NATIONAL AIR TOXICS TRENDS STATIONS QUALITY ASSURANCE ANNUAL REPORT CALENDER YEAR 2006

FINAL

Environmental Protection Agency
Office of Air Quality, Planning and Standards
Air Quality Analysis Division
109 TW Alexander Drive
Research Triangle Park, NC 27711

FORWARD

In the fall of 2007, Battelle Inc. prepared a final technical report under Contract No. 68-D-02-061 Work Assignment 5-01, Task 10b. The report was prepared for Margaret Dougherty, Project Officer and Candace Sorrell, Work Assignment Manager of the Air Quality Assessment Division (AQAD) within the Office of Air Quality Planning and Standards (OAQPS) in Research Triangle Park, North Carolina. The report was written by Ian C. MacGregor, Laura Aume, and Bradley P. Goodwin. That report was incorporated into this final report.

Additional work on this report was provided by AQAD staff.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Final Technical Report on
NATTS Quality Assurance Annual Report (QAAR)
for Calendar Year 2006

Work Assignment 5-01, Task 10b

1.0 INTRODUCTION

There are currently 188 hazardous air pollutants (HAPs), or air toxics, regulated under the Clean Air Act (CAA) that have been associated with a wide variety of adverse human health and ecological effects, including cancer, neurological effects, reproductive effects, and developmental effects. In keeping with the Government Performance Results Act (GPRA), the U.S. Environmental Protection Agency (U.S. EPA) is working to reduce air toxics emissions by 75 percent from 1993 levels in order to significantly reduce Americans' risk of cancer and of other serious health effects caused by airborne toxic chemicals. Early efforts toward this end have focused on emissions reductions through the assessment of technical feasibility. However, as new assessment tools are developed, more attention is being placed on the goal of risk reduction associated with exposure to air toxics.

To assess progress toward reducing air toxics ambient concentrations and corresponding exposure-associated risk, the National Air Toxics Trends Station (NATTS) network was established, currently consisting of 23 stations in the contiguous 48 states. Moreover, two additional sites have recently (in 2007) been added in Los Angeles, California. Having data of sufficient quality is paramount for a network such as the NATTS. As such, the U.S. EPA has established a Quality System (QS) for the NATTS, two aspects of which are Technical Systems Audits (TSAs) and Instrument Performance Audits (IPAs) of each network station and its affiliated laboratory tasked with sample analysis. Another integral part of the QS is the quarterly analysis of proficiency testing (PT) samples. Furthermore, the sampling and analytical techniques selected to collect and quantify the air toxics of concern must demonstrate acceptable analytical and overall sampling precision and laboratory bias, as well as suitable overall method detection limits (MDLs) that are compatible with expected ambient air toxics concentrations.

This report describes and summarizes the quality assurance (QA) data generated by the NATTS program for calendar year (CY) 2006. Although this report contains a great deal of information about 23 different chemicals of interest, it focuses in many respects on results for four key ambient air toxics: benzene, 1,3-butadiene, formaldehyde, and PM_{10} arsenic. These four pollutants were selected as principle pollutants of interest by virtue of associated health risk, frequency of occurrence at measurable concentrations, and the fact that they represent the three main categories of HAPs routinely measured in the NATTS program (volatile organic compounds (VOCs), carbonyls, and PM_{10} metals). If the program can meet the Data Quality Objectives (DQOs) for these four compounds, the additional 19 compounds of concern will have similar quality since the other 19 compounds are collected and analyzed using the same field and laboratory equipment.

Included in this Quality Assurance Annual Report (QAAR) are data from a number of different sources. Presented first is an assessment of the completeness of the data available in the Air Quality System (AQS) database. Entries into AQS also include results from replicate analyses of a given sample and from duplicate and collocated samplers. Data were retrieved from AQS, and analytical and overall sampling precision were calculated for as many of the 23 applicable compounds and for as many of the 23 NATTS sites as had such data posted to AQS in 2006. Data from the analysis of blind audit PT samples for many of the 23 compounds are also presented. With these data, an analytical laboratory's ability to accurately quantify samples generated at the NATTS sites was assessed. The accuracy achieved is also referred to as the amount of laboratory bias introduced during sample analysis. Moreover, field bias data, which are the differences between actual and measured sampler flow readings for each of the three different sampler types (VOCs, carbonyls, and PM_{10} metals), are presented for primary and collocated samplers (where available) at the three sites visited during the IPAs conducted in CY 2006. Finally, information regarding MDLs was solicited from all the NATTS state and local agencies and affiliated laboratories for the 23 compounds of interest. Taken together, the combination of all the above QA data summarizes the activities of the NATTS QS for the NATTS for CY 2006.

2.0 NATTS QUALITY ASSURANCE DATA FOR CALENDAR YEAR 2006

There are 23 sites in the NATTS network. The EPA Region in which the sites are located, the location of the sites (site identifier), whether the site is located in an urban or rural area, and the unique AQS identification code (site code) for all the sites are given in Table 1.

Table 1. NATTS sites with EPA region numbers and AQS site codes.

Region	Site Identifier	Type	AQS Site Code
I	Boston-Roxbury, MA	Urban	25-025-0042
I	Underhill, VT	Rural	50-007-0007
I	Providence, RI	Urban	44-007-0022
II	Bronx, NY	Urban	36-005-0110
II	Rochester, NY	Urban	36-055-1007
III	Washington, DC	Urban	11-001-0043
IV	Chesterfield, SC	Rural	45-025-0001
IV	Decatur, GA	Urban	13-089-0002
IV	Hazard, KY	Rural	21-193-0003
IV	Hillsborough Cty, Tampa, FL	Urban	12-057-3002
IV	Pinellas Cty, Tampa, FL	Urban	12-103-0026
V	Dearborn, MI	Urban	26-163-0033
V	Mayville, WI	Rural	55-027-0007
V	Northbrook, IL	Urban	17-031-4201
VI	Deer Park, TX	Urban	48-201-1039
VI	Harrison County, TX	Rural	48-203-0002
VII	St. Louis, MO	Urban	29-510-0085
VIII	Bountiful, UT	Urban	49-011-0004
VIII	Grand Junction, CO	Rural	08-077-0017, -0018
IX	Phoenix, AZ	Urban	04-013-9997
IX	San Jose, CA	Urban	06-085-0005
X	La Grande, OR	Rural	41-061-0119
X	Seattle, WA	Urban	53-033-0080

Though a city and state are typically used as the site identifier, the county name is used for the two Florida sites on either side of Tampa Bay. The Grand Junction, Colorado, site has two separate codes, one for VOCs and carbonyls (-0018), the other for the metals (-0017), since the organics and metals samplers are present at two separate physical locations at the sampling site. The 23 hazardous air pollutants measured in the NATTS program are compounds that have been identified by EPA as being cancer and non-cancer risk drivers. They are listed in Table 2. These include 14 VOCs, two carbonyls, and seven PM_{10} metals. Also included in Table 2 are the unique AQS identification codes for each compound. In the left-hand column are arbitrary compound numbers used throughout the report to identify the different HAPs in the various tables and graphs.

Table 2. The 23 HAPs and their AQS compound codes.

Compound Number	Compound Name	AQS Code
1	benzene	45201
2	1,3-butadiene	43218
3	carbon tetrachloride	43804
4	chloroform	43803
5	1,2-dibromoethane	43843
6	1,2-dichloropropane	43829
7	1,2-dichloroethane	43815
8	dichloromethane	43802
9	1,1,2,2-tetrachloroethane	43818
10	tetrachloroethylene	43817
11	trichloroethylene	43824
12	vinyl chloride	43860
13	cis-1,3-dichloropropene	43831
14	trans-1,3-dichloropropene	43830
15	formaldehyde	43502
16	acetaldehyde	43503
17	arsenic	82103
18	beryllium	82105
19	cadmium	82110
20	lead	82128
21	manganese	82132
22	mercury	82142
23	nickel	82136

2.1 Measurement Quality Objectives

Several different Measurement Quality Objectives (MQOs) have been established for the NATTS network in order to ensure that only data of the highest quality are collected by the NATTS network. The stated Data Quality Objective (DQO) for the NATTS program is “to be able to detect a 15 percent difference (trend) between two consecutive 3-year annual mean concentrations within acceptable levels of decision error” [1]. MQOs for the four compounds of primary importance to the NATTS program (benzene, 1,3-butadiene, formaldehyde, and PM_{10} arsenic) are summarized below in Table 3.

Table 3. Measurement Quality Objectives for the NATTS program.

Compound	Completeness	Precision (Coefficient of Variation)	Laboratory Bias	Method Detection Limit (MDL)
benzene	> 85 %	< 15 %	< 25 %	0.016 μg/m^3
1,3-butadiene	> 85 %	< 15 %	< 25 %	0.013 μg/m^3
formaldehyde	> 85 %	< 15 %	< 25 %	0.0074 μg/m^3†
arsenic	> 85 %	< 15 %	< 25 %	0.217 ng/m^3‡

† Assumes a sampling volume of 1,000 L.

‡ Assumes high-volume sampling with a sampling volume of 1,627 m^3 (1.13 m^3/min (40 ft^3/min) for 24 hours) and that 1/8 of the sampled area of the filter is extracted for analysis.

The MQOs require that (1) sampling occurs every sixth day and is successful 85 percent of the time; (2) precision as measured by the coefficient of variation (CV) is controlled to less than 15 percent; and (3) laboratory (measurement) bias is less than 25 percent. Furthermore, actual MDLs as reported by the laboratories supporting the NATTS sites are compared to the target MDLs as listed in the latest draft version of the NATTS Technical Assistance Document (TAD) [2].

Data acquired to assess compliance with the above stated MQOs are derived from a variety of sources. These sources are given in Table 4.

Table 4. Sources of data for the evaluation of MQOs for the NATTS program.

MQO	Data Source
Completeness	AQS
Analytical and Overall Precision	AQS
Bias - Laboratory	Proficiency Testing
Bias - Field	Audits of sampler flowrates
MDL	Laboratories

AQS contains data used to assess completeness, and to estimate precision from results of replicate analyses and collocated and duplicate sampling. PT samples were sent to participating laboratories for analysis and determination of analytical bias. Field bias was evaluated by measurement of sampler flow rates during on-site IPAs. Finally, MDL data were solicited from the individual laboratories.

2.2 Completeness of NATTS Data

The AQS database was accessed and the raw data records for calendar year 2006 were retrieved for the 23 NATTS sites using the site codes given in Table 1. AQS data were retrieved on July 2, 2007; thus, any data entered into AQS after this time are not reflected in the completeness calculations presented here. The completeness of the 2006 AQS dataset was assessed for four compounds: benzene, 1,3-butadiene, formaldehyde, and arsenic. The results are shown in Table 5. The presence of 61 concentration values in the database indicated 100 percent completeness for a 1 in 6 day sampling frequency. Zero values in the database indicated a valid data point and, thus, were counted toward total dataset completeness. Moreover, transactions where non-detects were indicated with the appropriate qualifier code were counted as complete. However, if the appropriate data fields were empty, if no data were found, or if one of several "null codes"[1] were found, then the sampling event was determined to be incomplete and data were understood to be missing. In these instances, the total completeness percentage decreased accordingly.

The completeness data presented here are composite values for both the primary and collocated sampler present at a given sampling site. One way to distinguish primary and collocated data in AQS is by use of different parameter occurrence codes (POCs). (POCs are discussed in further detail in Section 2.3.) The algorithm ensured that "double-counting" did not occur by disregarding data that appeared more frequently than every six days. In such cases where higher frequency data were present, such as at sites with collocated samplers, only samples separated by six days were counted toward the overall dataset completeness. For example, if the database contained records of sampling on days 1, 3, 5, 7, 10, and 13, all on a single POC, only three of these records would be counted toward the total completion percentage. The algorithm started with day 1, then ignored days 3 and 5 since only 2 and 4 days had elapsed after day 1, respectively. But the algorithm tallied the value at day 7 since six days had passed after day 1. Similarly, the value at day 10 would be skipped but day 13 would be counted.

Sorted by compound and taken across all the NATTS sites, the completeness data given in Table 5 are shown as a box and whisker plot in Figure 1. The "+" symbols indicate the mean completeness for each compound and the horizontal line "—" in the box represents the median. The upper and lower ends of the boxes represent the upper and lower quartiles; thus, the height of the box is the interquartile range. The upper whisker shows the maximum value less than the sum of the upper quartile value plus 1.5 times the interquartile range. Similarly, the lower whisker depicts the minimum value above the lower quartile minus 1.5 times the interquartile range. The squares show "outliers" that represent individual completeness values greater than 1.5 times the interquartile range from the upper or lower quartile.

The mean completeness values across all of the NATTS laboratories were 87 percent, 87 percent, 88 percent, and 70 percent for benzene, 1,3-butadiene, formaldehyde, and arsenic, respectively. The median completeness values were higher: 93 percent, 93 percent, 95 percent,

---

[1] Null codes and explanations of their meaning may be found at the following website: http://www.epa.gov/ttn/airs/airsaqs/manuals/qualifiers.htm.

and 92 percent for benzene, 1,3-butadiene, formaldehyde, and arsenic, respectively. Sites with markedly low completeness values include Washington, D.C., Phoenix, Arizona, and San Jose, California. Low network-wide completeness for metals is explained in part because metals analysis was not performed for samples collected in CY2006 at Underhill, Vermont, the sites in New York State, or San Jose, California.

Table 5. Percent completeness of the 2006 AQS dataset by site for four HAPs.

Site Identifier	Completeness of Compound by AQS number and by name, %			
	45201	43218	43502	82103
	benzene	1,3-butadiene	formaldehyde	arsenic
Boston-Roxbury, MA	92	92	100	90
Underhill, VT	89	89	93	No data
Providence, RI	87	87	95	97
Bronx, NY	70	70	97	No data
Rochester, NY	89	89	90	No data
Washington, DC	100	100	No data	No data
Chesterfield, SC	98	98	95	95
Decatur, GA	100	100	93	97
Hazard, KY	100	100	100	100
Hillsbourough Cty, Tampa, FL	93	93	98	100
Pinellas Cty, FL	98	98	98	93
Dearborn, MI	95	95	98	98
Mayville, WI	92	92	93	92
Northbrook, IL	97	97	100	98
Deer Park, TX	82	82	85	89
Harrison County, TX	98	98	97	98
St. Louis, MO	92	92	93	85
Bountiful, UT	97	97	98	92
Grand Junction, CO	97	97	97	97
Phoenix, AZ	No data	No data	82	No data
San Jose, CA	49	49	49	No data
La Grande, OR	93	95	85	95
Seattle, WA	83	83	90	90
Mean	**87**	**87**	**88**	**70**
Median	**93**	**93**	**95**	**92**

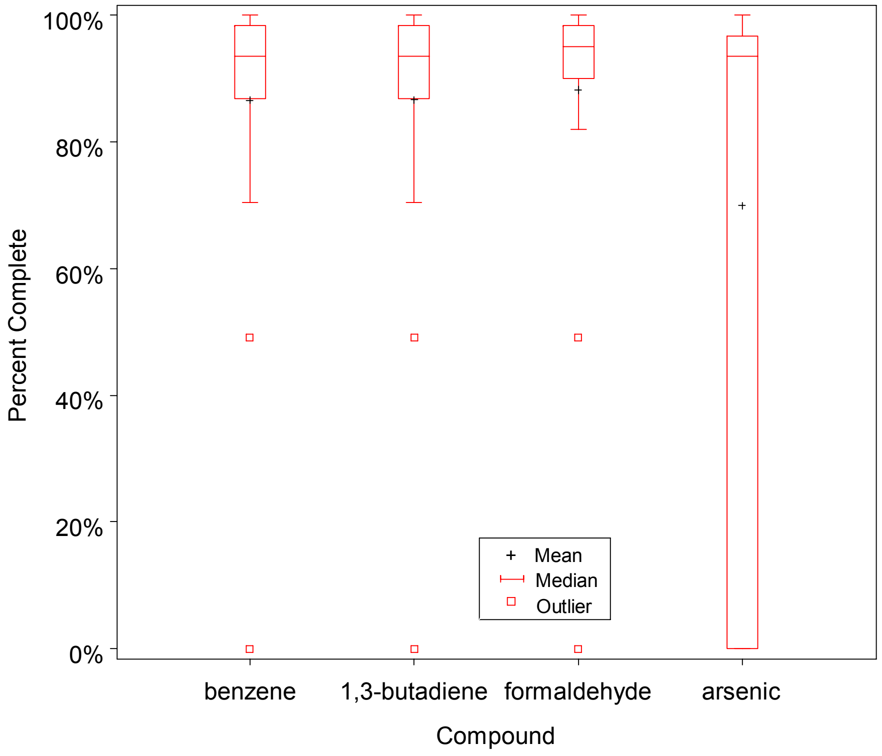

Figure 1. **Box and whisker plot of the completeness data for 2006 for 23 NATTS sites and for four compounds.**

2.3 Precision of NATTS Data

Both analytical and overall precision of the NATTS data are calculated and presented. Analytical (also sometimes referred to as instrumental) precision is a measure of the variability in reported results due to run-to-run differences on the analytical instrument. It is estimated by comparison of results from the replicate analysis of a single sample. Overall sampling precision, as measured by duplicate sampling, accounts for not only analytical variability but also for the variability inherent in sampling media. As given in the NATTS TAD [2], a duplicate sample “is collected simultaneously with a primary sample (i.e., on two separate cartridges through the same sampling system at the same time).” Moreover, by collection of collocated samples, a third type of variability – inter-sampler variability – is captured in the overall precision estimate (in addition to analytical and sampling media variations captured by duplicate sampling). The NATTS TAD defines collocated sampling as the “use of two separate sampling systems to generate two samples at the same location” [2]. Note that even though precision estimates calculated using duplicate and collocated data are collectively referred to as overall precision in this report, inter-sampler variability is not captured in overall precision determined from duplicate sampling. Only from collocated sampling results is such variability incorporated in overall precision estimates.

Ultimately, two different types of data were obtained from AQS in order to quantify both analytical and overall precision. The first is replicate (RP) data transactions. For a given sampling moment, site, and compound, AQS replicate data can have one of three different precision identifiers: IDs 1, 2, or 3. Concentration information from a collocated sampler is coded with Precision ID 1. Primary replicate data, that is, a concentration value from a second analysis of the primary sample, are coded with Precision ID 2. Collocated sampler replicate data are identified with Precision ID 3. Hence, the analytical precision is derived from the replicate pairs of data coded with Precision IDs 2 and 3. On the other hand, overall precision data are calculated using records with Precision ID 1.

Raw Data (RD) transactions are the second source of precision data in AQS. Instead of using RP transactions in the AQS database, some NATTS sites capture overall precision data with different Parameter Occurrence Codes (POCs) in the RD AQS transactions. For instance, collocated samplers operating at a given site may be assigned two separate POC values so that for each sampling moment, two RD records are generated for each compound measured. One RD record is generated for each of the collocated samplers, and each record has a unique POC value. Data from duplicate sampling may be similarly captured. Each NATTS site was contacted to ascertain which POCs they used to code collocated and/or duplicate data. In addition, if collocated and/or duplicate sampling was occurring at a non-NATTS site, but one in the same state/local/tribal network as a NATTS site, overall precision data were captured from these sites as surrogates for the affiliated NATTS site. The POCs for duplicate and collocated sampling records for AQS RD transactions are listed by NATTS (and NATTS-surrogate) site in Table 6. POCs are arbitrarily assigned, and collection of POC data for the purpose of estimating network precision was a time-intensive, non-automated process. To streamline the process of precision estimation, standardization of POC values across all NATTS sites is recommended.

Table 6. Parameter occurrence codes by NATTS site and compound type.

Region	Site Identifier	AQS Site Code	Parameter Occurrence Codes (POCs)							
			VOC			Carbonyls			Metals	
			P[a]	D[b]	C[c]	P	D	C	P	C
I	Boston, MA	25-025-0042	10	11		3			6	7
I	Underhill, VT	50-007-0007	1			1				
I	Providence, RI	44-007-0022	2			5		7	1	2
II	Bronx, NY	36-005-0110	2			2				
II	Rochester, NY	36-055-1007	2			2				
III	Washington, DC	11-001-0043	1	2						
IV	Chesterfield, SC	45-025-0001	1		2	1		2	1	2
IV	Decatur, GA[d]	13-089-0002	1,3		2,4	2		3	1	2
IV	Hazard, KY	21-193-0003	1	2		1	2		1	
IV	Hillsborough Cty, FL	12-057-3002	1			6			5	
IV	Pinellas Cty, FL	12-103-0026	1			6			5	
V	Dearborn, MI	26-163-0033	1	2		1	2		1	9
V	Mayville, WI	55-027-0007	1	2		1	2		1	2
V	Northbrook, IL	17-031-4201	6		7	6		7	6	
VI	Deer Park, TX	48-201-1039	2		3	3	5		1	
VI	Harrison County, TX	48-203-0002	1			1			1	
VII	St. Louis, MO	29-510-0085	6			6			6	7
VIII	Bountiful, UT	49-011-0004	6			6			1	2
VIII	Grand Junction, CO	08-077-0017, -0018	6			6			3	4
IX	Phoenix, AZ[e]	04-013-9997								
IX	San Jose, CA	06-085-0005	5			1				
X	La Grand, OR	41-061-0119	7			7			7	
X	Seattle, WA	53-033-0080	1			1			1	
I	Burlington, VT[f]	50-007-0014	1		2	1		2		
I	East Providence, RI[f]	44-007-1010	2		7					
IV	Ashland, KY[f]	21-019-0002							1	2

[a] P = Primary.
[b] D = Duplicate.
[c] C = Collocated.
[d] Benzene on POCs 3 & 4; all other VOCs on POCs 1 & 2.
[e] No 2006 data available.
[f] Non-NATTS sites, but affiliated with a NATTS site within same state.

2.3.1 Analytical Precision Results

The precision estimate is expressed in the form of the percent coefficient of variation (% CV). A smaller % CV indicates a more precise measurement. To assess the analytical precision, the % CV was calculated in the following manner:

$$\%CV = 100 \cdot \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{(p_i - r_i)}{0.5 \cdot (p_i + r_i)}\right]^2 + \sum_{j=1}^{m}\left[\frac{(c_j - cr_j)}{0.5 \cdot (c_j + cr_j)}\right]^2}{2 \cdot (n+m)}} \qquad \text{(Eq. 2.3.1)}$$

where p_i and r_i are the corresponding primary and replicate records, n is the number of such records, c_j and cr_j are the corresponding collocated and collocated replicate records, and m is the number of such records. These records were taken from RP transactions in the AQS database. Given in Table 7 are the analytical precision results.

Table 7. Analytical precision given as % CV determined from 2006 AQS data. Only those sites and compounds for which data were available are shown. HAPs are given by number; see Table 2 for cross-reference. Data in parentheses are the number of data pairs used for the % CV calculation.

Site Identifier	Compound Number						
	1	2	3	4	5	7	8
Pinellas Cty, FL	6% (90)	10% (71)	7% (90)	11% (51)	0% (2)	11% (45)	17% (90)
Dearborn, MI	7% (18)	14% (14)	8% (18)	6% (18)			10% (18)
Northbrook, IL	9% (23)	17% (8)	6% (12)	7% (11)			7% (10)
St. Louis, MO	6% (11)	12% (11)	31% (11)	13% (9)			7% (11)
Bountiful, UT	8% (24)	8% (14)	32% (12)	14% (8)			8% (12)
Grand Junction, CO	6% (12)	6% (12)	14% (12)	33% (8)			12% (12)
Weighted Mean	**7%**	**10%**	**11%**	**12%**	**0%**	**11%**	**14%**
Site Identifier	**Compound Number**						
	10	**11**	**12**	**13**	**14**	**15**	**16**
Hillsborough Cty, Tampa, FL						8% (14)	10% (14)
Pinellas Cty, FL	15% (72)	19% (26)		0% (2)	0% (4)	4% (12)	4% (12)
Dearborn, MI	5% (15)	0% (7)	0% (1)			1% (55)	1% (55)
Northbrook, IL	13% (7)	19% (7)				0% (16)	1% (16)
St. Louis, MO	14% (8)	27% (6)				3% (14)	1% (14)
Bountiful, UT	12% (8)	47% (1)	0% (1)			4% (12)	2% (12)
Grand Junction, CO	6% (8)					1% (10)	1% (10)
Weighted Mean	**13%**	**18%**	**0%**	**0%**	**0%**	**2%**	**2%**

2.3.2 Overall Precision Results

To calculate the % CV for the available overall precision data, the following relationship was employed:

$$\%CV = 100 \cdot \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{(p_i - c_i)}{0.5 \cdot (p_i + c_i)}\right]^2}{2 \cdot n}} \qquad \text{(Eq. 2.3.2)}$$

where p_i and c_i are the corresponding primary and collocated (or duplicate) records, and n is the number of such records. These records were taken from both RP transactions in the AQS database and RD transactions with different POCs.

A corresponding pair of records was not included in the calculation if one of the values in the pair was either zero or less than the MDL assigned for that compound in AQS. If no MDL was given and non-zero precision data were present, the precision data were included in the % CV calculation. The results of the overall precision calculations are shown in Table 8.

Table 8. Overall precision given as % CV determined from the 2006 AQS data. Only those sites and compounds for which data were available are shown. HAPs are given by number; see Table 2 for cross-reference. Data in parentheses are the number of data pairs used for the % CV calculation. Values in bold are RP data. Values in italic are from duplicate data.

Site Identifier	Compound Number						
	1	2	3	4	5	6	7
Boston-Roxbury, MA	*3% (10)*	*29% (10)*	*3% (10)*	*11% (10)*			*38% (6)*
Chesterfield, SC	**35% (29)**		**37% (7)**				
Decatur, GA	15% (29)		20% (25)	8% (2)			
Hazard, KY	*7% (45)*	*2% (1)*					
Pinellas Cty, FL	**8% (30)**	**12% (23)**	**9% (30)**	**14% (16)**	**0% (1)**		**8% (12)**
Dearborn, MI	**14% (18)**	**21% (5)**	**22% (12)**	**47% (9)**			
Mayville, WI	*10% (3)*						
Northbrook, IL	49% (6)	35% (4)	5% (7)	37% (6)			
St. Louis, MO	**6% (5)**	**7% (5)**	**40% (5)**	**0% (4)**			
Bountiful, UT	**6% (12)**	**11% (7)**	**46% (6)**	**24% (4)**			
Grand Junction, CO	**6% (6)**	**23% (5)**	**22% (6)**	**38% (3)**			
E. Providence, RI*	4% (56)	11% (41)	4% (56)	7% (41)			
Burlington, VT*	8% (22)	2% (3)	0% (2)	33% (2)		47% (1)	0% (1)
Weighted Mean	**12%**	**14%**	**13%**	**16%**	**0%**	**47%**	**17%**

Site Identifier	Compound Number						
	8	9	10	11	13	14	15
Boston-Roxbury, MA	*5% (10)*		*8% (10)*	*27% (5)*			
Providence, RI							8% (45)
Chesterfield, SC	**24% (4)**	**27% (10)**					**26% (53)**
Decatur, GA			19% (8)				45% (20)
Hazard, KY							*6% (29)*
Hillsborough Cty, Tampa, FL							**11% (7)**
Pinellas Cty, FL	**20% (29)**		**13% (24)**	**0% (6)**	**0% (1)**	**0% (2)**	**6% (6)**
Dearborn, MI	**34% (7)**		**9% (5)**	**0% (1)**			**29% (30)**
Mayville, WI	*11% (1)*						*3% (4)*
Northbrook, IL	54% (6)		36% (3)	48% (3)			71% (8)
St. Louis, MO	**13% (5)**		**14% (4)**	**0% (3)**			**4% (7)**
Bountiful, UT	**12% (6)**		**14% (5)**				**6% (6)**
Grand Junction, CO	**13% (6)**		**15% (4)**				**2% (5)**
E. Providence, RI*	7% (55)		8% (28)	12% (16)			
Burlington, VT*	5% (3)		0% (1)	0% (1)			**9% (23)**
Weighted Mean	**15%**	**27%**	**12%**	**14%**	**0%**	**0%**	**19%**

* Surrogate for a NATTS site.

Table 8. (Continued).

Site Identifier	Compound Number						
	16	17	18	19	20	21	23
Boston-Roxbury, MA		14% (27)		36% (27)	15% (27)	15% (27)	15% (27)
Providence, RI	9% (42)				9% (27)	8% (27)	14% (21)
Chesterfield, SC	**27% (52)**	**20% (55)**	**13% (32)**	**29% (53)**	**34% (55)**	**21% (54)**	**52% (43)**
Decatur, GA	22% (19)	16% (17)		48% (22)	27% (23)	35% (23)	49% (22)
Hillsbourough Cty, Tampa, FL	**13% (7)**				**13% (45)**	**12% (45)**	
Pinellas Cty, FL	**6% (6)**						
Dearborn, MI	**27% (30)**	28% (53)	22% (1)	26% (50)	32% (53)	38% (55)	38% (54)
Mayville, WI	*9% (4)*	45% (7)		8% (6)	47% (7)	36% (7)	50% (7)
Northbrook, IL	37% (8)						
St. Louis, MO	**2% (7)**	5% (13)		10% (13)	6% (13)	5% (13)	15% (12)
Bountiful, UT	**3% (6)**	**4% (2)**	**20% (2)**	**7% (2)**	**33% (4)**	**4% (2)**	**12% (4)**
Grand Junction, CO	**2% (5)**		13% (11)	9% (9)	12% (44)	14% (44)	8% (4)
Ashland, KY*		**5% (46)**		**6% (27)**	**6% (56)**	**16% (55)**	**19% (54)**
Burlington, VT*	**8% (23)**						
Weighted Mean	**18%**	**17%**	**13%**	**25%**	**19%**	**20%**	**31%**

* Surrogate for a NATTS site.

Precision data available in AQS varied widely by compound and by site. However, the precision data, when available, shows that MQOs are, in general, being attained. The mean analytical precision values for benzene (6 sites, 178 records), 1,3-butadiene (6 sites, 130 records), and formaldehyde (7 sites, 133 records) are 7 percent, 10 percent, and 2 percent, respectively (see Table 7). Moreover, the overall precision estimates for benzene (13 sites, 271 records), 1,3-butadiene (10 sites, 104 records), formaldehyde (13 sites, 243 records), and arsenic (8 sites, 220 records) are 12 percent, 14 percent, 19 percent, and 17 percent, respectively (see Table 8). The overall precision data for these four key air toxics are depicted graphically in Figure 2.

Only seven stations out of 23 reported precision data using RP transactions, with the remainder of the precision data coming from raw data with different POC values, either as duplicate or collocated data. That is, much more precision data are available when duplicate and collocated data contained in RD transactions are accessed. However, reduction of such data requires knowledge of site-specific POC values. Thus, to facilitate the future use of RD transactions to determine overall precision, the use of POCs should be standardized across the network. For instance, a simple coding scheme would have all data from primary samplers on POC 1, all duplicate data on POC 2, and all collocated data on POC 3.

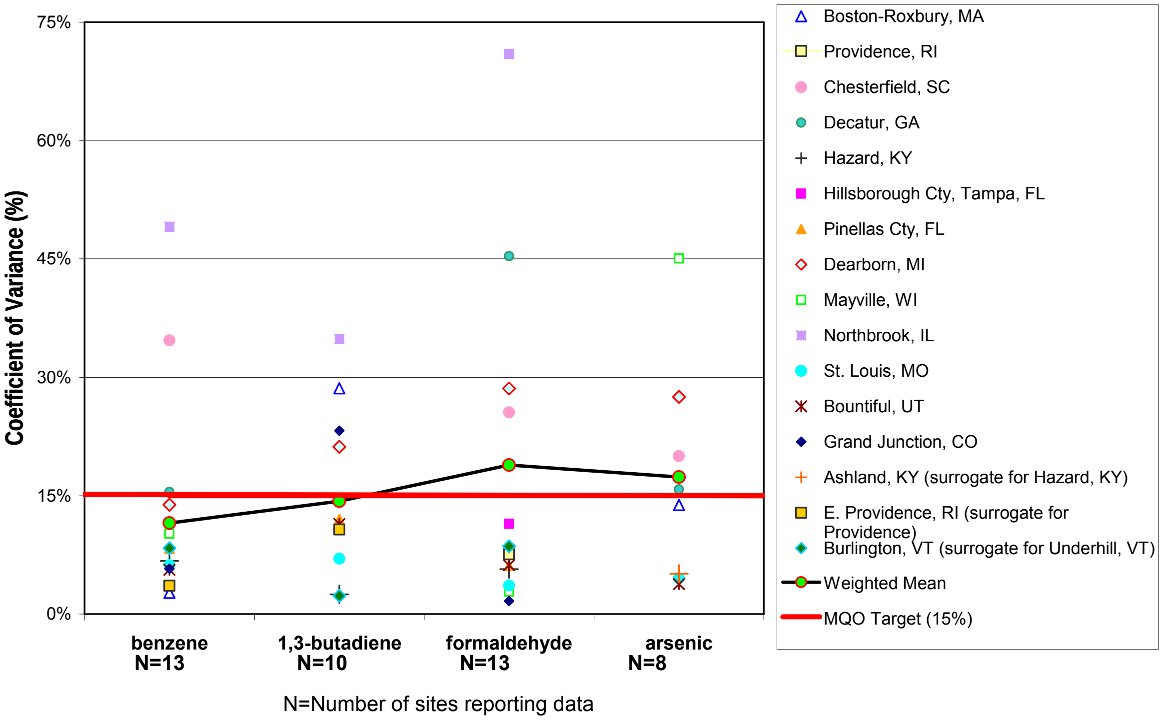

Figure 2. **Overall precision data for four key air toxics for 2006 by NATTS site. Shown are both the mean precision across sites reporting data and the goal precision of 15 percent.**

2.4 Laboratory Bias Data from Proficiency Testing (PT) Samples from Alion

Alion Science, Inc., is under contract (Contract No. 68-D03-006) to the U.S. EPA to conduct quarterly PT audits of the NATTS laboratories (twice per year for carbonyl samples). Spiked samples containing known amounts of the HAPs of interest were forwarded to each laboratory that was performing analyses for a NATTS site and that chose to participate in a given PT study. Participating laboratories forwarded their results to Alion, after which reports were prepared comparing the values measured by each laboratory to the stated (known) value. For calendar year 2006, four separate PT studies for VOCs and metals were conducted, whereas only two were performed for carbonyls. Alion provided Battelle with the results of the calendar year 2006 PT audits for inclusion in this report.

Laboratory bias is defined as the percent difference between the laboratory's measured value and the known value for audit sample:

$$\%Difference = \frac{Measured - Known}{Known} \cdot 100 \qquad \text{(Eq. 2.4.1)}$$

Given in Figures 3 through 6 are boxplots summarizing laboratory bias results for all the participating laboratories for the four compounds of interest: benzene, 1,3-butadiene, formaldehyde, and arsenic. The dashed line in these figures represents the goal bias of 25 percent. In Figures 3 through 6, the laboratories are identified by numbers assigned by Alion; a cross-reference between NATTS site and assigned laboratory codes is provided in Table 9. A laboratory's results are shown only if they support analysis of that sample type for at least one NATTS site.

Although individual laboratories continue to report PT sample concentrations with bias beyond the NATTS MQO, combined results across all laboratories for the PT program for CY2006 demonstrate that mean laboratory bias for benzene, 1,3-butadiene, formaldehyde, and arsenic is within the acceptable tolerance limit of ±25 percent.

Table 9. Cross-reference between laboratory codes and affiliated NATTS sites.

Laboratory Code	NATTS Site(s)
01-01	Providence, RI
01-02	Underhill, VT
01-03	Boston-Roxbury, MA
01-04	EPA Region 1 Laboratory*
02-01	Bronx & Rochester, NY
03-01	Washington, DC
04-01	Hillsborough & Pinellas Cty, Tampa, FL
04-02	Chesterfield, SC
04-03	Hazard, KY
04-04	Decatur, GA
05-01	Dearborn, MI
05-03	Mayville, WI
06-01	Deer Park & Harrison Cty, TX
08-02	Grand Junction, CO
09-02	Phoenix, AZ
09-03	San Jose, CA
10-01	Seattle, WA
10-02	La Grande, OR
11-01	ERG**

* The EPA Region 1 Laboratory does not operate a NATTS site.

** ERG serves as the analytical laboratory for several NATTS sites.

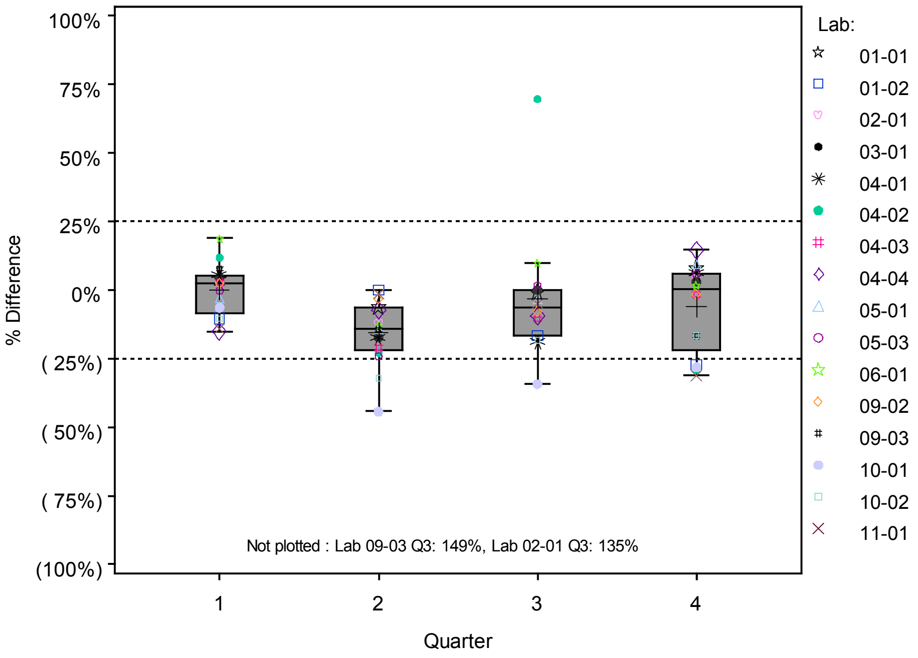

Figure 3. **Laboratory bias boxplot for benzene PT data from CY2006.**

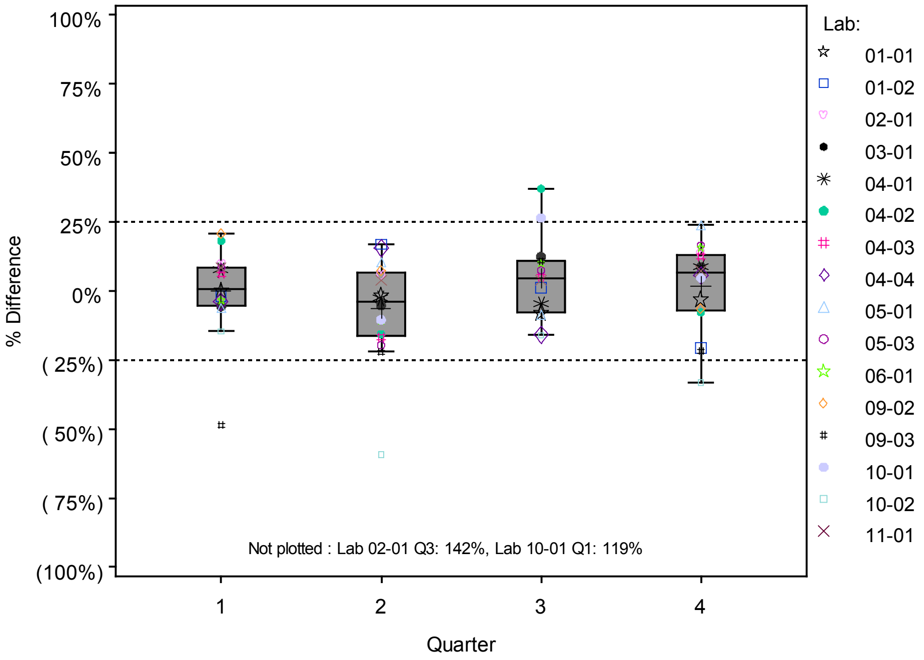

Figure 4. **Laboratory bias boxplot for 1,3-butadiene PT data from CY2006.**

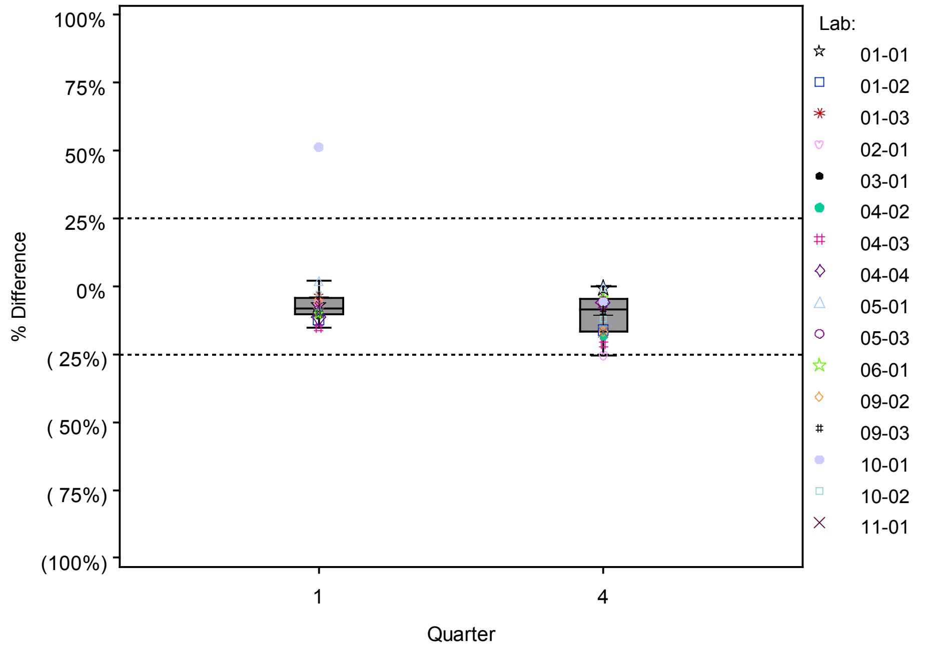

Figure 5. Laboratory bias boxplot for formaldehyde PT data from CY2006.

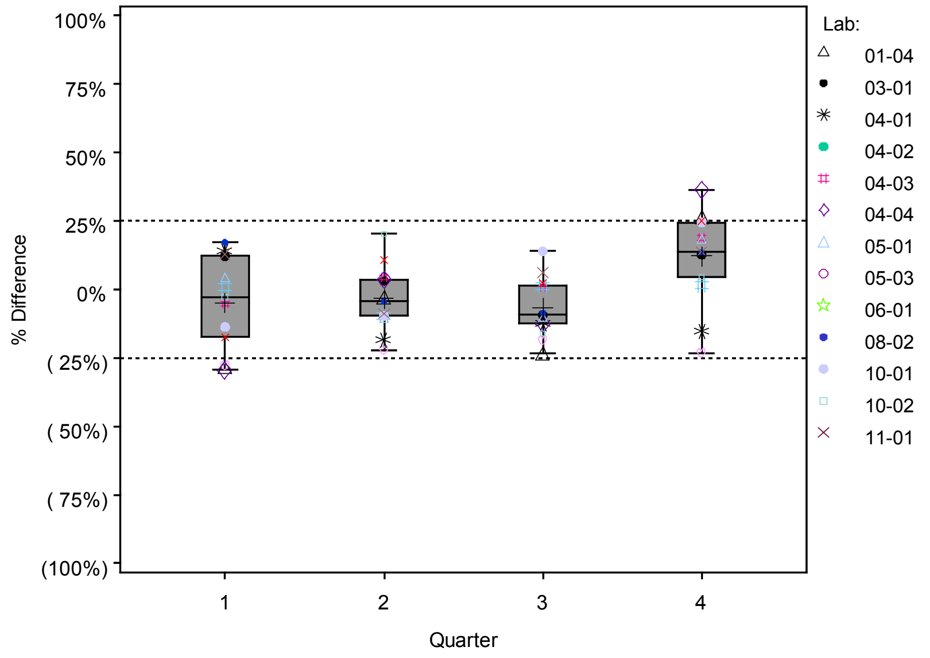

Figure 6. Laboratory bias boxplot for arsenic PT data from CY2006.

Participation in the Calendar Year 2006 laboratory PT program by all NATTS-affiliated laboratories was 100 percent for VOCs and carbonyls (see Table 10). Moreover, all of the metals laboratories that currently analyze samples for NATTS sites (13 in all) participated in every quarterly PT audit. However, overall participation for metals is lower compared to the other sample types because several sites did not analyze metals samples in CY2006. As such, these sites could not participate in the PT program. The sites include those in New York state, Underhill, Vermont, Phoenix, Arizona, and San Jose, California.

Table 10. Participation in PT program by quarter for CY2006.

Compound Class	Quarter, CY 2006			
	1	2	3	4
VOCs	100%	100%	100%	100%
Carbonyls	100%	--	--	100%
Metals	76%	76%	76%	76%

2.5. Field Bias Data from Flow Audits Performed During IPAs

Three NATTS field sites were audited during calendar year 2006. The IPA focuses on the sampling that occurs at the NATTS station. Flow rates through all three sampler types are confirmed using certified flow, temperature, and pressure instruments.

Flows were measured using a calibrated volumetric flow measurement device. Subsequently, the measured volumetric flow rates were corrected to the standard conditions of 25 C and 1 atm. Comparison of the site flow rate (also corrected to standard conditions) to the flow measured during the IPA allow for the calculation of what can be termed field bias. In this case, field bias is defined as the percent difference between the corrected site flow (Fs_c) and the corrected audit flow (Fa_c):

$$\%Difference = \frac{Fs_C - Fa_C}{Fa_C} \cdot 100 \qquad \text{(Eq. 2.5.1)}$$

The results from the flow audits conducted at three NATTS sites during calendar year 2006 are shown in Table 11. The sampling techniques are shown in column 2. The canister method signifies a VOC sampler; carbonyl indicates sampling onto cartridges for aldehydes; and PM_{10} represents filter sampling for PM_{10} metals. Every NATTS site is supposed to have at least one of each sampler type, which is designated as the primary sampler in column 3. If present, collocated samplers are also flow audited, and are designated as such in column 3. Canister and carbonyl samplers may have more than one flow channel in order to accommodate the collection of duplicate samples. If a NATTS site routinely collects a duplicate sample using a single sampler, but through a different flow channel, then this second flow channel was also subjected to a flow audit. PM_{10} samplers cannot have secondary flow channels and, hence, are marked with "NA" (not applicable) in column 4. The percent difference (field bias) as defined above is given in column 5.

Table 11. Flow audit results from 2006 Instrument Performance Audits.

Site Identifier	Method	Monitor	Channel	% Difference
Washington, DC	Canister	Primary	1	4.6
	Carbonyl	Primary	1	2.8
	Carbonyl	Primary	2	0.3
	PM10	Primary	NA	9.7
Chesterfield, SC	Canister	Primary	1	8.3
	Canister	Collocated	1	22.3
	Carbonyl	Primary	1	-0.2
	Carbonyl	Collocated	1	-2.9
	PM10	Primary	NA	7.8
	PM10	Collocated	NA	3.0
San Jose, CA	Canister	Primary	1	-1.5
	Carbonyl	Primary	1	0.2
	PM10	Primary	NA	-1.3

A summary of the IPA flow results is given in Figure 7. On the ordinate is given the absolute percent difference in flow rate (the absolute value of the field bias in Table 11, column 5). All but one of the 13 flow rate measurements were within ±10 percent of the audit flow rate.

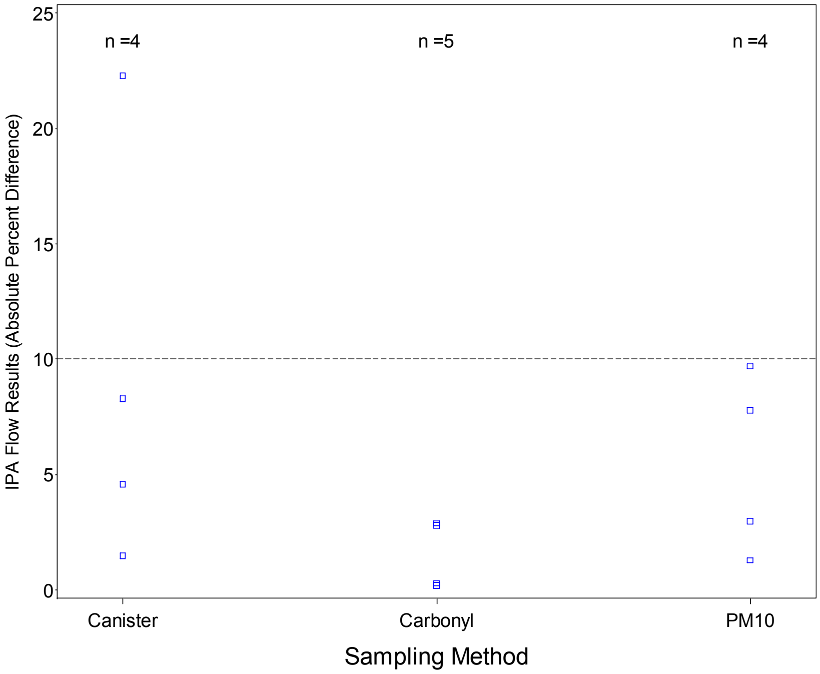

Figure 7. Summary of Instrument Performance Audit flow results sorted by sampling method. The number of observations is given by n.

While it is important that flow rates of carbonyl and PM_{10} samplers are accurate, the absolute accuracy of canister sampler flow rates are less important since these flows do not directly affect the outcome of the VOC concentration measurements. For VOC sampling, what matters most is whether the flow rate remains constant over the 24-hour sampling period to ensure collection of truly representative time-integrated samples. Although flow rate constancy over 24 hours is not explicitly verified during the field bias flow audit, the field bias flow audit of a VOC sampler flow rate may be interpreted as a spot check performed to assess whether the flow rate selected by site staff is in fact the actual sampler flow rate used in the field on the sampling instrument.

2.6 Method Detection Limit (MDL) Data

MDL data were requested from the points-of-contact at all 23 NATTS field sites for all three sample types: VOCs, carbonyls, and metals. Different information was requested depending on the sample type, but the fundamental objective for each was the same; i.e., to calculate the overall sampling and analytical MDL for each of the 23 HAPS listed in Table 2. This process was facilitated through a series of e-mail exchanges and telephone calls with NATTS station managers and analysts, as well as with QA personnel at laboratories affiliated with the NATTS sites. The required information was gathered, scrutinized for obvious errors, overall MDLs were calculated, converted to the appropriate units, and tabulated. The results are shown in Table 12. The marker “N/A” indicates where MDL information was unavailable because such compounds are not presently being analyzed at a particular laboratory.

Although referred to as overall sampling and analytical MDLs, the values tabulated in Table 12 are actually theoretical MDL values based on a calculation using the analytical MDLs and dilution factors (for VOCs, if applicable), other analysis parameters (extraction or digestion volumes), and average sampler flow rates, as discussed in the remainder of this section. Determining actual MDLs is a much more involved, difficult, and expensive process that requires challenging a sampler with a known amount of gas-phase analyte followed by extraction/digestion (if appropriate), and instrumental analysis.

Table 12. Method detection limits (MDLs) by site for the year 2006 for the 23 HAPs. HAPs are given by number (see Table 2 for cross-reference). MDLs for compounds 1-16 and 17-23 are in $\mu g/m^3$ and ng/m^3, respectively.

Site Identifier	1	2	3	4	5	6	7	8	9	10	11	12
Boston-Roxbury, MA	2.9E-02	2.7E-02	1.0E-01	7.3E-02	2.1E-01	5.5E-02	7.7E-02	5.6E-02	4.9E-01	1.8E-01	1.3E-01	4.1E-02
Underhill, VT	2.7E-01	1.9E-01	7.5E-01	3.7E-01	6.1E-01	3.1E-01	3.5E-01	3.1E-01	2.3E-01	7.1E-01	4.1E-01	2.0E-01
Providence, RI	2.9E-02	2.7E-02	1.0E-01	7.3E-02	2.1E-01	5.5E-02	7.7E-02	5.6E-02	4.9E-01	1.8E-01	1.3E-01	4.1E-02
Bronx, NY	9.6E-02	1.1E-01	1.9E-01	1.5E-01	1.5E-01	1.4E-01	8.1E-02	1.0E-01	2.1E-01	2.0E-01	2.1E-01	3.1E-01
Rochester, NY	9.6E-02	1.1E-01	1.9E-01	1.5E-01	1.5E-01	1.4E-01	8.1E-02	1.0E-01	2.1E-01	2.0E-01	2.1E-01	3.1E-01
Washington, DC	1.9E-02	3.3E-02	1.0E-01	7.3E-02	1.2E-01	7.9E-02	4.0E-02	4.9E-02	1.2E-01	4.1E-02	5.4E-02	4.1E-02
Chesterfield, SC	3.0E-01	2.0E-01	6.0E-01	5.0E-01	8.0E-01	5.0E-01	4.0E-01	4.0E-01	7.0E-01	7.0E-01	5.0E-01	3.0E-01
Decatur, GA	1.2E-01	6.6E-02	2.0E-01	2.0E-01	2.2E-01	2.6E-01	1.9E-01	2.3E-01	2.1E-01	1.9E-01	2.0E-01	6.1E-02
Hazard, KY	7.7E-01	5.3E-01	1.5E+00	1.2E+00	1.8E+00	1.1E+00	9.6E-01	8.2E-01	1.6E+00	1.6E+00	1.3E+00	6.0E-01
Hillsbrgh Cty, Tampa, FL	8.3E-02	9.0E-02	2.0E-01	1.6E-01	2.3E-01	1.6E-01	8.7E-02	2.1E-01	2.2E-01	1.6E-01	1.3E-01	1.3E-01
Pinellas Cty, Tampa, FL	8.3E-02	9.0E-02	2.0E-01	1.6E-01	2.3E-01	1.6E-01	8.7E-02	2.1E-01	2.2E-01	1.6E-01	1.3E-01	1.3E-01
Dearborn, MI	1.7E-02	1.3E-02	5.6E-02	1.8E-02	1.4E-01	1.5E-01	5.9E-02	5.9E-02	8.9E-02	7.2E-02	5.1E-02	2.0E-02
Mayville, WI	3.2E-01	2.2E-01	6.3E-01	4.9E-01	7.7E-01	4.6E-01	4.0E-01	3.5E-01	6.9E-01	6.8E-01	5.4E-01	2.6E-01
Northbrook, IL	1.7E-02	1.3E-02	5.6E-02	1.8E-02	1.4E-01	1.5E-01	5.9E-02	5.9E-02	8.9E-02	7.2E-02	5.1E-02	2.0E-02
Deer Park, TX	2.3E-01	2.0E-01	7.3E-01	3.9E-01	1.5E+00	7.9E-01	1.4E+00	4.9E-01	6.0E-01	5.4E-01	4.1E-01	2.3E-01
Harrison County, TX	2.3E-01	2.0E-01	7.3E-01	3.9E-01	1.5E+00	7.9E-01	1.4E+00	4.9E-01	6.0E-01	5.4E-01	4.1E-01	2.3E-01
St. Louis, MO	1.7E-02	1.3E-02	5.6E-02	1.8E-02	1.4E-01	1.5E-01	5.9E-02	5.9E-02	8.9E-02	7.2E-02	5.1E-02	2.0E-02
Bountiful, UT	1.7E-02	1.3E-02	5.6E-02	1.8E-02	1.4E-01	1.5E-01	5.9E-02	5.9E-02	8.9E-02	7.2E-02	5.1E-02	2.0E-02
Grand Junction, CO	6.7E-02	1.0E-01	2.5E-01	1.4E-01	2.5E-01	1.3E-01	1.1E-01	1.4E-01	2.5E-01	1.7E-01	2.2E-01	1.0E-01
Phoenix, AZ	6.4E-02	4.4E-02	1.3E-01	9.8E-02	1.5E-01	9.2E-02	8.1E-02	6.9E-02	1.4E-01	1.4E-01	1.1E-01	5.1E-02
San Jose, CA	1.6E-01	8.8E-02	1.3E-01	9.8E-02	7.7E-02	N/A	8.1E-01	3.5E-01	N/A	6.8E-02	1.1E-01	N/A
La Grande, OR	2.9E-01	4.2E-01	3.0E-01	4.5E-01	4.6E-01	4.1E-01	5.1E-01	2.6E-01	4.5E-01	4.0E-01	4.7E-01	1.6E-01
Seattle, WA	7.5E-02	4.4E-02	4.3E-02	4.1E-02	N/A	8.3E-02	N/A	7.0E-02	N/A	8.3E-02	5.4E-02	N/A
Geometric Mean	8.3E-02	7.2E-02	1.9E-01	1.2E-01	2.9E-01	2.0E-01	1.7E-01	1.5E-01	2.6E-01	2.0E-01	1.7E-01	9.6E-02
Arithmetic Mean	1.5E-01	1.2E-01	3.2E-01	2.3E-01	4.6E-01	2.9E-01	3.4E-01	2.2E-01	3.7E-01	3.1E-01	2.6E-01	1.6E-01
Median	8.3E-02	9.0E-02	1.9E-01	1.5E-01	2.1E-01	1.5E-01	8.7E-02	1.4E-01	2.2E-01	1.8E-01	1.3E-01	1.3E-01

Table 12. (Continued).

Site Identifier	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**
Boston-Roxbury, MA	7.7E-02	7.3E-02	3.7E-02	3.6E-02	2.6E-02	2.9E-02	2.3E-02	8.1E-02	1.5E-01	2.5E-01	2.2E-01
Underhill, VT	3.3E-01	3.2E-01	1.4E-02	2.0E-02	1.4E+00	3.0E-02	1.4E-01	1.7E+00	3.4E-01	N/A	8.5E-01
Providence, RI	7.7E-02	7.3E-02	3.8E-02	2.6E-02	2.3E+00	1.1E+00	5.5E-01	1.1E+00	1.1E+00	N/A	1.1E+00
Bronx, NY	9.1E-02	1.4E-01	8.6E-03	7.2E-03	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Rochester, NY	9.1E-02	1.4E-01	8.6E-03	7.2E-03	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Washington, DC	5.9E-02	8.6E-02	2.1E-02	1.3E-02	5.3E-01	2.2E-01	1.4E-01	6.5E-01	6.4E-01	N/A	8.2E-01
Chesterfield, SC	5.0E-01	5.0E-01	1.7E-01	1.7E-01	3.1E-02	1.5E-03	1.1E-03	2.7E-03	2.3E-03	N/A	2.8E-03
Decatur, GA	1.8E-01	1.6E-01	7.0E-01	7.9E-01	5.6E-01	6.3E-02	3.1E-02	1.3E-01	1.9E-01	N/A	2.5E-01
Hazard, KY	1.1E+00	1.1E+00	5.0E-02	6.8E-02	1.7E+00	8.3E-01	8.3E-01	8.3E-01	8.3E-01	N/A	8.3E-01
Hillsbrgh Cty, Tampa, FL	1.1E-01	9.9E-02	7.4E-03	9.5E-03	1.4E+00	9.9E-02	3.2E-01	8.1E-01	1.9E-01	N/A	4.9E+00
Pinellas Cty, Tampa, FL	1.1E-01	9.9E-02	6.6E-03	8.6E-03	1.3E+00	9.4E-02	3.1E-01	7.7E-01	1.8E-01	N/A	4.6E+00
Dearborn, MI	5.6E-02	4.2E-02	6.5E-03	8.4E-03	9.3E-02	9.2E-02	9.2E-02	1.3E-01	1.9E-01	N/A	1.3E-01
Mayville, WI	4.5E-01	4.5E-01	7.2E-02	7.7E-02	4.1E-02	1.5E-02	1.6E-02	6.1E-03	2.2E-02	N/A	1.4E-01
Northbrook, IL	5.6E-02	4.2E-02	3.4E-03	4.4E-03	2.4E-02	2.7E-02	2.1E-02	7.4E-02	1.4E-01	2.3E-01	2.0E-01
Deer Park, TX	3.3E-01	3.9E-01	8.0E-02	1.5E-01	2.2E+00	N/A	N/A	N/A	N/A	N/A	N/A
Harrison County, TX	3.3E-01	3.9E-01	8.0E-02	1.5E-01	2.2E+00	N/A	N/A	N/A	N/A	N/A	N/A
St. Louis, MO	5.6E-02	4.2E-02	6.0E-03	7.7E-03	2.7E-02	3.0E-02	2.3E-02	8.4E-02	1.5E-01	2.6E-01	2.3E-01
Bountiful, UT	5.6E-02	4.2E-02	8.0E-03	1.0E-02	3.7E-01	2.6E-01	2.7E-01	4.9E-01	4.4E-01	2.4E+00	1.1E+00
Grand Junction, CO	1.1E-01	1.8E-01	1.4E-03	1.8E-03	5.8E+00	7.9E-01	3.0E-01	4.0E-01	5.4E-01	N/A	1.5E+00
Phoenix, AZ	9.1E-02	9.1E-02	1.2E-01	1.8E-01	3.3E-01	2.4E-01	2.4E-01	4.4E-01	4.0E-01	2.1E+00	9.6E-01
San Jose, CA	4.5E-01	4.5E-01	9.9E-02	9.9E-02	N/A	N/A	N/A	N/A	N/A	N/A	N/A
La Grande, OR	4.2E-01	3.7E-02	2.5E-02	3.4E-02	3.5E-03	3.5E-03	3.5E-02	3.5E-01	3.5E-01	N/A	3.5E-01
Seattle, WA	N/A	N/A	9.5E-03	8.0E-03	6.6E-03	3.3E-03	2.9E-03	3.8E-02	5.5E-02	N/A	5.9E-02
Geometric Mean	1.5E-01	1.4E-01	2.3E-02	2.6E-02	2.4E-01	6.0E-02	6.8E-02	1.9E-01	1.9E-01	6.0E-01	4.0E-01
Arithmetic Mean	2.3E-01	2.2E-01	6.9E-02	8.2E-02	1.0E+00	2.2E-01	1.9E-01	4.5E-01	3.3E-01	1.1E+00	1.0E+00
Median	1.1E-01	1.2E-01	2.1E-02	2.0E-02	4.5E-01	7.7E-02	1.2E-01	3.8E-01	1.9E-01	2.6E-01	5.9E-01

For all three sample types, the analytical MDLs for the 23 compounds of interest were requested. Starting with these values, the overall sampling and analytical MDLs could be calculated given sufficient additional information depending on the sampler type. However, some laboratories simply provided overall sampling and analytical MDLs without further information. In many of these cases, the additional information described below was requested and received so that a consistent dataset was gathered and calculations could be verified. However, in some cases, only overall MDL information was received and reported. Shown in Table 13 are the laboratories that performed the analyses of the different sample types for the 23 NATTS sites for calendar year 2006.

In Table 14, the abbreviations used in Table 13 are given along with the full names of the laboratories.

Table 13. Laboratories performing analyses for the three different compound types for each of the NATTS sites in 2006. (See Table 14 for abbreviation cross-reference.)

Site Identifier	VOCs	Carbonyls	Metals
Boston-Roxbury, MA	RIDOH	MADEP	ERG
Underhill, VT	VTDEC	VTDEC	None
Providence, RI	RIDOH	RIDOH	EPAR1
Bronx, NY	NYSDEC	NYSDEC	None
Rochester, NY	NYSDEC	NYSDEC	None
Washington, DC	MDDE	PAMSL	WVDEP
Chesterfield, SC	SCDHEC	SCDHEC	SCDHEC
Decatur, GA	GADNR	GADNR	GADNR
Hazard, KY	KYDES	KYDES	KYDES
Hillsborough Cty, Tampa, FL	PCDEM	ERG	EPCHC
Pinellas Cty, Tampa, FL	PCDEM	ERG	EPCHC
Dearborn, MI	MDEQ/ERG	MDEQ	MDEQ
Mayville, WI	WSLH	WSLH	WSLH
Northbrook, IL	ERG	ERG	ERG
Deer Park, TX	TCEQ	TCEQ	TCEQ
Harrison County, TX	TCEQ	TCEQ	TCEQ
St. Louis, MO	ERG	ERG	ERG
Bountiful, UT	ERG	ERG	ERG
Grand Junction, CO	ERG	ERG	CDHE
Phoenix, AZ	SDAPCD	SDAPCD	None
San Jose, CA	BAAQMD	BAAQMD	None
La Grande, OR	ODEQ	ODEQ	ODEQ
Seattle, WA	RJLCLS	RJLCLS	RJLCLS

Table 14. Abbreviations and full names of laboratories performing analyses of NATTS samples.

Laboratory Abbreviation	Full Name of Analytical Laboratory
BAAQMD	Bay Area Air Quality Management District
CDHE	Colorado Department of Health and Environment
EPAR1	Environmental Protection Agency Region 1 Laboratories
EPCHC	Environmental Protection Commission of Hillsborough County
ERG	Eastern Research Group
GADNR	Georgia Department of Natural Resources
KYDES	Kentucky Division of Environmental Services
MADEP	Massachusetts Department of Environmental Protection
MDDE	Maryland Department of the Environment
MDEQ	Michigan Department of Environmental Quality
NYSDEC	New York State Department of Environmental Conservation
ODEQ	Oregon Department of Environmental Quality
PAMSL	Philadelphia Air Management Services Laboratory
PCDEM	Pinellas County Department of Environmental Management
RIDOH	Rhode Island Department of Health
RJLCLS	RJ Lee Group Center for Laboratory Sciences
SCDHEC	South Carolina Department of Health and Environmental Control
SDAPCD	San Diego Air Pollution Control Division
TCEQ	Texas Commission on Environmental Quality
VTDEC	Vermont Department of Environmental Conservation
WSLH	Wisconsin State Laboratory of Hygiene
WVDEP	West Virginia Department of Environmental Protection

For the VOCs, the amount that the canisters are diluted prior to analysis is required to calculate overall MDLs from analytical MDLs. The overall sampling and analytical MDL is linearly proportional to the analytical MDL, where the constant of proportionality is the dilution factor. Certain laboratories pressurize canisters with zero-grade nitrogen or air in preparation for analysis. However, others simply analyze canisters at subatmospheric pressure without further dilution. The dilution factor is calculated as follows: if the canister is received at a pressure of 10 psia (pounds per square inch absolute) and pressurized to 20 psia = 5.3 psig (pounds per square inch gauge), then the dilution factor is 20 psia/10 psia = 2. Hence, in this instance, the overall MDL is twice that of the analytical MDL.

Many of the laboratories reported their VOC MDLs in units of ppb (parts per billion by volume). Conversion to the preferred units of $\mu g/m^3$ was performed using the standard conditions of 25 C, 1 atm pressure.

For the carbonyls, in addition to the analytical MDL in units of mass per unit liquid volume, knowledge of three other parameters is required in order to determine overall MDLs. The first is the extraction volume, which is the total volume of liquid solvent used to extract the carbonyls from the sampling cartridge. The second is the average sampling time, which for the NATTS program should always be approximately 24 hours = 1,440 minutes. The final datum needed is the average volumetric flow rate through the carbonyl cartridge, preferably corrected to the standard conditions of 25 C, 1 atm, or with the average conditions of temperature and pressure reported so that correction can be made to standard conditions. If A_{MDL} is a compound-specific analytical MDL in μg/mL, V_E the extraction volume in mL, t the average sampling time in minutes, and F is the average volumetric flow rate through the carbonyl cartridge in m^3/min, then

$$O_{MDL} = \frac{A_{MDL} \cdot V_E}{t \cdot F} \qquad \text{(Eq. 2.6.1)}$$

where O_{MDL} is the compound-specific overall MDL in μg/m^3.

Calculation of the overall metals MDL is performed similarly. Along with compound-specific analytical MDLs, four additional parameters are needed. As with the carbonyls, the average sampling time and typical average sampler flow rate are required. Moreover, final volume of acid into which the filter is digested and metal ions diluted are required to calculate the overall MDL. Specific to PM_{10} metals analysis, however, is that a certain fraction of the quartz fiber filter is cut and digested for analysis. (Note that only high-volume filters are cut; several NATTS sites now use low-volume 47 mm filters that are not subsampled.) If A_{MDL} is a compound-specific analytical MDL in ng/mL, V_D is the digestion volume in mL, f is the fraction of filter digested, t is the average sampling time in minutes, and F is the average volumetric flow rate through the metals sampler in m^3/min, then

$$O_{MDL} = \frac{A_{MDL} \cdot V_D}{f \cdot t \cdot F} \qquad \text{(Eq. 2.6.2)}$$

where O_{MDL} is the compound-specific overall MDL in ng/m^3.

Of particular importance is the use of the correct value of the filter fraction. One should only consider the parts of the filter actually covered with particulate matter. For instance, if after sampling the typical 8- x 10-inch filter has a border 1 inch wide around the outer filter edge where no particulate matter was collected, then the total sampled area is 6 inches by 8 inches (48 in^2). Assuming that a 1- x 8-inch strip is cut from across the width of the filter, and realizing that along only 6 of the 8 inches will particulate matter be present, then this strip represents 6 in^2 / 48 in^2 = 1/8 of the sampled area of the filter and $f = 0.125$. (For low-volume 47 mm filters, the entire filter is digested, thus, $f = 1$.)

The box and whisker plots shown in Figures 8 and 9 depict graphically, by compound, and taken across all laboratories, the overall MDLs for the organic compounds (VOCs and carbonyls) and the metals, respectively. Shown are the mean, median, interquartile range, overall range, and location of any data outliers (data points that lie further than 1.5 times the interquartile range from the upper or lower quartile). Note the log scale on the ordinate of both plots. Otherwise, these figures are in the same format as Figures 1 and 3 through 6. See Table 2 for the cross-reference between compound number, name, and AQS compound code.

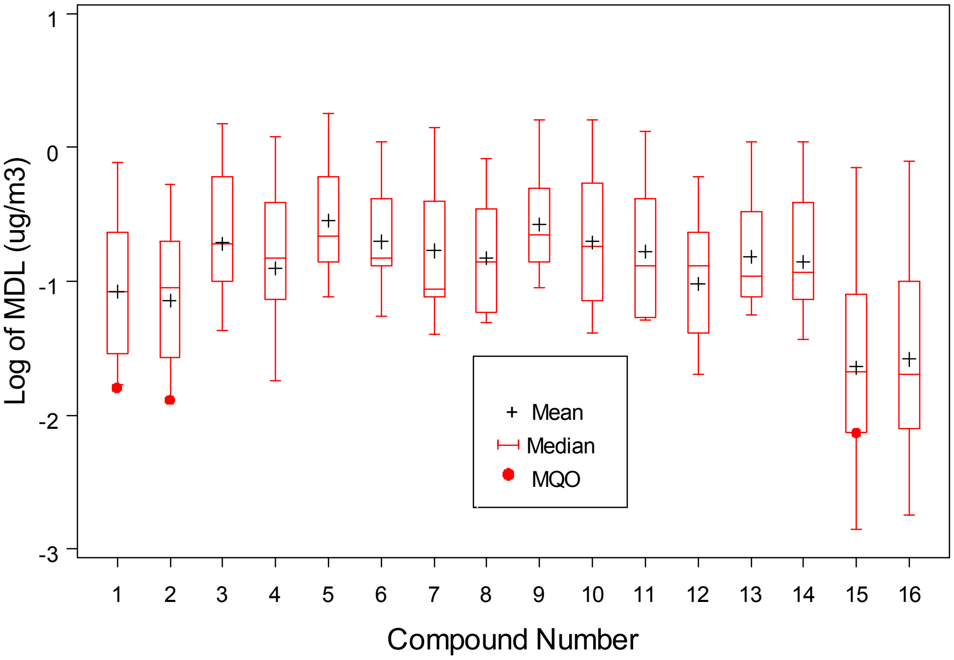

Figure 8. **Box and whisker plot of the VOC and carbonyl MDLs across all the NATTS sites. Also plotted are the MQOs for benzene, 1,3-butadiene, and formaldehyde.**

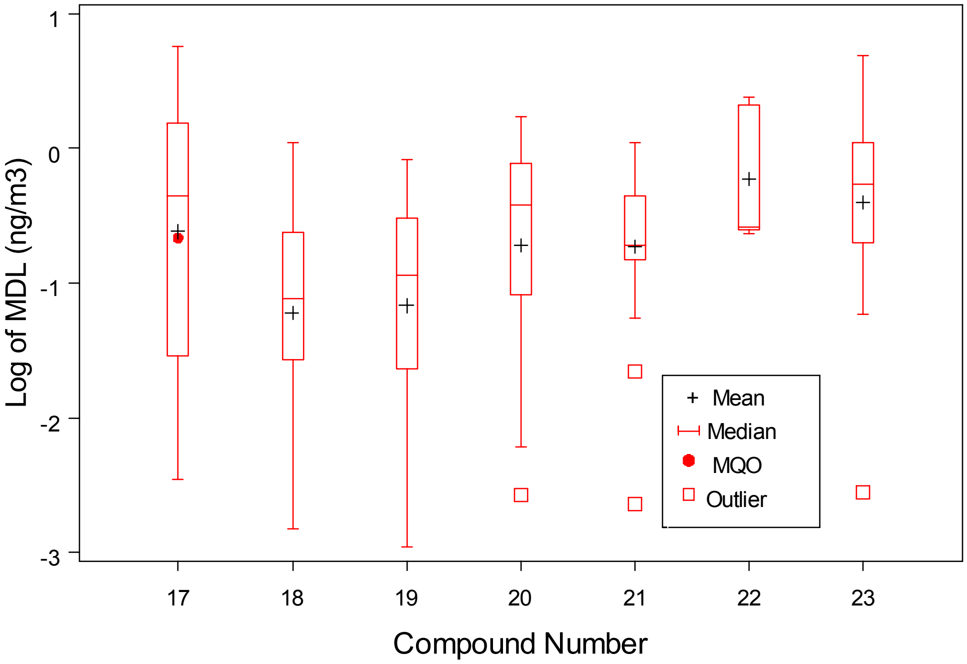

Figure 9. **Box and whisker plot of the metals MDLs across all of the NATTS sites. Also shown is the MQO for arsenic.**

The MDL data for individual laboratories, in addition to the mean across all laboratories reporting data, are presented graphically in Figures 10 and 11.

For CY2006, four sites (Hazard, Kentucky, Grand Junction, Colorado, Bountiful, Utah, and Phoenix, Arizona) collected low-volume PM_{10} metals samples on 47 mm Teflon filters. Of particular note is that target detectability of PM_{10} metals collected by high-volume sampling onto quartz 8- x 10-inch filters is quite comparable to low-volume sampling on 47 mm Teflon filters. See Table 15 for a comparison of detectability by sampling technique. Thus, for this report, all metals data were combined and treated without distinction to how metals sampling was performed.

Table 15. Comparison of high-volume and low-volume target PM_{10} metals detectability in mass/volume based on typical sampling parameters and target mass/filter MDLs given in the NATTS TAD.

Compound	Calculated MDLs, ng/m^3		High-volume to low-volume MDL ratio
	8- x 10-inch Quartz, high-volume sampling	47 mm Teflon, low-volume sampling	
Arsenic	0.217	0.329	0.66
Beryllium	0.244	0.237	1.03
Cadmium	0.186	0.241	0.77
Lead	0.672	0.437	1.54
Manganese	1.233	0.395	3.12
Mercury	2.088	2.137	0.98
Nickel	1.804	0.961	1.88

Note: Based on (1) high-volume sampling rate of 1.13 m^3/min and $f = 0.125$; (2) low-volume sampling rate of 16.7 L/min and $f = 1$; (3) sampling time of 24 hours; and (4) target metals MDLs in ng/filter as given in Table 4.3-2 of NATTS TAD [2].

As shown in Table 16, across all laboratories, the mean and median MDL for benzene, 1,3-butadiene, formaldehyde, and arsenic all exceed the target MDLs (the MQOs) given in and calculated from values in the most recent version of the NATTS TAD [2] (see Table 3). Ratios of geometric mean MDLs reported by NATTS sites to the target MDLs range from a factor of 1.1 for arsenic to 5.5 for 1,3-butadiene.

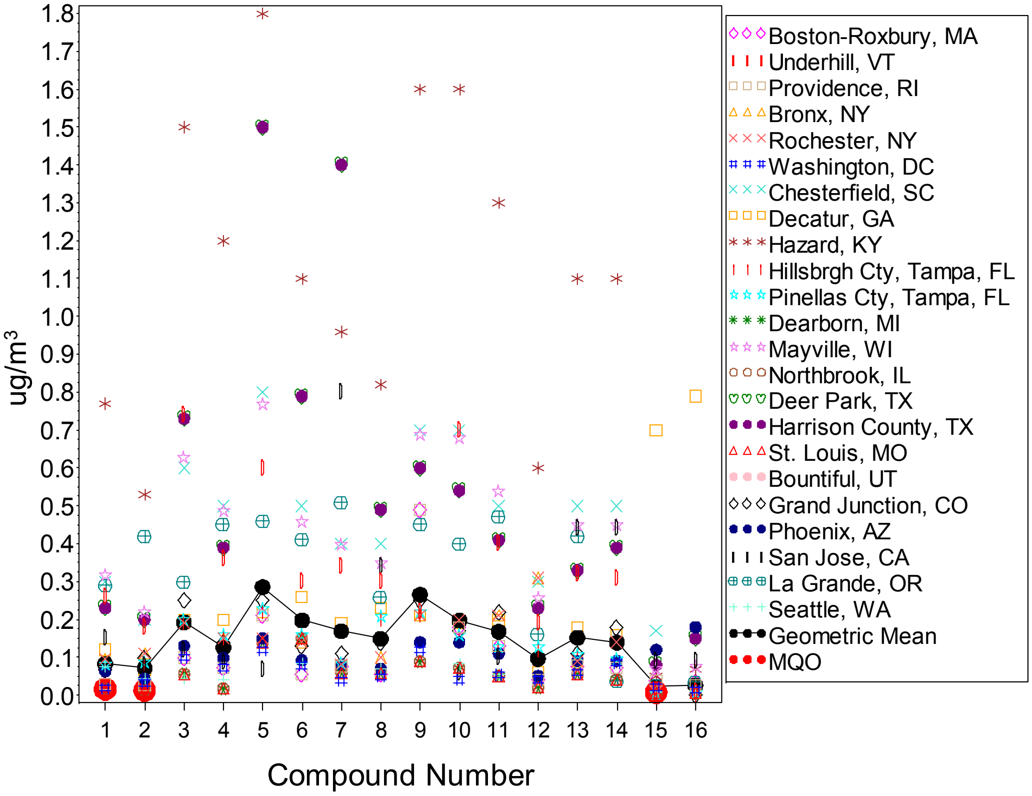

Figure 10. **Plot of the VOC and carbonyl MDLs for all of the NATTS sites. The geometric mean MDL for each compound is also shown. Moreover, MQOs for benzene, 1,3-butadiene, and formaldehyde are plotted.**

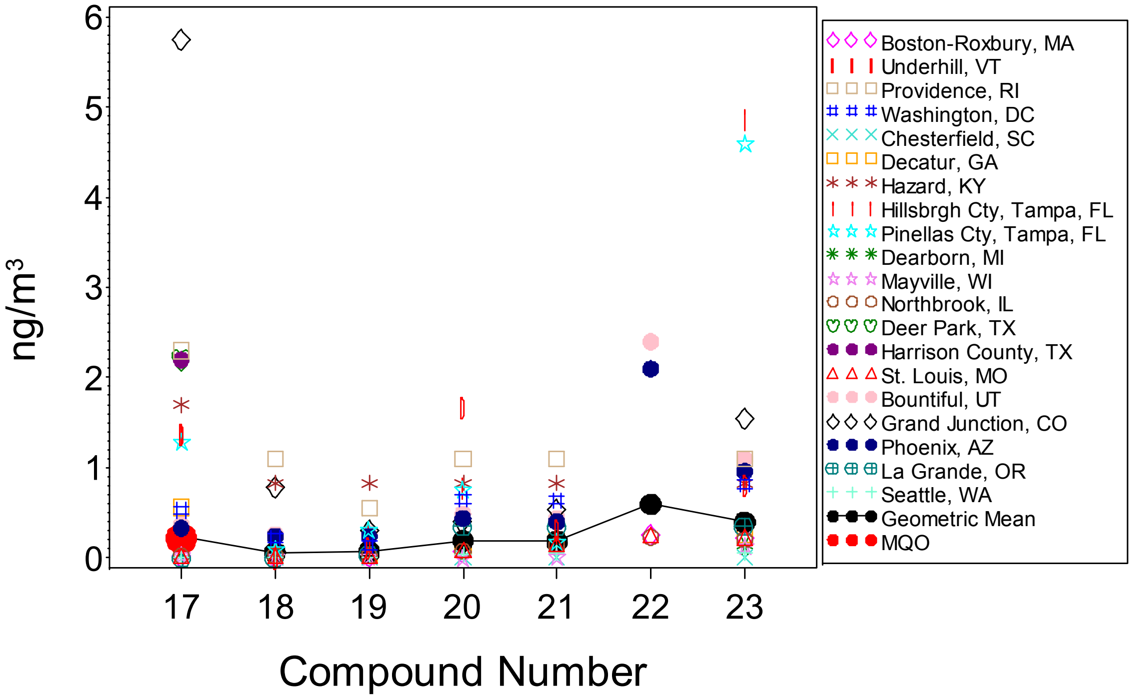

Figure 11. **Plot of the metals MDLs for all of the NATTS sites. The geometric mean MDL for each compound is also shown. The MQO for arsenic is also plotted.**

Table 16. **Geometric and arithmetic means, and median CY2006 MDLs across all NATTS laboratories for four compounds, and relevant detectability MQOs from Table 3.**

MDL	Compound			
	Benzene, µg/m^3	1,3-butadiene, µg/m^3	formaldehyde, µg/m^3	arsenic, ng/m^3
Geometric Mean	0.083	0.072	0.0228	0.240
Arithmetic Mean	0.147	0.124	0.0688	1.003
Median	0.083	0.090	0.0212	0.447
MQO	0.016	0.013	0.0074	0.217
Ratio of Geo Mean to MQO	5.2	5.5	3.1	1.1

3.0 SUMMARY

For calendar year 2006, across the entire NATTS network, and for the four target compounds (benzene, 1,3-butadiene, formaldehyde, and arsenic):

- Mean completeness of AQS data from the NATTS sites was 87 percent for benzene and 1,3-butadiene, and 88 percent for formaldehyde, all of which meet the NATTS DQO goal. However, mean completeness of the arsenic data was below goal at 70 percent. Median completeness values were all greater than 85 percent.

- In general, analytical and overall precision meet the MQO goal of a CV less than 15 percent. Only the overall precision of formaldehyde (19%) and arsenic (17%) exceeded the MQO goal. Much more precision data are available when duplicate and collocated data contained in raw data transactions are accessed, although reduction of such data requires knowledge of site-specific POC values. To simplify future, precision calculations, POC values should be standardized across the NATTS network. A simplified POC system would assign primary data to POC 1, duplicate data to POC 2, and collocated data to POC 3.

- Mean laboratory bias met the DQO of less than 25 percent for all four compounds. Maximum participation in the PT program was achieved for VOCs and carbonyls, but improvement is still needed for metals. All sites that analyzed metals in CY2006 participated in the PT program; however, several sites were collecting but not analyzing metals samples and, as such, could not participate in the PT program.

- Flow rates measured during IPAs at NATTS field sites demonstrated that field bias is acceptably low. Only one out of the 13 flow rate measurements made in 2006 showed greater than 10 percent bias.

- Mean MDLs across all NATTS sites for all compounds remain greater than target MDLs (the MQOs) given in the NATTS TAD. Ratios of geometric mean MDLs reported by NATTS sites to the target MDLs range from a factor of 1.1 for arsenic to 5.5 for 1-3-butadiene.

4.0 REFERENCES

[1] "Final Draft, July 2004, National Monitoring Strategy, Air Toxics Component." Available at http://www.epa.gov/ttn/amtic/files/ambient/airtox/atstrat804.pdf ; accessed July 26, 2007.

[2] "Technical Assistance Document for the National Ambient Air Toxics Trends and Assessment Program." Eastern Research Group, January 1, 2007.