State of Delaware, Department of Natural Resources and Environmental Control (DNREC), Division of Air Quality, Air Quality Management Section, Air Surveillance Branch, Ambient Air Monitoring Group

COMMUNITY AIR TOXICS STUDY (CATS)
FINAL REPORT, PART 1

FINAL REPORT GENERAL INFORMATION

Grant #:	XA-97358801
Category:	Community-Scale Monitoring
Agency:	**Delaware Department of Natural Resources and Environmental Control** (DNREC), Division of Air Quality (DAQ), Air Surveillance Branch, Ambient Air Monitoring Group
Award:	$231,187.30
Cost:	$365,998.34 (EPA Grant Award & DNREC Grant Support/Matching Funds)
Report Period:	**July 2007 - December 2011**

FINAL REPORT AUTHORS

Primary:	**Nicole Romisch, Environmental Scientist III**
Contributing:	*Constance Ewing, Analytical Chemist II* *Mark Prettyman, Environmental Scientist III*
Reviewed By:	*Charles Sarnoski, Program Manager I* *Betsy Frey, Quality Assurance/Quality Control Coordinator* *James Snead, Engineer IV*

FINAL REPORT TITLE

Community Air Toxics Study (CATS) Project Final Report, Part 1: Summary of Project Activities from 07/2007 to12/2011 for EPA Grant Number XA-97358801 & All Raw (NOT Validated) Project Data Files.

Document Contents

⊶ *Topic rows linked to document page: Simultaneously press the Control Key while selecting a topic row listed below with the left mouse button to navigate to the corresponding document location.*

1.0 Introduction

The Delaware Community Air Toxics Study (CATS) project was an enhanced community-level air toxics monitoring project primarily focused on mobile source impacts to the Wilmington, Delaware geographical area, and investigated temporal and spatial variability of ambient volatile organic compounds (VOCs) concentrations, also commonly referred to as volatile organic hazardous air pollutants (VOHAPs).

In 2003 the Delaware Air Toxics Assessment Study (DATAS) used speciated air toxics emission inventory data to model estimated ambient concentrations of VOCs and associated risk levels. Results for certain VOCs indicated potential elevated risk, particularly in the urban Wilmington area. These compounds are of particular concern because most are determined to be known or probable human carcinogens. The CATS project therefore focused specifically on the following five target VOC compounds identified by the DATAS project: 1,3-Butadiene, Benzene, Carbon tetrachloride, Ethylbenzene, and Toluene.

2.0 Sample Collection & Analysis

2.1 Sampling Frequency

During the calendar years 2007 through 2011, samples were collected in coordination with the corresponding Environmental Protection Agency (EPA) VOC 1-in-6-day Monitoring Schedules at the following five urban locations in Wilmington, Delaware, as well as a background site approximately 15 miles from the city. The 1-in-6-day frequency is equivalent to collecting samples for 24-hours every six days on the same schedule as the VOC 24-hour canister samples, as required by the EPA.

2.2 Monitoring Design

The CATS monitoring design was developed by following site selection criteria provided by the EPA and using dispersion model generated one-kilometer grid resolution (Figure 1) maps indicating areas with estimated elevated concentrations of the VOCs of concern to determine locations for five Wilmington monitoring sites.

Community-level VOC maps of the Wilmington area were overlaid with GIS maps indicating population density and sensitive points, such as schools and hospitals. Monitoring sites were selected from appropriate grids to consider proximity to sensitive points such as schools, source, and potential elevated VOC concentrations. Finally, a control site was selected using modeling results for the northern Delaware area to indicate background VOC levels.

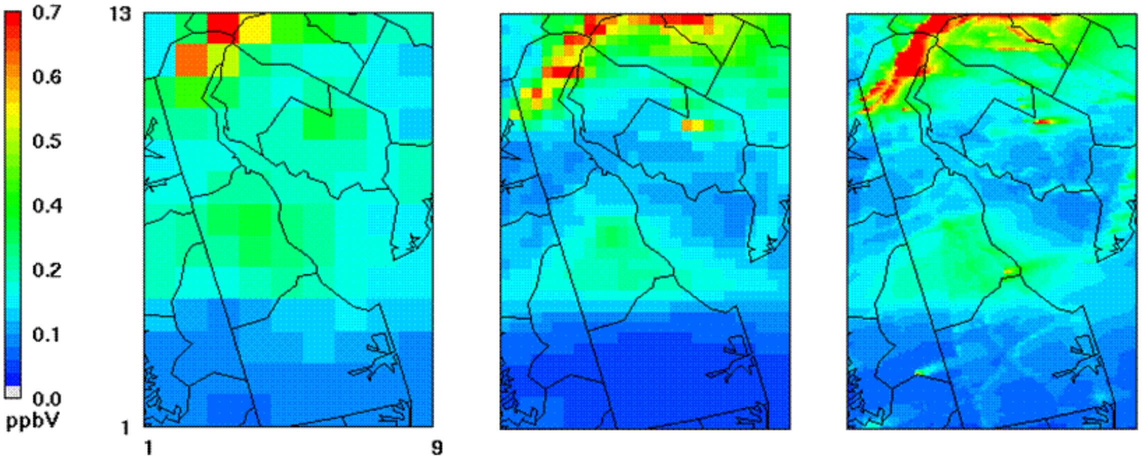


Figure 1: **Mapped modeling results indicating higher benzene concentrations in the Wilmington region. The maps, from left to right, indicate 12, 4, & 1-kilometer (km) grid resolutions, respectively.**

2.2.1 Site Locations

One location (MLK/MLC/MLD) collected samples with two side-by-side samplers per sampling event: a primary sampler (MLK) and the second sampler alternated collocated (MLC) and distributive volume pair (MLD) samples. The other four urban locations (PYL, NAT, NBS, ST6) and a nearby rural background location (LUM) collected samples with one primary sampler per sampling event. Please refer to **Appendix A** for a map of the site locations.

➢ **MLK**: **Martin Luther King Site (Urban, Primary)**

The MLK Site is an existing DNREC DAQ Ambient Air Monitoring Station (Delaware's NCORE site), located at the intersection of Martin Luther King Boulevard and Justison Street, in Wilmington, Delaware. Additional parameters collected at this location, during the grant-funded period, include the following:

- **Continuous:** Rainfall, Relative Humidity, Temperature, Wind Speed, Wind Direction, CO, CO_2, $NO_{x,y}$, SO_x, Ultrafine Particulate Matter (UFP), Fine Particulate Matter ($PM_{2.5}$);
- **Daily:** $PM_{2.5}$ Filters;
- **1-in-3-day (24-Hour Sample):** $PM_{2.5}$ Filters; and
- **1-in-6-day (24-Hour Sample):** Carbonyl Cartridges, Course Particulate Matter (PM_{10}-$PM_{2.5}$) Filters, Lead (Pb), Total Suspended Particulate (TSP) Filters, VOC Canisters.

. The CATS sampler housings were also located on the roof of the station during project activities on the Northwest corner of the station that coincided with the closest location to the intersection of MLK Boulevard and South Justison Street.

- **<u>MLC/D</u>: MLK Site (Urban, Collocate (MLC) and Distributive Volume Pair (MLD))**

  An additional sampler located at the MLK site, adjacent to the primary sampler housing, that enhances our field sampling quality control with the collection of collocated (MLC) and distributive volume pair (MLD) data on alternating sampling date cycle. Sampling procedures were identical to the primary samplers concerning sampling period, preparation, setup, and retrieval.

- **<u>PYL</u>: Pyle Site (Urban, School, Primary)**

  Sarah Pyle Academy for Academic Intensity located at 501 North Lombard Street, Wilmington, Delaware 19801. The sampler housing was secured on the third floor roof of the school, accessible via a permanently affixed metal ladder through a second floor, roof access, entry door secured with a keyed padlock to prevent unauthorized access to the rooftop locations of the school.

- **<u>NAT</u>: Nativity Site (Urban, School, Primary)**

  Nativity Preparatory School located at 1515 Linden Street, Wilmington, Delaware 19805. The samplers were secured to a fence located on the Northwest side of the school parking lot. No power was available for operation of the sampler; therefore portable batteries were charged and used to supply power to the sampler. Sampling setup included a site-specific timer transported to this site and programmed to turn the sampler on and off in accordance with the corresponding EPA schedule.

- **<u>NBS</u>: North Broom Street Site (Urban, School, Primary)**

  North Broom Street, Wilmington, Delaware: Electricity was available and provided. The sampler housing was secured behind a padlock secured gated fence.

- **<u>ST6</u>: Wilmington Union Street Fire Station 6 (Urban, Primary)**

  Wilmington Union Street Fire Station 6, 224 North Union Street, Wilmington, Delaware 19805. Electricity was available and provided for the sampler located on station roof with ladder access secured by a combination padlock and metal plate.

- **<u>LUM</u>: Lums Pond Site (Rural, State Park, Background)**

  An existing DNREC DAQ Ambient Air Monitoring Station and the rural, background sampling location. The Lums Pond Site was located approximately 15 miles from the urban Wilmington, Delaware area at the Lums Pond State Park Radio Control Field (R/C Field) in Summit Bridge, Delaware.

3.0 Procedure Summary

Sample collection, handling, and laboratory analysis were performed in accordance with the following analytical references:

- **Method TO-17 (Primary Method)**

  The framework for this GC/MS ATD System analysis procedure is in accordance with the Primary Method entitled, ***The EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-17, Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes*** (Method TO-17).

- **Method TO-15 (Secondary Method)**

  Further, a Secondary Method entitled, ***The Compendium of Methods for the Determination of Toxic Organic Air Pollutants, Second Edition, Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed by Gas Chromatography/ Mass Spectrometry (GCMS)***, dated January 1999 (Method TO-15) was cross-referenced as recommended per Method TO-17.

The Primary Method, or Method TO-17, specifically utilizes sorbent tube thermal desorption through Gas Chromatography/Mass Spectrometry (GCMS) analysis to quantify specifically identified air toxics analytes, also known as target VOCs, in ambient air.

3.1 Sample Collection

A Perkin Elmer STS 25 sequential tube sampler (Perkin Elmer Instrument; Shelton, CT) drew four liters of air for each two-hour sample, with the exception of the distributed volume pair sampler that collected two liters of ambient air. On January 14, 2010, the initial collection of one-liter distributed volume pair samples was increased to two-liters due to concerns with operation at the lowest volume threshold of the sampling pump and following cursory reviews of the Perkin Elmer Clarus 500 GC/MS with an ATD accessory (GC/MS ATD System) chromatograms. All samples were collected through pre-packed Air Toxics tubes (Supelco; Bellfonte, PA) containing sorbent selected to retain target VOCs. After sampling, tubes were recapped with Swagelok fittings using PTFE ferrules and placed them in a clean, opaque, airtight container for GC/MS ATD System analysis. Sorbent tubes were stored in laboratory freezer until analysis.

3.2 Analysis

For analysis, samples were loaded onto the Perkin Elmer Turbo Matrix Automated Thermal Desorber (ATD), where dry, inert gas purged the sorbent tubes before analysis to remove water vapor and air. The sample underwent thermal desorption of the sorbent tube (primary desorption), followed by analyte refocusing on a secondary trap and rapid desorption of the trap. The next step involved injection/transfer of target analytes into a Perkin Elmer Clarus 500 gas chromatograph (secondary desorption), and individual VOCs were then identified through separation of compounds by high resolution capillary gas chromatography (GC). A Perkin Elmer Clarus 500 mass spectrometer then quantified the individual VOCs. Data is exported as a csv file for data management. Please refer to **Appendix B** for the list of compounds included in the EPA VOC Mix.

3.3 Data Processing of csv Output

In order to evaluate the samples that were taken and analyzed, the resulting data had to be processed and imported into a database that was more suitable for examination. After being analyzed by the GC/MS, the sample results were exported into comma separated value (.csv) files, and grouped based upon the sample collection date. These .csv files were further grouped by quarters within a year, and processed before importing the data into a database which represented an entire quarter of analyzed samples. The steps for processing the .csv files and importing them into an Excel database are outlined in **Appendix D**.

3.4 Data Validation Process

Samples were collected from the third quarter of 2009 through the third quarter of 2011. These samples are pending data validation. Upon completion of data validation activities, Mohammed Majeed-Engineer, Betsy Frey-QA Coordinator, and Nicole Romisch- Environmental Scientist will collectively analyze the validated data. Please refer to **Appendix C** for a summary of data validation activities.

4.0 Project Objectives

The CATS project implemented state-of-the-art monitoring techniques complimented by a GC/MS ATD System analytical platform to effectively collect and interpret ambient concentrations of select VOCs. By implementing two-hour time resolutions that spatially characterized a 5 km x 5 km community centered at the existing Wilmington (Martin Luther King Blvd.) monitoring site, DAQ worked towards the following objectives:

- Established the framework for a VOC monitoring program capable of performing fast, accurate VOC measurements in communities identified through modeling as potential hotspots.

- Collected a dataset to investigate temporal and spatial variations in VOC concentrations at the community level. Much of the data currently available is based on 24-hour average concentrations across a large geographical area. The ability to identify temporal concentration variations throughout the day and spatial variability relative to a source of interest will serve as a valuable tool for evaluating community health risk.

- Constructed a time resolved VOC dataset to be used for improved model validation. Computer simulations have become one of the main resources when estimating pollutant concentrations in ambient air. Unfortunately, most of the monitoring data used to validate model results is based on annual or 24 hour averages at best. Creating data sets with better time resolution (i.e. one-hour or two-hour increments) will aid in developing simulation programs better capable of elucidating diurnal patterns in pollutant concentrations.

Upon completion of data validation and analysis activities, to be included in Part 2 of this report, DAQ hopes to achieve the following remaining objectives:

- Evaluate potential concentration changes in ambient air of specific VOCs resulting from reformulated gasoline (RFG) usage. In 2006 Delaware switched to gasoline with a 10% ethanol additive (E10 gasoline), as a result, the Wilmington area will likely experience a decline in concentrations of several VOCs. The Wilmington area is of particular interest due to the proximity of major highways and the percentage of VOC concentrations contributed by on-road mobile sources (estimated by DATAS to be approximately 38% statewide).
- Build community-level data set of specific VOCs to accomplish mutual health-risk assessment goals in cooperation with Delaware Department of Health and Social Services (DHSS). Delaware DAQ and DHSS continue to work very closely to assess to the potential health risk associated with exposure to VOC’s in Delaware communities.
- Timeline of Project Activities & Achievements Summary.

03/2007	Grant submitted by Mr. Terry Mead Project Lead
11/2007	Grant awarded
07/2008	Mr. Terry Mead accepts position with other agency
06/2008	Ms. Jill Winterling, Analytical Chemist begins sampling and analysis oversight.
11/2008	Perkin Provides new filament design for GC/MS to remediate service issues
03/2009	Mr. Charles Sarnoski begins project oversight
03/2009	Ms. Nicole Romisch, Environmental Scientist, introduced to project providing support activities.
06/2009	First useable quarter of collected data for statistical analysis.
01/14/2010	Ms. Betsy Frey, QA Coordinator, approved Ms. Winterling’s request to change the distributive volume pair sampler to collect 2L of air instead of 1L due to low flow sampler capability is approved.

07/2010	Mr. Charles Sarnoski, Program Manager began providing backup analytical support.
07/2011	Final sampling date, Mr. Charles Sarnoski makes decision to halt sampling due to equipment problems and backlog of samples to analyze.
08/2011	Ms. Winterling on unexpected leave of absence.
10/2011	Ms. Winterling returns to Analytical Chemist position part-time, transitioning into full-time role.
11/2011	Ms. Winterling officially resigned for another position.
02/2012	Ms. Constance Ewing fills vacant Analytical Chemist position.

4.1 Lessons Learned

The following comments describe the lessons learned, both positive and negative, regarding all technical aspects of the CATS project.

- **Analysis Equipment System Maintenance Requirements and Down Time**

  The time required to maintain the Perkin Elmer Clarus 500 GC/MS with the Turbomatrix ATD (GC/MS ATD System) exceeded assumptions made during the CATS Project Design. During the design phase of the CATS project, we did not have staff with the technical experience specific to the operation of this particular GC/MS ATD System. This lack of experience resulted in an unrealistic expectation for the time required for sample analysis and estimated frequency of maintenance and repair. The Analytical Chemist spent excess time troubleshooting and coordinating the scheduling for Perkin Elmer Service Technicians to perform emergency GC/MS-ATD System maintenance.

  We observed the operation of the GC/MS system to be particularly temperamental and labor intensive. The volume of service calls requiring Perkin Elmer Service Technicians and/or Product Specialists to travel onsite to correct problems with the GC/MS system delayed the analysis of many samples. In 2008 there were 11 emergency service visits between June and December. In 2009 there were 15 emergency service visits.

  This down time caused an analysis backlog on collected samples that resulted in the exceedance of the allotted holding time. Fortunately, a service contract was purchased so most of these cost were adsorbed by the contract.

  One of the more frequent issues was with the Mass Spectrometers source filament. This filament required frequent replacement that required recalibration of the system. Developing calibration curves for the system of 61 compounds became quite labor intensive and time consuming.

- **Smaller May Be Smarter**

  Sampling at five urban sites with an alternating collocate/distributive volume pair sampler and a background site pushed the limits for holding and analysis times with approximately 400 sorbent tubes sampled each month. Additionally, the holding time limit required analysis of the sampled sorbent tubes within 30 days of collection. A smaller study, for example decreasing the five urban sites to include two or three urban sites, would have been more manageable.

- **Benzene Resin and Residual Concentration on Sorbent**

  In mid-2010, we observed residual benzene concentrations on several blank tubes following tube analysis and additional baking cycles. According to Supelco, the sorbent manufacturer, one of the sorbent materials is a benzene resin derivative. The typical ambient air concentrations being sampled are below Supelco's standard QA/QC lower limit testing for benzene background on sorbent tubes. Supelco developed a sorbent prescreening to supply this study with sorbents that had lower benzene background levels.

  Supelco supplied 200 sorbent tubes with lower Benzene background. It was determined that all tubes should be analyzed prior to sampling to verify that each tube is blank and without residual background analyte concentrations. This verification is time and labor intensive.

  This blanking verification process is limited by GC/MS ATD System operation and availability, quantity of time sensitive samples collected, and labor availability. It may not be possible to verify every tube prior to sample analysis. In the event of partial verification, a primary (ideally coupled with a collocated and/or distributive volume pair sampler) site and a background site should be verified, at a minimum.

- **Calibration Standards Containing Only the Compounds of Interest**

  An EPA 524.2 VOC mix calibration standard that contained 60 compounds and a 1,3-Butadiene standard was used to develop calibration curves for this study. It may have been in the best interest of time to only include the compounds of interest in a custom standard. The amount of time required to address the target compounds in lieu of all 61 compounds would have greatly benefited this project.

- **Backup Analytical Personnel**

  During this study several changes in personnel occurred. In future projects it would be recommended that there be cross training of air monitoring staff. This training would reduce the lost time for sample analysis. As expected, with every personnel change the project incurred a set-back and loss of continuity.

It would also be beneficial to have additional people trained in the operation of the GC/MS for sample analysis. With the unforeseen medical leave, the analysis of collected samples was delayed.

5.0 Results

All raw data (not verified) is enclosed on electronic media (CD). All data is processed from csv GC/MS ATD System Output and organized into quarterly calendar year spreadsheets. DAQ is in the process of validating these data files and an additional report will be supplied when the data has been validated.

NOTE: Raw unvalidated data files are located on CD supplied with this report.

6.0 TO-17 Evaluation

6.1 Technical Effectiveness

The project proved this analytical method could be effective for VOC analysis of air samples. The increased resolution in the 2-hour samples versus a traditional 24-hour canister sample has obvious benefits to environmental research. We have conducted a preliminary review of the data for the third quarter of 2009. However, after discussion with Perkin Elmer there were discrepancies in our interpretation of data output concentrations. A great deal of effort has been made to address this issue and therefore all Level 2 & 3 data verification must be reviewed. The following is an excerpt from the Level 3 Data Validation Memo dated January 10, 2010(the entire Memo can be reviewed in **Appendix E**):

> ***Issues of concern identified in the 3Q09 dataset include****:*
>
> - *high number of samples flagged as "Out of Spec"*
> - *low percentage of samples above the MDL for most compounds*
> - *low percentage of samples above the field blank for most compounds*
> - *apparent trends and/or step changes in field blanks, collocated and distributed volume pair results that may or may not reflect actual changes in field or laboratory conditions/procedures*
>
> ***Issues indicating confidence in the data include*** *the consistent diurnal patterns and overall concentrations that fit with other air toxics studies of urban and mobile source influenced sites. Collocated samples and precision confidence intervals are also promising for some compounds.*

6.2 Economic Feasibility

It is our opinion that the analytical method is economically feasible if the instrumentation performs as specified by the manufacturer. Quality data capture should be considered over instrument cost.

The instruments purchased for this study was manufactured by Perkin Elmer. Perkin Elmer was selected because we had used their GC in a PAMS project many years earlier. Perkin Elmer had also been a forerunner in this type application since the 1980's.

The equipment purchased was from their demo inventory. This equipment was operated in their laboratory for application development. This instrumentation was purchased at a deeply discounted price making it a very attractive purchase. We have expended over $70,000 in equipment purchases. This cost would double if new equipment had been purchased and almost half of the grant budget would have been used. We suggest that future projects budget for new equipment to be purchased. We also suggest that the manufacturer supply references to other researchers that are performing the same type study. We have been unsuccessful in getting any references from Perkin Elmer.

When the analytical equipment was operating as specified the project moved along smoothly. Unfortunately, this was not always the case. Software issues were intermittent and the most troublesome, delaying the processing of chromatograms. The GC/MS hardware had a few minor issues throughout the project but could be resolved. The software issues had to be addressed by Perkin Elmer and there was no resolution. The application software used for this study is only used by a few researchers. It is our impression that Perkin Elmer didn't want to expend resources on an application that was not mainstream and had no significant payback.

The Service Contracts purchased from Perkin Elmer resulted in a net savings to DAQ when considering the cost of labor and materials to service the GC/MS ATD System. With the frequent visits in 2008 and 2009 we certainly got our money's worth. On more than one instance, the service technician said management complained about how much it was costing them.

7.0 Financial Statement

7.1 Initial Budget

Proposal Budget Summary

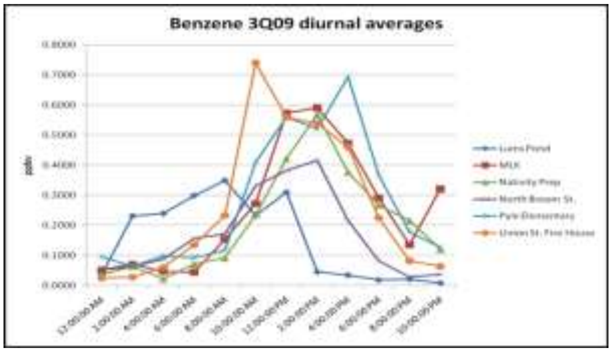
	Total	Requested Amount	Contractual Support
Total this Grant	**$365,998.34**	**$231,187.30**	**$134,811.04**
Personnel	**$212,774.64**	**$77,963.60**	**$134,811.04**
Salaries and Wages	$163,672.80	$59,972.00	$103,700.80
Fringe Benefits	$49,101.84	$17,991.60	$31,110.24
Non-Personnel	**$153,223.70**	**$153,223.70**	**$0.00**
Contract Services	$26,830.00	$26,830.00	$0.00
Equipment and supplies	$114,824.00	$114,824.00	$0.00
Travel	$8,255.00	$8,255.00	$0.00
Other	$3,314.70	$3,314.70	$0.00

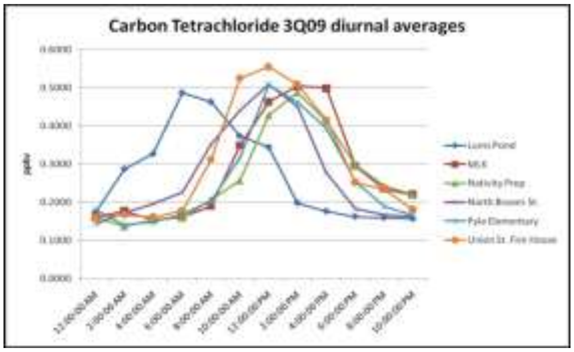
7.2 Final Budget

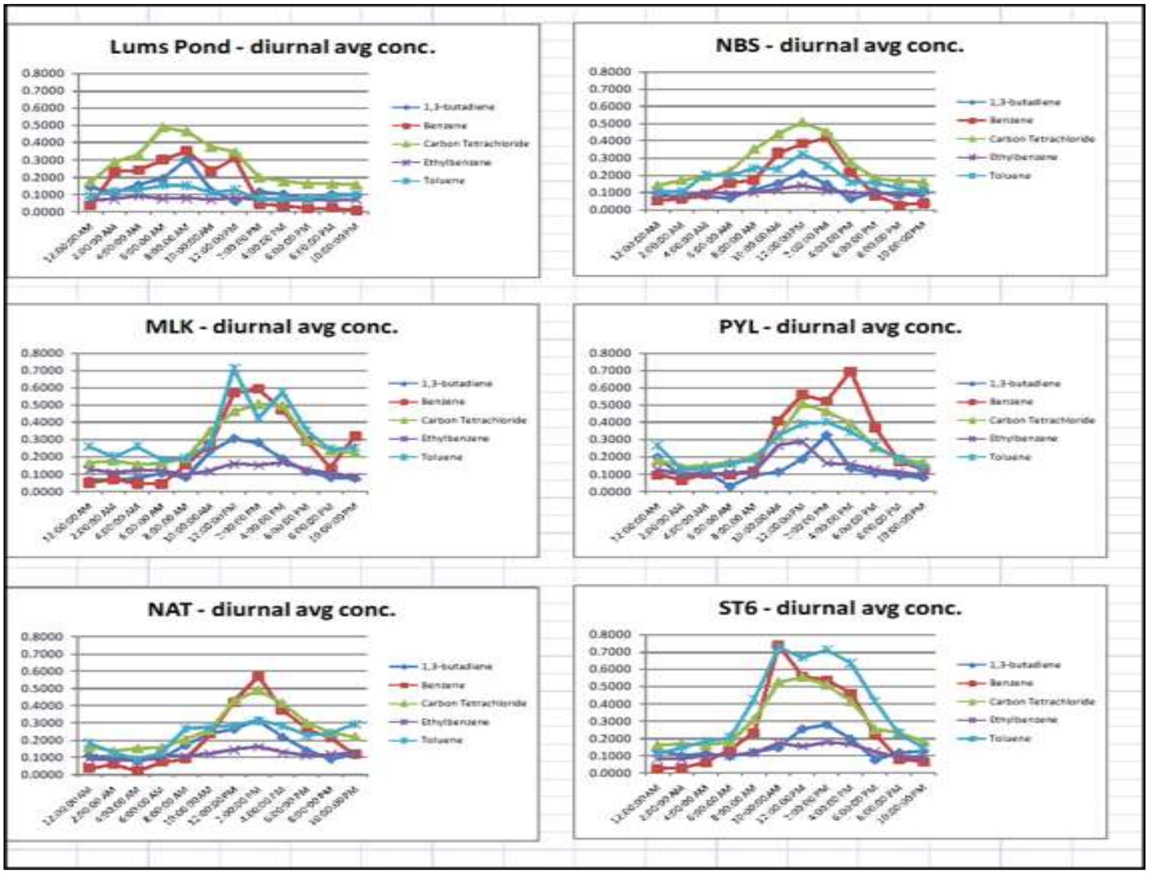
Statement of Account Balances									**11/28/2012**	
DAWM / XA-973588801-3 07040404										
GRANT DATES: 11/01/2007 - 12/31/2011										
2878 COMMUNITY AIR TOXICS AMBIENT MONITORING										
40521 Project # **2878**07040404001										
CATEGORY	ORGN	Rept. Cat	**Total Funds Awarded**	***Disbursements for the Month of December, 2011***	Disbursements In FSF thru December, 2011	Disbursements in DFMS thru June, 2010	**Total Disbursements to Date**	Encumbrances In FSF thru December, 2011	**Total Encumbrances to Date**	**Year to Date Balance as of December, 2011**
FEDERAL FUNDS										
SALARIES & OEC'S	0902	AT81	**25,964.00**	0.00	6,554.81	1,284.46	**7,839.27**	0.00	**0.00**	**18,124.73**
TRAVEL	0902	AT84	**7,774.00**	0.00	336.45	1,289.30	**1,625.75**	0.00	**0.00**	**6,148.25**
CONTRACTUAL	0902	AT85	**75,113.00**	0.00	22,245.92	63,058.08	**85,304.00**	0.00	**0.00**	**-10,191.00**
SUPPLIES	0902	AT86	**69,824.00**	0.00	820.09	62,054.70	**62,874.79**	0.00	**0.00**	**6,949.21**
EQUIPMENT	0902	AT87	**52,281.00**	0.00	36,000.00	37,312.00	**73,312.00**	0.00	**0.00**	**-21,031.00**
AUDIT COSTS	0902	AT88	**231.00**	0.00	231.19	0.00	**231.19**	0.00	**0.00**	**-0.19**
TOTAL FEDERAL FUNDS			**231,187.00**	0.00	66,188.46	164,998.54	**231,187.00**	0.00	**0.00**	**0.00**
MATCH	s/b 36.83%									
SALARIES & OEC'S - MATCH	0902	AS81	**134,811.00**	0.00	120,455.76	16,746.15	**137,201.91**	0.00	**0.00**	**-2,390.91**
TOTAL MATCH			**134,811.00**	0.00	120,455.76	16,746.15	**137,201.91**	0.00	**0.00**	**-2,390.91**
							37.24%			
TOTAL AWARD			**365,998.00**				**368,388.91**			

8.0 Conclusion

We feel that this type of analytical approach to VOC analysis can be an important one. A team is currently working on this project that is committed to developing an ongoing program for VOC analysis throughout the state. There have been some struggles with the analytical instrumentation but the results are worth the effort. The graphs below show typical diurnal patterns that the validated data will provide.







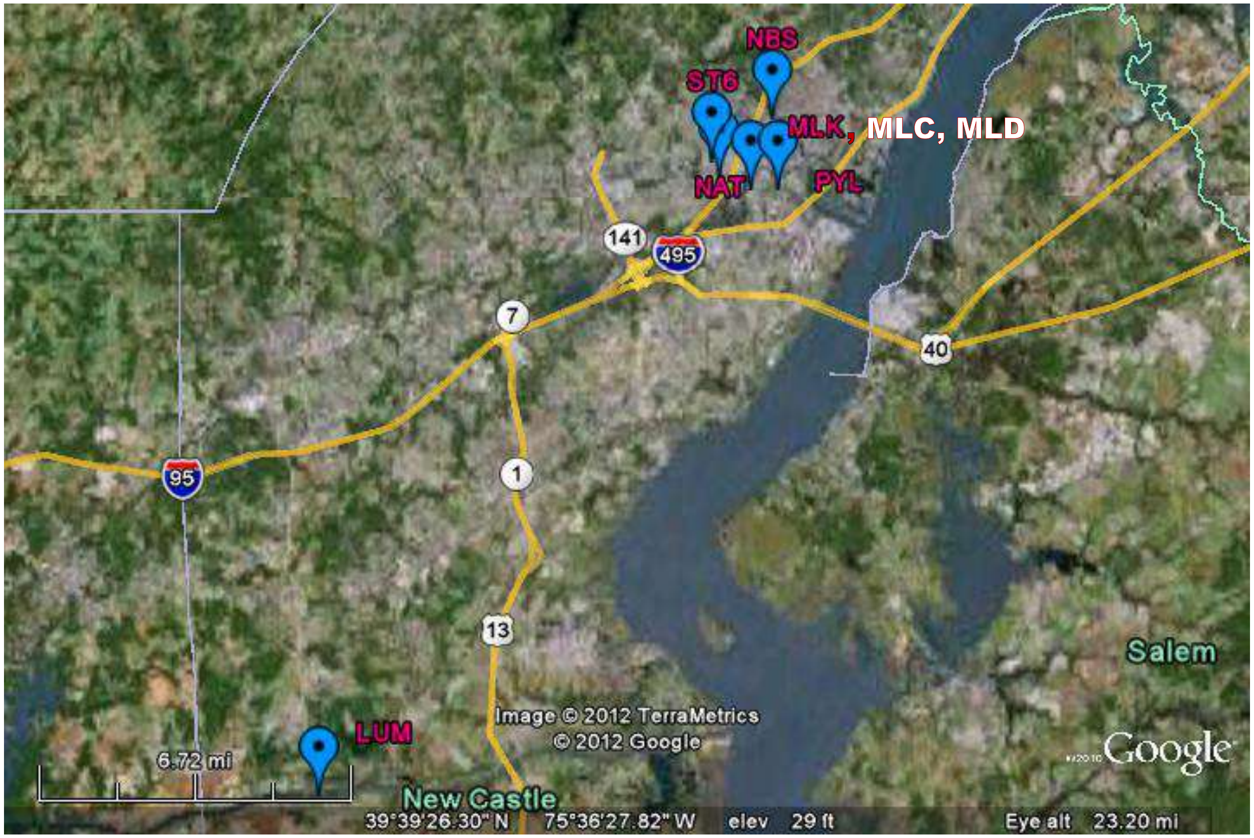
Future community air toxics studies will follow up on the CATS but on a smaller scale. In the meantime, two of the CATS sites are currently collecting VOC samples using vacuum canisters that are analyzed by the State of Maryland. We are planning on collecting a sorbent tube data set at these sites to compare with this canister data and plan to present the results at regional and/or national conferences in the near future.

The raw dataset will improve as the data is validated, and anticipate that Part 2 of this report will be better able to address the data analysis and analytical conclusions. Delivery of Part 2 to the EPA is planned to be completed by early in the first calendar quarter of 2014.

Appendix A

CATS Sampling Site Location Maps

All CATS Sampling Site Locations: Overview
(Includes Our One Background LUM Site & Two Alternating QA/QC MLC/MLD Samplers)



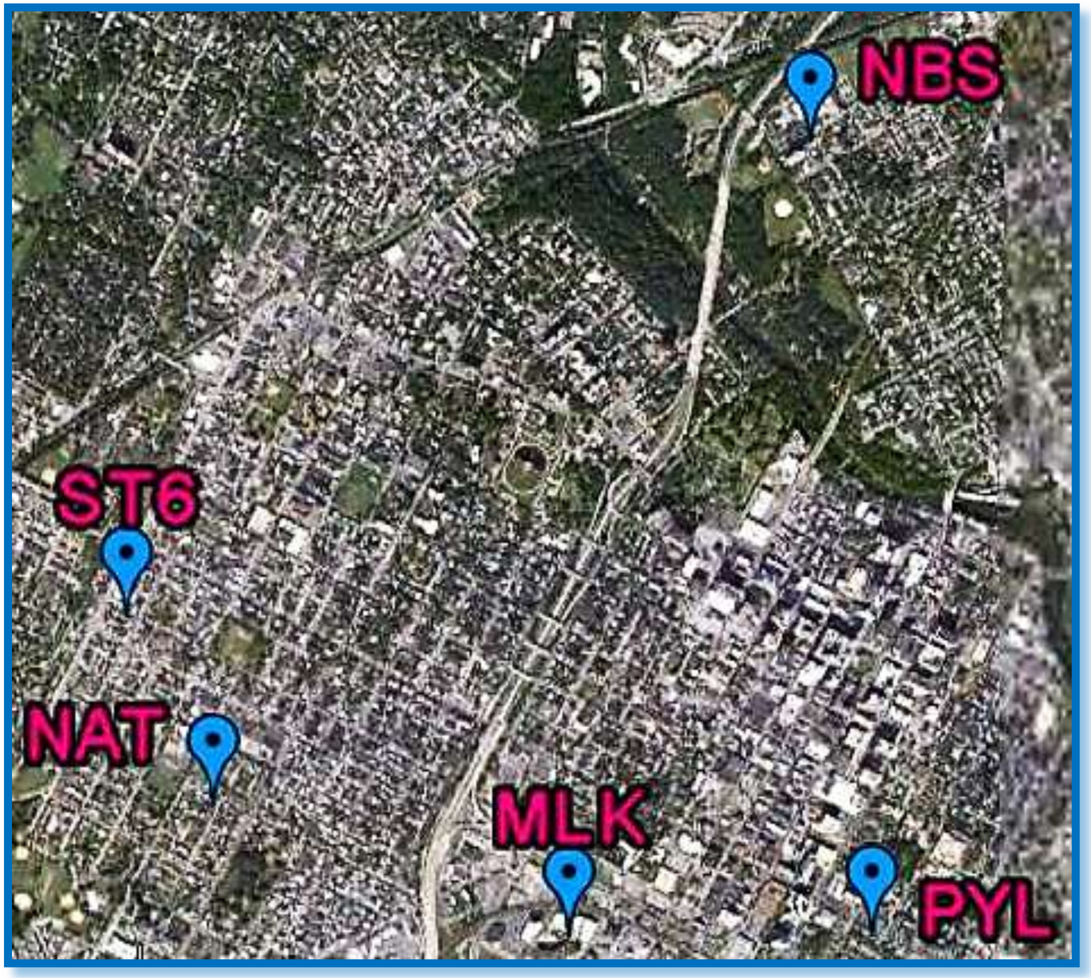
MAP KEY

** All Primary Sites are in Wilmington, DE (Urban)*

- **LUM**: Lums Pond State Park Radio Control Field (R/C Field) in Red Lion, DE (Background)
- **MLK**: DNREC Air Monitoring Station at Martin Luther King Boulevard & Justison Street
  - → **MLC**: Collocated Sampler
  - → **MLD**: Distributed Volume Pair Sampler
- **NAT**: Nativity Preparatory School
- **NBS**: North Broom Street School
- **PYL**: Sarah Pyle Academy School
- **ST6**: Union Street Fire Station 6

Primary Sampling Site Locations Detail

Local View



MAP KEY

** All Primary Sites are in Wilmington, DE (Urban)*

- **MLK**: DNREC Air Monitoring Station at Martin Luther King Boulevard & Justison Street
- **NAT**: Nativity Preparatory School
- **NBS**: North Broom Street School
- **PYL**: Sarah Pyle Academy School
- **ST6**: Union Street Fire Station 6

Background Sampling Site Location Detail

Local View

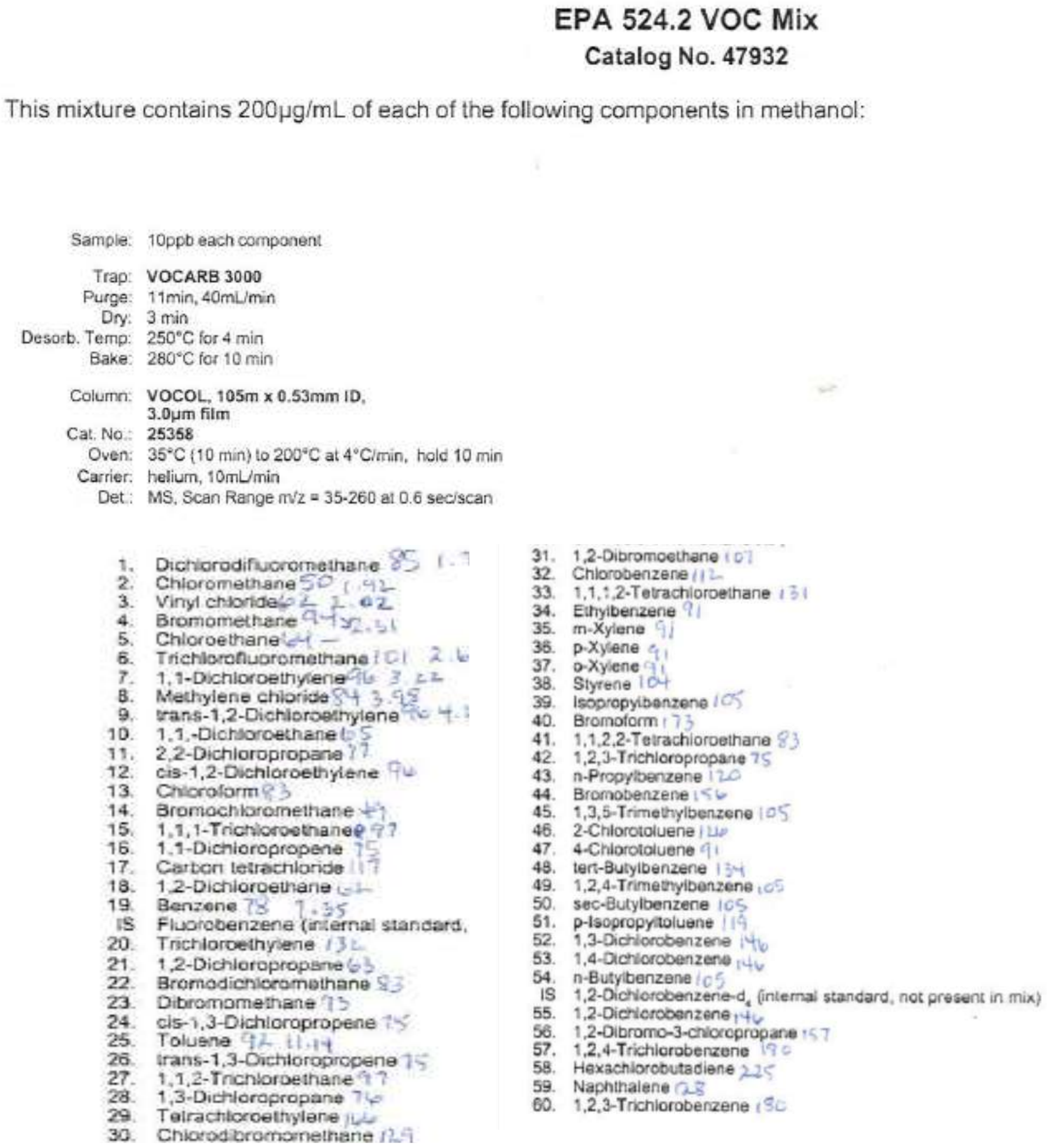
MAP KEY

- **LUM**: Lums Pond State Park Radio Control Field (R/C Field) in Red Lion, DE (Background)

Appendix B

EPA VOC Mix Datasheet

EPA 524.2 VOC Mix Datasheet Excerpt



EPA 524.2 VOC Mix

Catalog No. 47932

This mixture contains 200µg/mL of each of the following components in methanol:

Sample: 10ppb each component

Trap: **VOCARB 3000**
Purge: 11min, 40mL/min
Dry: 3 min
Desorb. Temp: 250°C for 4 min
Bake: 280°C for 10 min

Column: **VOCOL, 105m x 0.53mm ID, 3.0µm film**
Cat. No.: **25358**
Oven: 35°C (10 min) to 200°C at 4°C/min, hold 10 min
Carrier: helium, 10mL/min
Det.: MS, Scan Range m/z = 35-260 at 0.6 sec/scan

1. Dichlorodifluoromethane 85 1.7
2. Chloromethane 50 1.92
3. Vinyl chloride 62 2.02
4. Bromomethane 94 2.51
5. Chloroethane 64 —
6. Trichlorofluoromethane 101 2.6
7. 1,1-Dichloroethylene 96 3.22
8. Methylene chloride 84 3.95
9. trans-1,2-Dichloroethylene 96 4.1
10. 1,1,-Dichloroethane 65
11. 2,2-Dichloropropane 77
12. cis-1,2-Dichloroethylene 96
13. Chloroform 83
14. Bromochloromethane 49
15. 1,1,1-Trichloroethane 97
16. 1,1-Dichloropropene 75
17. Carbon tetrachloride 117
18. 1,2-Dichloroethane 62
19. Benzene 78 7.35

IS Fluorobenzene (internal standard,

20. Trichloroethylene 132
21. 1,2-Dichloropropane 63
22. Bromodichloromethane 83
23. Dibromomethane 93
24. cis-1,3-Dichloropropene 75
25. Toluene 92 11.14
26. trans-1,3-Dichloropropene 75
27. 1,1,2-Trichloroethane 97
28. 1,3-Dichloropropane 76
29. Tetrachloroethylene 166
30. Chlorodibromomethane 129
31. 1,2-Dibromoethane 107
32. Chlorobenzene 112
33. 1,1,1,2-Tetrachloroethane 131
34. Ethylbenzene 91
35. m-Xylene 91
36. p-Xylene 91
37. o-Xylene 91
38. Styrene 104
39. Isopropylbenzene 105
40. Bromoform 173
41. 1,1,2,2-Tetrachloroethane 83
42. 1,2,3-Trichloropropane 75
43. n-Propylbenzene 120
44. Bromobenzene 156
45. 1,3,5-Trimethylbenzene 105
46. 2-Chlorotoluene 126
47. 4-Chlorotoluene 91
48. tert-Butylbenzene 134
49. 1,2,4-Trimethylbenzene 105
50. sec-Butylbenzene 105
51. p-Isopropyltoluene 119
52. 1,3-Dichlorobenzene 146
53. 1,4-Dichlorobenzene 146
54. n-Butylbenzene 105

IS 1,2-Dichlorobenzene-d_4 (internal standard, not present in mix)

55. 1,2-Dichlorobenzene 146
56. 1,2-Dibromo-3-chloropropane 157
57. 1,2,4-Trichlorobenzene 180
58. Hexachlorobutadiene 225
59. Naphthalene 128
60. 1,2,3-Trichlorobenzene 180

Appendix C

Data Validation Summary

Data Validation Summary

All data validation activities should take place in accordance with the Community Air Toxics QAPP. The following description of the different data validation levels is based on the EPA RTI $PM_{2.5}$ speciation QAPP along with EPA guidance documents.

Since this technology includes some elements of method development (i.e., sorbent tubes for temporal variability), the acceptance limits or guidelines for validation of data may need to be adjusted based on experience. When necessary, updates will be made to the SOP and QAPP to reflect these changes.

Note: Recommendations on designating data as invalid can be made at any level, but the official validation decision is made at Level 3.

Level 1 Data Validation: Analytical Chemist

Level 1 Data Validation involves a basic review of the sampling and analysis data and associated records for compliance with stated sampling and analytical conditions.

This includes (but is not limited to) the elements below:

- **Data source attribution**: Verify that the site, date, time, and field sheet entries are correct. Logbooks, reporting forms, and data custody sheets should be consulted if a problem of attribution is suspected.
- **Holding times and conditions**: Field sheet and logbooks should be checked to verify that holding times have been met and that required storage conditions such as temperature met the requirements. Data should be flagged or notated if holding times and/or storage conditions were violated. The QAC, in consultation with the Analytical Chemist, will decide the validity of any samples for which these conditions have been violated.
- **Laboratory or Field Sampling flags or conditions**: Any operational or analytical flags generated or recorded in the field or laboratory records/logbooks will be entered into the Air Toxics database. A translation between these flags or codes and AQS validation flags will be developed as the program progresses.
- **Additional validation pertaining to laboratory analyses**: GC/MS data will be reviewed for technical acceptability and reasonableness based on information such as routine QC sample results, including standards, spikes, and blank results. Consult the SOP and QAPP for specific guidance on acceptance limits.

Findings from Level 1 Data Validation activities will be summarized on a periodic basis with a Level 1 Data Validation cover sheet for each run date analyzed and forwarded to the Air Toxics Coordinator for Level 2 Data Validation. Please find the cover sheet below.

CATS DATA VALIDATION

Run Date:________________

Level I	Yes	No	Notes
Flow Check Criteria Met (30 – 36 ml/min or 15.04 – 18.36 ml/mi)			
24 Hour Sample Run Completed			
Retrieval < 72 Hours After Run			
Proper Signatures			
Review of Sample Log on ATD			
Current Tune File Used			Tune Filename:
Current Calibration Curve Used			Curve Filename:
Leak Check Performed			
Laboratory Blank Performed			
Out-of-Spec Standards Recorded			
Tuning Mix Passed and Printed			
Data Uploaded to Database			
Samples Analyzed Within 30 Days			

Comments:

Reviewer Signature and Date:

Level 2 Data Validation: Air Toxics Coordinator (alt. Program Manager)

Level 2 Data Validation involves basic statistical evaluations of the data set for internal consistency. These comparisons include, for example, comparing collocated measurements and identification of outliers.

Level 2 validation of field data will involve the overall assessment of the validity of the data. Based on the information generated during the verification and validation process, some data may be recommended to be designated as invalid. Final designation of data as invalid takes place after Level 3 validation. Invalid data are not reported to AQS. Examples of Level 2 activities include:

- Performance evaluation (PE) samples, including internal and external audits.
- Statistical screening, internal consistency checks, and range checks. Examples include:
    - **Time Series Analysis***:* This analysis is typically the examination of a set of data for a single observable (e.g., a particular chemical species at a certain site) acquired over a period of time. Time series data are often best examined graphically, and it is often helpful to chart related variables together on the same graph.
    - **Outlier Checks***:* Statistical outlier checks for screening chemical concentration measurements (the actual environmental measurements, rather than QA quality control data) are another means of identifying potential problems. **An environmental observation should never be invalidated simply because it is identified as a possible outlier by statistical techniques.** Observed environmental concentration distributions tend to be somewhat skewed, so that a small number of concentrations significantly higher than the long-term average should be expected. Selecting the top 1 or 2 percent of values in a data set for investigation however is often a good rule of thumb for data assessment because high data values are sometimes the result of analytical, procedural, or calculation errors.

Findings from Level 2 data validation activities are summarized on a quarterly basis in memo form with electronically stored Excel spreadsheets made available to the QA/QC Coordinator for Level 3 validation.

Level 3 Data Validation: QA/QC Coordinator

Level 3 validation involves a more in-depth analysis that may include comparisons with external datasets as part of the data interpretation process. Unacceptable long-term performance of the analytical system can also be uncovered in the process of documenting the DQIs of completeness, precision, accuracy, and detection limits, and comparing those indicators with the program's goals or DQOs.

Level 3 activities will include precision and bias calculations, determination of confidence intervals, and other statistical tests that may be determined. The VOCDat tool developed for validation of the PAMS data is anticipated to be used at this level. Final data validation decisions will be made, and any associated null codes or data flags will be assigned to the data.

Level 3 findings are summarized on a quarterly basis in memo to the Program Manager and Air Toxics Coordinator, and validated data will be submitted to AQS using the VOCDat tool.

Appendix D

Steps for Adding Files to CATS Excel Database

Steps for Creating CATS Excel Database

1. For each quarter of data (i.e., Q3 2009), the raw output files, in .csv format, are downloaded from the DAQ server. These .csv files are grouped by each day of sampling that occurred in that quarter.
2. Each .csv file (representing a sample, standard, or blank) is opened in Excel, and a macro is run to populate the information contained in the file name into new fields. These new fields include the date of sample, hour of sample, site of sample (or if it is a Blank or Standard), date of file export, and time of file export.
3. Based upon the Level 1 data validation information, the .csv files of each day of samples, standards, and blanks are sorted into one of 4 folders (Standard 1_01, Standard 2_01, Standard 1_02, or Standard 2_02), depending on the order by which they are analyzed on the GC/MS. This ensures that the samples are grouped into the correct "bins" by which they can be compared to the actual standard that preceded the standards when being analyzed.
4. Using an MS-DOS command prompt, all .csv files within an individual folder, within each day of samples, are copied into a single .csv file, which contains all records of all other .csv files combined.
5. These single, combined .csv files are then opened in Excel, and resaved as an Excel file (.xlsx).
6. Once converted into an .xlsx file, the resulting records are filtered to remove the "header" records that appeared in each individual file that was combined into the current file, as well as remove the redundant "File Name" field.
7. In order to apply the "percent deviation" of each compound of the standard to all compounds of all samples within the single .xlsx file, the following steps are taken:

a. Since the percent deviation value is already calculated in each standard's .csv file, the percent deviation values are also included in the single .xlsx file. These values are labeled as "QC Pass" or "QC Fail" depending on if the percent deviation is less than 30% or greater than 30%, respectively.

b. For all other records in the .xlsx file, a lookup formula is used to populate two new fields to apply the same percent deviation and QC pass/fail value of the compounds of the standard, to every compound of in the file (i.e., all other samples that followed it when analyzed by the GC/MS, until the next standard was analyzed).

8. Another macro is run on the .xlsx file to format the date and time fields from text values to actual dates and times, using the formats of MM/DD/YY and ##:##:##, respectively.
9. The data from every .xlsx file (for each day of samples, and each set of samples/standards analyzed by the GC/MS) is then copied into a single, new Excel spreadsheet, representing an entire quarter of data. This new spreadsheet includes formulas to automatically calculate various information based upon the input data.
10. Once all data is copied into a new "final" spreadsheet, the data is cleaned up by performing the following steps:

a. Insert "ND" into all blank fields of columns J, K, L, M, and N, EXCEPT for field blank records in column K (concentration records); those values are changed to ZERO.
b. Truncate T, U, V, W, and X to 4 significant digits.
c. Lock header row (using the "Freeze" function).
d. Copy the Run Start and Run End times into columns B and C.
e. Double check the number of records with the number of records in the raw data.
f. Change all instances of "FB" to "13" in the run number and the Run Start and Run End times.
g. Change all records in the "Sample_V L" column to a value of "1" for all compounds that are part of a BLANK or a field blank (Run = 13).
h. Delete the entries in the columns of Run_Start_Time, Run_End_Time, and Flow Outside Range for all records for BLANK1 and BLANK2.
i. Delete entries in "FB Value" and "<FB" for BLANK1 and BLANK2.
j. Delete data in all fields after O for BFB and Fluorobenzene.

CATS Excel Database – Field Descriptions

FIELD NAME	DESCRIPTION OF FIELD
DateSiteRunName	A merging of the Date, Site, Run, and Name records for use as a unique identifier for calculations in other fields.
Run_Start_Time	The hour at which the sampling is started.
Run_End_Time	The hour at which the sampling is ended.
Test_Date	The date that the analyzed sample is exported by the GC/MS to a .csv file.
Test_Time	The time of day that the analyzed sample is exported by the GC/MS to a .csv file.
Sample_Date	The day which the sample is taken.
Site	The site at which the sample is taken.
Run	The number which corresponds to the 2-hour sampling period over which a sample is taken (i.e., 1 = 12am-2am, 2 = 2am-4am, etc.)
Name	The name of the compound.
RT	Retention time. "ND" if the value is missing (no data).
[μg/m^3] 1L	The analyzed concentration of a sample. "ND" if the value is missing (no data).
Area	GC-MS Chromatogram concentration peak area. "ND" if the value is missing (no data).
Post_Flow ml/min	The average of three (3) collected flow measurements using a calibrated flow meter, collected after sample retrieval. "ND" if the value is missing (no data).
Pre_Flow ml/min	The average of three (3) collected flow measurements using a calibrated flow meter, collected before sample setup. "ND" if the value is missing (no data).
%QC_01	The percent deviation for a specific compound which relates to the percent deviation of a compound analyzed within a standard.
QC>30%	"QC Pass" if the percent deviation is less than 30%. "QC Fail" if the percent deviation is greater than 30%.
Ave_Flow ml/min	The average of the "Post_Flow" and "Pre_Flow" fields. "ND" if either of the flow values are missing (no data).

FIELD NAME	DESCRIPTION OF FIELD
Sample_V L	Total sample volume, expressed in Liters.
MW	The molecular weight of the compound.
24.46/MW	Conversion factor.
[PPBV]	Concentration, expressed in parts-per-billion-by-volume. "ND" if either the concentration or flow values are missing (no data).
[µg/m^3]	Concentration, expressed in micrograms per cubic meter. "ND" if either the concentration or flow values are missing (no data).
MDL (ug/m3)	The calculated MDL value for the compound, in micrograms per cubic meter.
MDL (ppbv)	The calculated MDL value for the compound, in parts per billion, by volume.
<MDL	"BELOW MDL" if the analyzed concentration is less than the MDL value. "ABOVE MDL" if the analyzed concentration is greater than the MDL value. "NA" if the analyzed concentration is missing (no data).
FB Value	The concentration of the field blank that corresponds to the specific compound, the date of the sample, and the run value of the sample.
<FB	"FB_SMALLER" if the field blank value is smaller than the analyzed concentration, for the specific compound, sample day, and run time. "FB_GREATER" if the field blank value is greater than the analyzed concentration, for the specific compound, sample day, and run time. "BOTH_ZERO" if the field blank value and the analyzed concentration are both zero, for the specific compound, sample day, and run time. "ND" if either the field blank value or the analyzed concentration are missing (no data), for the specific compound, sample day, and run time.
Flow Outside Range	"FALSE" if the average flow is between the acceptable values of 30 and 36. "TRUE" if the average flow is less than 30, or greater than 36. "ND" if either of the flow values are missing (no data).
BFB Tune Pass	"Fail" if the test fails for an entire standard. Noted for all samples that follow that specific standard.
Comments	To be added if there are any comments to be noted about any of the samples.

Appendix E

CATS 3Q09 Level 3 Data Validation Memo

DELAWARE DEPARTMENT OF NATURAL RESOURCES AND ENVIRONMENTAL CONTROL

Division of Air and Waste Management
Air Quality Management Section
Air Surveillance Branch

MEMORANDUM

To: Nicole Romisch

From: Betsy Frey

Cc: Chuck Sarnoski, Jill Winterling, Joe Martini

Subject: CATS 3Q09 data validation

Date: January 12, 2010

I have reviewed the July – September 2009 Delaware Community Air Toxics Study Data Review memorandum dated 11/18/09 and the associated data files on the "F" drive. Issues identified in the original memo and my comments follow.

Quality Control Review. A specific comment summarizing sample collection and laboratory analysis activities was not included in the initial memo; I recommend that a statement be included in future memos regarding sample completeness and/or verification of sample collection and laboratory analyses.

A. Laboratory data flags – It was noted that the most common data flag was "Out of Spec" for one or both spiked standards. Review of associated data files for the five primary compounds indicates the following "Out of Spec" flag frequency:

    1,3-butadiene: 13 of 15 sample dates flagged
    Benzene: 13 of 15 sample dates flagged
    Carbon Tetrachloride: 9 out of 15 sample dates flagged
    Ethylbenzene: 14 of 15 samples dates flagged
    Toluene: 14 of 15 sample dates flagged

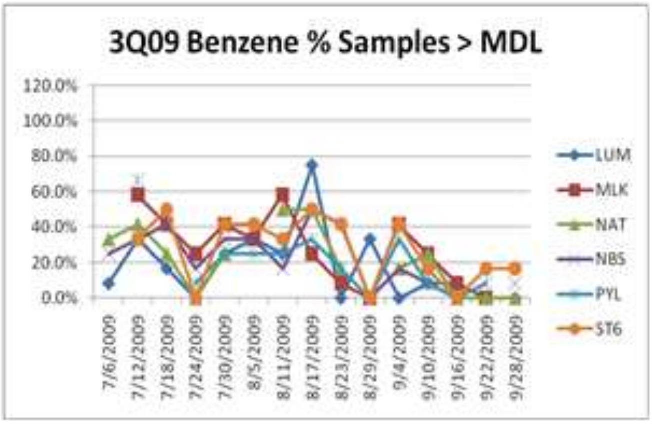
   The high number of samples flagged is a concern, and may reflect continuing problems with the GC/MS analysis.

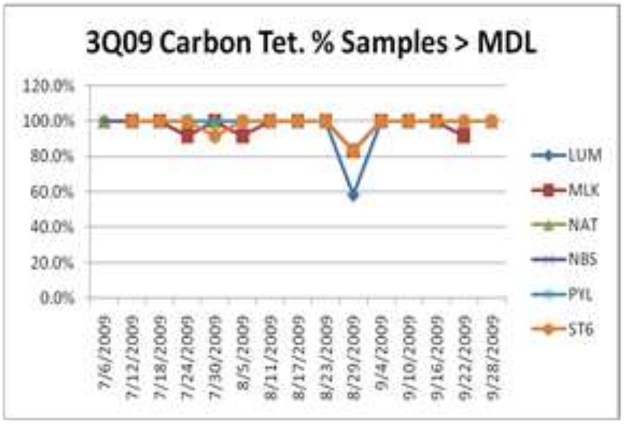
B. Data review – Sample data was graphed and statistical summary data included in the data files. Outliers were identified as exceeding three standard deviations; It was noted that there was one sample ≥ 3 standard deviations from the mean for Carbon Tetrachloride on August 29, 2009. The corresponding Carbon Tetrachloride field blank sample on this date was also ≥ 3 from the mean for field blank data.

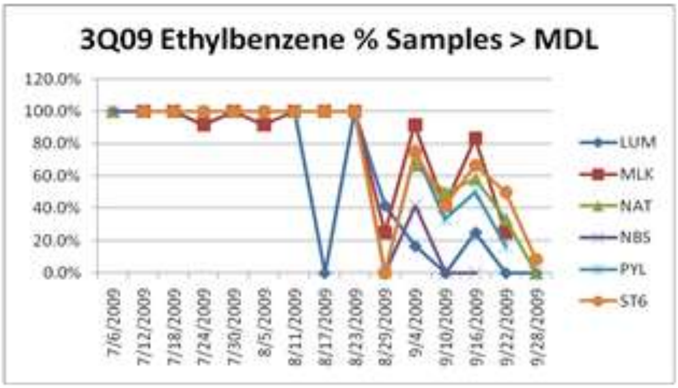
C. Field Quality Control Review – Results for field blanks and collocated/distributed volume samples were included in the data files. Associated summary statistics were also included.

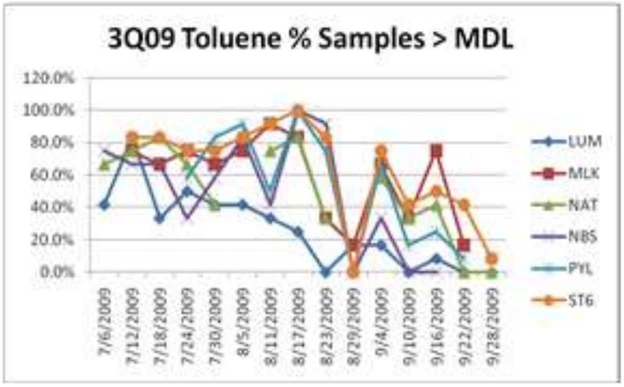
Data Quality Assessment. Individual 2-hour sample results, as well as daily averages, were evaluated for the five target compounds (1,3-buitadiene, benzene, carbon tetrachloride, ethylbenzene, and toluene). Following are my comments regarding the data:

A. Individual sample concentrations were evaluated with regard to minimum detection limits (MDLs), and the daily results graphed for each site/compound as shown below. The exception is 1,3-butadiene for which no MDL had been determined.









For benzene and toluene, a significant portion of sample results throughout the quarter were less than the MDL, with the percentage decreasing near the end of the quarter. Ethylbenzene results were largely above the MDL prior to August, then the percentage decreased. Almost all carbon tetrachloride samples were above the MDL.

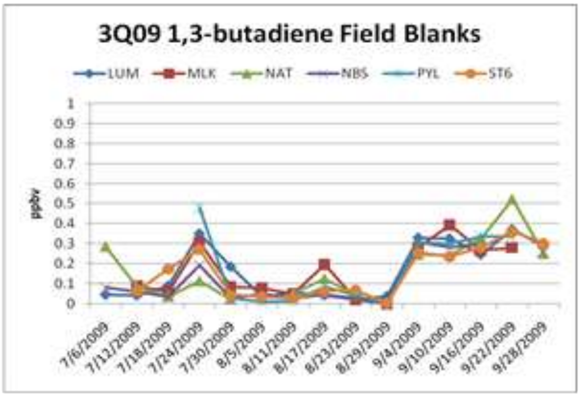
The change in the percentage of samples above the MDL over the quarter may indicate either a seasonal change in ambient concentrations or a change in sampling or analytical techniques. Because this study represents new sampling and analytical methodology, no final conclusion is drawn at this time.

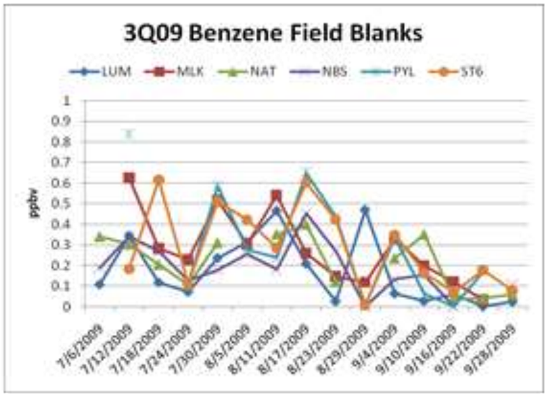
A. Individual sample concentrations were evaluated with regard to field blanks. The table below indicates the average percentage of samples at each site that were above the field blanks results for each compound. Field blank results are calculated as ppbv using average sample volume for compairson to field sample results.

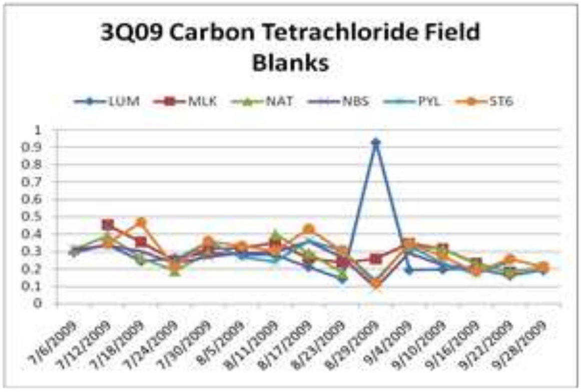
Parameter	LUM	MLK	NAT	NBS	PYL	ST6
1,3-butadiene	25%	23%	18%	20%	23%	30%
Benzene	25%	29%	30%	28%	23%	30%
Carbon Tetrachloride	37%	40%	39%	39%	39%	38%
Ethylbenzene	44%	38%	42%	49%	42%	42%
Toluene	38%	35%	40%	34%	35%	36%

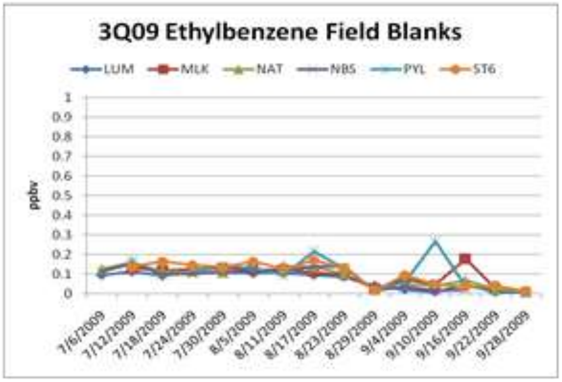
Field blank results were also charted to look for trends.

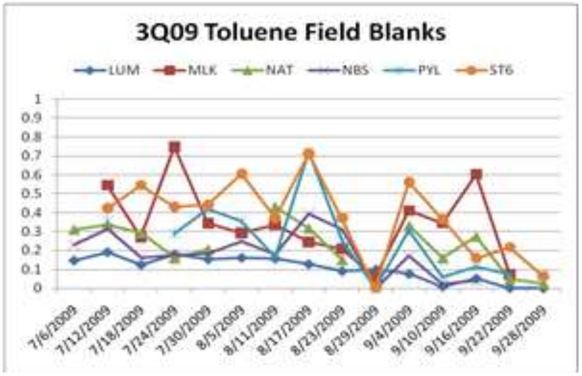
Field blank results for benzene, carbon tetrachl











oride, ethylbenzene, and toluene show a downward trend throughout the quarter. Field blanks for 1,3-butadiene, however, show a step increase in concentration at the end of August.

Field blank results are also similar among all sites with the exception of toluene. Statistical analysis of results (ANOVA and pair wise multiple comparison using Holm-Sidak method) indicates that MLK and NBS field blanks are significantly higher than blanks from the other locations.

Because this study represents new sampling and analytical methodology, no final conclusion regarding field blanks is drawn at this time.

C. Collocated samples and distributed volume pairs were evaluated. Individual 2-hour sample results were graphed and examined for trends as well as incorporated into precision calculations.

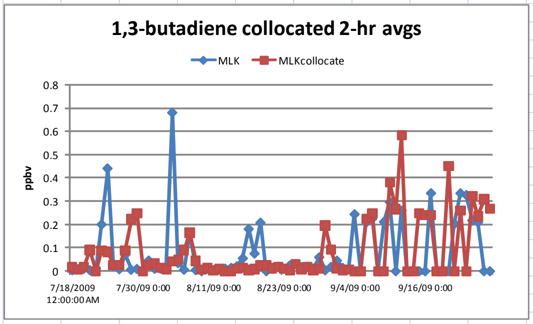
Precision is a measure of mutual agreement among individual measurements of the same property usually under prescribed similar conditions. This is the random component of error. For most air toxics sampling programs, precision is estimated via duplicate measurements from collocated samplers. For each collocated data pair, the relative percent difference d_i is calculated. The precision upper bound statistic, CV_{UB}, is a standard deviation on d_i with a 90 percent upper confidence limit. These results were calculated for the third quarter 2009 and are shown below.

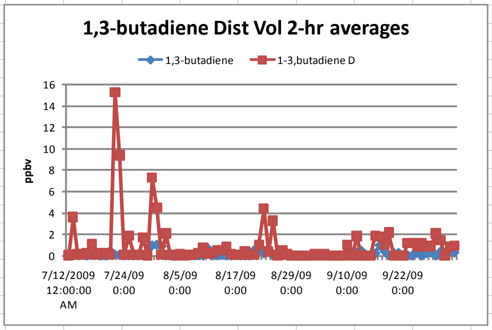
Compound	**Precision Estimate CV_{UB}**
1,3-butadiene	76.6
Benzene	96.5
Carbon Tetrachloride	25.2
Ethylbenzene	38.8
Toluene	52.2

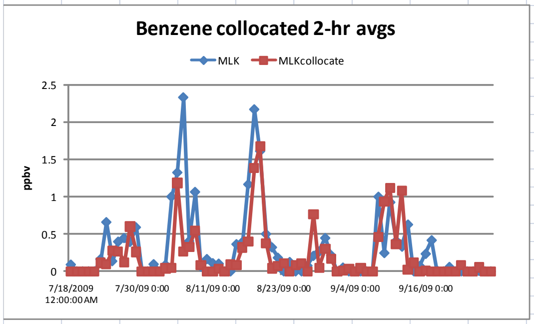
Collocated differences and distributed volume pair differences were charted as shown in the following graphic. For most samples, there is greater agreement between the collocated samples than between the distributed volume pairs. There are significant differences in the collocated samples for ethylbenzene and toluene on 9/16/09, but the remaining samples show closer agreement.

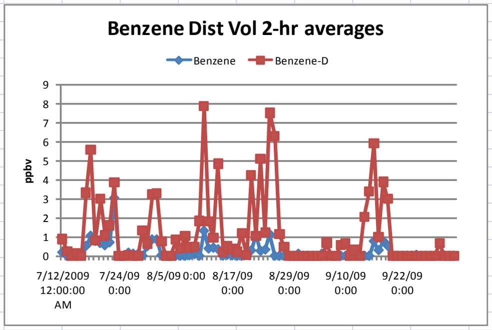
One potential issue identified in the use of distributed volume pairs is the low flow rate in the duplicate sample; the current SOP indicates the use of 8 liters per minute which is close to the lower limit of the sample pump. Inaccurate or poorly controlled flow rate might account for some of the differences in the distributed volume pairs. Use of a higher flow rate is under consideration for future sampling.

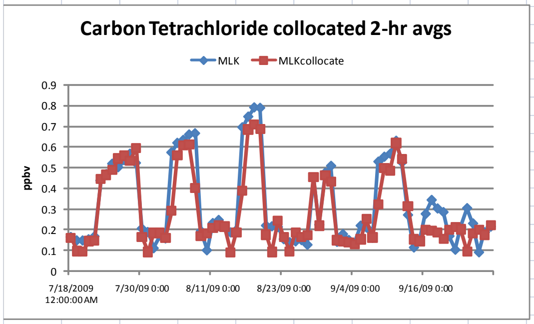
Because this study represents new sampling and analytical methodology, no final conclusion regarding collocated or distributed volume sampling is drawn at this time.

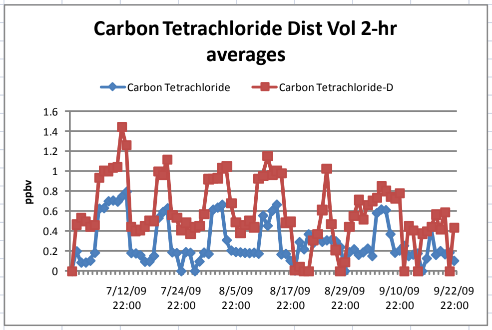

1,3-butadiene collocated 2-hr avgs

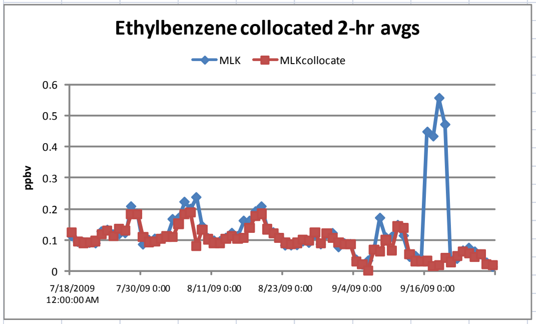

1,3-butadiene Dist Vol 2-hr averages

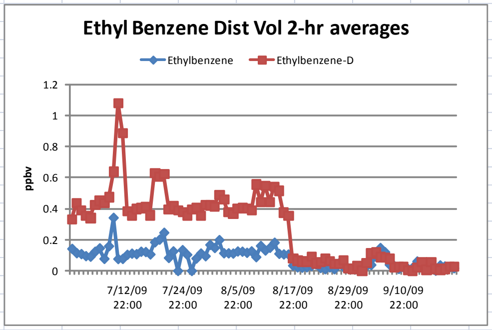

Benzene collocated 2-hr avgs

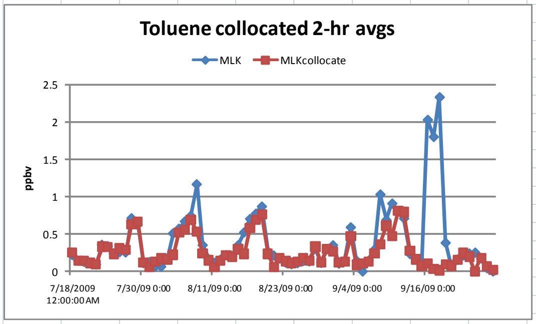

Benzene Dist Vol 2-hr averages

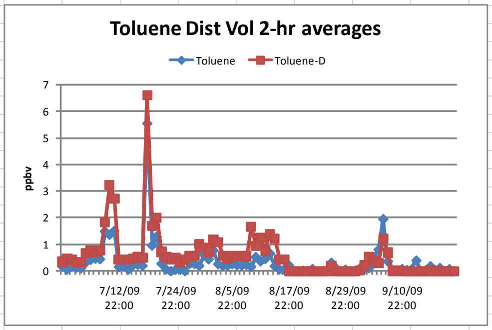

Carbon Tetrachloride collocated 2-hr avgs


Carbon Tetrachloride Dist Vol 2-hr averages

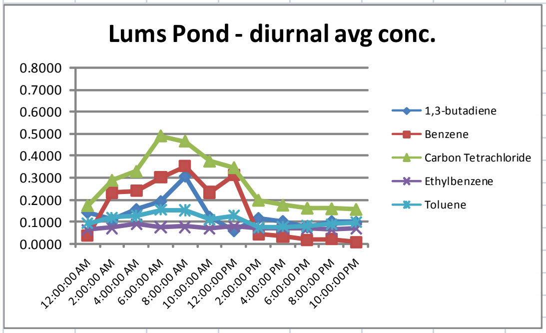

Ethylbenzene collocated 2-hr avgs

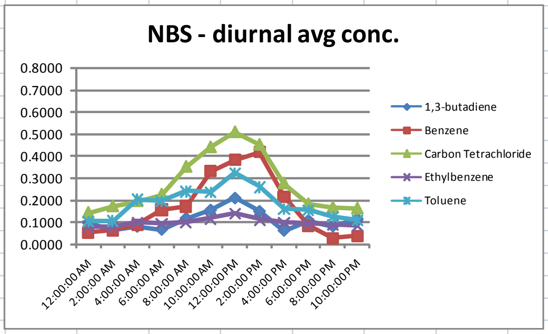

Ethyl Benzene Dist Vol 2-hr averages

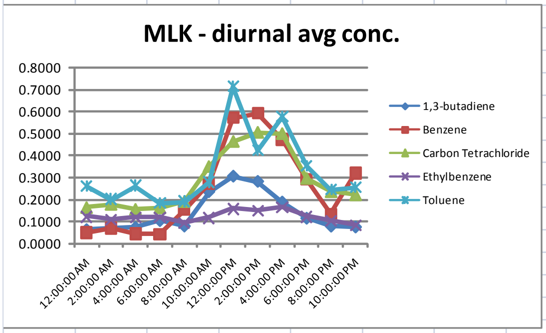

Toluene collocated 2-hr avgs

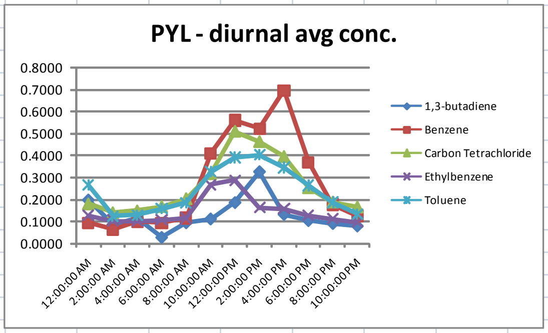

Toluene Dist Vol 2-hr averages

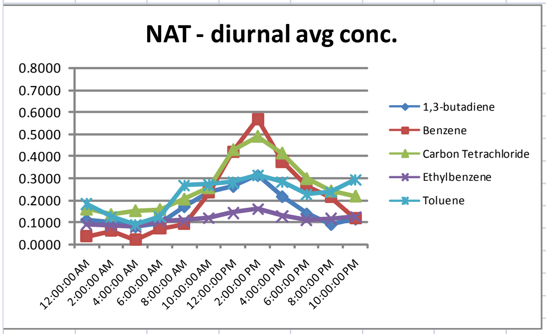
D. Other approaches to evaluating data quality. To become more familiar with this dataset, sample results were graphed as diurnal averages. These graphs can be used to evaluate the “reasonableness” of the data as well as to examine expected patterns and differences/similarities between sites. Graphs of compounds by site are shown below.

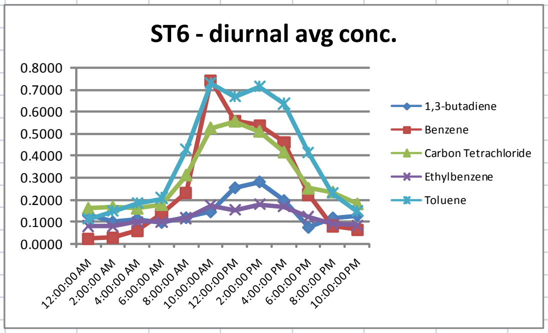

Lums Pond - diurnal avg conc.


NBS - diurnal avg conc.


MLK - diurnal avg conc.


PYL - diurnal avg conc.


NAT - diurnal avg conc.


ST6 - diurnal avg conc.

The diurnal patterns are generally reasonable, with the more rural Lums Pond site showing lower concentrations, earlier and broader peaks than the more urban sites. Sites most strongly influenced by mobile sources (MLK and ST6) show diurnal patterns typical of mobile source influenced sites.

Summary.

Issues of concern identified in the 3Q09 dataset include:

- high number of samples flagged as “Out of Spec”
- low percentage of samples above the MDL for most compounds
- low percentage of samples above the field blank for most compounds
- apparent trends and/or step changes in field blanks, collocated and distributed volume pair results that may or may not reflect actual changes in field or laboratory conditions/procedures

Issues indicating confidence in the data include the consistent diurnal patterns and overall concentrations that fit with other air toxics studies of urban and mobile source influenced sites. Collocated samples and precision confidence intervals are also promising for some compounds.

Conclusion. No final conclusions on data validity are being drawn at this time due to the fact that both the sample collection method and laboratory analysis methods are new. More data is needed to establish clearer estimates of data variability and internal consistency. As additional data is collected in future calendar quarters, and improvements are made to the field sampling and laboratory analysis methods, data quality assessments will continue and validity decisions will be made at that time.

Data will be submitted to AQS after data validity determinations are made.