



**NATIONAL AIR TOXICS TRENDS STATIONS
QUALITY ASSURANCE ANNUAL REPORT
CALENDER YEAR 2007**

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 Spring of 2009, Research Triangle Institute (RTI) prepared a final technical report under Contract No. EP-D-08-047 Work Assignment 0-05, Task 10. The report was prepared for Jeff Curry, Project Officer and Dennis Mikel, Work Assignment Manager within the Office of Air Quality Planning and Standards (OAQPS) in Research Triangle Park, North Carolina. The report was written by Larry Michael and Cary Eaton of RTI. That report was incorporated into this draft final report

Additional work on this report was provided by AQAD staff.

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**Prepared by:
RTI International**

**For:
U.S. Environmental Protection Agency
Office of Air Quality, Planning and Standards
Air Quality Analysis Division
109 TW Alexander Drive
Research Triangle Park, NC 27711**

**Under:
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TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION	1
2.0 NATTS QUALITY ASSURANCE DATA FOR CALENDAR YEAR 2007	2
2.1 Measurement Quality Objectives	4
2.2 Completeness of NATTS Data	6
2.3 Precision of NATTS Data	10
2.3.1 Analytical Precision Results	15
2.3.2 Overall Precision Results	20
2.4 Laboratory Bias Data from Proficiency Testing (PT) Samples	28
2.5 Flow Audits Results from Instrument Performance Audits	33
2.6 Method Detection Limit (MDL) Data	35
3.0 SUMMARY	45
4.0 RECOMMENDATIONS	46
5.0 REFERENCES	47
Appendix A Data Analysis Results for Acrolein	
Appendix B Method Detection Limit Request Letter Sent to Each NATTS-Participating Laboratory	

LIST OF TABLES

Table 1.	NATTS sites with EPA Region numbers and AQS site codes	3
Table 2.	The 23 HAPS Air Pollutants and their AQS parameter codes	4
Table 3.	Measurement Quality Objectives for the NATTS program	5
Table 4.	Data Sources employed for the evaluation of MQOs	5
Table 5.	Percent completeness of the 2007 AQS dataset by site for four HAPs	7
Table 6.	Parameter occurrence codes by NATTS sites and analyte type	12
Table 7.	Laboratories Performing Analyses for the Different Compound Types for Each NATTS Site in 2007	13
Table 8.	Laboratory Abbreviations and Descriptions for NATTS Laboratories	14
Table 9.	Analytical Precision ^a for Replicate Analyses of 2007 NATTS Data	16
Table 10.	Overall Precision (% CV) for Primary and Collocated Samples from 2007.	21
Table 11.	Proficiency Testing Bias Results for Carbonyls in 2007 NATTS Laboratories	29
Table 12.	Proficiency Testing Bias Results for Metals in 2007 NATTS Laboratories	29
Table 13.	Performance Testing Bias Results for VOCs in 2007 NATTS Laboratories	30
Table 14.	Percent Participation in Proficiency Testing Program by Quarter for 2007	33
Table 15.	Flow Audit Results from 2007 Instrument Performance Audits	34

Table 16.	Method Detection Limits by Site and Overall for Calendar Year 2007 (VOCs and Carbonyls: $\mu\text{g}/\text{m}^3$; Metals: ng/m^3).	38
Table 17.	Comparison of Method Detection Limits for High- and Low-Volume Sampling of PM_{10} Metals in 2007.....	44
Table 18.	Summary Statistics for MDLs Across All Reporting NATTS Laboratories for 2007.....	45

LIST OF FIGURES

Figure 1.	Completeness for Arsenic at NATTS Sample Collection Sites in 2007.....	8
Figure 2.	Completeness for Benzene at NATTS Sample Collection Sites in 2007.....	8
Figure 3.	Completeness for 1,3-Butadiene at NATTS Sample Collection Sites in 2007.....	9
Figure 4.	Completeness for Formaldehyde at NATTS Sample Collection Sites in 2007	9
Figure 5.	Analytical Precision Summary for Arsenic at NATTS Sample Collection Sites in 2007	18
Figure 6.	Analytical Precision Summary for Benzene at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).....	18
Figure 7.	Analytical Precision Summary for 1,3-Butadiene at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).....	19
Figure 8.	Analytical Precision Summary for Formaldehyde at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).....	19
Figure 9.	Overall Precision Summary for Arsenic at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).....	26
Figure 10.	Overall Precision Summary for Benzene at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).....	26
Figure 11.	Overall Precision Summary for 1,3-Butadiene at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).....	27
Figure 12.	Overall Precision Summary for Formaldehyde at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).....	27
Figure 13.	Distribution of Laboratory Bias by Quarter for Arsenic Proficiency Testing Data from 2007	31
Figure 14.	Distribution of Laboratory Bias by Quarter for Benzene Proficiency Testing Data from 2007	31
Figure 15.	Distribution of Laboratory Bias by Quarter for 1,3-Butadiene Proficiency Testing Data from 2007.....	32
Figure 16.	Distribution of Laboratory Bias by Quarter for Formaldehyde Proficiency Testing Data from 2007	32
Figure 17.	Summary of Instrument Performance Flow Audit Results By Sample Type and Site Id	34
Figure 18.	Distribution of Method Detection Limits for Carbonyls for 2007 NATTS Data (dotted line indicates MQO target MDL for formaldehyde; $>1.5 \times \text{IQR}$ are identified as stars)....	41

Figure 19.	Distribution of Method Detection Limits for Metals for 2007 NATTS Data (dotted line indicates MQO target MDL for arsenic; $>1.5 \times \text{IQR}$ are identified)	42
Figure 20.	Distribution of Method Detection Limits for VOCs for 2007 NATTS Data (dotted line indicates MQO target MDL for benzene; $>1.5 \times \text{IQR}$ are identified)	43

1.0 INTRODUCTION

As mandated under the Government Performance Results Act, the U.S Environmental Protection Agency is focused on reducing risk of cancer and other serious health effects associated with hazardous air pollutants (HAPS) by achieving a 75% reduction in air toxics emissions chemicals, based on 1993 levels. The current inventory of hazardous air pollutants includes 188 chemicals regulated under the Clean Air Act which have been linked to numerous adverse human health and ecological effects, including cancer, neurological effects, reproductive effects, and developmental effects. Current agency attention is targeting risk reduction associated with human exposure to air toxics.

The National Air Toxics Trends Station (NATTS) network was established to create a database of air quality data toward assessment of progress in reducing ambient concentrations of air toxics and concomitant exposure-associated risk. Presently, the NATTS network consists of 25 stations in the contiguous 48 states, with Los Angeles and Rubidoux, CA added in 2007. To ensure the quality of the data collected under the NATTS network, the U.S. EPA has implemented a Quality System comprised of two primary components: 1.) Technical Systems Audits (TSAs) and 2.) Instrument Performance Audits (IPAs) for both the network stations and the associated sample analysis laboratories. As an integral part of the Quality System, EPA has also instituted quarterly analysis of proficiency testing samples to provide quantitative assessment of laboratory performance and to ensure that sampling and analysis techniques are consistent with precision, bias, and method detection limits specified by the NATTS measurement quality objectives.

This report describes and summarizes the quality assurance (QA) data generated by the NATTS program during calendar year (CY) 2007. For data retrieved from EPA's Air Quality Systems database (AQS), only data collected in 2007 and posted prior to July 1, 2008 are included. Although this report contains substantive information about air concentrations of 23 different chemicals of interest, it focuses primarily on results for four key toxic ambient air constituents: benzene, 1,3-butadiene, formaldehyde, and PM₁₀ arsenic. At the request of EPA, these four pollutants were selected as having particular 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 PM₁₀ metals). It is presumed that if the NATTS program can meet the Data Quality Objectives (DQOs) for these four compounds, the additional 18 compounds of concern will be of comparable quality by virtue of the representativeness of the physicochemical properties and the consistency of the collection and analysis methodologies of these four compounds.

The comprehensive information in this Quality Assurance Annual Report (QAAR) was compiled from data acquired from numerous sources. The following general categories of information are presented:

- Descriptive background information on the AQS site identities, compounds of interest, and measurement quality objectives;
- Assessment of the completeness of the data available in the Air Quality System (AQS) database;
- Precision estimates for, independently, analytical and overall sampling error computed for as many of the 23 applicable compounds and for as many of the 25 NATTS sites as available for calendar year 2007;
- Evaluation of an analytical laboratory's accuracy (or bias), based on analysis of blind audit PT samples for many of the 23 compounds;
- Additionally, field bias data, which are expressed as the differences between actual and measured sampler flow readings for each of the three different sampler types (VOCs, carbonyls, and PM₁₀ metals), are presented for primary and collocated samplers (where available) at the three sites visited during the instrument performance audits conducted during calendar year 2007;
- Method detection limit (MDL) data are presented for each site and/or analytical laboratory. Detailed information regarding MDLs was solicited, directly, from all the NATTS state and local agencies and affiliated laboratories for the 23 compounds of interest.

Where possible, all data analyses were performed in SAS, version 9.1.3. Initial compilation of MDLs, by laboratory, was performed using Microsoft Excel.

2.0 NATTS QUALITY ASSURANCE DATA FOR CALENDAR YEAR 2007

There are 25 sites in the NATTS network. Table 1 presents the EPA Regions in which the sites are located, a descriptive location of the sites (site identifier), the urban or rural character of each site, and the unique AQS identification code.

Table 1. NATTS Sites, EPA Region Numbers, and AQS Site Codes.

EPA 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 County, FL	Urban	12-057-3002
IV	Pinellas County, 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
IX	Rubidoux, CA	Urban	06-065-8001
IX	Los Angeles, CA	Urban	06-037-1103
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 and for Harrison County, Texas. Historical consistency has been maintained for the Grand Junction, Colorado, site where two separate codes are used, one for VOCs and carbonyls (-0018), the other for the metals (-0017). This convention is unique to this site and is based on the fact that the organics and metals samplers are present at two separate physical locations at the sampling site.

The 23 specific and hazardous air pollutants measured in the NATTS program, presented in Table 2 along with their unique AQS identification codes, are compounds that have been identified by EPA as being of significant health concern. These include 15 VOCs, two carbonyls, and six PM₁₀ metals. Succinct abbreviations of each chemical name are provided to facilitate table and figure creation and interpretation throughout this report.

Table 2. The 23 Hazardous Air Pollutants^a and their AQS Parameter Codes.

Analyte Abbreviation	Compound Name	AQS Code
BENZ	benzene	45201
BUTA	1,3-butadiene	43218
CTET	carbon tetrachloride	43804
CLFRM	chloroform	43803
EDB	1,2-dibromoethane	43843
DCP	1,2-dichloropropane	43829
EDC	1,2-dichloroethane	43815
MECL	dichloromethane	43802
TCE1122	1,1,2,2-tetrachloroethane	43818
PERC	tetrachloroethylene	43817
TCE	trichloroethylene	43824
VCM	vinyl chloride	43860
cDCPEN	cis-1,3-dichloropropene	43831
tDCPEN	trans-1,3-dichloropropene	43830
ACRO	acrolein ^b	43505
FORM	formaldehyde	43502
ACET	acetaldehyde	43503
As	arsenic	82103
Be	beryllium	82105
Cd	cadmium	82110
Pb	lead	82128
Mn	manganese	82132
Ni	nickel	82136

^a Mercury has been excluded.

^b All acrolein results are presented in Appendix A.

2.1 Measurement Quality Objectives

Measurement Quality Objectives (MQOs) for completeness, precision, laboratory bias, and method detection limits, established for the NATTS network in order to ensure data quality within the NATTS network, were unchanged from 2006. 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 PM₁₀ 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 ^{3a}
arsenic	> 85 %	< 15 %	< 25 %	0.217 ng/m ^{3b}

^a Assumes a sampling volume of 1,000 L.

^b Assumes high-volume sampling with a sampling volume of 1,627 m³ (1.13 m³/min (40 ft³/min) for 24 hours) and that 1/8 of the sampled area of the filter is extracted for analysis.

As intended by the NATTS network, the MQOs require that:

- (1) sampling occurs every sixth day;
- (2) sampling is successful 85 percent of the time;
- (3) precision, as measured by the coefficient of variation (CV), is within 15 percent based on duplicate and collocated samples;
- (4) laboratory (measurement) bias is less than 25 percent, based on laboratory proficiency testing results.

Furthermore, actual MDLs as reported by the laboratories supporting the NATTS sites, or their sponsoring federal, state, or municipal agencies, are compared to the target MDLs as listed in the January 2007 edition 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. Data Sources Employed for the Evaluation of MQOs.

Measurement Quality Objective	Data Source
Completeness	AQS
Analytical and Overall Precision	AQS
Bias - Laboratory	Proficiency Testing results reported by Alion
Bias - Field	Audits of sampler flow rates
MDL	Federal, state and contract laboratories

Data retrievals from AQS for relevant samples collected in 2007 and uploaded to the AQS database prior to July 1, 2008 were analyzed to assess completeness, and to estimate precision from results of replicate analyses and collocated and duplicate sampling. Proficiency testing (PT) samples were distributed by Alion Science, Inc., U.S.EPA contractor, to participating laboratories for determination of analytical bias. Field bias was evaluated by independent measurement of sampler flow rates with NIST-traceable flowmeters during on-site

Instrument Performance Audits (IPAs). Finally, MDL data were acquired by direct contact with the individual laboratories.

2.2 Completeness of NATTS Data

The AQS database was queried for data records corresponding to relevant samples collected from the 25 NATTS sites during calendar year 2007 and entered into the AQS database prior to July 1, 2008. Data contributed to AQS by participating laboratories after July 1, 2008 are not reflected in the completeness calculations presented in Table 5, below. Specifically, completeness of the 2007 AQS dataset was assessed for four compounds representative of the entire suite of 23 compounds presented previously in Table 2: benzene, 1,3-butadiene, formaldehyde, and arsenic. Based on the NATTS requirement of a 1 in 6 day sample collection frequency, 60 records for the primary parameter occurrence code (POC) would represent 100 percent completeness. For purposes of this completeness calculation, non-detects were counted equivalently with measurable values. Conversely, missing values were not counted toward the percent complete.

Completeness statistics were computed for primary samples or, if the primary measurement was missing, for the collocated samples collected at the same location during the same sampling period. To ensure that only a single record was included for each site and date, the maximum value of the measurements was retained across primary and collocated samples. In this way, if one of the measurements was missing and the other was not detected/measured, the maximum would capture the not detected/measured record. If both primary and collocated records contained a missing value, only one record would be tallied for the completeness count. Finally, if both records contained a not detected or measured value, the larger of the two would be captured for the completeness count. Since sample collection at some locations was performed more frequently to meet the requirements of other sampling networks, or for other specific purposes, only records which occurred at a 1 in 6 sample collection frequency (i.e., days 0, 6, 12, 18, 24, 30, etc.), starting with the first collection date for each site in calendar year 2007, were counted. In cases where the interval of days since the last collection event was greater than 6 (e.g., 9) but the subsequent interval (e.g., 3) summed to a multiple of 6 (in this case, 12), only one of the two sampling events was counted toward completeness. No correction was applied for compound-specific missing data (i.e., the value for benzene was missing but the value for dichloromethane was non-missing). It is assumed that this discrepancy does not significantly distort the percent completeness.

The results of the completeness assessment are presented for each collection location and representative compound in Table 5 and in Figures 1 through 4. Mean and median completeness values across all NATTS laboratories for a given analyte and across all analytes for a given site, are also presented. Where footnoted, in cases where no data were reported, the particular analyte class was not collected at that NATTS site.

Table 5. Percent Completeness of the 2007 AQS Dataset by Site for Four Hazardous Air Pollutants.

AQS Site Id.	Parameter Code → Site Name	82103	45201	43218	43502
		AS	BENZ	BUTA	FORM
25-025-0042	Boston, MA	90	90	90	98
49-011-0004	Bountiful, UT	93	102	102	100
36-005-0110	Bronx, NY	100	100	100	100
45-025-0001	Chesterfield, SC	100	100	100	100
26-163-0033	Dearborn, MI	107	95	95	88
13-089-0002	Decatur, GA	100	100	100	98
48-201-1039	Deer Park, TX	98	100	100	93
08-077-0017	Grand Junction, CO	92	100	100	100
48-203-0002	Harrison County, TX	100	93	93	92
21-193-0003	Hazard, KY	100	100	100	100
41-061-0119	La Grande, OR	93	87	88	83
06-037-1103	Los Angeles, CA	N.C. ^a	87	87	115
55-027-0007	Mayville, WI	82	87	87	37
17-031-4201	Northbrook, IL	97	98	98	100
04-013-9997	Phoenix, AZ	97	88	88	100
12-103-0026	Pinellas County, FL	97	98	98	100
12-057-3002	Hillsborough County, FL	100	100	100	98
44-007-0022	Providence, RI	100	98	98	100
36-055-1007	Rochester, NY	88	100	100	100
06-065-8001	Rubidoux, CA	N.C. ^a	87	87	100
06-085-0005	San Jose, CA	N.C. ^a	85	85	100
53-033-0080	Seattle, WA	100	100	100	100
29-510-0085	St. Louis, MO	98	100	100	100
50-007-0007	Underhill, VT	N.C. ^a	100	100	97
11-001-0043	Washington, DC	100	98	72	N.C. ^a
	<i>Mean</i>	96	96	95	96
	<i>Std. Dev.</i>	6	6	7	14
	<i>Median</i>	98	98	98	100

^a Not collected at this site.

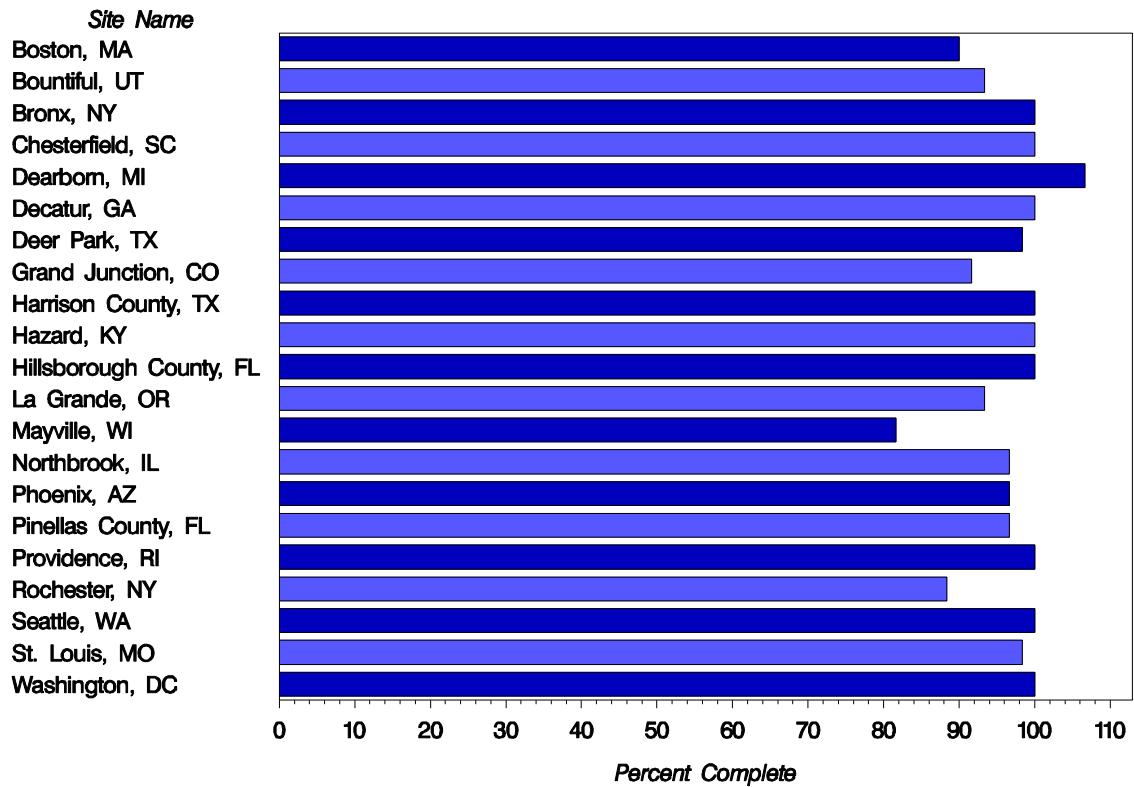


Figure 1. Completeness for Arsenic at NATTS Sample Collection Sites in 2007.

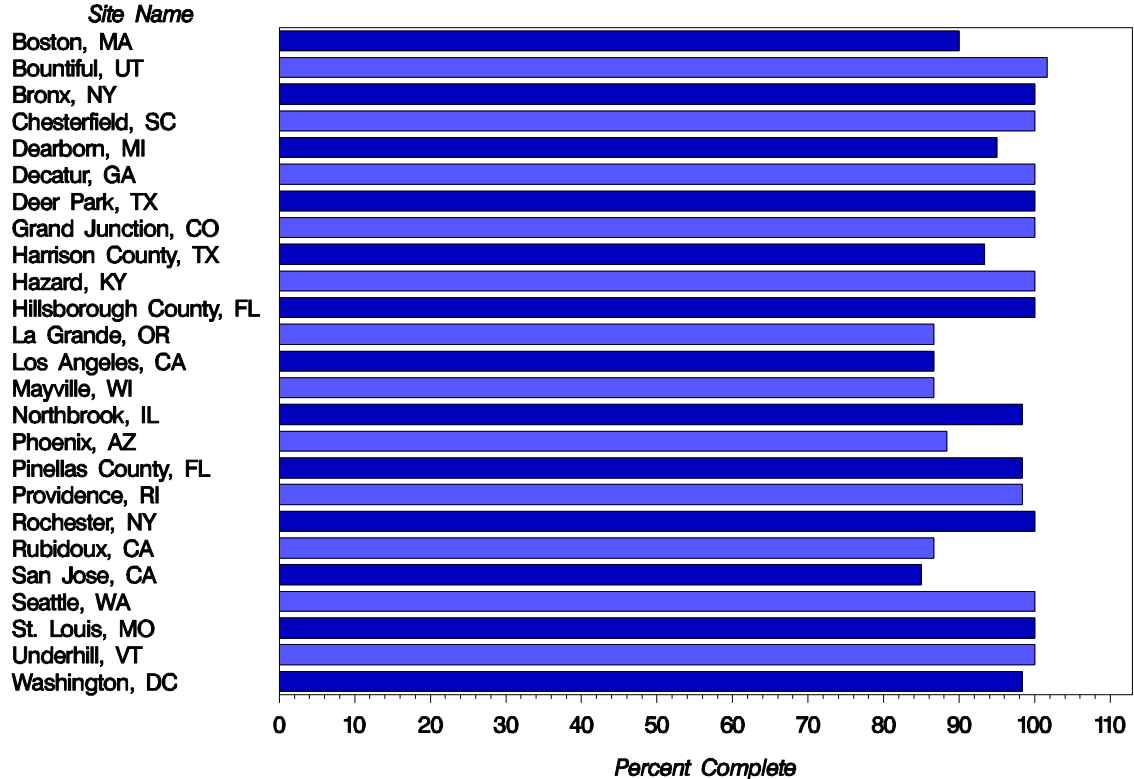


Figure 2. Completeness for Benzene at NATTS Sample Collection Sites in 2007.

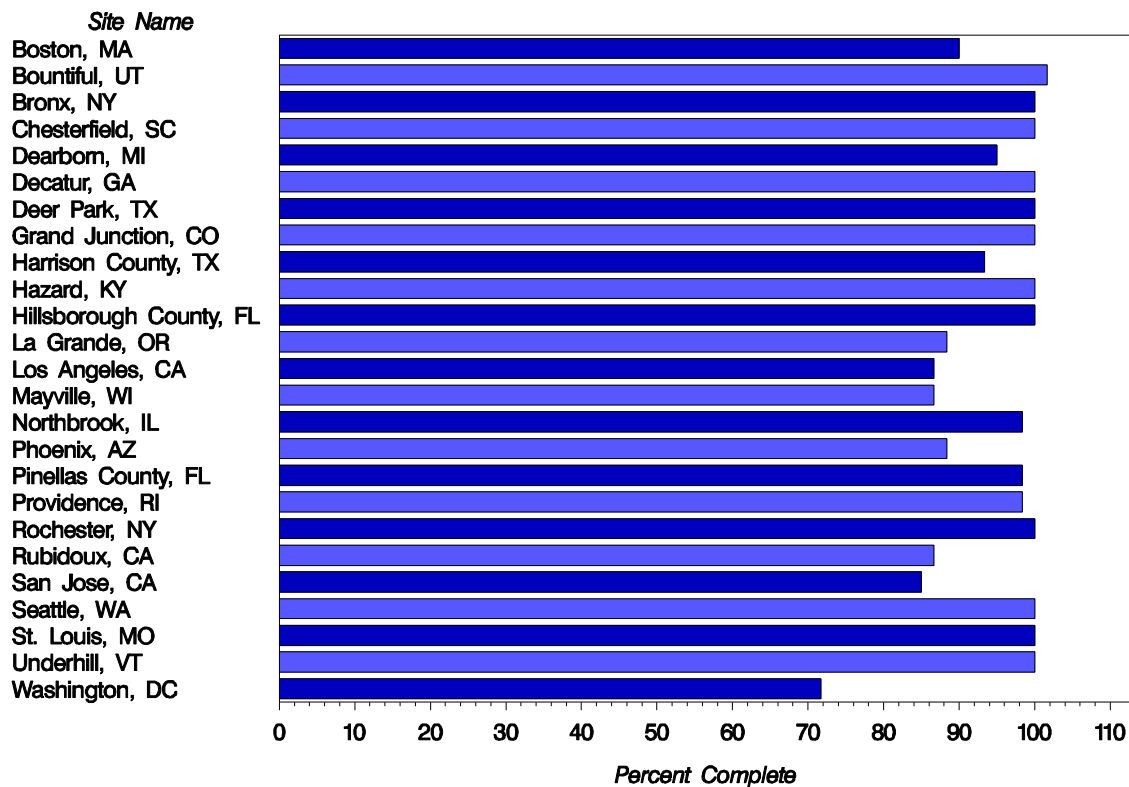


Figure 3. Completeness for 1,3-Butadiene at NATTS Sample Collection Sites in 2007.

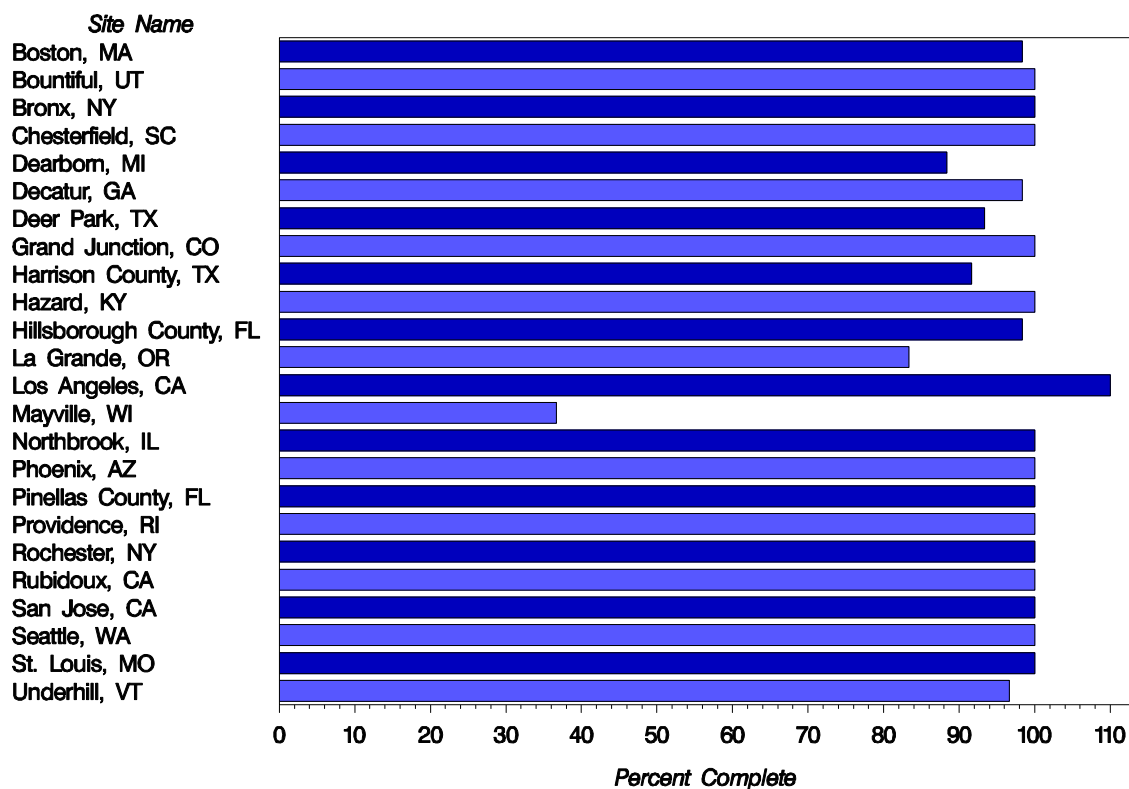


Figure 4. Completeness for Formaldehyde at NATTS Sample Collection Sites in 2007.

With the notable exceptions of Washington, DC (1,3-butadiene), and Mayville, WI (formaldehyde), all sites exhibited consistently high completeness statistics across all reported analytes and met the MQO of 85% completeness.

2.3 Precision of NATTS Data

Three basic sample types are collected at NATTS sites:

- Primary samples – a single sample which represents a particular sampling event;
- Duplicate samples – a replicate sample, collected simultaneously with the primary sample, which represents a second measurement from the same sample stream (e.g., the inlet stream of an outdoor air monitor) but employing an independent sample collection device (e.g., sampling pump) and collection substrate (e.g., filter) from the primary sample. Duplicate samples provide the basis for assessment of the aggregate variability associated with the collection device, sampling substrate, and sample analysis;
- Collocated samples – a replicate sample, collected simultaneously with the primary sample, which represents a second measurement from a completely independent (but spatially close, usually 1 to 2 meters away from the primary sampler) sample stream, collection device and collection substrate from the primary sample. Collocated samples provide the basis for assessment of the total variability associated with all components of the sample collection and analysis scheme.

Precision analyses were performed exclusively on NATTS sites. Assessment of methodological precision for the NATTS data is accomplished from both analytical (i.e., instrumental) and overall (i.e., instrumental + sampling) perspectives. In the former case, analytical precision is a measure of the variability in reported results due exclusively to differences in analytical instrument performance and is estimated by comparison of results from the replicate analyses of a single sample, whether that sample be primary, duplicate, or collocated. Overall sampling precision is assessed by comparison of the results from primary and collocated samples and accounts for the combined variability associated with sample collection and sample analysis. Despite the differences, albeit subtle, between duplicate and collocated samples, this report will reflect overall precision estimates based on both duplicate and collocated samples.

For the purposes of these precision assessments, the AQS database was queried for two distinct record types: RP records and RD records. RP records contain data for various types of replicate samples and analyses associated with a particular sampling date, site, and chemical parameter. Different types of replicates are identified by the value of the precision Id. variable (PCRECISID) according to the following scheme:

- PRECISID=1: Collocated sample data;
- PRECISID=2: Replicate analysis of a primary sample;
- PRECISID=3: Replicate analysis of a collocated sample.

For this report, analytical precision is computed from the replicate pairs of data coded with either Precision Id. 2 or 3. Overall precision is computed using the data in the raw data records as described below.

In addition to the replicate records, raw data (AQS RD) transactions provide a second source of primary and collocated data in AQS. Using the parameter occurrence codes (POCs) shown for each NATTS site listed in Table 6, it is possible to distinguish among primary, duplicate and collocated sampling events. For example, primary samples collected at the Chesterfield, SC NATTS site are assigned a parameter occurrence code of 1, while collocated samples collected at the same site are assigned a parameter occurrence code of 2. This results in the creation of two distinct records for each sampling event at which a collocated sample is collected. Duplicate samples are similarly identified. Since the assignment of a particular POC is at the discretion of each NATTS site, extensive effort was required to ensure that the POCs for each site were correctly identified. To this end, a representative at each NATTS site was contacted by email and by telephone to determine the specific POC used for each of the primary, duplicate, and collocated samples and for the three chemical classes (i.e., VOCs, carbonyls, and metals). Multiple POCs for a given site, analyte and sample type reflect a number of factors unique to a site during 2007, largely made for reasons known only to the NATTS site administrators. Overall precision estimates were computed by comparing primary and collocated records for a particular site, chemical parameter and sample collection date.

Table 7, complemented by Table 8, presents the laboratories performing analysis of specific sample types for each NATTS site. Of particular note is the fact that some laboratories provided analytical chemistry services for multiple NATTS sites. Laboratory codes presented in Table 8 were assigned by Alion Science, Inc. to track proficiency testing samples and their results.

Table 6. Parameter Occurrence Codes by NATTS Site and Analyte Type.

Region	Site Identifier	AQS Site Code	Parameter Occurrence Codes (POCs) ^a							
			VOC			Carbonyls			Metals	
			P ^b	D ^c	C ^d	P	D	C	P	C
I	Boston, MA	25-025-0042	10	11		3	4		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	20	10	1	2
II	Rochester, NY	36-055-1007	2			2			1	
III	Washington, DC	11-001-0043	1	2		1			1	
IV	Chesterfield, SC	45-025-0001	1		2	1		2	1	2
IV	Decatur, GA ^e	13-089-0002	1,3		2,4	2		3	1	2
IV	Hazard, KY	21-193-0003	1	2		1	2		1	
IV	Hillsborough County, FL	12-057-3002	1			6	6		5	6
IV	Pinellas County, FL	12-103-0026	1		2	6			5	
V	Dearborn, MI	26-163-0033	1	2	2	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	04-013-9997	6		7	1,30		2,31	1	
IX	Los Angeles, CA	06-037-1103	4		5	4		5		
IX	Rubidoux, CA	06-065-8001	4		5	4		5		
IX	San Jose, CA	06-085-0005	3,5		5	1,3,4		1	1	
X	La Grande, OR	41-061-0119	7			7			7	
X	Seattle, WA	53-033-0080	6		7	6		7	6	7

^a As reported by the NATTS site administrator. Multiple POCs reflect different analytes or changes in assignments during the monitoring year

^b P = Primary.

^c D = Duplicate.

^d C = Collocated.

^e Benzene on POCs 3 & 4; all other VOCs on POCs 1 & 2.

Table 7. Laboratories Performing Analyses for the Different Compound Types for Each NATTS Site in 2007.

AQS Site Id.	VOCs	Carbonyls	Metals
Boston-Roxbury, MA	RIDOH	MADEP	ERG
Underhill, VT	VTDEC	VTDEC	--- ^a
Providence, RI	RIDOH	RIDOH	USEPAR1
Bronx, NY	NYSDEC	NYSDEC	RTI
Rochester, NY	NYSDEC	NYSDEC	RTI
Washington, DC	MDE	PAMSL	WVDEP
Chesterfield, SC	SCDHEC	SCDHEC	SCDHEC
Decatur, GA	GADNR	GADNR	GADNR
Hazard, KY	KYDES	KYDES	KYDES
Hillsborough County, FL	PCDEM	ERG	EPCHC
Pinellas County, FL	PCDEM	ERG	EPCHC
Dearborn, MI	ERG	ERG	MIDPH
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	IMLAS
Phoenix, AZ	SDCAPCD	SDCAPCD	ERG
San Jose, CA	BAAQMD	BAAQMD	--- ^a
Los Angeles, CA	SCAQMD	SCAQMD	SCAQMD
Rubidoux, CA	SCAQMD	SCAQMD	SCAQMD
La Grande, OR	ODEQ	ODEQ	ODEQ
Seattle, WA	ERG	ERG	ERG

^aNot provided

Table 8. Laboratory Abbreviations and Descriptions for NATTS Laboratories.

Laboratory Code(s)	Laboratory Abbreviation	Laboratory Description
01-01-C	RIDOH	Rhode Island Department of Health
01-02-C,V	VTDEC	Vermont Department of Environmental Conservation
01-03-C	MADEP	Massachusetts Department of Environmental Protection
01-04-M	USEPAR1	U.S. EPA Region 1 Laboratory
02-01-C,V	NYSDEC	New York State Department of Environmental Conservation
03-01-V	MDE	Maryland Department of the Environment
03-01-C	PAMSL	Philadelphia Air Management Services Laboratory
03-01-M	WVDEP	West Virginia Department of Environmental Protection
04-01-M	EPCHC	Environmental Protection Commission of Hillsborough County
04-01-V	PCDEM	Pinellas County Department of Environmental Management
04-02-C,M,V	SCDHEC	South Carolina Department of Health and Environmental Control
04-03-C,M,V	KYDES	Kentucky Division of Environmental Services
04-04-C,M,V	GADNR	Georgia Department of Natural Resources
05-01-M	MIDPH	Michigan Department of Public Health
05-03-C,M,V	WSLH	Wisconsin State Laboratory of Hygiene
06-01-C,M,V	TCEQ	Texas Commission on Environmental Quality
08-02-M,V	IMLAS	IML Air Science Laboratory
09-03-C,V	BAAQMD	Bay Area Air Quality Management District
09-06-C,V	SDCAPCD	San Diego County Air Pollution Control District
10-02-C,M,V	ODEQ	Oregon Department of Environmental Quality
11-01-C,M,V; 09-02-V	ERG ^a	Eastern Research Group
11-02-M	RTI	RTI International
--- ^b	SCAQMD	South Coast Air Quality Management District

^a ERG provides analytical laboratory support for several NATTS sites.

^b Did not participate in Proficiency Testing program.

2.3.1 Analytical Precision Results

Analytical precision was computed from the results of the primary and collocated samples and their respective replicate analyses extracted from RP records in the AQS database. This measure of agreement, expressed as the percent coefficient of variation (% CV), is defined algebraically in Eq. 1, below.

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

where:

p_i = the result of the principal analysis on sample i ;

r_i = the result of the replicate analysis on sample i ;

n = the number of principal-replicate analysis pairs

The analytical precision for all measured hazardous air pollutants analyzed in samples collected in calendar year 2007 are presented in Table 9 with selected analytes summarized graphically in Figures 5 through 8.

Table 9. Analytical Precision^a for Replicate Analyses of 2007 NATTS Data.

AQS SiteCode	Site Description	Analyte Abbreviation								
		BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122
04-013-9997	Phoenix, AZ	14.1 (6)	6.2 (6)	9.8 (6)	7.8 (6)	-- ^b	--	--	8 (6)	--
06-085-0005	San Jose, CA	3.5 (7)	15.7 (1)	3.8 (7)	<0.5 (3)	--	--	--	4.6 (1)	--
08-077-0018	Grand Junction, CO	6.5 (12)	6.2 (12)	10.4 (12)	7.2 (12)	--	--	--	4.2 (12)	--
12-057-3002	Hillsborough County, FL	--	--	--	--	--	--	--	--	--
12-103-0026	Pinellas County, Tampa, FL	4.8 (83)	10.8 (83)	5.9 (83)	12.8 (83)	34.9 (36)	52.8 (22)	22 (83)	21.7 (83)	32.2 (74)
17-031-4201	Northbrook, IL	17 (19)	10.4 (10)	5.6 (9)	4.7 (9)	--	--	--	5.7 (9)	--
25-025-0042	Boston, MA	--	--	--	--	--	--	--	--	--
26-163-0033	Dearborn, MI	4.9 (12)	5.3 (12)	4.4 (12)	6.5 (12)	--	--	--	6.3 (12)	--
29-510-0085	St. Louis, MO	34.6 (11)	16.7 (10)	6.9 (10)	3.7 (10)	--	--	--	11.4 (10)	--
48-201-1039	Deer Park, TX	5.5 (47)	6.7 (47)	5.9 (47)	9.7 (43)	--	--	7.1 (15)	6.4 (47)	--
48-203-0002	Harrison County, TX	3.3 (2)	<0.5 (2)	<0.5 (2)	33.3 (2)	--	--	3.4 (2)	<0.5 (2)	--
49-011-0004	Bountiful, UT	4.3 (24)	7.4 (24)	11.9 (12)	6.5 (10)	--	--	--	4.4 (12)	--
53-033-0080	Seattle, WA	9.7 (14)	9.3 (14)	4.8 (14)	7.3 (13)	--	--	--	11 (14)	--
	Overall Mean	10.4 (235)	9.4 (221)	6.7 (214)	10.6 (203)	34.9 (36)	52.8 (22)	20.2 (100)	14.8 (208)	32.2 (74)

Table 9 Analytical Precision^a for Replicate Analyses of 2007 NATTS Data (additional analytes).

AQS SiteCode	Site Description	PERC	TCE	VC	cDCPEN	tDCPEN	FORM	ACET	AS	BE	CD	PB	MN	NI
04-013-9997	Phoenix, AZ	13.3 (6)	4.9 (2)	<0.5 (2)	--	--	0.6 (6)	1.3 (6)	--	--	--	--	--	--
06-085-0005	San Jose, CA	2.5 (7)	<0.5 (3)	--	--	--	1 (10)	3.7 (10)	--	--	--	--	--	--
08-077-0018	Grand Junction, CO	6.9 (12)	20.2 (6)	--	--	--	1.6 (12)	0.5 (12)	--	--	--	--	--	--
12-057-3002	Hillsborough County, FL	--	--	--	--	--	31.4 (14)	26.4 (14)	--	--	--	--	--	--
12-103-0026	Pinellas County, Tampa, FL	13.2 (82)	37.6 (71)	34 (53)	36.5 (41)	39.3 (49)	2 (14)	4 (14)	--	--	--	--	--	--
17-031-4201	Northbrook, IL	6.4 (9)	9.1 (7)	10.9 (1)	--	--	0.9 (12)	1.1 (12)	--	--	--	--	--	--
25-025-0042	Boston, MA	--	--	--	--	--	--	--	5.3 (56)	35 (53)	1.7 (56)	2 (56)	2.2 (55)	2.9 (56)
26-163-0033	Dearborn, MI	8.1 (10)	18.3 (5)	<0.5 (1)	--	--	0.6 (12)	0.9 (12)	--	--	--	--	--	--
29-510-0085	St. Louis, MO	10.7 (10)			--	--	1.8 (12)	5 (12)	0.9 (23)	16.1 (23)	1 (23)	0.6 (23)	1.7 (23)	1.1 (23)
48-201-1039	Deer Park, TX	10.7 (42)	10.6 (18)	7.3 (30)	--	--	--	--	--	--	--	--	--	--
48-203-0002	Harrison, County, TX	<0.5 (2)		<0.5 (1)	--	--	--	--	--	--	--	--	--	--
49-011-0004	Bountiful, UT	6.4 (12)	1 (6)	12 (4)	--	--	4.1 (12)	1.3 (12)	--	--	--	--	--	--
53-033-0080	Seattle, WA	7 (12)	4.5 (7)	--	--	--	1.5 (14)	1 (14)	2.7 (2)	9.1 (2)	6.3 (2)	1.2 (2)	3.1 (2)	7.6 (2)
	Overall Mean^c	10.9 (204)	29.3 (125)	26.3 (92)	36.5 (41)	39.3 (49)	11 (118)	9.4 (118)	4.4 (81)	30.2 (78)	1.8 (81)	1.7 (81)	2.1 (80)	2.8 (81)

^a Expressed as %CV with number of contributing data pairs presented in parentheses. Metals results are reported at STP at most sites and local conditions at others.

^b Sample not collected or analyte not reported.

^c Across all sites.

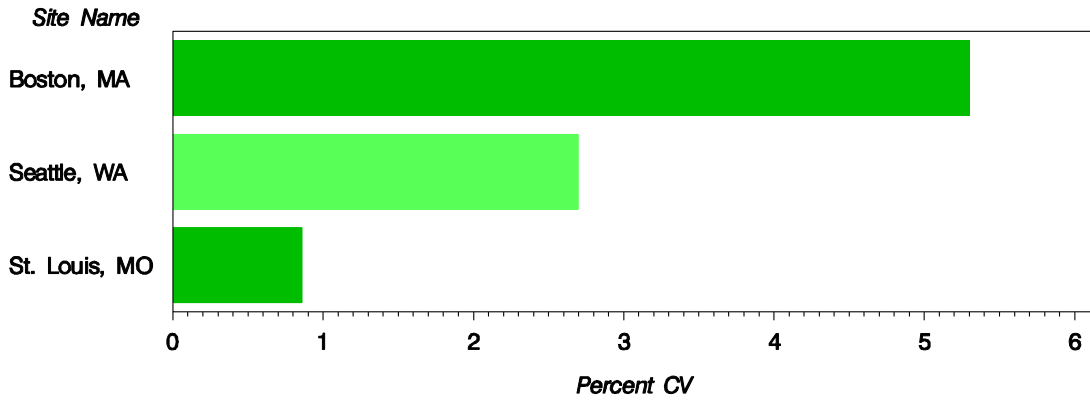


Figure 5. Analytical Precision Summary for Arsenic at NATTS Sample Collection Sites in 2007.

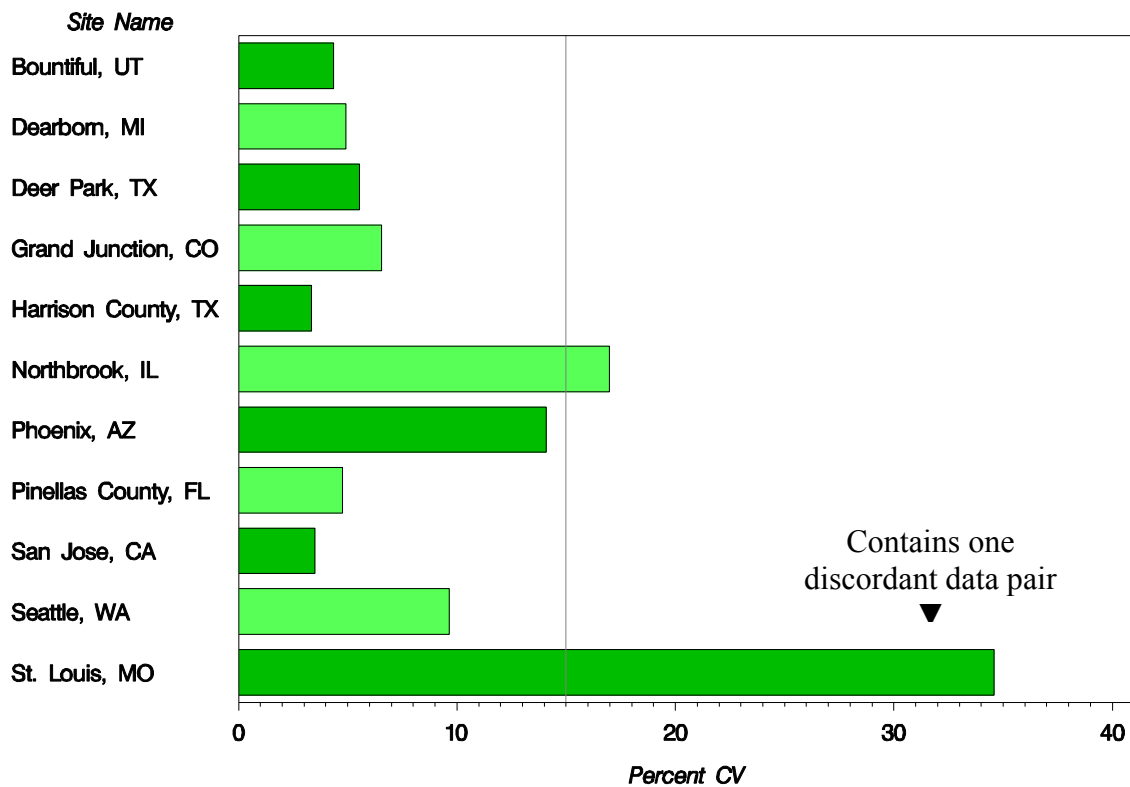


Figure 6. Analytical Precision Summary for Benzene at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).

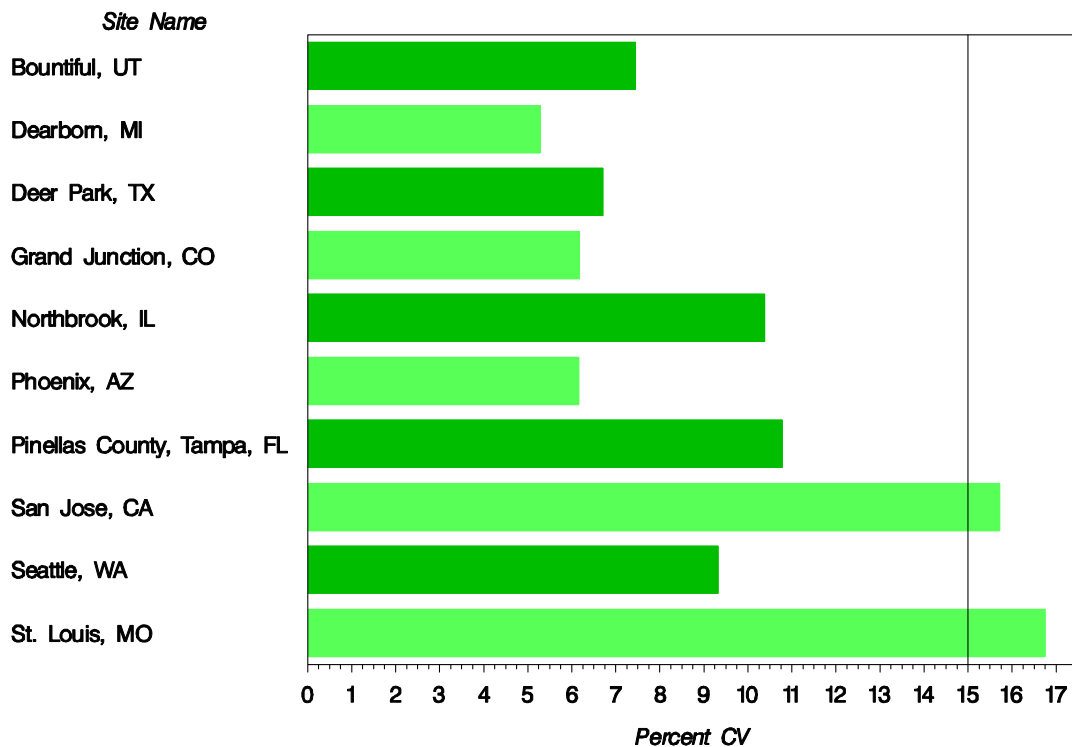


Figure 7. Analytical Precision Summary for 1,3-Butadiene at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).

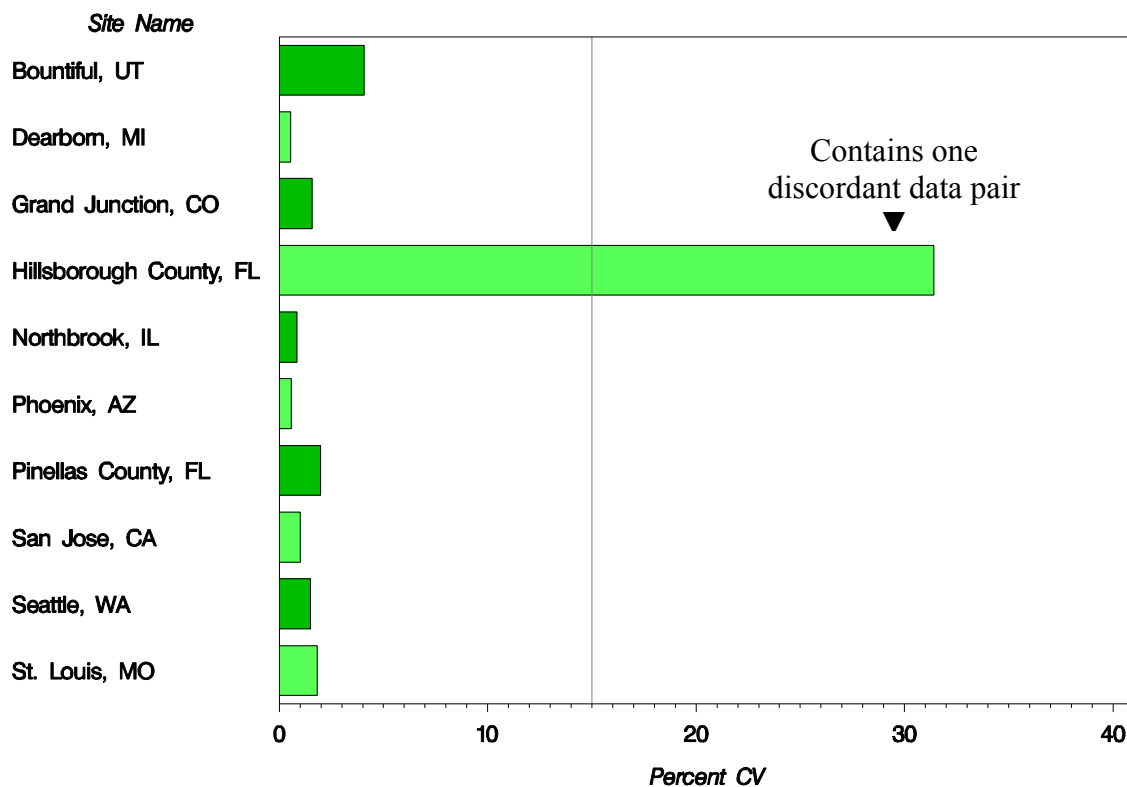


Figure 8. Analytical Precision Summary for Formaldehyde at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).

Overall, the agreement between replicate analyses of the same samples was within the MQO guidelines and, in most cases, much less than 10 percent. Notable exceptions to this were replicate measurements of benzene in samples collected at the St. Louis site (35% CV) and formaldehyde in samples collected at the Hillsborough County, FL site (31% CV). Examination of the individual data records revealed that these high CVs are the result of one extreme value in each case.

2.3.2 Overall Precision Results

Overall precision was computed from the results of the primary, duplicate and collocated samples extracted from RD records in the AQS database. This measure of agreement, expressed as the percent coefficient of variation (% CV), is defined algebraically in Eq. 2, below.

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

where:

- p_i = the result of the principal analysis on primary sample i ;
- r_i = the result of the principal analysis on collocated sample i ;
- n = the number of primary-collocated sample pairs

The overall precision results for samples collected in calendar year 2007 are presented in Table 10 and summarized graphically in Figures 9 through 12. For cases where either the primary or collocated sample yielded a result of zero or had a value below the reported method detection limit, the data pairs were excluded from the overall precision estimate. All data pairs with measurable values were included in the computation.

Table 10. Overall Precision^a for Primary and Collocated Samples from 2007.

AQS Site Id.	Site Description	Duplicate Type	Analyte Abbreviation								
			BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122
04-013-9997	Phoenix, AZ	Collocated	10.4 (13)	7.0 (13)	5.2 (13)	3.0 (13)	22.3 (1)	-- ^b	7.4 (10)	9.1 (13)	--
04-013-9997	Phoenix, AZ	Duplicate	--	--	--	--	--	--	--	--	--
06-037-1103	Los Angeles, CA	Collocated	14.4 (21)	37.3 (21)	--	22.1 (21)	--	--	--	12.4 (21)	--
06-037-1103	Los Angeles, CA	Duplicate	--	--	--	--	--	--	--	--	--
06-065-8001	Rubidoux, CA	Collocated	16.6 (27)	35.7 (27)	--	18.2 (27)	--	--	--	19.8 (27)	--
06-065-8001	Rubidoux, CA	Duplicate	17.0 (25)	37.4 (25)	--	20.9 (25)	--	--	--	28.9 (25)	--
06-085-0005	San Jose, CA	Collocated	17.4 (29)	58.5 (21)	--	41.6 (26)	--	--	--	23.7 (6)	--
06-085-0005	San Jose, CA	Duplicate	--	--	--	--	--	--	--	--	--
08-077-0017	Grand Junction, CO	Collocated	--	--	--	--	--	--	--	--	--
08-077-0017	Grand Junction, CO	Duplicate	--	--	--	--	--	--	--	--	--
08-077-0018	Grand Junction, CO	Collocated	--	--	--	--	--	--	--	--	--
08-077-0018	Grand Junction, CO	Duplicate	--	--	--	--	--	--	--	--	--
11-001-0043	Washington, DC	Collocated	--	--	--	--	--	--	--	--	--
11-001-0043	Washington, DC	Duplicate	--	--	--	--	--	--	--	--	--
12-057-3002	Hillsborough County, FL	Collocated	--	--	--	--	--	--	--	--	--
12-057-3002	Hillsborough County, FL	Duplicate	--	--	--	--	--	--	--	--	--
12-103-0026	Pinellas County, Tampa, FL	Collocated	5.2 (37)	14.6 (37)	5.3 (37)	12.5 (37)	46.6 (12)	37.3 (11)	23 (37)	22.5 (37)	40.9 (25)
12-103-0026	Pinellas County, Tampa, FL	Duplicate	--	--	--	--	--	--	--	--	--
13-089-0002	Decatur, GA	Collocated	88.6 (81)	--	14.9 (27)	22.1 (7)	--	--	--	--	--
13-089-0002	Decatur, GA	Duplicate	--	--	--	--	--	--	--	--	--
17-031-4201	Northbrook, IL	Collocated	18.5 (6)	32.3 (5)	18.8 (6)	92.3 (6)	--	--	--	15.1 (6)	--
17-031-4201	Northbrook, IL	Duplicate	--	--	--	--	--	--	--	--	--
21-193-0003	Hazard, KY	Collocated	--	--	--	--	--	--	--	--	--
21-193-0003	Hazard, KY	Duplicate	12.4 (35)	--	--	--	--	--	--	--	--

Table 10. Overall Precision^a for Primary and Collocated Samples from 2007, continued.

AQS Site Id.	Site Description	Duplicate Type	Analyte Abbreviation								
			BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122
25-025-0042	Boston, MA	Collocated	--	--	--	--	--	--	--	--	--
25-025-0042	Boston, MA	Duplicate	4.5 (8)	36.6 (8)	2.5 (8)	6.3 (8)	--	--	36.2 (5)	2.5 (8)	--
26-163-0033	Dearborn, MI	Collocated	40.9 (6)	5.4 (5)	43.7 (6)	44.8 (5)	--	--	--	49.9 (6)	--
26-163-0033	Dearborn, MI	Duplicate	--	--	--	--	--	--	--	--	--
29-510-0085	St. Louis, MO	Collocated	--	--	--	--	--	--	--	--	--
29-510-0085	St. Louis, MO	Duplicate	--	--	--	--	--	--	--	--	--
36-005-0110	Bronx, NY	Collocated	--	--	--	--	--	--	--	--	--
36-005-0110	Bronx, NY	Duplicate	--	--	--	--	--	--	--	--	--
36-055-1007	Rochester, NY	Collocated	--	--	--	--	--	--	--	--	--
36-055-1007	Rochester, NY	Duplicate	--	--	--	--	--	--	--	--	--
41-061-0119	La Grande, OR	Collocated	--	--	--	--	--	--	--	--	--
41-061-0119	La Grande, OR	Duplicate	--	--	--	--	--	--	--	--	--
44-007-0022	Providence, RI	Collocated	--	--	--	--	--	--	--	--	--
44-007-0022	Providence, RI	Duplicate	--	--	--	--	--	--	--	--	--
45-025-0001	Chesterfield, SC	Collocated	25.4 (33)	--	34.6 (6)	--	--	--	--	31.4 (3)	--
45-025-0001	Chesterfield, SC	Duplicate	--	--	--	--	--	--	--	--	--
48-201-1039	Deer Park, TX	Collocated	5.5 (57)	45.9 (57)	15.4 (57)	23.2 (57)	6.2 (57)	12.1 (57)	36.6 (57)	38.7 (57)	8.8 (57)
48-201-1039	Deer Park, TX	Duplicate	--	--	--	--	--	--	--	--	--
48-203-0002	Harrison County, TX	Collocated	--	--	--	--	--	--	--	--	--
48-203-0002	Harrison County, TX	Duplicate	--	--	--	--	--	--	--	--	--
49-011-0004	Bountiful, UT	Collocated	--	--	--	--	--	--	--	--	--
49-011-0004	Bountiful, UT	Duplicate	--	--	--	--	--	--	--	--	--
50-007-0007	Underhill, VT	Collocated	--	--	--	--	--	--	--	--	--
50-007-0007	Underhill, VT	Duplicate	--	--	--	--	--	--	--	--	--
53-033-0080	Seattle, WA	Collocated	9.7 (7)	9.6 (7)	7.6 (7)	35.9 (7)	--	--	--	8.0 (7)	--
53-033-0080	Seattle, WA	Duplicate	--	--	--	--	--	--	--	--	--
55-027-0007	Mayville, WI	Collocated	--	--	--	--	--	--	--	--	--

Table 10. Overall Precision^a for Primary and Collocated Samples from 2007, continued.

AQS Site Id.	Site Description	Duplicate Type	Analyte Abbreviation									
			BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122	
55-027-0007	Mayville, WI	Duplicate	--	--	--	--	--	--	--	--	--	--
	<i>Overall Mean</i> ^c	All Dups.	42.8 (385)	37.4 (226)	15.9 (167)	27.9 (239)	20.3 (70)	18.9 (68)	30.7 (109)	27.5 (216)	23.7 (82)	

^a Expressed as %CV with number of contributing data pairs presented in parentheses. Metals results are reported at STP at most sites and local conditions at others.

^b Sample either not collected or analyte not reported

^c Across all sites

Table 10. Overall Precision^a for Primary and Collocated Samples from 2007 (additional analytes).

AQS Site Id.	Site Description	Duplicate Type	PERC	TCE	VCM	cDCPEN	tDCPEN	FORM	ACET	AS	BE	CD	PB	MN	NI
04-013-9997	Phoenix, AZ	Collocated	10.1 (13)	16.9 (11)	<0.5 (1)	--	--	27.1 (28)	28.7 (28)	--	--	--	--	--	--
04-013-9997	Phoenix, AZ	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
06-037-1103	Los Angeles, CA	Collocated	21.9 (21)	45.2 (21)	--	--	--	45.8 (27)	59.3 (27)	--	--	--	--	--	--
06-037-1103	Los Angeles, CA	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
06-065-8001	Rubidoux, CA	Collocated	20.9 (27)	15.9 (12)	--	--	--	35 (25)	39.3 (25)	--	--	--	--	--	--
06-065-8001	Rubidoux, CA	Duplicate	22.8 (25)	20.9 (12)	--	--	--	--	--	--	--	--	--	--	--
06-085-0005	San Jose, CA	Collocated	33.6 (30)	35.2 (26)	--	--	--	24.9 (30)	55.3 (30)	--	--	--	--	--	--
06-085-0005	San Jose, CA	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
08-077-0017	Grand Junction, CO	Collocated	--	--	--	--	--	--	--	--	6.1 (9)	1.8 (2)	7.6 (31)	8.3 (34)	2.4 (5)
08-077-0017	Grand Junction, CO	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
08-077-0018	Grand Junction, CO	Collocated	--	--	--	--	--	--	--	--	--	--	--	--	--
08-077-0018	Grand Junction, CO	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
11-001-0043	Washington, DC	Collocated	--	--	--	--	--	--	--	--	--	--	--	--	--
11-001-0043	Washington, DC	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
12-057-3002	Hillsborough County, FL	Collocated	--	--	--	--	--	--	--	--	--	--	--	--	--
12-057-3002	Hillsborough County, FL	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--

Table 10. Additional Analytes, continued.

AQS Site Id.	Site Description	Duplicate Type	PERC	TCE	VCM	cDCPEN	tDCPEN	FORM	ACET	AS	BE	CD	PB	MN	NI
12-103-0026	Pinellas County, Tampa, FL	Collocated	13.7 (37)	45.2 (26)	37.1 (19)	35.1 (13)	44 (19)	--	--	--	--	--	--	--	--
12-103-0026	Pinellas County, Tampa, FL	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
13-089-0002	Decatur, GA	Collocated	20.0 (2)	--	--	--	--	42.9 (27)	31.5 (27)	28.4 (18)	--	33 (27)	26.5 (28)	27.5 (28)	33.7 (28)
13-089-0002	Decatur, GA	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
17-031-4201	Northbrook, IL	Collocated	28.1 (6)	37.6 (3)	--	--	--	75.7 (6)	78.3 (6)	--	--	--	--	--	--
17-031-4201	Northbrook, IL	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
21-193-0003	Hazard, KY	Collocated	--	--	--	--	--	--	--	--	--	--	--	--	--
21-193-0003	Hazard, KY	Duplicate	--	--	--	--	--	7.2 (31)	--	--	--	--	--	--	--
25-025-0042	Boston, MA	Collocated	--	--	--	--	--	--	--	4.1 (30)	32.1 (28)	18 (30)	8.3 (30)	5.7 (29)	13.8 (30)
25-025-0042	Boston, MA	Duplicate	12.2 (8)	36.3 (2)	--	--	--	11.5 (10)	21.9 (10)	--	--	--	--	--	--
26-163-0033	Dearborn, MI	Collocated	4.4 (4)	11.6 (2)	--	--	--	27.3 (2)	4.4 (1)	10.9 (50)	30.7 (50)	11.8 (50)	8.4 (50)	24.8 (50)	10.9 (50)
26-163-0033	Dearborn, MI	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
29-510-0085	St. Louis, MO	Collocated	--	--	--	--	--	--	--	5.9 (11)	16.7 (11)	14.8 (11)	8.8 (11)	7.0 (11)	10.4 (11)
29-510-0085	St. Louis, MO	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
36-005-0110	Bronx, NY	Collocated	--	--	--	--	--	--	--	--	--	--	--	--	--
36-005-0110	Bronx, NY	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
36-055-1007	Rochester, NY	Collocated	--	--	--	--	--	--	--	--	--	--	--	--	--
36-055-1007	Rochester, NY	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
41-061-0119	La Grande, OR	Collocated	--	--	--	--	--	--	--	--	--	--	--	--	--
41-061-0119	La Grande, OR	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
44-007-0022	Providence, RI	Collocated	--	--	--	--	--	6.1 (28)	5.7 (28)	9.4 (2)	17.2 (2)	5.9 (2)	7.7 (29)	8.1 (28)	8.2 (24)
44-007-0022	Providence, RI	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
45-025-0001	Chesterfield, SC	Collocated	9.4 (1)	--	--	--	--	17.6 (54)	19.6 (54)	19.0 (53)	10.8 (13)	40.1 (35)	27.3 (52)	27.4 (53)	72.2 (42)
45-025-0001	Chesterfield, SC	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
48-201-1039	Deer Park, TX	Collocated	33.5 (57)	19.2 (57)	35.1 (57)	6.2 (57)	<0.5 (57)	--	--	--	--	--	--	--	--
48-201-1039	Deer Park, TX	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
48-203-0002	Harrison County, TX	Collocated	--	--	--	--	--	--	--	--	--	--	--	--	--
48-203-0002	Harrison County, TX	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--

Table 10. Additional Analytes, continued.

AQS Site Id.	Site Description	Duplicate Type	PERC	TCE	VCM	cDCPEN	tDCPEN	FORM	ACET	AS	BE	CD	PB	MN	NI
49-011-0004	Bountiful, UT	Collocated	--	--	--	--	--	--	--	8.6 (3)	13.8 (3)	4.7 (3)	3.8 (3)	9.8 (3)	34.8 (3)
49-011-0004	Bountiful, UT	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
50-007-0007	Underhill, VT	Collocated	--	--	--	--	--	--	--	--	--	--	--	--	--
50-007-0007	Underhill, VT	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
53-033-0080	Seattle, WA	Collocated	3.4 (5)	38.3 (4)	--	--	--	8.0 (7)	3.1 (7)	2.4 (1)	<0.5 (1)	6.3 (1)	0.6 (1)	0.8 (1)	7.0 (1)
53-033-0080	Seattle, WA	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
55-027-0007	Mayville, WI	Collocated	--	--	--	--	--	--	--	22.8 (4)	--	33.1 (4)	34.8 (4)	53.1 (4)	32.3 (4)
55-027-0007	Mayville, WI	Duplicate	--	--	--	--	--	--	--	--	--	--	--	--	--
	Overall Mean ^b	All Dups.	24.9 (236)	31.4 (176)	35.4 (77)	16.2 (70)	22.0 (76)	29.1 (275)	37.3 (24)	16.9 (218)	26.9 (162)	23.0 (217)	15.9 (292)	20.3 (294)	34.5 (251)

^a Expressed as %CV with number of contributing data pairs presented in parentheses. Metals results are reported at STP at most sites and local conditions at others.

^b Sample either not collected or analyte not reported.

^c Across all sites.

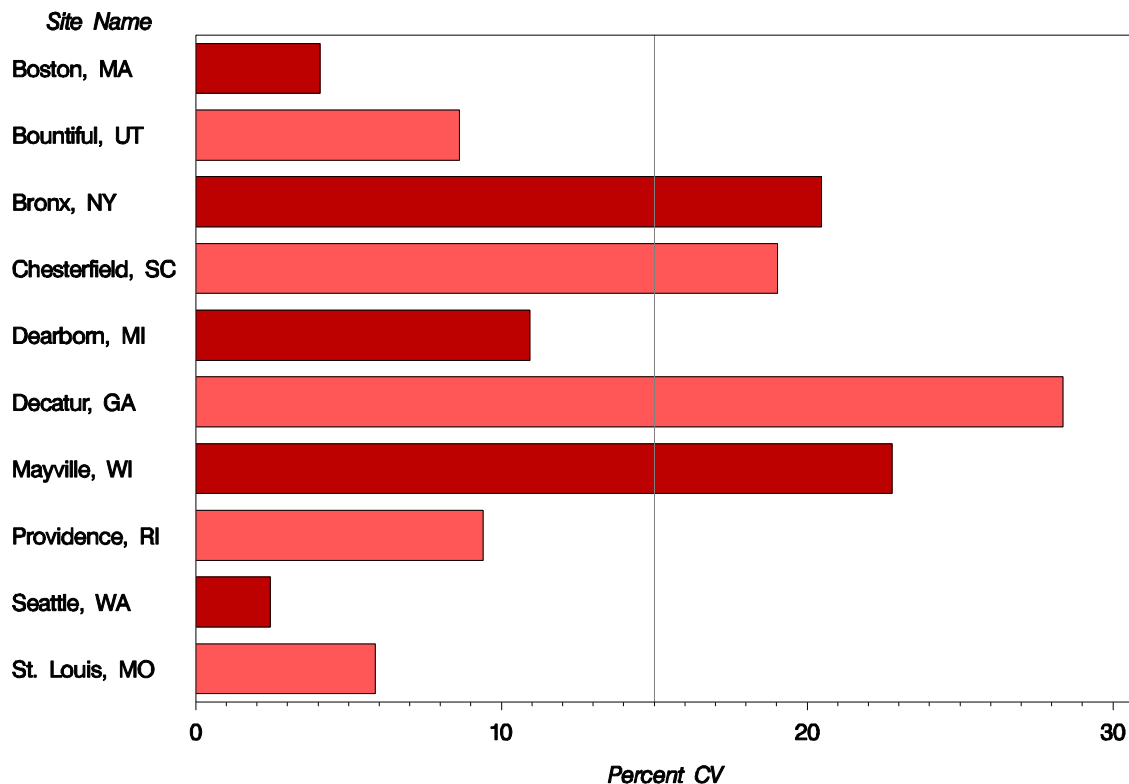


Figure 9. Overall Precision Summary for Arsenic at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).

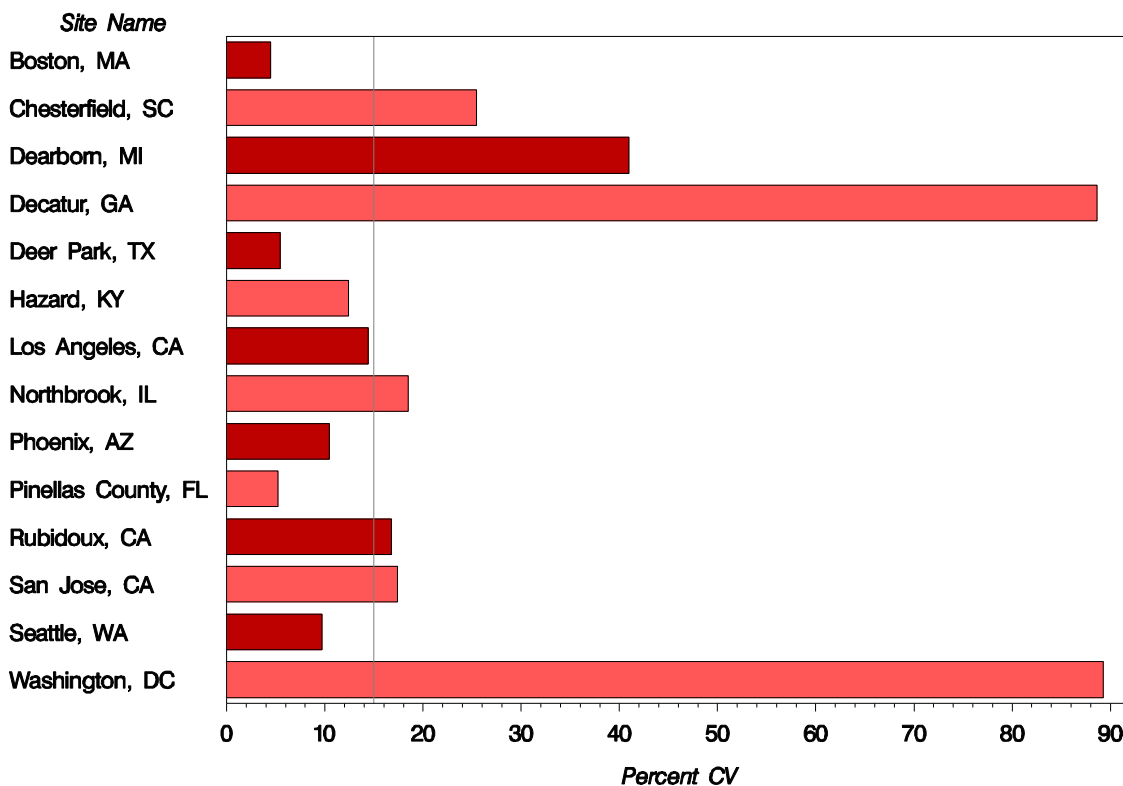


Figure 10. Overall Precision Summary for Benzene at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).

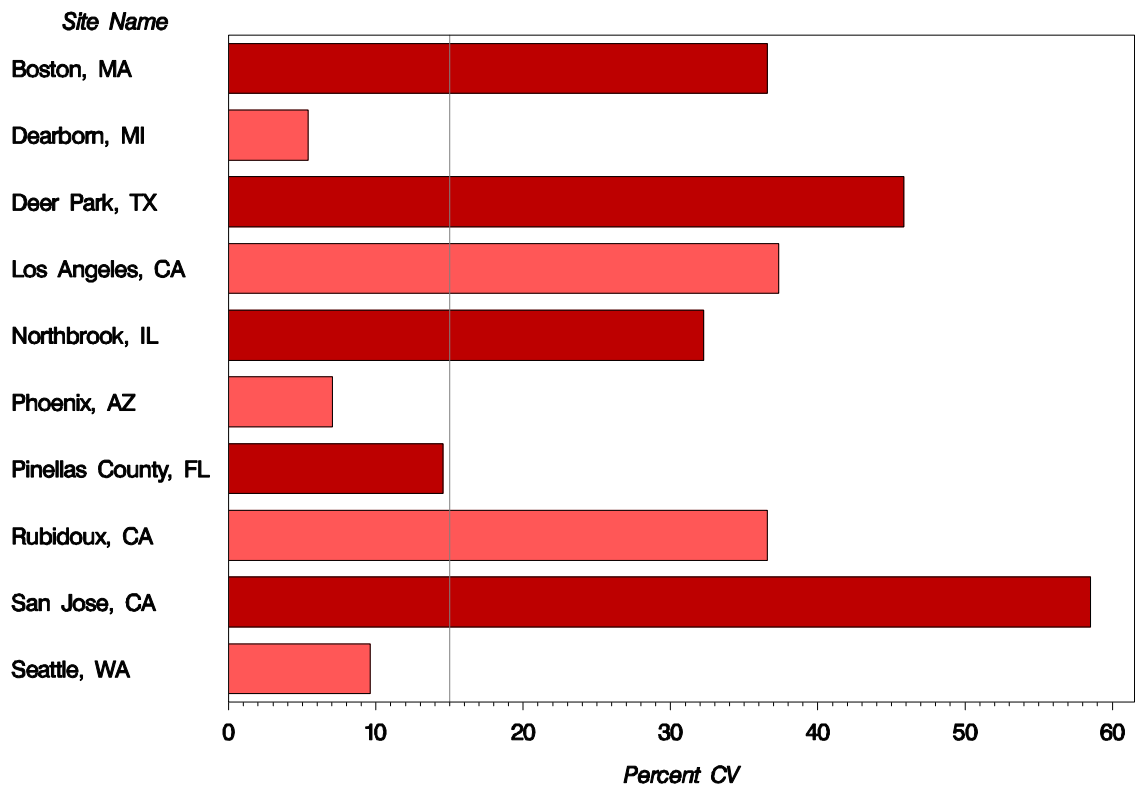


Figure 11. Overall Precision Summary for 1,3-Butadiene at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).

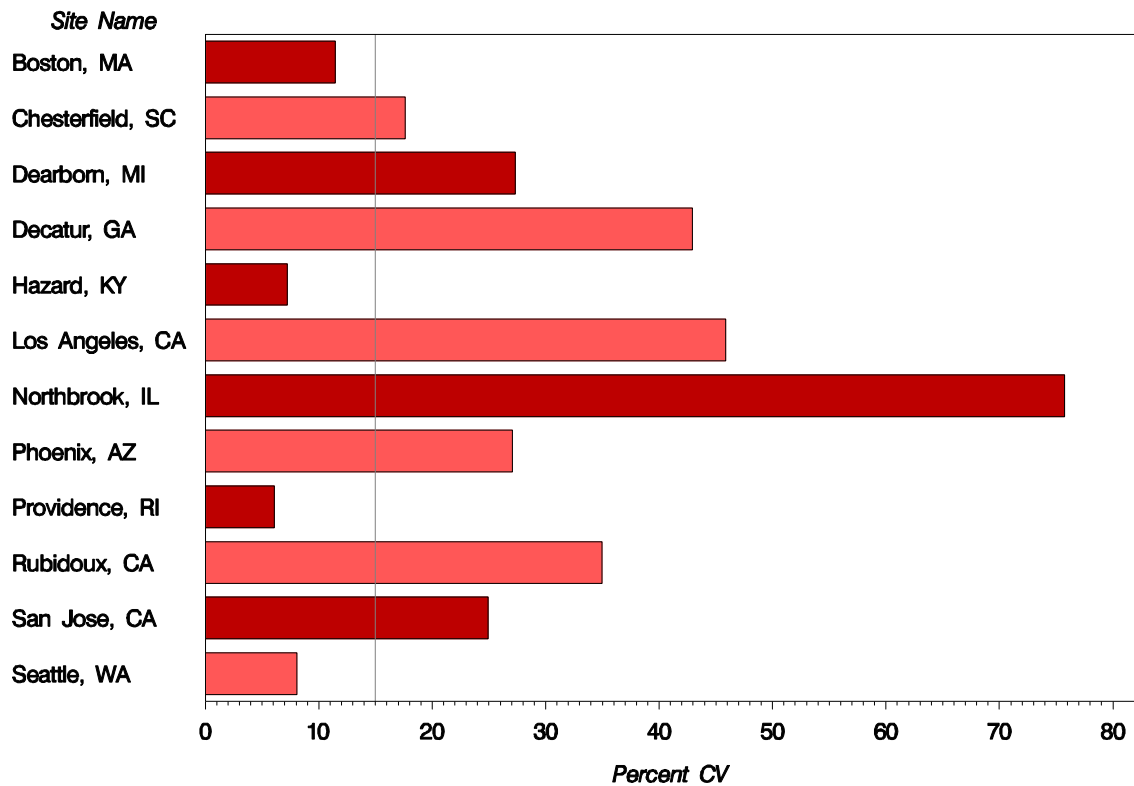


Figure 12. Overall Precision Summary for Formaldehyde at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).

Examination of Figures 9 through 12 reveals that aggregate precision associated with sample collection and analysis varies widely by collection site and analyte. Not unexpectedly, the aggregate variability observed is substantially greater than the analytical variability shown in Figures 5 through 8. With that being said, it is possible that the large variability seen for many sites reflects one or more extreme values which are strongly influencing the overall results. This would require a careful review of the distributions of CVs for the individual data pairs for each analyte and site and is considered beyond the scope of this report. Nevertheless, the fact that many sites exhibit percent CVs above the MQO target level suggests that the collection methodology is contributing significantly to the overall variability in the data for a given site and analyte. Without identifying specific sites, the percentages of sites with %CV above the MQO threshold are 33, 43, 73, and 62% for arsenic, benzene, 1,3-butadiene, and formaldehyde, respectively. The %CVs computed across sites, by analyte, are somewhat misleading as they are clearly influenced by large CVs at selected sites. The QA report of the NATTS stations for 2006 warned of the danger in extracting duplicate and collocated results using only the RP records. For that reason and despite the considerable difficulty in determining the specific primary, duplicate, and collocated parameter occurrence codes (POCs) for each site, the data presented here are based exclusively on the RD records.

2.4 Laboratory Bias Data Based on Proficiency Testing (PT) Samples

Quarterly proficiency testing audits of participating NATTS sample analysis laboratories were conducted by Alion Science, Inc., under contract to the U.S. EPA (Contract No. 68-D03-006). Spiked samples containing known amounts of the hazardous air pollutants of interest were delivered to each laboratory. Following chemical analyses, the participating laboratories returned their results to Alion, which, in turn, prepared reports comparing the laboratory-measured values to the stated (known) values for each proficiency testing sample. During calendar year 2007, four separate proficiency testing cycles were conducted for VOCs and metals; two cycles were performed for carbonyls. The results of these proficiency testing sample analyses were provided to RTI International by EPA for CY 2007.

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

$$\%Difference = \frac{Measured - Known}{Known} \cdot 100 \quad (\text{Eq. 3})$$

Tables 11 through 13 present the results of the proficiency testing samples for all compounds analyzed; Figures 13 through 16 present 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 MQO bias goal of 25 percent. In Figures 13 through 16, the laboratories are identified by numbers assigned by Alion; a cross-reference between NATTS site and assigned laboratory codes is provided above in Tables 7 and 8. A laboratory's results were included in the summary analysis only if the laboratory provided analysis of a particular sample type. To maintain figure clarity, only labs whose results fell outside of a window defined by $1.5 \times IQR$ are identified on the graphical display. The inter-quartile range (IQR) is defined as the distance between the 25th and 75th percentiles of the distribution of values. Despite the fact that some individual laboratories report

PT sample concentrations which exhibit bias beyond the NATTS MQO, the profound majority of laboratories demonstrate laboratory biases for benzene, 1,3-butadiene, formaldehyde, and arsenic that are well within the MQO limit of ± 25 percent.

Table 11. Proficiency Testing Bias Results for Carbonyls in 2007 NATTS Laboratories

Laboratory Code	Laboratory Description	FORM	ACET	Overall (across analytes)
01-01-C	RI Dept. of Health Laboratories	-2.80	-0.55	-1.68
01-02-C	Vermont DEC Environmental Lab	-2.88	-3.48	-3.18
01-03-C	MA DEP	-6.75	-8.95	-7.85
02-01-C	NYS DEC BAQS	-23.1	-17.6	-20.38
03-01-C	Philadelphia Air Management Services Laboratory	-13.2	0.75	-6.23
04-02-C	SC Dept of HEC, Div. of AQ Analysis	-10.2	-5.80	-8.00
04-03-C	KY Div. of Environmental Services	-20.2	-21.9	-21.08
04-04-C	GA DNR,EPD Laboratory	-16.6	-26.6	-21.63
05-01-C	MI DEQ Lab	-5.00	-4.00	-4.50
05-03-C	Wisconsin DNR	-8.15	2.00	-3.08
06-01-C	Texas CEQ	-2.80	-4.65	-3.73
09-02-C	County of San Diego Air Pollution Control District	-11.3	-5.64	-8.45
09-03-C	Bay Area Air Quality Management District	-12.6	-6.85	-9.70
10-02-C	Oregon DEQ Lab	-8.95	-5.15	-7.05
11-01-C	ERG	-3.20	-1.85	-2.53
	<i>Overall (across laboratories)</i>	-9.97	-7.54	-8.75

Table 12. Proficiency Testing Bias Results for Metals in 2007 NATTS Laboratories

Laboratory Code	Lab Description	AS	BE	CD	PB	MN	NI	Overall (across analytes)
01-04-M	US EPA Region 1 Lab	12.52	12.72	9.59	4.03	-8.65	-1.02	4.52
03-01-M	DEP Division of Air Quality	-3.07	9.62	1.63	5.62	-0.42	7.39	3.46
04-01-M	Environmental Protection Comm. of Hillsborough Co.	8.09	18.41	3.90	-6.19	-14.6	-8.54	0.18
04-02-M	SC Dept of HEC, Div. of AQ Analysis	11.33	12.53	-6.45	2.22	-1.07	-3.36	2.53
04-03-M	KY Div. Of Environmental Services	9.26	13.13	3.21	-7.27	8.75	1.69	4.79
04-04-M	GA DNR EPD Laboratory	8.21	19.86	7.30	6.16	-10.1	-2.77	4.78
05-01-M	MI DEQ Lab	-0.04	9.26	-2.97	-8.32	-0.65	-12.8	-2.59
05-03-M	Wisconsin DNR	7.31	10.61	1.86	-4.42	-15.1	-8.38	-1.36
06-01-M	Texas CEQ	8.12	18.90	3.58	-1.42	-14.1	-10.1	0.84
08-02-M	IML Air Science	3.14	18.13	8.56	-1.27	-11.3	-5.15	2.02
10-01-M	R.J Lee Group, Central Laboratory Services	1.23	15.12	17.03	11.54	-5.70	0.72	-2.96
10-02-M	Oregon DEQ Lab	7.77	12.78	2.23	-6.12	-19.1	-10.3	-2.13
11-01-M	ERG	11.60	18.71	5.42	-1.53	-13.7	-8.45	2.34
11-02-M	RTI International	19.81	21.44	8.98	-2.55	-13.9	-6.30	3.51
	<i>Overall (across laboratories)</i>	7.88	15.18	3.89	-1.28	-8.50	-5.03	1.73

Table 13. Performance Testing Bias Results for VOCs in 2007 NATTS Laboratories

LABCODE	LABNAME	BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122	PERC	TCE	VCM	cDCPEN	tDCPEN	Overall (across analytes)
01-01-V	RI Dept. of Health Laboratories	-2.98	-3.73	0.60	-7.50	-4.19	-8.09	-3.53	-4.74	7.09	-3.88	-3.37	3.11	2.46	9.36	-1.43
01-02-V	Vermont DEC Environmental Lab	-9.51	-3.37	-2.86	5.52	-7.31	-14.8	-5.19	5.21	-4.18	-23.1	-12.9	-1.91	-22.1	-6.54	-6.94
02-01-V	NYS DEC BAQS	0.59	4.84	11.80	4.23	5.20	-6.28	3.23	-6.39	3.25	-2.84	0.27	3.70	-5.05	3.14	1.66
03-01-V	Philadelphia Air Management Services Laboratory	-3.28	2.97	5.30	-3.81	-1.76	-3.31	2.30	9.04	-4.71	-3.23	2.26	3.30	3.61	-3.35	0.64
04-01-V	Pinellas County DEM AQ	-21.6	-8.53	-9.73	-17.7	-7.18	-20.8	-11.0	-13.3	-10.4	-23.5	-15.3	-15.6	-9.65	-6.13	-13.20
04-02-V	SC Dept of HEC, Div. of AQ Analysis	-0.13	-17.1	11.71	-3.72	-14.8	-3.66	-23.0	-8.78	5.94	0.73	-7.57	4.48	4.61	-1.44	-4.32
04-03-V	KY Div. of Environmental Services	6.73	5.54	7.48	8.50	7.50	9.06	8.83	3.02	5.34	3.86	5.81	0.03	3.75	12.75	6.29
04-04-V	GA DNR EPD Laboratory	-9.89	-14.0	1.63	-4.02	0.35	-6.72	-0.45	-5.44	-5.10	-9.51	-2.28	-1.32	-3.65	3.08	-4.03
05-01-V	MI DEQ Lab	-12.4	44.88	-10.3	-13.1	-3.92	-11.2	-12.4	0.00	-1.83	-17.7	-7.83	0.00	-10.2	7.32	-3.48
05-03-V	Wisconsin DNR	6.26	10.65	7.89	-8.49	6.91	12.51	-9.42	6.59	2.97	1.55	2.67	25.60	12.88	21.86	6.72
06-01-V	Texas CEQ	-6.26	1.31	3.47	-14.3	-17.2	-23.5	-17.1	-0.79	-15.3	-22.1	-16.3	-6.18	-22.1	-13.5	-11.66
09-02-V	ERG	-1.74	-1.33	-0.65	0.33	10.98	-3.09	-1.48	-0.54	1.95	2.19	-0.38	-5.09	6.31	20.27	1.98
09-03-V	Bay Area Air Quality Management District	-12.6	-4.35	3.10	0.00	.	.	13.40	.	.	.	-3.87
09-06-V	County of San Diego Air Pollution Control District	4.20	-13.1	1.35	6.70	11.85	1.40	-0.85	-2.65	0.90	5.80	2.70	-0.40	6.20	9.90	1.63
10-02-V	Oregon DEQ Lab	-19.7	-18.5	-17.2	-19.4	-10.2	-19.1	-12.5	14.53	-21.2	-21.1	-19.7	-12.7	-12.8	0.01	-13.33
11-01-V	ERG	-5.83	2.53	10.44	9.12	4.04	-3.32	7.65	7.87	-4.58	-3.73	5.51	1.04	0.77	0.73	2.66
	Overall (across laboratories)	-5.72	-2.65	2.14	-4.00	-2.14	-7.01	-4.72	0.39	-3.01	-8.21	-4.32	0.00	-3.33	2.94	-2.73

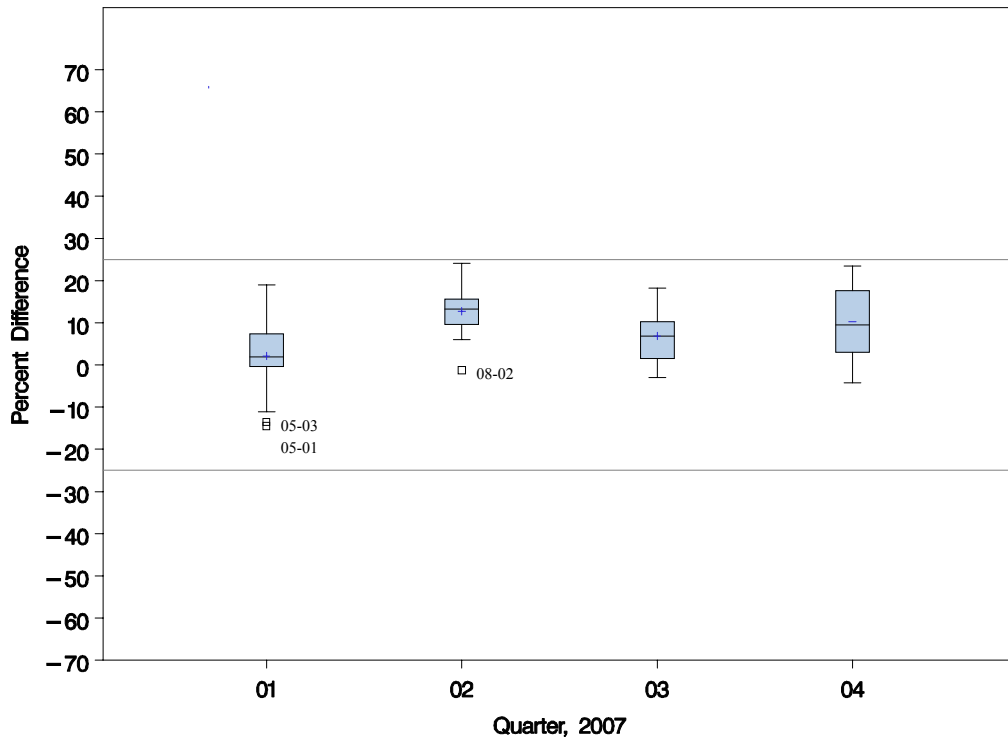


Figure 13. Distribution of Laboratory Bias by Quarter for Arsenic Proficiency Testing Data from 2007.

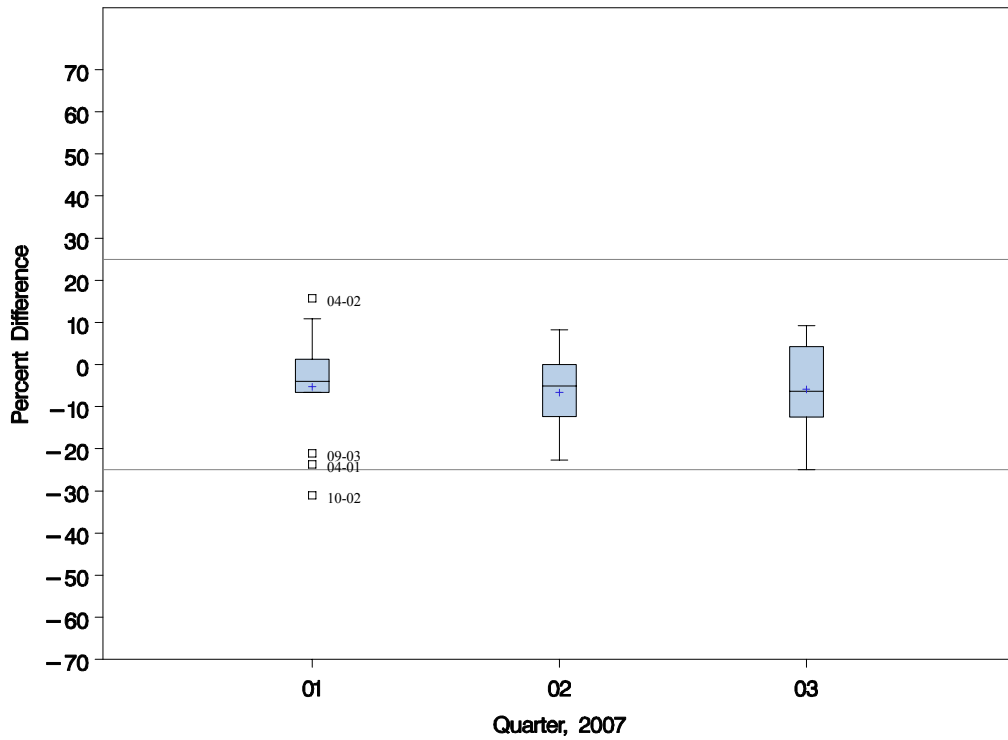


Figure 14. Distribution of Laboratory Bias by Quarter for Benzene Proficiency Testing Data from 2007.

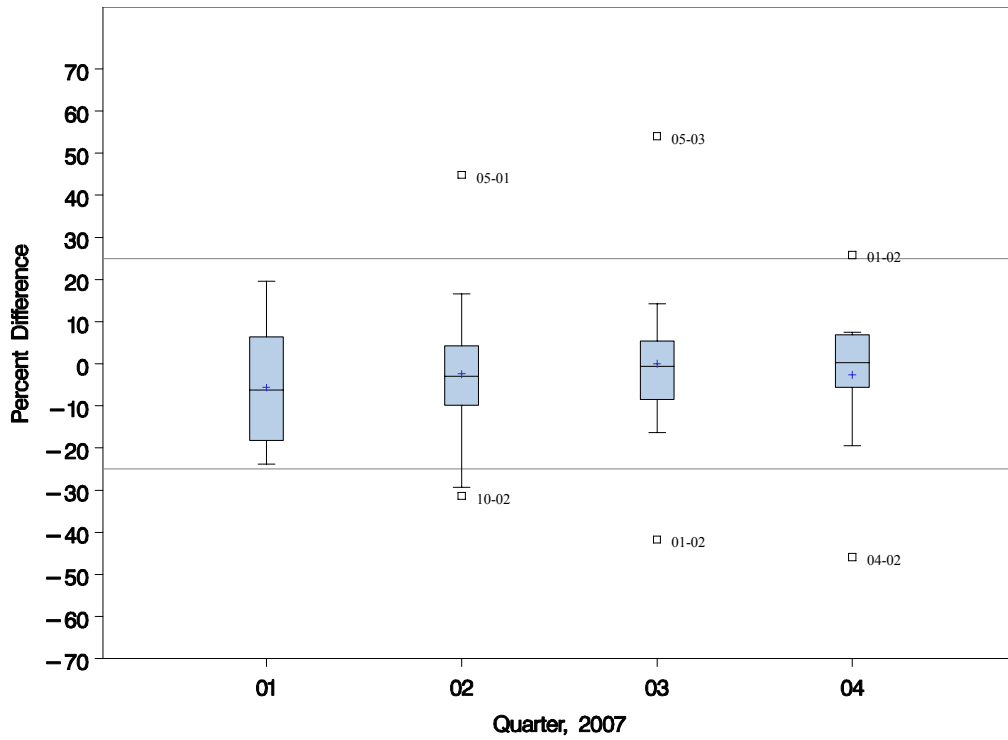


Figure 15. Distribution of Laboratory Bias by Quarter for 1,3-Butadiene Proficiency Testing Data from 2007.

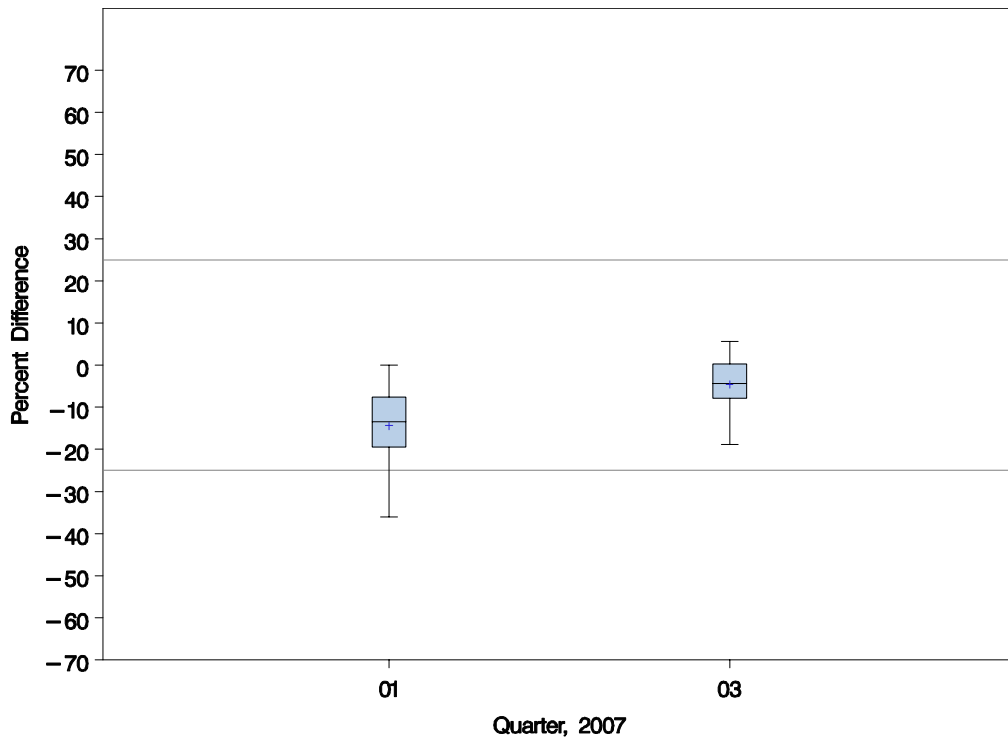


Figure 16. Distribution of Laboratory Bias by Quarter for Formaldehyde Proficiency Testing Data from 2007.

Participation in the laboratory PT program during 2007 by all NATTS-affiliated laboratories is shown in Table 14. These percentages are somewhat attenuated by the fact that two new NAATS sites, and their laboratories, were added in 2007.

Table 14. Percent Participation in Proficiency Testing Program by Quarter for 2007.

Compound Class	Quarter, CY 2007			
	1	2	3	4
Carbonyls	100	--- ^a	100	--- ^a
Metals	100	100	100	92
VOCs	100	100	100	100

^a Carbonyl PT samples not sent to laboratories in Q2 and Q4

2.5. Flow Audits Results from Instrument Performance Audits

Four NATTS field sites were audited during calendar year 2007: Hazard, KY; Underhill, VT; Pinellas County, FL; Hillsborough County, FL. The Instrument Performance Audit involves independent measurements of flow rates on all resident sampler types at the NATTS site using certified flow, temperature, and pressure instruments.

Sampler flows were measured using a calibrated volumetric flow measurement device with flow rates subsequently corrected to the standard conditions of 25 °C and 1 atm. Comparison of the site-recorded and similarly-corrected flow rate to the audited flow rate afforded calculation of field bias. For this purpose, field bias is defined as the percent difference between the corrected site flow (F_{s_c}) and the corrected audit flow (F_{a_c}):

$$\%Difference = \frac{F_{s_c} - F_{a_c}}{F_{a_c}} \cdot 100 \quad (\text{Eq. 4})$$

The results from the flow audits conducted at four sites during calendar year 2007, along with the relevant sampling techniques, are shown in Table 15. The specific sampler audited (i.e., primary or collocated) is identified in column 3. If present during the audit, collocated samplers were also audited. Since canister and carbonyl samplers may have multiple flow channels to facilitate duplicate sampling, all active channels were also subjected to a flow audit. PM₁₀ samplers have only primary channels.

Table 15. Flow audit results from 2007 Instrument Performance Audits.

Site Identifier	Method	Sampler	Channel	% Difference
Hazard, KY	Canister ^a	Primary	1	Not performed
	Carbonyl ^b	Primary	1	-0.3
	Carbonyl	Primary	2	0.3
	PM10 ^c	Primary	NA ^d	-1.2
	PM10	Collocated	NA	-1.8
Underhill, VT	Canister	Primary	1	-1.1
	Carbonyl	Primary	1	0.1
	PM10	Primary	NA	4.8
Pinellas County, FL	Canister	Primary	1	Not performed
	Carbonyl	Primary	1	-12
	Carbonyl	Primary	2	-14.4
	PM10	Primary	NA	2.9
Hillsborough County, FL	Canister	Primary	1	Not performed
	Carbonyl	Primary	1	9.6
	Carbonyl	Primary	2	-10.2
	PM10	Primary	NA	2.6
	PM10	Collocated	NA	5.7

^a VOC sampler.

^b Carbonyl cartridge.

^c Filter sample for PM₁₀ metals.

^d Not applicable.

A graphical summary of the flow audit results is presented in Figure 17. All but one of the 14 flow rate measurements were within ± 10 percent of the audit flow rate.

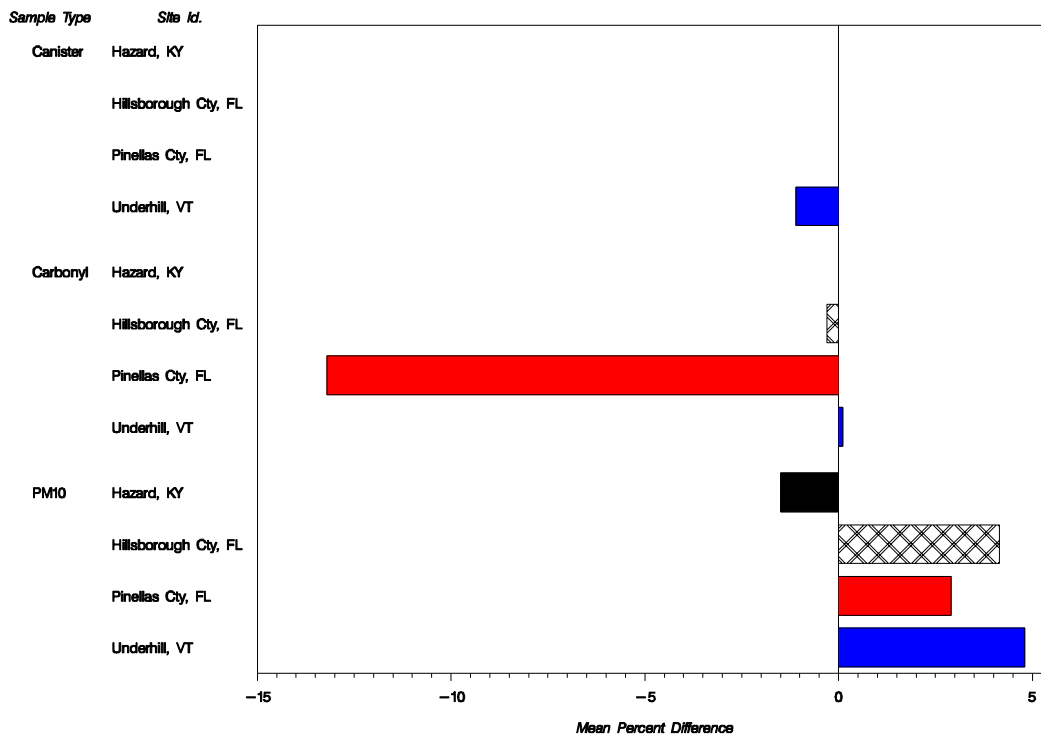


Figure 17. Summary of Instrument Performance Flow Audit Results by Sample Type and Site Id.

Accuracy of flow rates for carbonyl and PM₁₀ samplers is critical for the determination of sample concentration. Conversely, since only an aliquot of the canister volume is analyzed, the accuracy of canister sampler flow rates is less important. However, a constant flow rate across the 24-hour sampling interval is critical to achieving a linearly-representative integrated sample. The field bias audit of a VOC sampler flow rate is a random check of this time integrated value.

2.6 Method Detection Limit (MDL) Data

Significant effort was invested in the acquisition of the method detection limit data and the assistance of U.S. EPA in this effort is gratefully acknowledged. In particular, Agency staff provided invaluable assistance in linking the specific analytical laboratories with the NATTS monitoring sites for the three chemical classifications (i.e., carbonyls, metals, VOCs). MDL data were requested from direct contact with each laboratory known to be providing analytical services. A four-phase approach was used to acquire the MDL and supporting information from each laboratory:

1. The analytical laboratory believed to be associated with each NATTS site was identified and the supervisory individual at that laboratory identified. Every effort was made to obtain correct address and telephone numbers for these individuals. This was often a complex and tedious task as laboratories and associated personnel change significantly from year to year.
2. A specific request for information was made to each laboratory. Very explicit instructions were provided electronically (Appendix B) along with a spreadsheet template, created with pages for direct entry of carbonyl, metal and VOC MDL data. This template, along with a letter of introduction, was sent to each laboratory.
3. A follow-up telephone call was made within one week of sending the template spreadsheet to determine if the addressee was the appropriate recipient and, if not, to whom the template should be sent. Alternate contacts were sent the template and also contacted by telephone.
4. Finally, after careful review of the received materials from each laboratory, the spreadsheet information was compiled into a database from which subsequent data analyses could be performed. In numerous cases, follow-up emails were required to request information not provided or to clarify information provided.

For this report and by generally accepted convention, method detection limits are defined as the detection threshold for a given analyte based on the mathematical combination of all aspects of the sample collection and analysis process. As such, they reflect, among other factors, the collected sample volume for each sample, the size of the sub-sample subjected to analysis and any sample dilutions which may be associated with the analysis methodology. Previous NATTS QA reports have drawn a distinction between “overall” method detection limits and “analytical” method detection limits, both ambiguously referred to as MDLs, although sometimes with an analytical or method qualifier. This lack of measurement threshold clarity has almost assuredly degraded the quality and consistency of the data received from some laboratories. In addition, each laboratory was requested to provide MDL (with units), MDL COMPUTATIONAL FORMULA, AVERAGE SAMPLING TIME, and VOLUMETRIC FLOW RATE (with units), but there is no unequivocal way to discern from the existing data if the MDLs provided reflect the method detection limit (i.e., taking into account sampling and

analysis components) or if they reflect only instrumental detection limits. These concerns notwithstanding, the MDL results presented in this report are presented under the assumption that each laboratory provided actual *method* detection limits which incorporated both instrumental and sampling considerations.

For the sake of comprehensiveness and clarity, the computations required to convert instrumental detection limits to method detection limits are presented for clarity in the following paragraphs. However, to avoid the ambiguities associated with obtaining the component variables for these computations, the laboratories were specifically instructed to provide the actual method detection limits for the samples they analyzed. In addition to the MDLs, information for each of the 23 hazardous air pollutants listed in Table 2, each laboratory was asked to provide additional information on the relevant sampling and analysis methods used. For a given chemical class (i.e., carbonyls, metals, VOCs), MDL units, as received from each laboratory, were converted to a consistent value of $\mu\text{g}/\text{m}^3$.

VOCs from Canisters:

Samples collected in canisters for the analysis of VOCs require knowledge of the final canister pressure in order to compute MDLs from analytical detection limits. Canisters sampled to sub-ambient or ambient pressure require the addition of nitrogen or air to facilitate removal of aliquots for analysis. This dilution (i.e., ratio of pressure at the time of canister aliquoting to the pressure at the time of canister receipt) must be accounted for in the MDL.

Carbonyls:

Additional parameters are necessary to compute MDLs for carbonyl samples: 1.) the volume of solvent used to extract the carbonyls from the sampling cartridge; 2.) the nominal (i.e., target) sampling time (ca. 1440 min.); 3.) the average (or nominal) air flow rate through the carbonyl cartridge, corrected to the standard conditions of 25 °C, 1 atm. Equation 5 shows the algebraic relationship between these elements for each carbonyl analyte.

$$MDL_C = \frac{IDL_C \cdot V}{\bar{T}_s \cdot \bar{F}_s} \quad (\text{Eq. 5})$$

where: MDL_C = method detection limit for each carbonyl analyte ($\mu\text{g}/\text{m}^3$)

IDL_C = instrumental detection limit

V = volume of extraction solvent

\bar{T}_s = mean (or nominal) sample collection time

\bar{F}_s = mean (or nominal) air flow rate through the cartridge

Metals:

Method detection limits for metals are computed in a manner similar to that used for carbonyls. In addition to the mean sampling time and sampler flow rate, the fraction of filter subjected to analysis and the volume of acid digest solution are required to compute the MDL. Equation 6 shows the algebraic relationship between these elements for each metal analyte. Specific to most 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, S 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

$$MDL_M = \frac{IDL_M \cdot V}{\bar{T}_s \cdot \bar{F}_s \cdot S_f} \quad (\text{Eq. 6})$$

where: MDL_M = method detection limit for each analyte (ng/m^3)

IDL_M = instrumental detection limit

V = volume of extraction solvent

\bar{T}_s = mean (or nominal) sample collection time

\bar{F}_s = mean (or nominal) air flow rate through the filter

S_f = fraction of sampled filter area subjected to analysis

The MDL data for individual sites, in addition to the mean across all sites reporting data, are shown in Table 16.

Box and whisker plots and complementary scatter plots, shown in Figures 18 through 20, illustrate the method detection limits for VOCs, carbonyls, and metals, respectively. The measurement quality objective for benzene, 1,3-butadiene, formaldehyde, and arsenic are added to each plot for reference. As reported previously, only labs whose results fell outside of a window defined by $1.5 \times IQR$ are identified by blue stars on the graphical display. The inter-quartile range (IQR) is defined as the distance between the 25th and 75th percentiles of the distribution of values.

**Table 16. Method Detection Limits by Site and Overall for Calendar Year 2007
(VOCs and Carbonyls: $\mu\text{g}/\text{m}^3$; Metals: ng/m^3).**

Site Name	AQS Site Code	BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122
Boston, MA	25-025-0042	0.012 ^a	0.016	0.014	0.014	0.019	0.012	0.017	0.015	0.046
Bountiful, UT	49-011-0004	0.031	0.011 ^a	0.024	0.033	0.055	0.046	0.035	0.061	0.063
Bronx, NY	36-005-0110	0.053	0.037	0.063	0.046	0.118	0.086	0.051	0.066	0.093
Chesterfield, SC	45-025-0001	0.349	0.191	0.944	0.664	1.306	0.738	0.501	0.269	1.791
Dearborn, MI	26-163-0033	0.031	0.011 ^a	0.024	0.033	0.055	0.046	0.035	0.061	0.063
Decatur, GA	13-089-0002	0.104	0.054	0.129	0.139	0.219	0.192	0.155	0.175	0.175
Deer Park, TX	48-201-1039	0.864	0.595	1.703	1.026	1.533	0.787	0.727	0.486	1.372
Grand Junction, CO	08-077-0017	0.031	0.011 ^a	0.024	0.033	0.055	0.046	0.035	0.061	0.063
Grand Junction, CO	08-077-0018	0.094	0.062	0.100	0.098	0.131	0.115	0.109	0.058	0.128
Harris County, TX	48-203-0002	0.864	0.595	1.703	1.026	1.533	0.787	0.727	0.486	1.372
Hazard, KY	21-193-0003	0.031	0.011 ^a	0.024	0.033	0.055	0.046	0.035	0.061	0.063
La Grande, OR	41-061-0119	0.286	0.451	0.299	0.448	0.464	0.409	0.508	0.262	0.451
Los Angeles, CA	06-037-1103	0.320	0.222	0.630	0.489	0.055	0.046	0.035	0.061	0.063
Mayville, WI	55-027-0007	0.320	0.221	0.631	0.488	0.767	0.463	0.404	0.347	0.686
Northbrook, IL	17-031-4201	0.031	0.011 ^a	0.024	0.033	0.055	0.046	0.035	0.061	0.063
Phoenix, AZ	04-013-9997	0.031	0.011 ^a	0.024	0.033	0.055	0.046	0.035	0.061	0.063
Pinellas County, Tampa, F	12-103-0026	0.064	0.086	0.164	0.127	0.184	0.125	0.105	0.205	0.199
Hillsborough County, FL	12-057-3002	0.064	0.086	0.164	0.127	0.184	0.125	0.105	0.205	0.199
Providence, RI	44-007-0022	0.286	0.451	0.299	0.448	0.464	0.409	0.508	0.262	0.451
Rochester, NY	36-055-1007	0.053	0.037	0.063	0.046	0.118	0.086	0.051	0.066	0.093
Rubidoux, CA	06-065-8001	0.320	0.222	0.630	0.489	0.055	0.046	0.035	0.061	0.063
San Jose, CA	06-085-0005	0.960	0.355	0.630	0.098	0.055	0.046	0.035	0.061	0.063
Seattle, WA	53-033-0080	0.031	0.011 ^a	0.024	0.033	0.055	0.046	0.035	0.061	0.063
Site Name	AQS Site Code	BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122
St. Louis, MO	29-510-0085	0.031	0.011 ^a	0.024	0.033	0.055	0.046	0.035	0.061	0.063
Underhill, VT	50-007-0007	0.078	0.084	0.123	0.138	0.201	0.110	0.092	0.109	0.491
Washington, DC	11-001-0043	0.331	0.207	0.158	0.122	0.131	0.115	0.109	0.058	0.128

**Table 16. Method Detection Limits by Site and Overall for Calendar Year 2007
(VOCs and Carbonyls: $\mu\text{g}/\text{m}^3$; Metals: ng/m^3), continued.**

<i>Geometric Mean</i>	0.103	0.075	0.122	0.113	0.139	0.104	0.086	0.101	0.153
<i>Arithmetic Mean</i>	0.218	0.168	0.332	0.242	0.307	0.195	0.175	0.144	0.322
<i>Standard Deviation</i>	0.278	0.189	0.478	0.300	0.457	0.244	0.227	0.134	0.473
<i>Median</i>	0.071	0.085	0.126	0.110	0.118	0.086	0.051	0.061	0.093

^a Meets measurement quality objective.

Table 16 (additional analytes).

Site Name	AQS Site Code	PERC	TCE	VCM	cDCPEN	tDCPEN	FORM	ACET	AS	BE	CD	PB	MN	NI
Phoenix, AZ	04-013-9997	0.039	0.019	0.012	0.027	0.030	0.007 ^a	0.009	0.077 ^a	0.154	0.089	0.387	0.127	0.375
Los Angeles, CA	06-037-1103	0.680	0.538	0.102	0.027	0.030	0.123	1.083	0.077 ^a	0.154	0.089	0.387	0.127	0.375
Rubidoux, CA	06-065-8001	0.680	0.538	0.102	0.027	0.030	0.123	1.083	0.077 ^a	0.154	0.089	0.387	0.127	0.375
San Jose, CA	06-085-0005	0.136	0.215	0.102	0.027	0.030	0.123	0.361	0.077 ^a	0.154	0.089	0.387	0.127	0.375
Grand Junction, CO	08-077-0017	0.039	0.019	0.012	0.027	0.030	0.007 ^a	0.009	5.573	0.674	0.276	0.206	0.397	1.570
Grand Junction, CO	08-077-0018	0.093	0.119	0.075	0.114	0.114	0.015	0.013	5.573	0.674	0.276	0.206	0.397	1.570
Washington, DC	11-001-0043	0.340	0.323	0.128	0.114	0.114	0.123	1.083	0.130	0.040	0.010	0.010	0.060	0.070
Hillsborough County, FL	12-057-3002	0.197	0.129	0.100	0.109	0.095	0.007 ^a	0.009	0.560	0.020	0.150	0.380	0.190	0.600
Pinellas County, Tampa, FL	12-103-0026	0.197	0.129	0.100	0.109	0.095	0.007 ^a	0.009	0.560	0.020	0.150	0.380	0.190	0.600
Decatur, GA	13-089-0002	0.166	0.196	0.338	0.164	0.161	0.634	0.671	0.170 ^a	0.009	0.006	0.005	0.012	0.016
Northbrook, IL	17-031-4201	0.039	0.019	0.012	0.027	0.030	0.007 ^a	0.009	0.010 ^a	0.012	0.008	0.107	0.021	0.110
Hazard, KY	21-193-0003	0.039	0.019	0.012	0.027	0.030	0.007 ^a	0.009	0.010 ^a	0.012	0.008	0.107	0.021	0.110
Boston, MA	25-025-0042	0.021	0.021	0.017	0.013	0.014	0.044	0.036	0.010 ^a	0.012	0.008	0.107	0.021	0.110
Dearborn, MI	26-163-0033	0.039	0.019	0.012	0.027	0.030	0.007 ^a	0.009	0.150 ^a	0.210	0.140	0.200	0.350	0.140
St. Louis, MO	29-510-0085	0.039	0.019	0.012	0.027	0.030	0.007 ^a	0.009	0.010 ^a	0.012	0.008	0.107	0.021	0.110
Bronx, NY	36-005-0110	0.063	0.061	0.026	0.047	0.032	0.015	0.015	0.052 ^a	0.026	0.026	0.026	0.026	0.026
Rochester, NY	36-055-1007	0.063	0.061	0.026	0.047	0.032	0.015	0.015	0.052 ^a	0.026	0.026	0.026	0.026	0.026
La Grande, OR	41-061-0119	0.398	0.467	0.156	0.417	0.370	0.007 ^a	0.010	0.035 ^a	0.004	0.035	0.350	0.350	0.350
Providence, RI	44-007-0022	0.398	0.467	0.156	0.417	0.370	0.007 ^a	0.010	0.035 ^a	0.004	0.035	0.350	0.350	0.350
Chesterfield, SC	45-025-0001	1.265	0.965	0.295	0.814	0.796	0.194	0.178	0.031 ^a	0.001	0.001	0.003	0.002	0.003
Deer Park, TX	48-201-1039	1.630	1.559	0.436	0.908	0.905	0.074	0.178	0.013 ^a	0.001	0.001	0.003	0.002	0.003
Harrison County, TX	48-203-0002	1.630	1.559	0.436	0.908	0.905	0.074	0.144	0.014 ^a	0.001	0.001	0.003	0.002	0.003
Bountiful, UT	49-011-0004	0.039	0.019	0.012	0.027	0.030	0.007 ^a	0.009	0.077 ^a	0.154	0.089	0.387	0.127	0.375

Table 16. Additional analytes, continued.

Site Name	AQS Site Code	PERC	TCE	VCM	cDCPEN	tDCPEN	FORM	ACET	AS	BE	CD	PB	MN	NI
Underhill, VT	50-007-0007	0.146	0.116	0.066	0.115	0.141	0.014	0.009	0.077 ^a	0.154	0.089	0.387	0.127	0.375
Seattle, WA	53-033-0080	0.039	0.019	0.012	0.027	0.030	0.007 ^a	0.009	0.010 ^a	0.012	0.008	0.107	0.021	0.110
Mayville, WI	55-027-0007	0.679	0.538	0.256	0.454	0.452	0.390	0.078	0.040 ^a	0.014	0.016	0.006	0.021	0.131
<i>Geometric Mean</i>		0.149	0.114	0.057	0.079	0.080	0.073	0.036	0.068	0.026	0.025	0.081	0.052	0.122
<i>Arithmetic Mean</i>		0.350	0.314	0.116	0.194	0.189	0.140	0.195	0.519	0.104	0.066	0.193	0.125	0.318
<i>Standard Deviation</i>		0.479	0.438	0.131	0.282	0.277	0.173	0.358	1.495	0.181	0.079	0.161	0.135	0.411
<i>Median</i>		0.141	0.124	0.088	0.047	0.032	0.099	0.012	0.065	0.020	0.031	0.154	0.094	0.136

^a Meets measurement quality objective.

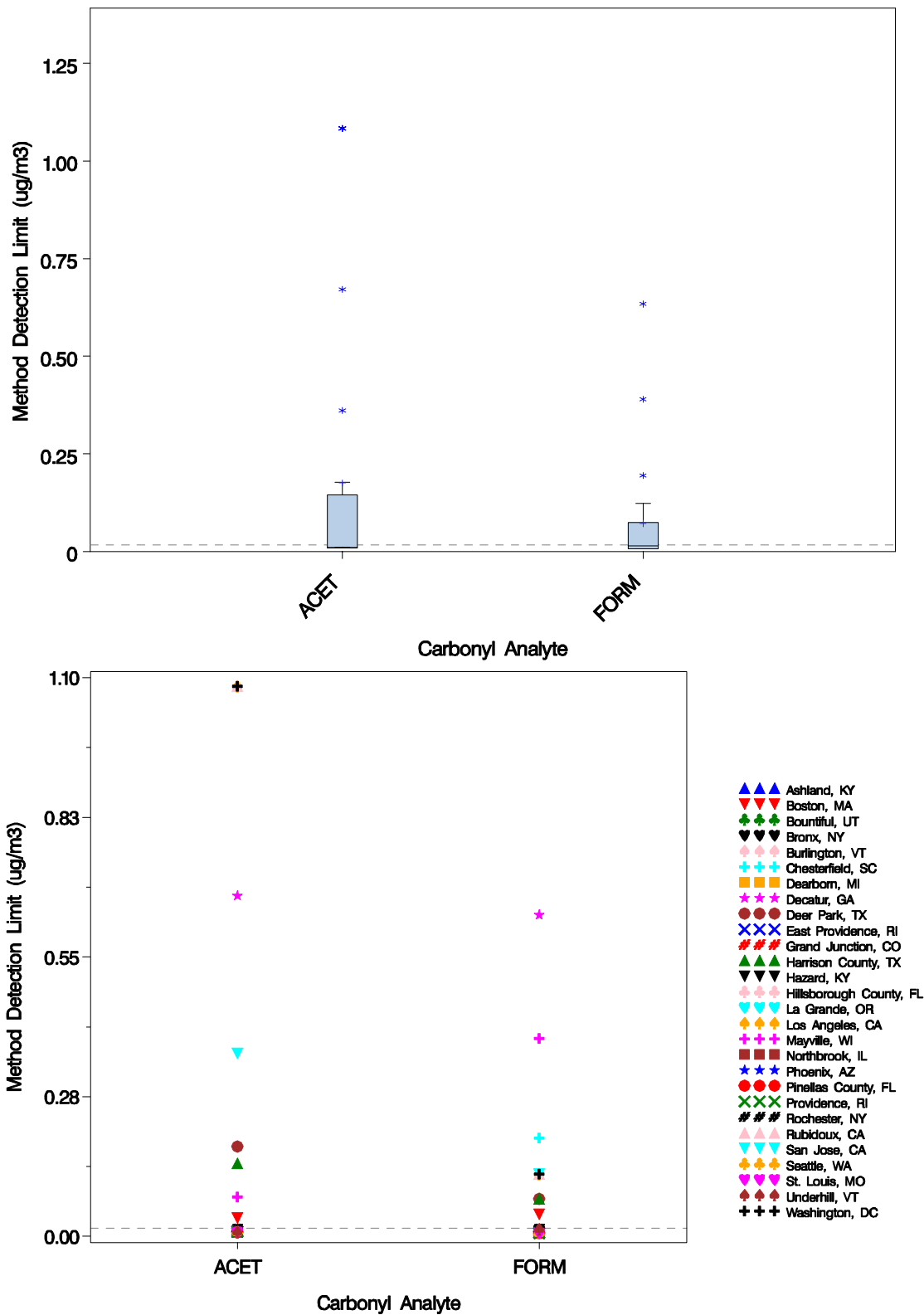


Figure 18. Distribution of Method Detection Limits for Carbonyls for 2007 NATTS Data (dotted line indicates MQO target MDL for formaldehyde; >1.5×IQR are identified as blue stars in top display).

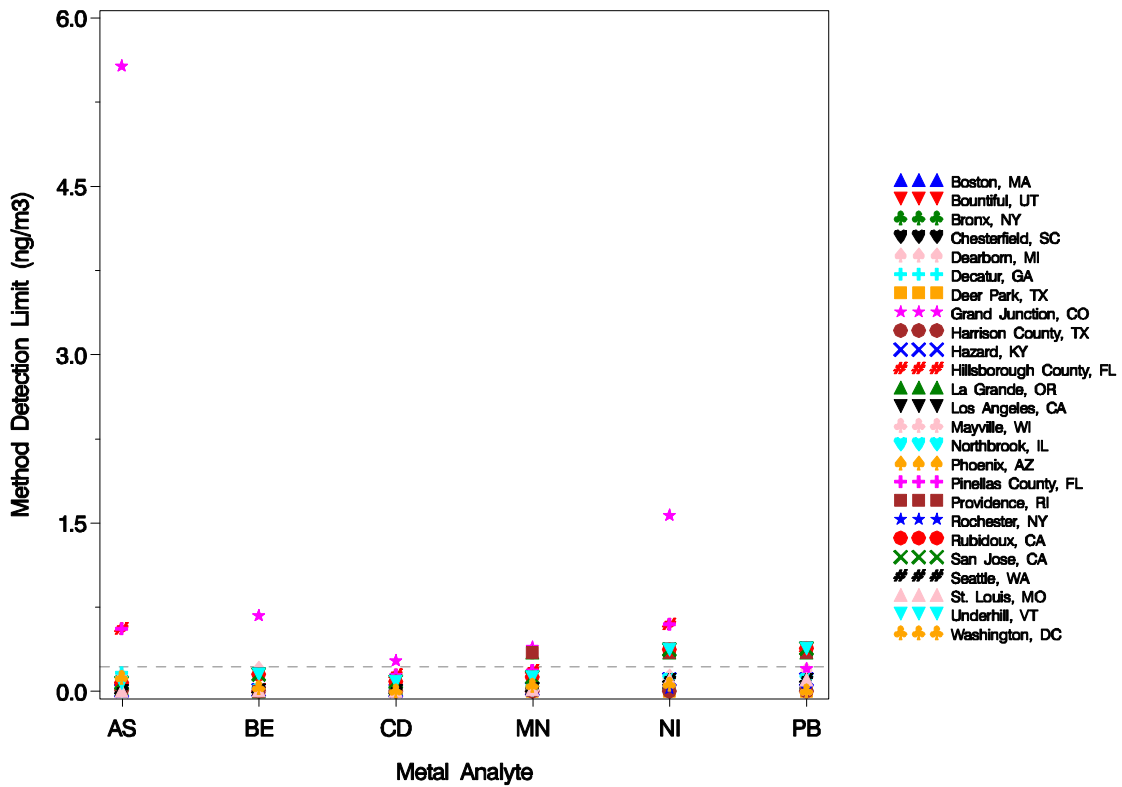
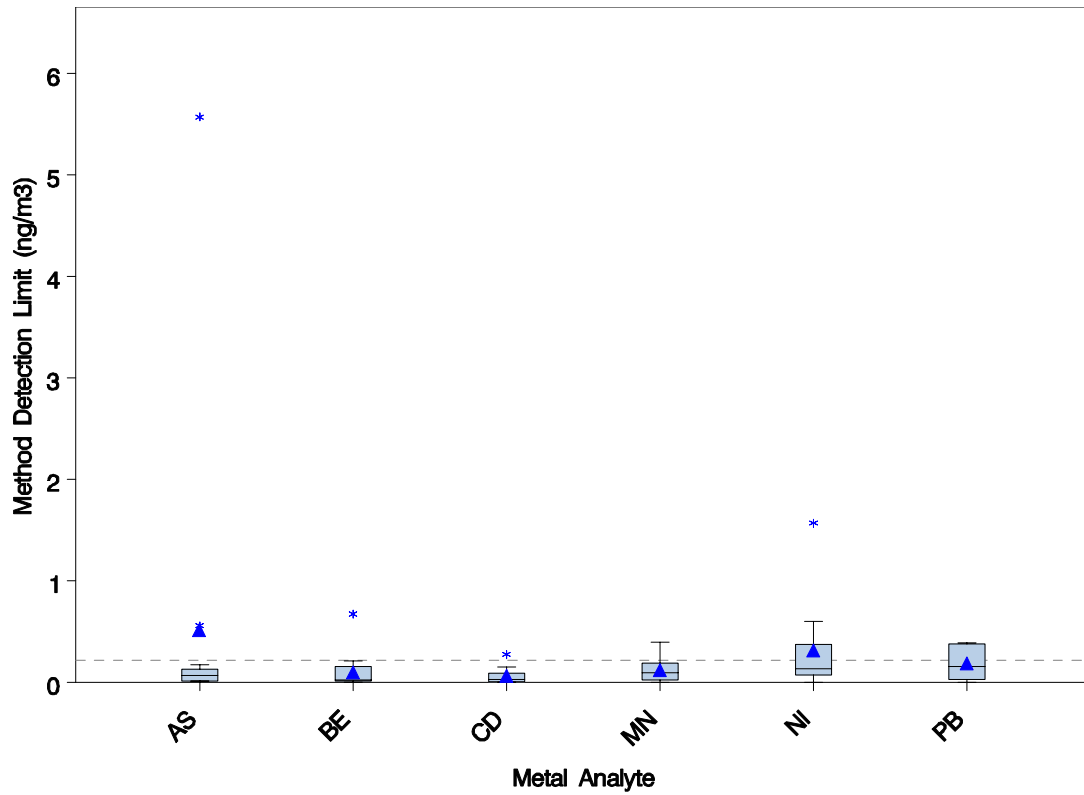


Figure 19. Distribution of Method Detection Limits for Metals for 2007 NATTS Data (dotted line indicates MQO target MDL for arsenic; $>1.5 \times \text{IQR}$ are identified as blue stars in top display).

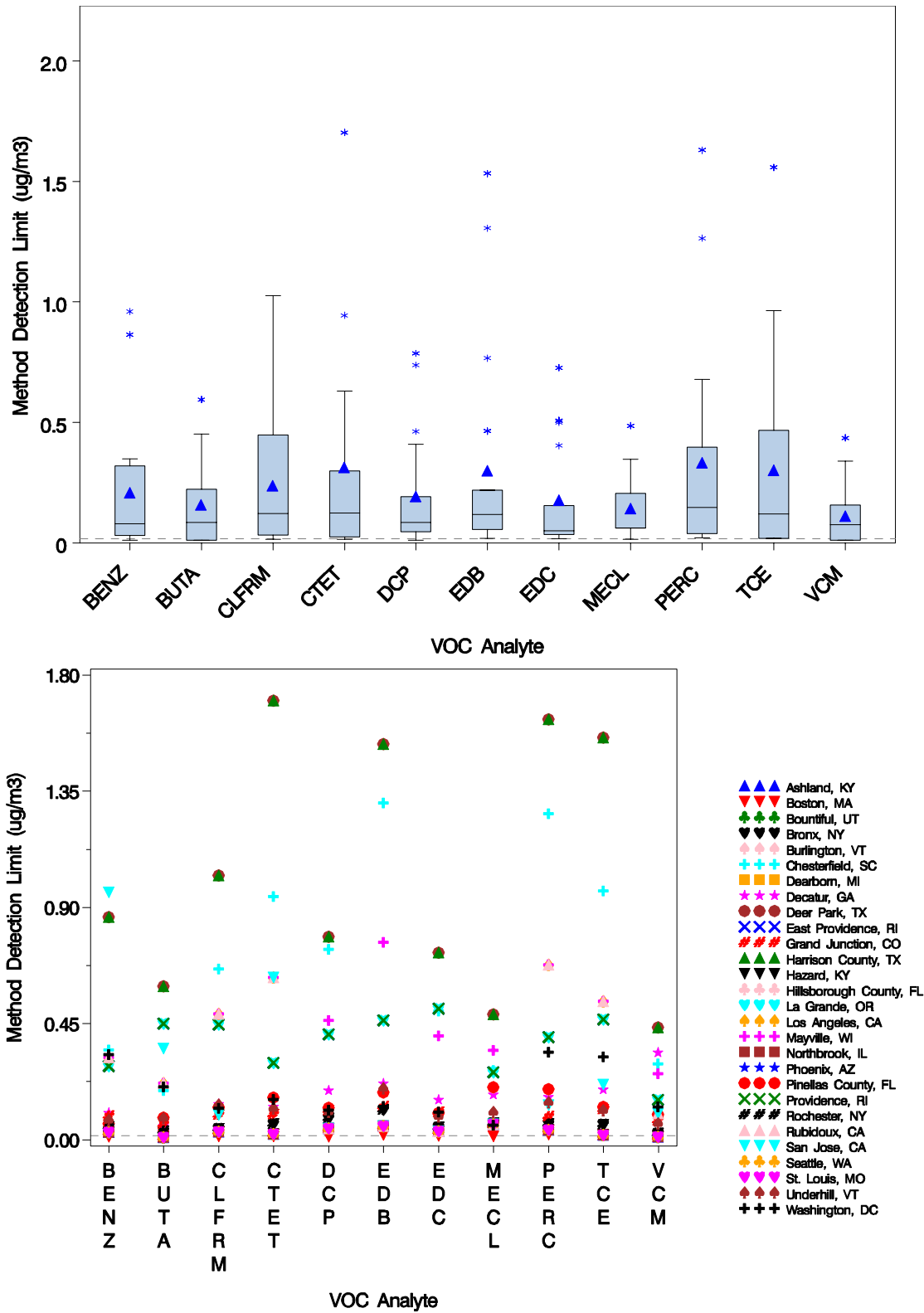


Figure 20. Distribution of Method Detection Limits for VOCs for 2007 NATTS Data (dotted line indicates MQO target MDL for benzene; $>1.5 \times \text{IQR}$ are identified as blue stars in top display).

As reported by the metals analysis laboratories for 2007, twelve NATTS sites (Boston-Roxbury, MA; Decatur, GA; Hillsborough Cty, FL; Pinellas Cty, FL; Dearborn, MI; Mayville, WI; Northbrook, IL; Harrison County, TX; St. Louis, MO; Grand Junction, CO, La Grande, OR; Seattle, WA; Providence, RI) collected high-volume PM₁₀ metals on 8x10 in. quartz fiber filters. Five sites reported using low-volume PM₁₀ metals sampling on 47 mm Teflon filters (Bronx, NY; Rochester, NY; Bountiful, UT; Grand Junction, CO; Phoenix, AZ). The remaining sites either did not collect PM₁₀ samples for metals analysis or did not report the type of sampling implemented.

Comparison of method detection limits for the two sampling approaches is meaningful only when the analysis laboratory is the same for the two sites; otherwise the variability in method detection limits is an aggregate effect of sample collection and sample analysis. The metals results provided by the ERG laboratory offer a unique opportunity to examine method detection limits between high and low volume sampling without the influence of cross-laboratory instrumental detection limit variability. Table 17, below, shows the method detection limits for each of the PM₁₀ metal analytes. As expected from the 100-fold differential in collected air volume, the method detection limits for the high-volume sampling are from 3 to 12 times lower than those for the low-volume sampling for the same analyte. However, given the variability in MDLs among laboratories, all metals data were combined for the summary analyses presented in this report (Table 16 and Figures 18 through 20).

Table 17. Comparison of Method Detection Limits for High- and Low-Volume Sampling of PM₁₀ Metals in 2007.

Analyte	Method Detection Limits (ng/m ³)		MDL ratio (High/Low)
	2000 m ³ samples	20 m ³ samples	
Arsenic	0.0102	0.0766	7.51
Beryllium	0.0124	0.1538	12.40
Cadmium	0.0076	0.0892	11.74
Lead	0.1066	0.3866	3.63
Manganese	0.0214	0.1267	5.92
Nickel	0.1103	0.3749	3.40

The geometric mean MDLs (Table 18) for the select analytes: benzene, 1,3-butadiene, and formaldehyde do not meet the target measurement quality objective MDL. Conversely, the MDL for arsenic falls within the target MQO.

Table 18. Summary Statistics for MDLs Across All Reporting NATTS Laboratories for 2007.

MDL	Selected Analyte			
	Benzene, ($\mu\text{g}/\text{m}^3$)	1,3-butadiene, ($\mu\text{g}/\text{m}^3$)	formaldehyde, ($\mu\text{g}/\text{m}^3$)	arsenic, (ng/m^3)
Geometric Mean	0.101	0.065	0.022	0.050
Arithmetic Mean	0.209	0.159	0.071	0.465
Median	0.078	0.084	0.014	0.052
MQO	0.016	0.013	0.0074	0.217
Ratio of Geo. Mean to MQO	6.3	5.0	3.0	0.230

3.0 SUMMARY

Based on four hazardous air pollutants representative of the various chemical classes: benzene, 1,3-butadiene, formaldehyde, and arsenic, the following summary comments are appropriate for the 2007 NATTS data.

1. Excluding NATTS sites intentionally not collecting data for a particular analyte class (e.g., PM₁₀ metals), the mean percent completeness of data reported into AQS across all NATTS sites were 88, 90, 89, and 93 for benzene, 1,3-butadiene, formaldehyde, and arsenic, respectively. Data from specific sites were found to fall within the MQO. Overall, the measurement quality objective was achieved for all four analytes.
2. Among sites for which replicate analyses were available, analytical precision was found to be below the 15% MQO threshold for benzene, 1,3-butadiene, formaldehyde, and arsenic. There were a few notable exceptions to this achievement for specific sites which might be reflective of extreme disagreements between measurements for selected samples and not necessarily indicative of a general lack of analytical precision. As certainly expected, the frequency of cases where the MQO threshold was exceeded was distinctly greater for overall precision (i.e., including sampling and analysis), particularly for 1,3-butadiene and formaldehyde. Estimates of overall precision included both duplicate and collocated samples.
3. Laboratory performance, as assessed by percent difference between the laboratory measurement and the certified sample concentration of the proficiency testing samples, was within the $\pm 25\%$ MQO for all analytes (i.e., benzene, 1,3-butadiene, formaldehyde, and arsenic) for available data from all quarters in 2007. The proportion of laboratories participating in the performance testing program was, overall, slightly below 100% for carbonyls, 90% for VOCs, and 86% for metals; a participation decline was observed in Q3 and Q4 of 2007. Laboratories not performing analyses of a particular analyte were excluded from these statistics.

4. With a single exception, sampler flows measured during instrument performance audits conducted at NATTS field sites showed less than $\pm 5\%$ difference from their site-recorded values. Flow rates of samplers employed for collection of carbonyls showed the greatest deviations from their recorded values.
5. Among all measures of data quality, method detection limits were substantially greater than the corresponding measurement quality objectives and showed substantial variability for any given analyte across sites (i.e., laboratories). Only arsenic showed detectability within the MQO threshold. The ratios of the geometric means to the corresponding MQOs were 6.3, 5.0, 3.3, and 0.23 for benzene, 1,3-butadiene, formaldehyde, and arsenic, respectively.

4.0 RECOMMENDATIONS

The acquisition of information, both analytical results and site characteristics, for the NATTS network samples present in the AQS database was accomplished successfully, based upon a thorough understanding of the database structure. However, two very important pieces of information were quite difficult to obtain and required significant, and repeated, effort as well as EPA support to realize. These included: 1.) the linkages between the parameter occurrence codes (POCs) and the primary, duplicate, and collocated samples, and 2.) the MDL data.

The parameter occurrence codes (POCs) are present in the AQS database but the associated sampler information is not. Since POCs are arbitrarily assigned by the agency monitoring a particular NATTS site and are in no way standardized across NATTS sites, the inclusion of a field in the AQS database to specify whether a particular POC is “primary”, “duplicate”, or “collocated” would be of enormous benefit to the utility of the AQS data. Alternatively, POCs might be standardized so that a POC indicating a primary sample (e.g.) at one site would be exactly the same for all sites. While this might seem attractive from a consistency perspective, it would be much more difficult to implement due to suspected entrenchment of POC assignments at many NATTS sites and the possible conflicts with POCs for other monitoring networks. Since for many sites specific POCs are historically entrenched with particular sample types, resistance from site administrators to making POCs equivalent at all sites would likely be very high. Alternatively, a complementary field to the POC field might be added in the AQS database which would allow the inclusion of a text value (e.g., “P”, “D”, or “C”) to identify whether a particular AQS record was associated with a primary, duplicate, or collocated sampling event.

Summary statistics created for this report reflect the overall condition of the data but may, in some cases, be unduly influenced by selected extreme values. Instances where the summary statistics fall outside of the MQOs warrant further investigation of the individual data points and, possibly, direct discussions with the laboratory performing the analyses.

The acquisition and assembly of method detection limit information was, by far, the most labor-intensive task and yielded the least reliable data. Since the sample analysis laboratory is presumably responsible for uploading the analysis results to AQS, the method detection limit information associated with a given measurement could easily be uploaded with the

measurement result. Furthermore, a text field could be added that contained an indication of the laboratory contributing the result. While direct person-to-person contact with the laboratory may still be required to clarify specific issues, the association between the NATTS site and the laboratory would already be established in AQS.

Lastly, the definition of method detection limit needs to be clearly stated, both in grammatical and algebraic language, and any ambiguity between the method detection limit and the instrumental detection limit should be eliminated.

5.0 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>.
2. "Technical Assistance Document for the National Ambient Air Toxics Trends and Assessment Program." Eastern Research Group, January 1, 2007.
3. "National Air Toxics Trends Stations Quality Assurance Annual Report – Calendar Year 2006" prepared by Battelle Memorial Institute for U.S.EPA, 2007.

APPENDIX A

Data Analysis Results for Acrolein

This appendix summarizes quality assurance information for the VOC compound, acrolein. Completeness, analytical precision, overall precision, laboratory bias, and method detection limit results are presented for calendar year 2007 for the NATTS network.

Completeness

Percent completeness statistics for acrolein are presented in Table A-1 and in Figure A-1. For comparison, completeness statistics for arsenic, benzene, 1,3-butadiene, and formaldehyde are also given. Five sites did not report acrolein results at all and one site, Phoenix, AZ, reported it in fewer than 50% of the samples. All other sites achieved the completeness measurement quality objective for acrolein. With these noted exceptions, sites which reported acrolein did so at frequencies similar to other VOC analytes.

Table A-1. Percent Completeness^a of the 2007 AQS Dataset by Site for Five Hazardous Air Pollutants.

AQS Site Id.	Site Name	Parameter Code →	82103	45201	43218	43502	43505
		AS	BENZ	BUTA	FORM	ACRO	
25-025-0042	Boston, MA		90	90	90	98	90
49-011-0004	Bountiful, UT		93	102	102	100	102
36-005-0110	Bronx, NY		100	100	100	100	100
45-025-0001	Chesterfield, SC		100	100	100	100	100
26-163-0033	Dearborn, MI		107	95	95	88	95
13-089-0002	Decatur, GA		100	100	100	98	N.R. ^b
48-201-1039	Deer Park, TX		98	100	100	93	N.R. ^b
08-077-0017	Grand Junction, CO		92	100	100	100	100
48-203-0002	Harrison County, TX		100	93	93	92	92
21-193-0003	Hazard, KY		100	100	100	100	100
41-061-0119	La Grande, OR		93	87	88	83	N.R. ^b
06-037-1103	Los Angeles, CA		N.C. ^c	87	87	115	87
55-027-0007	Mayville, WI		82	87	87	37	87
17-031-4201	Northbrook, IL		97	98	98	100	98
04-013-9997	Phoenix, AZ		97	88	88	100	42
12-103-0026	Pinellas County, FL		97	98	98	100	98
12-057-3002	Hillsborough County, FL		100	100	100	98	100
44-007-0022	Providence, RI		100	98	98	100	98
36-055-1007	Rochester, NY		88	100	100	100	100
06-065-8001	Rubidoux, CA		N.C. ^c	87	87	100	87
06-085-0005	San Jose, CA		N.C. ^c	85	85	100	N.R. ^b
53-033-0080	Seattle, WA		100	100	100	100	100
29-510-0085	St. Louis, MO		98	100	100	100	100
50-007-0007	Underhill, VT		N.C. ^c	100	100	97	N.R. ^b
11-001-0043	Washington, DC		100	98	72	N.C. ^c	100
		<i>Mean</i>	96	96	95	96	94
		<i>Std. Dev.</i>	6	6	7	14	13
		<i>Median</i>	98	98	98	100	99

^a Based on 60 collections/analyses = 100%.

^b Not reported.

^c Not collected at this site.

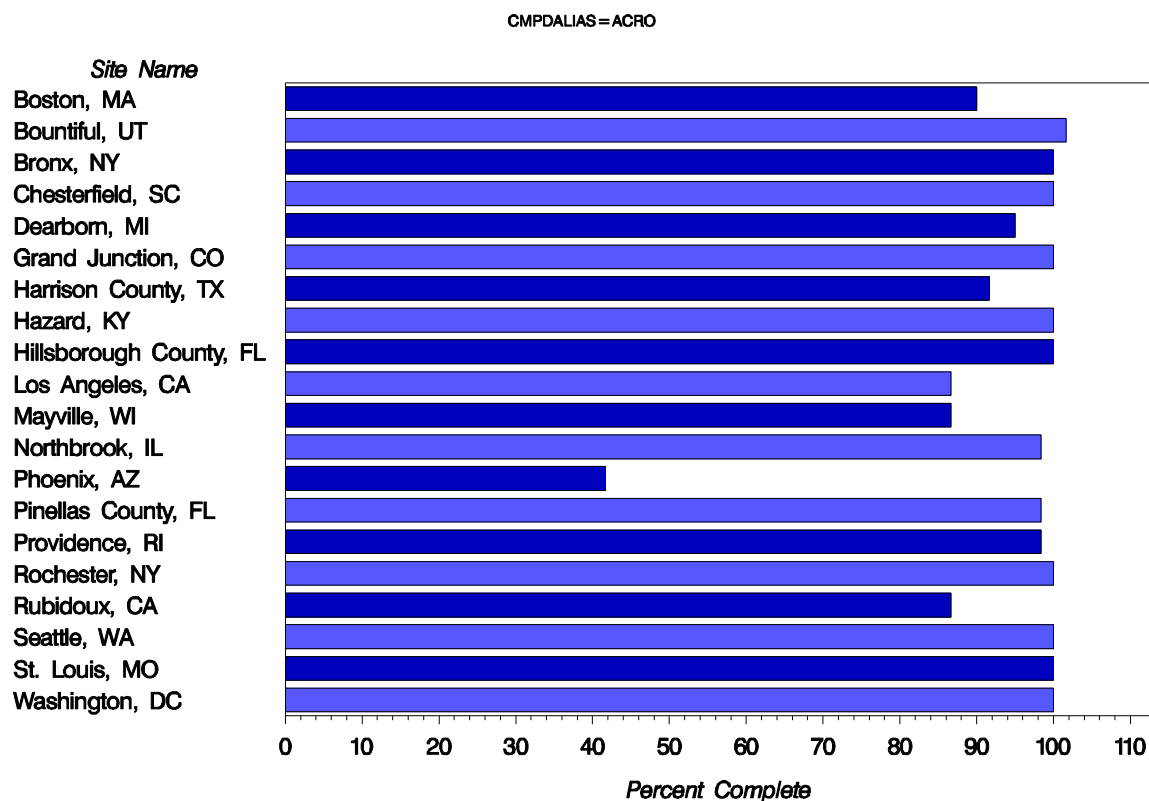


Figure A-1. Completeness for Acrolein at NATTS Sample Collection Sites in 2007.

Analytical Precision

Laboratories associated with nine sites reported analytical precision for acrolein. Seven of these sites employed the services of the same laboratory for VOC analyses. Overall, the CV for acrolein (20%), shown in Table A-2, is well within the range seen for other VOCs (Table 9); however, Figure A-2 illustrates that only four of the nine sites achieved the measurement quality objective of 15% for analytical precision, a most surprising finding based on the fact that a single lab performed most of the analyses. In this light, it seems possible that the range of %CVs for acrolein (4.4-39.7) reflects differences in the magnitude of the individual measurements across sites as well as differences associated with laboratory performance.

Table A-2. Analytical Precision^{a,b} for Acrolein for Replicate Analyses of 2007 NATTS Data.

AQS		
Site Id.	Site Description	Acrolein
04-013-9997	Phoenix, AZ	11.1 (6)
08-077-0018	Grand Junction, CO	39.7 (12)
12-103-0026	Pinellas County, FL	22 (83)
17-031-4201	Northbrook, IL	10.6 (9)
26-163-0033	Dearborn, MI	4.4 (12)
29-510-0085	St. Louis, MO	28.2 (10)

AQS		
Site Id.	Site Description	Acrolein
48-203-0002	Harrison County, TX	12.9 (2)
49-011-0004	Bountiful, UT	18 (12)
53-033-0080	Seattle, WA	22 (14)
<i>Overall Mean^c</i>		20 (207)

^a Expressed as %CV with number of contributing data pairs presented in parentheses.

^b Sites not presented in the table reported no duplicate analysis results.

^c Across all reporting sites.

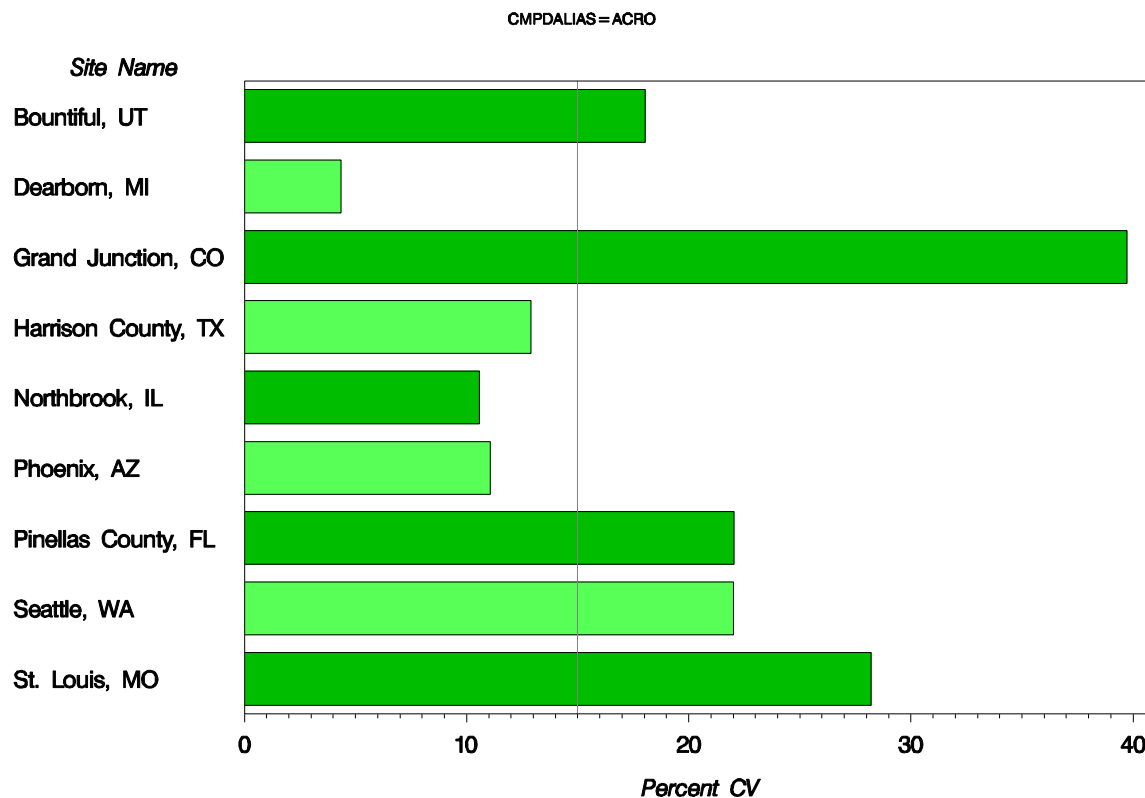


Figure A-2. Analytical Precision Summary for Acrolein at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).

Overall Precision

Seven sites reported overall precision for acrolein for collocated samples, with two sites reporting duplicate precision. The overall CV for acrolein (52.7%), shown in Table A-3, is significantly and predictably larger than that seen for the corresponding analytical precision. It is also well above the range seen for other VOCs (Table 10). This observation may be attributable to the relative difficulty associated with the collection of this analyte and its instability during containment in canisters. Figure A-3 illustrates that only one of the eight sites achieved the measurement quality objective of 15% for overall precision.

Table A-3. Overall Precision^{a,b} for Acrolein for Primary and Collocated Samples from 2007.

AQS Site Id.	Site Description	Duplicate Type	Acrolein
04-013-9997	Phoenix, AZ	Collocate	14 (3)
06-037-1103	Los Angeles, CA	Collocate	73 (21)
06-065-8001	Rubidoux, CA	Collocate	65.2 (27)
06-065-8001	Rubidoux, CA	Duplicate	60.4 (25)
12-103-0026	Pinellas County, FL	Collocate	31.9 (37)
17-031-4201	Northbrook, IL	Collocate	34.5 (6)
25-025-0042	Boston, MA	Duplicate	16 (8)
26-163-0033	Dearborn, MI	Collocate	36.8 (5)
53-033-0080	Seattle, WA	Collocate	44.5 (7)
<i>Overall Mean^c All Dups.</i>			52.7 (139)

^a Expressed as %CV with number of contributing data pairs presented in parentheses. Metals results are reported at STP at most sites and local conditions at others.

^b Sites and/or duplicate types not presented in the table represent no duplicate and/or collocated sample results reported.

^c Across all reporting sites and duplicate types

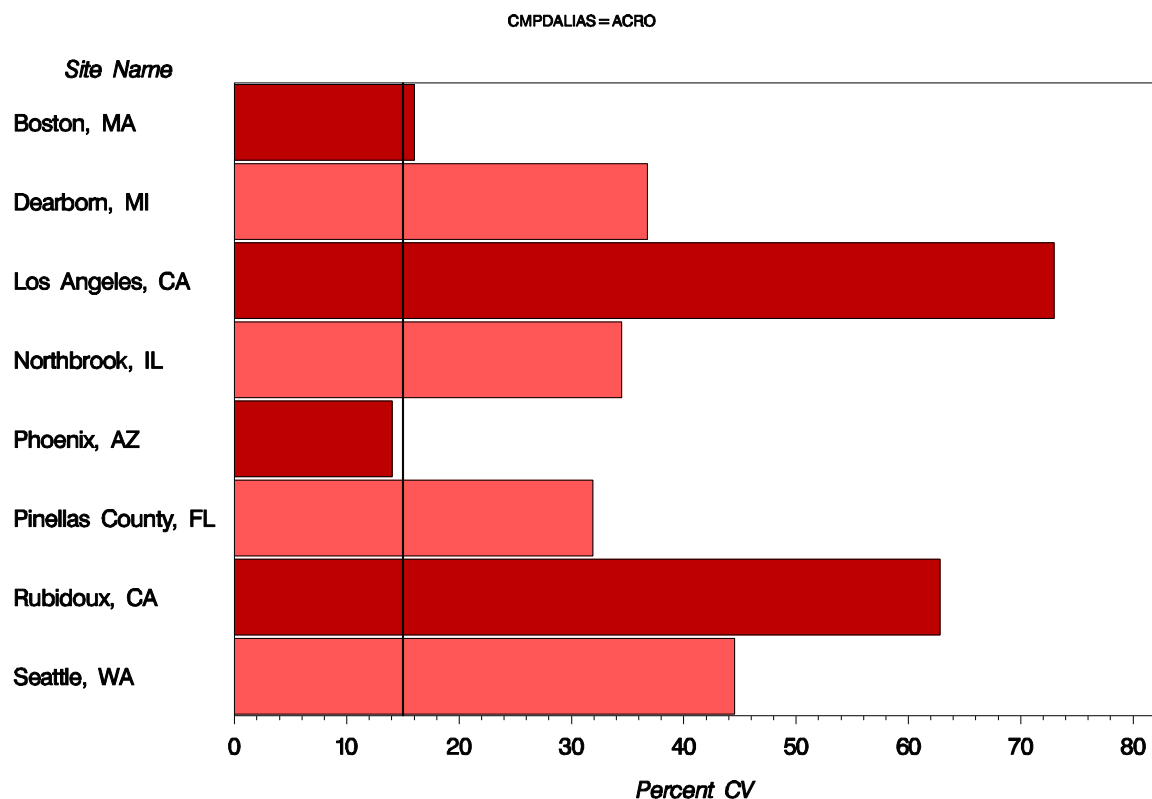


Figure A-3. Overall Precision Summary for Acrolein at NATTS Sample Collection Sites in 2007 (MQO reference indicated at 15%).

Laboratory Bias

Proficiency testing results for acrolein, shown in Table A-4, were available from 13 laboratories in 2007. Overall, the results reveal a profoundly positive bias, indicating that the laboratories are reporting values appreciably higher than what was reputed to have been loaded into the canisters. Examination of the distribution of percent differences for acrolein by quarter in 2007 (Figure A-4) reveals a much different perspective, with the first and last quarters showing relatively good agreement with the loaded amounts and quarters 2 and 3 showing a strong positive bias and at least one extreme value for Pinellas County.

Table A-4. Proficiency Testing Bias^a Results for Acrolein in 2007 NATTS Laboratories

Laboratory		Acrolein
Code	Laboratory Name	
01-01-V	RI Dept. of Health Laboratories	-7.04
01-02-V	Vermont DEC Environmental Lab	4.80
02-01-V	NYS DEC BAQS	2.72
03-01-V	Philadelphia Air Management Services Laboratory	1.58
04-01-V	Pinellas County DEM AQ	44.14

Laboratory Code	Laboratory Name	Acrolein
04-02-V	SC Dept of HEC, Div. of AQ Analysis	-11.2
04-03-V	KY Div. of Environmental Services	19.28
04-04-V	GA DNR EPD Laboratory	-4.03
05-03-V	Wisconsin DNR	50.16
06-01-V	Texas CEQ	-13.2
09-03-V	Bay Area Air Quality Management District	59.15
09-06-V	County of San Diego Air Pollution Control District	5.05
11-01-V	ERG	-7.46
<i>Overall Mean^b</i>		10.14

^a Expressed as % difference.

^b Across all reporting sites

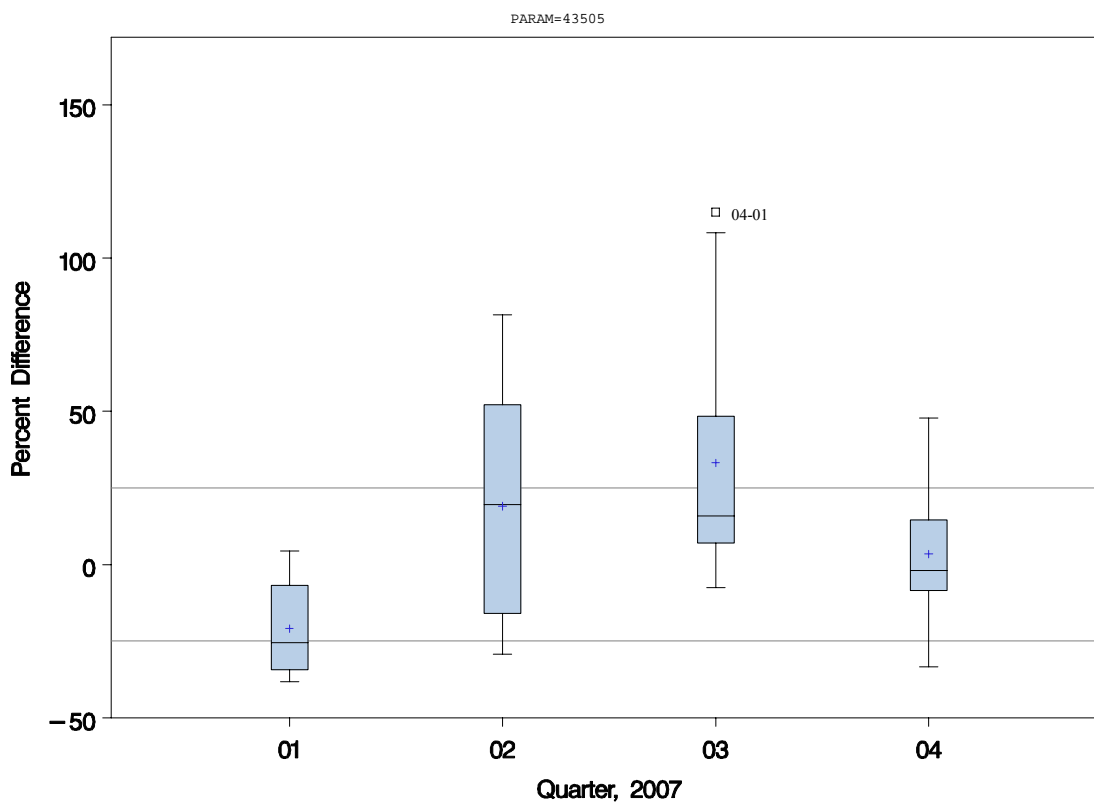


Figure A-4. Distribution of Percent Difference for Acrolein in Proficiency Testing Results in 2007.

Method Detection Limits

The method detection limit data for acrolein, acquired directly from the laboratories, is presented in Table A-5. Only two laboratories reported an MDL for this analyte, ERG and the South

Carolina Department of Health and Environmental Control. The ERG laboratory performed the acrolein analyses for all sites listed in Table A-5 except Chesterfield, SC.

Table A-5. Method Detection Limits^{a,b} for Acrolein by Site and Overall for Calendar Year 2007

Site Name	AQS Site Code	Acrolein ^c
Phoenix, AZ	04-013-9997	0.057
Grand Junction, CO	08-077-0017	0.057
Northbrook, IL	17-031-4201	0.057
Dearborn, MI	26-163-0033	0.057
St. Louis, MO	29-510-0085	0.057
Chesterfield, SC	45-025-0001	0.203
Bountiful, UT	49-011-0004	0.057
Seattle, WA	53-033-0080	0.057
	<i>Geometric Mean^d</i>	0.067
	<i>Arithmetic Mean^d</i>	0.075
	<i>Standard Deviation^d</i>	0.052
	<i>Median^d</i>	0.057

^a Expressed as $\mu\text{g}/\text{m}^3$.

^b Sites not presented in the table reported no MDL for acrolein.

^c MDL measurement quality objective = $0.11 \mu\text{g}/\text{m}^3$ (See reference A-1).

^d Across all reporting sites

Reference

A-1. "Final Acrolein Method Development Report and Standard Operating Procedure for the Determination of Acrolein in Ambient Air by Method TO-15", Posted 5/31/06. Available at <http://www.epa.gov/ttn/amtic/files/ambient/airtox/finacrolein.pdf>.

APPENDIX B

Method Detection Limit Request Letter Sent to Each NATTS-Participating Laboratory

NATTS Network Affiliated Laboratory:

Under contract to the US E.P.A., RTI International is preparing the quality assurance report for the NATTS network for QA data collected in calendar year 2007. Specifically, this work is being performed under Work Assignment 0-05, Task 10 for EPA contract EP-D-08-047. In order to prepare a summary of the quality assurance (QA) data generated by the NATTS program for calendar year (CY) 2007, RTI has been tasked to collect information for each site regarding method detection limits (MDLs) for the three main categories of hazardous air pollutants (HAPs) routinely measured in the NATTS program (volatile organic compounds (VOCs), carbonyls, and PM₁₀ metals). Because of possible variations in sampling and/or analytical methods and computational routines used by the reporting agencies, certain additional data and supporting information are requested as well.

For each NATTS site operated by your reporting organization, please provide the following (see attached template):

1. *Site Identifier*

2. *PM₁₀ Metals*

- a. Sampling method (e.g., low-volume 47mm filter, hi-volume 8x10 inch filter)
- b. Average sampling time and volumetric flow rate at standard conditions used for MDL computation.
- c. Analytical method (include any deviations/modifications from EPA guidance such as size of strip cut from 8x10 filter or digestate final dilution volumes).
- d. MDLs reported for each metal in $\mu\text{g}/\text{m}^3$ at 25°C, 1 atm. (provide description of how MDLs were calculated including formulas/algorithms).
- e. Dates for which the reported MDLs apply. If the MDLs changed during the time period (e.g. as the result of routine redetermination, method change, or equipment change). If so, please record the appropriate dates and the individual MDL values.
- f. Treatment of measurements that are below the MDL (e.g., reported as measured, Zero, MDL, MDL/2, etc.)

3. *Carbonyls*

- a. Sampling method (note any deviations/modifications from EPA guidance)
- b. Average sampling time and volumetric flow rate at standard conditions used for MDL computation.
- c. Analytical method (include any deviations/modifications from EPA guidance. Note final extraction volume prior to analyses.)
- d. MDLs reported for each compound in $\mu\text{g}/\text{m}^3$ at 25°C, 1atm. (provide description of how MDLs were calculated including formulas/algorithms).
- e. Dates for which the reported MDLs apply. If the MDLs changed during the time period (e.g. as the result of routine redetermination, method change, or equipment change). If so, please record the appropriate dates and the individual MDL values.

- f. Treatment of measurements that are below the MDL (e.g., reported as measured, Zero, MDL, MDL/2, etc.)
4. *VOCs*
- a. Sampling method (note any deviations/modifications from EPA guidance. Are canister samples collected and then analyzed at subambient pressure or are they pressurized prior to analysis?)
 - b. Average sampling time and volumetric flow rate at standard conditions used for MDL computation.
 - c. Analytical method (include any deviations/modifications from EPA guidance. Provide sample dilution factor.)
 - d. MDLs reported for each compound in $\mu\text{g}/\text{m}^3$ at 25°C, 1 atm. (provide description of how MDLs were calculated including formulas/algorithms).
 - e. Dates for which the reported MDLs apply. If the MDLs changed during the time period (e.g. as the result of routine redetermination, method change, or equipment change). If so, please record the appropriate dates and the individual MDL values.
 - f. Treatment of measurements that are below the MDL (e.g., reported as measured, Zero, MDL, MDL/2, etc.)

For further information on the intended use of the information requested, please refer to the CY 2006 Annual NATTS Quality Assurance Annual Report which can be found at:

<http://www.epa.gov/ttn/amtic/files/ambient/airtox/Final%20NATTS%202006%20QA%20Annual%20Rept%2010.10.07.pdf>

Also please review Tables 13 and 14 in the CY2006 report and provide any changes in laboratories identified as performing your NATTS analyses.

Please provide the information in tabular, electronic format directly to:

Mr. Larry Michael
RTI International
LCM@RTI.ORG
(919) 541-6150

For your convenience, I have provided a Microsoft Excel template for entry of the information we require to compile the data and perform the summary statistical analyses. Please feel free to repeat analyte names, as needed, to accommodate multiple MDLs for the same analyte. When returning the templates, please include the words "NATTS QA Data" in the email subject line and provide the name of the individual providing the data. Mr. James Homolya, a consultant on this effort, will be contacting you in the next few days to assist you in providing this information.

Thank you for your important assistance.

Larry C. Michael