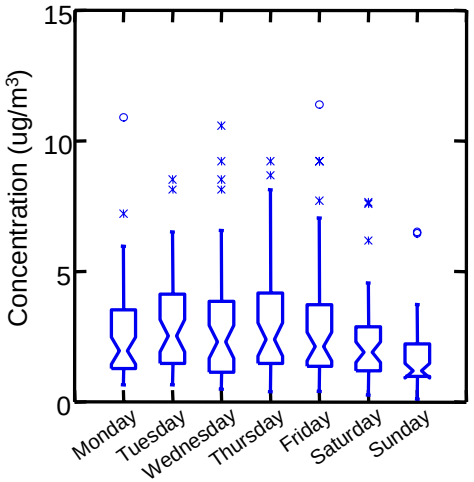
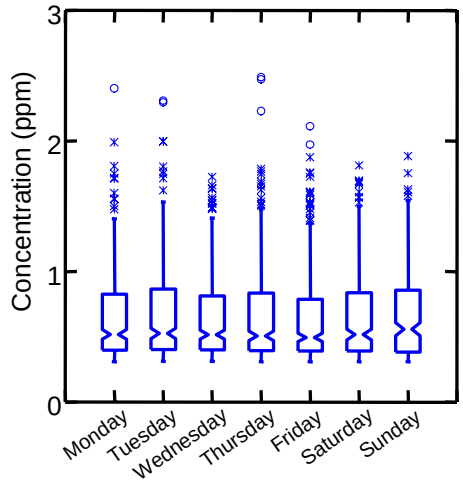


Day of Week Trends (6 of 6)

Carbon monoxide

121030018



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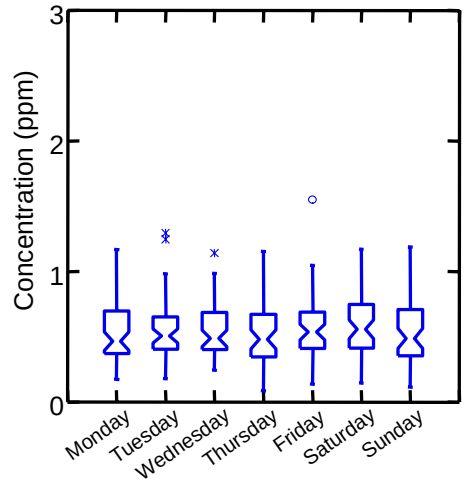
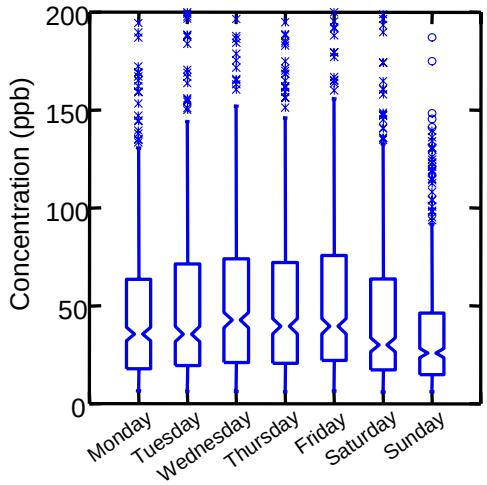


NO_x

130890002



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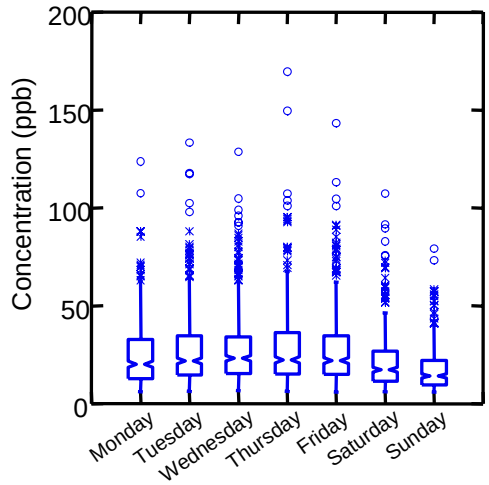


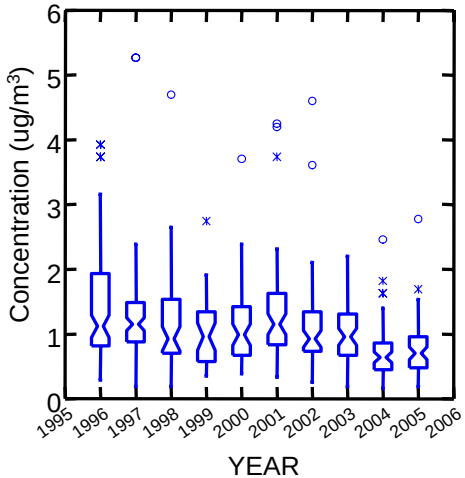
Day of Week Trends – Implications

- MSAT concentrations should follow typical day-of-week traffic patterns if a site is influenced by mobile sources.
  - 121030084 (FL) is strongly influenced by mobile sources
  - 130843001 (GA) is influenced by mobile sources
  - 130840002 (GA) is less strongly influenced by mobile sources
- Formaldehyde and acetaldehyde are both primarily emitted and secondarily formed through photochemistry. The significant influence of secondary formation was apparent in the data as concentrations of these compounds were consistent for all days of the week and did not follow traffic patterns.

Annual Trends (1 of 7)

Benzene

121030018



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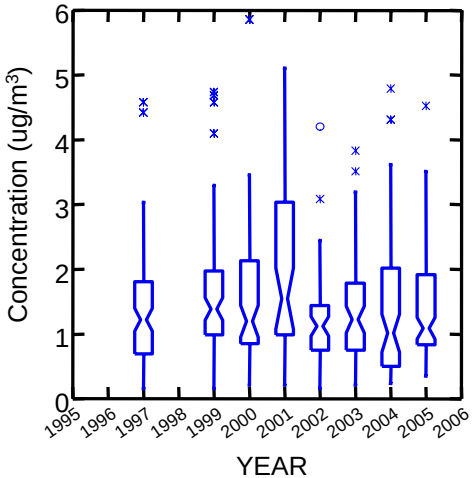

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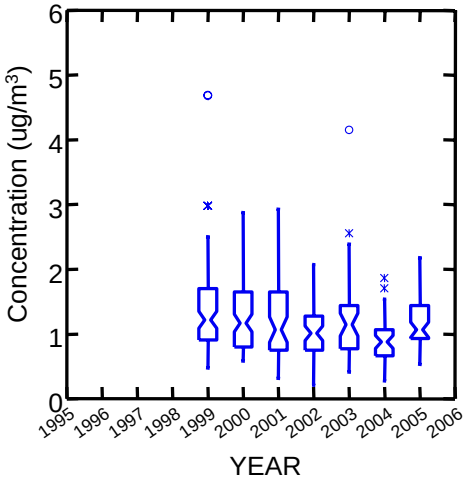
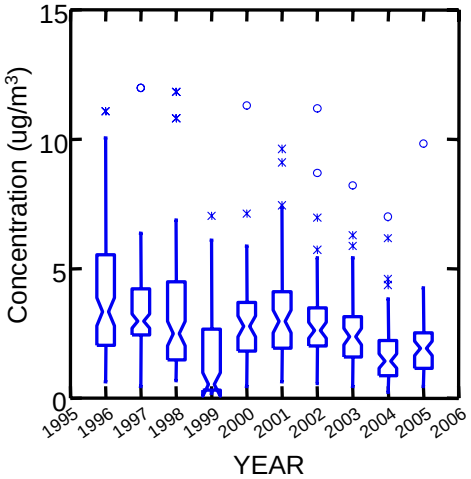


Toluene

121030018



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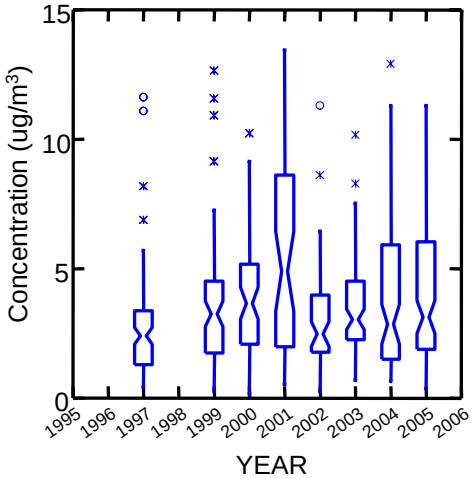

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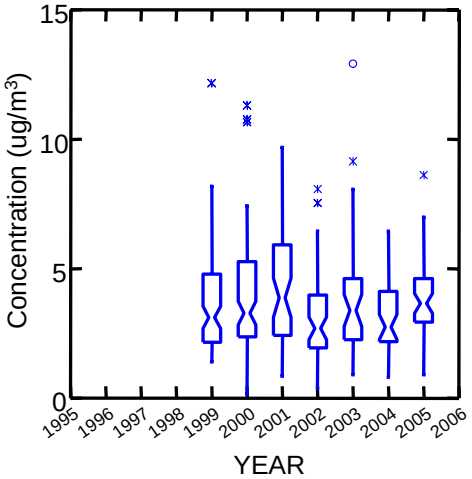
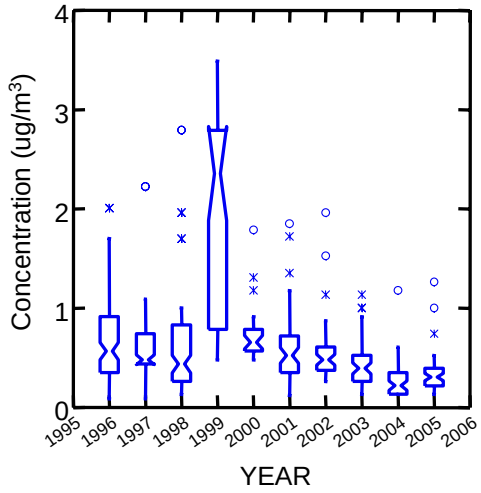


Annual Trends (2 of 7)

Ethylbenzene

121030018



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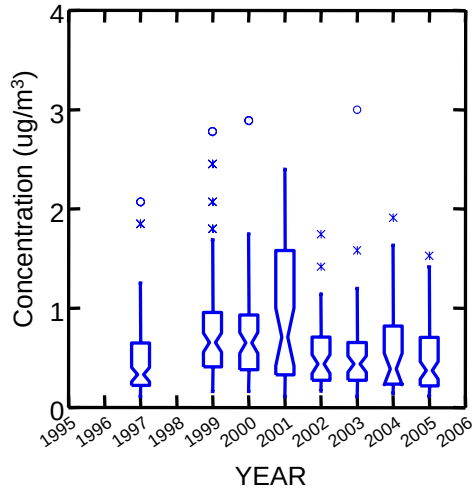

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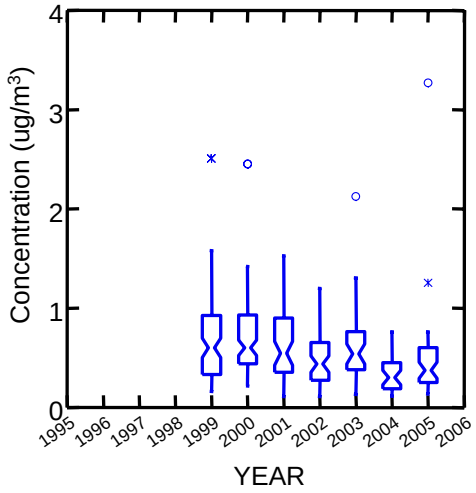
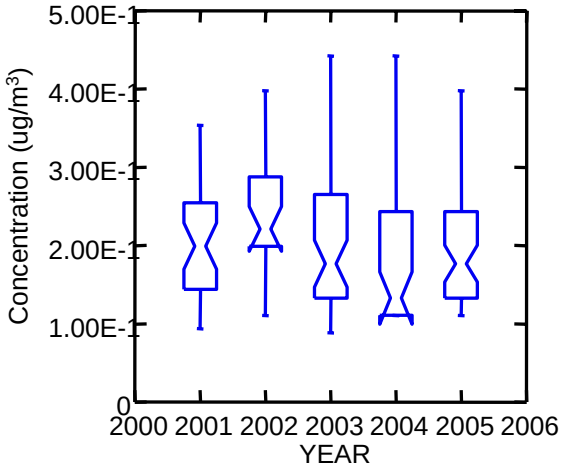


1,3-Butadiene

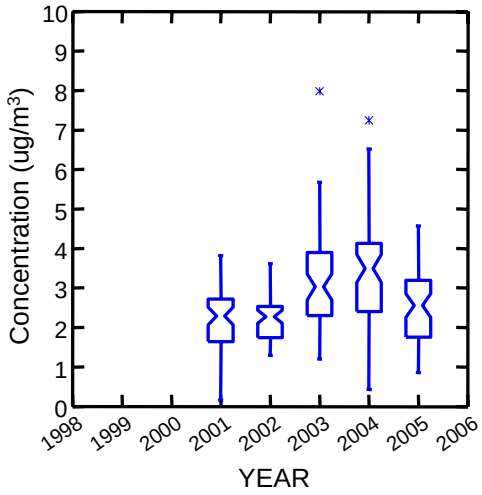
121030018



Annual Trends (3 of 7)

Acetaldehyde

121030018



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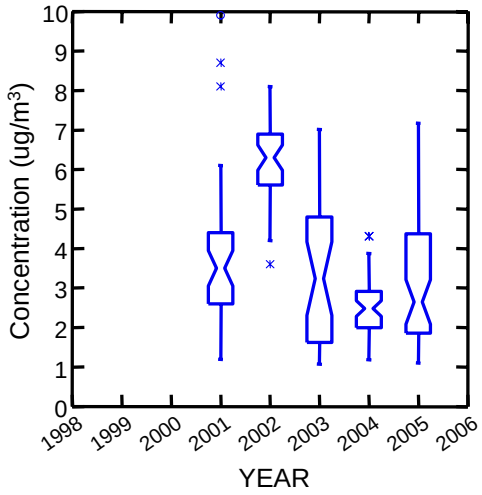

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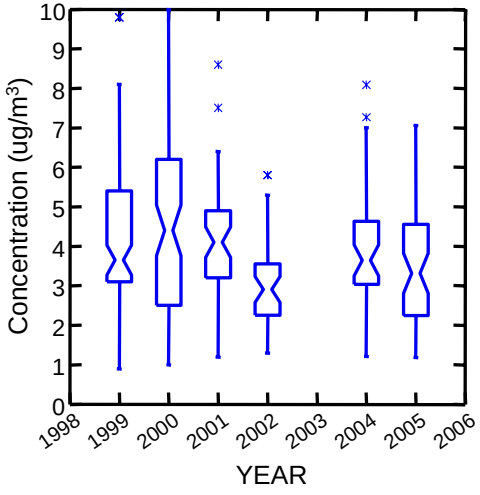
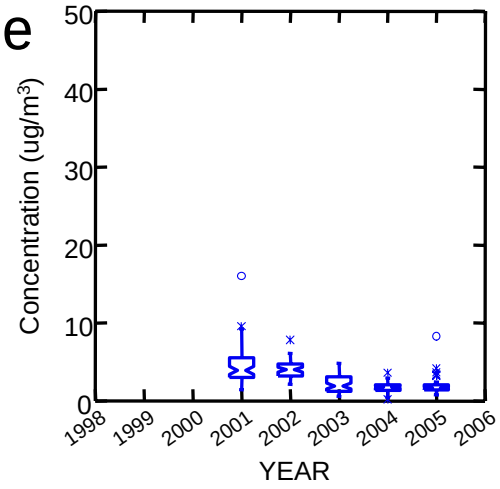


Formaldehyde

121030018



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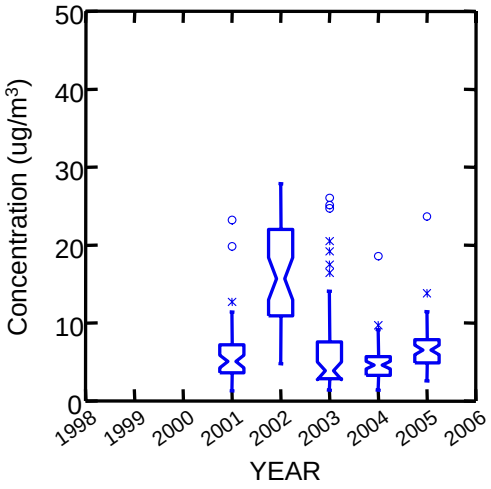

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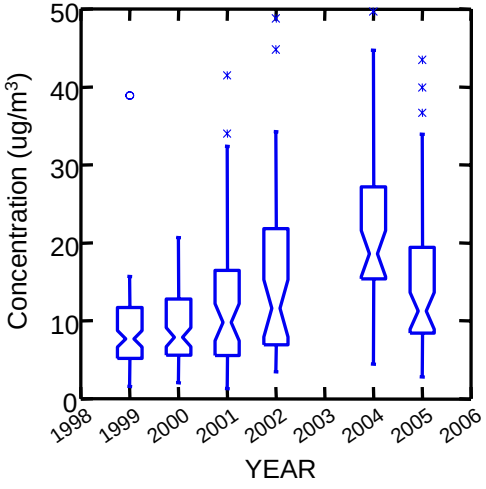
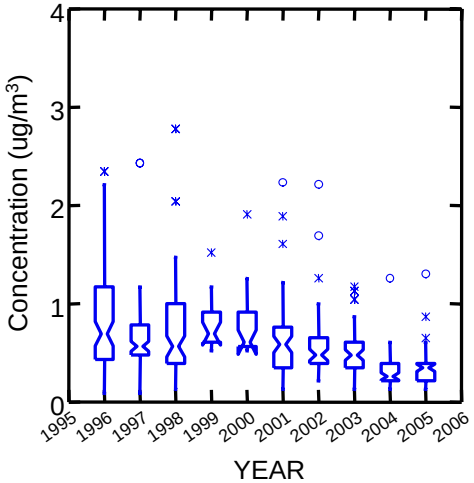


Annual Trends (4 of 7)

o-Xylene

121030018



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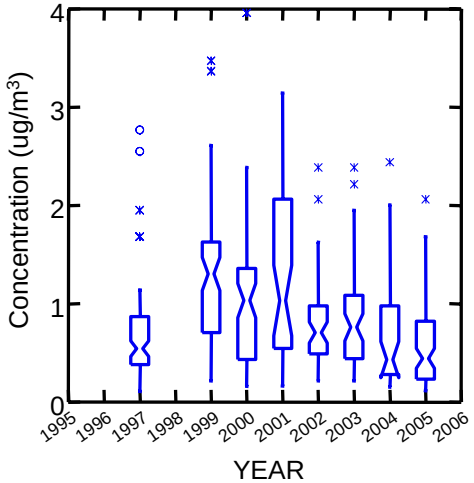

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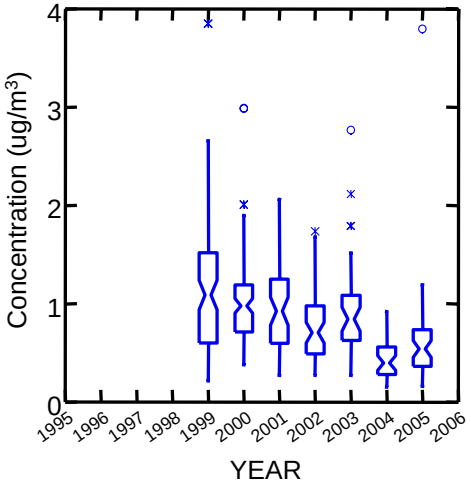
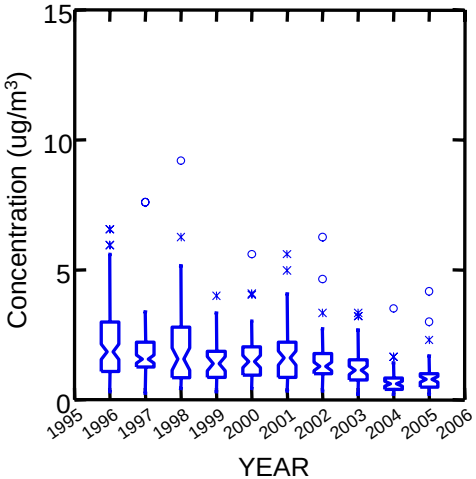


m-&p-Xylene

121030018



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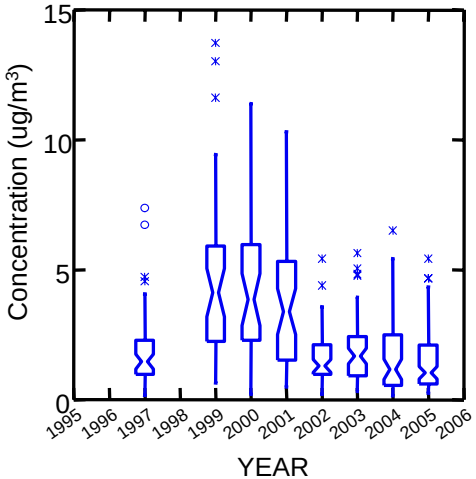

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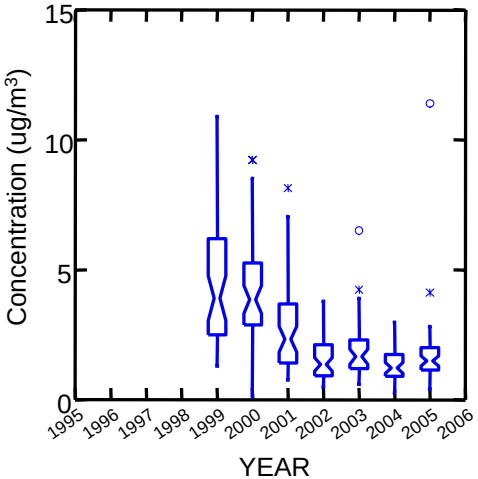
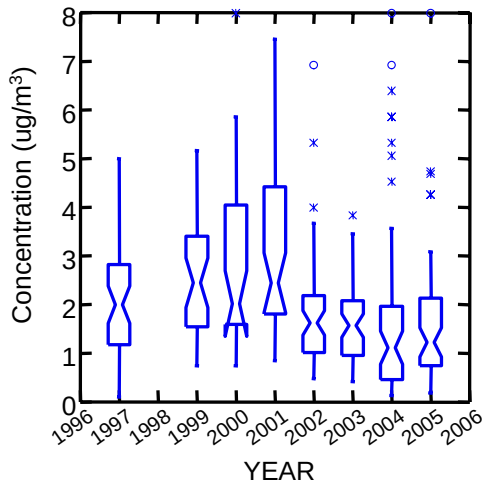


Annual Trends (5 of 7)

Acetylene

130890002



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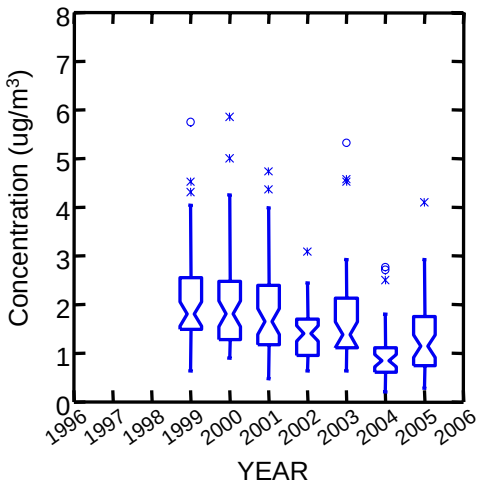
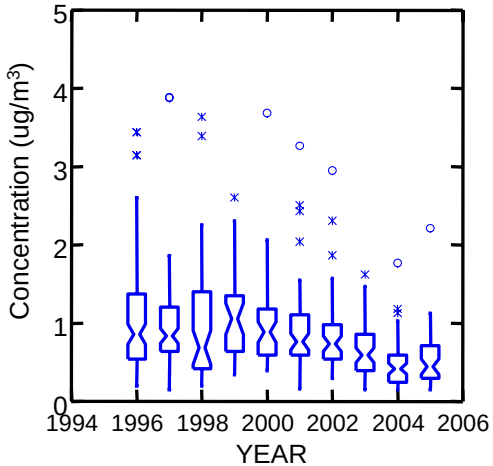


1,2,4-Trimethylbenzene

121030018



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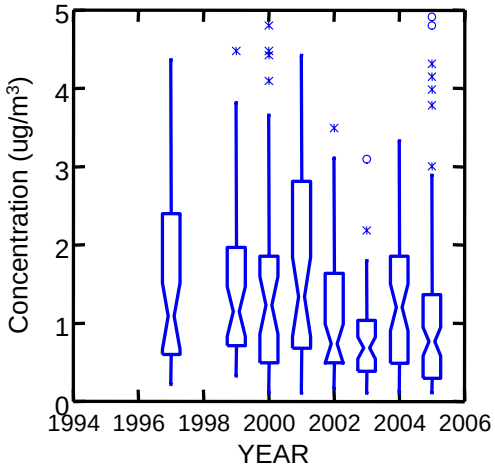

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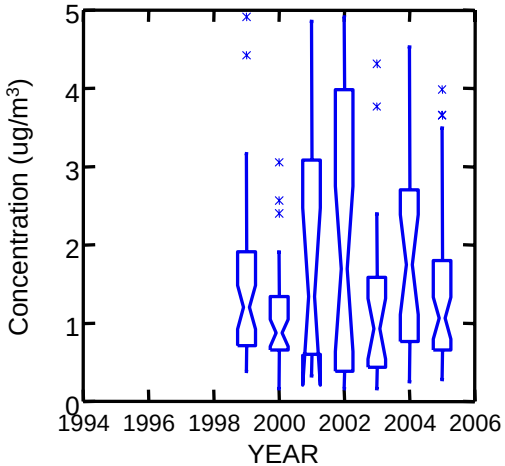
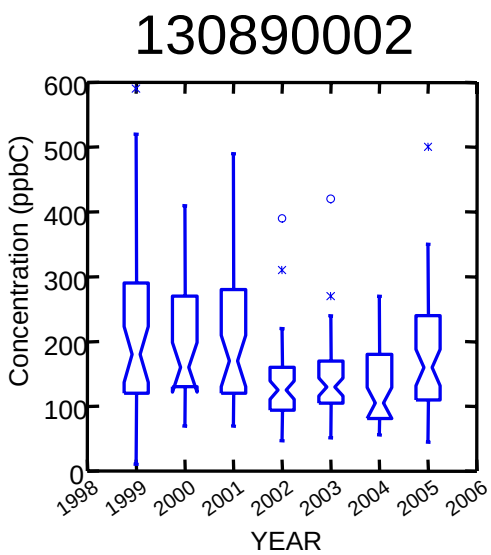
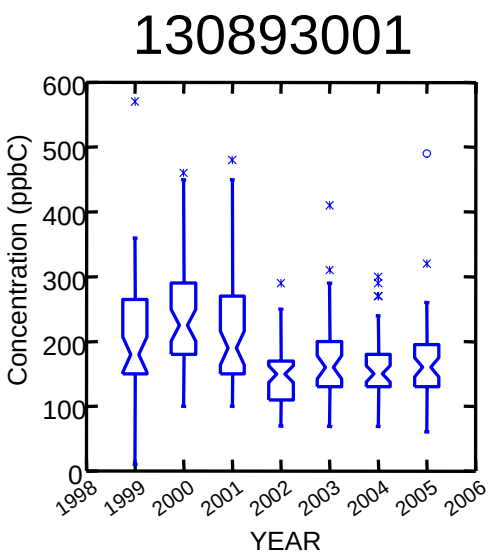


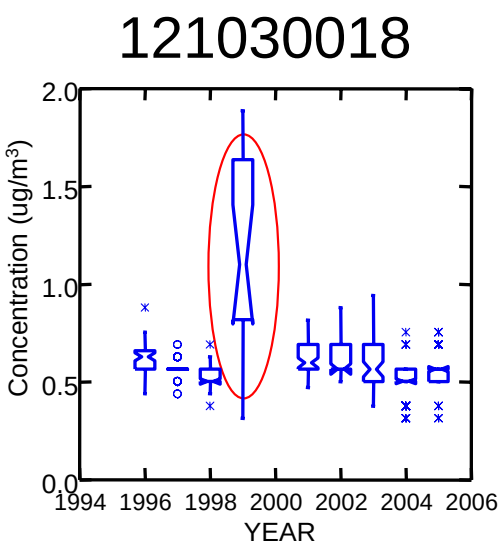
Annual Trends (6 of 7)

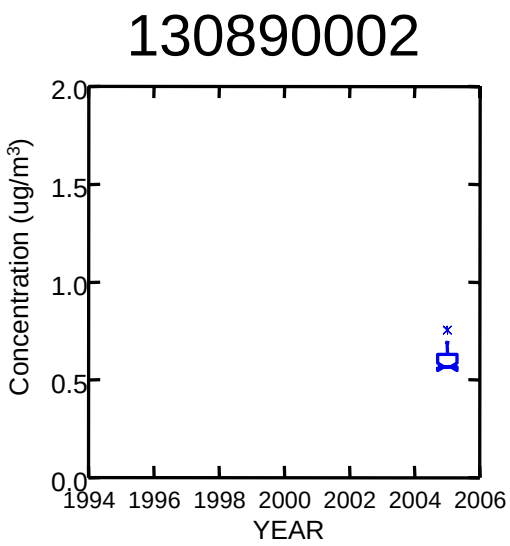
Total NMOC





Carbon tetrachloride



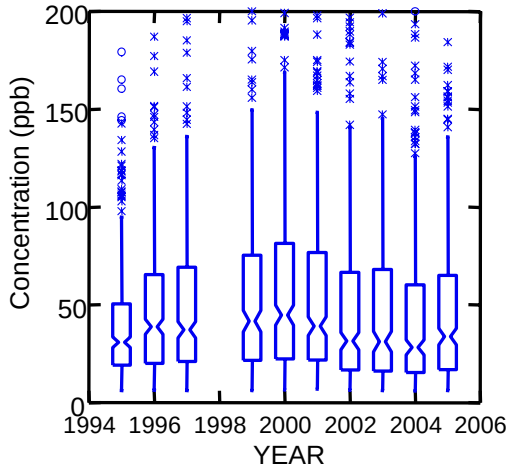


1999 data are unreliable (circled); such a large change in Carbon Tet. concentration within one year highly improbable. Graphs have been cut off at 2 ug/m^3 for clarity.

Annual Trends (7 of 7)

NO_x

130890002



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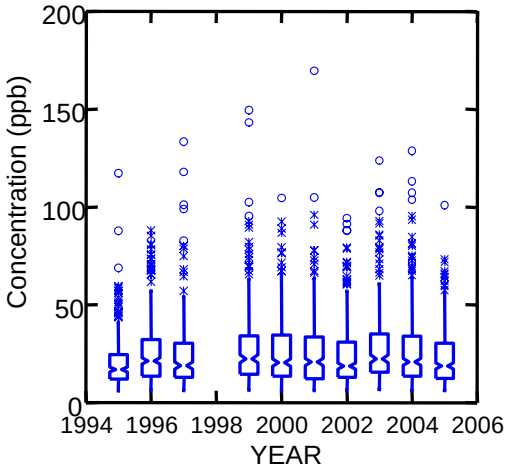
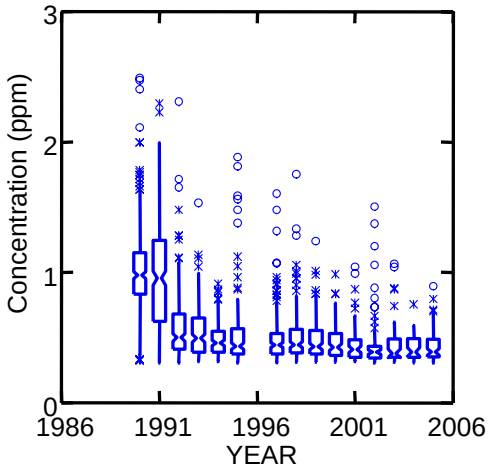


Carbon monoxide

121030018



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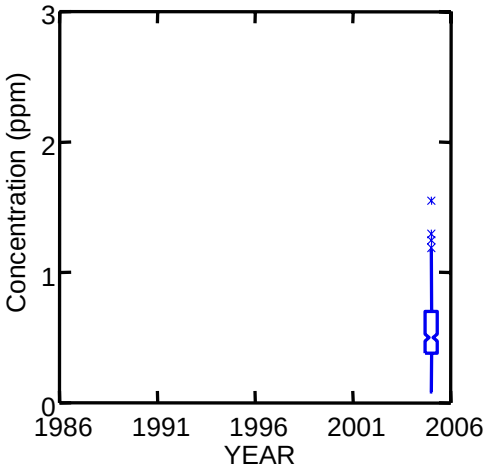


Annual Trends – Implications

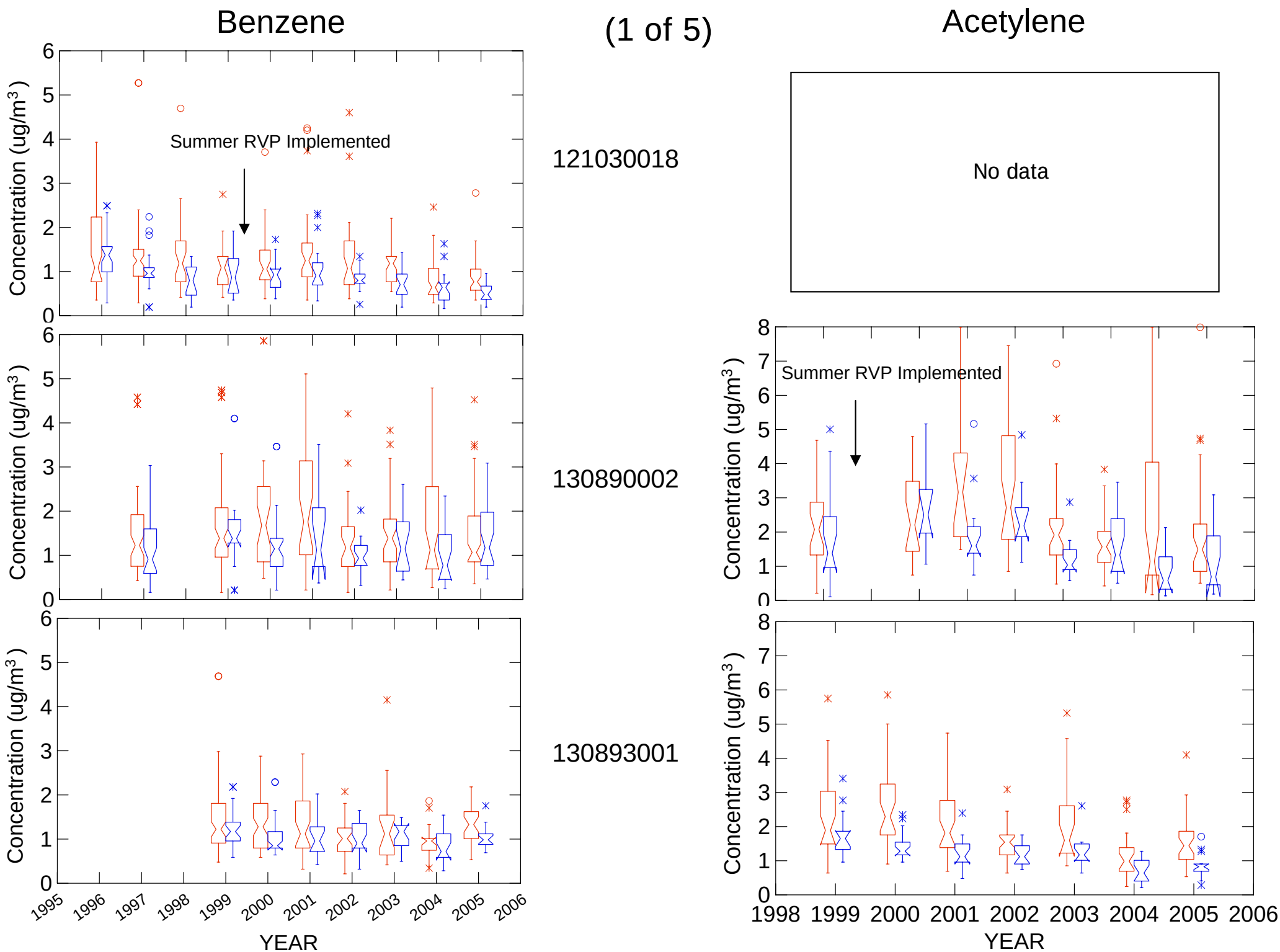
- Most MSATs show a small decrease in concentration over time.
- The increase in acetaldehyde and decrease in formaldehyde in Florida are consistent with the removal of methyl-t-butyl ether (MTBE) from gasoline. However, the change in fuel composition could not be verified.
- A significant step change was observed in the concentrations of o-xylene, m-&p-xylenes, acetylene and total NMOC between 2001 and 2002 in Georgia. The regulations researched in this report do not account for these changes.
- The large drop in CO concentrations in 1992 may be due to the 1990 Clean Air Act which required new tailpipe standards in 1990 and the introduction of oxyfuels to high CO cities 1992 (U.S. Environmental Protection Agency, 2007).

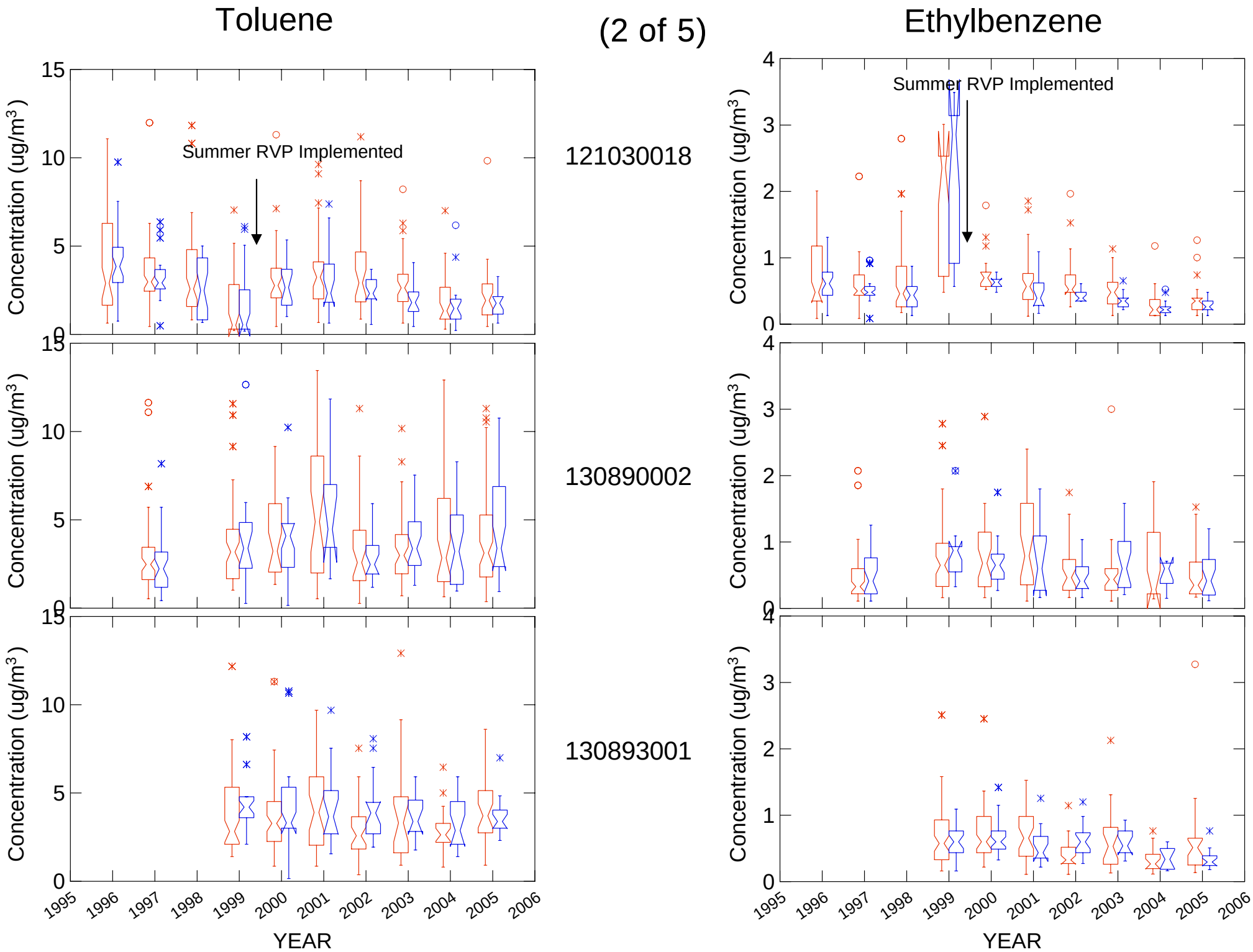
RVP Comparisons

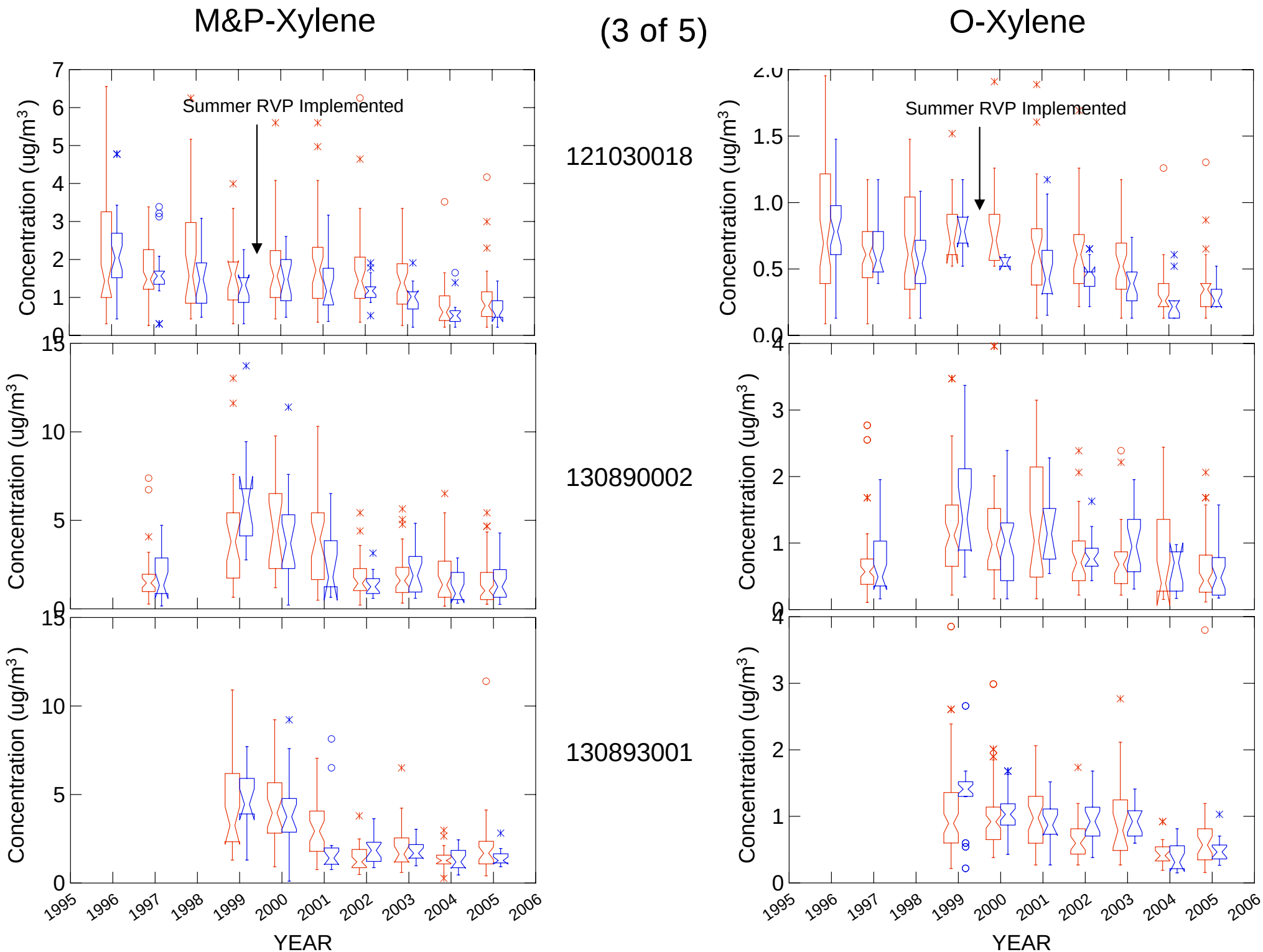
Red = Non-RVP Months

Blue = RVP Months (June, July, August, September)

Do changes in ambient concentrations coincide with changes in RVP?


Benzene
(1 of 5)
Acetylene
121030018
130890002
130893001
Summer RVP Implemented
No data
Concentration (ug/m3)
YEAR
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006


Toluene
Ethylbenzene
121030018
130890002
130893001
Summer RVP Implemented
Summer RVP Implemented
Concentration (ug/m3)
YEAR
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006


M&P-Xylene
O-Xylene
121030018
130890002
130893001
Summer RVP Implemented
Concentration (ug/m3)
YEAR
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006

1,2,4-Trimethylbenzene

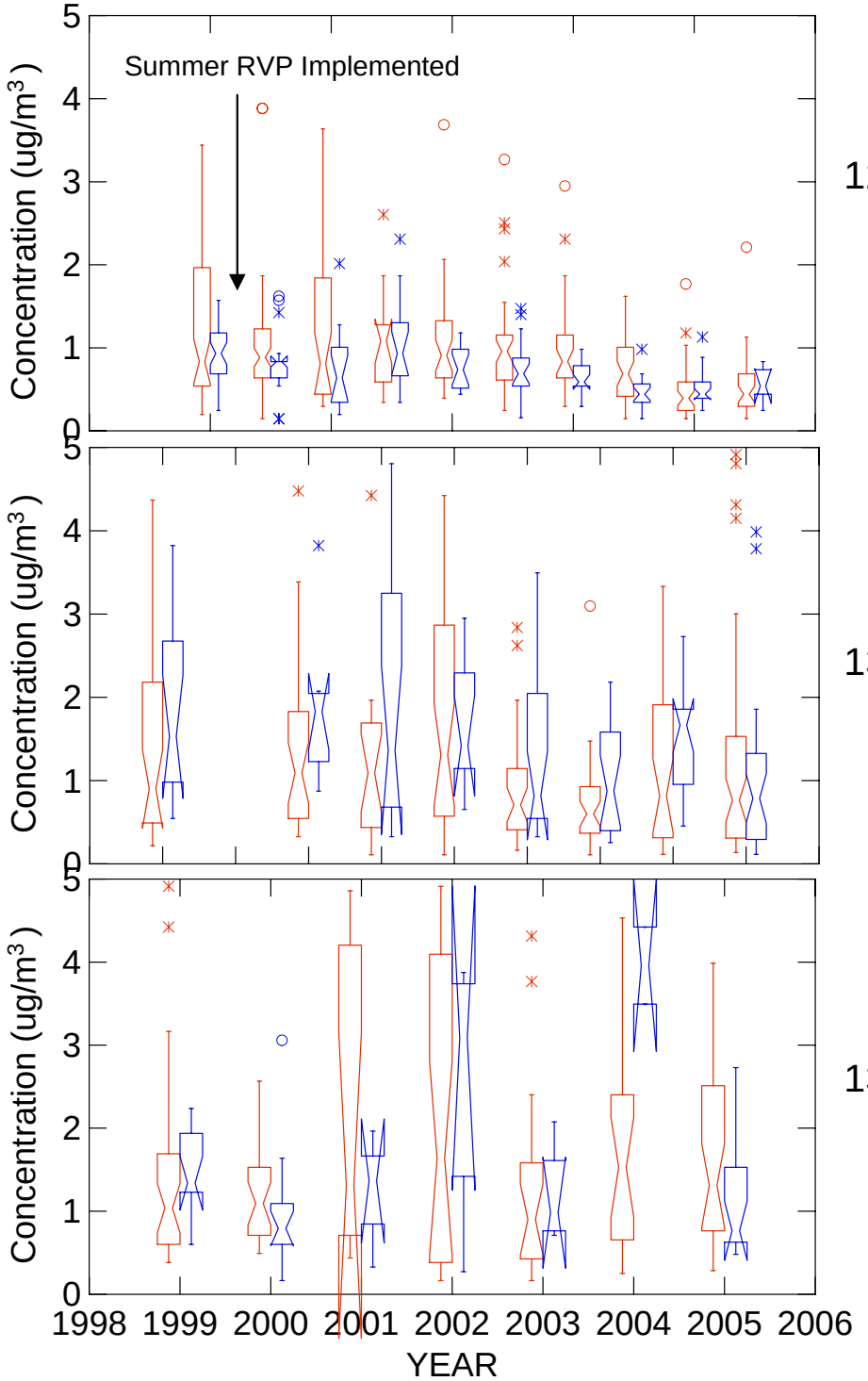
(4 of 5)

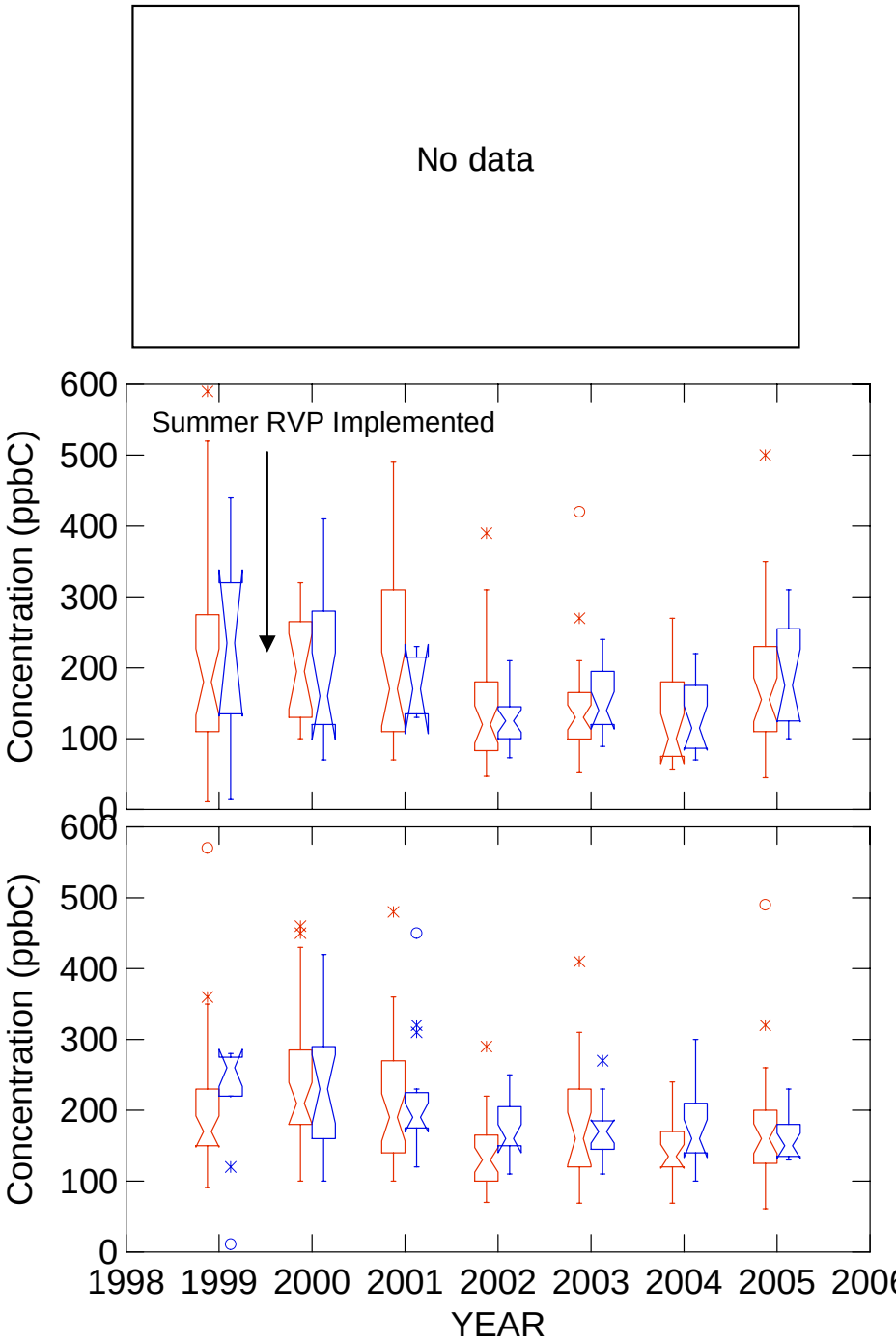
Total NMOC

121030018

130890002

130893001

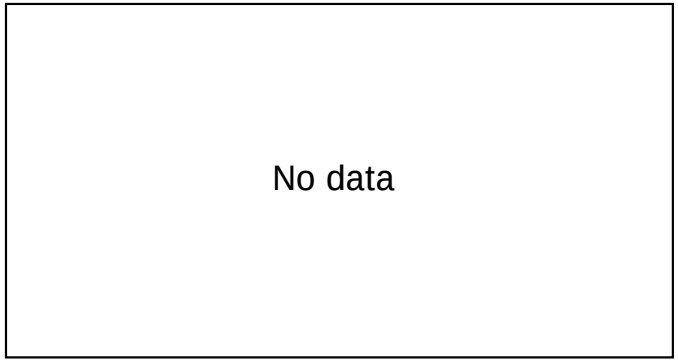




N-Butane

N-Pentane

121030018



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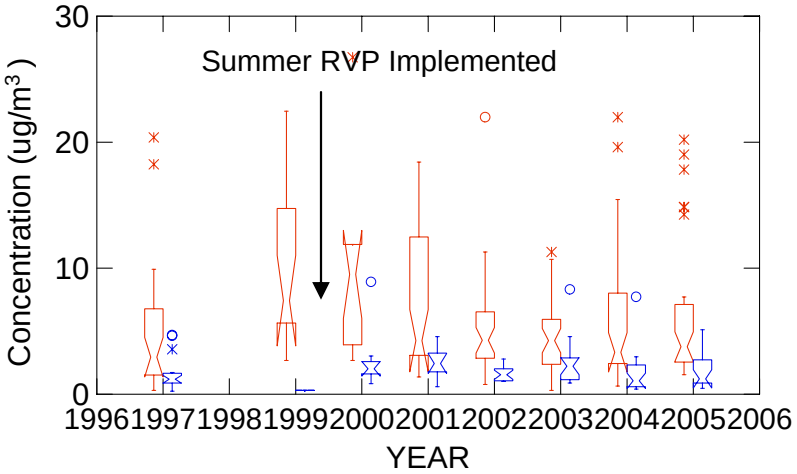

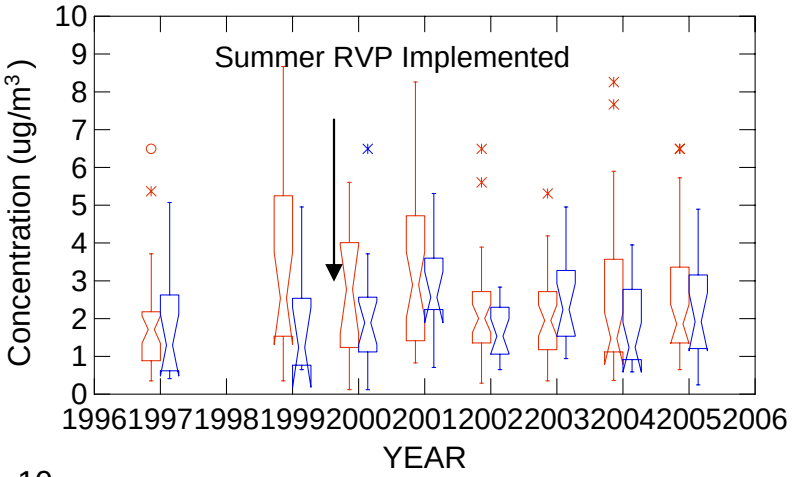

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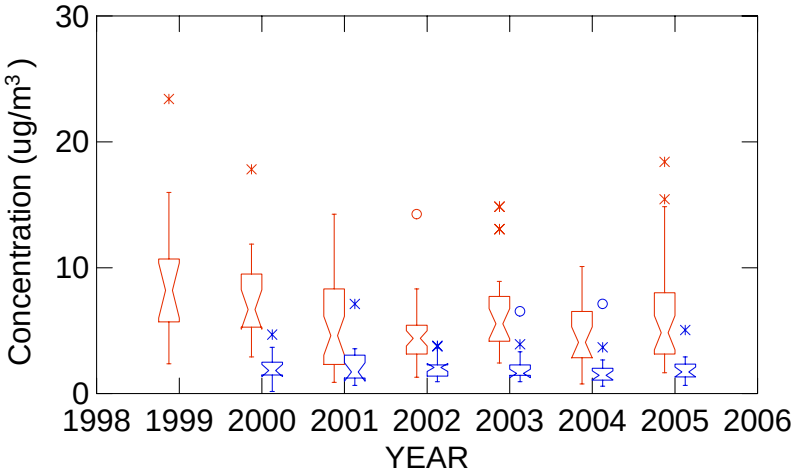
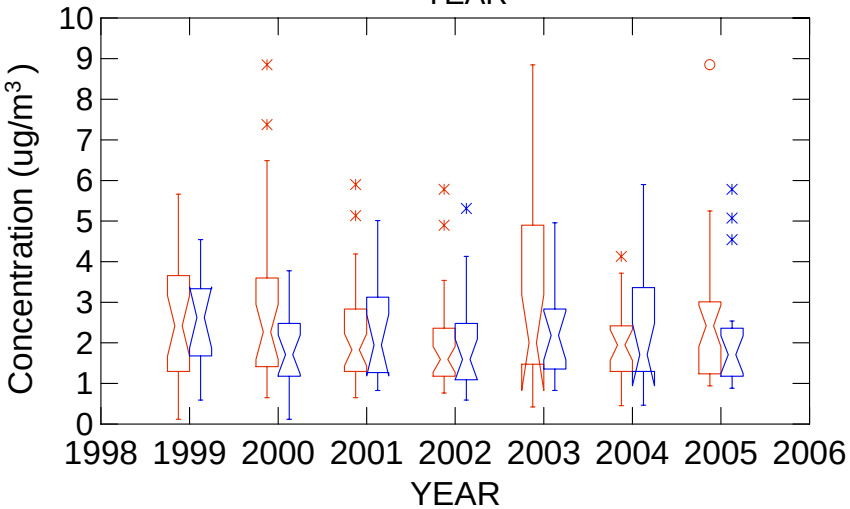


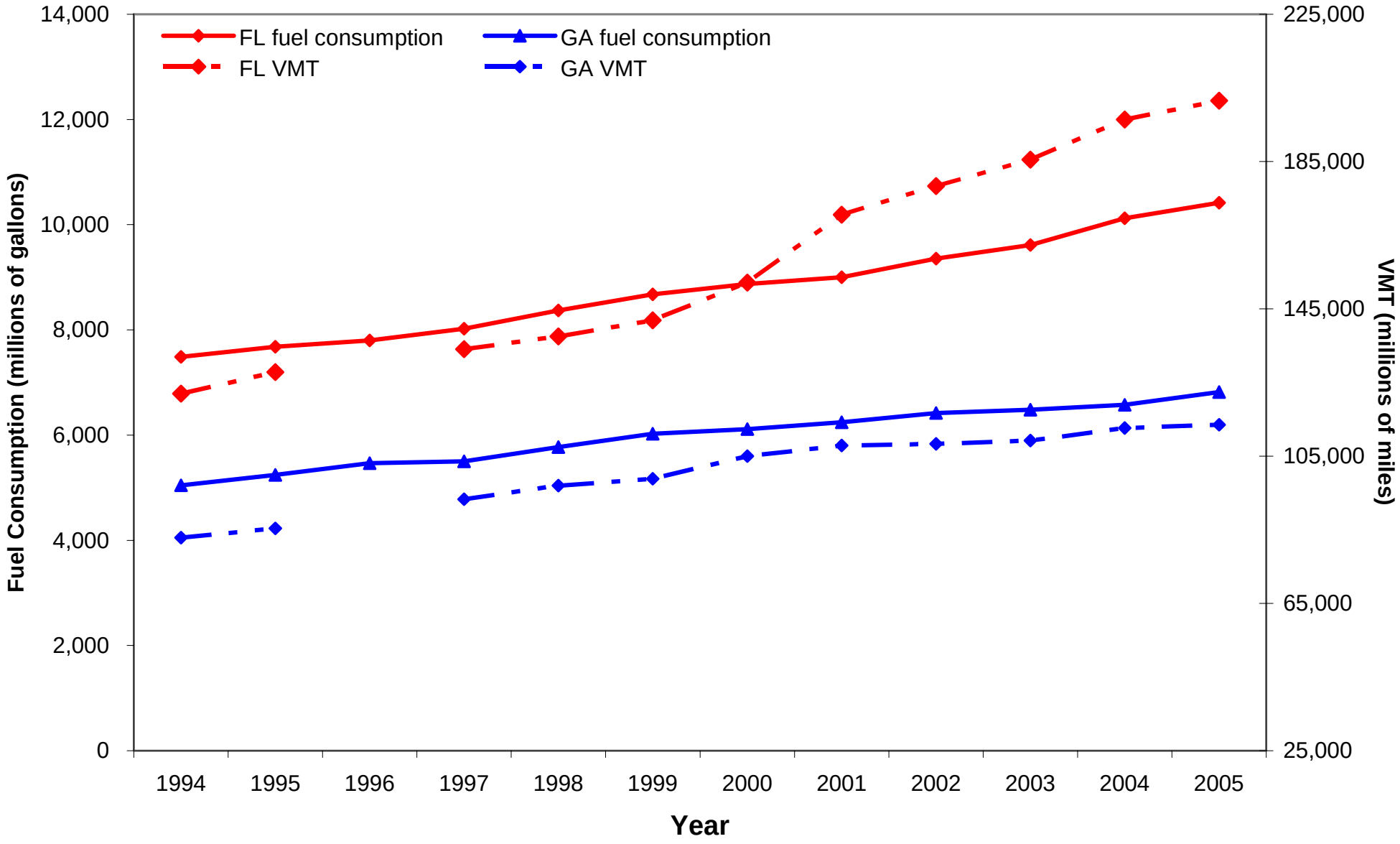


RVP Trends – Implications

- RVP is typically reduced by removing the most volatile fraction of the fuel such as butanes and pentanes.*
  - N-butane ambient concentrations are consistently lower during lower RVP months in Georgia after 1999. However, pre-1999 data are insufficient to tell if RVP regulations are causing this difference.
  - N-pentane concentrations are similar for RVP and non-RVP months.
- MSATs do not show a significant change coincident with changes in RVP regulations.

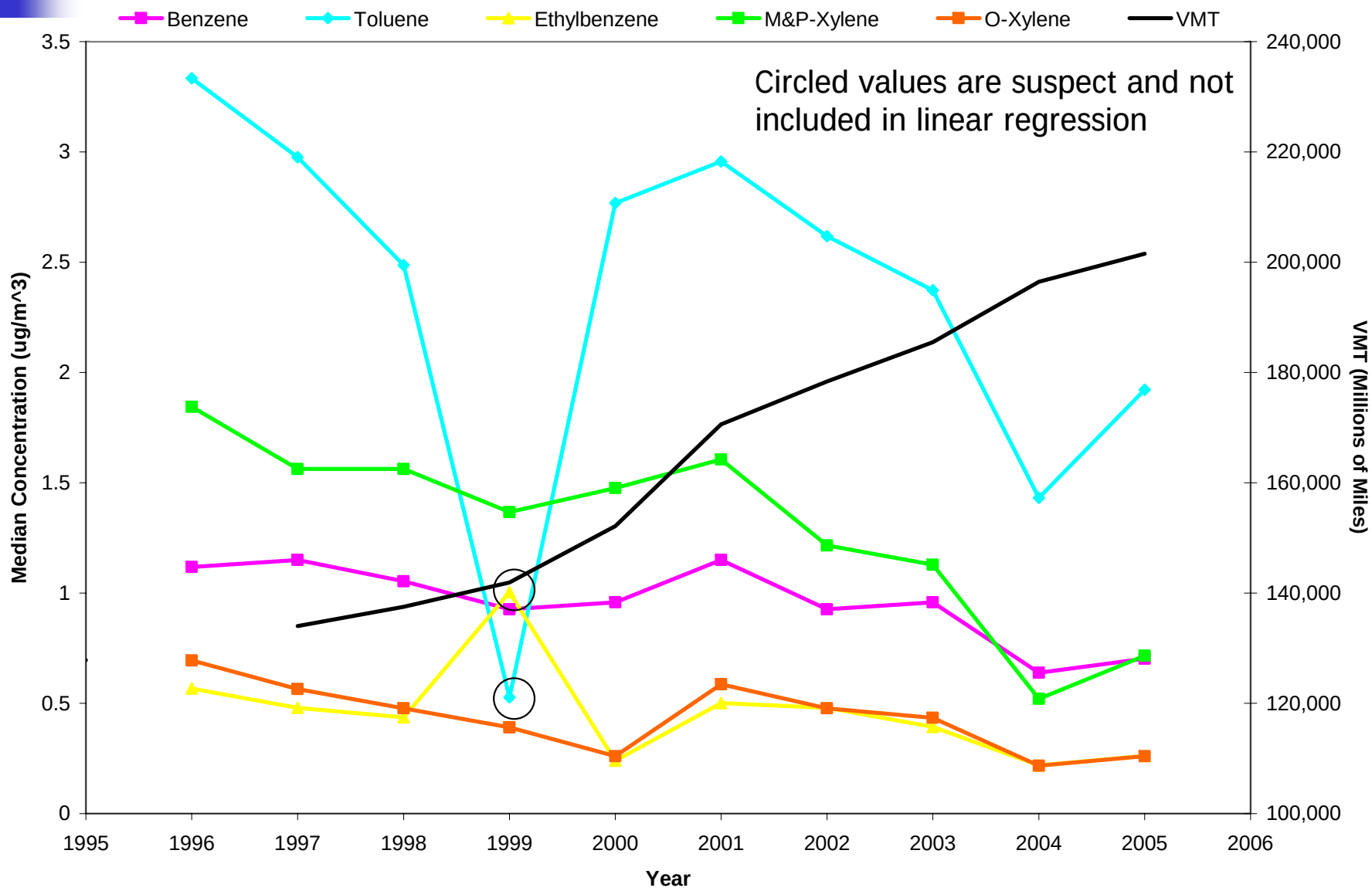
* These parameters are not measured at the Florida site.

Fuel consumption and vehicle miles traveled (VMT) by state.
Both VMT and fuel consumption are increasing over 1994-2005.



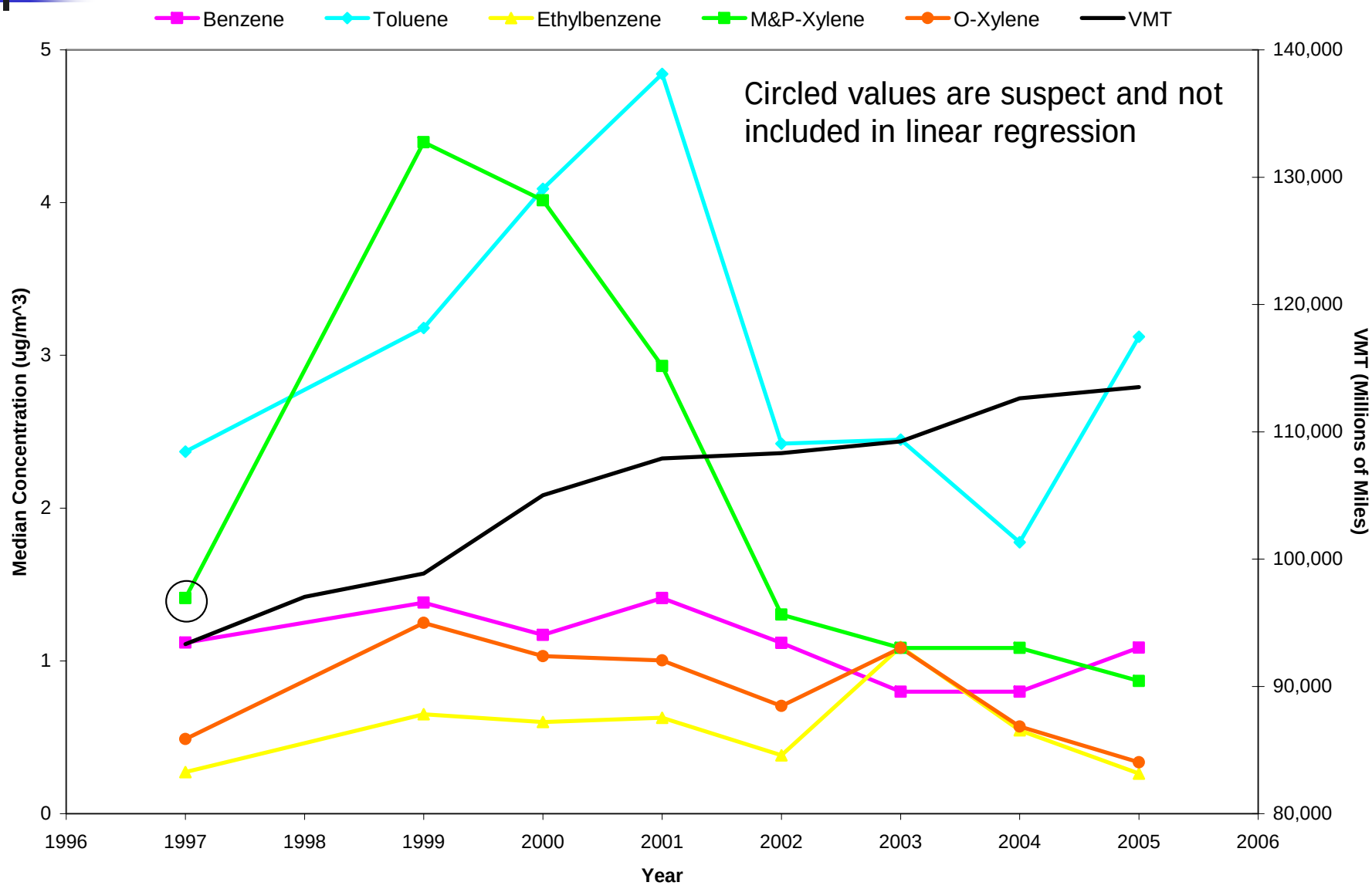
Source: U.S. Department of Transportation (2006a, 2006b)

Florida MSAT Trends – 121030018



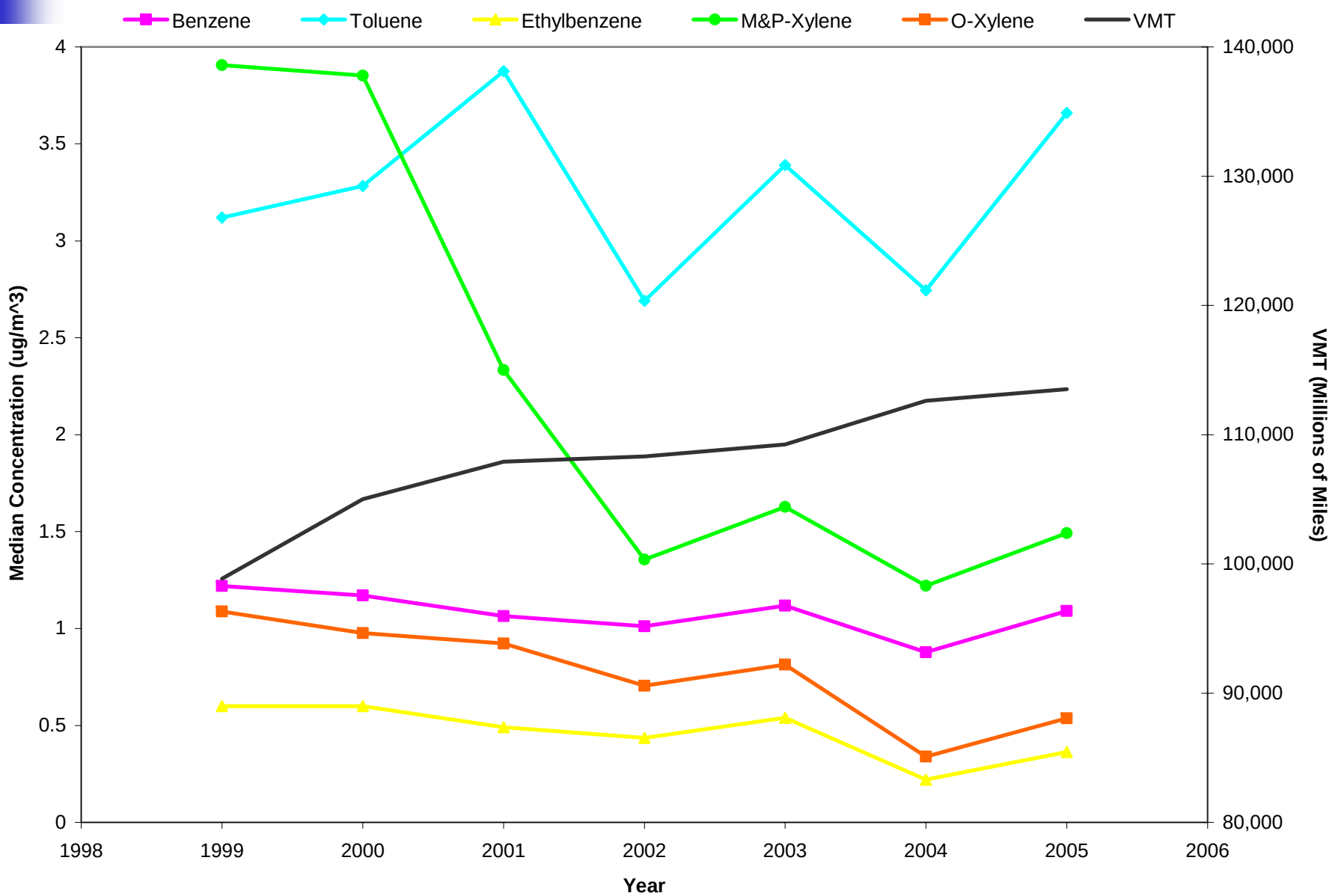
Benzene % Change: **- 38%** Toluene % Change: **- 40%** Ethylbenzene % Change: **- 44%**

Georgia MSAT Trends – 130890002



Benzene % Change: **- 29%** Toluene % Change: **- 19%** Ethylbenzene % Change: **21%**

Georgia MSAT Trends – 130893001



Benzene % Change: **- 18%** Toluene % Change: **0%** Ethylbenzene % Change: **- 43%**

Annual Trends Summary

- Regression equations were applied to annual medians and calculated using Microsoft Excel
- Percent change was calculated from the regression equation

Compound	Site	Regression Constants		R^2	Overall % Change	Average % Change per Year
		m (µg/m³ / Year)	b (µg/m³)			
Benzene	121030018	-0.0461	93.1	0.63	-38	-4
Ethylbenzene*		-0.0268	54.0	0.44	-44	-4
Toluene*		-0.148	299	0.65	-40	-4
Benzene	130890002	-0.0459	92.9	0.23	-29	-3
Ethylbenzene		0.0119	-23.3	0.01	21	2
Toluene		-0.0780	159	0.04	-19	-2
Benzene	130893001	-0.0328	66.7	0.40	-18	-3
Ethylbenzene		-0.0507	102	0.63	-43	-6
Toluene		0.00210	0.854	0.0001	0	0

Linear regression may not be the best fit of data in all cases.

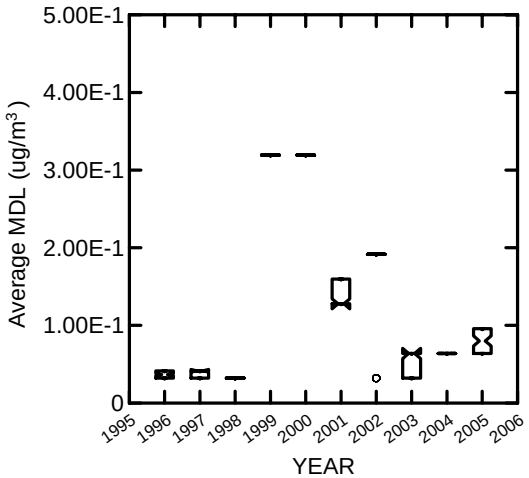
*1999 data were removed for regression analysis

Annual Average MDL

Did changes in MDL over time influence concentration trends?

Benzene

121030018



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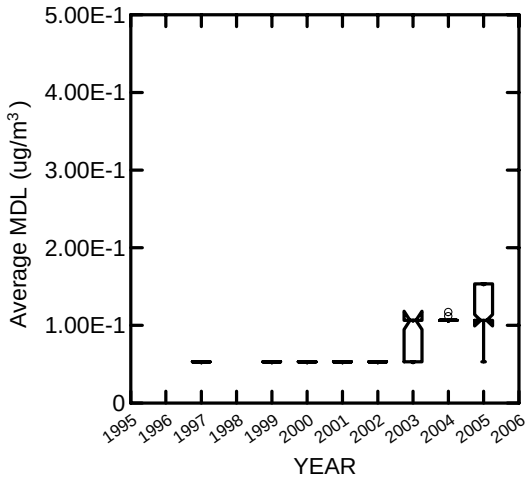

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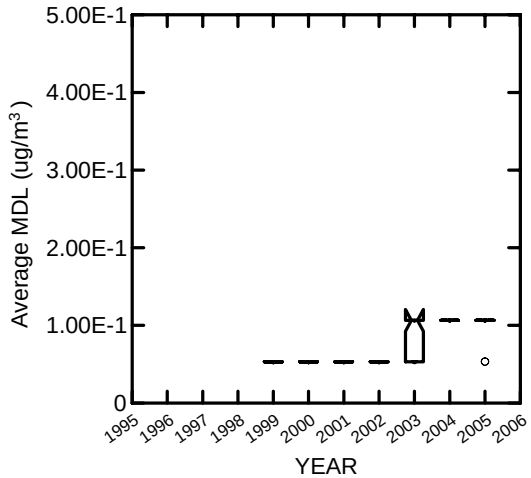
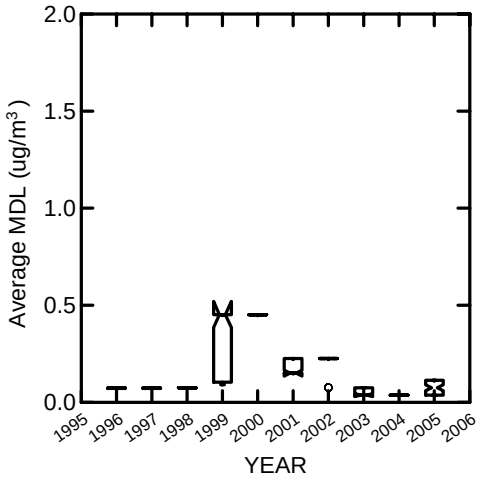


Toluene

121030018



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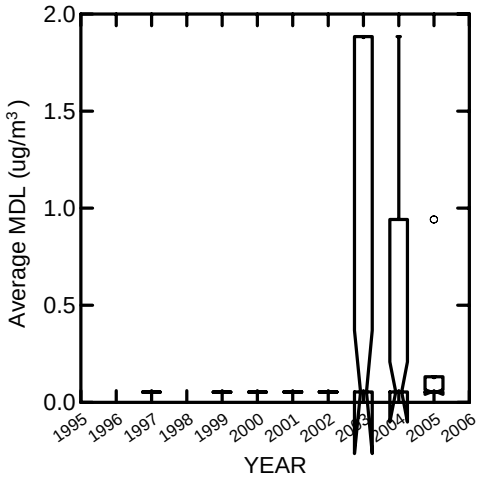

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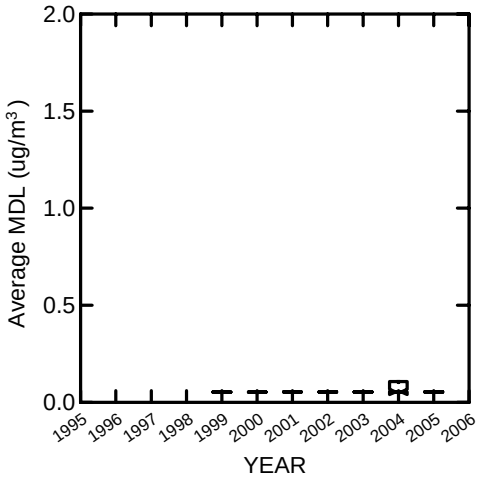
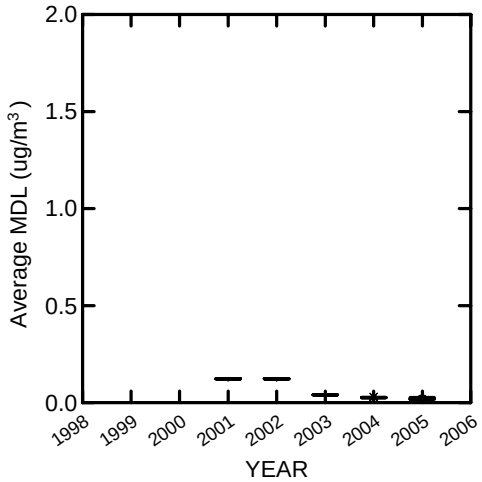


Formaldehyde

121030018



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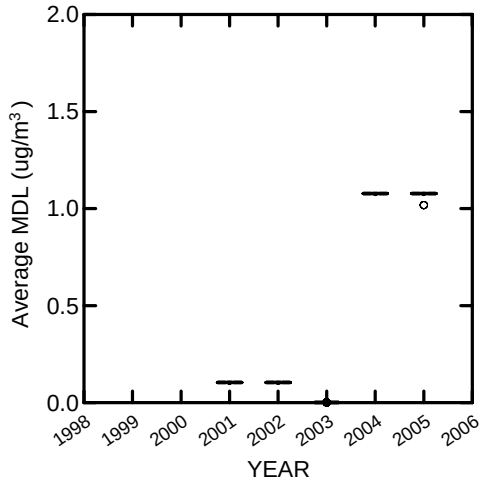

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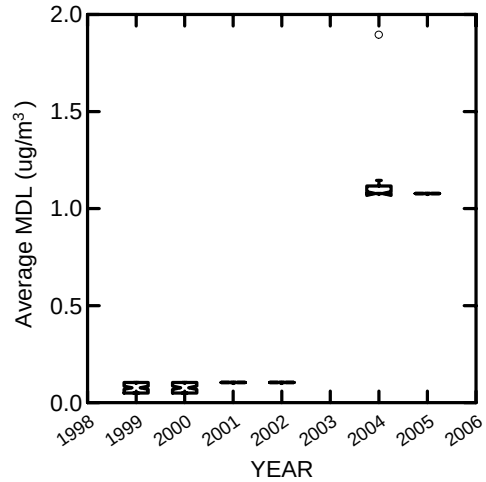
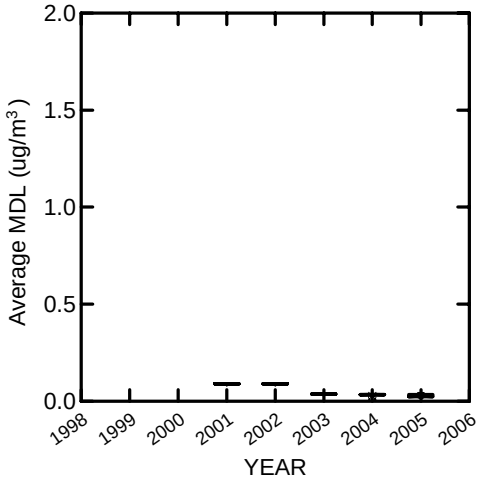


Acetaldehyde

121030018



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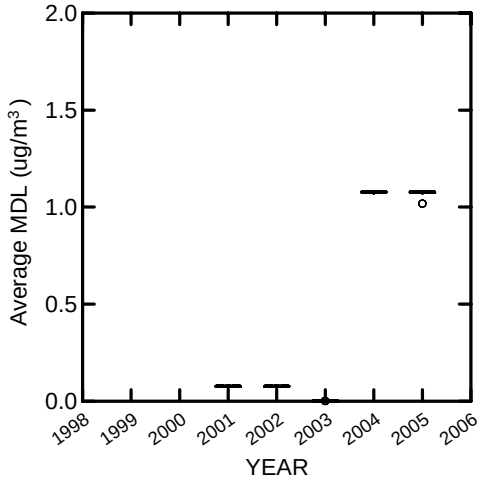

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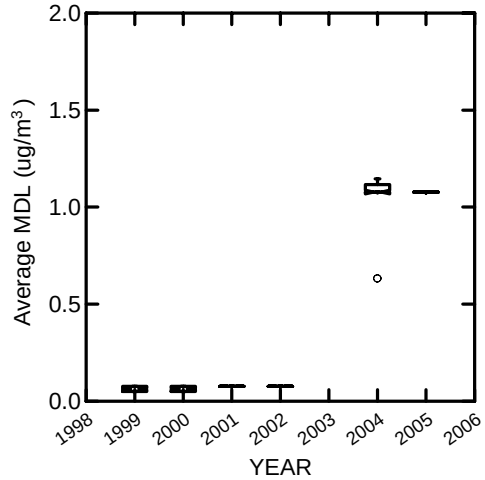
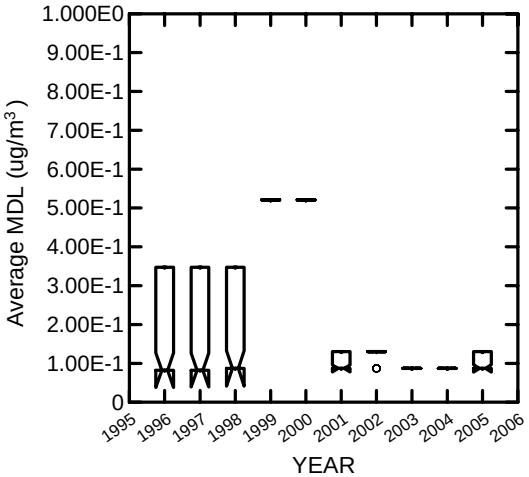


O-Xylene

121030018



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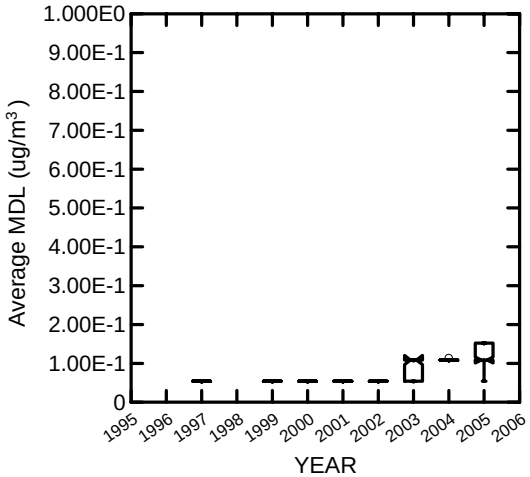

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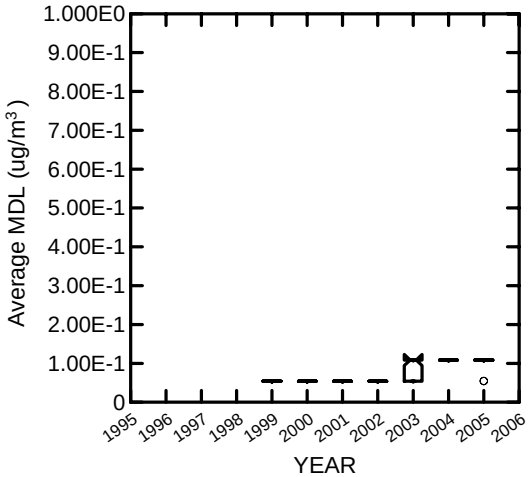
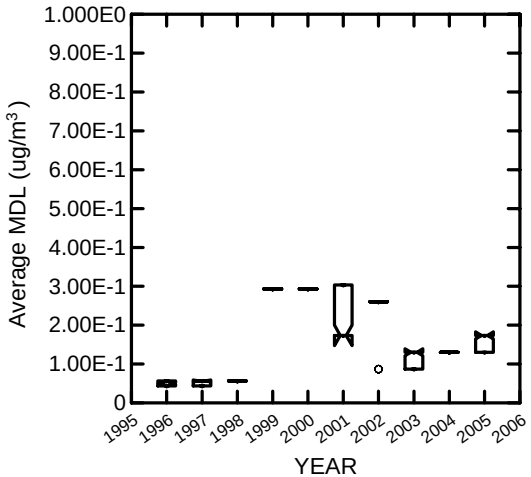


M & P-Xylene

121030018



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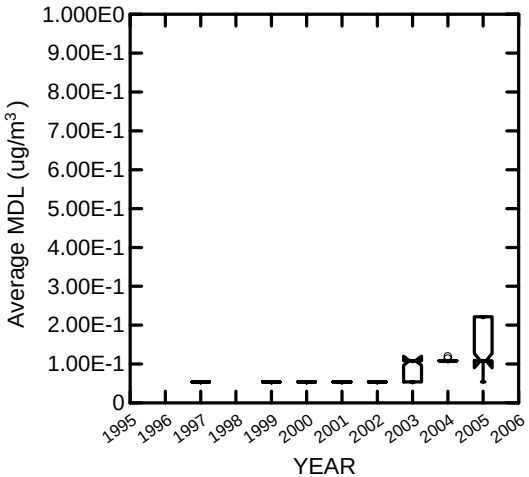

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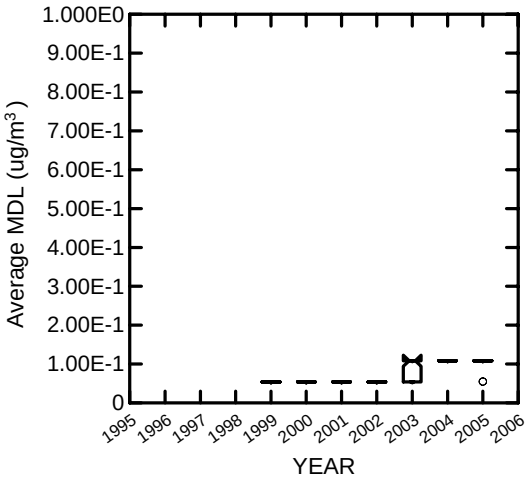
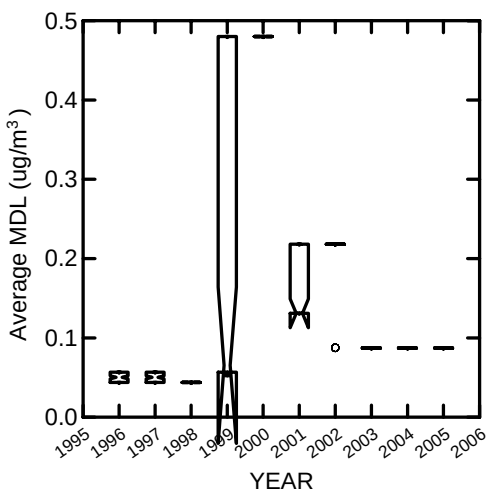


Ethylbenzene

121030018



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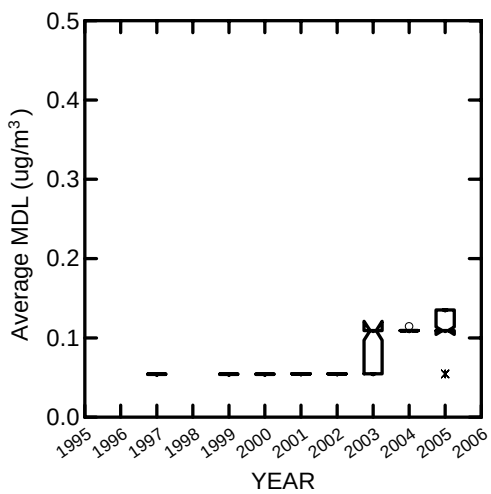

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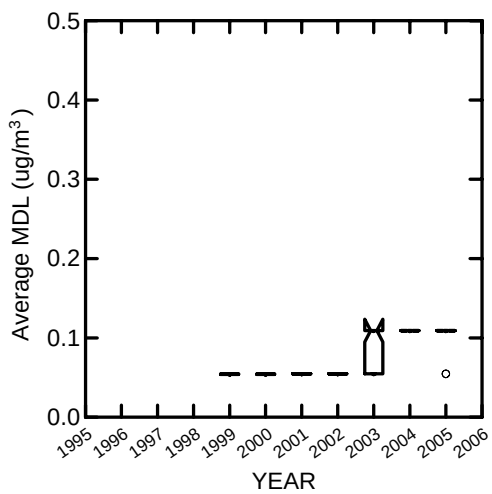

Trends in MDL - Implications

- Large intra-annual MDL differences were observed at all sites
- However, MSAT concentrations were typically far enough above the MDL not to be effected by these MDL changes
- The principal exceptions were a small effect observed in the 1999 and 2000 Annual Box Plots for Ethylbenzene and O-Xylene in Florida

Conclusions

- The annual benzene percent change of -4% is consistent with fleet turnover (Harley, 2006)
  - Ethylbenzene and toluene show a similar percent change per year for reasonable regression fits
  - Fleet turnover is the best explanation for the decrease observed in these species
  - The large decrease in m-&p-xylene concentrations in Georgia may not be mobile source-related. Have other regulations been put in place? Did a nearby emitter shut down?
- RVP regulation effects are difficult to observe based on the data available at these sites
  - RVP affects summer concentrations of some pollutants but will not cause a decrease in concentration over time

References

Harley, RA *et al*. (2006) Effects of reformulated gasoline and motor vehicle fleet turnover on emissions and ambient concentrations of benzene. *Environ. Sci. Technol*., **40**, 5084.

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