NATIONAL AIR TOXICS TRENDS STATIONS QUALITY ASSURANCE ANNUAL REPORT CALENDER YEAR 2009

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 Spring of 2011, Research Triangle Institute (RTI) prepared a technical report under Contract No. EP-D-08-047 Work Assignment 03-04. The report describes the Quality Assurance (QA) data collected within the calendar year 2009. The report was prepared for Dennis K. Mikel, Work Assignment Manager within the Office of Air Quality Planning and Standards (OAQPS) in Research Triangle Park, North Carolina. The draft report was written by Larry Michael and Jeff Nichols of RTI. EPA staff submitted it to the State and Local air toxics community for review and comment. RTI addressed the comments that were submitted and sent this final report to the Work Assignment Manager. This is the final report.

Additional work on this report was provided by AQAD staff.

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FINAL REPORT

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:
U.S. EPA Contract EP-D-08-047
Work Assignment 03-04, Task 10

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1.0 INTRODUCTION

As mandated under the Government Performance Results Act, the U.S. Environmental Protection Agency (EPA) 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 HAPs includes 188 chemicals regulated under the Clean Air Act that 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 to assess progress in reducing ambient concentrations of air toxics and concomitant exposure-associated risk. During 2009, the NATTS network consisted of 27 stations in the contiguous 48 states. To ensure the quality of the data collected under the NATTS network, EPA has implemented a Quality System comprising 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 semiannual analysis of proficiency testing (PT) samples for volatile organic compounds (VOCs) and carbonyls and annual analysis of PT samples for metals and polycyclic aromatic hydrocarbons (PAHs) to provide quantitative assessment of laboratory performance and to ensure that sampling and analysis techniques are consistent with precision, bias, and method detection limits (MDLs) specified by the NATTS Measurement Quality Objectives (MQOs).

This report describes and summarizes the quality assurance (QA) data generated by the NATTS program during calendar year 2009. For data retrieved from EPA's Air Quality Systems (AQS) database, only data collected in 2009 and posted prior to August 31, 2011, are included. Although this report contains substantive information about air concentrations of 2 different chemicals of interest, it focuses primarily on results for four classes of toxic ambient air constituents (VOCs, carbonyls, PAHs, and PM_{10} metals) as represented by seven pollutants: benzene, 1,3-butadiene, formaldehyde, acrolein, naphthalene, chromium (VI), and PM_{10} arsenic. At the request of EPA, these seven pollutants were selected as having particular interest by virtue of associated health risk and the frequency of their occurrence at measurable concentrations. Although no group of compounds can provide unequivocal representation of their respective compound groups, these seven analytes were selected by EPA as reasonable representatives of the four main categories of HAPs routinely measured in the NATTS program and thus provide the framework for this summary report. It is presumed that if the NATTS program can meet the Data Quality Objectives (DQOs) for these seven compounds, the additional 20 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 seven compounds. Because monitoring for PAHs and chromium (VI) is new, or relatively new, at many sites, QA results may be unavailable for some MQOs at some sites.

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 MQOs;
- Assessment of the completeness of the data available in the AQS database;
- Precision estimates, independently, for analytical and overall sampling error computed for as many of the 27 applicable compounds and for as many of the 27 NATTS sites as available for calendar year 2009;
- Evaluation of an analytical laboratory's accuracy (or bias), based on analysis of blind audit PT samples for many of the 27 compounds;
- Field bias data, which are expressed as the differences between actual and measured sampler flow readings for each of the four different sampler types associated with VOCs, carbonyls, PAHs, and PM_{10} metals, for primary and collocated samplers (where available) at the three sites visited during the IPAs conducted during calendar year 2009; and
- MDL data for each site and/or analytical laboratory. The AQS database, specifically the ALT_MDL variable, was used as the primary source of MDLs for 2009. However, because this MDL field in AQS is not a required field, it was necessary to augment the information with direct contacts to several NATTS state and local agencies and affiliated laboratories to compile MDL data for the 27 compounds of interest at all sites. This modification improved both acquisition efficiency and the accuracy of the MDL data.

Where possible, all data analyses were performed in SAS, version 9.2. Method Detection Limits obtained from individual laboratories and Proficiency Testing data wwere recorded and compiled using Microsoft Excel.

2.0 NATTS QUALITY ASSURANCE DATA FOR CALENDAR YEAR 2009

The NATTS network included 27 sites in 2009. 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 [1].

Although 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, TX. Historical consistency has been maintained for the Grand Junction, CO, site, where two separate codes are used, one for VOCs, carbonyls, and PAHs (-0018) and the other for metals (-0017). This convention is unique to this site and is used because the organics and metals samplers are present at two separate physical locations at the sampling site.

Table 1. EPA Region Numbers, NATTS Sites, Site Type, and Air Quality Systems 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
III	Richmond, VA	Urban	51-087-0014
IV	Chesterfield, SC	Rural	45-025-0001
IV	Decatur, GA	Urban	13-089-0002
IV	Grayson Lake, KY	Rural	21-043-0500
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[a], -0018[b]
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	Portland, OR	Urban	41-051-0246
X	Seattle, WA	Urban	53-033-0080

[a] Metals only.
[b] VOCs, carbonyls, PAHs, and Cr(VI) only.

The 27 specific HAPs measured in the NATTS program, presented in Table 2 along with their unique AQS identification codes, are compounds that EPA has identified as being of significant health concern. These include 16 VOCs, 2 carbonyls, 2 PAHs, 6 PM_{10} metals, and chromium (VI). Succinct abbreviations of each chemical name are provided to facilitate table and figure creation and interpretation throughout this report.

Table 2. The 23 Unique Hazardous Air Pollutants[a] and their Air Quality Systems Parameter Codes.

Analyte Abbreviation[a]	Compound Name	Exact AQS Label	AQS Code	Compound Group
BENZ[b]	benzene	Benzene	45201	VOC
BUTA[b]	1,3-butadiene	1,3-Butadiene	43218	VOC
CTET	carbon tetrachloride	Carbon Tetrachloride	43804	VOC
CLFRM	chloroform	Chloroform	43803	VOC
EDB	1,2-dibromoethane	Ethylene Dibromide	43843	VOC
DCP	1,2-dichloropropane	1,2-Dichloropropane	43829	VOC
EDC	1,2-dichloroethane	Ethylene Dichloride	43815	VOC
MECL	dichloromethane	Dichloromethane	43802	VOC
TCE1122	1,1,2,2-tetrachloroethane	1,1,2,2-Tetrachloroethane	43818	VOC
PERC	tetrachloroethylene	Tetrachloroethylene	43817	VOC
TCE	trichloroethylene	Trichloroethylene	43824	VOC
VCM	vinyl chloride	Vinyl Chloride	43860	VOC
cDCPEN	cis-1,3-dichloropropene	Cis-1,3-Dichloropropylene	43831	VOC
tDCPEN	trans-1,3-dichloropropene	Trans-1,3-Dichloropropylene	43830	VOC
ACRO[c,e]	acrolein	Acrolein	43505[d]	VOC[c]
ACRO[d,e]	acrolein	Acrolein	43509[e]	VOC[c]
ACRY	acrylonitrile	Acrylonitrile	43704	VOC
NAPH[b]	naphthalene	Naphthalene (Tsp) Stp		PAH
BaP	benzo[a]pyrene	Benzo[A]Pyrene (Tsp) Stp		PAH
FORM[b]	formaldehyde	Formaldehyde	43502	Carbonyl
ACET	acetaldehyde	Acetaldehyde	43503	Carbonyl
As[b]	arsenic	Arsenic Pm10 Stp	82103	Metal
Be	beryllium	Beryllium Pm10 Stp	82105	Metal
Cd	cadmium	Cadmium Pm10 Stp	82110	Metal
Pb	lead	Lead Pm10 Stp	82128	Metal
Mn	manganese	Manganese Pm10 Stp	82132	Metal
Ni	nickel	Nickel Pm10 Stp	82136	Metal
CrVI[b]	chromium (VI)	Chromium (VI) Tsp Stp	12115	Metal
As[f]	arsenic	Arsenic Pm10 Lc	85103	Metal
Be[f]	beryllium	Beryllium Pm10 Lc	85105	Metal
Cd[f]	cadmium	Cadmium Pm10 Lc	85110	Metal
Pb[f]	lead	Lead Pm10 Lc	85128	Metal
Mn[f]	manganese	Manganese Pm10 Lc	85132	Metal
Ni[f]	nickel	Nickel Pm10 Lc	85136	Metal
CrVI[f]	chromium (VI)	Chromium (VI) Tsp Lc	14115	Metal

[a] Mercury has been intentionally excluded from all data analyses in this report, per U.S. EPA directive.
[b] Results presented are representative of completeness for other chemicals in this class.
[c] Unverified results.
[d] Verified results.
[e] Completeness based on verified and unverified results.
[f] Some sites reported results for metal analytes at local conditions (Lc), instead of STP (Stp), using these parameter codes. For this report, data reported in Stp and Lc units are combined, under the assumption that the difference between the two values is negligible.

2.1 Measurement Quality Objectives

MQOs for completeness, precision, laboratory bias, and MDLs, established for the NATTS network to ensure data quality within the network, were unchanged from 2008 and were based on the Technical Assistance Document [2] applicable on January 1, 2009. The stated 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" [3]. MQOs for the four compounds of primary importance to the NATTS program (benzene, 1,3-butadiene, formaldehyde, PM_{10} arsenic) are summarized in Table 3. MQOs for the three additional analytes of interest (acrolein, naphthalene, and chromium [VI]) have not been assigned by EPA.

Table 3. Measurement Quality Objectives for the NATTS Program.

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

[a] Assumes a sampling volume of 1,000 L.
[b] Assumes high-volume sampling with a sampling volume of 1,627 m^3 (1.13 m^3/min [40 ft^3/min] for 24 hours) and that one-eighth 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 6th day;
(2) sampling is successful 85% of the time;
(3) precision, as measured by the coefficient of variation (CV), is within 15% based on duplicate and collocated samples; and
(4) laboratory (measurement) bias is less than 25%, based on laboratory PT results.

Furthermore, actual MDLs, as reported by the laboratories supporting the NATTS sites or their sponsoring federal, state, or municipal agencies, are compared with the target MDLs as listed in the applicable edition of the NATTS Technical Assistance Document (TAD) [2].

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

Table 4. Data Sources Used to Evaluate Measurement Quality Objectives.

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 conducted by RTI International
MDL	AQS augmented with information from the analytical laboratories

Data retrievals from AQS for relevant samples collected in 2009 and uploaded to the AQS database prior to May 7, 2011, were analyzed to assess completeness and to estimate precision from results of replicate analyses and collocated and duplicate sampling. PT samples were distributed by EPA contractor Alion Science, Inc., to participating laboratories for determination of analytical bias. Field bias was evaluated by independent measurement of sampler flow rates with National Institute of Standards and Technology (NIST)-traceable flowmeters during on-site IPAs. Finally, MDL data were extracted from AQS, where present, and augmented by values obtained 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 27 NATTS sites during calendar year 2009 and entered into the AQS database prior to May 7, 2011. This posting period to AQS was extended from the original July 1, 2010 deadline for the 2009 report to allow for posting of data unintentionally excluded by a single NATTS site. Any data that might have been contributed to AQS by participating laboratories after May 7, 2011, are not reflected in the completeness calculations presented in Table 5 below. Specifically, completeness of the 2009 AQS dataset was assessed for seven compounds representative of the entire suite of 27 compounds presented previously in Table 2: benzene, 1,3-butadiene, acrolein, formaldehyde, naphthalene, chromium (VI), 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% completeness. Depending on the first date of collection in 2009, some sites might exhibit slightly greater than 100% completeness if 61 samples were collected during that year. For purposes of this completeness calculation, non-detects were counted equivalently with measurable values. Conversely, missing values were not counted toward the percentage complete. Completeness statistics were not adjusted for abbreviated collection periods because all sites were operated for the entire 12 months during 2009.

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. Because sample collection at some locations was performed more frequently to meet the requirements of other sampling networks or for other specific purposes, only records that occurred at the required 1-in-6 day sample collection frequency (days 0, 6, 12, 18, 24, 30, etc.), starting with the first collection date for each site in calendar year 2009, were counted. For this and other reasons, it is not possible to discern from the AQS database when makeup samples are collected. The individual enumeration of valid samples from each and every site would be an extremely tedious task and presumes that only NATTS sample records are present in the database for a given parameter occurrence code. Therefore, to account for makeup samples collected near the time of the scheduled collection date, the interval of days since the last collection event was allowed to vary between 4 and 8. No correction was applied for compound-specific missing data (e.g., 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 percentage completeness.

The results of the completeness assessment are presented for each collection location and representative compound in Table 5 and in Figures 1 through 7. Mean and median completeness values across all NATTS laboratories for a given analyte and across all analytes for a given site are also presented. In cases where no data were reported, the particular analyte class was not collected at that NATTS site, as indicated by table notes.

Table 5. Percentage Completeness[a] of the 2009 AQS Dataset by Site for Seven Hazardous Air Pollutants.

AQS Site ID	Parameter Code → Site Name	45201 BENZ	43218 BUTA	43502 FORM	43505 ACRO	17141 NAPH	12115 CRVI	82103 AS
25-025-0042	Boston-Roxbury, MA	97	97	102	97	100	98	95
49-011-0004	Bountiful, UT	95	95	95	95	100	97	92
36-005-0110	Bronx, NY	102	102	102	102	97	98	102
45-025-0001	Chesterfield, SC	102	102	102	102	102	100	102
26-163-0033	Dearborn, MI	93	93	97	93	97	97	102
13-089-0002	Decatur, GA	102	102	102	102	100	95	102
48-201-1039	Deer Park, TX	102	102	98	102	100	100	102
08-077-0017[b], -0018[c]	Grand Junction, CO	85	85	95	85	98	98	102
21-043-0500	Grayson Lake, KY	93	93	87	93	97	98	95
48-203-0002	Harrison County, TX	100	100	97	97	95	98	102
12-057-3002	Hillsborough County, FL	100	100	100	100	102	102	102
41-061-0119	La Grande, OR	93	93	97	NR[d]	98	92	88
06-037-1103	Los Angeles, CA	100	100	100	100	100	NR	NR
55-027-0007	Mayville, WI	88	88	92	88	98	97	72
17-031-4201	Northbrook, IL	102	102	102	102	97	100	102
04-013-9997	Phoenix, AZ	95	95	98	95	95	97	95
12-103-0026	Pinellas County, FL	102	102	102	102	98	102	102
41-051-0246	Portland, OR	77	90	102	NR	95	100	98
44-007-0022	Providence, RI	102	102	102	102	90	102	102
51-087-0014	Richmond, VA	100	100	102	100	100	100	100
36-055-1007	Rochester, NY	102	102	102	102	100	100	102
06-065-8001	Rubidoux, CA	98	98	102	98	95	NR	NR
06-085-0005	San Jose, CA	93	93	102	93	102	NR	100
53-033-0080	Seattle, WA	93	93	93	93	97	100	93
29-510-0085	St. Louis, MO	102	102	100	102	95	97	102
50-007-0007	Underhill, VT	102	102	102	102	97	98	102
11-001-0043	Washington, DC	100	100	NR	100	97	102	102
	Mean	97	98	99	98	98	99	98
	Std. Dev.	6	5	4	5	3	2	7
	Median	100	100	101	100	98	98	102

[a] Data pulled from AQS on 8/31/2011.
Metals only.
Carbonyls, VOCs, and PAHs only.
[d] Not reported for this site.

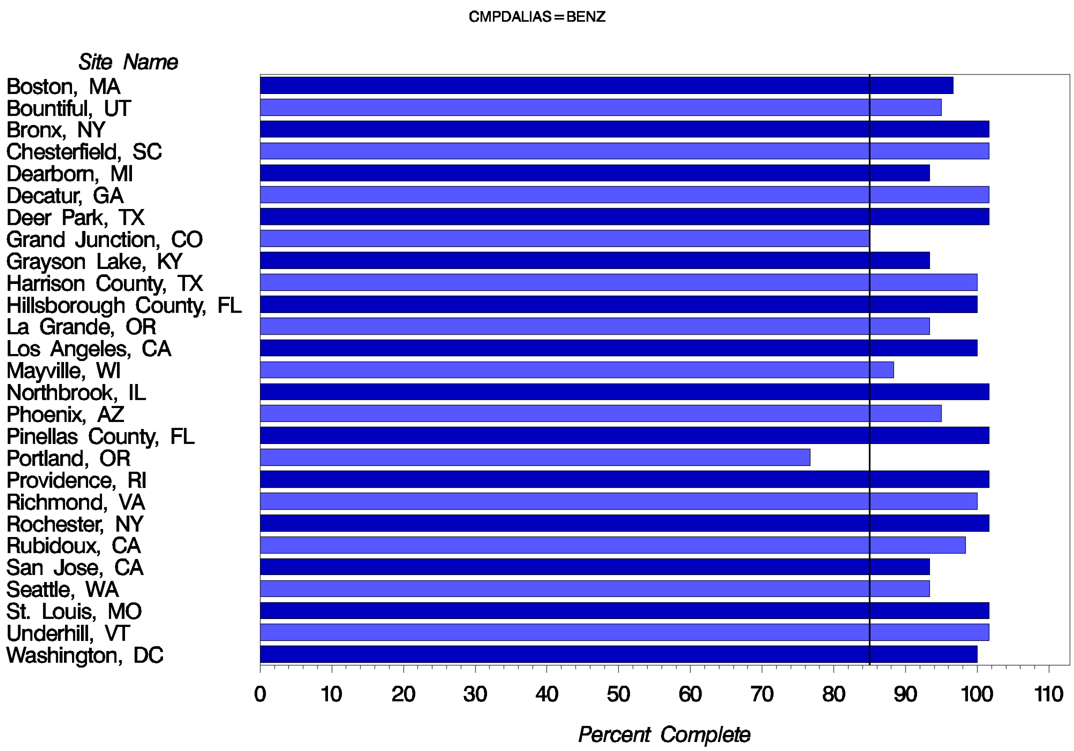


Figure 1. Completeness for Benzene at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 85%).

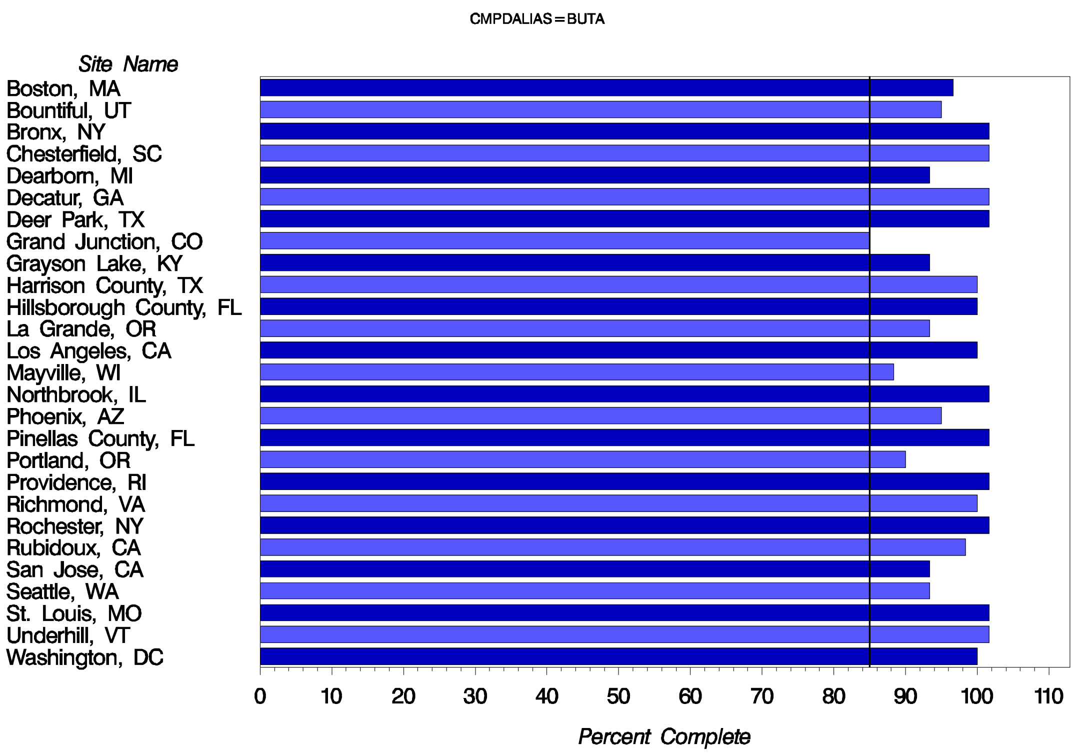


Figure 2. Completeness for 1,3-Butadiene at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 85%).

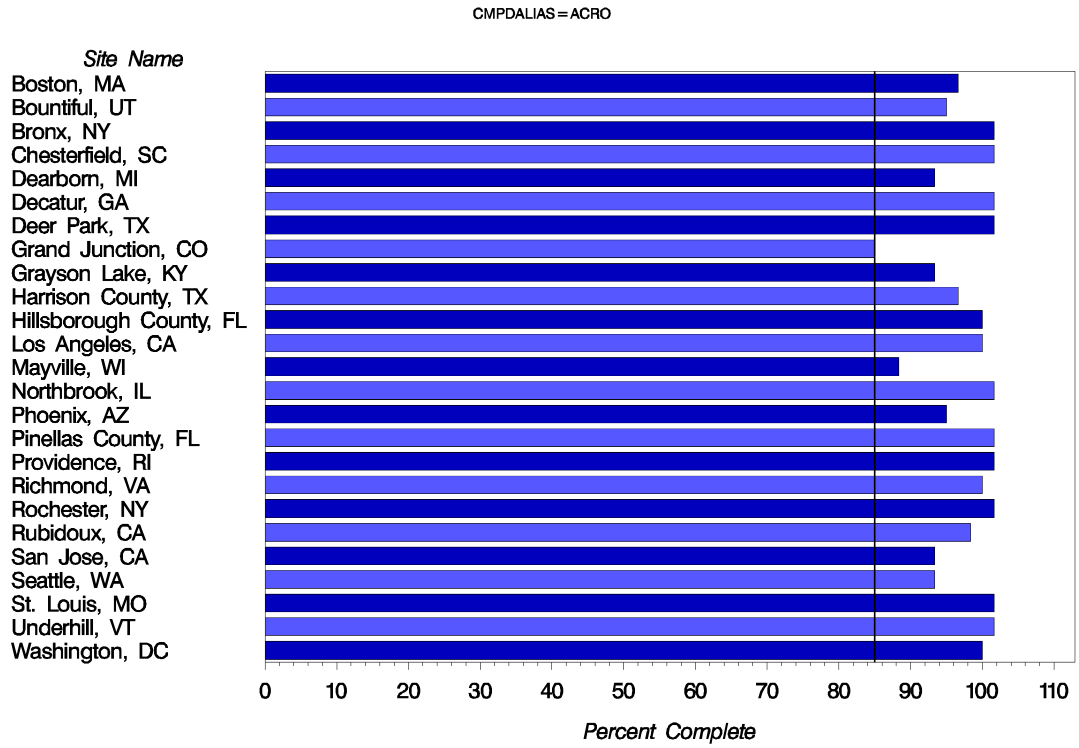


Figure 3. Completeness for Acrolein at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 85%).

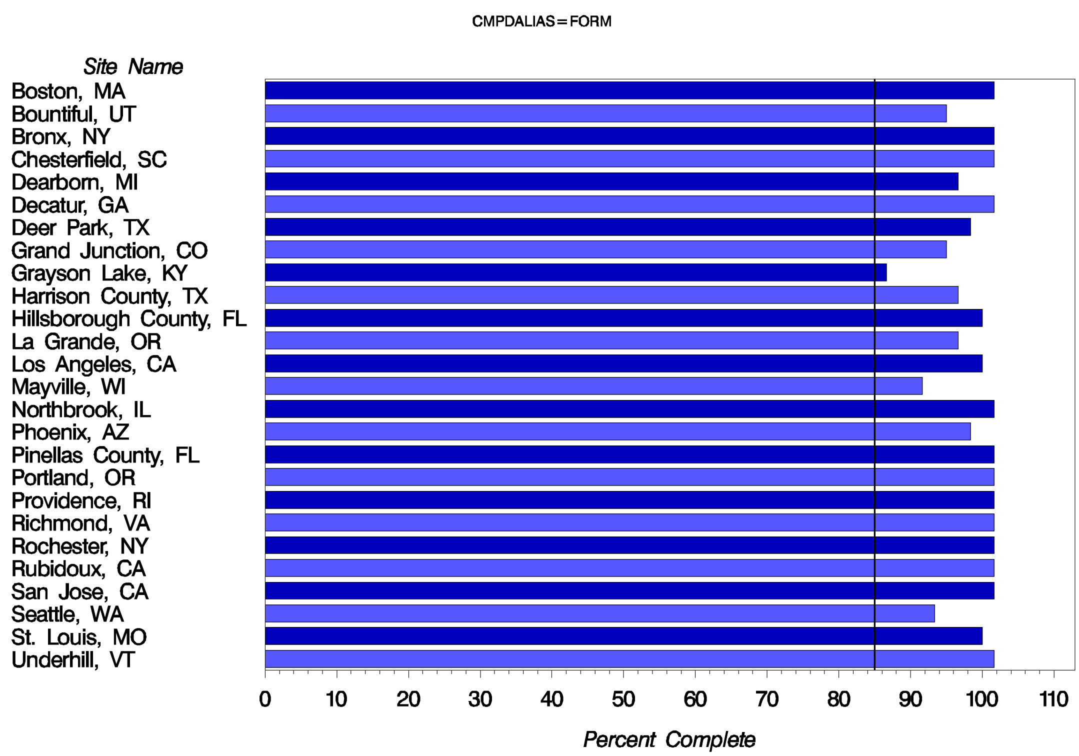


Figure 4. Completeness for Formaldehyde at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 85%).

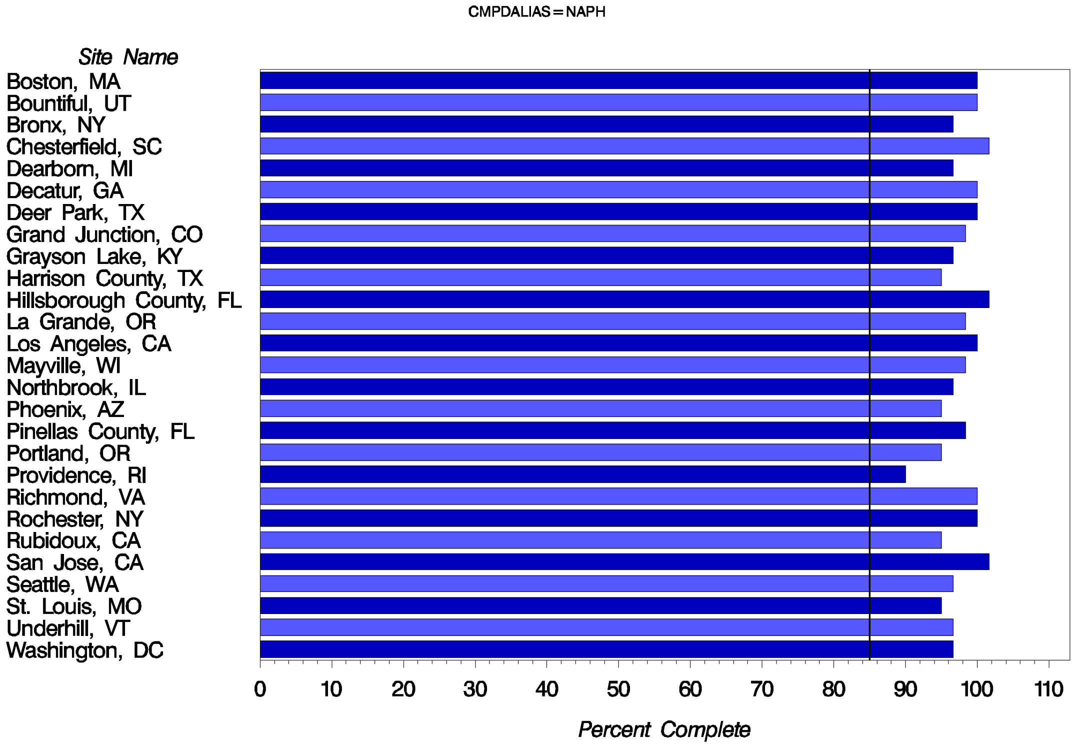


Figure 5. Completeness for Naphthalene at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 85%).

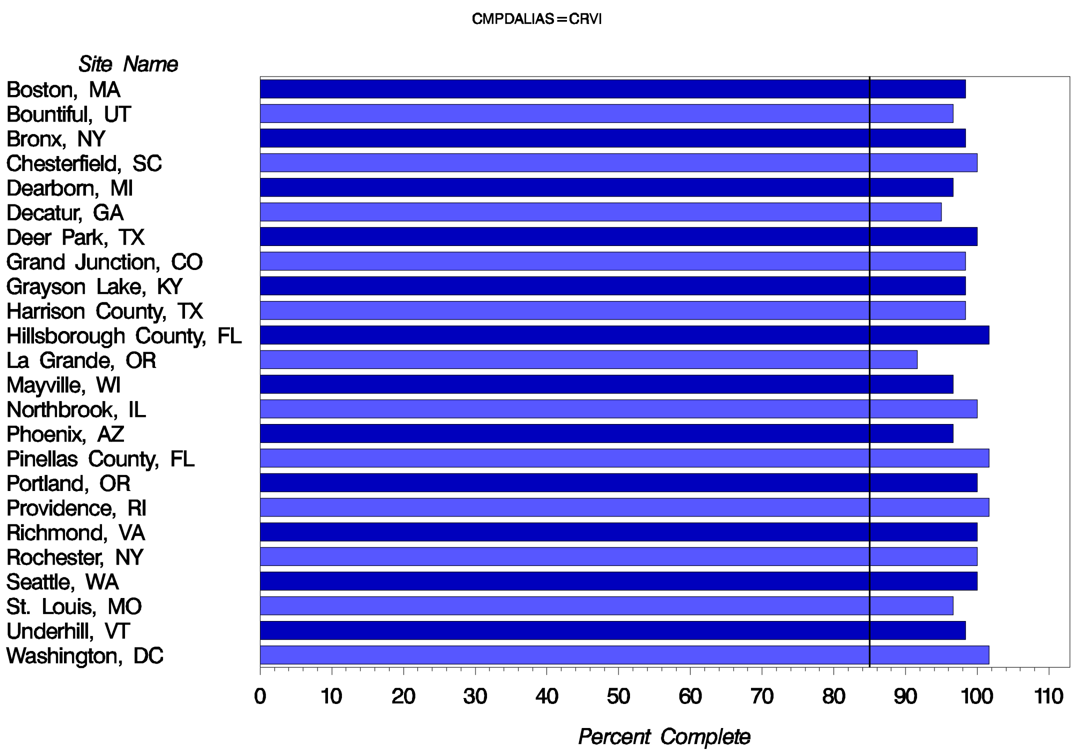


Figure 6. Completeness for Chromium (VI) at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 85%).

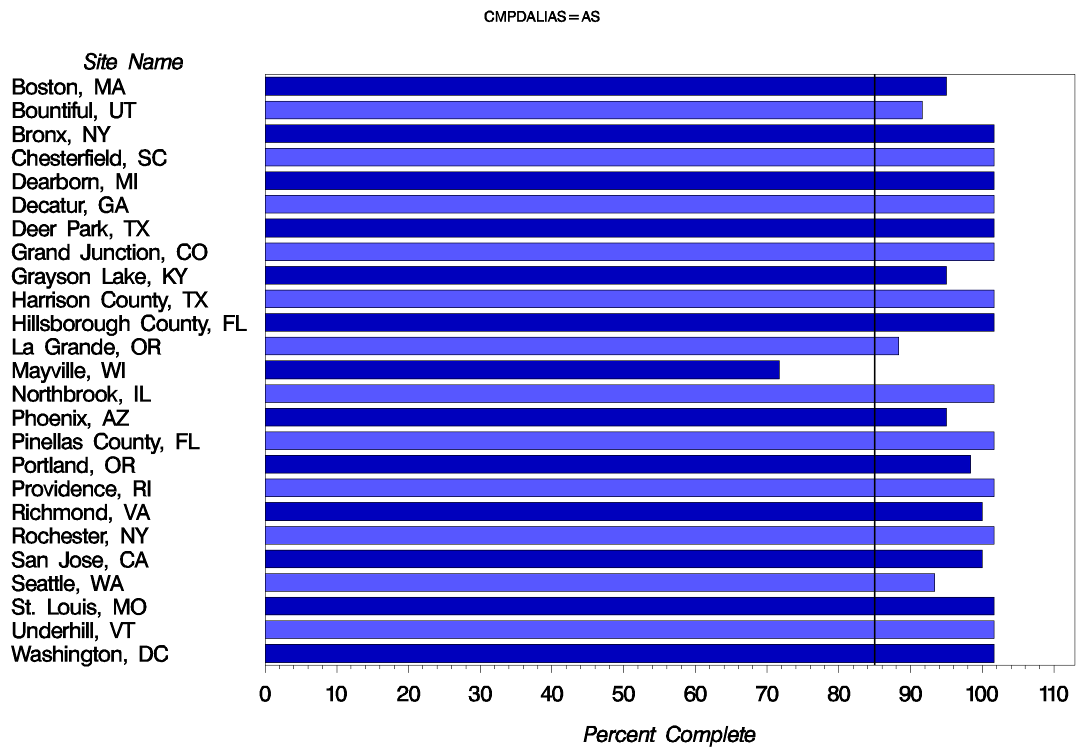


Figure 7. Completeness for Arsenic at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 85%).

With the exceptions of benzene at the Portland, OR site and arsenic at the Mayville, WI, site, all sites exhibited consistently high completeness statistics for all analytes and met the MQO of 85% completeness. The preponderance of completeness metrics at 102% reflects the fact that most sites collected 61 samples during 2009 and completeness is based on the collection of 60 samples.

2.3 Precision of NATTS Data

Three basic sample types are collected at NATTS sites:

- Primary samples—a single sample that represents a particular sampling event.
- Duplicate samples—a replicate sample, collected simultaneously with the primary sample, that represents a second measurement from the same sample stream (e.g., the inlet stream of an outdoor air monitor) but employs 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 assessing the aggregate variability associated with the collection device, sampling substrate, and sample analysis.
- Collocated samples—a replicate sample, collected simultaneously with the primary sample, that 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 assessing the total variability associated with all

components of the sample collection and analysis scheme; thus, the analyst can assume that the air collected by the primary and collocated samplers is absolutely identical in its composition. Samples collected at different sites violate this basic premise of collocation and were excluded from these precision analyses at the direction of EPA.

- Replicate Sampling:

Replicate sampling refers, generally, to both duplicate and collocated sample collections as described above and as differentiated within the AQS database. Precision assessments associated with replicate sampling are distinctly different from those associated with replicate analyses as the latter are derived from a second chemical analysis of a single sample and the former are derived from single chemical analyses of two different samples. For this report, precision analyses were performed exclusively on NATTS sites; surrogate, non-NATTS sites with collocated samplers have not been included. The methodological precision for the NATTS data was assessed from both analytical (i.e., instrumental) and overall (i.e., instrumental + sampling) perspectives. Analytical precision measures the variability in reported results due exclusively to differences in analytical instrument performance and was estimated by comparing results from two analyses of a single sample, whether that sample be primary, duplicate, or collocated. Overall sampling precision was assessed by comparing the results from primary and collocated samples or from primary and duplicate 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 provides separate overall precision estimates for these two replicate sample types.

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 (PRECISID) 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

With the exception of the Pinellas County, FL site, analytical precision for this report was computed from the replicate pairs of data coded with either Precision Id. 2 or 3. Additional Precision Ids. were employed for Pinellas County. Overall precision was 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 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. Because the assignment of a particular POC is made at the discretion of each NATTS site, extensive effort was required to ensure that the POCs for each site were correctly identified. POCs for primary, duplicate, and collocated samples of each chemical class were determined by hierarchical exploration of three principal pieces of information:

1) POCs used by each NATTS collection site in 2007 and 2008 were used as the reference for POCs assigned in 2009.
2) POCs assigned in previous years were confirmed by results of frequency analysis performed on RD records for samples collected in 2009.
3) Discrepancies and/or uncertainties about POC assignments were resolved by direct contact with NATTS administrators for specific collection sites.

Multiple POCs for a given site, analyte, and sample type reflect a number of factors unique to a site during 200 , 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 6. Parameter Occurrence Codes by NATTS Site and Analyte Type.

Region	Site Identifier	AQS Site Code	Parameter Occurrence Codes (POCs)[a]														
			VOC			Carbonyls			Metals			PAHs			Chromium (VI)		
			P[b]	D[c]	C[d]	P	D	C	P	D	C	P	D	C	P	D	C
I	Boston, MA	25-025-0042	10	11		3	4		6	7		6			6	7	
I	Underhill, VT	50-007-0007	1			1			1			6			6	7	
I	Providence, RI	44-007-0022	2			5		7	1		2	6			6		7
II	Bronx, NY	36-005-0110	2			2			1		2	6			6		7
II	Rochester, NY	36-055-1007	2			2			1			6			6		7
III	Washington, DC	11-001-0043	4			1			1			1			1		2
III	Richmond, VA	51-087-0014	4	1		2			1			6			6		7
IV	Chesterfield, SC	45-025-0001	1		2	1		2	1		2	6			6	7	
IV	Decatur, GA[e]	13-089-0002	1,3		2,4	2		3	1		2	6		7	6		7
IV	Grayson Lake, KY	21-043-0500	1	2		1	2		1	2		6			6		7
IV	Hillsborough County, FL	12-057-3002	1			6			5			6		7	6		7
IV	Pinellas County, FL	12-103-0026	1			6			5			6		7	6		7
V	Dearborn, MI	26-163-0033	1		2	1		2	1		9	1		2	1		2
V	Mayville, WI	55-027-0007	1			1	2		1		2	6			6		7
V	Northbrook, IL	17-031-4201	6		7	6		7	6		7	6			6		7
VI	Deer Park, TX	48-201-1039	2		3	3			1			1	2	6	1		2
VI	Harrison County, TX	48-203-0002	1			1			1			1			1		
VII	St. Louis, MO	29-510-0085	6			6			6		7	6			6		7
VIII	Bountiful, UT	49-011-0004	6			6			1		2	6			6		7
VIII	Grand Junction, CO	08-077-0017, -0018	6			6			3		4	6			6		7
IX	Phoenix, AZ	04-013-9997	6		7	30		31	1			3			6		7
IX	Los Angeles, CA	06-037-1103	4		5	4		5				6					
IX	Rubidoux, CA	06-065-8001	4		5	4		5				6	7				
IX	San Jose, CA	06-085-0005	3		5	3		1	1			1					
X	La Grande, OR	41-061-0119	7			7			7			7			7		
X	Portland, OR	41-051-0246	7		9	7		9	7		9	7		9	7		
X	Seattle, WA	53-033-0080	6		7	6		7	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 and 4; all other VOCs on POCs 1 and 2.

Table 7, complemented by Table 8, presents the laboratories that analyzed 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 PT samples and their results.

Table 7. Laboratories Performing Analyses for the Different Analyte Types for Each NATTS Site in 2009.

Site Identifier	VOCs[a]	Carbonyls	Metals	PAHs	Chromium (VI)
Boston-Roxbury, MA	RIDOH	MADEP	ERG	ERG	ERG
Underhill, VT	ERG	VTDEC	ERG	ERG	ERG
Providence, RI	RIDOH	RIDOH	RIDOH	ERG	ERG
Bronx, NY	NYSDEC	NYSDEC	RTI	ERG	ERG
Rochester, NY	NYSDEC	NYSDEC	RTI	ERG	ERG
Washington, DC	MDE	PAMSL	WVDEP	ERG	ERG
Richmond, VA	VA DCLS	VA DCLS	VA DCLS	ERG	ERG
Chesterfield, SC	SCDHEC	SCDHEC	SCDHEC	ERG	ERG
Decatur, GA	GADNR	GADNR	GADNR	ERG	ERG
Grayson Lake, KY	KYDES	KYDES	KYDES	ERG	ERG
Hillsborough County, FL	PCDEM	ERG	EPCHC	ERG	ERG
Pinellas County, FL	PCDEM	ERG	EPCHC	ERG	ERG
Dearborn, MI	ERG	ERG	MIDEQ	ERG	ERG
Mayville, WI	WSLH	WSLH	WSLH	ERG	ERG
Northbrook, IL	ERG	ERG	ERG	ERG	ERG
Deer Park, TX	TCEQ	TCEQ	TCEQ	TCEQ	TCEQ
Harrison County, TX	TCEQ	TCEQ	TCEQ	TCEQ	TCEQ
St. Louis, MO	ERG	ERG	ERG	ERG	ERG
Bountiful, UT	ERG	ERG	ERG	ERG	ERG
Grand Junction, CO	ERG	ERG	IMLAS[b]	ERG	ERG
Phoenix, AZ	ERG	ERG	ERG	ERG	ERG
San Jose, CA	BAAQMD	BAAQMD	ERG	ERG	CARB
Rubidoux, CA	SCAQMD	SCAQMD	SCAQMD	ERG	CARB
Los Angeles, CA	SCAQMD	SCAQMD	SCAQMD	ERG	CARB
La Grande, OR	ODEQ	ODEQ	ODEQ	ODEQ	ODEQ
Portland, OR	ODEQ	ODEQ	ODEQ	ODEQ	ODEQ
Seattle, WA	ERG	ERG	ERG	ERG	ERG

[a] Includes acrolein.
[b] Switching from IMLAS to CO State Lab effective January 2010.

Table 8. Laboratory Abbreviations and Descriptions for NATTS Laboratories.

Laboratory Code(s)	Laboratory Abbreviation	Laboratory Description
01-01-C,V,M	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,P	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	MIDEQ	Michigan Department of Environmental Quality
05-03-C,M,V	WSLH	Wisconsin State Laboratory of Hygiene
06-01-C,M,V,P	TCEQ	Texas Commission on Environmental Quality
08-02-M	IMLAS	IML Air Science Laboratory
09-03-C,V	BAAQMD	Bay Area Air Quality Management District
10-02-C,M,V	ODEQ	Oregon Department of Environmental Quality
11-01-C,M,V;	ERG[a]	Eastern Research Group
11-02-M	RTI	RTI International
—[a]	VA DCLS	Virginia Division of Consolidated Laboratory Services
—[a]	SCAQMD	South Coast Air Quality Management District
—[b]	CARB	California Air Resources Board

[a] Did not participate in the PT program in 2009.
[b] Cr(VI) not included in the PT program during 2009.

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 percentage coefficient of variation (% CV), is defined algebraically in Eq. 1:

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

where

p_i = the result of the principal analysis on sample *i*,

r_i = the result of the replicate analysis on sample *i*, and

n = the number of principal-replicate analysis pairs.

The analytical precision for all measurable HAPs analyzed in samples collected in calendar year 200 is presented in Table 9 with selected analytes summarized graphically in Figures 8 through 14.

As in previous reporting years, the agreement between replicate analyses of the same samples is highly variable across sites/laboratories but largely still within the MQO guidelines. Although only reported for three sites, arsenic agreement is below 2%. Showing marked improvement since 2008, nearly all laboratories show agreement within the MQO for chromium (VI). Conversely, agreement between formaldehyde reanalyses is quite variable, albeit consistently well within the MQO for all sites. Although an MQO is not assigned for PAHs, naphthalene exhibits agreements below 3% for all reporting sites, well below CVs reported for VOCs.

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 % CV, is defined algebraically in Eq. 2:

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

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*, and

n = the number of primary-collocated sample pairs.

The overall precision results for samples collected in calendar year 2009 are presented in Table 10 and summarized graphically in Figures 15 through 21. For cases where either the primary or collocated sample yielded a result of zero, the data pairs were excluded from the overall precision estimate. All data pairs with reported values were included in the computation.

Table 9. Analytical Precision[a] for Replicate Analyses of 2009 NATTS Data.

AQS Site Code	Site Description	BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122	PERC	TCE	VCM
04-013-9997	Phoenix, AZ	5.1 (11)	7.5 (11)	9.1 (11)	6.2 (9)	—	—	—	6.8 (11)	—	5.8 (11)	15.1 (2)	20.2 (1)
06-065-8001	Rubidoux, CA	—[b]	—	—	—	—	—	—	—	—	—	—	—
06-085-0005	San Jose, CA	7.2 (12)	0 (2)	6.2 (12)	8.5 (9)	—	—	—	9.9 (9)	—	2.8 (11)	0 (6)	—
08-077-0017	Grand Junction, CO	—	—	—	—	—	—	—	—	—	—	—	—
08-077-0018	Grand Junction, CO	10.3 (10)	4.8 (10)	5.8 (10)	11.4 (10)	—	—	—	5.5 (10)	—	18.5 (10	4.7 (6)	—
11-001-0043	Washington, DC	—	—	—	—	—	—	—	—	—	—	—	—
12-057-3002	Hillsborough County, FL	—	—	—	—	—	—	—	—	—	—	—	—
12-103-0026	Pinellas County, FL	3.3 (92)	13.8 (92)	2.9 (92)	17.4 (92)	27.4 (44)	20 (4)	9.3 (90)	23.5 (92)	25.4 (69)	11.8 (92)	24 (73)	31.1 (43)
13-089-0002	Decatur, GA	—	—	—	—	—	—	—	—	—	—	—	—
17-031-4201	Northbrook, IL	5.4 (5)	13.1 (3)	2.7 (3)	4.7 (3)	—	—	12.8 (2)	2.8 (3)	—	9.6 (3)	11.3 (3)	—
21-043-0500	Grayson Lake, KY	—	—	—	—	—	—	—	—	—	—	—	—
25-025-0042	Boston, MA	—	—	—	—	—	—	—	—	—	—	—	—
26-163-0033	Dearborn, MI	6.6 (16)	7.2 (16)	4.7 (16)	5.8 (16)	—	—	—	4.2 (16)	—	7.3 (16)	17 (4)	0 (3)
29-510-0085	St. Louis, MO	5.2 (12)	11.6 (12	13.8 (12	9.1 (12)	—	—	—	12.3 (12)	—	4.9 (12)	8.5 (6)	20.4 (3)
36-005-0110	Bronx, NY	—	—	—	—	—	—	—	—	—	—	—	—
36-055-1007	Rochester, NY	—	—	—	—	—	—	—	—	—	—	—	—
44-007-0022	Providence, RI	—	—	—	—	—	—	—	—	—	—	—	—
45-025-0001	Chesterfield, SC	—	—	—	—	—	—	—	—	—	—	—	—
49-011-0004	Bountiful, UT	30.9 (10)	11.3 (9)	13 (6)	12.1 (6)	—	—	—	14.1 (6)	—	13 (6)	54.7 (4)	—
50-007-0007	Underhill, VT	—	—	—	—	—	—	—	—	—	—	—	—
51-087-0014	Richmond, VA	—	—	—	—	—	—	—	—	—	—	—	—
53-033-0080	Seattle, WA	6.5 (8)	8.5 (8)	4.4 (8)	10.7 (8)	—	—	—	4.1 (8)	—	4.6 (8)	6.7 (2)	—
55-027-0007	Mayville, WI	—	—	—	—	—	—	—	—	—	—	—	—
	Overall Mean	8.9 (176)	11.9 (163)	6.4 (170)	14.3 (165)	27.4 (44)	20 (4)	9.3 (92)	18.3 (167)	25.4 (69)	10.7 (169)	26.8 (106)	29.4 (50)

(continued)

Table 9. Analytical Precision[a] for Replicate Analyses of 2009 NATTS Data (continued).

AQS Site Code	Site Description	cDCPEN	tDCPEN	ACRO	ACRY	NAPH	BaP	FORM	ACET	AS	BE	CD	PB	MN	NI	CRVI
04-013-9997	Phoenix, AZ	—	—	7.4 (11)	8.9 (3)	—[b]	—	0.5 (13)	0.8 (13)	—	—	—	—	—	—	6 (12)
06-065-8001	Rubidoux, CA	—	—	—	—	4.2 (8)	8.6 (3)	—	—	—	—	—	—	—	—	—
06-085-0005	San Jose, CA	—	—	—	—	—	—	1.3 (10)	0.6 (10)	—	—	—	—	—	—	—
08-077-0017	Grand Junction, CO	—	—	—	—	—	—	—	—	—	—	—	—	—	—	10.8 (6)
08-077-0018	Grand Junction, CO	—	—	13.6 (10)	12.6 (2)	—	—	1.5 (8)	0.9 (8)	—	—	—	—	—	—	—
11-001-0043	Washington, DC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	9.4 (6)
12-057-3002	Hillsborough County, FL	—	—	—	—	3.2 (66)	7.7 (18)	4.9 (12)	1.5 (12)	—	—	—	—	—	—	12.8 (6)
12-103-0026	Pinellas County, FL	34.1 (46)	36.4 (51)	16.3 (92)	40.3 (89)	—	—	3.4 (12)	4.4 (12)	—	—	—	—	—	—	7.3 (4)
13-089-0002	Decatur, GA	—	—	—	—	2.7 (12)	3.6 (1)	—	—	—	—	—	—	—	—	8.5 (9)
17-031-4201	Northbrook, IL	—	—	10.5 (3)	—	—	—	0.5 (10)	0.4 (10)	1.2 (48)	18.6 (43)	6 (48)	1 (48)	1.1 (48)	4 (48)	10.5 (6)
21-043-0500	Grayson Lake, KY	—	—	—	—	—	—	—	—	—	—	—	—	—	—	7.2 (4)
25-025-0042	Boston, MA	—	—	—	—	—	—	—	—	1.4 (66)	36.6 (52)	9.1 (66)	0.8 (66)	1.1 (66)	1.7 (66)	9.1 (7)
26-163-0033	Dearborn, MI	—	—	6.7 (16)	—	1.3 (11)	3.7 (11)	0.3 (10)	0.6 (10)	—	—	—	—	—	—	4.2 (12)
29-510-0085	St. Louis, MO	—	—	25.3 (12)	13.9 (6)	—	—	1.5 (14)	1.8 (14)	2 (19)	22.6 (19)	0.7 (19)	1.4 (19)	0.7 (19)	1.8 (19)	6.7 (11)
36-005-0110	Bronx, NY	—	—	—	—	—	—	—	—	—	—	—	—	—	—	4.5 (10)
36-055-1007	Rochester, NY	—	—	—	—	—	—	—	—	—	—	—	—	—	—	10.2 (2)

(continued)

Table 9. Analytical Precision[a] for Replicate Analyses of 2009 NATTS Data (continued).

AQS Site Code	Site Description	cDCPEN	tDCPEN	ACRO	ACRY	NAPH	BaP	FORM	ACET	AS	BE	CD	PB	MN	NI	CRVI
44-007-0022	Providence, RI	—	—	—	—	—	—	—	—	—	—	—	—	—	—	7.2 (4)
45-025-0001	Chesterfield, SC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	15 (6)
49-011-0004	Bountiful, UT	—	—	16.9 (6)	13.9 (2)	—	—	7.6 (10)	3.4 (10)	—	—	—	—	—	—	4.4 (8)
50-007-0007	Underhill, VT	—	—	—	—	—	—	—	—	—	—	—	—	—	—	8.5 (2)
51-087-0014	Richmond, VA	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3.1 (5)
53-033-0080	Seattle, WA	—	—	7.3 (8)	—	2 (11)	3.7 (4)	0.5 (12)	1.3 (12)	—	—	—	—	—	—	4.7 (9)
55-027-0007	Mayville, WI	—	—	—	—	—	—	—	—	—	—	—	—	—	—	10.6 (4)
	Overall Mean	34.1 (46)	36.4 (51)	15.4 (159)	37.9 (102)	3 (108)	6.4 (37)	3.1 (111)	2 (111)	1.4 (133)	28.8 (114)	7.4 (133)	1 (133)	1.1 (133)	2.8 (133)	8.1 (133)

[a] Expressed as percentage coefficient of variation (%CV) with number of contributing data pairs presented in parentheses. Metals results are reported at STP at most sites and lcs at others.
[b] Sample not collected or analyte not reported.
[c] Across all sites.

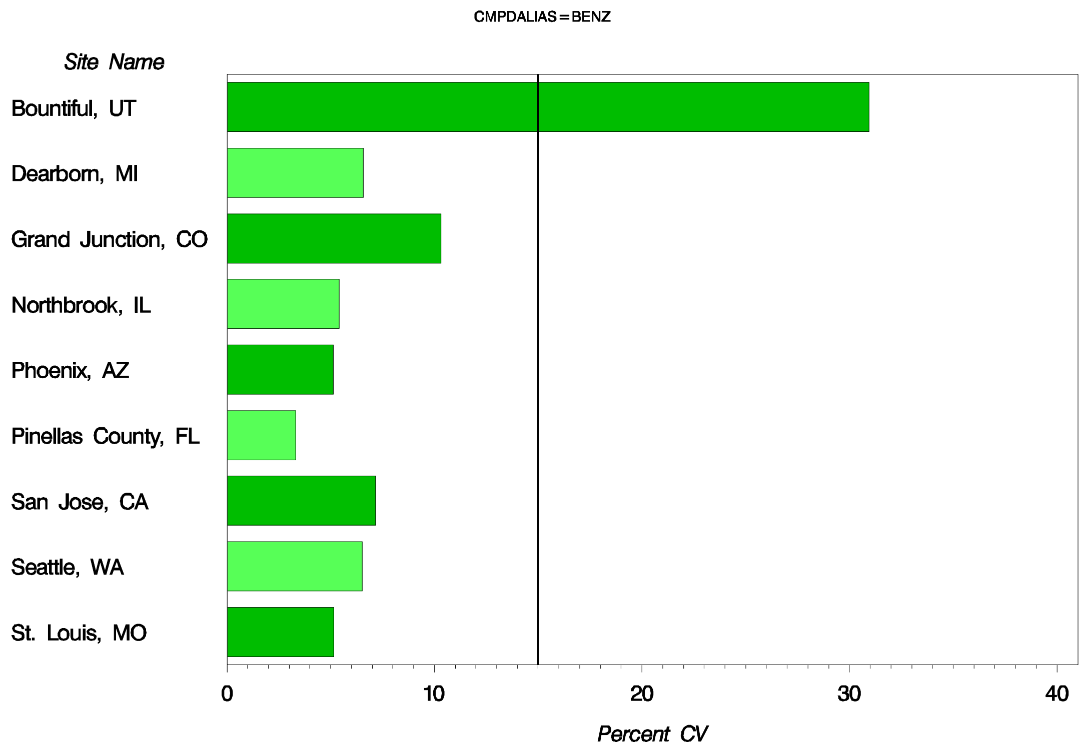


Figure 8. Analytical Precision Summary for Benzene at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 15%).

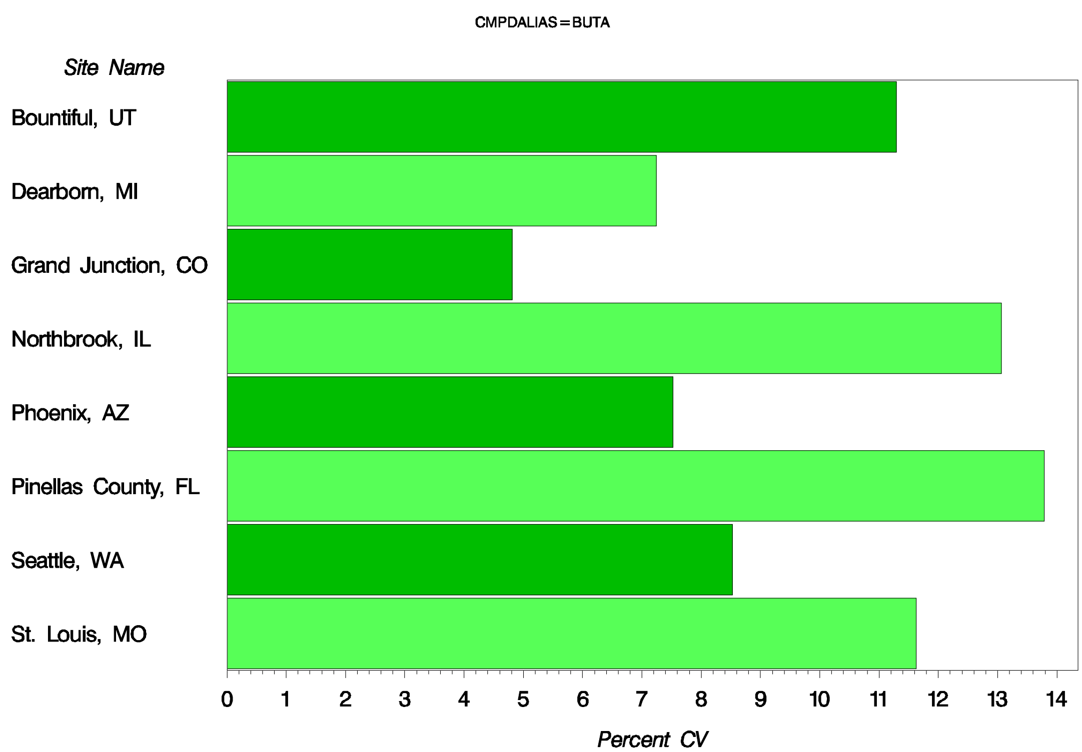


Figure 9. Analytical Precision Summary for 1,3-Butadiene at NATTS Sample Collection Sites in 2009.

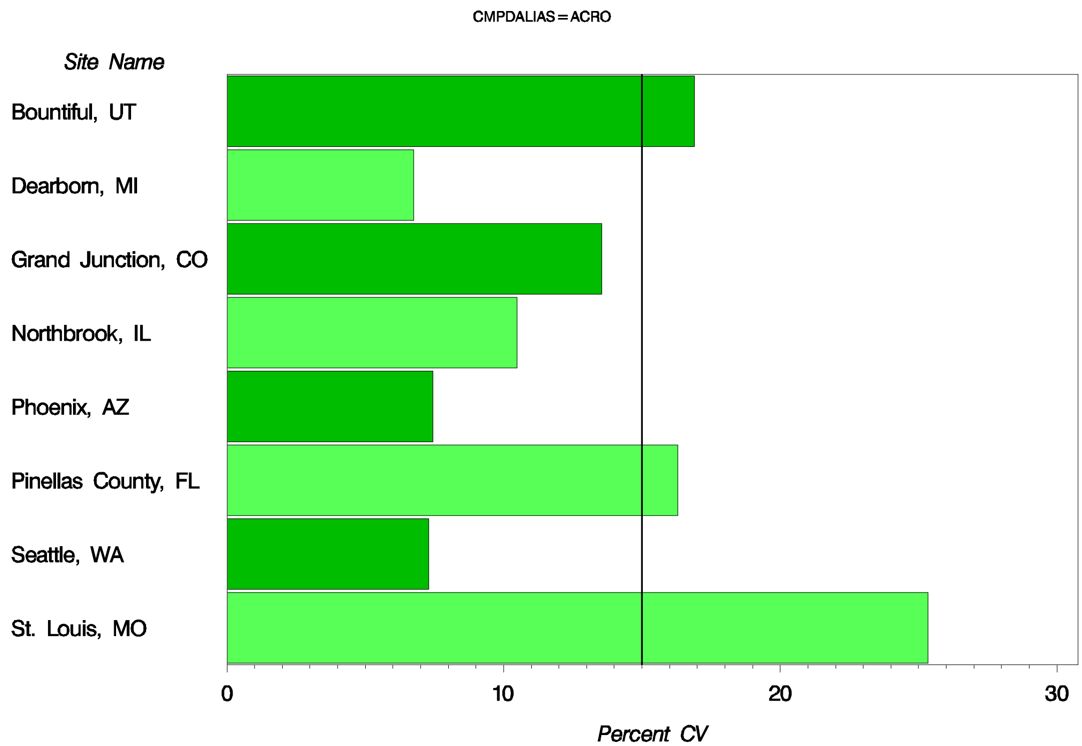


Figure 10. Analytical Precision Summary for Acrolein at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 15%).

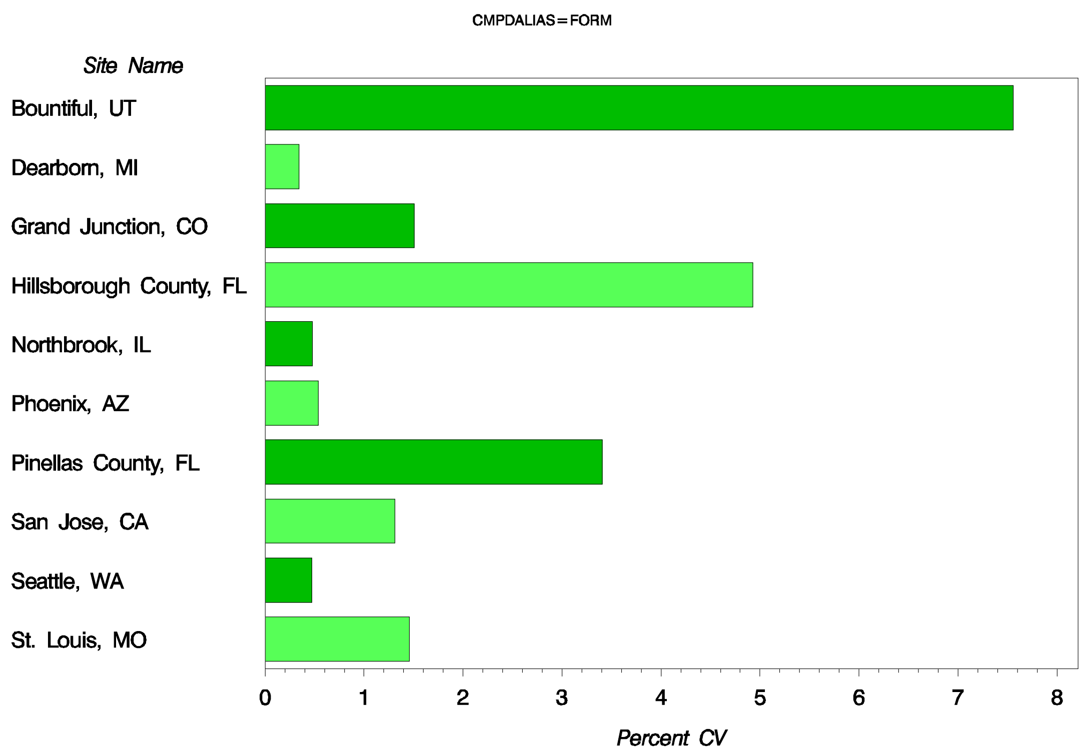


Figure 11. Analytical Precision Summary for Formaldehyde at NATTS Sample Collection Sites in 2009.

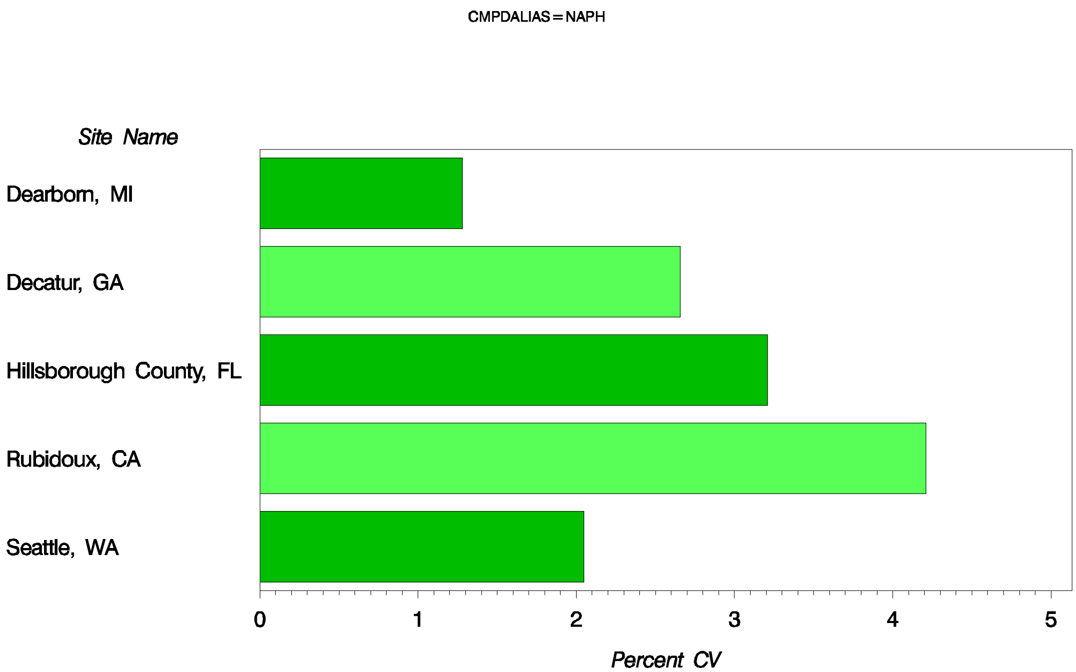


Figure 12. Analytical Precision Summary for Naphthalene at NATTS Sample Collection Sites in 2009.

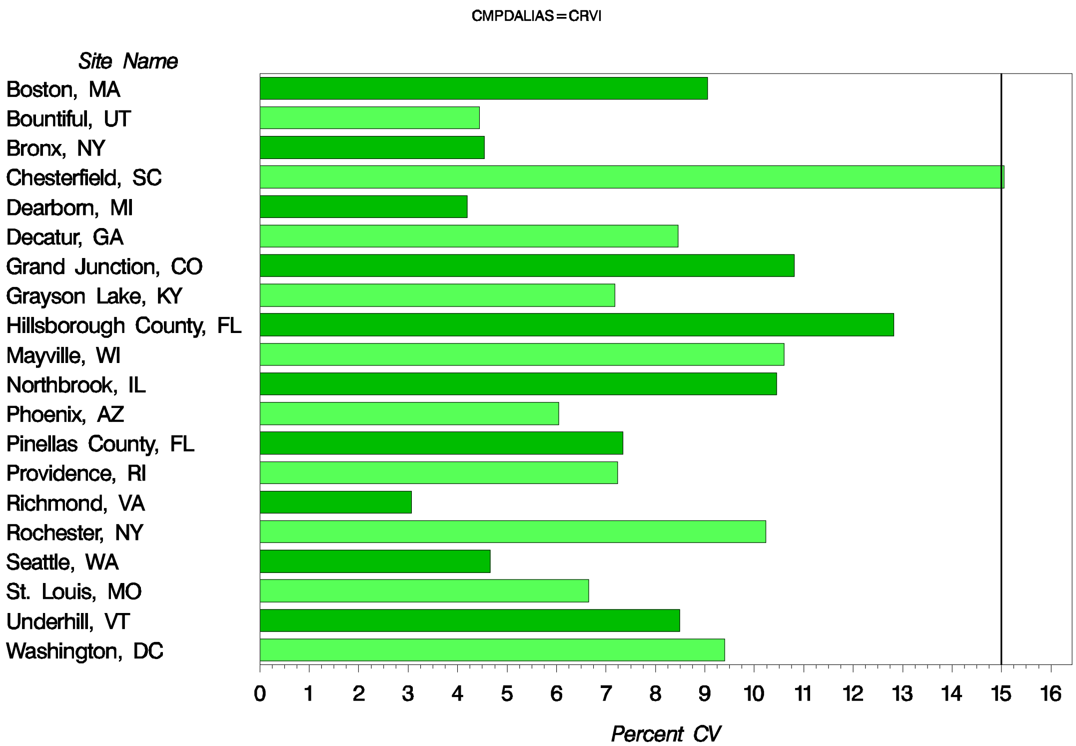


Figure 13. Analytical Precision Summary for Chromium (VI) at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 15%).

CMPDALIAS=AS

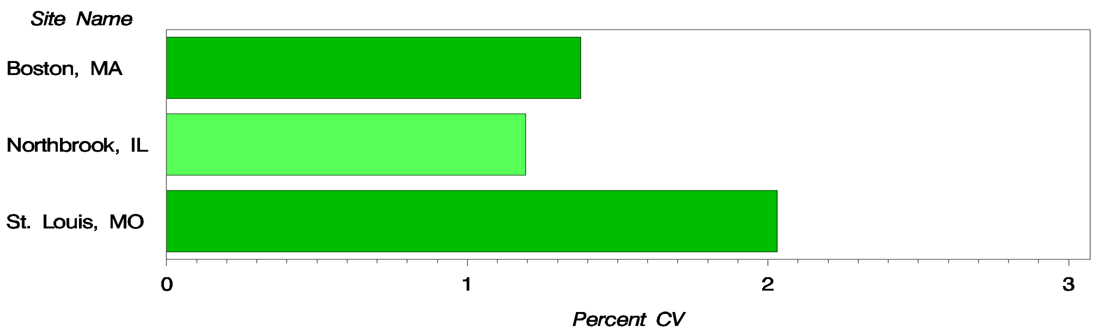


Figure 14. Analytical Precision Summary for Arsenic at NATTS Sample Collection Sites in 200 .

Examination of Figures 15 through 21 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 8 through 14. Variability seen for many sites may reflect the presence of extreme values. No attempt has been made to elucidate this cause through careful review of the individual data pairs for each analyte and site. With the exception of acrolein where only one site achieved the MQO in 2009, some sites achieve the MQOs, and some sites do not for most analytes, suggesting that the 15% threshold is a reasonable target for the MQO. The fact that many sites exhibit percentage CVs above the MQO target level suggests that the collection methodology contributes significantly to the overall variability in the data for a given site and analyte. Without identifying specific sites, the percentages of reporting sites with percentage CV above the MQO threshold are 46%, 35%, 30%, 55%, 91%, and 36% for arsenic, chromium (VI), benzene, 1,3-butadiene, acrolein, and formaldehyde, respectively. These percentages are consistent with variations in collection and analysis challenges posed by different analytes, with more problematic analytes (e.g., butadiene, and acrolein) showing poorer attainment of the MQO. That fact not withstanding, the percentage CVs computed across sites by analyte are somewhat misleading because they may be influenced by atypically large CVs at selected sites. The QA report of the NATTS stations for 2006 [4] warned of the danger of 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 POCs for each site—the data presented here are based primarily on the RD records. The two exceptions were the duplicate data for VOCs from the Washington, DC and Pinellas County, FL sites that were uploaded to AQS only as RP records and were, therefore, extracted as such.

Table 10. Overall Precision[a] for Primary and Collocated Samples from 2009.

AQS Site ID	Site Description	Duplicate Type	BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122	PERC	TCE	VCM
04-013-9997	Phoenix, AZ	Collocate	14.7 (7)	9.2 (7)	14.4 (7)	6.8 (6)	—[b]	—	—	50.7 (7)	—	9.9 (7)	6.1 (1)	—
04-013-9997	Phoenix, AZ	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
06-037-1103	Los Angeles, CA	Collocate	10.8 (27)	24.5 (28)	—	23.4 (28)	—	—	—	27 (28)	—	28.7 (25	26 (26)	—
06-037-1103	Los Angeles, CA	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
06-065-8001	Rubidoux, CA	Collocate	19 (23)	25.5 (24)	—	23.7 (24)	—	—	—	62.6 (2)	—	41.7 (23)	0 (3)	—
06-065-8001	Rubidoux, CA	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
06-085-0005	San Jose, CA	Collocate	13 (25)	60 (4)	—	55.6 (20)	—	—	—	48.8 (22)	—	44.6 (25)	37.9 (11)	—
06-085-0005	San Jose, CA	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
08-077-0017	Grand Junction, CO	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
08-077-0017	Grand Junction, CO	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
08-077-0018	Grand Junction, CO	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
08-077-0018	Grand Junction, CO	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
11-001-0043	Washington, DC	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
11-001-0043	Washington, DC	Duplicate	7.4 (59)	23.9 (58)	6.9 (59)	6 (59)	0 (6)	15.7 (27)	17.6 (59)	12.5 (47)	10.8 (19)	6.8 (59)	0 (41)	13.1 (13)
12-057-3002	Hillsborough County, FL	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
12-057-3002	Hillsborough County, FL	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
12-103-0026	Pinellas County, FL	Collocate	3.7 (31)	14.7 (31)	5 (31)	26.2 (31)	36.1 (12)	28.3 (1)	11.3 (30)	36.7 (31)	30.4 (22)	14.9 (31)	34.2 (25)	43.1 (14)
12-103-0026	Pinellas County, FL	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
13-089-0002	Decatur, GA	Collocate	24.2 (60)	—	9.5 (21)	15 (9)	—	—	0 (1)	88.7 (1)	—	21.9 (4)	0 (1)	—
13-089-0002	Decatur, GA	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—

(continued)

Table 10. Overall Precision[a] for Primary and Collocated Samples from 2009 (continued).

AQS Site ID	Site Description	Duplicate Type	BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122	PERC	TCE	VCM
17-031-4201	Northbrook, IL	Collocate	25.8 (1)	—	9.1 (1)	23.6 (1)	—	—	0 (1)	107 (1)	—	34.4 (1)	31.4 (1)	—
17-031-4201	Northbrook, IL	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
21-043-0500	Grayson Lake, KY	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
21-043-0500	Grayson Lake, KY	Duplicate	4.7 (4)	—	—	—	—	—	—	44.7 (11)	—	—	—	—
25-025-0042	Boston, MA	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
25-025-0042	Boston, MA	Duplicate	4.8 (31)	27.3 (31)	3.2 (31)	3.6 (31)	23.6 (4)	11.2 (23	4.3 (31)	19.3 (31)	26.2 (10)	5.1 (31)	9.7 (30)	4.5 (20)
26-163-0033	Dearborn, MI	Collocate	9.3 (8)	10.5 (8)	3.8 (8)	39.4 (8)	—	—	—	10.1 (8)	—	6.9 (8)	15.5 (2)	0 (1)
26-163-0033	Dearborn, MI	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
29-510-0085	St. Louis, MO	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
29-510-0085	St. Louis, MO	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
36-005-0110	Bronx, NY	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
36-005-0110	Bronx, NY	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
36-055-1007	Rochester, NY	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
36-055-1007	Rochester, NY	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
41-051-0246	Portland, OR	Collocate	33.3 (23)	5.9 (3)	8.9 (22)	19.6 (3)	—	0 (2)	—	38.6 (39)	—	19.6 (8)	—	—
41-051-0246	Portland, OR	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
41-061-0119	La Grande, OR	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
41-061-0119	La Grande, OR	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
44-007-0022	Providence, RI	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
44-007-0022	Providence, RI	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
45-025-0001	Chesterfield, SC	Collocate	36.4 (12)	—	0 (11)	—	—	—	—	31.3 (24)	—	—	—	—
45-025-0001	Chesterfield, SC	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—

(continued)

Table 10. Overall Precision[a] for Primary and Collocated Samples from 2009 (continued).

AQS Site ID	Site Description	Duplicate Type	BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122	PERC	TCE	VCM
48-201-1039	Deer Park, TX	Collocate	11.6 (55)	26 (16)	7 (55)	12.5 (53)	23.6 (4)	34.6 (5)	17.3 (29)	10.7 (51)	21.1 (5)	15.7 (42)	28.3 (20)	15.8 (20)
48-201-1039	Deer Park, TX	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
48-203-0002	Harrison County, TX	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
48-203-0002	Harrison County, TX	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
49-011-0004	Bountiful, UT	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
49-011-0004	Bountiful, UT	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
50-007-0007	Underhill, VT	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
50-007-0007	Underhill, VT	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
51-087-0014	Richmond, VA	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
51-087-0014	Richmond, VA	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
53-033-0080	Seattle, WA	Collocate	9.8 (4)	4.5 (4)	5.3 (4)	32.6 (4)	—	—	—	40.5 (4)	—	5.2 (4)	9.4 (1)	—
53-033-0080	Seattle, WA	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
55-027-0007	Mayville, WI	Collocate	—	—	—	—	—	—	—	—	—	—	—	—
55-027-0007	Mayville, WI	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—
	Overall Mean	All Dups.	18.3 (311)	23.9 (156)	6.9 (191)	25.5 (218)	31.7 (20)	17.7 (31)	11.9 (92)	36.4 (282)	28.2 (37)	25.5 (209)	26.2 (121)	23.9 (55)

(continued)

Table 10. Overall Precision[a] for Primary and Collocated Samples from 2009 (continued).

AQS Site ID	Site Description	Duplicate Type	cDCPEN	tDCPEN	ACRO	ACRY	NAPH	BaP	FORM	ACET	AS	BE	CD	PB	MN	NI	CRVI
04-013-9997	Phoenix, AZ	Collocate	—	—	20.7 (7)	118 (1)	—	—	4.2 (6)	5.8 (6)	—	—	—	—	—	—	15.1 (6)
04-013-9997	Phoenix, AZ	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
06-037-1103	Los Angeles, CA	Collocate	—	—	89.9 (28)	—	—	—	36 (26)	31.2 (26)	—	—	—	—	—	—	15.1 (6)
06-037-1103	Los Angeles, CA	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
06-065-8001	Rubidoux, CA	Collocate	—	—	85.9 (24)	—	—	—	24.4 (29)	28.2 (29)	—	—	—	—	—	—	15.1 (6)
06-065-8001	Rubidoux, CA	Duplicate	—	—	—	—	17.2 (3)	27 (1)	—	—	—	—	—	—	—	—	—
06-085-0005	San Jose, CA	Collocate	—	—	42.9 (24)	—	—	—	24.1 (30)	26.7 (30)	—	—	—	—	—	—	15.1 (6)
06-085-0005	San Jose, CA	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
08-077-0017	Grand Junction, CO	Collocate	—	—	—	—	—	—	—	—	—	4.7 (6)	5.1 (6)	29.4 (34	7.1 (92)	37.1 (46)	34.3 (3)
08-077-0017	Grand Junction, CO	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
08-077-0018	Grand Junction, CO	Collocate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
08-077-0018	Grand Junction, CO	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
11-001-0043	Washington, DC	Collocate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	8 (3)
11-001-0043	Washington, DC	Duplicate	0 (3)	0 (3)	26.1 (50)	37.2 (49)	—	—	—	—	—	—	—	—	—	—	—
12-057-3002	Hillsborough County, FL	Collocate	—	—	—	—	20.8 (33)	39.6 (8)	—	—	15.2 (59)	0 (59)	22.3 (59)	16.1 (59)	12.8 (59)	12 (59)	20.7 (3)
12-057-3002	Hillsborough County, FL	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

(continued)

Table 10. Overall Precision[a] for Primary and Collocated Samples from 2009 (continued).

AQS Site ID	Site Description	Duplicate Type	cDCPEN	tDCPEN	ACRO	ACRY	NAPH	BaP	FORM	ACET	AS	BE	CD	PB	MN	NI	CRVI
12-103-0026	Pinellas County, FL	Collocate	34.3 (16)	35.2 (17)	24.7 (31)	69.1 (29)	—	—	—	—	—	—	—	—	—	—	7.5 (2)
12-103-0026	Pinellas County, FL	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
13-089-0002	Decatur, GA	Collocate	—	—	—	—	11.8 (5)	—	41.5 (24)	14.3 (22)	18.3 (16)	84.9 (1)	22 (24)	27.2 (25)	24.6 (25)	15.2 (25)	14.1 (4)
13-089-0002	Decatur, GA	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
17-031-4201	Northbrook, IL	Collocate	—	—	3.7 (1)	—	—	—	4.9 (5)	2.5 (5)	17.3 (23)	43.9 (20)	24 (23)	19 (23)	10.7 (23)	23.8 (23)	35 (3)
17-031-4201	Northbrook, IL	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
21-043-0500	Grayson Lake, KY	Collocate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	9.4 (2)
21-043-0500	Grayson Lake, KY	Duplicate	—	—	—	—	—	—	15.4 (27)	15.2 (27)	6.6 (26)	—	—	6.8 (56)	45.7 (50)	44.9 (3)	—
25-025-0042	Boston, MA	Collocate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
25-025-0042	Boston, MA	Duplicate	0 (2)	47.1 (1)	19.1 (31)	58.5 (27)	—	—	7.5 (31)	28.5 (31)	3 (33)	45.3 (25)	27.9 (33)	5.9 (33)	5.9 (33)	8.7 (33)	10.8 (3)
26-163-0033	Dearborn, MI	Collocate	—	—	26.9 (8)	—	5.3 (5)	13.8 (5)	5.3 (5)	3.8 (5)	12.3 (56)	21 (48)	15 (54)	10.8 (112)	7.8 (56)	24.3 (55)	8.9 (6)
26-163-0033	Dearborn, MI	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
29-510-0085	St. Louis, MO	Collocate	—	—	—	—	—	—	—	—	4.7 (11)	21.5 (11)	20.9 (11)	9.1 (11)	7.4 (11)	17.6 (11)	11.4 (6)
29-510-0085	St. Louis, MO	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
36-005-0110	Bronx, NY	Collocate	—	—	—	—	—	—	—	—	7.4 (51)	15.8 (51)	37.4 (49)	4.1 (51)	3.7 (51)	7.3 (51)	7.6 (5)
36-005-0110	Bronx, NY	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
36-055-1007	Rochester, NY	Collocate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
36-055-1007	Rochester, NY	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
41-051-0246	Portland, OR	Collocate	—	—	—	—	21.8 (44)	12.3 (12)	7 (47)	6.7 (47)	8.6 (40)	17.4 (40)	17.7 (40)	8.4 (40)	8.7 (40)	8.1 (40)	—
41-051-0246	Portland, OR	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

(continued)

Table 10. Overall Precision[a] for Primary and Collocated Samples from 2009 (continued).

AQS Site ID	Site Description	Duplicate Type	cDCPEN	tDCPEN	ACRO	ACRY	NAPH	BaP	FORM	ACET	AS	BE	CD	PB	MN	NI	CRVI
41-061-0119	La Grande, OR	Collocate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
41-061-0119	La Grande, OR	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
44-007-0022	Providence, RI	Collocate	—	—	—	—	—	—	10.6 (24)	15.5 (24)	25.6 (24)	34.1 (16)	55.4 (12)	15.2 (26)	11.8 (26)	16.4 (26)	10.1 (1)
44-007-0022	Providence, RI	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
45-025-0001	Chesterfield, SC	Collocate	—	—	—	—	—	—	10.4 (61)	12.7 (60)	25.8 (48)	—	45.7 (60)	39.1 (70)	14.4 (96)	66.6 (72)	—
45-025-0001	Chesterfield, SC	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	26.5 (3)
48-201-1039	Deer Park, TX	Collocate	23.6 (4)	33.3 (2)	102 (53)	—	37.4 (56	36.1 (30)	—	—	—	—	—	—	—	—	33.1 (23)
48-201-1039	Deer Park, TX	Duplicate	—	—	—	—	11.1 (56	35.1 (49)	—	—	—	—	—	—	—	—	—
48-203-0002	Harrison County, TX	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
48-203-0002	Harrison County, TX	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
49-011-0004	Bountiful, UT	Collocate	—	—	—	—	—	—	—	—	27.4 (2)	—	0 (1)	7.2 (3)	14.5 (3)	69.9 (1)	41.9 (4)
49-011-0004	Bountiful, UT	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
50-007-0007	Underhill, VT	Collocate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
50-007-0007	Underhill, VT	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	7.5 (1)
51-087-0014	Richmond, VA	Collocate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	6.7 (2)
51-087-0014	Richmond, VA	Duplicate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
53-033-0080	Seattle, WA	Collocate	—	—	28.7 (4)	—	—	—	5.7 (6)	2.7 (6)	—	—	—	—	—	—	—
53-033-0080	Seattle, WA	Duplicate	—	—	—	—	13.2 (6)	5 (2)	—	—	—	—	—	—	—	—	16.8 (4)

(continued)

Table 10. Overall Precision[a] for Primary and Collocated Samples from 2009 (continued).

AQS Site ID	Site Description	Duplicate Type	cDCPEN	tDCPEN	ACRO	ACRY	NAPH	BaP	FORM	ACET	AS	BE	CD	PB	MN	NI	CRVI
55-027-0007	Mayville, WI	Collocate	—	—	—	—	—	—	—	—	12.5 (2)	—	2.6 (1)	35.5 (1)	21.7 (1)	12.8 (2)	7.5 (2)
55-027-0007	Mayville, WI	Duplicate	—	—	—	—	—	—	3.8 (5)	4.5 (5)	—	—	—	—	—	—	—
	Overall Mean	All Dups.	31 (22)	35.7 (20)	70.1 (211)	65.5 (57)	24.3 (208)	32.9 (107)	20 (326)	19.6 (323)	15.3 (391)	24.6 (277)	30.2 (373)	19.5 (544)	17.6 (546)	32.5 (447)	24.2 (83)

[a] Expressed as percentage coefficient of variation (%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.

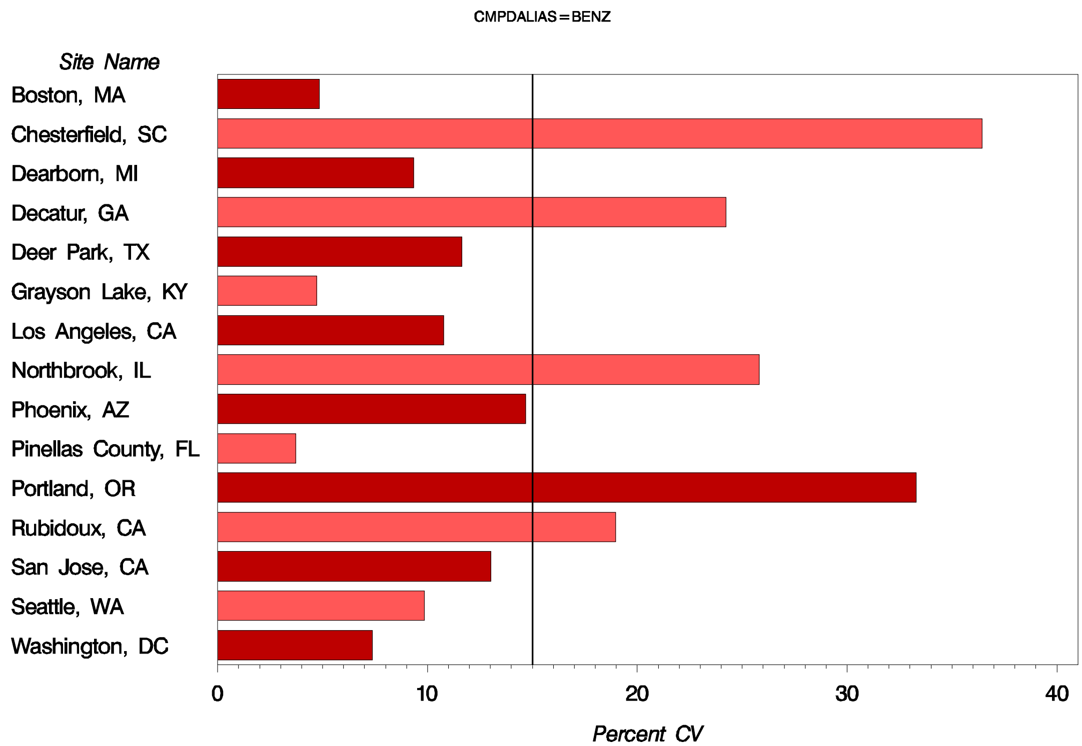


Figure 15. Overall Precision Summary for Benzene at NATTS Sample Collection Sites in 200 (MQO reference indicated at 15%).

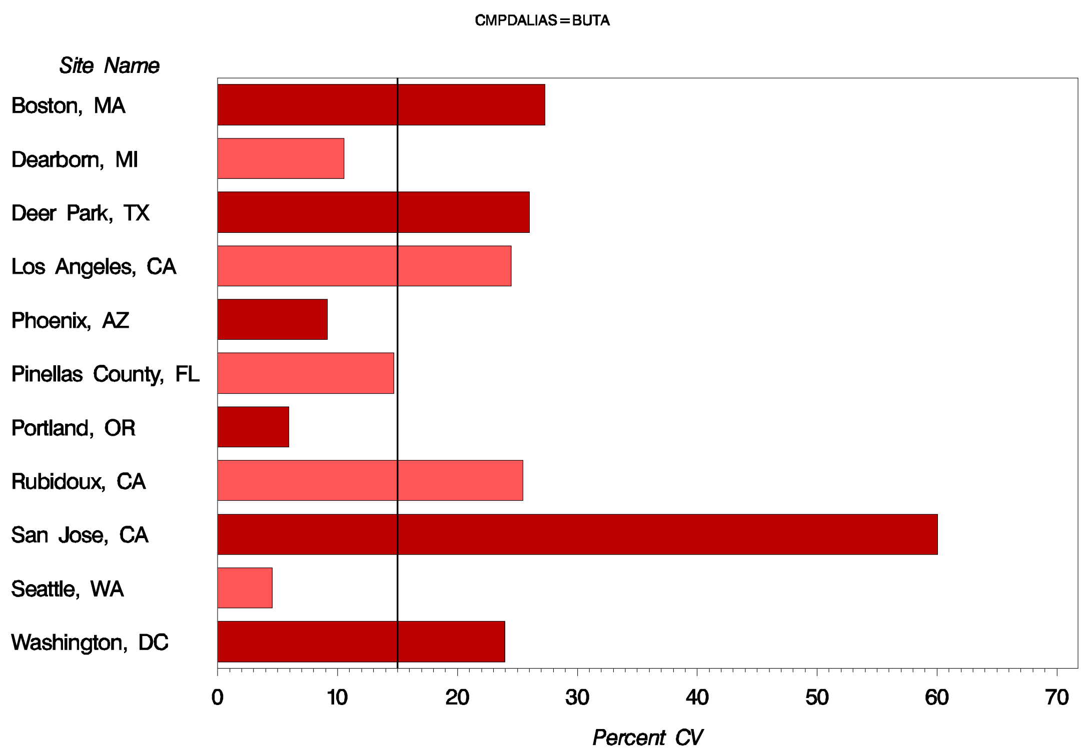


Figure 16. Overall Precision Summary for 1,3-Butadiene at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 15%).

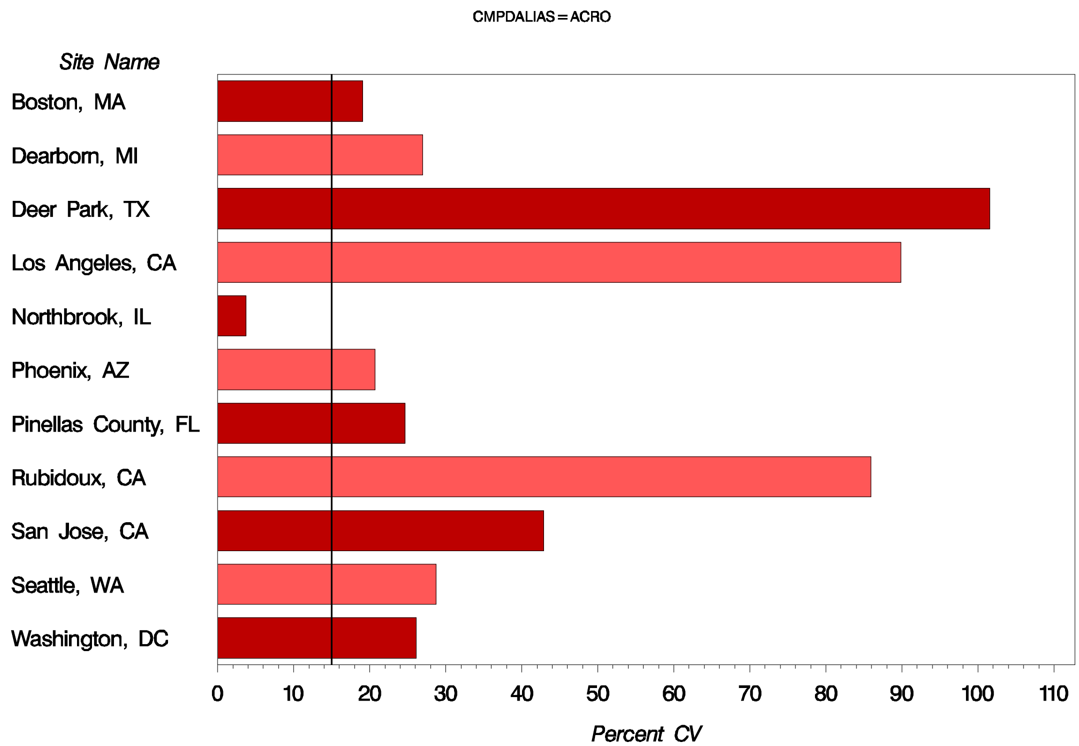


Figure 17. Overall Precision Summary for Acrolein at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 15%).

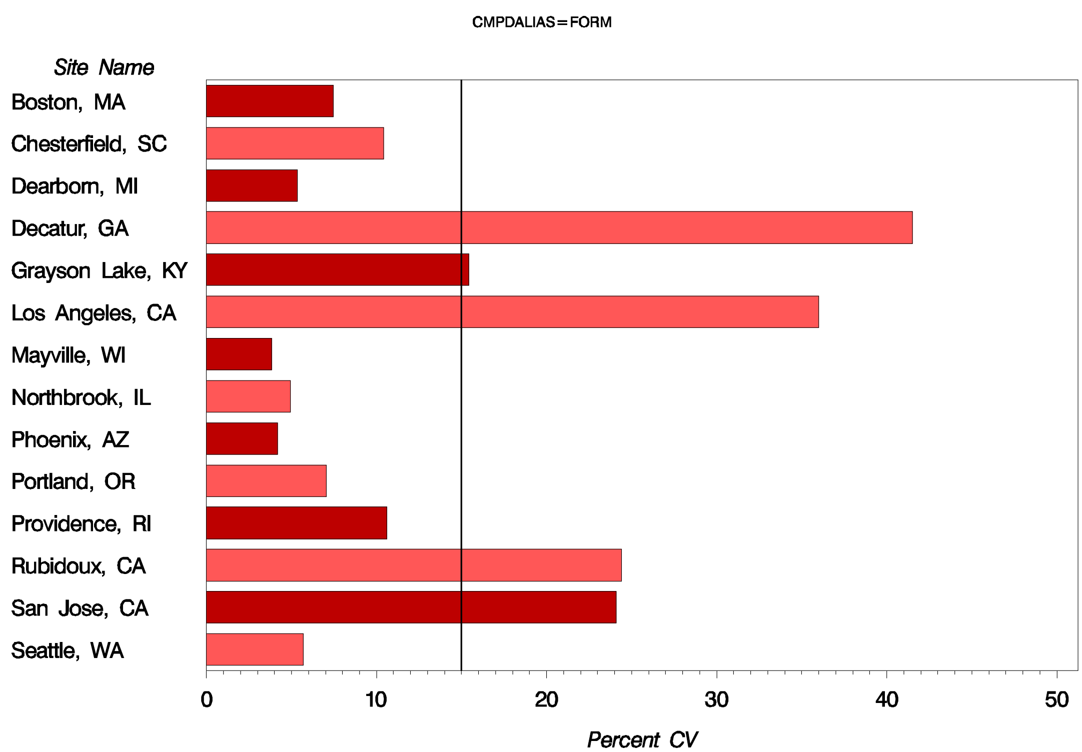


Figure 18. Overall Precision Summary for Formaldehyde at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 15%).

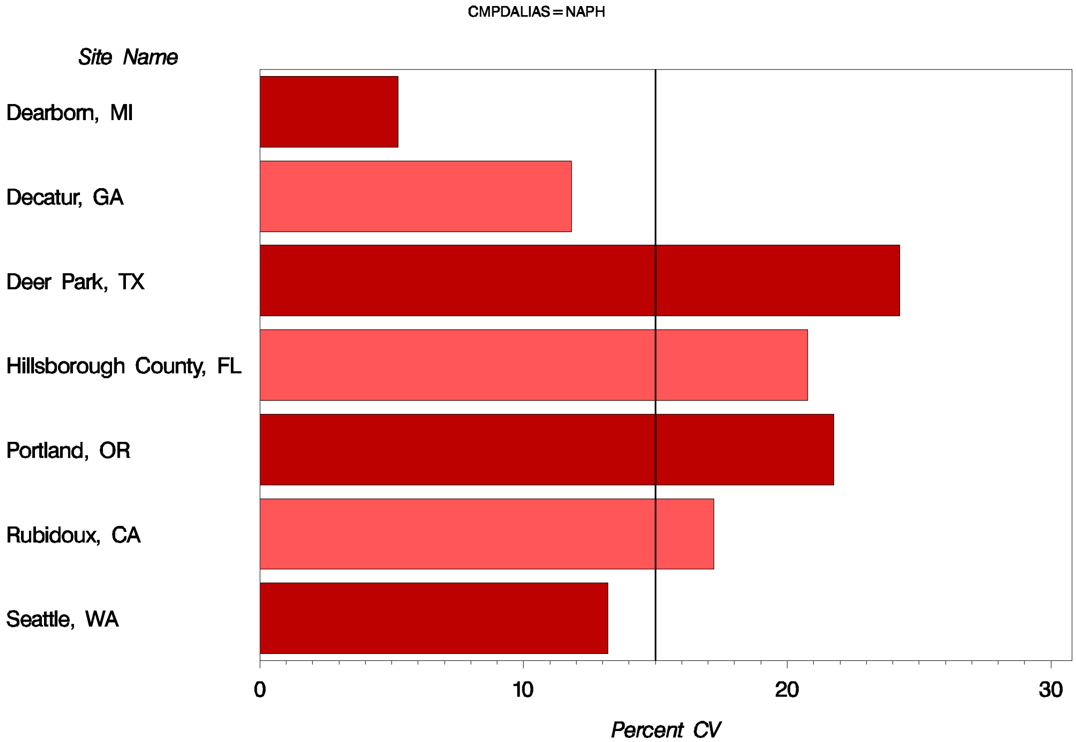


Figure 19. Overall Precision Summary for Naphthalene at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 15%).

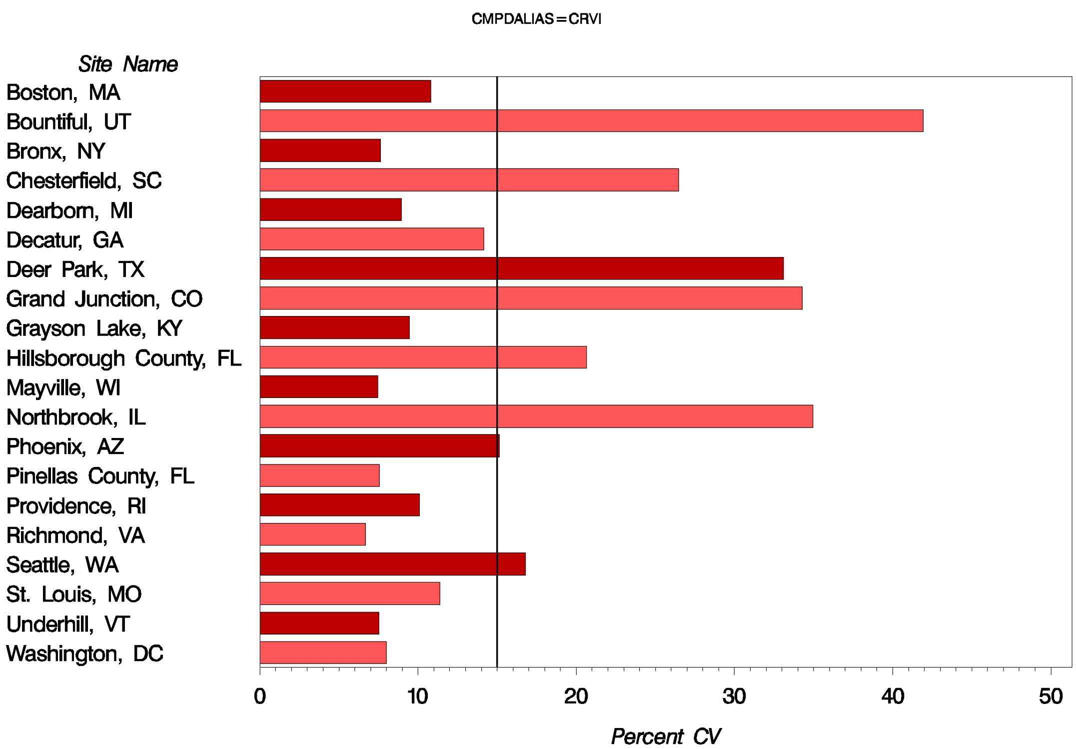


Figure 20. Overall Precision Summary for Chromium (VI) at NATTS Sample Collection Sites in 200 (MQO reference indicated at 15%).

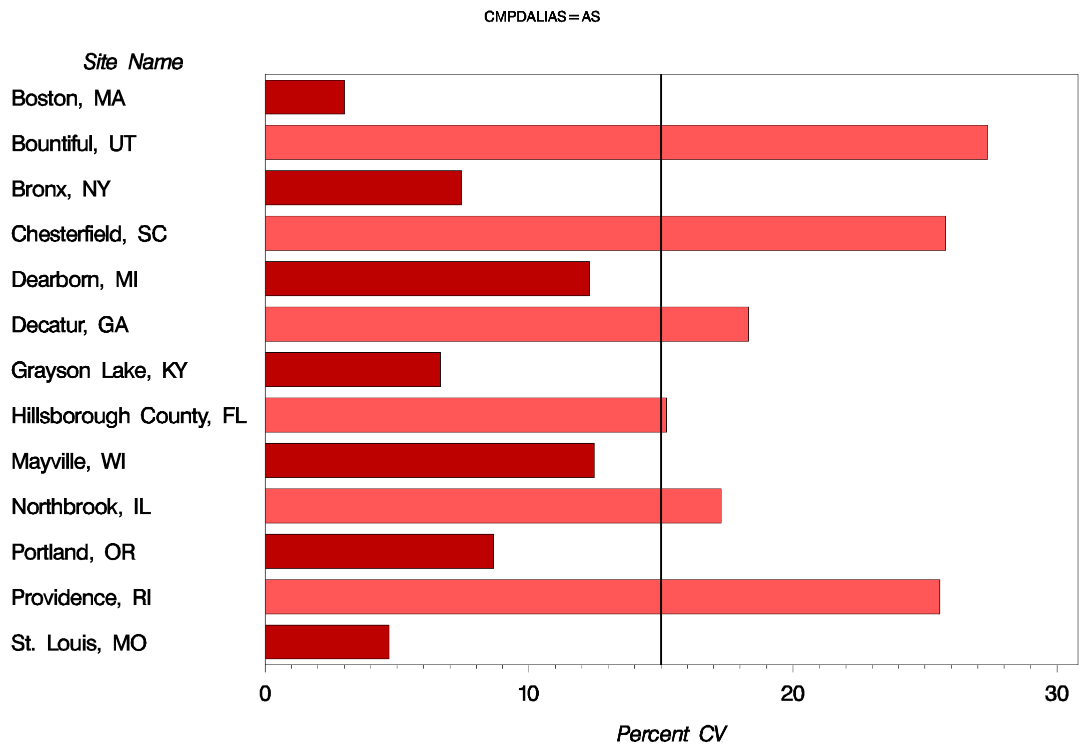


Figure 21. Overall Precision Summary for Arsenic at NATTS Sample Collection Sites in 2009 (MQO reference indicated at 15%).

2.4 Laboratory Bias Data Based on Proficiency Testing Samples

PT audits of participating NATTS sample analysis laboratories were conducted semiannually for VOCs and carbonyls and annually for metals and PAHs in 2009. Alion Science, Inc., under contract to EPA (Contract No. 68-D03-006), generated "spiked" samples containing known amounts of the HAPs of interest and delivered these spiked samples to each laboratory in 2009 for each of the VOC, carbonyl, and metals analyte groups. 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. The results of these PT sample analyses were provided to RTI International by EPA for calendar year 2009.

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

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

Tables 11 through 13 present the results of the PT samples for all compounds analyzed. To reflect overall bias independent of direction, the mean of the absolute value of the bias, along with the minimum and maximum bias values, is presented in the bottom and right-hand summaries for the individual tabulated values. Figure 22 shows boxplots summarizing laboratory bias results for all the participating laboratories across the five compounds for which PT data

Table 11. Performance Testing Bias Results[a] for VOCs in 2009 NATTS Laboratories.

Laboratory Code	Lab Description	BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE1122	PERC	TCE	VCM	c-CPEN	t-CPEN	ACRO	*Mean Abs. Bias (across analytes)*[b]	*Min.*	*Max.*
01-01-V	RI Dept. of Health Laboratories	0.41	-11.9	-9.21	-3.43	-9.36	-8.72	-11.7	-10.7	1.79	-9.66	-13.7	-10.3	-12.1	-12.4	87.9	15.3	-21.0	186.22
02-01-C	NYS DEC BAQS	-0.77	-12.2	0.26	-15.4	-11.4	-11.3	-11.6	-6.86	1.55	-9.62	-15.9	-9.83	-17.2	-13.4	-6.09	10.6	-24.8	7.00
03-01-V	Maryland Department of the Environment	5.98	2.26	4.61	6.00	-8.32	-2.28	-1.90	10.7	-2.56	6.82	-3.04	12.8	-12.3	-9.17	3.41	6.97	-15.9	13.4
03-02-V	Virginia Division of Consolidated Laboratory Services	-21.2	-16.6	-17.6	-29.0	-0.19	-7.84	-24.1	-23.0	-4.26	-6.50	-9.36	-20.6	-14.5	-3.80	14.2	18.8	-32.5	51.9
04-01-V	Pinellas County DEM AQ	-9.12	-6.76	-9.57	-13.1	-5.95	-12.4	-13.4	-15.5	-6.91	-11.3	-10.3	-5.84	-7.86	-8.08	-0.71	10.5	-27.6	14.1
04-02-V	SC Dept of HEC, Div. of AQ Analysis	-24.3	19.7	-34.5	-27.9	16.8	-8.37	-7.23	-10.3	97.5	-5.96	-8.62	-20.7	-25.6	9.88	67.1	26.8	-38.0	112
04-03-V	KY Div. of Environmental Services	-3.08	-5.83	-4.87	-4.06	-2.18	-11.7	-7.56	-4.88	-1.99	-1.10	-3.28	1.75	-4.53	-4.61	11.3	6.80	-16.9	15.2
04-04-V	GA DNR EPD Laboratory	-15.3	-17.8	-12.3	-17.5	-11.8	-15.7	-13.5	-12.4	-19.8	-15.9	-12.1	-8.55	-15.8	-13.7	3.15	14.3	-21.7	15.6
05-01-V	MI DEQ Lab	-9.51	8.89	-2.22	-9.37	-6.76	-11.2	-12.2	-13.0	-0.76	-3.05	-3.22	11.7	-12.7	-3.60		10.3	-24.4	20.9
05-03-V	Wisconsin DNR	-12.2	-12.8	10.9	-19.3	-24.0	-2.37	-14.8	10.3	-25.6	-18.2	-9.47	-1.28	-21.0	-12.2	27.3	15.3	-29.5	34.3
06-01-V	Texas CEQ	-3.44	-1.44	4.35	-17.9	-17.9	-28.0	-20.3	-15.1	-1.27	-21.9	-13.4	-3.91	2.78	3.80	6.67	12.2	-30.5	14.8
09-03-V	Bay Area Air Quality Management District	-10.2	-23.1	0.56	-9.69	-4.06	--[c]	-17.2	-21.0	--	-9.58	4.09	-5.32	--	--	117	21.5	-32.2	152
09-06-C	San Diego County Air Pollution Control District	-10.9	-9.62	-6.14	-14.4	-3.29	-14.9	-9.29	-10.3	-7.40	-8.64	-9.74	-10.8	-3.39	6.25	1.03	8.95	-25.6	13.2
10-02-V	Oregon DEQ Lab	-31.8	-10.9	-45.9	-26.7	-41.6	-30.2	-24.2	14.0	-45.2	-43.	-36.8	1.03	-35.4	-42.5	--	33.4	-61.6	29.7
11-01-V	ERG	6.16	-0.52	1.85	5.44	-1.50	-2.22	2.69	5.66	-7.25	1.11	2.71	-0.06	1.63	-4.02	-14.7	4.66	-18.5	10.4
	Mean Abs. Bias (across laboratories)	11.8	15.3	12.7	14.9	11.8	12.9	12.8	12.4	16.4	14.0	12.6	9.67	13.3	12.5	30.3	14.1		
	Minimum	-35.3	-42.9	-52.8	-30.3	-45.8	-33.7	-32.5	-32.2	-61.6	-32.5	-40.3	-26.8	-40.2	-50.5	-23.6			
	Maximum	12.0	21.1	20.0	7.45	16.8	5.26	3.42	29.7	112	3.42	14.6	20.9	11.0	14.8	186			

[a] Computed as the mean of the individual percent differences.
[b] Computed as the mean of the absolute values of the individual percent differences.
[c] Analyte not reported.

Table 12. Proficiency Testing Bias Results[a] for Carbonyls in 2009 NATTS Laboratories.

Laboratory Code	Laboratory Description	FORM	ACET	*Mean Abs. Bias (across analytes)[b]*	*Min.*	*Max.*
01-01-C	RI Dept. of Health Laboratories	-5.30	-1.15	9.22	-14.3	12.0
01-02-C	Vermont DEC Environmental Lab	-23.7	-25.6	24.7	-36.3	-11.1
01-03-C	MADEP	-9.56	-10.9	10.2	-15.4	-6.40
02-01-C	NYSDEC BAQS	-13.4	-15.4	14.4	-22.9	-8.00
03-01-C	Philadelphia Air Management Services Laboratory	-6.83	-9.37	8.10	-13.1	-5.60
03-02-C	Virginia Division of Consolidated Laboratory Services	-6.54	-11.0	8.79	-14.9	-6.22
04-02-C	SC Dept of HEC, Div. of AQ Analysis	1.62	-7.95	4.83	-14.3	2.67
04-03-C	KY Div. of Environmental Services	-13.7	-20.0	16.8	-40.0	0.00
04-04-C	GADNR,EPD Laboratory	-7.78	-22.1	14.9	-25.7	-3.56
05-01-C	MI DEQ Lab	-2.73	-8.00	5.37	-12.0	-0.57
05-03-C	Wisconsin DNR	-5.40	-9.15	10.3	-14.3	-2.22
06-01-C	Texas CEQ	-12.4	-17.4	14.9	-21.1	-11.6
09-03-C	Bay Area Air Quality Management District	-7.84	0.06	4.75	-11.1	1.71
09-06-C	San Diego County Air Pollution Control District	-2.74	-6.94	4.84	-13.7	-0.16
09-08-C	South Coast Air Quality Management District	-15.7	-14.2	15.0	-21.1	-10.2
10-02-C	Oregon DEQ Lab	-10.8	-14.3	12.5	-20.6	-8.00
11-01-C	ERG	-7.81	-10.1	8.93	-17.7	-2.40
	Mean Abs.Bias (across laboratories)	9.66	12.7	11.2		
	Minimum	-36.3	-40.0			
	Maximum	2.67	12.0			

[a] Computed as the mean of the individual percent differences.
[b] Computed as the mean of the absolute values of the individual percent differences.

were compiled: 1,3-butadiene, formaldehyde, acrolein, benzene, and arsenic. In this figure, the bottom and top of the "box" represent the 25th and 75th percentiles, respectively; the horizontal line inside the box represents the median value; the diamond symbol represents the mean; the top and bottom "whiskers" extend to a length of 1.5 times the interquartile range (IQR). The IQR is defined as the distance between the 25th and 75th percentiles of the distribution of values. The reference line in this figure represents the MQO bias goal of 25%. To maintain figure clarity, only labs whose results fell outside of a window defined by 1.5 × IQR are identified on the graphical display. Selected results that fell outside of the IQR are identified by their laboratory ID number assigned by Alion; a cross-reference between the 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. Although some individual laboratories report PT sample concentrations that 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%. The biases for benzene, 1,3-butadiene, and formaldehyde are slightly negative, implying a smaller measured result than expected; biases for acrolein and arsenic are nominally positive. Percentage participation in the PT program (Table 14) was 100% for all compound classes.

Table 13. Proficiency Testing Bias[a] Results for Metals in 2009 NATTS Laboratories.

Laboratory Code	Lab Description	AS	BE	CD	PB	MN	NI	*Mean Abs. Bias (across analytes)*[b]	*Min.*	*Max.*
01-01-M	RI Dept. of Health Laboratories	-24.4	-8.46	-21.5	-36.3	-41.2	-32.9	27.5	-41.2	-8.46
03-01-M	WVDEP Division of Air Quality	23.7	41.6	27.7	182	3.690	25.7	50.7	3.69	182
03-02-C	Virginia Division of Consolidated Laboratory Services	25.6	37.8	27.2	156	-5.30	35.6	48.0	-5.30	156
04-01-M	Environmental Protection Comm. of Hillsborough Co.	12.5	37.3	24.1	-3.79	4.84	12.9	15.9	-3.79	37.3
04-02-M	SC Dept of HEC, Div. of AQ Analysis	3.95	9.67	-0.55	-5.15	0.81	-9.29	4.90	-9.29	9.67
04-03-M	KY Div. of Environmental Services	12.0	32.0	17.2	-6.23	-4.84	4.86	12.8	-6.23	32.0
04-04-M	GA DNR EPD Laboratory	-0.34	2.94	-6.93	32.4	-27.8	-13.9	14.0	-27.8	32.4
05-01-M	MI DEQ Lab	-22.7	-11.9	-17.9	-32.3	-11.3	-18.6	19.1	-32.3	-11.3
05-03-M	Wisconsin DNR	-3.40	10.5	9.12	-14.1	-28.3	-13.1	13.2	-28.3	10.5
06-01-M	Texas CEQ	4.81	10.6	6.57	-15.8	-26.2	-6.21	11.7	-26.2	10.6
08-02-M	IML Air Science	2.75	19.9	6.57	0.00	-0.23	-8.00	6.24	-8.00	19.9
09-08-M	South Coast Air Quality Management District	-28.2	-47.7	-19.9	-29.7	-44.0	-40.4	35.0	-47.7	-19.9
10-02-M	Oregon DEQ Lab	-12.5	-7.08	-8.94	-32.9	-41.9	-32.9	22.7	-41.9	-7.08
11-01-M	ERG	-14.8	-5.53	-16.2	-30.6	-37.7	-28.9	22. 3	-37.7	-5.53
11-02-M	RTI International	-1.37	3.45	-4.74	-24.5	-34.8	-29.3	16.4	-34.8	3.45
	Mean Abs.Bias (across laboratories)	13.5	20.4	15.1	37.6	20.0	20.4	21.2		
	Minimum	-28.2	-47.7	-21.5	-36.3	-44.0	-40.4			
	Maximum	25.6	41.6	27.7	181	7.83	35.6			

[a] Computed as the mean of the individual percent differences.
[b] Computed as the mean of the absolute values of the individual percent differences.

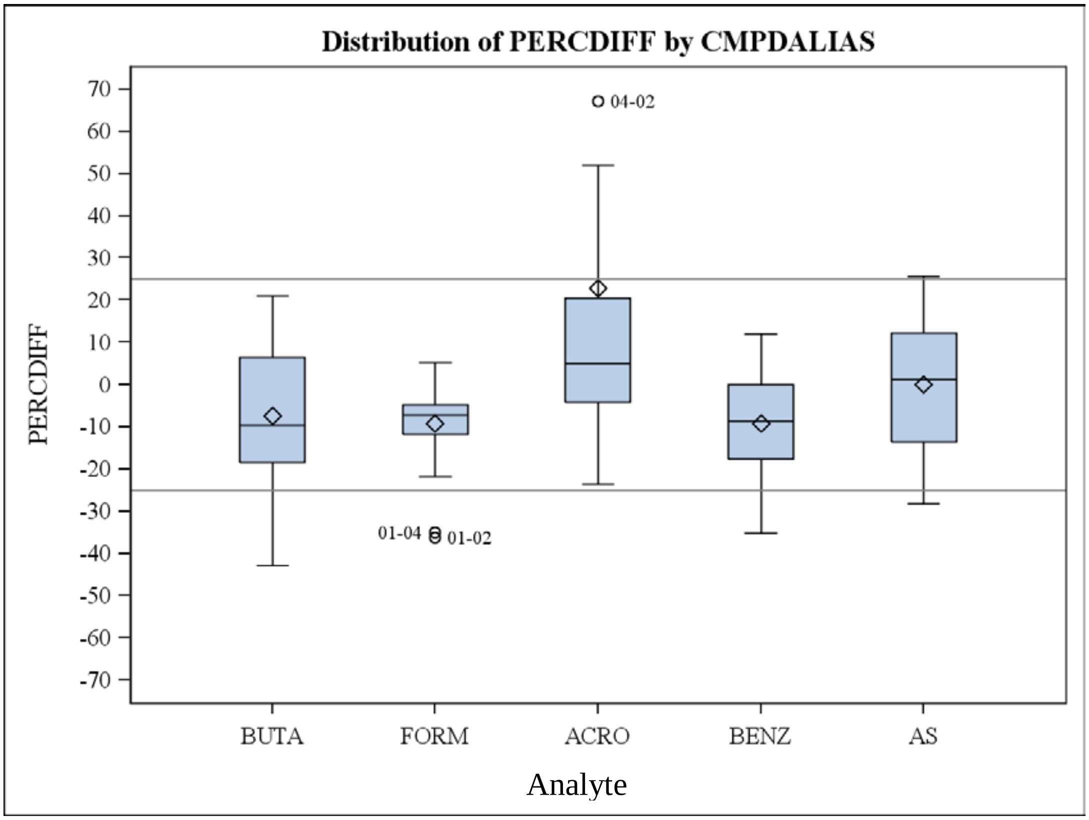


Figure 22. Distribution of Laboratory Bias by Analyte for Proficiency Testing Data from 200 .

Participation in the laboratory PT program during 200 by all NATTS-affiliated laboratories is shown in Table 14. All participating laboratories completed the PT sample analyses.

Table 14. Proficiency Testing Program Participation for 2009.

Compound Class	Percentage Participation
Carbonyls	100
Metals	100
VOCs	100

2.5 Flow Audit Results from Instrument Performance Audits

Six NATTS field sites (Dearborn, MI; Deer Park, TX; Harrison County, TX; Mayville, WI; Northbrook, IL; St. Louis MO) were audited during calendar year 200 for canister, carbonyl, PM_{10}, chromium (VI), and PAH samplers. The IPA 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 EC 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 percentage difference between the corrected site flow (Fs_c) and the corrected audit flow (Fa_c):

$$\%Difference = \frac{Fs_C - Fa_C}{Fa_C} \cdot 100 \qquad \text{(Eq. 4)}$$

The results from the flow audits conducted at six sites during calendar year 2009, 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, with no audits performed on canister samplers. If present during the audit, collocated samplers were also audited. Because canister and carbonyl samplers may have multiple flow channels to facilitate duplicate sampling, all active channels were also subjected to a flow audit. PM_{10} samplers have only primary channels.

Table 15. Flow Audit Results from 2009 Instrument Performance Audits.

Site Identifier	Method	Sampler	Channel	Measurements	Percentage Difference
Dearborn, MI	Canister[a]	Primary	NA	Not performed[c]	
	Carbonyl[b]	Primary	1	Site: 0.7412 L/min (actual) Audit[d]: 0.7488 L/min (actual)	−1.0
	Carbonyl	Duplicate/Collocated	2	Site: 0.7500 L/min (actual) Audit: 0.7635 L/min (actual)	-1.8
	PM_{10}[e]	Primary	NA	Site: 41.66 ft^3/min (STP) Audit: 40.63 ft^3/min (STP)	2.5
	PM_{10}[e]	Duplicate/Collocated	NA	Site: 40.71 ft^3/min (STP) Audit: 39.23 ft^3/min (STP)	3.8
	Cr(VI)	Primary	NA	Site: 14.4 L/min (actual) Audit: 13.58 L/min (actual)	6.0
	Cr(VI)	Duplicate/Collocated	NA	Site: 14.7 L/min (actual) Audit: 13.8 L/min (actual)	6.6
	PAH	Primary	NA	Site: 6.91 ft^3/min (STP) Audit: 7.25 ft^3/min (STP)	-4.7
	PAH	Duplicate/Collocated	NA	Site: 7.30 ft^3/min (STP) Audit: 7.32 ft^3/min (STP)	−0.3
Deer Park, TX	Canister[a]	Primary	NA	Not performed	
	Carbonyl[b]	Primary	1	Site: 1.125 L/min (actual) Audit: 1.09 L/min (actual)	3.2
	Carbonyl	Duplicate/Collocated	2	Site: 1.134 L/min (actual) Audit: 1.08 L/min (actual)	5.0
	PM_{10}[e]	Primary	NA	Site: 40.29 ft^3/min (STP) Audit: 40.29 ft^3/min (STP)	0.0
	PM_{10}	Duplicate/Collocated	NA	Site: 40.29 ft^3/min (STP) Audit: 40.41 ft^3/min (STP)	-0.3

(continued)

Table 15. Flow Audit Results from 2009 Instrument Performance Audits (continued).

Site Identifier	Method	Sampler	Channel	Measurements	Percentage Difference
Deer Park, TX (continued)	Cr(VI)	Primary	NA	Site: 11.51 L/min (actual) Audit: 11.58 L/min (actual)	-0.6
	Cr(VI)	Duplicate/Collocated	NA	Site: 11.51 L/min (actual) Audit: 11.58 L/min (actual)	-0.6
	PAH	Primary	NA	Site: 9.83 ft^3/min (STP) Audit: 9.84 ft^3/min (STP)	-0.1
	PAH	Duplicate/Collocated	NA	Site: 8.3 ft^3/min (STP) Audit: 8.4 ft^3/min (STP)	-1.2
Harrison County, TX	Canister[a]	Primary	NA	Not performed	
	Carbonyl[b]	Primary	1	Site: 1.099 L/min (actual) AuditI: 1.109 L/min (actual)	-0.9
	Carbonyl	Duplicate/Collocated	2	Site: 1.107 L/min (actual) Audit: 1.112 L/min (actual)	-0.4
	PM_{10}[e]	Primary	NA	Site: 39.98 ft^3/min (STP) Audit: 39.96 ft^3/min (STP)	0.1
	Cr(VI)	Primary	NA	Site: 11.86 L/min (actual) Audit: 12.13 L/min (actual)	-2.2
	PAH	Primary	NA	Site: 8.57 ft^3/min (STP) Audit: 8.49 ft^3/min (STP)	0.9
Mayville, WI	Canister[a]	Primary	NA	Not performed	
	Carbonyl[b]	Primary	1	Site: 0.6997 L/min (actual) Audit: 0.7356 L/min (actual)	-4.9
	Carbonyl	Duplicate/Collocated	2	Site: 0.7 L/min (actual) Audit: 0.7196 L/min (actual)	-2.7
	PM_{10}[e]	Primary	NA	Site: 32.96 ft^3/min (STP) Audit: 32.16 ft^3/min (STP)	2.5
	PM_{10}[e]	Duplicate/Collocated	NA	Site: 32.96 ft^3/min (STP) Audit: 32.59 ft^3/min (STP)	1.1
	Cr(VI)	Primary	NA	Site: 14.7 L/min (actual) Audit: 15.15 L/min (actual)	-3.0
	Cr(VI)	Duplicate/Collocated	NA	Site: 14.7 L/min (actual) Audit: 15.01 L/min (actual)	-2.1
	PAH	Primary	NA	Site: 6.36 ft^3/min (STP) Audit: 6.52 ft^3/min (STP)	-2.5
	PAH	Duplicate/Collocated	NA	Site: 6.61 ft^3/min (STP) Audit: 6.61 ft^3/min (STP)	0.0
Northbrook, IL	Canister[a]	Primary	NA	Not performed	
	Carbonyl[b]	Primary	1	Site: 1.18 L/min (actual) Audit: 1.21 L/min (actual)	-2.5
	PM_{10}[e]	Primary	NA	Site: 41.7 ft^3/min (STP) Audit: 42.8 ft^3/min (STP)	-2.6
	Cr(VI)	Primary	NA	Site: 14.4 L/min (actual) Audit: 13.86 L/min (actual)	3.9
	Cr(VI)	Duplicate/Collocated	NA	Site: 15.1 L/min (actual) Audit: 14.76 L/min (actual)	2.3
	PAH	Primary	NA	Site: 8.08 ft^3/min (STP) Audit: 8.23 ft^3/min (STP)	-1.8

(continued)

Table 15. Flow Audit Results from 2009 Instrument Performance Audits (continued).

Site Identifier	Method	Sampler	Channel	Measurements	Percentage Difference
St. Louis, MO	Canister[a]	Primary	NA	Not performed	
	Carbonyl[b]	Primary	1	Site: 0.7493 L/min (actual) Audit:0.771 L/min (actual)	-2.8
	Carbonyl[b]	Collocated/Duplicate	1	Site: 0.8897 L/min (actual) Audit:0.9222 L/min (actual)	-3.5
	PM_{10}[e]	Primary	NA	Site: 41.32 ft^3/min (STP) Audit: 39.71 ft^3/min (STP)	4.1
	Cr(VI)	Primary	NA	Site: 14.26 L/min (actual) Audit: 14.31 L/min (actual)	-0.3
	Cr(VI)	Duplicate/Collocated	NA	Site: 14.72 L/min (actual) Audit: 14.46 L/min (actual)	1.8
	PAH	Primary	NA	Site: 7.77 ft^3/min (STP) Audit: 7.78 ft^3/min (STP)	-0.1

[a] VOC sampler.
[b] Carbonyl cartridge.
[d] Performed by RTI International.
[d]Audit not performed for this sampler type.
[e] Filter sample for PM_{10} metals.

A graphical summary of the flow audit results is presented in Figure 23. All flow rate measurements were within ±10% of the audit flow rate; most were within 5%.

Accuracy of flow rates for carbonyl and PM_{10} samplers is critical for determining sample concentration. Conversely, because 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 Data

During compilation of 2007 QA data, substantial effort was invested in acquiring the MDL data through direct contacts with each contributing laboratory. For the 2008 and 2009 results, the AQS database, specifically the ALT_MDL variable in the RD record types, served as the primary source of laboratory-based MDL data. Although this is not a required field in AQS, approximately 85% of the MDL data were acquired from this source. Because AQS allows the posting of MDL data in a variety of units, even within chemical classes, all AQS-acquired MDLs were standardized to ng/m^3 for metals, PAHs, and chromium (VI) and μg/m^3 for carbonyls and VOCs. The balance of the MDLs (i.e., those values not posted to AQS) was requested from direct contact with each laboratory known to be providing analytical services. Multiple e-mail requests with some laboratory contacts were needed to obtain the full complement of MDL data. 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.

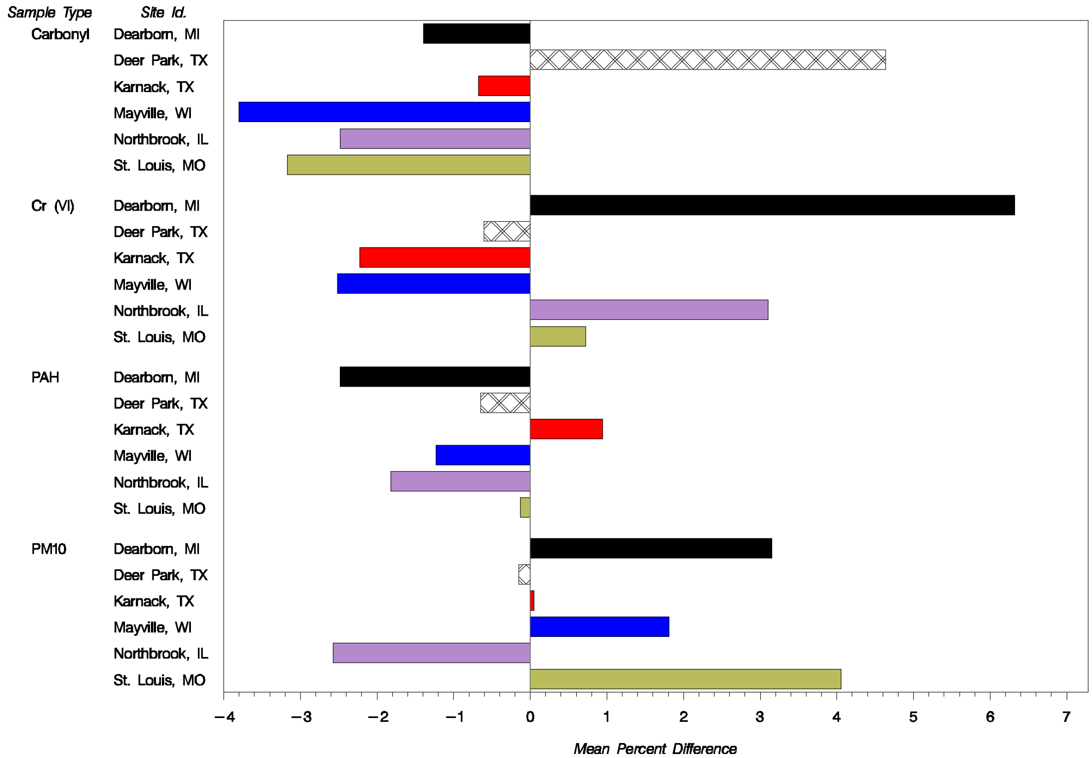


Figure 23. Summary of Instrument Performance Flow Audit Results for 2009.

For this report and by generally accepted conventions, MDLs 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. Thus, they reflect, among other factors, the collected sample volume for each sample, the size of the subsample subjected to analysis, and any sample dilutions that may be associated with the analysis methodology. Using the AQS database as the primary source of the MDL information does not, in and of itself, ensure consistency of the data, but consistency of the data derived largely from posted information is considered vastly improved over the same data obtained through individual laboratory requests. There is, however, no unequivocal way to discern from the existing data if the MDLs provided reflect the MDL (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 mean values computed from either individual AQS-posted values or directly from laboratory contacts and are presented under the assumption that each laboratory reported actual method detection limits that incorporated both instrumental and sampling considerations. In cases where the data were acquired by direct laboratory contact and unit conversions were needed, the data were converted to the same units specified above. The MDL data for individual sites, in addition to the mean across all sites reporting data, are shown in Table 16. Because ERG serves as the analytical laboratory for numerous NATTS sites (Table 7) for VOCs, carbonyls, metals, and particularly for chromium (VI) and PAHs, the method detection limits shown in Table 16 and in Figures 24 - 28 reflect a consistency in instrumental detection limits associated with an analytical laboratory common to multiple sites.

Box and whisker plots and complementary scatter plots, shown in Figures 24 through 28, illustrate the MDLs for carbonyls, metals, arsenic, VOCs, and PAHs, respectively. The MQOs for benzene, 1,3-butadiene, formaldehyde, and arsenic are added to each plot for reference. Labs whose results fell outside of a window defined by 1.5 × IQR are identified by blue asterisks on

Table 16. Method Detection Limits by Site and Overall for Calendar Year 2009 (VOCs and Carbonyls: µg/m^3; Metals: ng/m^3).

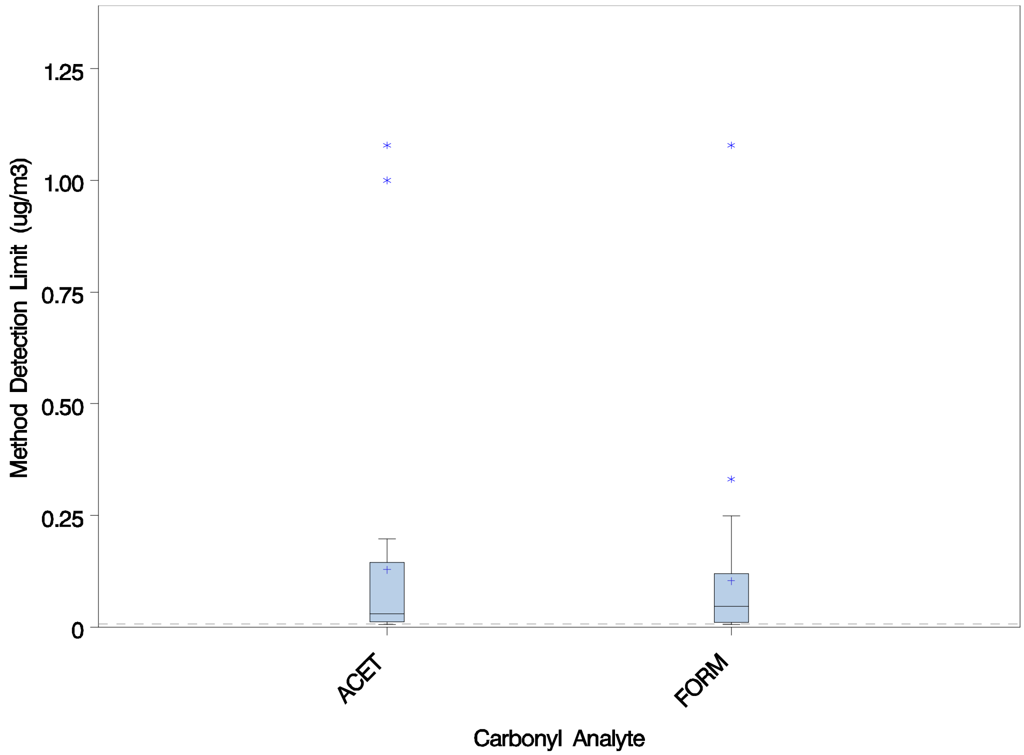
Site Name	AQS Site Code	BENZ	BUTA	CTET	CLFRM	EDB	DCP	EDC	MECL	TCE_1122	PERC	TCE	VCM	c_DCPEN	t_DCPEN
Phoenix, AZ	04-013-9997	0.125	0.122	0.014	0.011	0.008	0.015	0.009	0.03	0.023	0.022	0.012	0.006	0.015	0.015
Los Angeles, CA	06-037-1103	—[b]	0.176	0.63	0.355	0.77	0.463	0.406	0.348	—[b]	0.469	0.39	0.256	0.455	0.455
Rubidoux, CA	06-065-8001	—[b]	0.172	0.63	0.344	0.77	0.463	0.406	0.348	—[b]	0.452	0.378	0.256	0.455	0.455
San Jose, CA	06-085-0005	0.112	0.113	0.063	0.068	0.077	.	0.406	0.348	—[b]	0.047	0.074	0.256	0.455	0.455
Grand Junction, CO	08-077-0017	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]
Grand Junction, CO	08-077-0018	0.021	0.007	0.013	0.01	0.008	0.014	0.008	0.028	0.021	0.02	0.011	0.005	0.014	0.014
Washington, DC	11-001-0043	0.059	0.055	0.157	0.122	0.23	0.138	0.121	0.121	0.239	0.203	0.134	0.076	0.067	0.113
Hillsborough County, FL	12-057-3002	0.064	0.053	0.139	0.083	0.123	0.083	0.061	0.084	0.089	0.122	0.108	0.051	0.068	0.073
Pinellas County, FL	12-103-0026	0.064	0.053	0.139	0.083	0.123	0.083	0.061	0.084	0.089	0.122	0.108	0.051	0.068	0.073
Decatur, GA	13-089-0002	0.119	0.074	0.053	0.097	0.142	0.16	0.113	6.959	0.169	0.149	0.231	0.052	0.116	0.11
Northbrook, IL	17-031-4201	0.125	0.122	0.013	0.01	0.008	0.014	0.008	0.028	0.021	0.02	0.011	0.005	0.014	0.014
Grayson Lake, KY	21-043-0500	0.128	0.2	0.189	0.098	0.231	0.185	0.284	0.07	0.275	0.204	0.108	0.256	0.182	0.227
Boston, MA	25-025-0042	0.022	0.014	0.055	0.037	0.087	0.034	0.043	0.047	0.235	0.059	0.044	0.022	0.029	0.022
Dearborn, MI	26-163-0033	0.021	0.007	0.013	0.01	0.008	0.014	0.008	0.028	0.021	0.02	0.011	0.005	0.014	0.014
St. Louis, MO	29-510-0085	0.021	0.007	0.013	0.01	0.008	0.014	0.008	0.028	0.021	0.02	0.011	0.005	0.014	0.014
Bronx, NY	36-005-0110	0.032	0.044	0.063	0.049	0.077	0.093	0.041	0.035	0.069	0.068	0.054	0.026	0.045	0.045
Rochester, NY	36-055-1007	0.032	0.044	0.063	0.049	0.077	0.093	0.041	0.035	0.069	0.068	0.054	0.026	0.045	0.045
Portland, OR	41-051-0246	0.143	0.222	0.315	0.245	—[b]	0.232	—[b]	0.261	—[b]	0.34	0.269	0.154	—[b]	—[b]
La Grande, OR	41-061-0119	0.143	0.222	0.315	0.245	—[b]	0.232	—[b]	0.261	—[b]	0.34	0.269	0.154	—[b]	—[b]
Providence, RI	44-007-0022	0.024	0.014	0.055	0.037	0.087	0.034	0.043	0.047	0.235	0.059	0.044	0.022	0.029	0.022
Chesterfield, SC	45-025-0001	0.576	0.532	1.072	0.44	1.925	0.741	2.434	0.626	0.895	1.155	0.969	0.41	0.455	0.546
Deer Park, TX	48-201-1039	0.864	0.599	1.702	1.028	1.54	0.787	1.095	0.487	1.376	1.631	1.562	0.435	0.91	0.91
Harrison County, TX	48-203-0002	0.864	0.599	1.702	1.028	1.54	0.787	1.095	0.487	1.376	1.631	1.562	0.435	0.91	0.91
Bountiful, UT	49-011-0004	0.125	0.122	0.013	0.01	0.008	0.014	0.008	0.028	0.021	0.02	0.011	0.005	0.014	0.014
Underhill, VT	50-007-0007	0.019	0.02	0.027	0.021	0.049	0.018	0.017	0.034	0.085	0.028	0.02	0.015	0.02	0.026
Richmond, VA	51-087-0014	0.193	0.069	0.195	0.176	0.416	0.144	0.089	0.153	0.275	0.231	0.14	0.087	0.209	0.136
Seattle, WA	53-033-0080	0.021	0.007	0.013	0.01	0.008	0.014	0.008	0.028	0.021	0.02	0.011	0.005	0.014	0.014
Mayville, WI	55-027-0007	0.357	0.222	0.63	0.489	0.77	0.463	0.406	0.348	0.688	0.68	0.539	0.256	0.455	0.455
Geometric Mean		0.089	0.071	0.104	0.076	0.103	0.091	0.075	0.114	0.121	0.122	0.091	0.049	0.08	0.081
Arithmetic Mean		0.179	0.147	0.318	0.202	0.379	0.215	0.293	0.419	0.304	0.317	0.274	0.128	0.212	0.217
Standard Deviation		0.24	0.169	0.473	0.279	0.546	0.252	0.531	1.294	0.415	0.456	0.425	0.143	0.271	0.274
Median		0.116	0.093	0.101	0.083	0.105	0.093	0.061	0.084	0.089	0.122	0.108	0.051	0.068	0.073

(continued)

Table 16. Method Detection Limits by Site and Overall for Calendar Year 2009 (VOCs and Carbonyls: µg/m^3; Metals: ng/m^3) (additional analytes) (continued).

Site Name	AQS Site Code	ACRY	ACRO	FORM	ACET	NAPH	BaP	AS	BE	CD	PB	MN	NI	CRVI
Phoenix, AZ	04-013-9997	0.036	0.038	0.046	0.042	0.384	0.092	0.014	0.03	0.226	0.07	0.231	1.066	0.004
Los Angeles, CA	06-037-1103	0.653	0.388	—[b]	—[b]	0.378	0.093	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]
Rubidoux, CA	06-065-8001	0.653	0.401	0.123	0.181	0.28	0.069	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]
San Jose, CA	06-085-0005	0.324	0.426	0.123	0.181	0.337	0.082	0.024	0.002	0.046	0.438	0.378	0.658	—[b]
Grand Junction, CO	08-077-0017	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	1.583	0.205	0.179	1.112	0.392	0.45	0.004
Grand Junction, CO	08-077-0018	0.033	0.034	0.01	0.009	0.408	0.099	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]	—[b]
Washington, DC	11-001-0043	0.054	—[b]	0.026	0.029	0.383	0.093	1.18	0.18	0.31	0.84	0.19	0.78	0.005
Hillsborough County, FL	12-057-3002	0.061	0.143	0.011	0.01	0.336	0.081	0.46	0.2	0.15	1.04	0.14	0.92	0.005
Pinellas County, FL	12-103-0026	0.061	0.143	0.01	0.009	0.294	0.072	0.46	0.2	0.15	1.04	0.14	0.92	0.005
Decatur, GA	13-089-0002	—[b]	0.052	1.079	1.079	0.332	0.081	0.268	0.018	0.009	0.027	0.036	0.059	0.005
Northbrook, IL	17-031-4201	0.033	0.034	0.006	0.005	0.278	0.067	0.009	0.002	0.029	0.056	0.057	0.132	0.005
Grayson Lake, KY	21-043-0500	—[b]	0.391	0.008	0.022	0.277	0.067	0.413	0.253	0.243	0.247	0.414	0.578	0.4
Boston, MA	25-025-0042	—[b]	0.116	0.08	0.108	0.258	0.062	0.009	0.002	0.029	0.056	0.057	0.138	0.005
Dearborn, MI	26-163-0033	0.033	0.034	0.009	0.009	0.324	0.079	0.173	0.244	0.166	0.22	0.412	0.16	0.005
St. Louis, MO	29-510-0085	0.033	0.034	0.01	0.009	0.27	0.067	0.016	0.002	0.037	0.816	0.108	0.517	0.005
Bronx, NY	36-005-0110	—[b]	0.069	0.012	0.018	0.302	0.075	0.521	0.521	0.26	0.26	0.521	0.521	0.005
Rochester, NY	36-055-1007	—[b]	0.069	0.012	0.018	0.231	0.056	0.521	0.521	0.26	0.26	0.521	0.521	0.005
Portland, OR	41-051-0246	—[b]	—[b]	0.118	0.03	1.206	0.251	0.033	0.003	0.033	0.334	0.334	0.334	0.033
La Grande, OR	41-061-0119	—[b]	—[b]	0.122	0.03	1.801	0.255	0.037	0.004	0.037	0.367	0.367	0.367	0.036
Providence, RI	44-007-0022	0.265	0.116	0.046	0.027	0.381	0.094	0.057	0.014	0.016	0.024	0.026	0.017	0.005
Chesterfield, SC	45-025-0001	—[b]	1.953	0.249	0.197	0.347	0.085	0.031	0.001	0.001	0.003	0.002	0.003	0.005
Deer Park, TX	48-201-1039	—[b]	0.23	0.098	0.145	0.341	0.083	0.015	0.18	0.098	1.3	0.57	2.3	0.012
Harrison County, TX	48-203-0002	—[b]	0.23	0.098	0.145	—[b]	—[b]	0.015	0.18	0.098	1.3	0.57	2.3	0.012
Bountiful, UT	49-011-0004	0.033	0.034	0.009	0.008	0.431	0.105	0.031	0.045	0.19	0.098	0.205	0.835	0.004
Underhill, VT	50-007-0007	0.037	0.04	0.014	0.017	0.33	0.081	0.011	0.001	0.066	0.591	0.258	1.223	0.005
Richmond, VA	51-087-0014	0.089	0.179	0.055	0.043	0.379	0.092	0.037	0.011	0.007	0.032	0.042	0.312	0.005
Seattle, WA	53-033-0080	0.033	0.034	0.014	0.013	0.276	0.067	0.01	0.003	0.027	0.062	0.073	0.138	0.005
Mayville, WI	55-027-0007	—[b]	0.23	0.331	1	0.283	0.069	0.028	0.01	0.011	0.004	0.015	0.093	0.005
Geometric Mean		0.075	0.116	0.04	0.042	0.358	0.085	0.062	0.023	0.053	0.159	0.138	0.304	0.007
Arithmetic Mean		0.152	0.226	0.115	0.162	0.412	0.092	0.23	0.109	0.104	0.409	0.237	0.594	0.023
Standard Deviation		0.214	0.383	0.217	0.317	0.329	0.048	0.388	0.152	0.097	0.441	0.189	0.609	0.079
Median		0.046	0.116	0.046	0.029	0.332	0.081	0.032	0.016	0.056	0.254	0.197	0.484	0.005

[a] Meets MQO.
[b] Not reported.



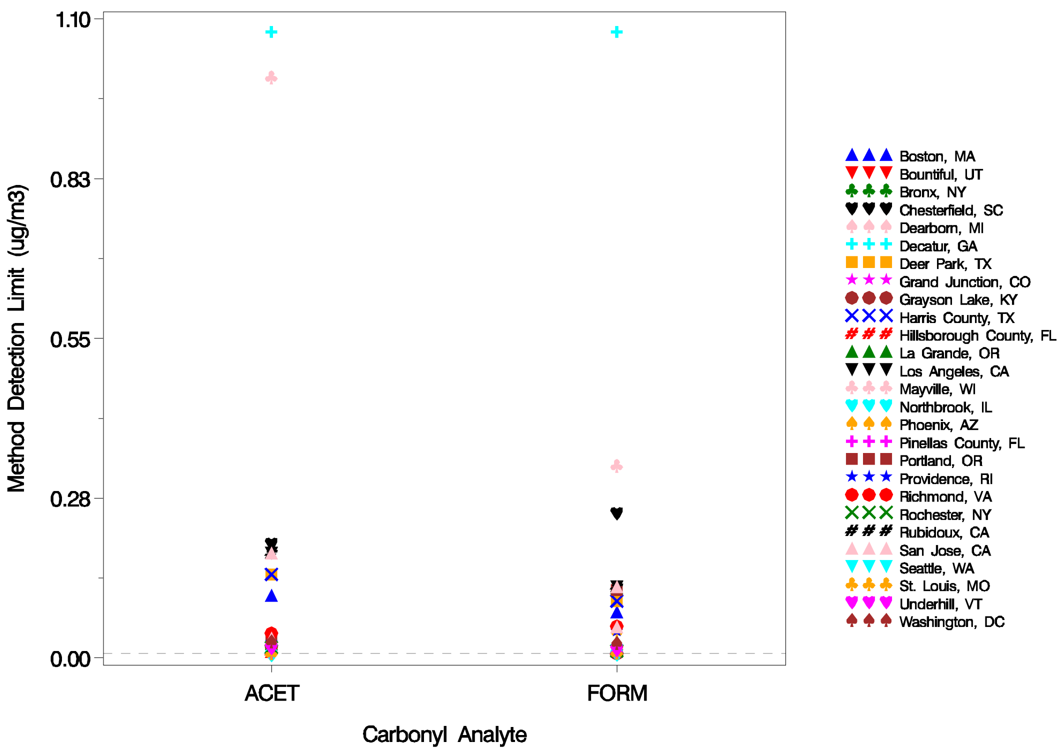


Figure 24. Distribution of Method Detection Limits for Carbonyls for 2009 NATTS Data (dashed line indicates MQO target MDL for formaldehyde; > 1.5 × IQR are identified as blue stars in top display).

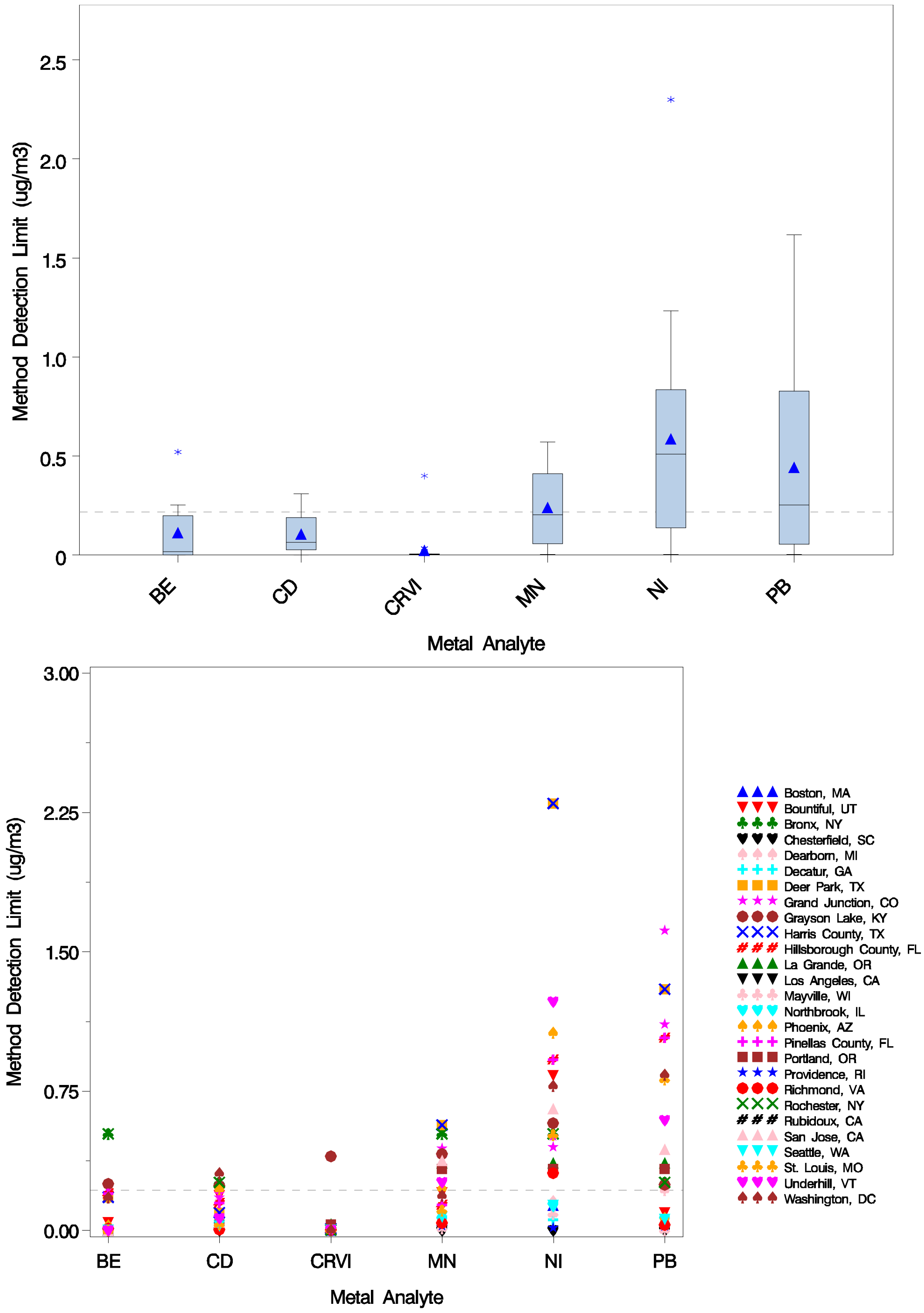


Figure 25. Distribution of Method Detection Limits for Metals for 2009 NATTS Data (dashed line indicates MQO target MDL for arsenic; > 1.5 × IQR are identified as blue stars in top display).

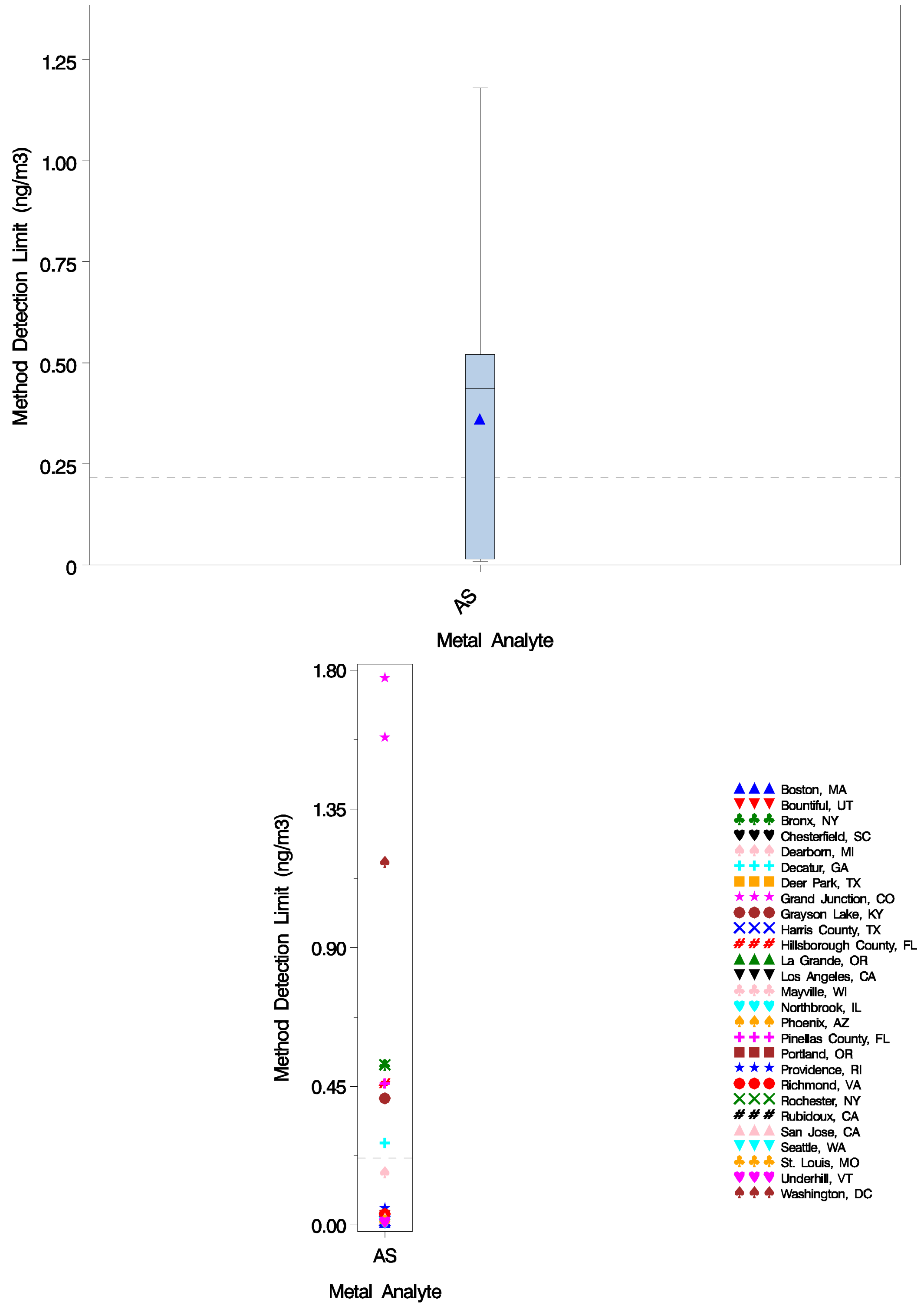


Figure 26. Distribution of Method Detection Limits for Arsenic for 2009 NATTS Data (dashed line indicates MQO target MDL for arsenic.

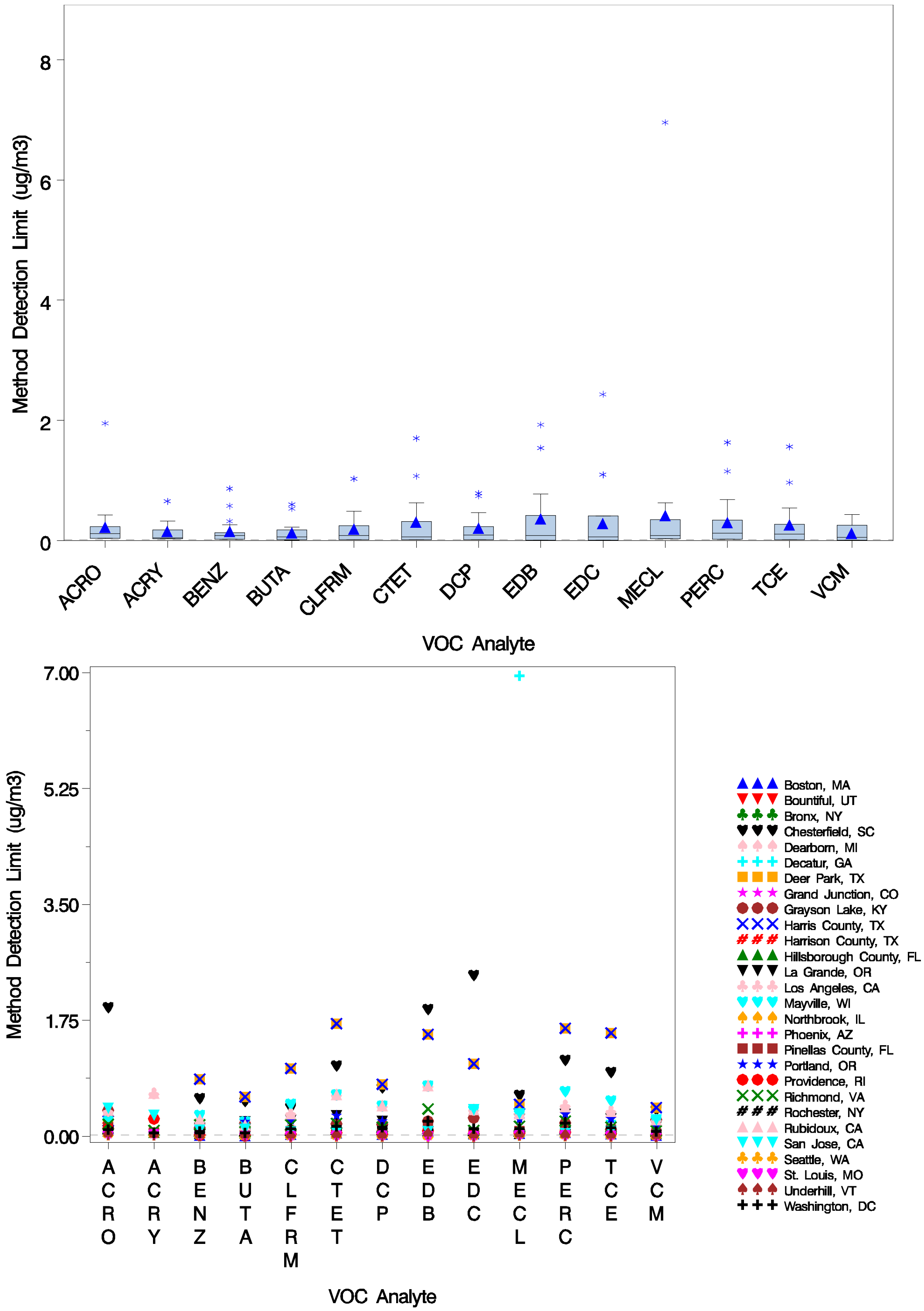


Figure 27. Distribution of Method Detection Limits for VOCs for 2009 NATTS Data (dashed line indicates MQO target MDL for benzene; > 1.5 × IQR are identified as blue stars in top display).

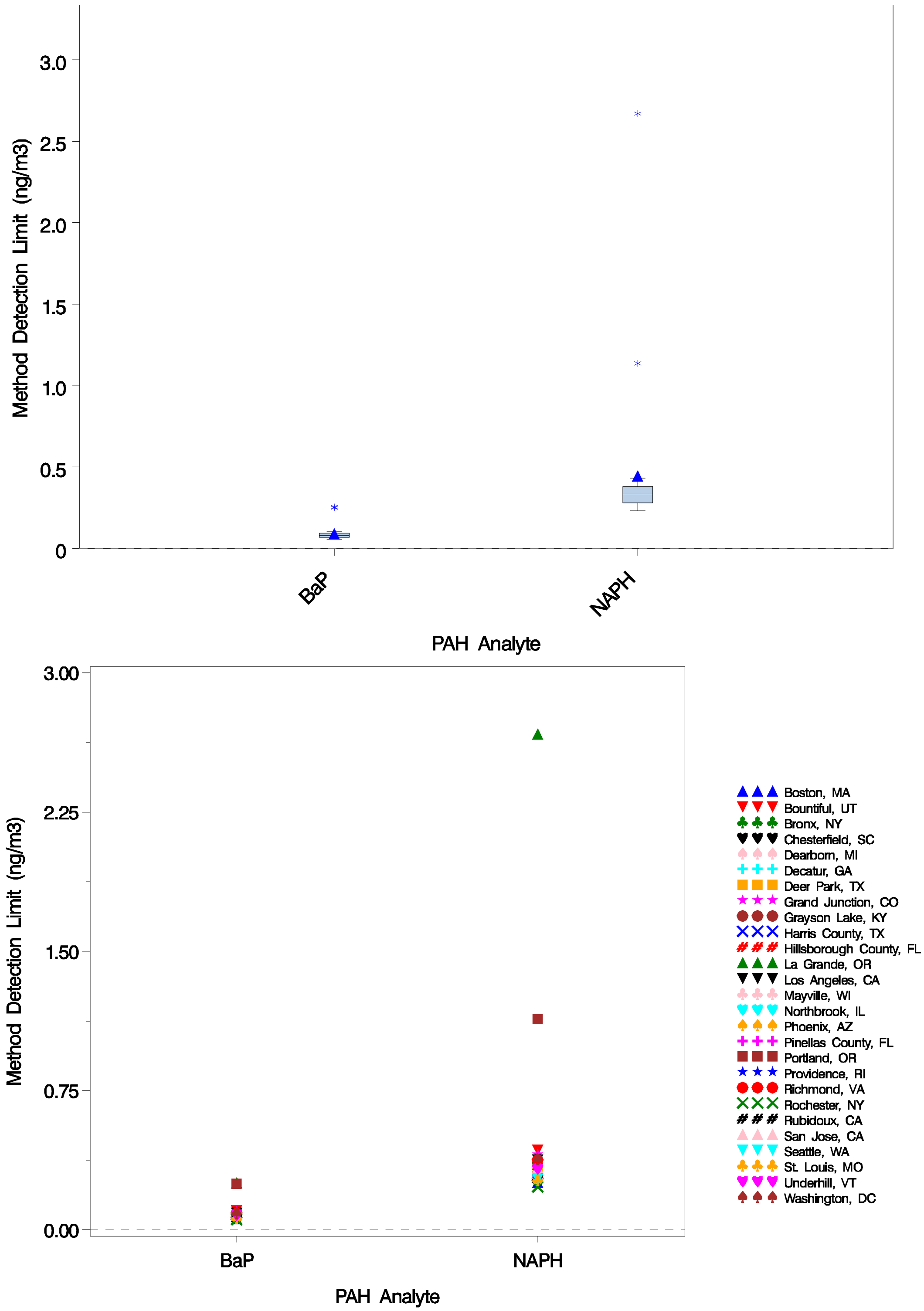


Figure 28. Distribution of Method Detection Limits for PAHs for 2009 NATTS Data.

the graphical display. The IQR is defined as the distance between the 25^{th} and 75^{th} percentiles of the distribution of values.

Review of the graphically displayed MDL results reveals a number of interesting features largely consistent with previous reporting years. MDLs for carbonyls (Figure 24) show appreciable spread across laboratories but almost universally greater than the MQO. The proximity of the mean MDL to the bottom of the distribution reflects the MDLs for many laboratories close to, albeit above, the MQO; values for two laboratories are significantly higher, particularly for acetaldehyde. Metals results in Figures 25 and 26 show MDL values falling within the MQO for some analytes, notably Be, Cd, and chromium (VI), but substantially above for others (Mn, Ni, Pb), with relatively few values outside the IQR. Arsenic performance was well within the MQOs for some laboratories but substantially outside for others. The consistency and magnitude of MDLs reported for chromium (VI) is particularly noteworthy and may reflect the fact that only three laboratories are performing this analysis for all NATTS sites. VOCs show much greater variability in MDLs across laboratories than other analyte groups, with a few sites accounting for most of the spread in the distribution (Figure 27). As was found for most analytes, a high proportion of MDLs for VOCs occurred above the MQO. Lastly, MDLs for PAHs, while universally above the MQO, tended to be clustered for both benzo[a]pyrene and naphthalene, again reflecting that the analysis was performed by only three labs (Figure 28).

As reported by the metals analysis laboratories for 2008, 19 NATTS sites (San Jose, CA; Washington, DC; Boston-Roxbury, MA; Decatur, GA; Hillsborough County, FL; Pinellas County, FL; Dearborn, MI; Mayville, WI; Northbrook, IL; Harrison County, TX; St. Louis, MO; La Grande, OR; Portland, OR; Seattle, WA; Providence, RI; Chesterfield, SC; Deer Park, TX; Underhill, VT; Richmond, VA) collected high-volume PM_{10} metals on 8 in. x 10 in. quartz fiber filters. Seven sites reported using low-volume PM_{10} metals sampling on 47 mm Teflon filters (Bronx, NY; Rochester, NY; Bountiful, UT; Grand Junction, CO; Phoenix, AZ; Hazard, KY; Grayson Lake, KY). The remaining sites either did not collect PM_{10} samples for metals analysis or did not report the type of sampling implemented.

Comparison of MDLs for the two sampling approaches is meaningful only when the analysis laboratory is the same for the two sites; otherwise the variability in MDLs is an aggregate effect of sample collection and sample analysis. The metals results provided by the ERG laboratory, which analyzes samples of both types, offer a unique opportunity to examine MDLs between high- and low-volume sampling without the influence of cross-laboratory instrumental detection limit variability. Table 17 shows the MDLs for each of the PM_{10} metal analytes. The enhanced MDLs for the higher volume samples are consistent with the 100-fold increase in sample size over the lower volume samples. At the direction of EPA, the computation of the MDLs by the laboratories for quartz sampling media was changed, allowing for adjustment of the significantly higher background levels for this collection medium. Overall, variability in MDLs among laboratories, shown in Table 18, is very large and suggests significant differences in analytical performance as well as collection volumes.

Table 17. Comparison of Method Detection Limits Reported by ERG Laboratory for Metals between High- and Low-Volume Samplers in Calendar Year 2009.

Analyte	Method Detection Limits (ng/m³) Median (Std. Dev.) 2000 m³ Samples[a]	20 m³ Samples[b]	MDL Ratio (High/Low)
Arsenic	0.0090 (0.0239)	0.0200 (0.0169)	0.45
Beryllium	0.0020 (0.0014)	0.0300 (0.0259)	0.067
Cadmium	0.0290 (0.0185)	0.2300 (0.0713)	0.13
Chromium (VI)	0.0046 (0.0008)	0.0043 (0.0006)	1.07
	0.0170 (0.0170)	1.1600 (0.0381)	0.015
Manganese	0.0570 (0.2795)	0.2400 (0.0630)	0.24
Nickel	0.1320 (0.6573)	1.0300 (0.4958)	0.13
Lead	0.0560 (0.7785)	0.0700 (0.0677)	0.80

[a] Based on six sites conducting high-volume PM_{10} sampling.
[b] Based on two sites conducting low-volume PM_{10} sampling.

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

Table 18. Summary Statistics for Method Detection Limits across All Reporting NATTS Laboratories for 2009.

MDL	Selected Analyte: Benzene, (µg/m³)	1,3-butadiene, (µg/m³)	Formaldehyde, (µg/m³)	Arsenic, (ng/m³)
Geometric Mean	0.063	0.0369	0.0402	0.0639
Arithmetic Mean	0.103	0.0773	0.1132	0.5119
Standard Deviation	0.102	0.0786	0.2377	1.1656
Minimum	0.010	0.0067	0.0049	0.0090
Median	0.071	0.0532	0.0400	0.0340
Maximum	0.357	0.2217	1.0800	5.3311
MQO	0.016	0.013	0.0074	0.217
Ratio of Geo. Mean to MQO	3.9	2.8	5.4	0.3

3.0 SUMMARY

Based on four HAPs representative of the various chemical classes—benzene, 1,3-butadiene, formaldehyde, and arsenic, the following summary comments are appropriate for the 2009 NATTS data.

1. Excluding NATTS sites intentionally not collecting data for a particular analyte class (e.g., PM_{10} metals), the mean completeness percentages of data reported into AQS across all NATTS sites were 97%, 98%, 98%, 98%, 99%, 99%, and 98% for benzene, 1,3-butadiene, acrolein, naphthalene, formaldehyde, chromium (VI), and arsenic, respectively. Completeness statistics reported in 2009 for naphthalene and chromium (VI) were dramatically improved over those reported in 2008, exceeding the MQO for nearly every site. Overall, the MQO was achieved for all seven analytes.
2. With a few exceptions as noted in the text of this report, analytical precision among sites for which replicate analyses were available was found to be below the 15% MQO threshold for all analytes used to reflect their respective chemical classes. Analytical precision for acrolein was somewhat more variable than other analytes but still within the 15% threshold. As expected, the frequency of cases where the MQO threshold was exceeded was distinctly greater for overall precision (i.e., including sampling and analysis) among all analytes and particularly for acrolein, an analyte presenting unique collection and analysis challenges. Estimates of overall precision included both duplicate and collocated samples.
3. Laboratory performance, as assessed by the percentage difference between the laboratory measurement and the certified sample concentration of the proficiency testing samples, was within the ±25% MQO for most analytes (i.e., benzene, 1,3-butadiene, formaldehyde, and arsenic) and for laboratories with available data from 2009. The poorest performance across all laboratories and analytes was observed for lead (37.6%) and acrolein (30.3%). The proportion of laboratories participating in the 2009 performance testing program was 100% for all chemical classes—a significant improvement over participation in 2008. Laboratories not performing analyses of a particular analyte were excluded from these statistics.
4. Without exception, sampler flows measured during IPAs conducted at NATTS field sites showed less than ±10% difference from their site-recorded values.
5. Among all measures of data quality, MDLs were substantially greater than the corresponding MQOs and showed substantial variability for any given analyte across sites (i.e., laboratories). Only the mean value for arsenic fell within the MQO threshold when all laboratories were considered together. The ratios of the cross-network geometric means to the corresponding MQOs were 3.9, 2.8, 5.4, and 0.3 for benzene, 1,3-butadiene, formaldehyde, and arsenic, respectively.

4.0 RECOMMENDATIONS

The information, both analytical results and site characteristics, for the NATTS network samples present in the AQS database was acquired successfully, based on a thorough understanding of the database structure. Based on knowledge of POC assignments in previous years, the POCs for the primary, duplicate, and collocated samples were assigned with greater facility than in previous years. However, as in previous years, acquiring MDL data for laboratories not posting MDLs to AQS directly was still problematic.

The POCs are present in the AQS database, but the associated sample type information (e.g., primary, duplicate, or collocated) is not. Because POCs are assigned by either the agency monitoring a particular NATTS site or the laboratory uploading the data to AQS, and are largely nonstandardized across NATTS sites [5, 6] (see Table 6), 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 and would greatly streamline the analyses reported here.

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 as deemed appropriate by EPA.

The acquisition and assembly of MDL information was again aided dramatically through the extraction of the ALT_MDL field for RD records in the AQS database. Only instances where this optional field was not populated by the contributing laboratory (~15%) required direct contacts with individual laboratory supervisors. Changing the character of this AQS field to "required" would completely eliminate the need for this follow-up step. Lastly, AQS accepts data in a variety of units at the discretion of the agency performing the upload. This requires very careful scrutiny of the UNIT variable so that MDL measurements can be standardized algebraically prior to data analysis. Standardization of MDLs posted in the ambiguous "ppbC" unit is particularly problematic.

5.0 REFERENCES

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