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Final Report

on

**NATTS QUALITY ASSURANCE ANNUAL REPORT
FOR CALENDAR YEAR 2004**

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for

**Vickie Presnell
Project Officer**

**Candace Sorrell
Work Assignment Manager**

**Emissions, Monitoring, and Analysis Division
Office of Air Quality Planning and Standards
U.S. ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina 27711**

Prepared by

Ian C. MacGregor and Laura L. Aume

**BATTELLE
505 King Avenue
Columbus, Ohio 43201-2693**

DISCLAIMER

This is the final report on the quality assurance information provided to the U.S. Environmental Protection Agency for the National Air Toxics Trends Stations (NATTS). The final technical report was sent to the agencies that support the NATTS network. Comments were received on that technical report from the contractor throughout October 2005 and these comments have been incorporated in this final version of this document.

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on
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1.0 INTRODUCTION

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

To meet the GPRA goals, the National Air Toxics Trends Station (NATTS) network has been established, consisting of 23 stations in the contiguous 48 states. Having data of sufficient quality is paramount for a network such as the NATTS. As such, the U.S. EPA has established a Quality System (QS) for the NATTS, two aspects of which are Technical Systems Audits (TSAs) and Instrument Performance Audits (IPAs) of each network station and its affiliated laboratory tasked with sample analysis. Another integral part of the QS is the quarterly analysis of performance evaluation (PE) samples. Furthermore, the sampling and analytical techniques selected to collect and quantify the air toxics of concern must demonstrate acceptable analytical and overall sampling precision as well as suitable overall method detection limits that are compatible with expected ambient air toxics concentrations.

This report describes and summarizes the quality assurance (QA) data generated by the NATTS QS for calendar year (CY) 2004. Included in this Quality Assurance Annual Report (QAAR) are data from a number of different sources. Presented first is an assessment of the completeness of the data available in Air Quality System (AQS) database for four ambient air toxics: benzene, 1,3-butadiene, formaldehyde, and PM_{10} arsenic. Sites may also enter into AQS results of replicate analyses of a given sample and from collocated samplers. Such information allows for the calculation of analytical and overall sampling and analysis precision, respectively. Thus, such precision data were retrieved from AQS, and analytical and overall sampling as well as analysis precision were calculated for as many of the 23 applicable compounds and for as many of the 23 NATTS sites as had such data posted to AQS. However, such precision data were available for only a few compounds from a few sites.

Data from the analysis of blind audit (performance evaluation) samples for many of the 23 compounds are also presented. Such analyses document a given analytical laboratory's ability to accurately quantify samples generated at the NATTS sites. The accuracy achieved is

also referred to as the amount of laboratory bias introduced during sample analysis. Similarly, field bias data, which are the differences between actual and measured sampler flow readings for each of the three different sampler types (volatile organic compounds (VOCs), carbonyls, and PM_{10} metals), are presented for primary and collocated samplers (where available) at nine sites visited during the IPAs conducted during CY 2004. Finally, information regarding method detection limits (MDLs) was solicited from all the sites and affiliated laboratories for the 23 compounds of interest. Taken together, the combination of all the above QA data summarizes the activities of the QS for the NATTS for CY 2004.

2.0 NATTS QUALITY ASSURANCE DATA FOR CALENDAR YEAR 2004

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

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

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

Typically a city and state are used as the site identifier, but, in the case of the two Florida sites that are both in the city of Tampa, the county name is appended to eliminate confusion. The rural Vermont site near Underhill, Vermont, is also referred to as the county where the site is located, since this appellation is the one found in the AQS database. The Grande Junction, Colorado, site has two separate codes, one for VOCs and carbonyls (-0018), the other for the metals (-0017), since the organics and metals samplers are present at two separate physical locations at the sampling site. The 23 hazardous air pollutants measured of interest for this work are given in Table 2. These include 14 VOCs, two carbonyls, and seven PM_{10} metals. Also included in Table 2 are the unique AQS identification codes for each compound.

Table 2.   23 HAPs and their AQS compound codes.

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

2.1   Completeness and Precision of Data in the AQS Database

The AQS database was accessed and the raw data records for calendar year 2004 were retrieved for the 23 NATTS sites using the site codes given in Table 1 and for the 23 compounds having the AQS codes given in Table 2. The completeness of the 2004 AQS dataset was assessed for four compounds: benzene, 1,3-butadiene, formaldehyde, and arsenic.[1] The results are shown in Table 3. Depending on the day sampling commenced in 2004, the presence of 60 or 61 concentration values in the database would indicate 100 percent completeness, since sampling is to occur every sixth day. Zero values in the database were taken as data being present and were, thus, counted toward total dataset completeness. However, if the appropriate data field was empty, or if one of several "null codes"[2] were found, then the sampling event was determined to be incomplete and data were understood to be missing. In these instances, the total completeness percentage decreased accordingly. Furthermore, in many instances, data appeared in the database more frequently than every six days. Sampling for this program should only be occurring every sixth day. In such cases where higher frequency data were present, an algorithm was developed to calculate the elapsed time between samples such that only samples separated by six days were counted toward the overall dataset completeness. For example, if the database contained records of sampling on day 1, 3, 5, 7, 10, and 13, only three of these records would be counted toward the total completion percentage. The algorithm started with day 1, then ignored days 3 and 5 since only 2 and 4 days had elapsed since day 1, respectively. But the algorithm tallied the value at day 7 since six days had passed since day 1. Similarly, the value at day 10 would be skipped but day 13 would be counted.

Sorted by compound and taken across all the NATTS sites, the completeness data given in Table 3 is shown as a box and whisker plot in Figure 1. The "+" symbols indicate the mean completeness for each compound and the horizontal line "—" in the box represents the median. The upper and lower ends of the boxes represent the upper and lower quartiles; thus, the height of the box is the interquartile range. The upper whisker shows the maximum value less than the sum of the upper quartile value plus 1.5 times the interquartile range. Similarly, the lower whisker depicts the minimum value above the lower quartile minus 1.5 times the interquartile range. The squares shown for the 1,3-butadiene data represent individual completeness values greater than 1.5 times the interquartile range from the upper or lower quartile.

The mean completeness values across all the laboratories for which data were present in AQS were 78 percent, 80 percent, 80 percent, and 79 percent for benzene, 1,3-butadiene, formaldehyde, and arsenic, respectively. The median completeness values were higher: 90 percent, 92 percent, 92 percent, and 95 percent for the same four compounds, respectively.

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[1]   The completeness data presented in this report only include those data available online from AQS, not from any other offline source, including data made available by individual sites and laboratories.

[2]   Null codes and explanations of their meaning may be found at the following website: http://www.epa.gov/ttn/airs/airsaqs/manuals/OldNullCodes.htm. Bronx, NY, twice used the null code "BJ" (which is not given on the website) for formaldehyde data.

Table 3.   Percent completeness of the 2004 AQS data set by site for four HAPs.

| Site Identifier	Completeness of Compound by AQS number and by name, %			
	45201	**43218**	**43502**	**82103**
	benzene	**1,3-butadiene**	**formaldehyde**	**arsenic**
Boston-Roxbury, MA	98	98	80	No data
Chittenden Cty, VT	90	90	48	No data
Providence, RI	98	98	77	100
Bronx, NY	100	100	45	No data
Rochester, NY	72	72	50	No data
Washington, DC	98	98	100	No data
Chesterfield, SC	50	50	92	47
Decatur, GA	98	93	100	95
Hazard, KY	33	97	97	98
Hillsborough Cty, Tampa, FL	97	97	92	98
Pinellas Cty, Tampa, FL	43	43	47	47
Dearborn, MI	90	90	89	95
Mayville, WI	93	93	98	No data
Northbrook, IL	83	82	100	No data
Deer Park, TX	97	97	98	25
Harrison County, TX	90	90	85	No data
St. Louis, MO	97	97	92	No data
Bountiful, UT	93	93	92	100
Grand Junction, CO	88	88	92	97
Phoenix, AZ	20	20	No data	No data
San Jose, CA	50	50	48	No data
La Grande, OR	80	80	78	77
Seattle, WA	77	75	75	No data
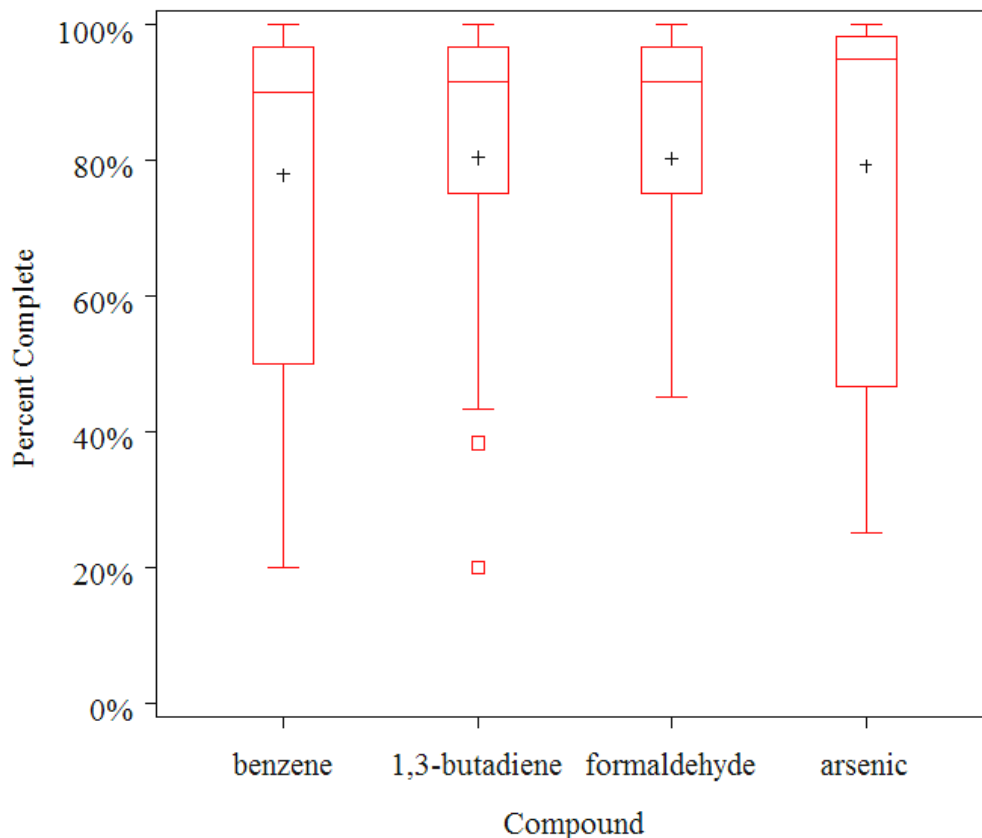
Figure 1. **Box and whisker plot of the completeness data for 2004 for 23 NATTS sites and for four compounds. (See Table 3 for the raw data.)**

The precision of the data in AQS was assessed for all 23 compounds identified in Table 2 and is listed in Tables 4 and 5. Replicate data transactions were retrieved from AQS. For a given sampling moment, site, and compound, AQS replicate data can have three separate transactions with Precision IDs of 1, 2, or 3. Concentration information from a collocated sampler is given in the transaction labeled with Precision ID 1; the value obtained from the replicate analysis of the primary sample is recorded with Precision ID 2; and the replicate analysis of the collocated sample is given in the transaction with Precision ID 3. Thus, both the analytical and overall sampling and analysis precision can be determined.

The precision is expressed in the form of the percent coefficient of variation (% CV). A smaller percent CV indicates a more precise measurement.

To assess the analytical precision, the percent CV was calculated in the following manner:

$$\%CV = 100 \cdot \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{(p_i - r_i)}{0.5 \cdot (p_i + r_i)}\right]^2 + \sum_{j=1}^{m}\left[\frac{(c_j - cr_j)}{0.5 \cdot (c_j + cr_j)}\right]^2}{2 \cdot (n + m)}} \qquad \text{(Eq. 2.1.1)}$$

where p_i and r_i are the corresponding primary and replicate records, n is the number of such records, c_j and cr_j are the corresponding collocated and collocated replicate records, and m is the number of such records.

Table 4. **Analytical precision given as % CV determined from 2004 AQS data. Only those sites and compounds for which data were available are shown. HAPs are given by number; see Table 2 for cross-reference. See text for additional details.**

	Compound #					
	1	**2**	**3**	**4**	**5**	**8**
Pinellas Cty, Tampa, FL	5% (38)	14% (36)	8% (38)	9% (38)	0% (2)	11% (38)
Northbrook, IL	53% (65)		21% (6)	63% (6)		69% (3)
St. Louis, MO	5% (14)	15% (7)	7% (10)	9% (4)		9% (12)
Bountiful, UT	4% (24)	11% (7)	12% (9)			8% (4)
Grand Junction, CO	14% (9)	9% (5)	13% (5)			
Phoenix, AZ	1% (2)	5% (2)	11% (2)			11% (2)
	Compound #					
Site identifier	**10**	**13**	**14**	**15**	**16**	
Pinellas Cty, Tampa, FL	13% (33)	0% (1)	0% (1)	1% (4)	2% (4)	
Northbrook, IL	22% (3)					
St. Louis, MO	0% (2)			1% (12)	0% (12)	
Bountiful, UT	7% (2)			1% (12)	1% (12)	
Grand Junction, CO	14% (2)			1% (10)	1% (10)	
Phoenix, AZ	14% (2)					

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

$$\%CV = 100 \cdot \sqrt{\frac{\sum_{i=1}^{n}\left[\frac{(p_i - c_i)}{0.5 \cdot (p_i + c_i)}\right]^2}{2 \cdot n}} \qquad \text{(Eq. 2.1.2)}$$

where p_i and c_i are the corresponding primary and collocated records, and n is the number of such records.

A corresponding pair of records was not included in the calculation if one of the values in the pair was zero or less than the MDL assigned for that compound in AQS. If no MDL was given and non-zero precision data were present, the precision data were included in the percent CV calculation. The results of the analytical and overall precision calculations for the data available in AQS are shown in Tables 4 and 5, respectively. Values in parentheses indicate the number of records used in the precision calculation.

Table 5. **Overall precision given as % CV determined from the 2004 AQS data. Only those sites and compounds for which data were available are shown. HAPs are given by number; see Table 2 for cross-reference. See text for additional details.**

Site Identifier	Compound #						
	1	2	3	4	5	8	10
Pinellas Cty, Tampa, FL	12% (13)	23% (12)	10% (13)	16% (13)	0% (1)	15% (13)	16% (11)
Mayville, WI	0% (1)		10% (2)				
Northbrook, IL	59% (59)		67% (6)	126% (6)		94% (4)	33% (2)
St. Louis, MO	8% (7)	12% (3)	10% (5)	9% (2)		9% (6)	13% (1)
Bountiful, UT	4% (12)	7% (4)	12% (4)			5% (2)	0% (1)
Grand Junction, CO	9% (6)	16% (4)	16% (3)				0% (1)
Phoenix, AZ	1% (1)	0% (1)	7% (1)			6% (1)	0% (1)

Site Identifier	Compound #						
	15	16	17	20	21	23	
Pinellas Cty, Tampa, FL	15% (2)	19% (2)					
Mayville, WI	0% (2)	5% (2)					
St. Louis, MO	5% (6)	2% (6)					
Bountiful, UT	10% (6)	9% (6)	7% (14)	17% (16)	13% (16)	20% (8)	
Grand Junction, CO	2% (5)	3% (5)					

Precision data available in AQS varied widely by compound and by site. Pinellas County, Tampa, Florida, and Northbrook, Illinois, had the most precision data available. The compound with the most precision data available was benzene. When evaluating the quality of the precision data, the typical acceptability criterion is for compounds to have a % CV of less than 15 percent. Across all laboratories reporting precision data into AQS, and across all compounds for which such data were reported, 88 percent (37/42) and 73 percent (35/48) of the analytical and overall precision data, respectively, meets the 15 percent acceptability criterion. However, the most important finding was that very little precision data, either for replicate analyses of a single sample or for analyses of collocated sampling, was available in AQS, as data were only available for seven of the 23 stations.

2.2   Laboratory Bias Data – Bias Data from Performance Evaluation Samples from Alion (formerly Mantech)

Alion (previously Mantech) is under contract (Contract No. 68-D03-006) to the U.S. EPA to conduct quarterly performance evaluation (PE) audits of the NATTS laboratories. Alion provided to Battelle the results of the calendar year 2004 PE audits for inclusion in the present work. Much of the information presented below describing the specific procedures involved in performing the PE audits was adapted from the Alion report by Kenneth J. Caviston, "National Air Toxics Trends Stations Proficiency Testing Program 2004 Data Report (Studies 200401 and 200402)." Additional details of the NATTS PE program may be found in the Caviston report.

For calendar year 2004, two separate carbonyl and VOC PE studies were conducted. The first of each of the studies (200401-C and 200401-V, where C designates carbonyl and V stands for VOC) were performed during September and October 2004. The second set of performance evaluation studies (200402-C and 200402-V) took place in November and December 2004. Only one metals PE study (200401-M) was conducted in the Fall of 2004, because several laboratories required additional time for analysis of this first metals PE sample.

Spiked samples containing known amounts of the HAPs of interest were forwarded to each laboratory that was performing analyses for a NATTS site and that chose to participate in a given PE study. Participating laboratories forwarded their results to Alion, after which reports were prepared comparing the values measured by the laboratory to the stated value.

For the VOCs PE samples, participating laboratories sent clean Summa canisters to Alion that were subsequently filled with humidified air containing the volatile organics of interest. Two different sets of VOC PE samples were prepared for 200401-V; each lot contained only seven of the 14 target compounds. Six of the 14 laboratories that participated were sent Lot 1, the remaining eight received Lot 2. All fourteen target compounds were present in the canisters sent to the 11 participating laboratories for 200402-V. For the 200401-V Lot 1 and 200401-V Lot 2 PE samples, Alion filled a single canister and analyzed it immediately. Similarly, Alion filled and analyzed immediately two canisters for 200402-V. The single-canister results from 200401-V Lots 1 and 2 and the mean results from 200402-V were the stated values against which the laboratories' results were compared. The VOC PE results are sorted by compound and presented in Figures 2 through 29.

In all of the PE figures, the results are identified, for the sake of consistency, by the NATTS site name. Notable exceptions are New York and Texas, which each have two NATTS sites, and ERG, which performed analyses in 2004 for several sample types for several of the NATTS stations. Table 9 provides cross references identifying which NATTS sites were affiliated with which laboratory for a given sample type. The abbreviations used in Table 9 are explained in Table 10. (These two tables are found in Section 2.4 of this report.)

The format for all the PE figures for all three sample types is the same. The dashed vertical line represents the stated value for the target given compound in the PE sample. The value obtained by a given laboratory is indicated next to the colored bar in the bar chart. Finally, the color of the bar indicates the percentage bias between the laboratory result and the stated value of the PE sample. Bias is calculated as the absolute percent difference from the stated value: % bias = |Stated value – Reported value|/Stated value * 100. For bias less than 20 percent, the bar is green; for 20 percent < bias < 25 percent, the bar is colored yellow; and, if the percent bias is greater than 25 percent, then the bar is red.
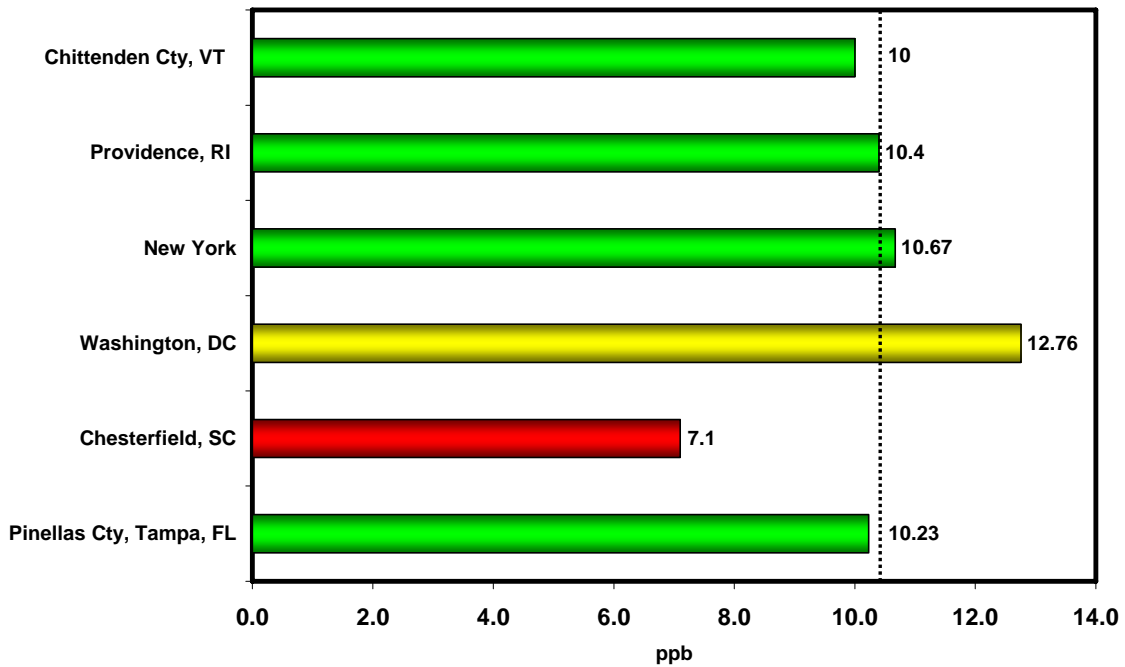
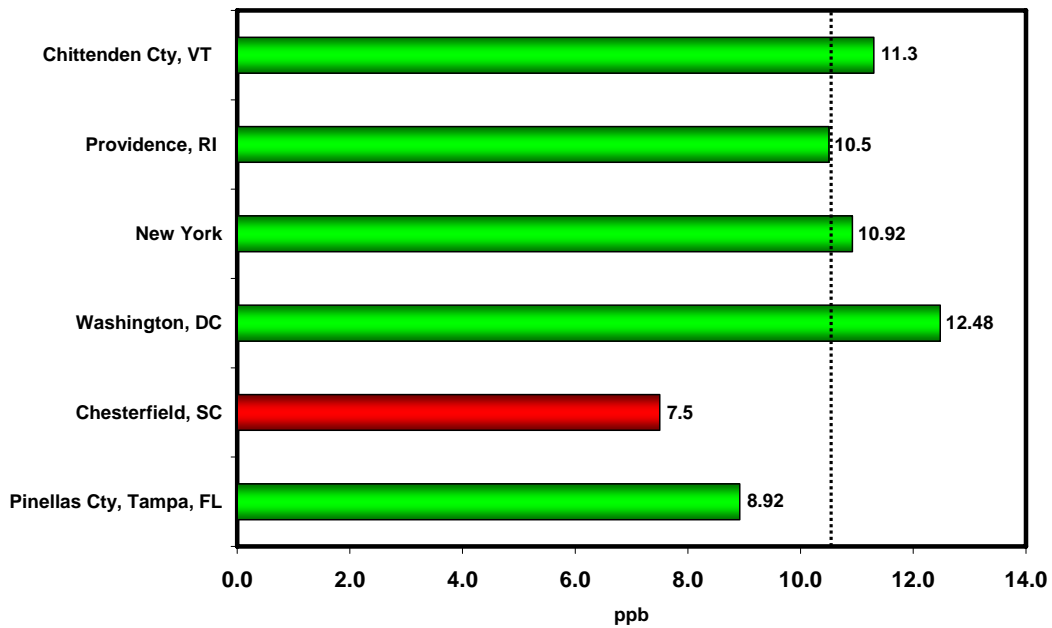**Figure 2.   200401-V Lot 1 laboratory bias data for benzene.**

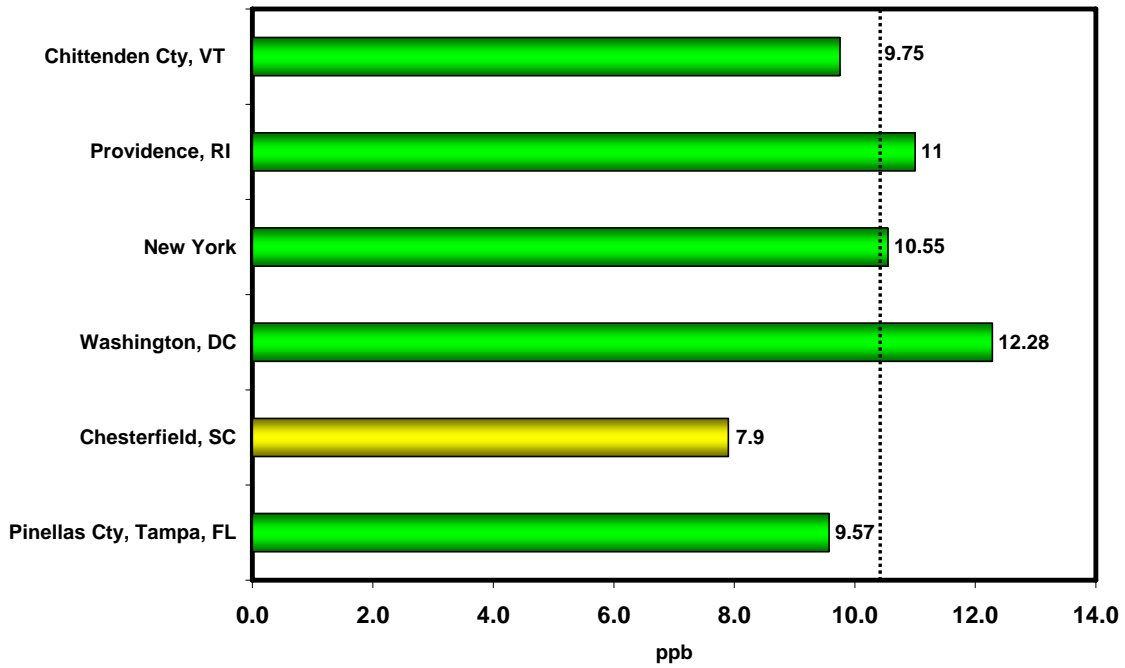**Figure 3.   200401-V Lot 1 laboratory bias data for chloroform.**

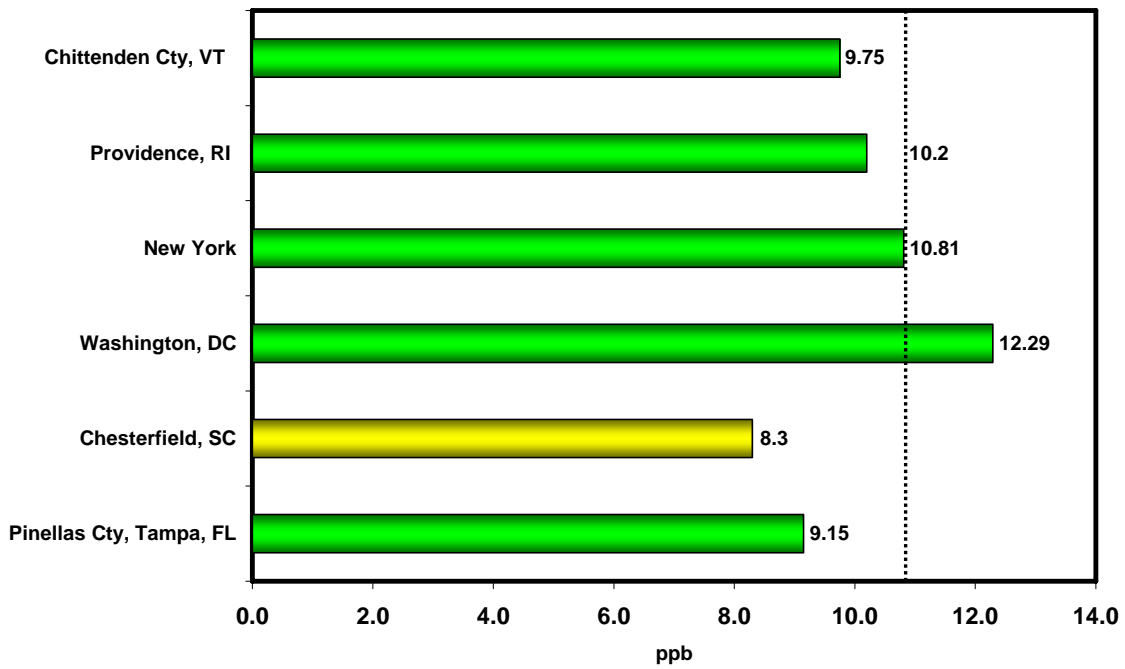**Figure 4.**   **200401-V Lot 1 laboratory bias data for 1,2-dichloropropane.**

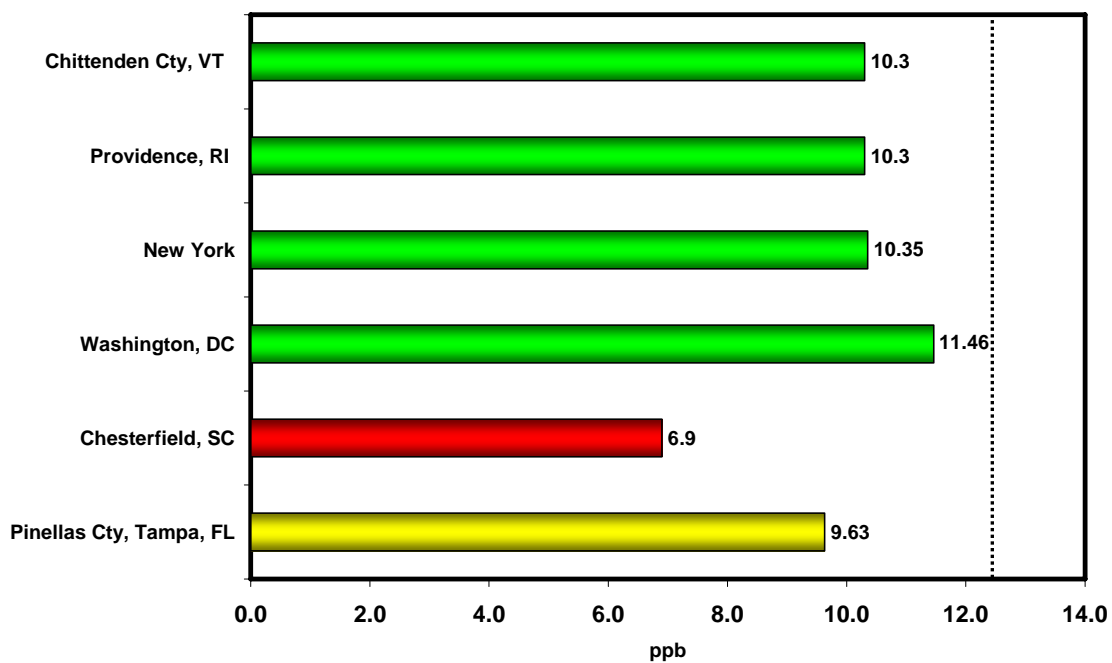**Figure 5.**   **200401-V Lot 1 laboratory bias data for tetrachloroethylene.**

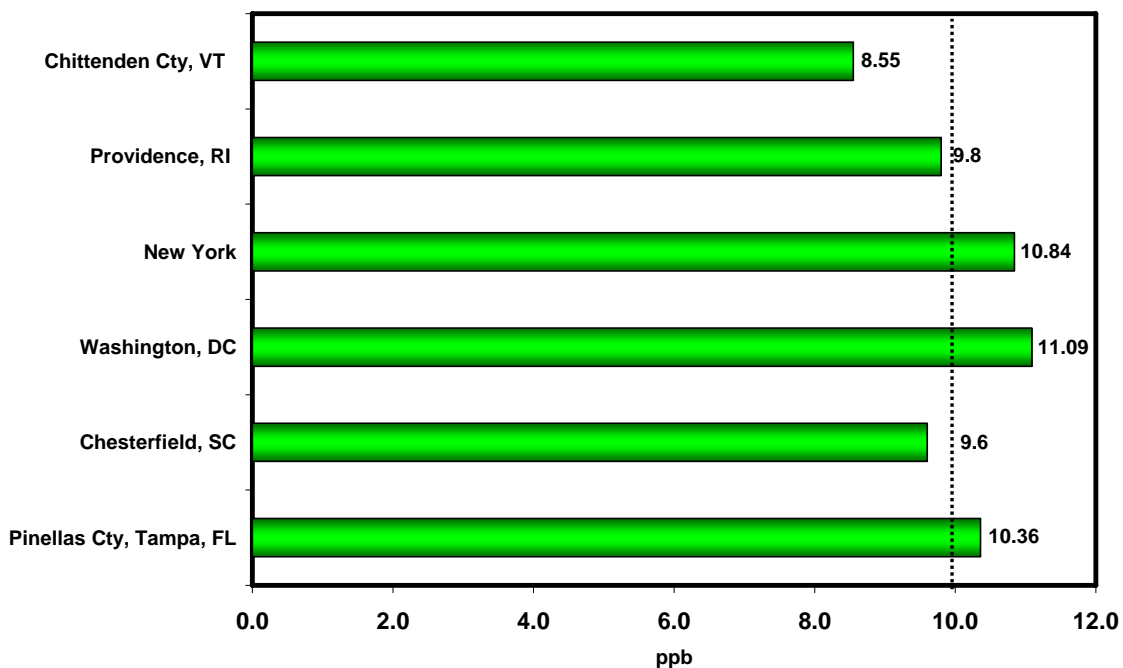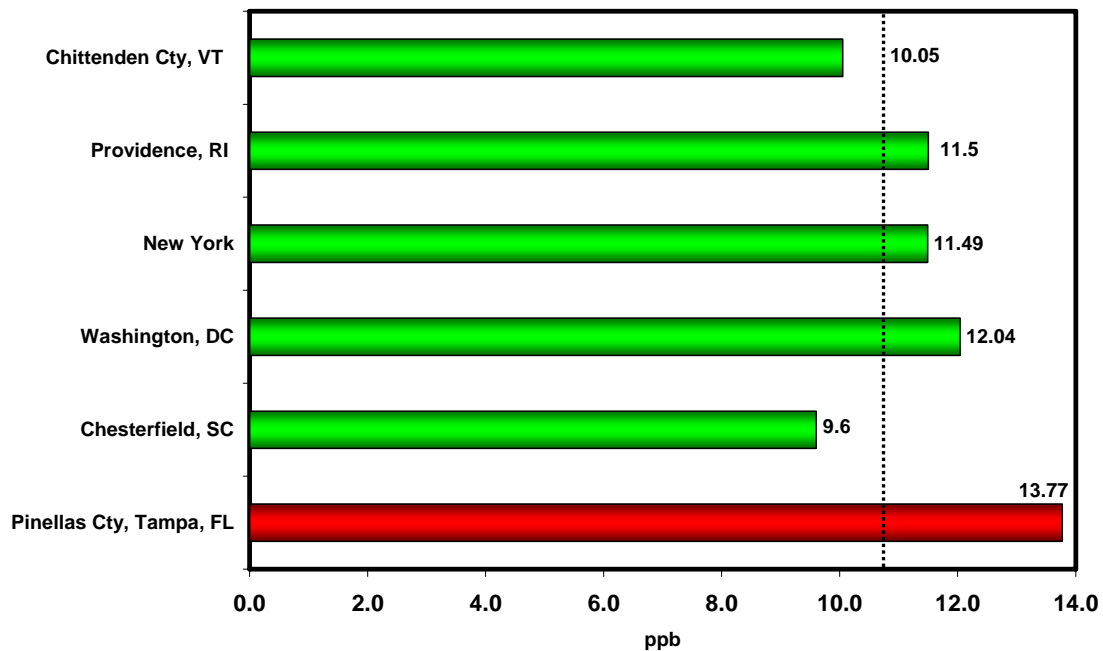**Figure 6.** **200401-V Lot 1 laboratory bias data for vinyl chloride.**

Figure 7. **200401-V Lot 1 laboratory bias data for cis-1,3-dichloropropene.**

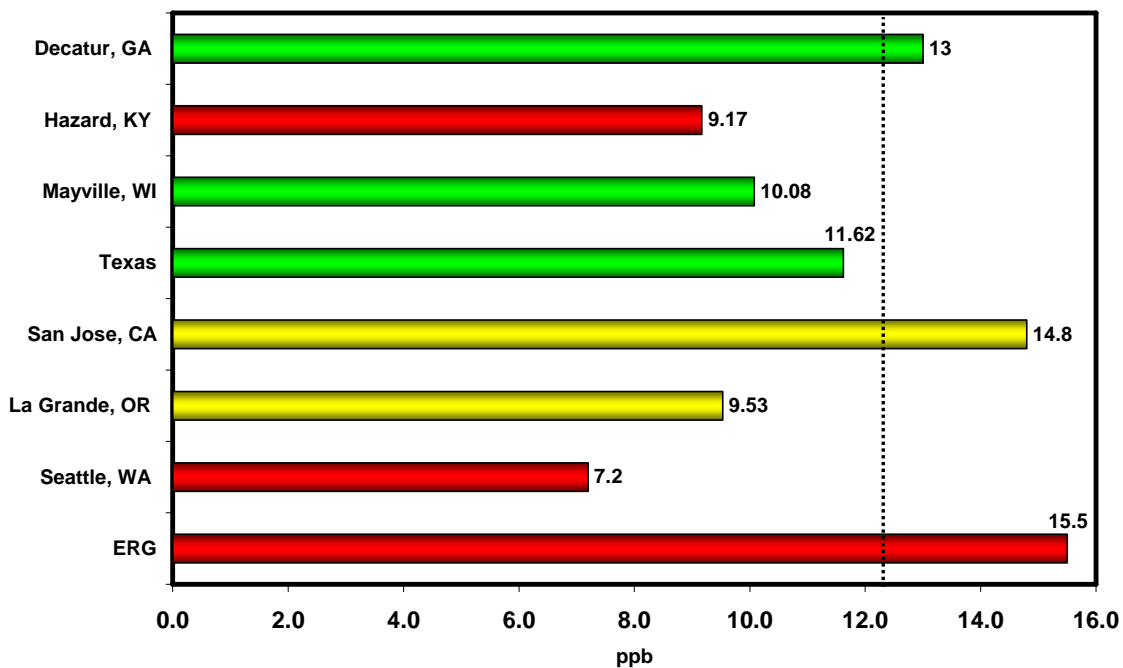**Figure 8.**   **200401-V Lot 1 laboratory bias data for trans-1,3-dichloropropene.**

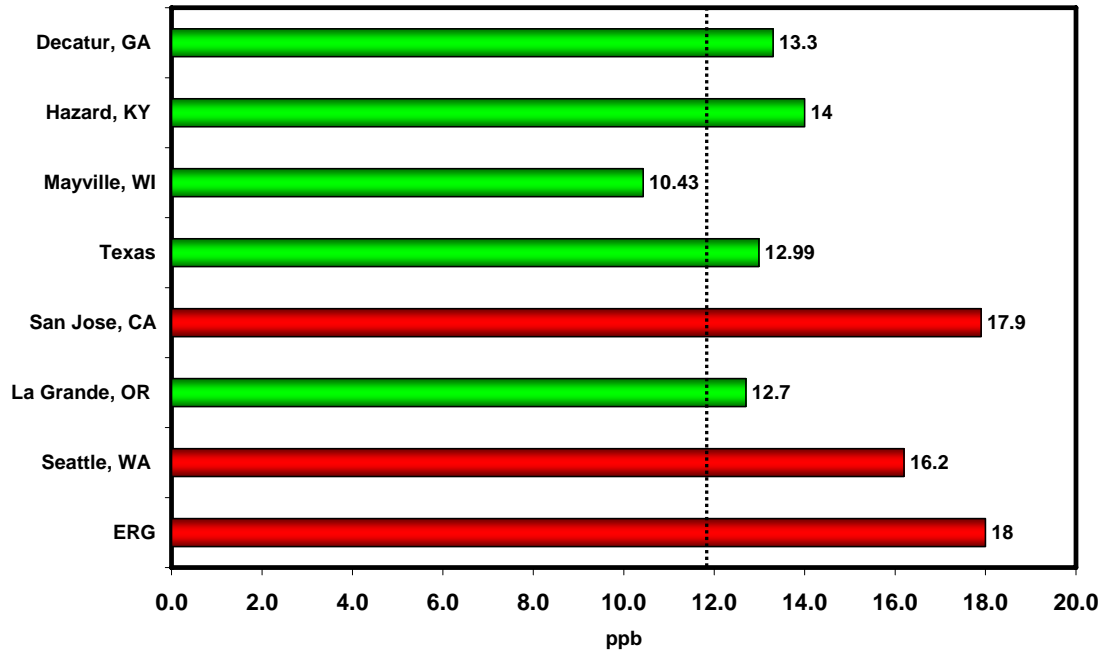**Figure 9.**   **200401-V Lot 2 laboratory bias data for 1,3-butadiene.**

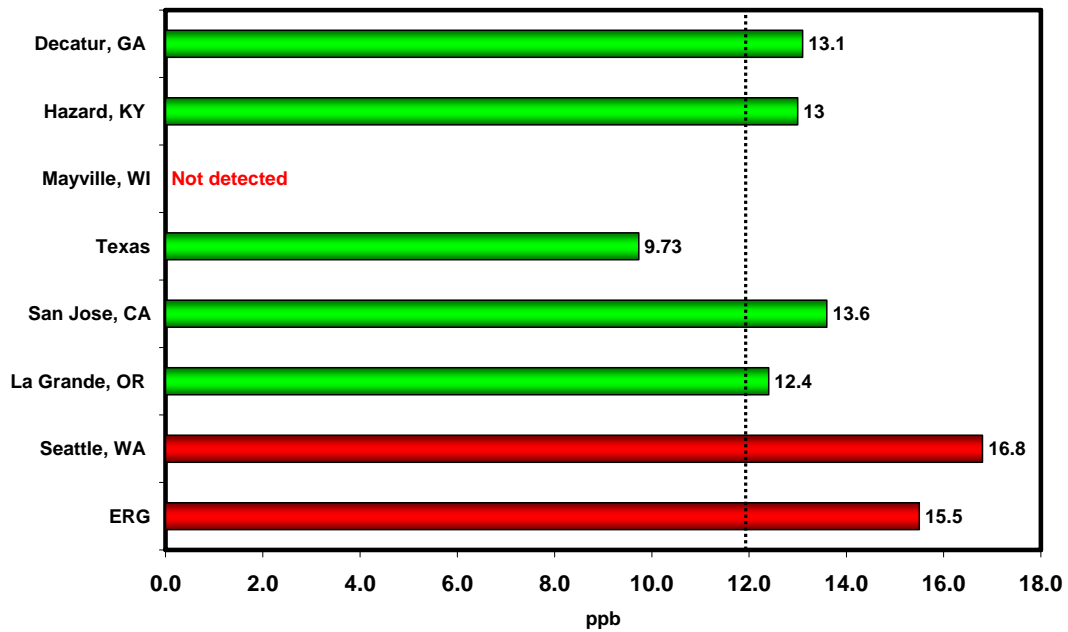**Figure 10.** **200401-V Lot 2 laboratory bias data for carbon tetrachloride.**

Figure 11. **200401-V Lot 2 laboratory bias data for 1,2-dibromoethane.**

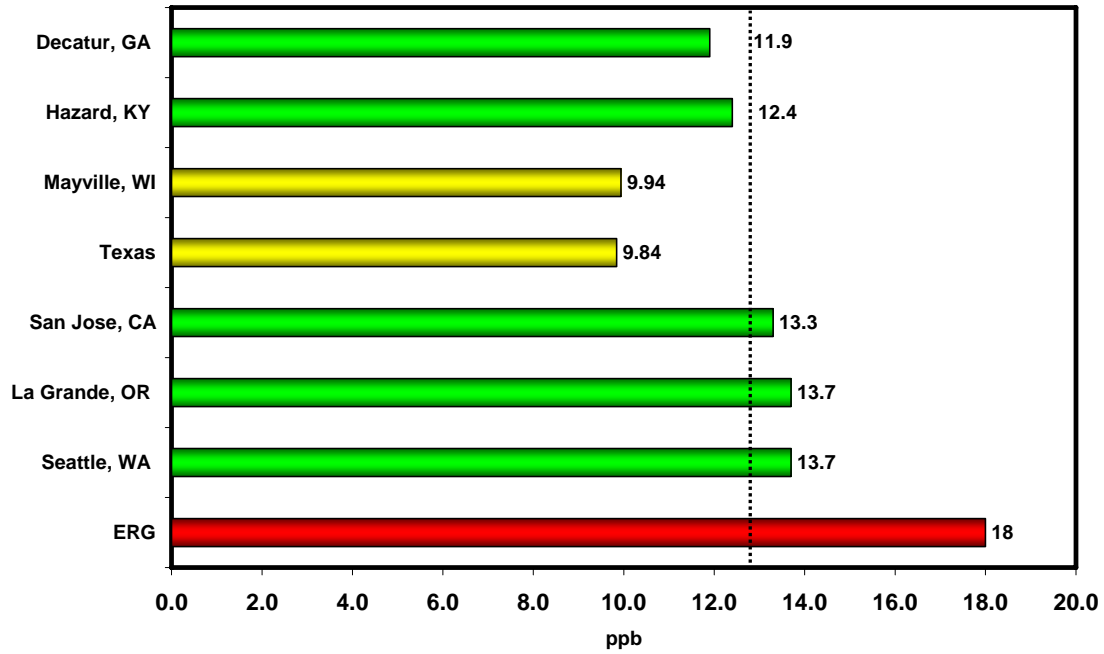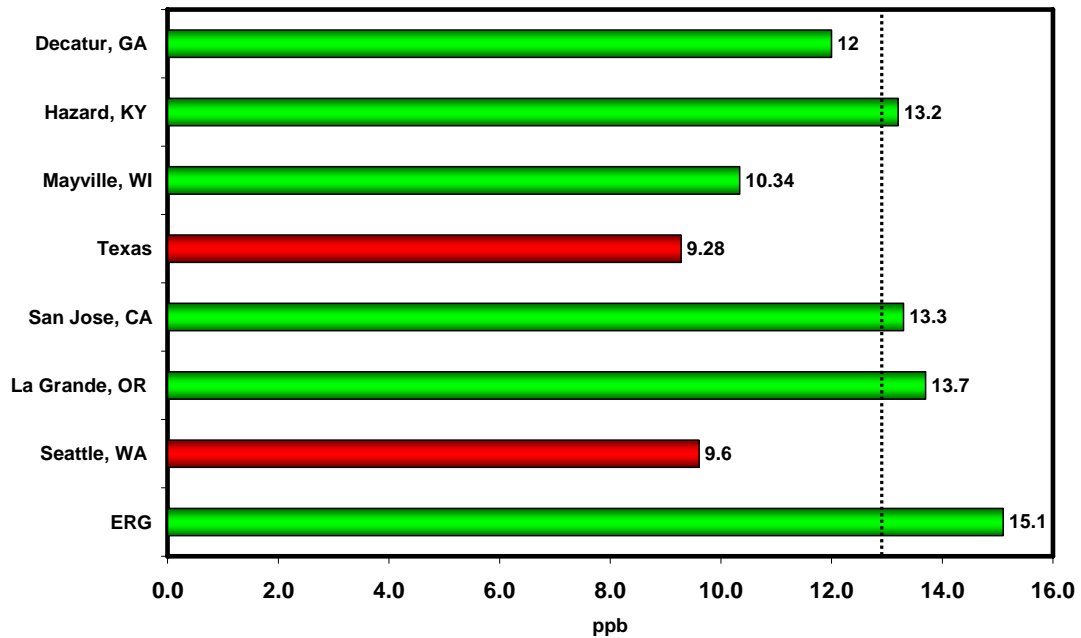**Figure 12.   200401-V Lot 2 laboratory bias data for 1,2-dichloroethane.**

Figure 13.   200401-V Lot 2 laboratory bias data for dichloromethane.
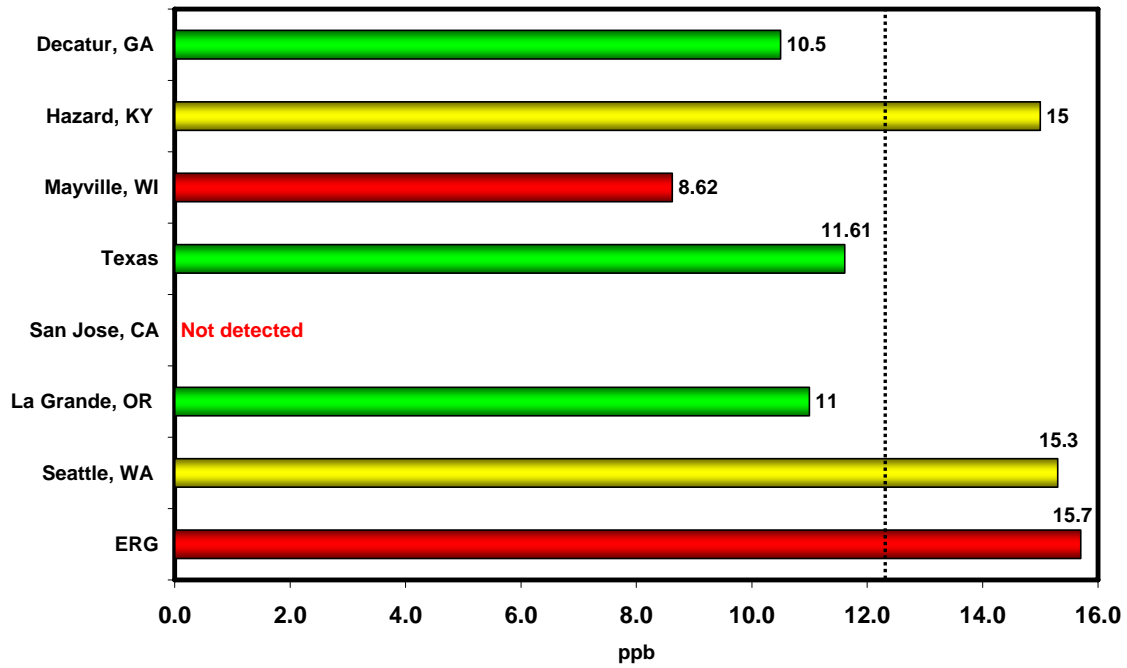
Figure 14.   200401-V Lot 2 laboratory bias data for 1,1,2,2-tetrachloroethane.
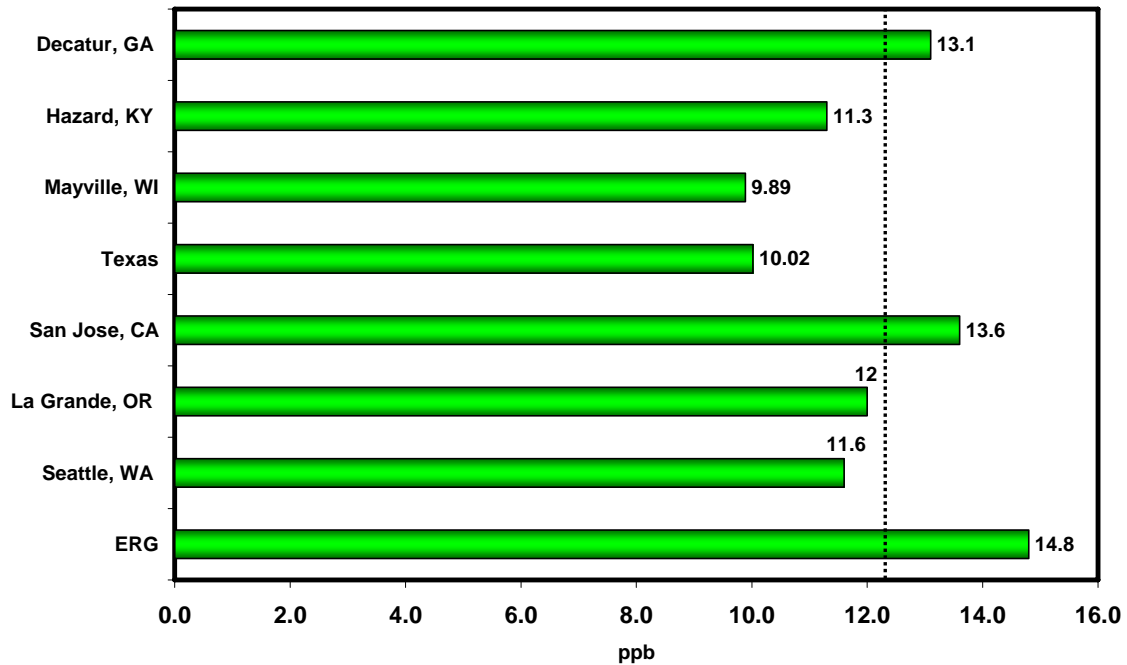

Figure 15.   200401-V Lot 2 laboratory bias data for trichloroethylene.

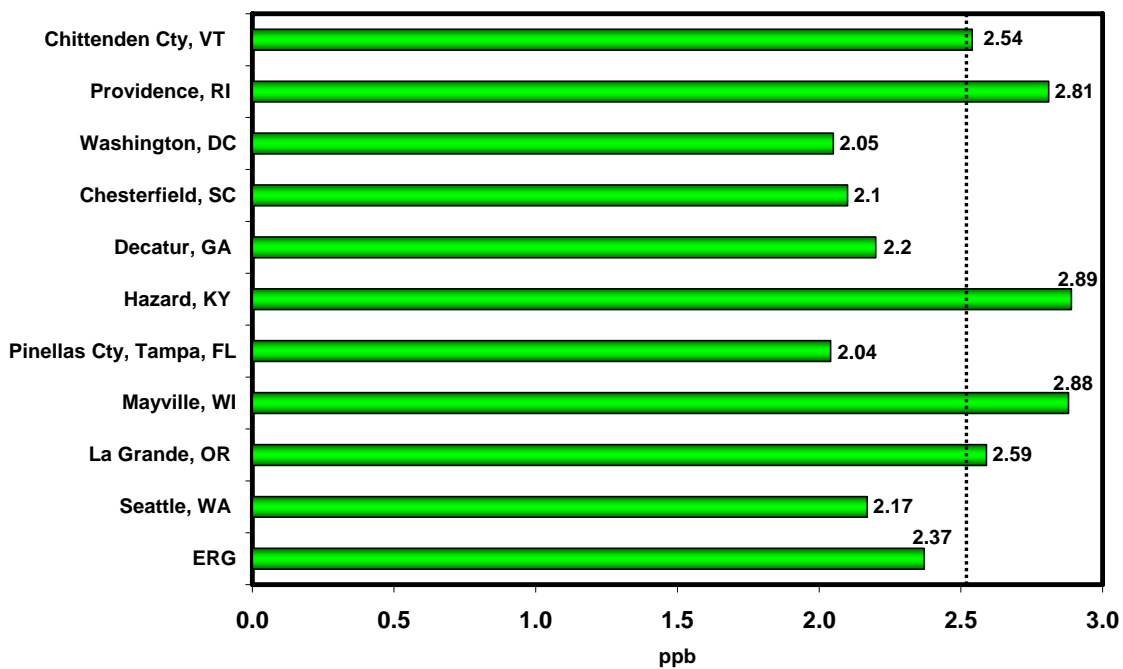**Figure 16.   200402-V laboratory bias data for benzene.**

Figure 17.   200402-V laboratory bias data for 1,3-butadiene.
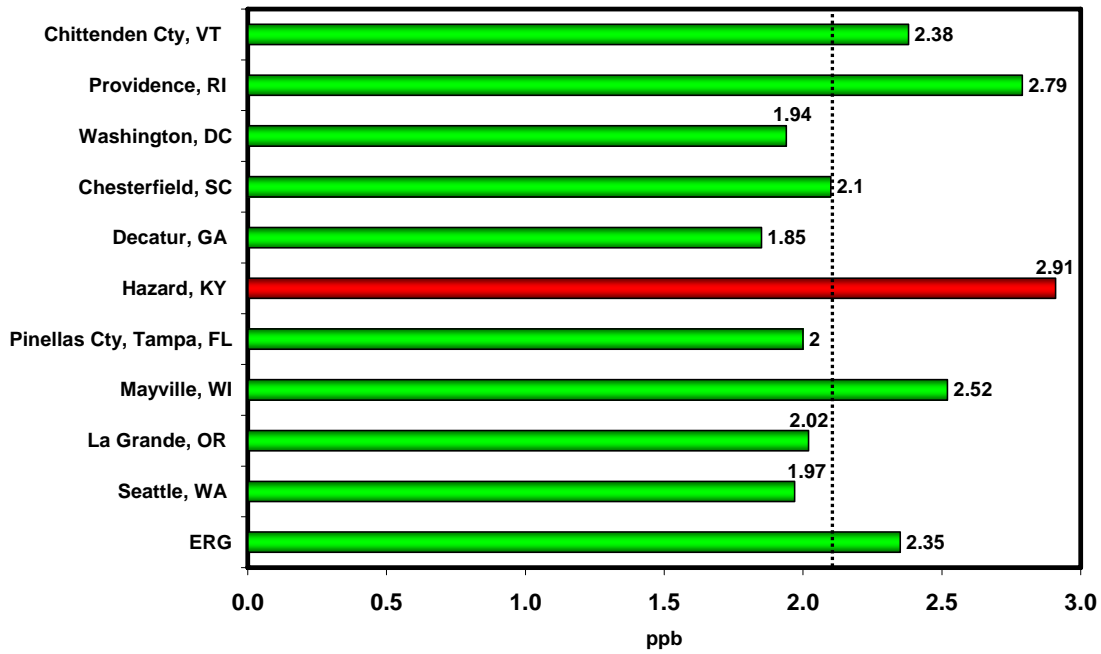
Figure 18.   200402-V laboratory bias data for carbon tetrachloride.
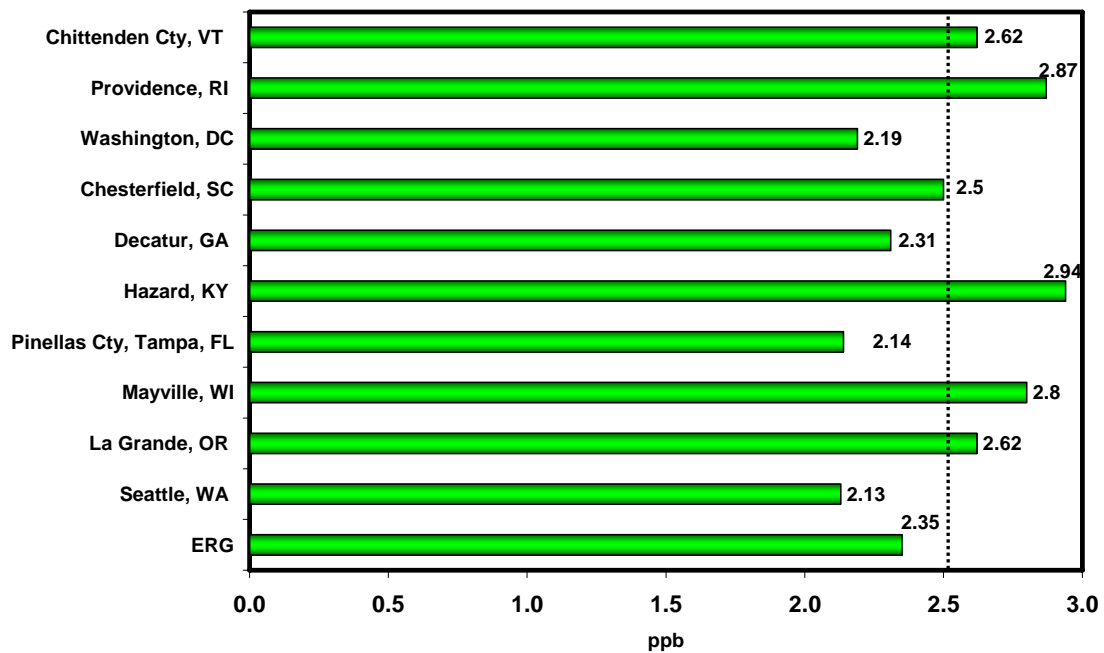
Figure 19.   200402-V laboratory bias data for chloroform.
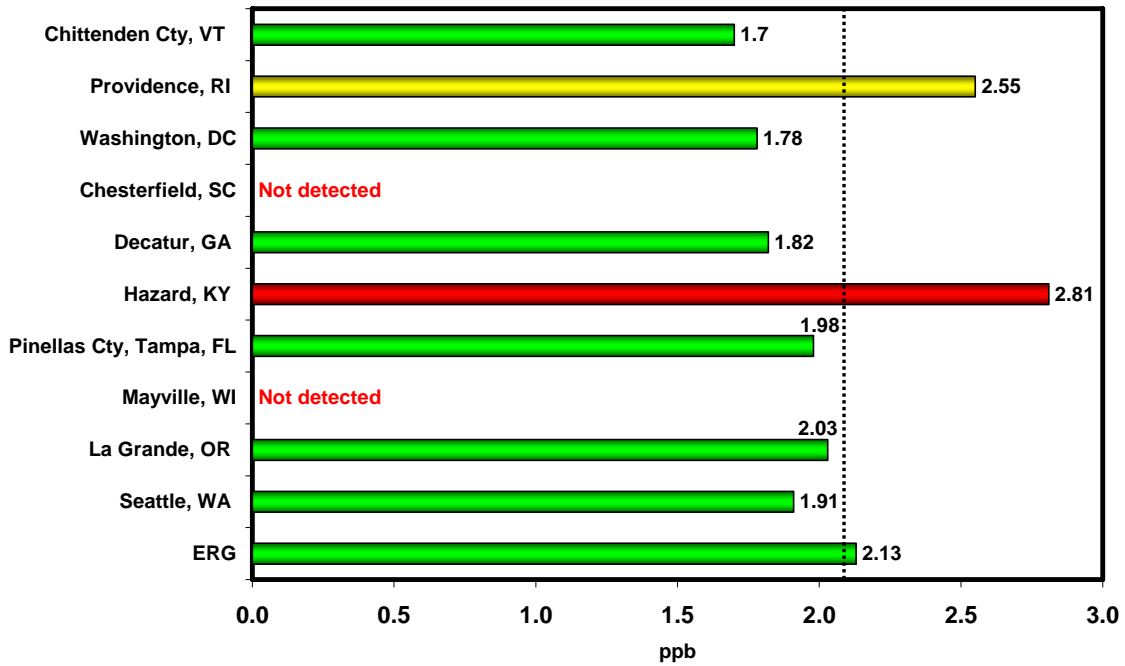
Figure 20.   200402-V laboratory bias data for 1,2-dibromoethane.
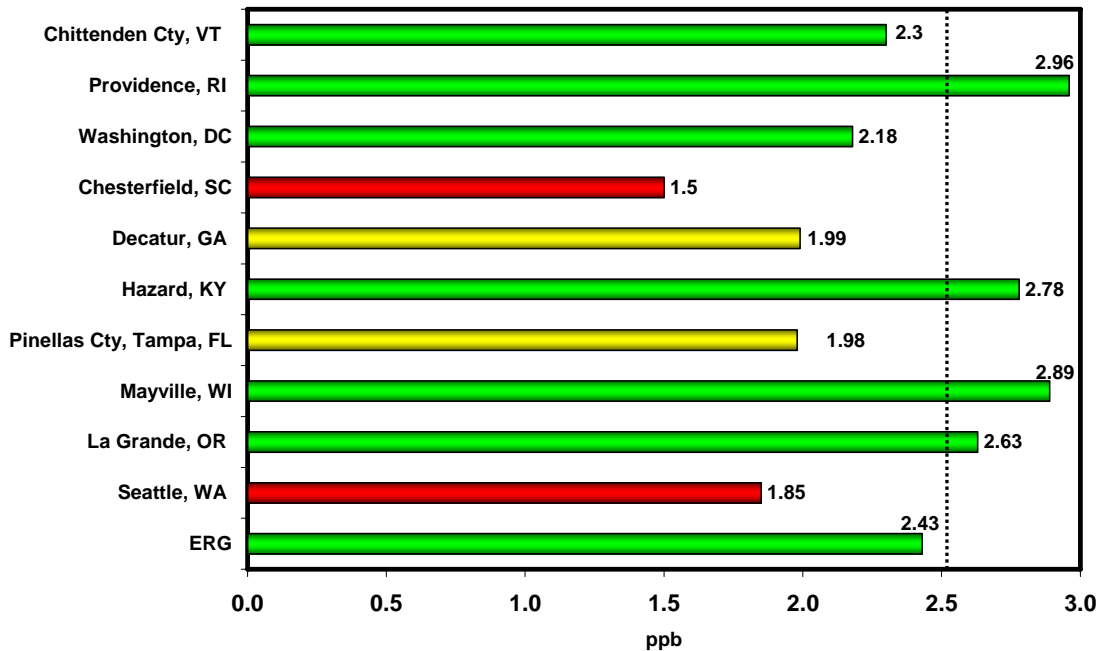
Figure 21.   200402-V laboratory bias data for 1,2-dichloropropane.
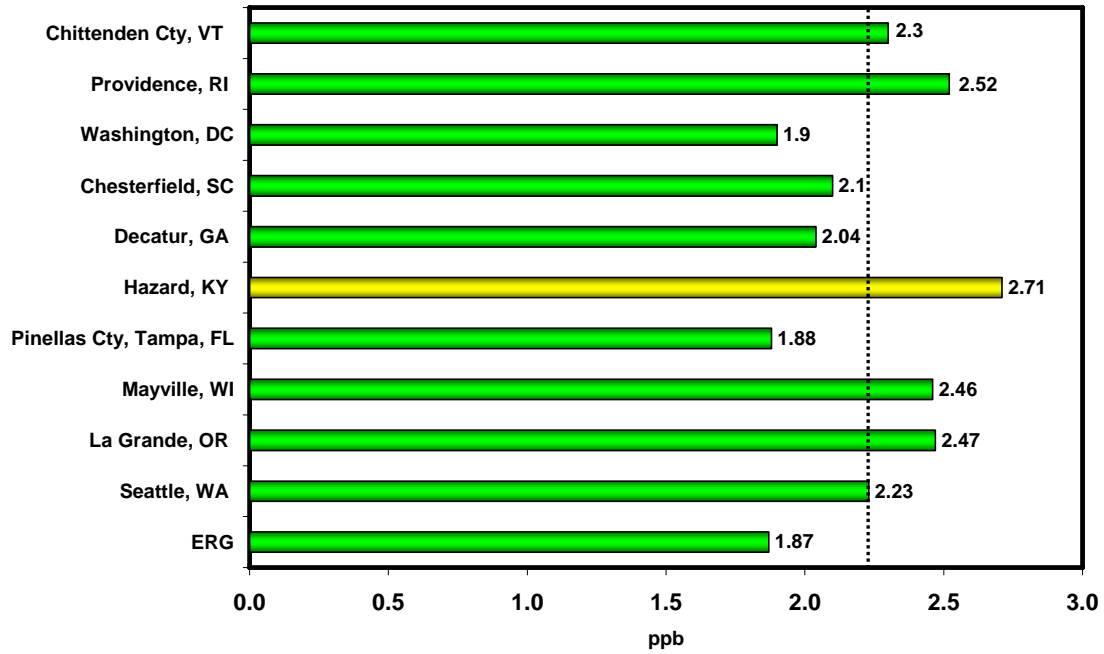
Figure 22. **200402-V laboratory bias data for 1,2-dichloroethane.**
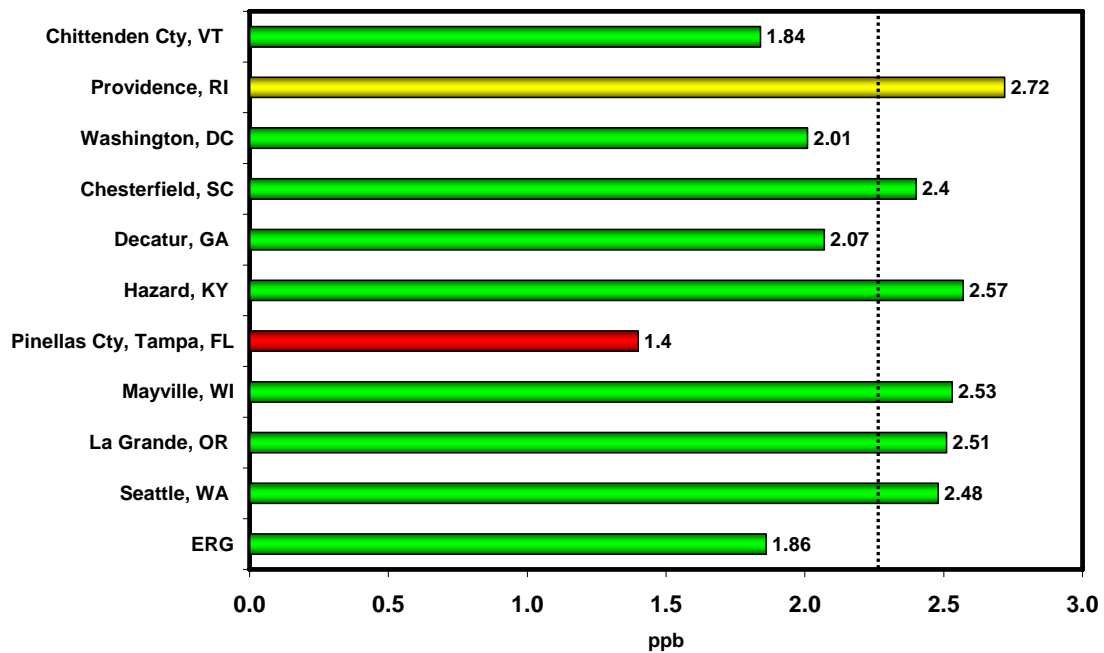
Figure 23. **200402-V laboratory bias data for dichloromethane.**
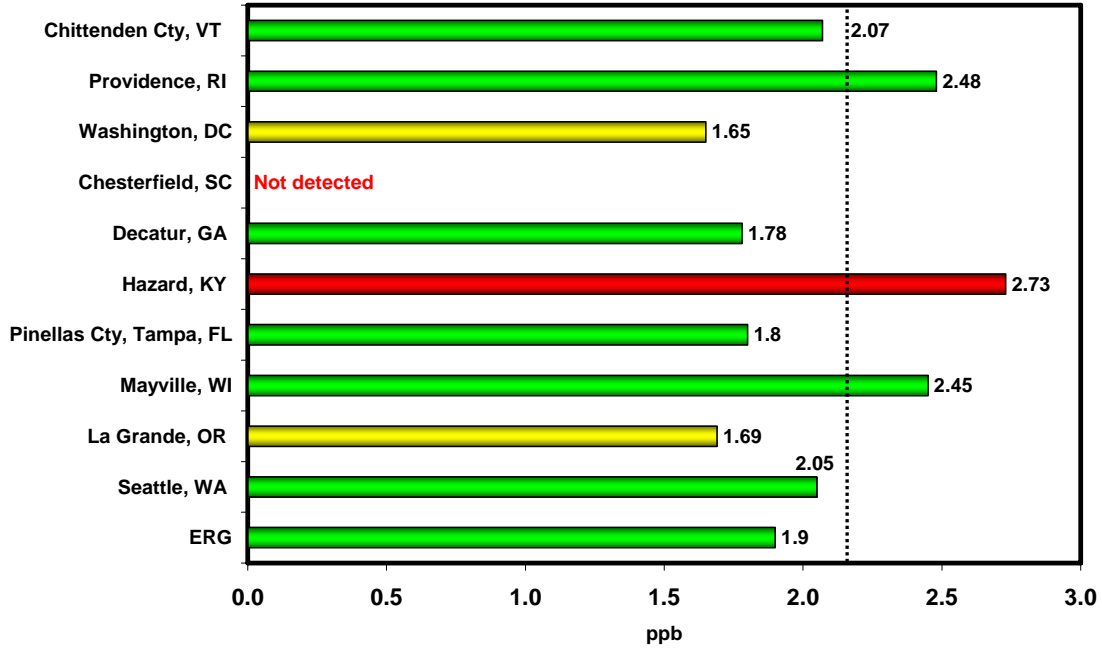
Figure 24.   200402-V laboratory bias data for 1,1,2,2-tetrachloroethane.
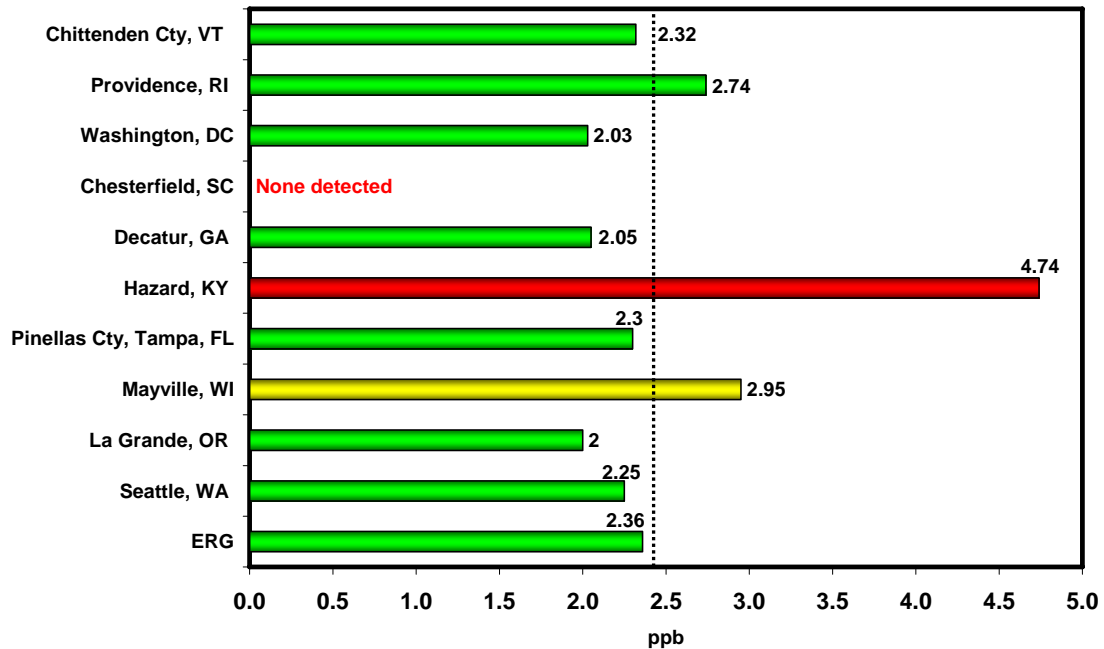
Figure 25.   200402-V laboratory bias data for tetrachloroethylene.
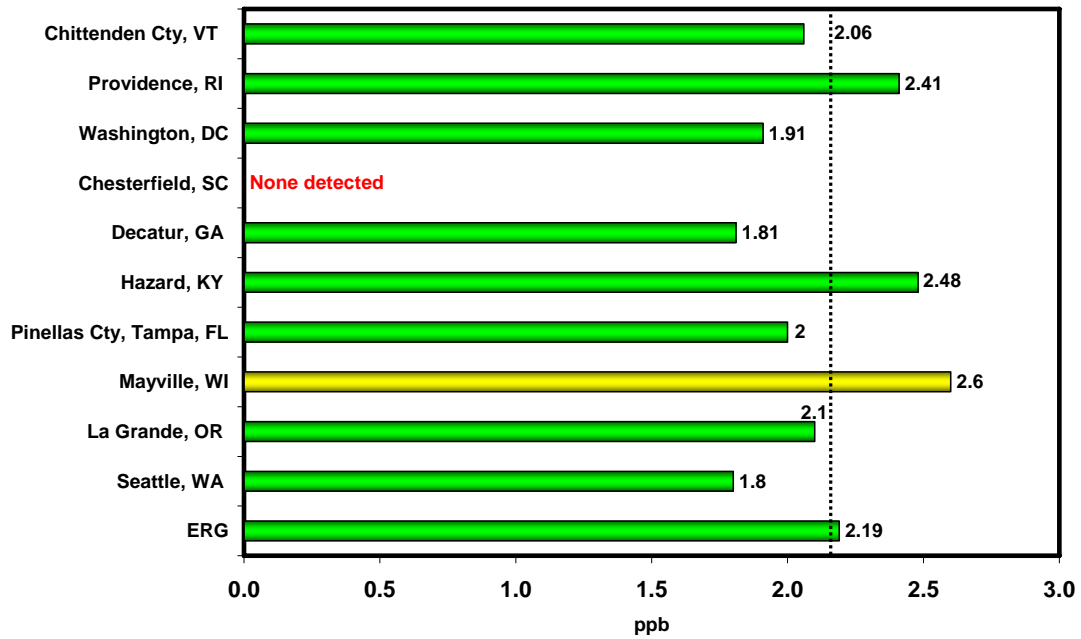
Figure 26.   200402-V laboratory bias data for trichloroethylene.
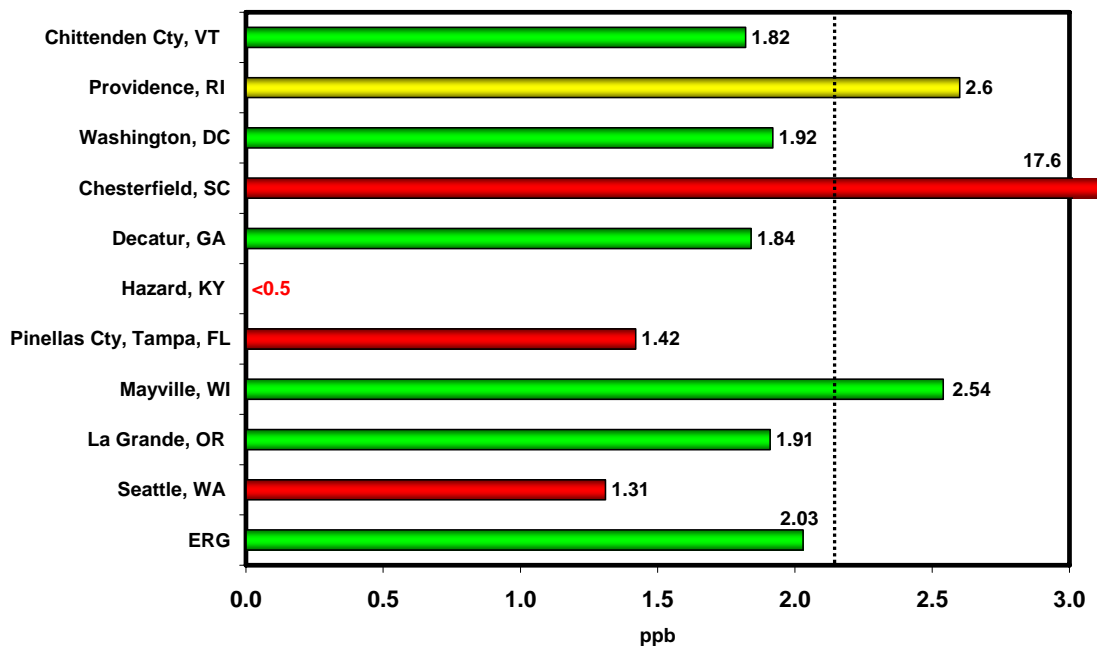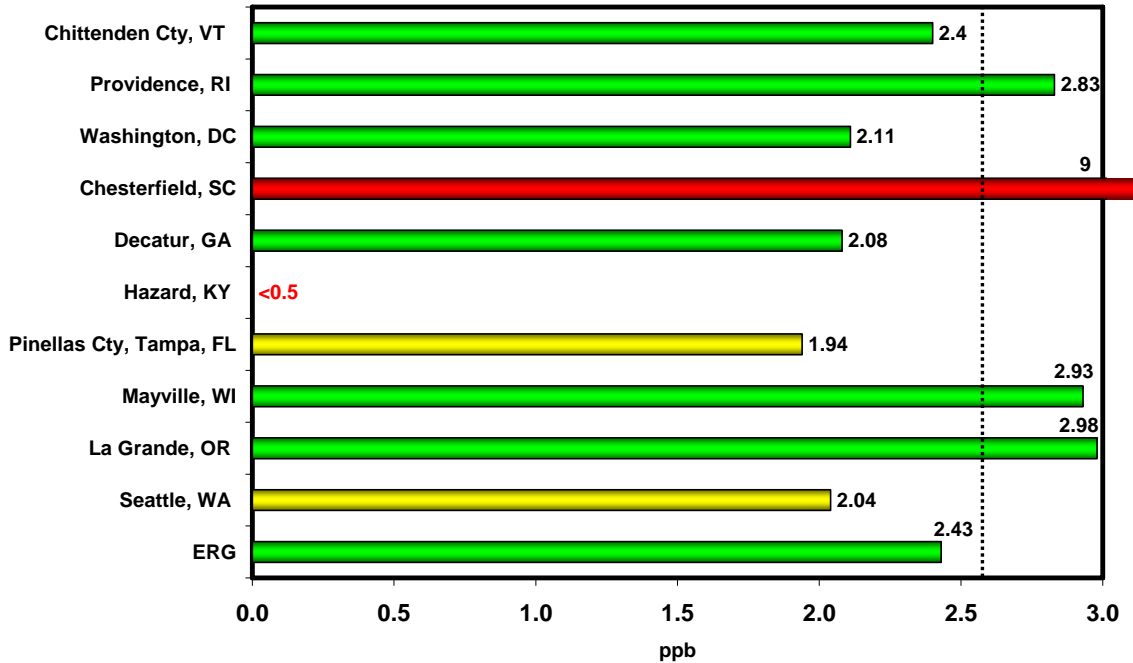

Figure 27.   200402-V laboratory bias data for vinyl chloride.
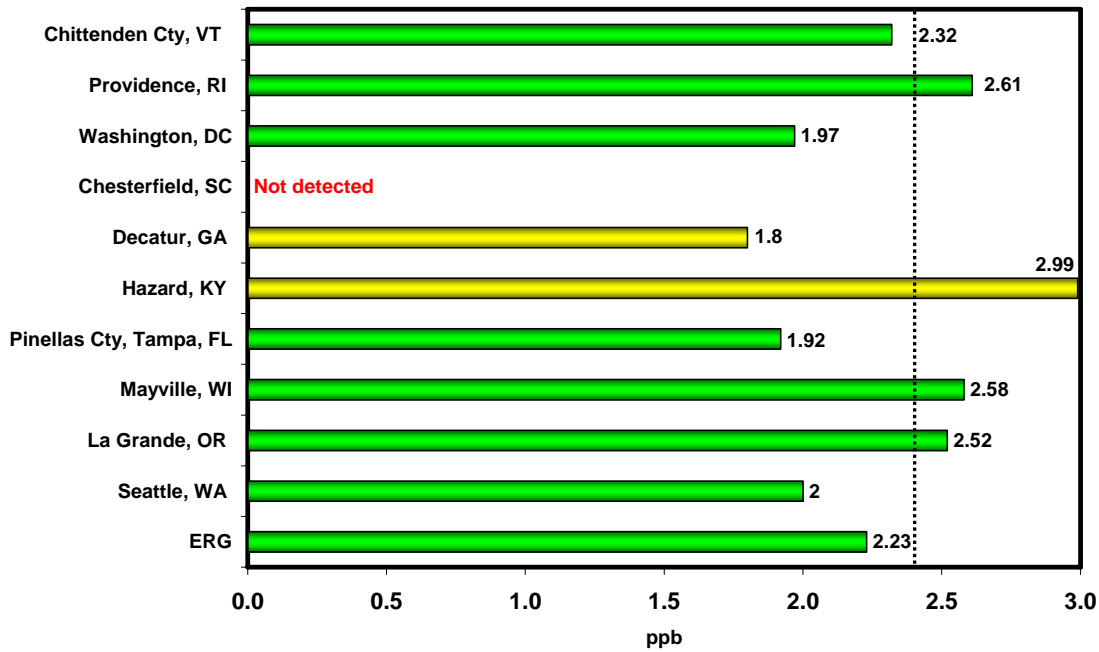
Figure 28.   200402-V laboratory bias data for cis-1,3-dichloropropene.
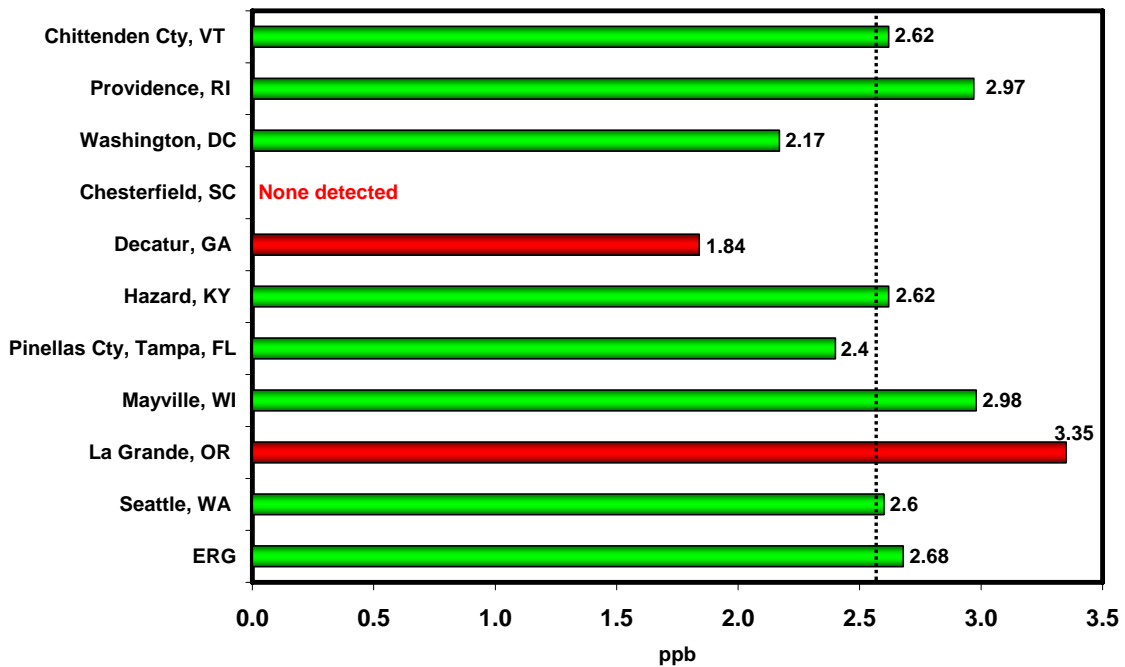
Figure 29.   200402-V laboratory bias data for trans-1,3-dichloropropene.

For the carbonyls, the 200401-C PE samples consisted of cartridges spiked with known amounts of formaldehyde, acetaldehyde, and acrolein. The 200402-C PE cartridges also were spiked with known amounts of formaldehyde, acetaldehyde, and acetone. All compounds were spiked as their dinitrophenyl hydrazine (DNPH) derivations in liquid solution. The amount of compound spiked onto a given cartridge was taken as the true value against which the laboratories' results were compared. Seventeen laboratories participated in both CY 2004 carbonyl PE studies. The results are summarized by compound in Figures 30 through 33. Only data for the two carbonyls that are currently of the most importance to the NATTS program, formaldehyde and acetaldehyde, are shown.
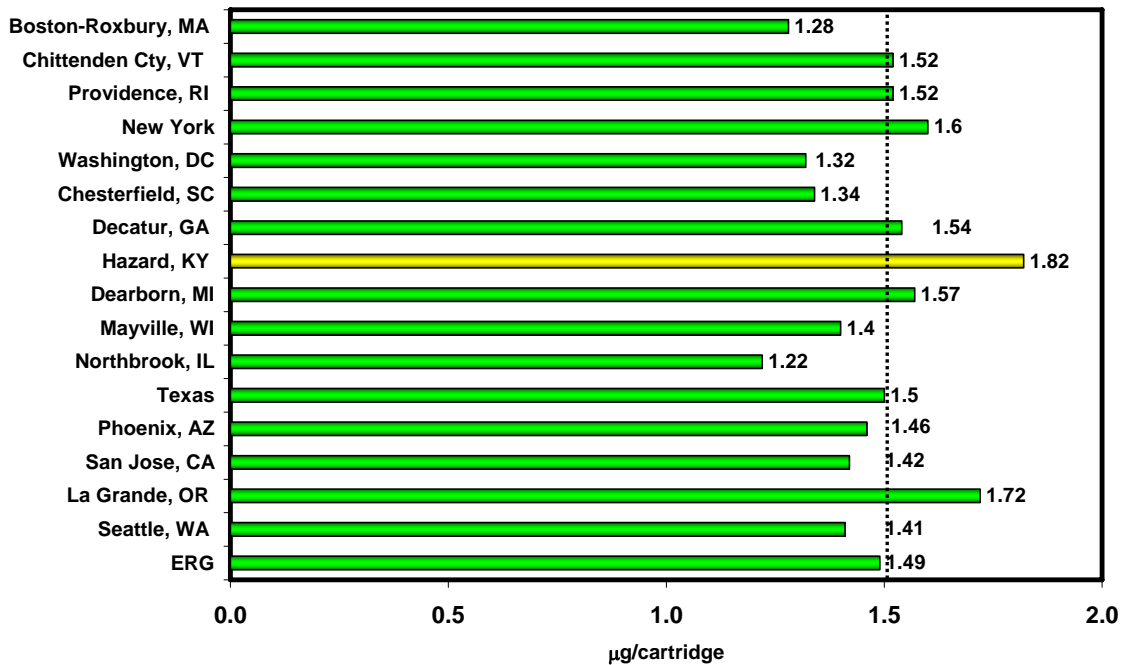
Figure 30.   200401-C laboratory bias data for formaldehyde.
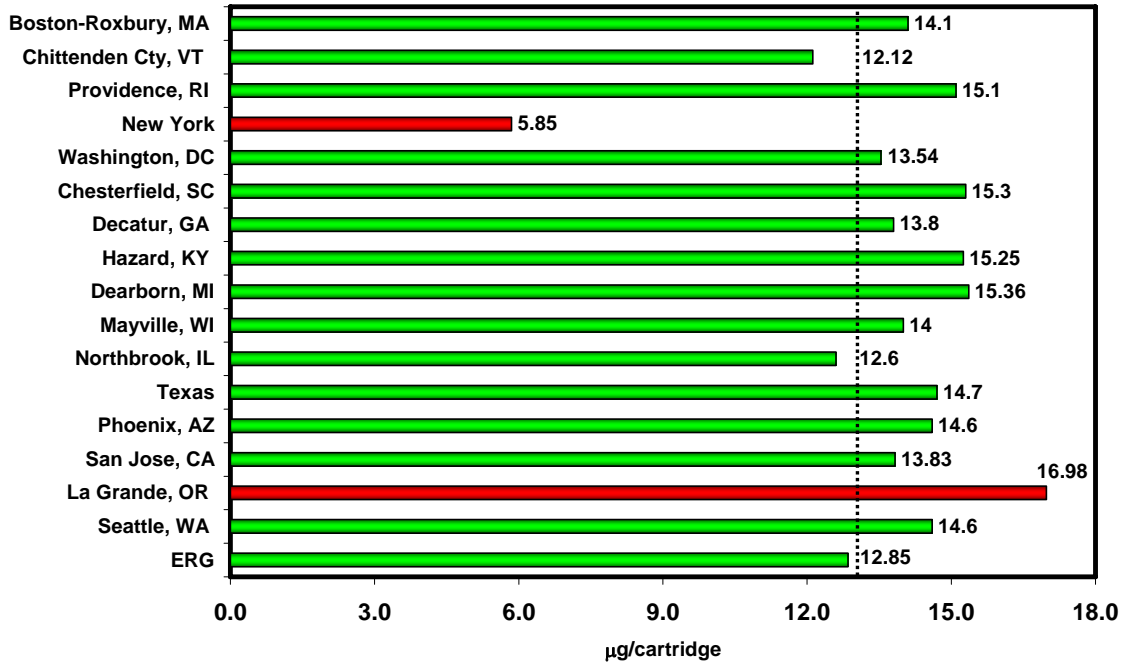
Figure 31.   200402-C laboratory bias data for formaldehyde.
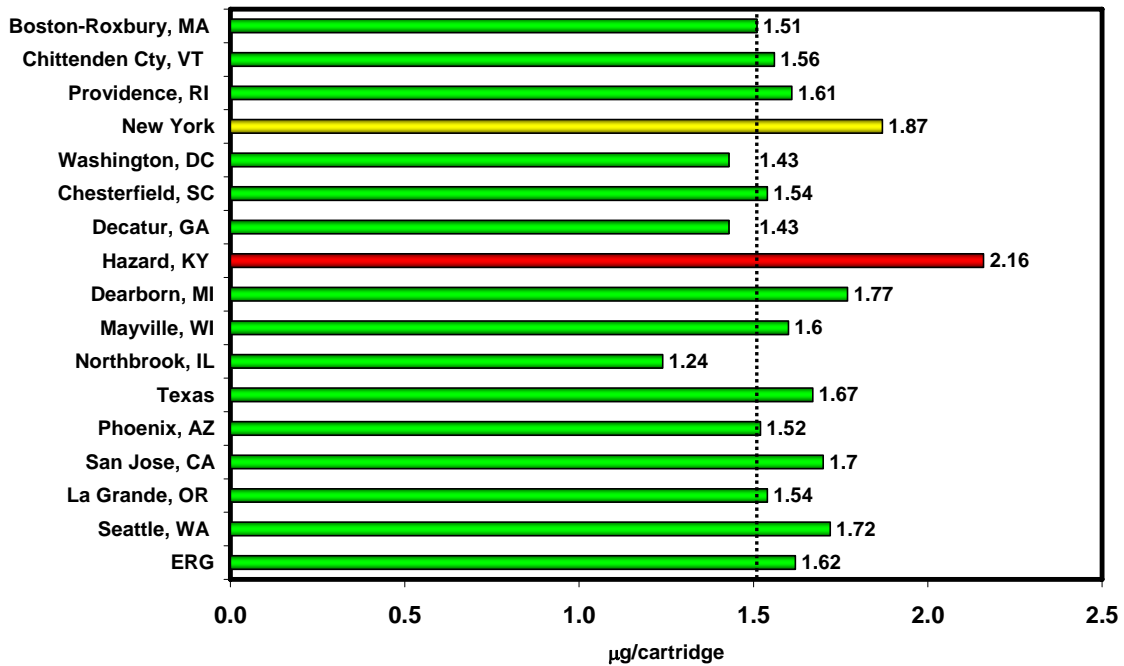
Figure 32.   200401-C laboratory bias data for acetaldehyde.
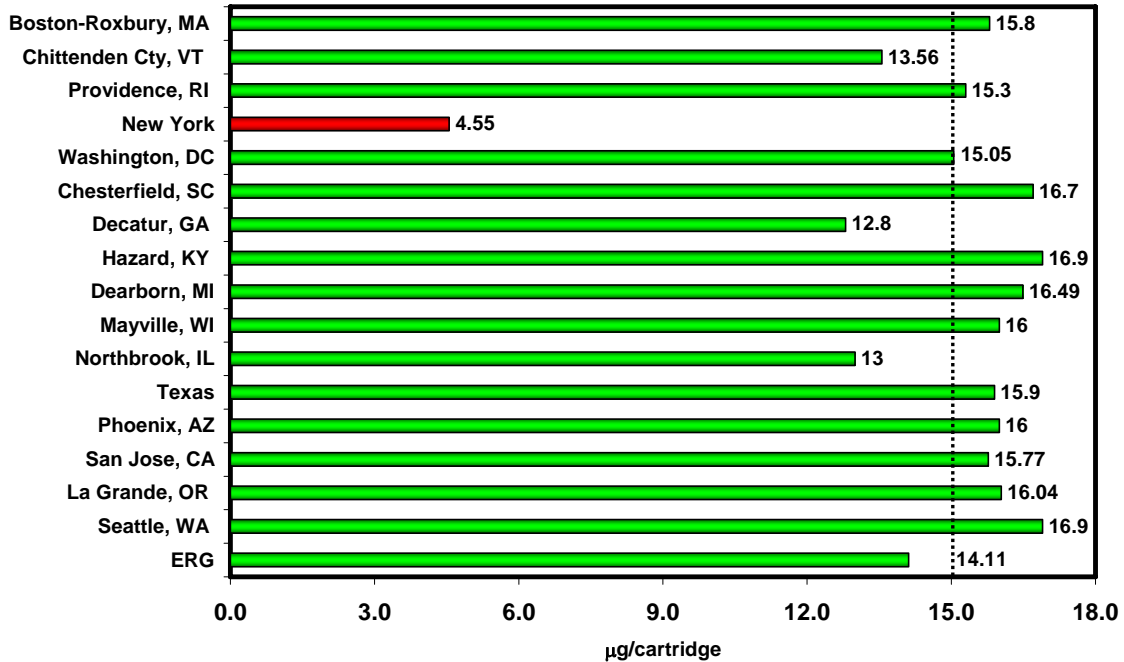
Figure 33.   200402-C laboratory bias data for acetaldehyde.

For the metals, the 200401-M PE samples consisted of Teflon filters spiked using an air stream containing aerosolized solutions of salts of seven target metals: arsenic, beryllium, cadmium, lead, manganese, nickel, and chromium. An independent laboratory under subcontract to Alion determined the filter concentrations (the stated values). Because many of the NATTS laboratories do not routinely analyze Teflon filters, only eight laboratories participated. Furthermore, ERG was sent a sample from a different lot that contained only arsenic (at a different spike concentration than the filters forwarded to the other laboratories), beryllium, and chromium. Results are summarized by compound in Figures 34 through 40.
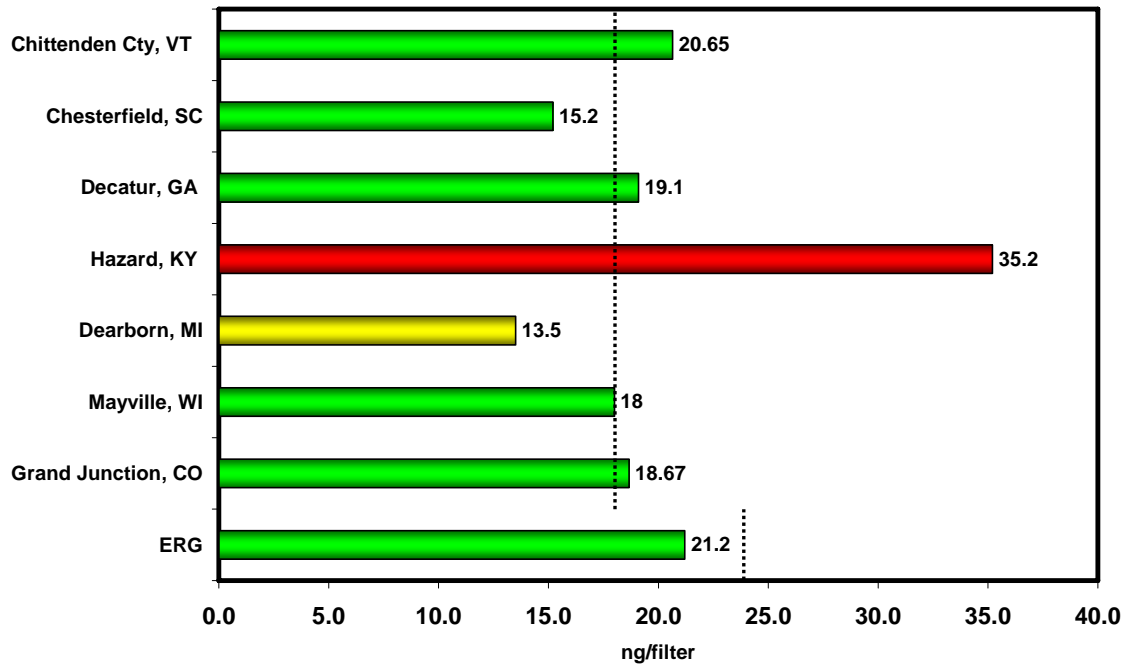
Figure 34.   200401-M laboratory bias data for arsenic.
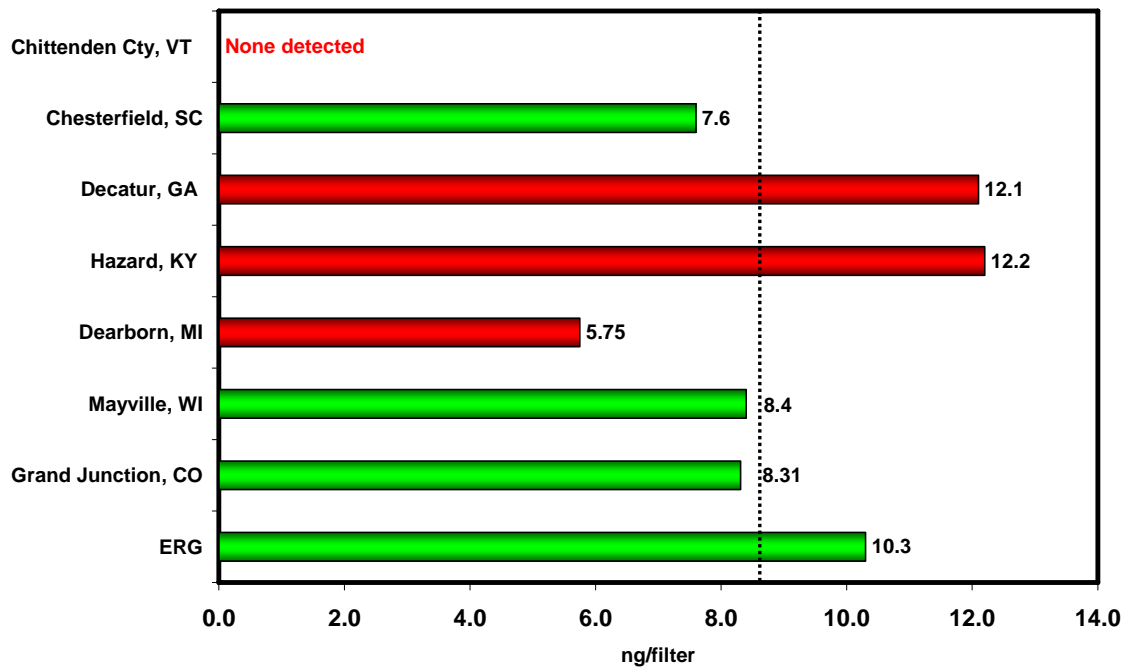
Figure 35.   200401-M laboratory bias data for beryllium.
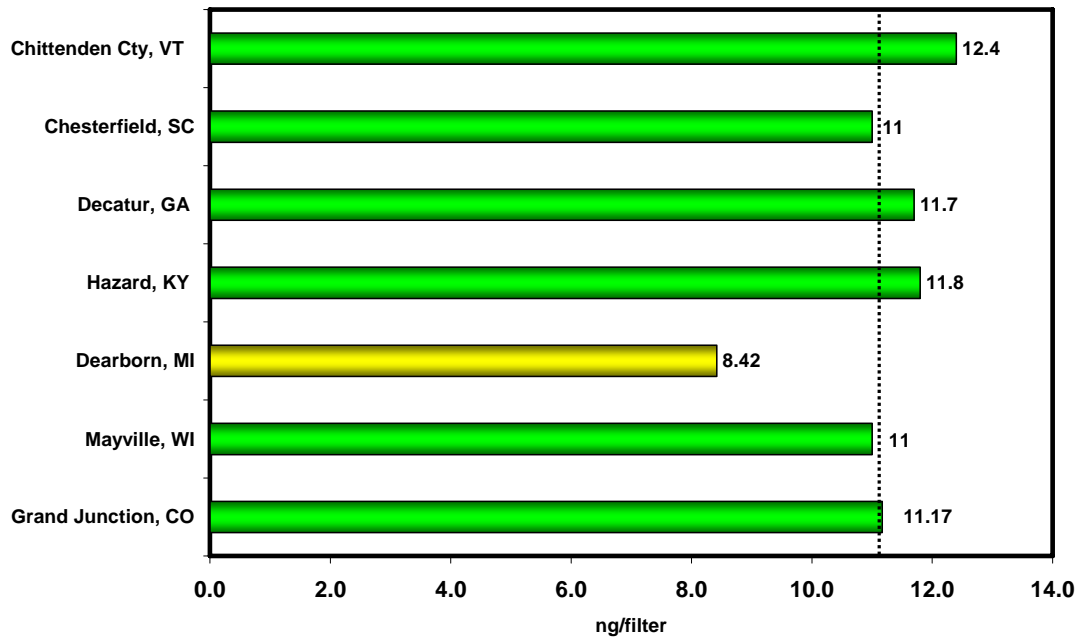
Figure 36.   200401-M laboratory bias data for cadmium.
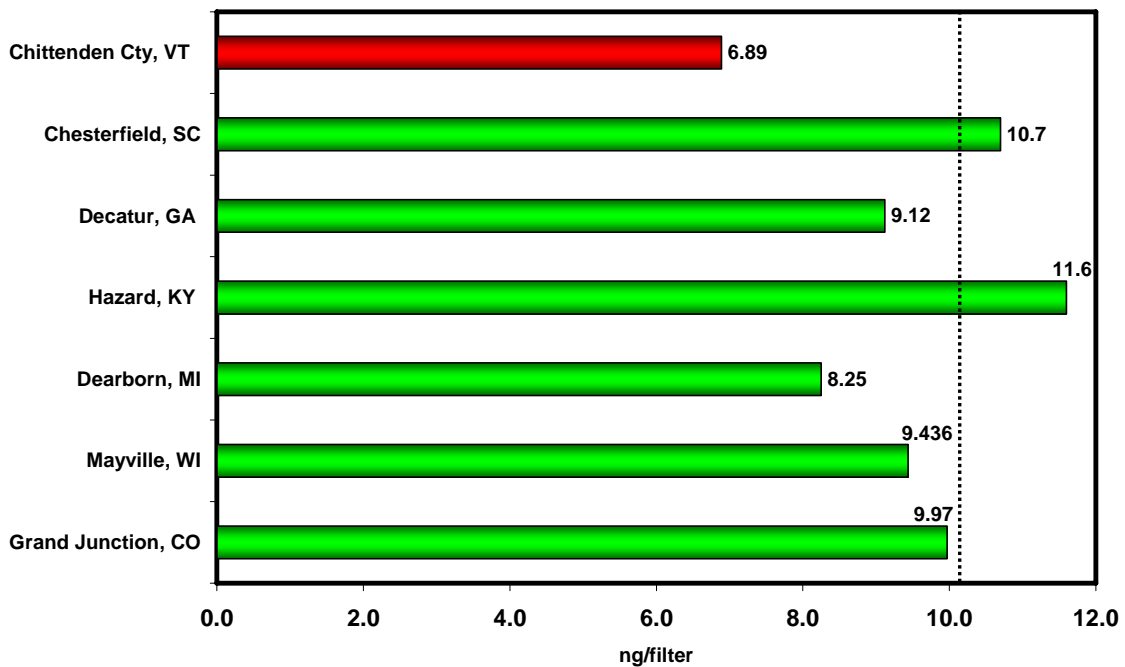
Figure 37.   200401-M laboratory bias data for lead.
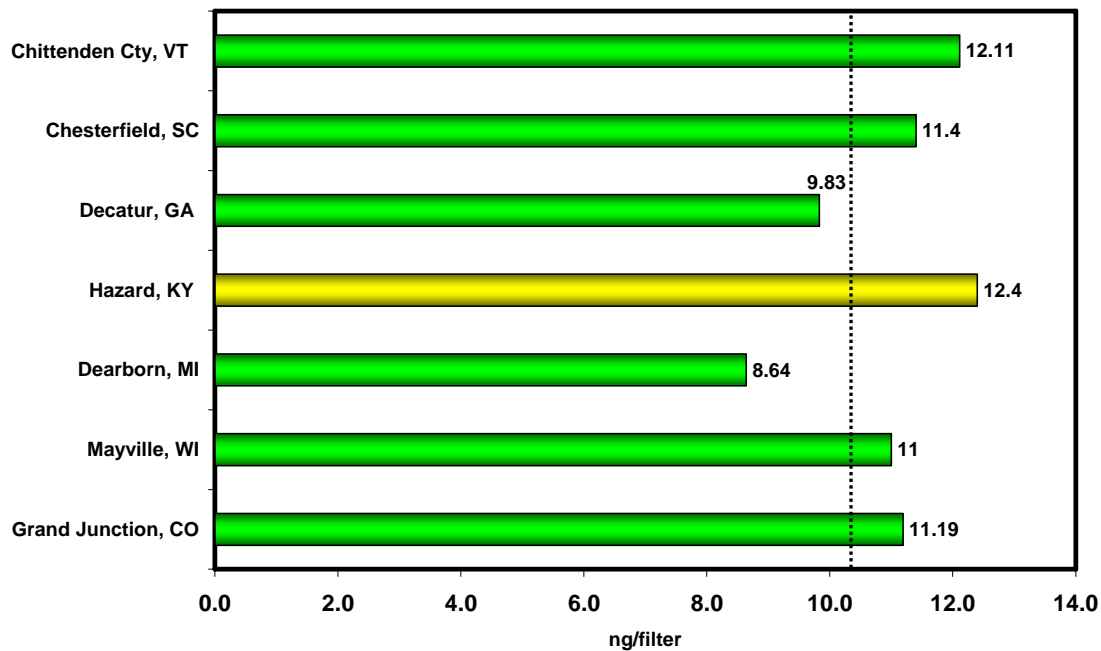
Figure 38.   200401-M laboratory bias data for manganese.
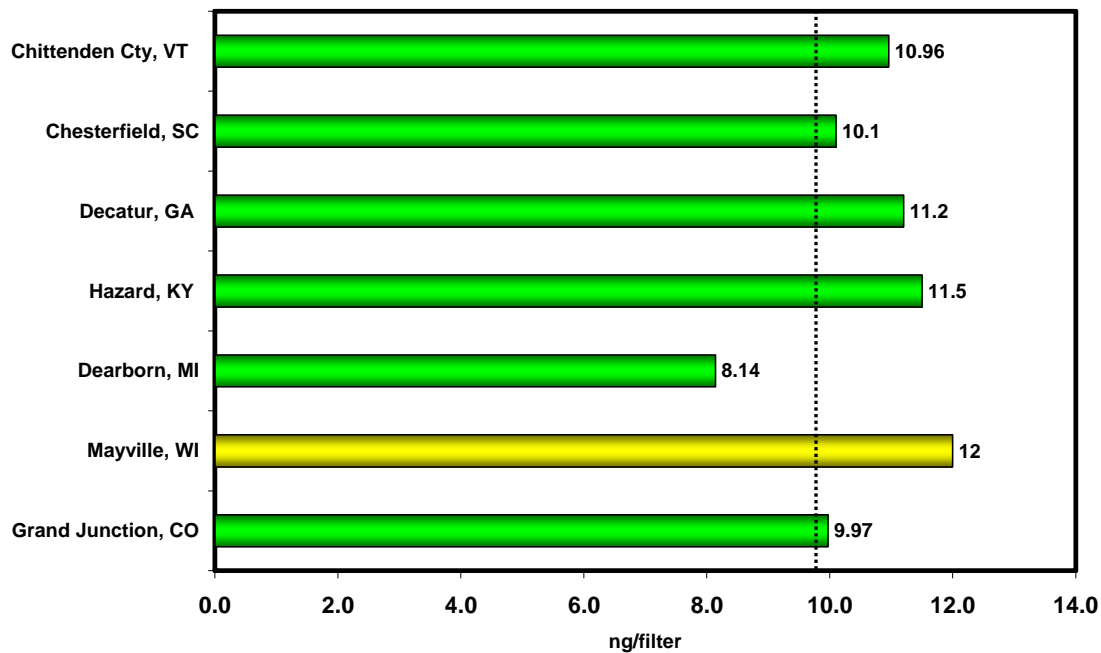
Figure 39.   200401-M laboratory bias data for nickel.
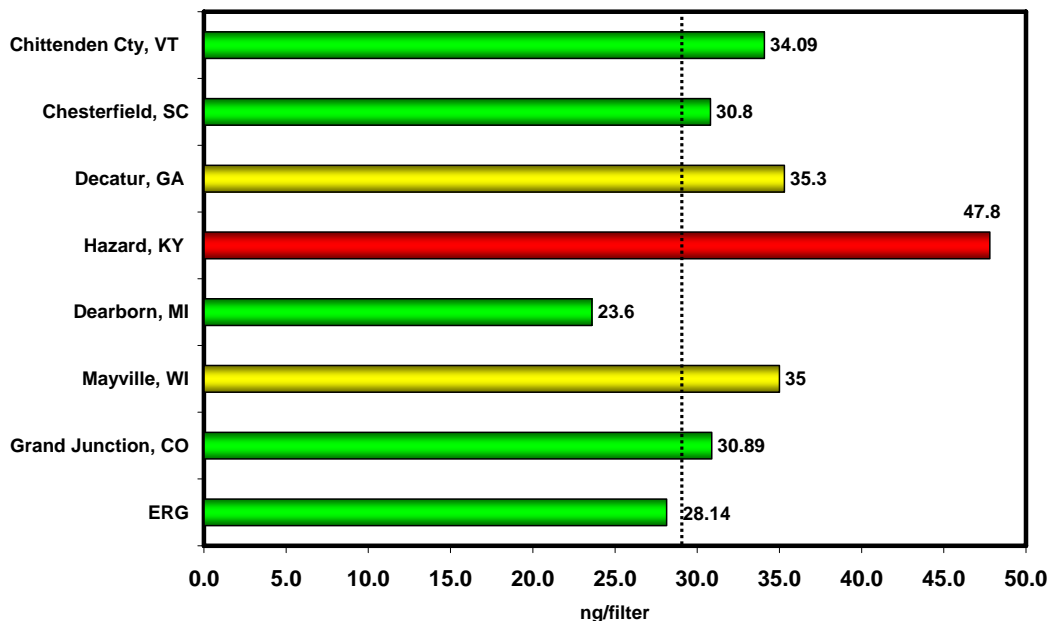
Figure 40.   200401-M laboratory bias data for chromium.

A summary of the performance evaluation results for calendar year 2004 is shown in Table 6. The total number of analyses summarized in this work, across all participating laboratories and for all audit compounds, is given in the second column. Since 17 laboratories participated in the 200401-C study, 34 analyses were performed. An analysis is still counted in column two even if a given laboratory intentionally did not attempt to identify and quantify a particular compound. Such was the case for 200402-V in which 1,2-dibromoethane was present in the volatiles mixture. The Wisconsin State Laboratory of Hygiene made no attempt to analyze for this compound, but, for the purpose of summary, it is still counted as an analysis.

As can be seen in Table 6, the best overall PE results were obtained for the carbonyls, with 91 percent of the laboratory results for both studies being reported within 20 percent of the stated values. It appears that VOC and metals analyses are comparatively more difficult: only 70 percent of the analyses performed during the 200401-V study were within the 20 percent bias range. Furthermore, 17 percent of the VOC analyses showed bias greater than 25 percent, the highest value for all five 2004 PE studies. The compound 1,3-butadiene (Figure 9) appears to be particularly difficult to quantify. Overall improvement was demonstrated for the second set VOC PE samples, with the number of analyses within 20 percent bias increasing to 77 percent and the percentage most out of tolerance dropped to 10 percent. However, 1,3-butadiene remained problematic (Figure 17). For the metals, 75 percent of the laboratory results were within 20 percent of the stated values. In addition, an equal number of metals analyses had absolute biases beyond 25 percent of the stated value. Beryllium proved to be the most difficult (Figure 35).

Table 6.   Summary of laboratory bias results by quarter for all three sample types.

Audit	Total Analyses	Bias < 20 % N	Bias < 20 % %	20 < Bias < 25 % N	20 < Bias < 25 % %	Bias > 25 % N	Bias > 25 % %	Not Reported N	Not Reported %
200401-V	98	69	70	10	10	17	17	2	2
200402-V	154	118	77	14	9	15	10	7	5
200401-C	34	31	91	2	6	1	3	0	0
200402-C	34	31	91	0	0	3	9	0	0
200401-M	52	39	75	6	12	6	12	1	2
Percentages may not add to 100 percent due to rounding.									

2.3.   Field Bias Data from Flow Audits Performed During IPAs

Ten NATTS field sites were audited during calendar year 2004. The field audits consisted of two parts: a Technical Systems Audit (TSA) and an Instrument Performance Audit (IPA). The TSA is defined as a thorough, on-site, qualitative audit of facilities and it focuses on the sampling aspects of the three targeted measurement methods: VOCs, carbonyls, and PM_{10} metals. The IPA maintains its focus on the sampling that occurs at the NATTS station. During the IPA portion of the site visit, a site assessment is conducted in which photos are taken, a sketch of the facility is drawn, and siting criteria are confirmed. Moreover, flow rates through all three sampler types are confirmed using certified flow, temperature, and pressure instruments.

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

$$\% \, Difference = \frac{Fs_C - Fa_C}{Fa_C} \cdot 100 \qquad \text{(Eq. 2.3.1)}$$

The results from the flow audits conducted at ten NATTS sites during calendar year 2004 are shown in Table 7. Sites are given by their identifiers; see Table 1 for a cross-reference to the site AQS codes. The sampling techniques are shown in column 2. The canister method signifies a VOC sampler; carbonyl indicates sampling onto cartridges for aldehydes, and PM_{10} represents filter sampling for PM_{10} metals. Every NATTS site is supposed to have at least one of each sampler type, which is designated as the primary sampler in column 3. If present, collocated samplers are also flow audited, and are designated as such in column 3. Canister and carbonyl samplers may have more than one flow channel in order to accommodate the collection of duplicate samples. If a NATTS site routinely collects a duplicate sample using a single sampler, but through a different flow channel, then this second flow channel was also subjected to a flow audit. PM_{10} samplers cannot have secondary flow channels and are, hence, marked with "NA"

(not applicable) in column 4. The percent difference (field bias) as defined above is given in column 5.

Table 7. **Flow audit results from 2004 Instrument Performance Audits.**

Site Identifier	Method	Monitor	Channel	% Difference
Boston-Roxbury, MA	PM_{10}	Primary	NA	0.4
Boston-Roxbury, MA	PM_{10}	Collocated	NA	2.1
Boston-Roxbury, MA	Canister	Primary	1	-14
Boston-Roxbury, MA	Carbonyl	Primary	1	-6.3
Boston-Roxbury, MA	Carbonyl	Primary	2	-4.9
Chittenden Cty, VT	PM_{10}	Primary	NA	0.2
Chittenden Cty, VT	Canister	Primary	1	-0.8
Chittenden Cty, VT	Carbonyl	Primary	1	-0.2
Providence, RI	PM_{10}	Primary	NA	-6.7
Providence, RI	Canister	Primary	1	-3.3
Providence, RI	Carbonyl	Primary	1	1.8
Providence, RI	Carbonyl	Primary	2	8.7
Bronx, NY	PM_{10}	Primary	NA	-19.3
Bronx, NY	PM_{10}	Collocated	NA	-11.7
Bronx, NY	Canister	Primary	1	2.3
Bronx, NY	Carbonyl	Primary	1	-6.8
Rochester, NY	Canister	Primary	1	-2.7
Rochester, NY	Carbonyl	Primary	1	-2.3
Washington, DC	PM_{10}	Primary	NA	-9.5
Washington, DC	Canister	Primary	1	-0.7
Washington, DC	Carbonyl	Primary	1	-7.6
Washington, DC	Carbonyl	Primary	2	-0.4
Decatur, GA	PM_{10}	Primary	NA	1.5
Decatur, GA	Canister	Primary	1	0.1
Decatur, GA	Carbonyl	Primary	1	-0.8
Hazard, KY	PM_{10}	Primary	NA	0.1
Hazard, KY	Canister	Primary	1	10.5
Hazard, KY	Canister	Primary	2	2.7
Hazard, KY	Carbonyl	Primary	1	-9
Hazard, KY	Carbonyl	Primary	2	-9.7
Hillsborough Cty, Tampa, FL	PM_{10}	Primary	NA	6.4
Hillsborough Cty, Tampa, FL	PM_{10}	Collocated	NA	12.7
Hillsborough Cty, Tampa, FL	Carbonyl	Primary	1	-9.1
Hillsborough Cty, Tampa, FL	Carbonyl	Primary	2	-2.9
Pinellas Cty, Tampa, FL	PM_{10}	Primary	NA	1.2
Pinellas Cty, Tampa, FL	Carbonyl	Primary	1	4.7
Pinellas Cty, Tampa, FL	Carbonyl	Primary	2	-7.9

A summary of the IPA flow results is given in Figure 41. On the ordinate is given the absolute percent difference in flow rate (the absolute value of the field bias in Table 7, column 5). All 16 of the carbonyl flow rates provided by the field sampling crew were within ± 10 percent of the audit flow rate. Seven of the nine canister sampler flow audits were within ± 5 percent, but two showed greater than 10 percent bias. Nine of the 12 metals sampler results are within ±10 percent, but three lay outside the 10 percent range, and one of these three was a 19 percent error. Overall, only ~14 percent of all the audits (5 out of 37) demonstrated a bias greater than 10 percent.
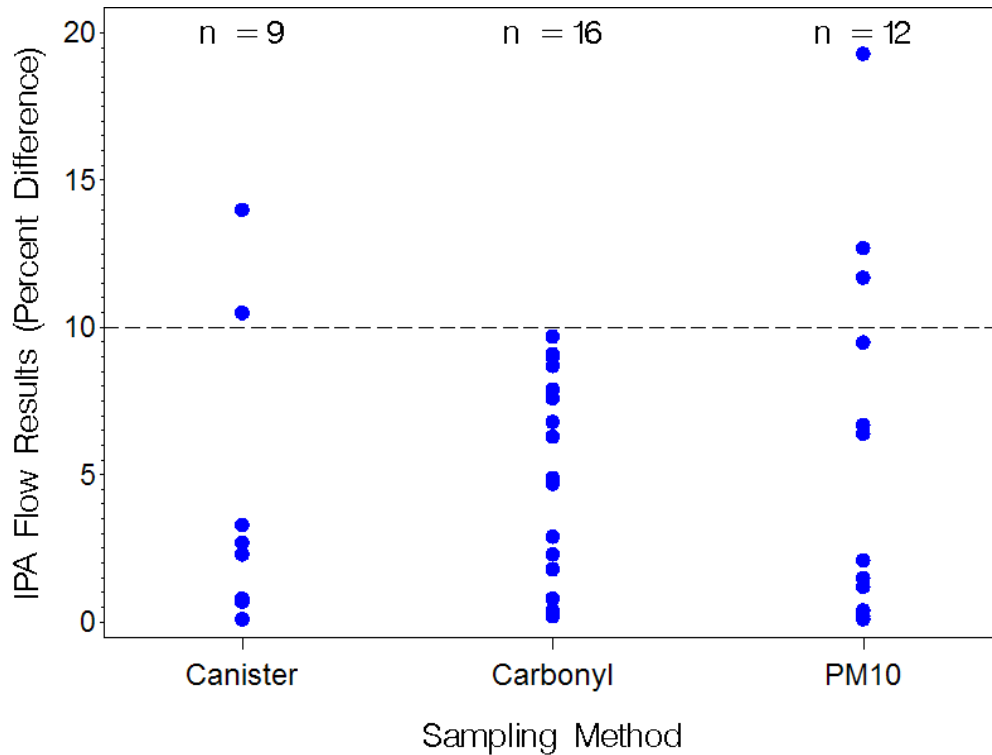
Figure 41. Summary of Instrument Performance Audit flow results sorted by sampling method. The number of observations is given by n.

Of the ten sites at which IPAs were conducted in CY 2004, relatively few are performing duplicate or collocated sampling. Eight of the ten sites collect only a single canister per sampling moment: Hazard, Kentucky, collects duplicates and Pinellas County, Tampa, Florida, performs collocated collection. (Due to technical considerations, flow audits could not be performed on the canister samplers in either Hillsborough County or Pinellas County in Tampa, Florida.) Six of the ten sites (Boston-Roxbury, Massachusetts; Providence, Rhode Island; Washington, D.C.; Hazard, Kentucky; Hillsborough County and Pinellas County, Tampa, Florida) are performing duplicate sampling using secondary channels on their carbonyl samplers. However, only three sites are performing collocated sampling for PM_{10} metals (Boston-Roxbury, Massachusetts; Bronx, New York; and Hillsborough County, Tampa, Florida).

2.4   Method Detection Limit (MDL) Data

Method detection limit data were requested from the points-of-contact at all 23 NATTS field sites for all three sample types: VOCs, carbonyls, and metals. Different information was requested depending on the sample type, but the fundamental objective for each was the same; i.e., to calculate the overall sampling and analytical MDL for each of the 23 HAPS listed in Table 2. Mainly through a series of e-mail exchanges with NATTS station managers and analysts, as well as with QA personnel at laboratories affiliated with the NATTS sites, the required information was gathered, scrutinized for obvious errors, overall MDLs were calculated, converted to the appropriate units, and tabulated. The results are shown in Table 8. The marker "NA" indicates where MDL information was unavailable because laboratories are not presently analyzing for a given compound whereas "NR" indicates that no data were received.

Table 8. Method detection limits (MDLs) by site for the year 2004 for the 23 HAPs. HAPs are given by number (see Table 2 for cross-reference). MDLs for compounds 1-16 and 17-23 are in $\mu g/m^3$ and ng/m^3, respectively.

Site Identifier	1	2	3	4	5	6	7	8	9	10	11	12
Boston-Roxbury, MA	1.4E-02	2.8E-02	5.8E-02	3.0E-02	4.9E-02	6.3E-02	3.8E-02	4.5E-02	1.8E-01	3.6E-02	4.9E-02	2.4E-02
Chittenden Cty, VT	3.1E-01	2.2E-01	5.1E-01	2.8E-01	6.7E-01	5.2E-01	4.3E-01	2.4E-01	4.7E-01	6.4E-01	4.1E-01	2.3E-01
Providence, RI	1.4E-02	2.8E-02	5.8E-02	3.0E-02	4.9E-02	6.3E-02	3.8E-02	4.5E-02	1.8E-01	3.6E-02	4.9E-02	2.4E-02
Bronx, NY	9.6E-02	8.8E-02	1.9E-01	1.5E-01	3.1E-01	1.8E-01	1.6E-01	6.9E-02	2.1E-01	2.0E-01	1.6E-01	1.3E-01
Rochester, NY	9.6E-02	8.8E-02	1.9E-01	1.5E-01	3.1E-01	1.8E-01	1.6E-01	6.9E-02	2.1E-01	2.0E-01	1.6E-01	1.3E-01
Washington, DC	3.2E-02	3.3E-01	2.5E-01	1.5E-01	2.3E-01	1.4E-01	8.1E-02	1.7E-01	1.4E-01	1.4E-01	1.1E-01	1.0E-01
Chesterfield, SC	3.0E-01	2.0E-01	6.0E-01	5.0E-01	8.0E-01	5.0E-01	4.0E-01	4.0E-01	7.0E-01	7.0E-01	5.0E-01	3.0E-01
Decatur, GA	8.0E-01	5.5E-01	1.6E+00	1.2E+00	1.9E+00	1.2E+00	1.0E+00	6.9E+00	1.7E+00	1.7E+00	1.3E+00	6.4E-01
Hazard, KY	3.2E+00	2.2E+00	6.2E+00	4.8E+00	7.6E+00	4.6E+00	4.0E+00	3.4E+00	6.8E+00	6.8E+00	5.4E+00	2.6E+00
Hillsbrgh Cty, Tampa, FL	6.0E-02	7.0E-02	1.3E-01	1.0E-01	1.5E-01	9.0E-02	2.0E-01	1.0E-01	2.1E-01	1.4E-01	1.6E-01	8.0E-02
Pinellas Cty, Tampa, FL	6.0E-02	7.0E-02	1.3E-01	1.0E-01	1.5E-01	9.0E-02	2.0E-01	1.0E-01	2.1E-01	1.4E-01	1.6E-01	8.0E-02
Dearborn, MI	1.1E-01	7.1E-02	1.3E+00	2.3E-01	7.7E-01	3.0E-01	4.2E-01	9.4E-01	3.2E-01	8.1E-01	5.8E-01	6.2E-02
Mayville, WI	1.6E-01	2.2E-01	3.1E-01	2.4E-01	NA	4.6E-01	4.0E-01	3.5E-01	6.9E-01	3.4E-01	5.4E-01	2.6E-01
Northbrook, IL	1.6E-01	1.3E-01	3.9E-01	2.1E-01	4.0E-01	3.3E-01	2.6E-01	2.6E-01	3.6E-01	3.4E-01	2.5E-01	1.1E-01
Deer Park, TX	9.9E-01	6.0E-01	2.5E+00	1.0E+00	1.5E+00	7.9E-01	1.4E+00	4.9E-01	1.4E+00	1.6E+00	1.6E+00	4.3E-01
Harrison County, TX	9.9E-01	6.0E-01	2.5E+00	1.0E+00	1.5E+00	7.9E-01	1.4E+00	4.9E-01	1.4E+00	1.6E+00	1.6E+00	4.3E-01
St. Louis, MO	1.6E-01	1.3E-01	3.9E-01	2.1E-01	4.0E-01	3.3E-01	2.6E-01	2.6E-01	3.6E-01	3.4E-01	2.5E-01	1.1E-01
Bountiful, UT	1.6E-01	1.3E-01	3.9E-01	2.1E-01	4.0E-01	3.3E-01	2.6E-01	2.6E-01	3.6E-01	3.4E-01	2.5E-01	1.1E-01
Grand Junction, CO	1.6E-01	1.3E-01	3.9E-01	2.1E-01	4.0E-01	3.3E-01	2.6E-01	2.6E-01	3.6E-01	3.4E-01	2.5E-01	1.1E-01
Phoenix, AZ	6.4E-02	4.4E-02	1.3E-01	9.8E-02	1.5E-01	9.2E-02	8.1E-02	6.9E-02	1.4E-01	1.4E-01	1.1E-01	5.1E-02
San Jose, CA	1.6E-01	8.8E-02	1.3E-01	9.8E-02	7.7E-02	NA	8.1E-01	3.5E-01	NA	6.8E-02	1.1E-01	NA
La Grande, OR	1.3E-01	1.1E-01	2.8E-01	2.3E-01	2.6E-01	2.0E-01	1.6E-01	1.4E-01	2.8E-01	3.0E-01	2.5E-01	1.0E-01
Seattle, WA	3.0E-02	4.0E-02	6.0E-02	1.0E-01	3.8E-01	1.8E-01	2.0E-01	2.8E-01	3.4E-01	7.0E-02	5.0E-02	1.3E-01

Table 8.   (Continued)

Site Identifier	13	14	15	16	17	18	19	20	21	22	23
Boston-Roxbury, MA	3.7E-02	6.7E-02	4.9E-02	7.2E-02	2.0E-02	2.8E-02	2.1E-02	1.5E+00	2.0E-01	1.8E-01	2.1E-01
Chittenden Cty, VT	4.1E-01	4.2E-01	2.0E-02	1.4E-02	2.0E-01	3.0E-02	1.4E-01	8.0E-02	3.4E-01	NA	8.5E-01
Providence, RI	3.7E-02	6.7E-02	4.9E-02	1.1E-01	2.3E+00	1.1E+00	5.5E-01	1.1E+00	1.1E+00	NA	1.1E+00
Bronx, NY	1.8E-01	1.8E-01	2.1E-02	3.2E-02	NR	NR	NR	NR	NR	NR	NR
Rochester, NY	1.8E-01	1.8E-01	2.1E-02	3.2E-02	NR	NR	NR	NR	NR	NR	NR
Washington, DC	1.4E-01	2.3E-01	4.1E-02	3.2E-02	1.2E+00	3.4E-01	3.5E-01	1.0E+00	8.7E-01	N/A	1.4E+00
Chesterfield, SC	5.0E-01	5.0E-01	1.6E-01	1.6E-01	1.4E+00	2.8E-01	1.4E-02	5.7E-02	5.7E-02	1.1E-01	1.4E+00
Decatur, GA	1.1E+00	1.1E+00	1.1E+00	1.1E+00	5.5E-01	6.1E-02	3.1E-02	1.2E-01	1.8E-01	NA	2.5E-01
Hazard, KY	4.6E+00	4.6E+00	5.0E-02	6.8E-02	1.7E+00	8.3E-01	8.3E-01	8.3E-01	8.3E-01	NA	8.3E-01
Hillsbrgh Cty, Tampa, FL	9.0E-02	9.0E-02	2.1E-02	2.6E-02	2.0E+00	3.6E-02	5.9E-02	7.8E-01	8.3E-02	NA	3.0E+00
Pinellas Cty, Tampa, FL	9.0E-02	9.0E-02	1.9E-02	2.3E-02	1.9E+00	3.5E-02	5.8E-02	7.7E-01	8.2E-02	NA	2.9E+00
Dearborn, MI	2.8E-01	3.0E-01	3.3E-02	8.0E-02	2.0E-03	3.9E-02	4.0E-03	2.4E-02	2.9E-01	NA	1.9E-01
Mayville, WI	4.5E-01	4.5E-01	1.3E-01	1.3E-01	5.2E-02	NA	1.2E-02	5.5E-02	7.7E-02	NA	NA
Northbrook, IL	2.2E-01	2.3E-01	7.4E-02	7.4E-02	4.6E-02	2.7E-02	1.1E-02	4.9E-02	6.8E-02	1.4E-02	2.7E-01
Deer Park, TX	9.1E-01	9.1E-01	7.4E-02	1.4E-01	8.6E-01	NA	NA	NA	NA	NA	NA
Harrison County, TX	9.1E-01	9.1E-01	7.4E-02	1.4E-01	8.6E-01	NA	NA	NA	NA	NA	NA
St. Louis, MO	2.2E-01	2.3E-01	1.9E-02	2.3E-02	2.0E-02	2.7E-02	2.1E-02	1.5E+00	1.9E-01	1.7E-01	2.0E-01
Bountiful, UT	2.2E-01	2.3E-01	2.3E-02	2.8E-02	1.4E-01	9.3E-02	1.0E-01	4.3E-01	1.2E-01	3.3E-01	9.6E-01
Grand Junction, CO	2.2E-01	2.3E-01	1.9E-02	2.4E-02	1.4E-01	1.6E-01	7.0E-02	1.2E-01	1.9E-01	NA	1.8E-01
Phoenix, AZ	9.1E-02	9.1E-02	1.2E-01	1.8E-01	NA	NA	NA	NA	NA	NA	NA
San Jose, CA	4.5E-01	4.5E-01	9.9E-02	9.9E-02	3.8E+00	NA	9.8E+00	8.9E+00	2.8E+00	6.8E+00	1.6E+00
La Grande, OR	1.9E-01	1.8E-01	2.5E-02	3.4E-02	1.8E-02	3.1E-03	1.2E-02	1.2E-01	4.9E-02	NA	1.2E-01
Seattle, WA	1.8E-01	1.8E-01	1.9E-02	1.6E-02	7.6E-03	2.1E-03	1.0E-03	6.9E-02	9.1E-02	NA	8.4E-02

For all three sample types, the analytical MDLs for the 23 compounds of interest were requested. Starting with these values, the overall sampling and analytical MDLs could be calculated given sufficient additional information depending on the sampler type. However, some laboratories simply provided overall sampling and analytical MDLs without further information. In many of these cases, the additional information described below was requested and received as well so that a consistent dataset was gathered and calculations could be verified. Shown in Table 9 are the laboratories that performed the analyses of the different sample types for the 23 NATTS sites for calendar year 2004.

In Table 10, the abbreviations used in Table 9 are given along with the full names of the laboratories.

Table 9. **Laboratories performing analyses for the three different compound types for each of the NATTS sites in 2004. (See Table 10 for abbreviation cross-reference.)**

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

Table 10.   Abbreviations and full names of laboratories performing analyses of NATTS samples.

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

For the VOCs, the amount that the canisters are diluted prior to analysis is required to calculate overall MDLs from analytical MDLs. Certain laboratories pressurize canisters with zero-grade nitrogen or air in preparation for analysis. However, others simply analyze canisters at subatmospheric pressure without further dilution. The overall sampling and analytical MDL is linearly proportional to the analytical MDL, where the constant of proportionality is the dilution factor. The dilution factor is calculated as follows: if the canister is received at a pressure of 10 psia (pounds per square inch absolute) and pressurized to 20 psia = 4.3 psig (pounds per square inch gauge), then the dilution factor is 20 psia/10 psia = 2. Hence, in this instance, the overall MDL is twice that of the analytical MDL.

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

For the carbonyls, in addition to the analytical MDL in units of mass per unit liquid volume, knowledge of three other parameters is required in order to determine overall MDLs. The first is the extraction volume, which is the total volume of liquid solvent used to extract the carbonyls from the sampling cartridge. The second is the average sampling time, which for the NATTS program should always be approximately 24 hours = 1,440 minutes. The final datum needed is the average volumetric flow rate through the carbonyl cartridge, preferably corrected to the standard conditions of 25 C, 1 atm, or with the average conditions of temperature and pressure reported so that correction can be made to standard conditions. In as many instances as possible, the flow was either reported at or corrected to standard conditions. If A_{MDL} is a compound-specific analytical MDL in μg/mL, V_E the extraction volume in mL, t the average sampling time in minutes, and F is the average volumetric flow rate through the carbonyl cartridge in m³/min, then

$$O_{MDL} = \frac{A_{MDL} \cdot V_E}{t \cdot F}$$
(Eq. 2.4.1)

where O_{MDL} is the compound-specific overall MDL in μg/m³.

Calculation of the overall metals MDL is similar to Equation 2.4.1. Along with compound-specific analytical MDLs, four additional parameters are needed. As with the carbonyls, the average sampling time and typical average sampler flow rate are required. Specific to PM_{10} metals analysis, however, is that a certain fraction of the quartz fiber filter is cut and digested for analysis. Both the size of the filter fraction and the final volume of acid into which the filter is digested and metals ions diluted are required to calculate the overall MDL. If A_{MDL} is a compound-specific analytical MDL in ng/mL, V_D the digestion volume in mL, f the fraction of filter digested, t the average sampling time in minutes, and F the average volumetric flow rate through the metals sampler in m³/min, then

$$O_{MDL} = \frac{A_{MDL} \cdot V_D}{f \cdot t \cdot F}$$
(Eq. 2.4.2)

where O_{MDL} is the compound-specific overall MDL in ng/m³.

Of particular importance is to use the correct value of the filter fraction. The denominator should be that part of the filter that is actually covered with particulate matter. For instance, if after sampling the typical 8- x 10 -inch filter has a border 1 inch wide around the outer filter edge where no particulate matter was collected, then the total sampled area is 6 inches by 8 inches. Assuming that a 1- x 8-inch strip is cut from the filter (including the 1 inch border), this represents one-eighth of the sampled filter.

The box and whisker plots shown in Figures 42 and 43 depict graphically, by compound and taken across all laboratories, the overall MDLs for the organic compounds (VOCs and carbonyls) and the metals, respectively. Shown are the mean, median, interquartile range, overall range, and location of any data outliers (data points that lie further than 1.5 times the interquartile range from the upper or lower quartile). The ordinate is the logarithm of the MDL.

See Table 2 for the cross-reference between compound number, name, and AQS compound code.

Across all laboratories, the mean and median MDL for all 14 VOCs fall between 0.1 to 1 $\mu g/m^3$. The mean and median MDLs for formaldehyde and acetaldehyde lie between 0.03 to 0.1 $\mu g/m^3$. Across all the laboratories for the seven metals of interest, more scatter is evident in the data, and the mean and median metals MDLs vary from 0.03 to 1 ng/m^3.

Although referred to as overall sampling and analyses MDLs, the values tabulated here are actually theoretical MDL values based on a calculation using the analytical MDLs and dilution factors (for VOCs, if applicable), other analysis parameters (extraction or digestion volumes), and average sampler flow rates. Determining actual MDLs is a much more involved, difficult, and expensive process that requires challenging a sampler with a known amount of gas-phase analyte followed by extraction/digestion (if appropriate), and instrumental analysis.
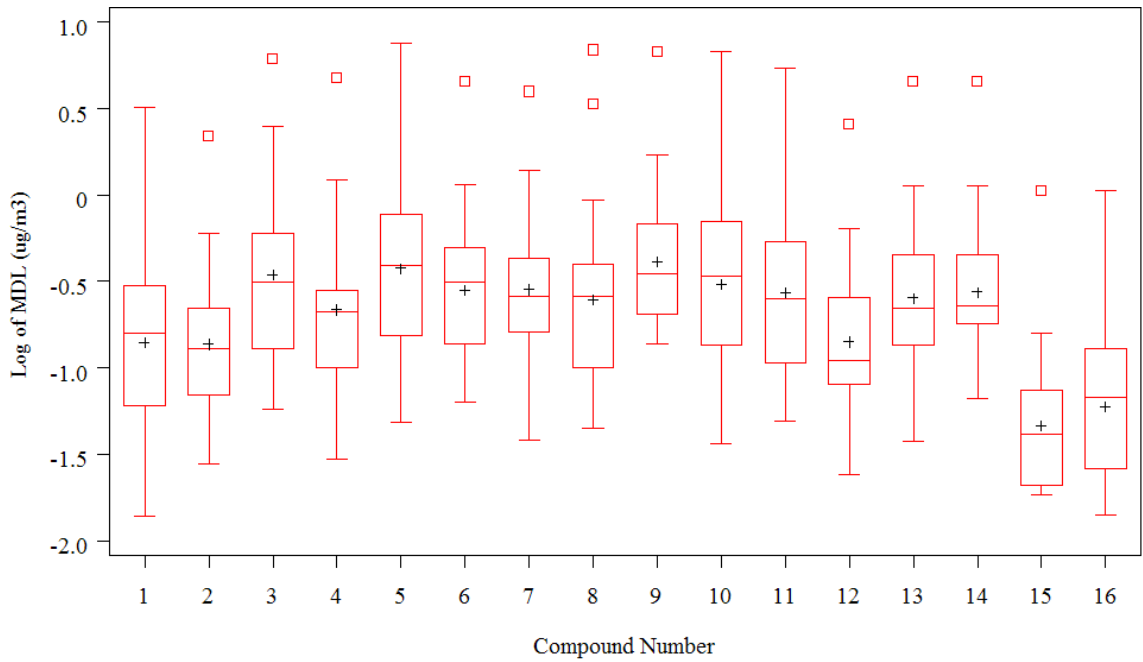
Figure 42. Box and whisker plot of the VOC and carbonyl MDLs across all the NATTS sites. (See Table 8 for the raw data.)
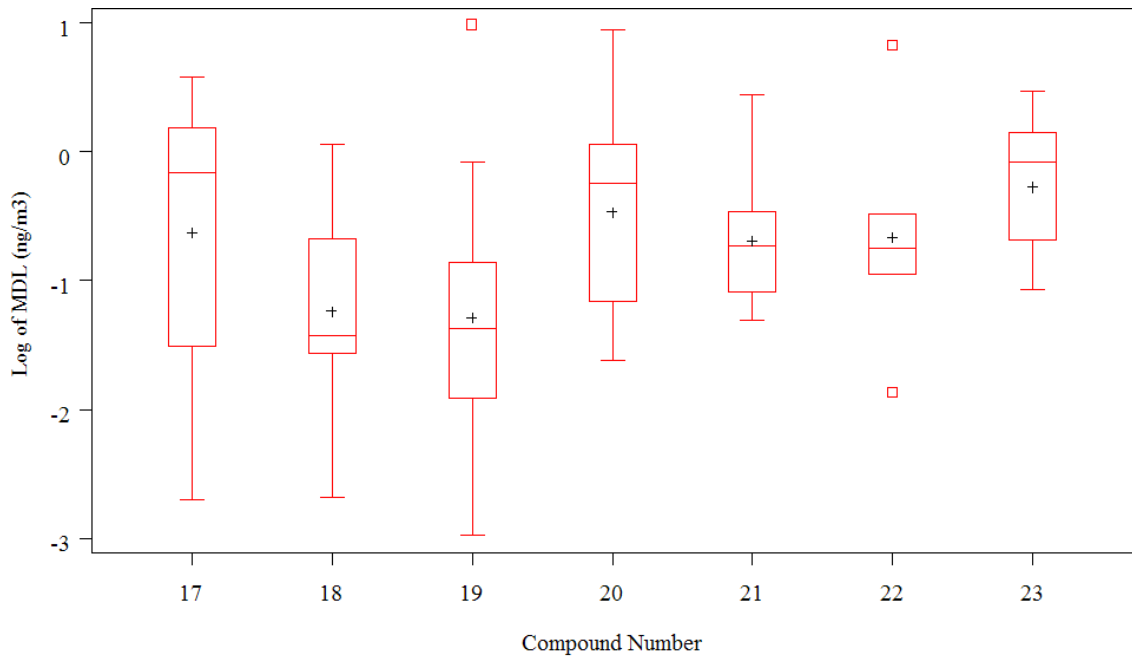
Figure 43. Box and whisker plot of the metals MDLs across all of the NATTS sites. (See Table 8 for the raw data.)

3.0 SUMMARY

This work summarizes the activities of the Quality System for the National Air Toxics Trends Station (NATTS) network for calendar year 2004. For the sites with data reported in the AQS database, the completeness of the dataset for the four HAPs of interest — benzene, 1,3-butadiene, formaldehyde, and arsenic — ranges between 78 and 80 percent (mean) and 90 and 95 percent (median). Precision data available in AQS varied widely by compound and by site. However, the most important finding was that very little precision data, either for replicate analyses of a single sample or for analyses of collocated sampling, were available in AQS, as data were only available for seven of the 23 stations. The laboratory bias data showed that the analytical laboratories performed the best with the carbonyl cartridges. The laboratories' performance improved for the VOCs from PE audit 1 to 2, but room for further improvement still exists for both the VOCs and metals. The flow audit checks showed that only five of the 37 stated site flows were greater than 10 percent different than the measured audit flows, with the carbonyl samplers performing the best of the three sampler types. Method detection limit data demonstrated that, on average, most laboratories perform fairly similarly and most sites employ generally similar techniques with regard to flow rates through the carbonyl and metals samplers. However, the range of values shows that a considerable interlaboratory and intersite variation does exist.

Appendix A:

Box and Whisker Plots of Laboratory Bias Data

Appendix A: Box and Whisker Plots of Laboratory Bias Data

Shown in this Appendix are box and whisker plots of the laboratory bias data given in Section 2.2. The plots are presented by compound in the order given in Table 1. The "+" symbols indicate the mean percent bias for each compound and the horizontal line "—" in the box represents the median. The upper and lower ends of the boxes represent the upper and lower quartiles; thus, the height of the box is the interquartile range. The upper whisker shows the maximum percent bias value less than the sum of the upper quartile value plus 1.5 times the interquartile range. Similarly, the lower whisker depicts the minimum percent bias value above the lower quartile minus 1.5 times the interquartile range. Outliers beyond 1.5 times the interquartile distance from the upper or lower quartile are given by red asterisks. If outliers lay beyond ± 100 percent difference, the point was not plotted but the location of the outlier is given as text on the figure. As the measurement quality objective for the laboratory bias data is that the bias be less than 25 percent, the ± 25 percent difference levels are marked on the plots with a dashed green line.
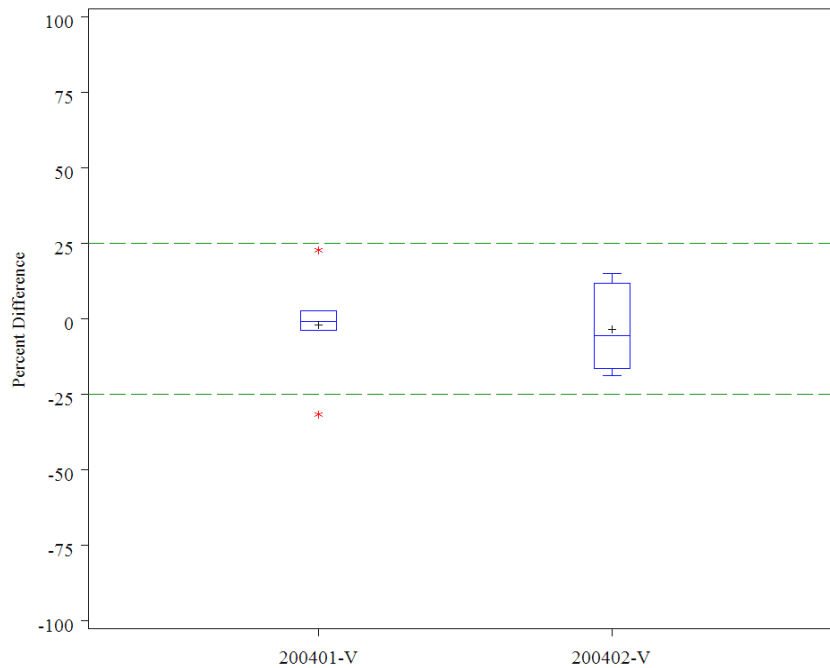
Figure A-1.   Box and whisker plot of laboratory bias data for benzene.
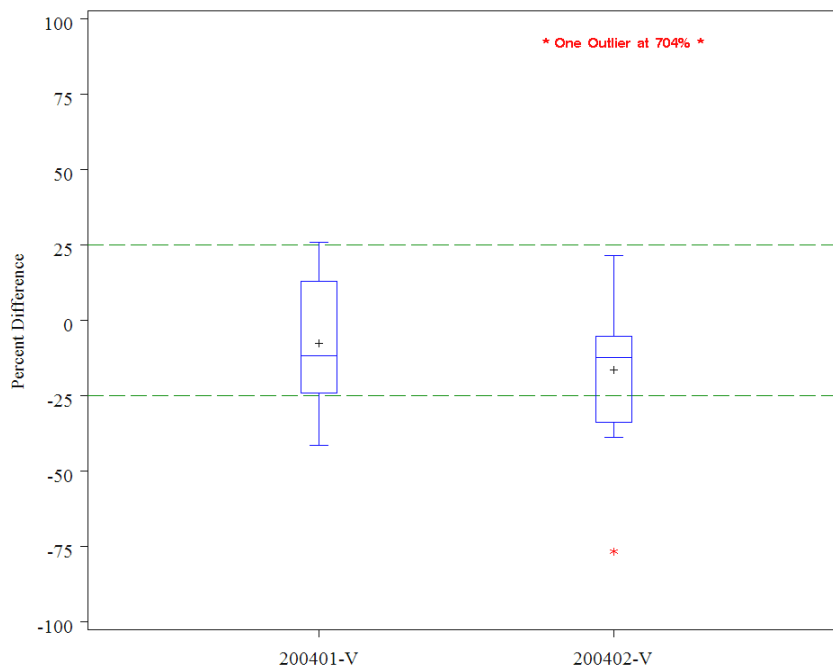
Figure A-2. Box and whisker plot of laboratory bias data for 1,3-butadiene.
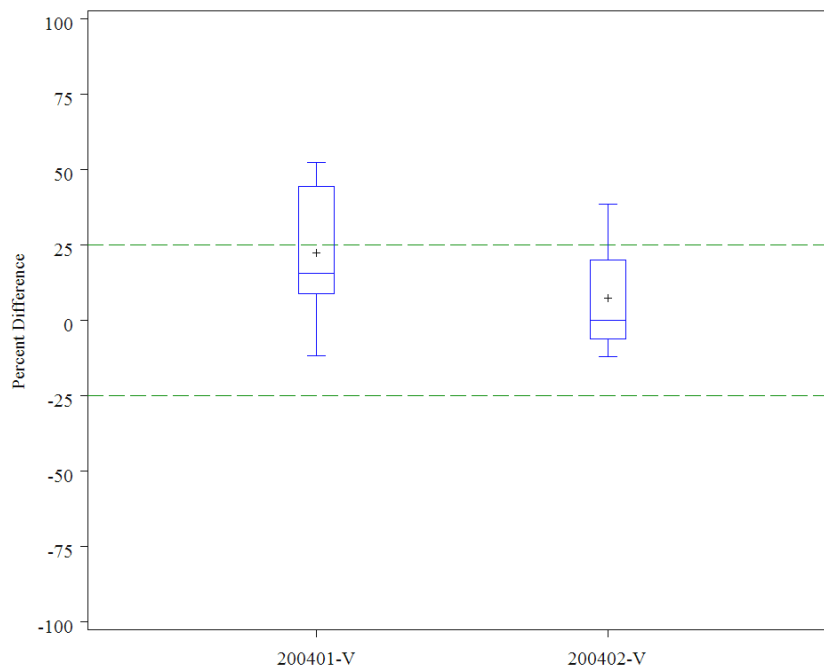
Figure A-3. Box and whisker plot of laboratory bias data for carbon tetrachloride.
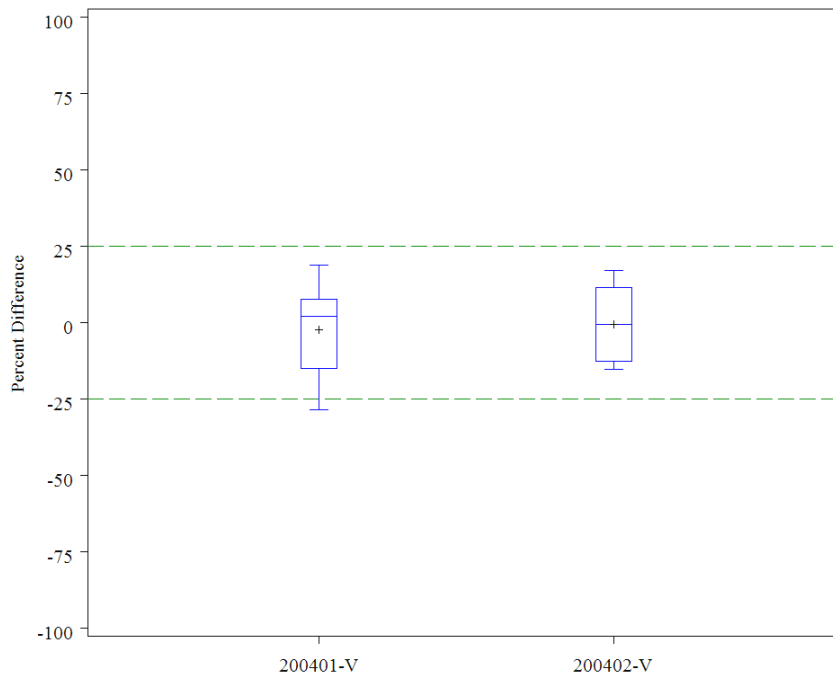
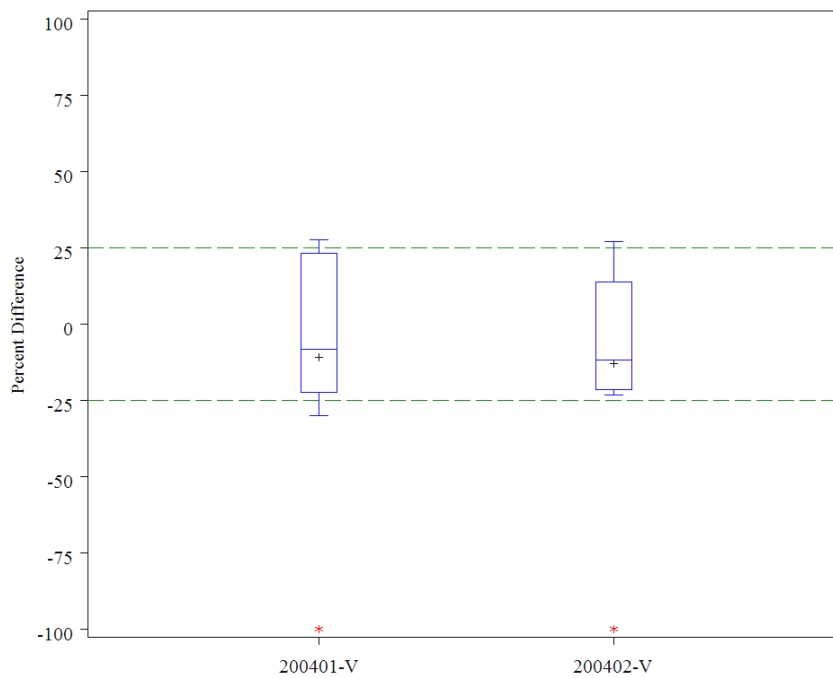**Figure A-4.** Box and whisker plot of laboratory bias data for chloroform.
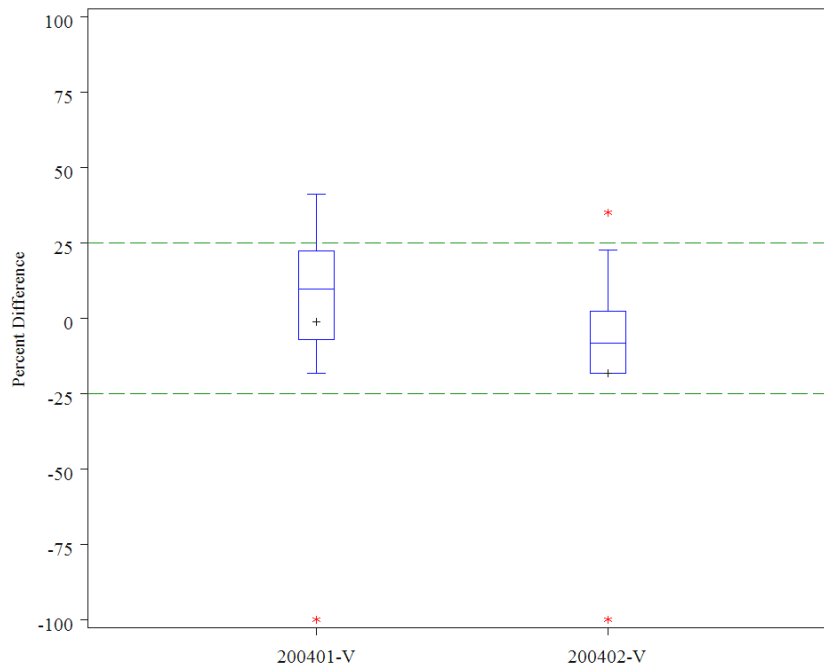
Figure A-5. Box and whisker plot of laboratory bias data for 1,2-dibromoethane.
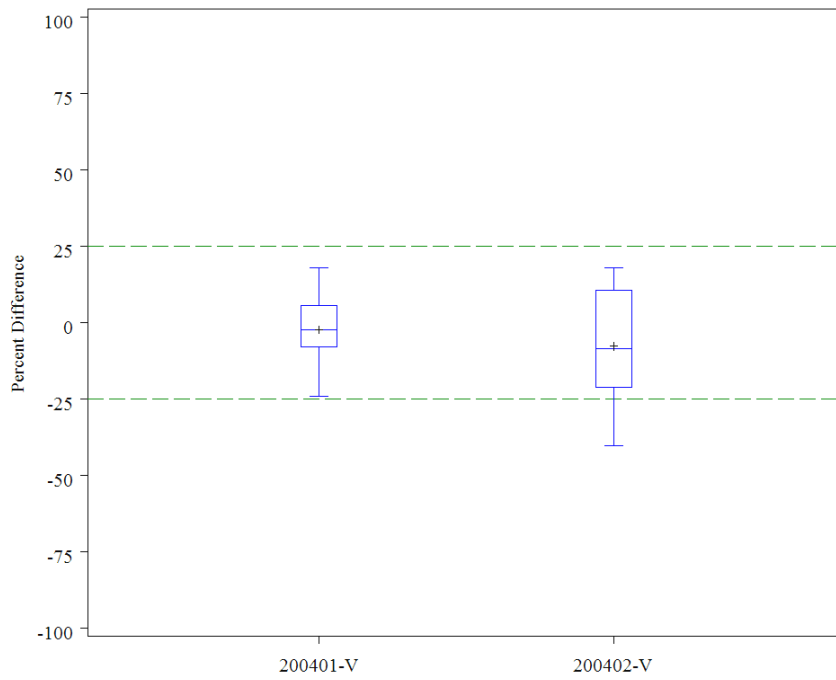
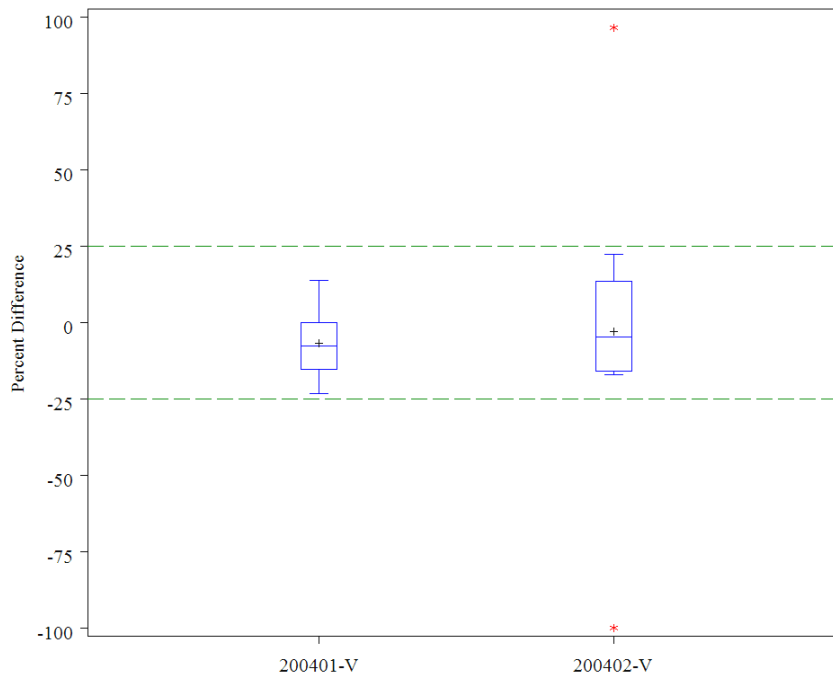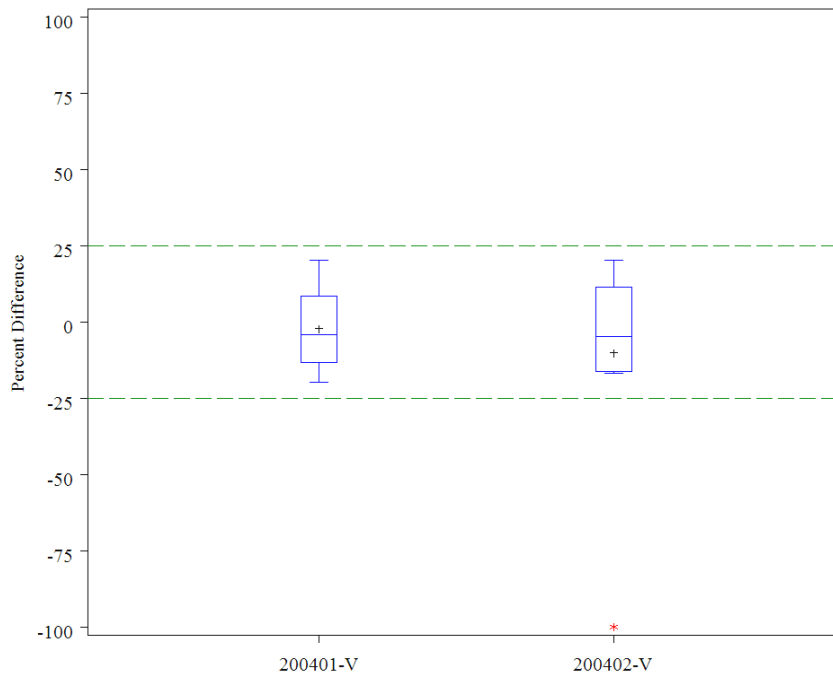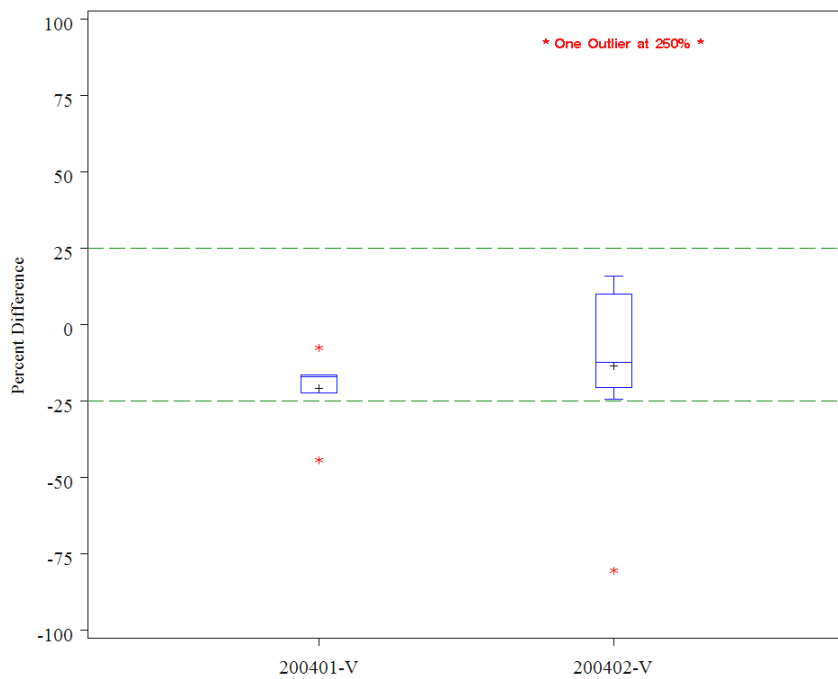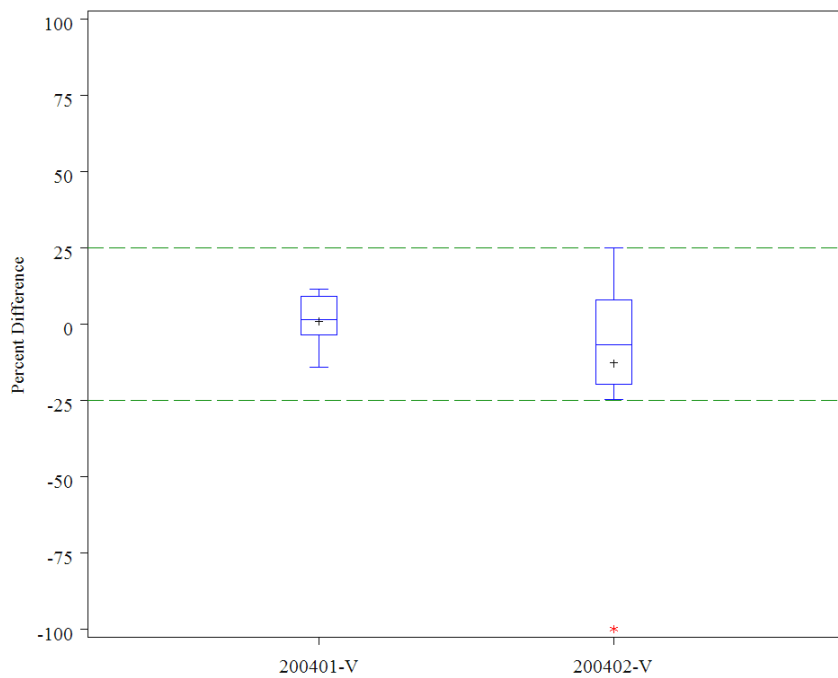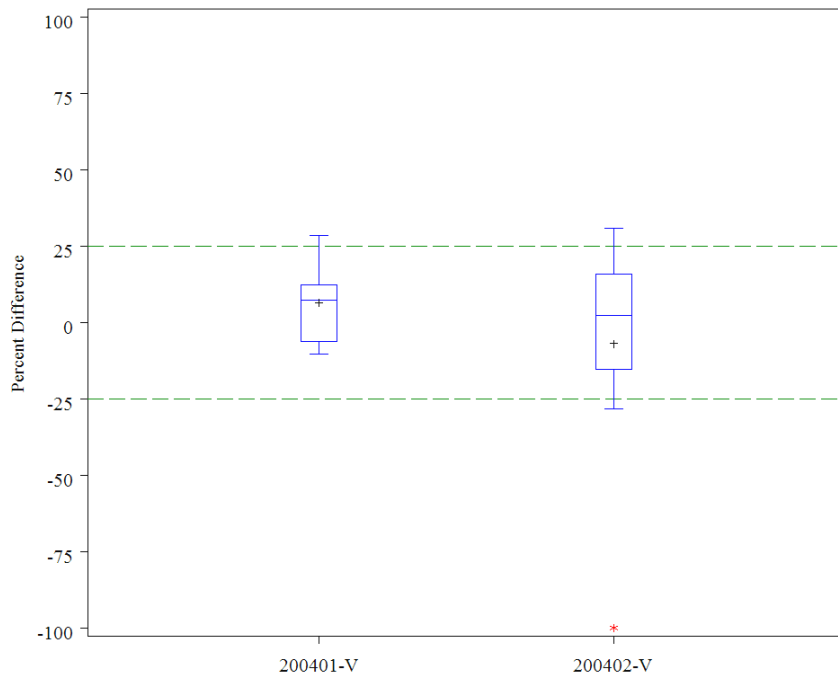**Figure A-6.   Box and whisker plot of laboratory bias data for 1,2-dichloropropane.**
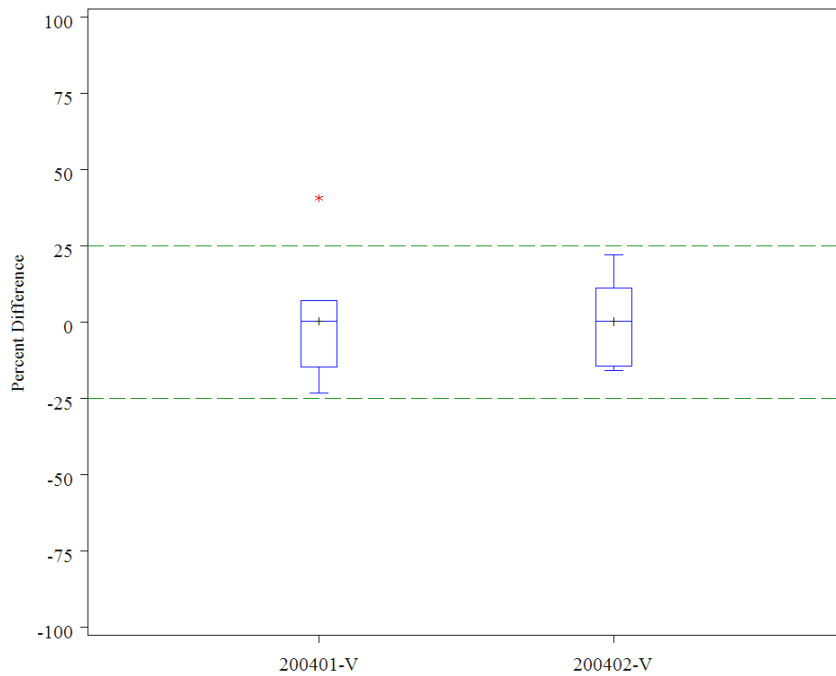
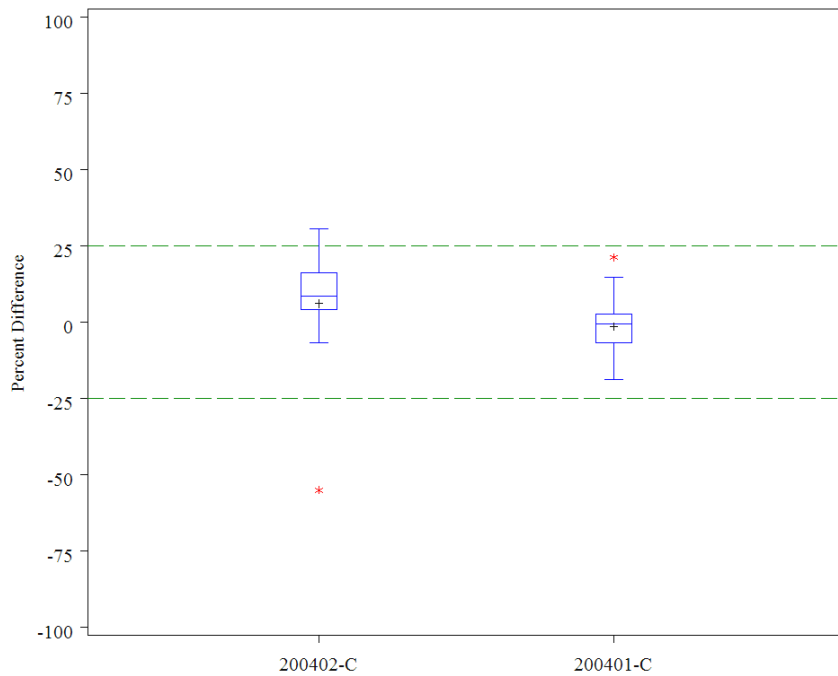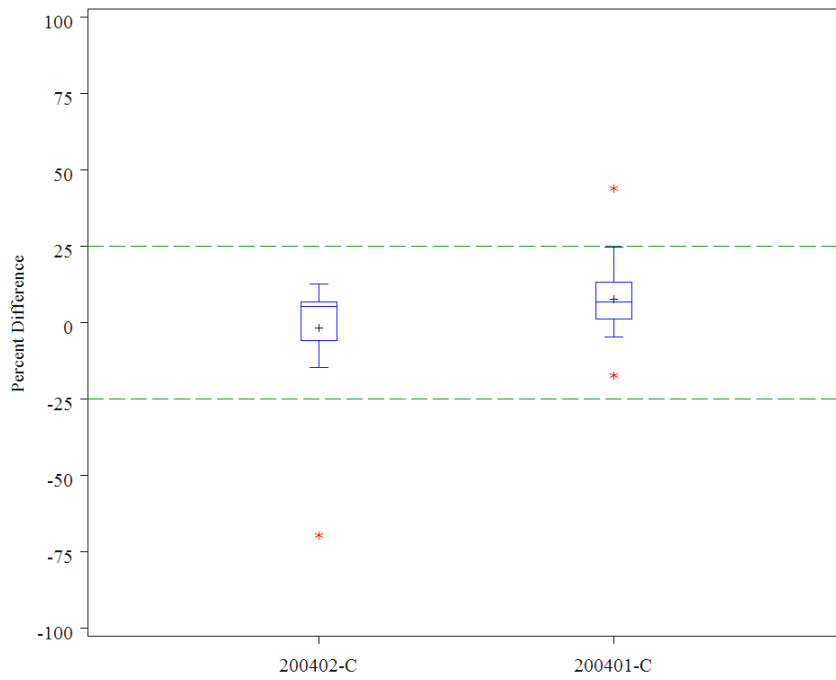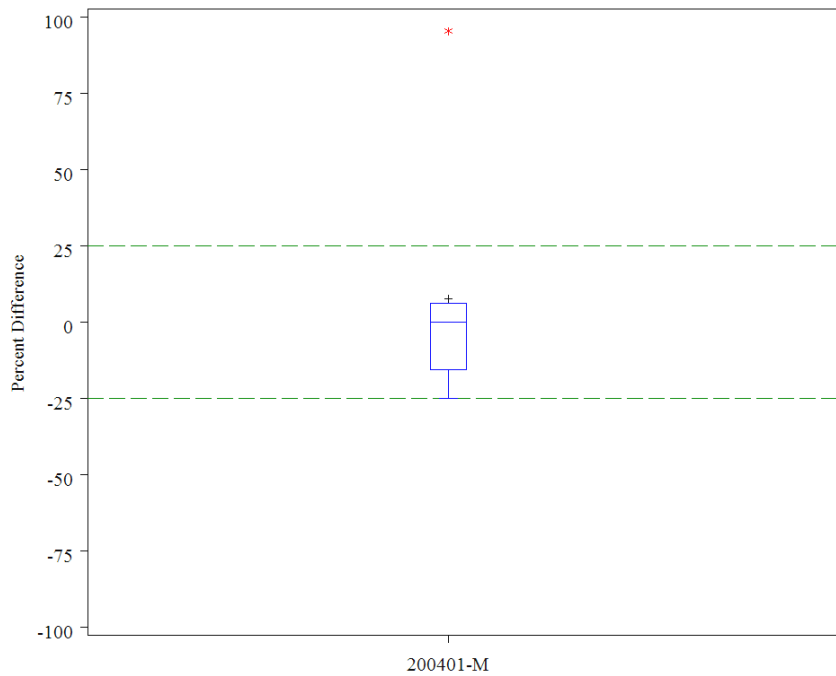**Figure A-7.   Box and whisker plot of laboratory bias data for 1,2-dichloroethane.**
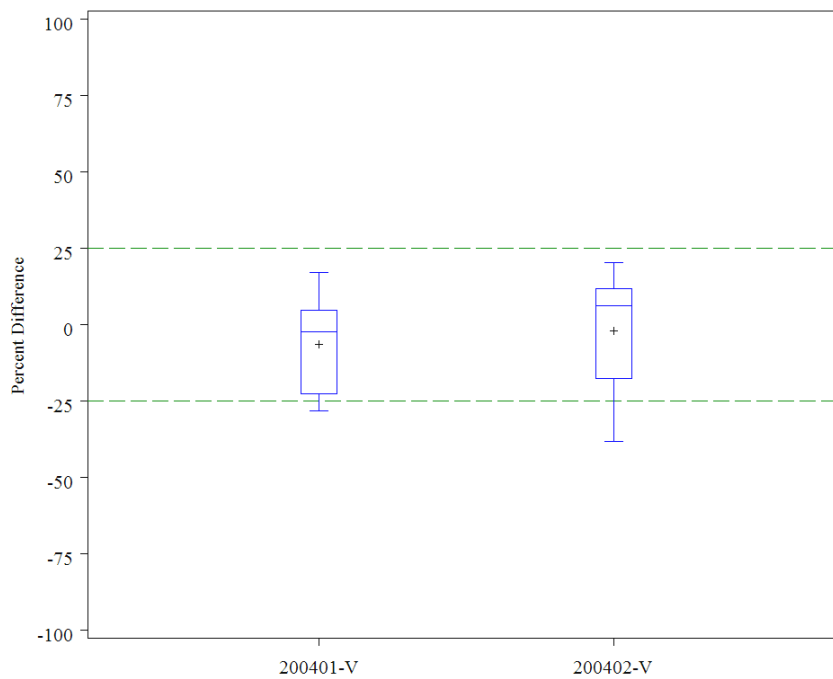
Figure A-8.   Box and whisker plot of laboratory bias data for dichloromethane.

Figure A-9.   Box and whisker plot of laboratory bias data for 1,1,2,2-tetrachloroethane.

Figure A-10. Box and whisker plot of laboratory bias data for tetrachloroethylene.

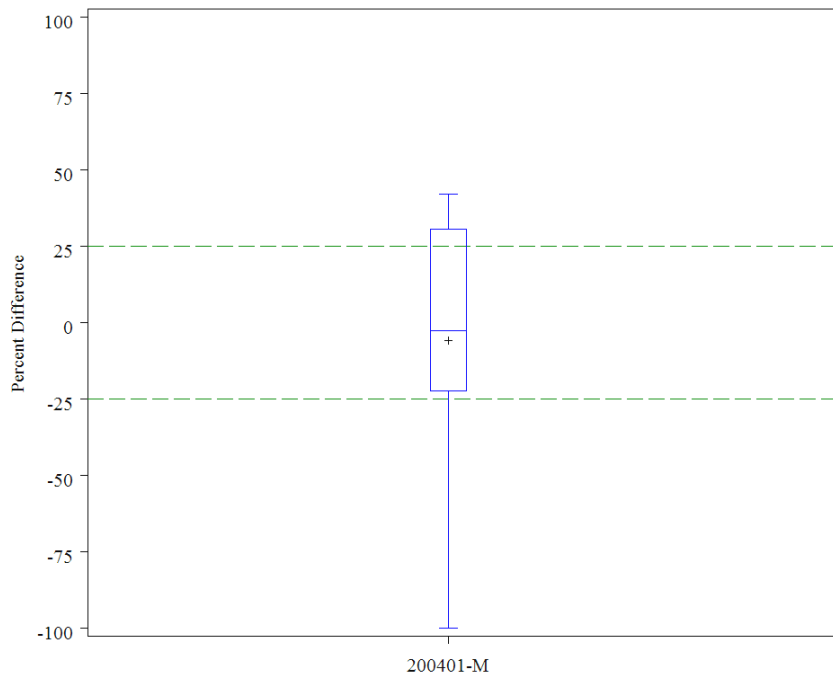**Figure A-11. Box and whisker plot of laboratory bias data for trichloroethylene.**

Figure A-12. Box and whisker plot of laboratory bias data for vinyl chloride.

Figure A-13. Box and whisker plot of laboratory bias data for cis-1,3-dichloropropene.
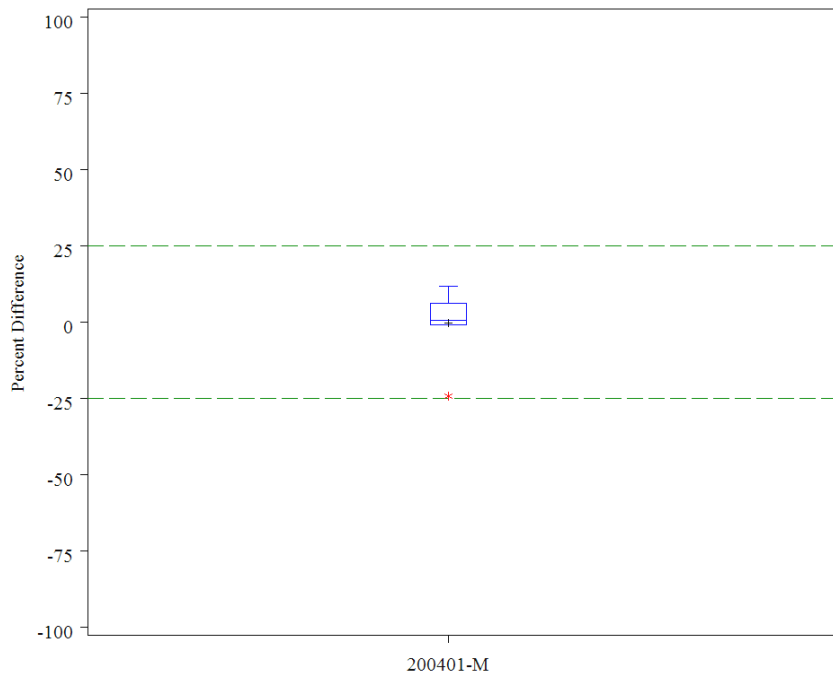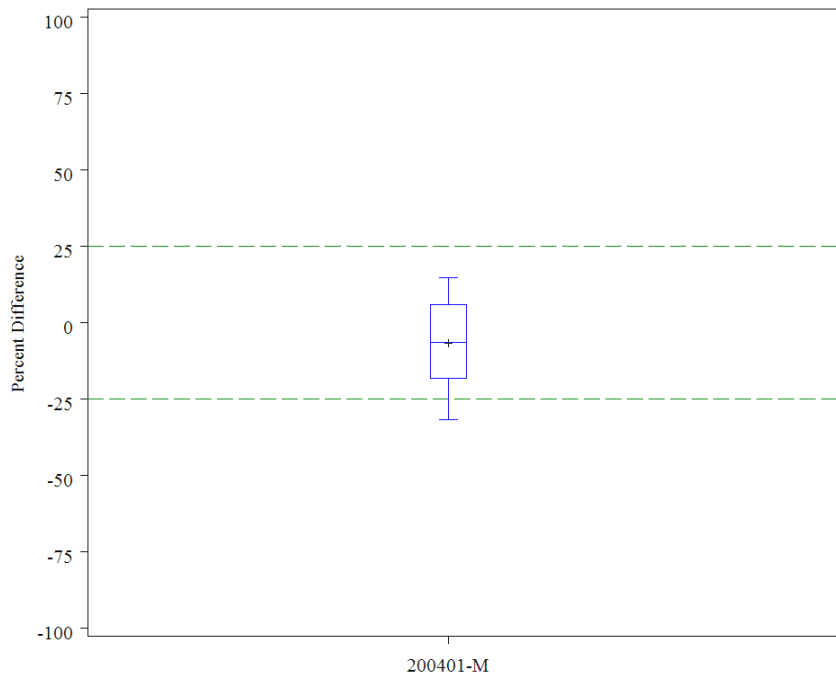
Figure A-14. Box and whisker plot of laboratory bias data for trans-1.3,dichloropropene.

Figure A-15. Box and whisker plot of laboratory bias data for formaldehyde.

Figure A-16. Box and whisker plot of laboratory bias data for acetaldehyde.

Figure A-17. Box and whisker plot of laboratory bias data for arsenic.

Figure A-18.   Box and whisker plot of laboratory bias data for beryllium.

Figure A-19.   Box and whisker plot of laboratory bias data for cadmium.

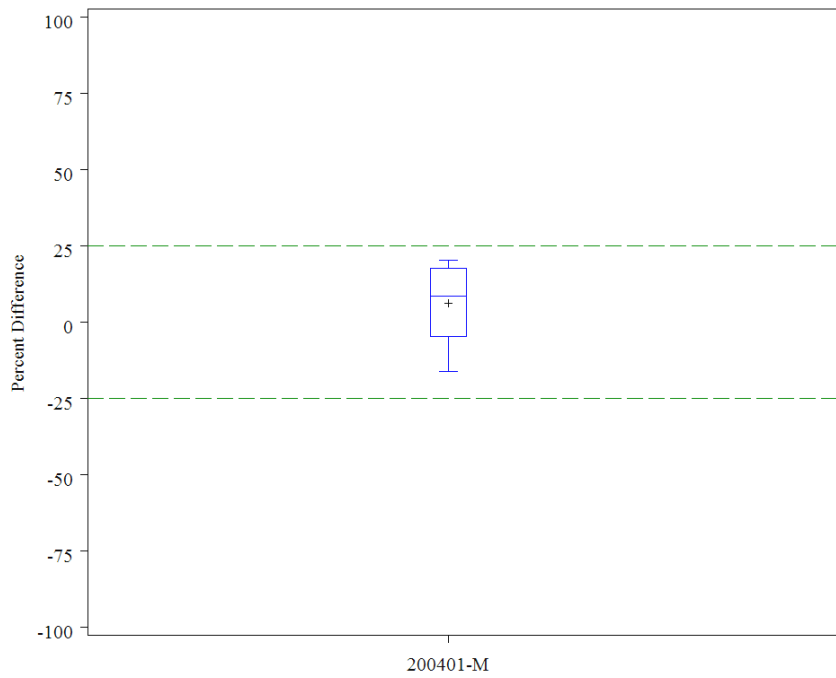**Figure A-20. Box and whisker plot of laboratory bias data for lead.**

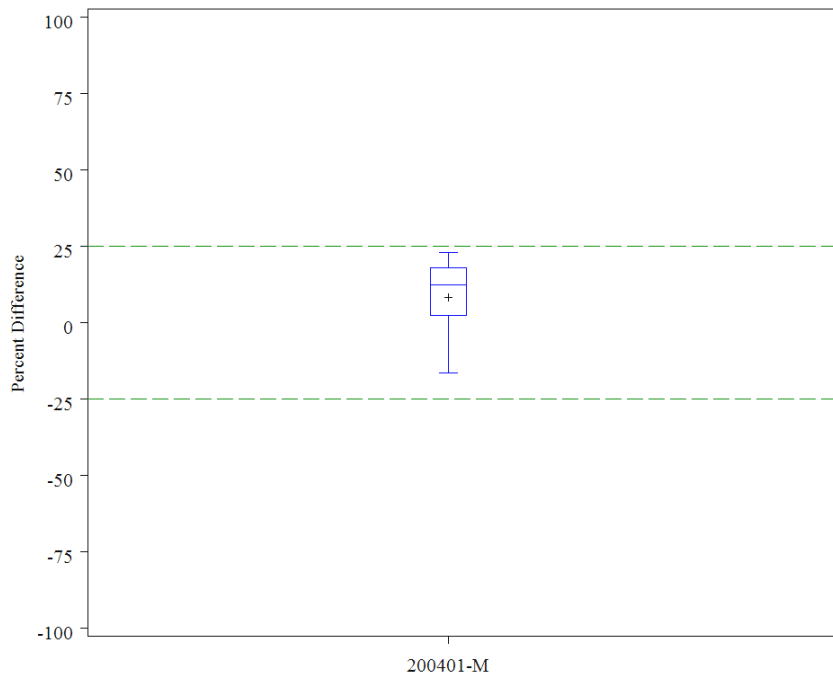**Figure A-21. Box and whisker plot of laboratory bias data for manganese.**

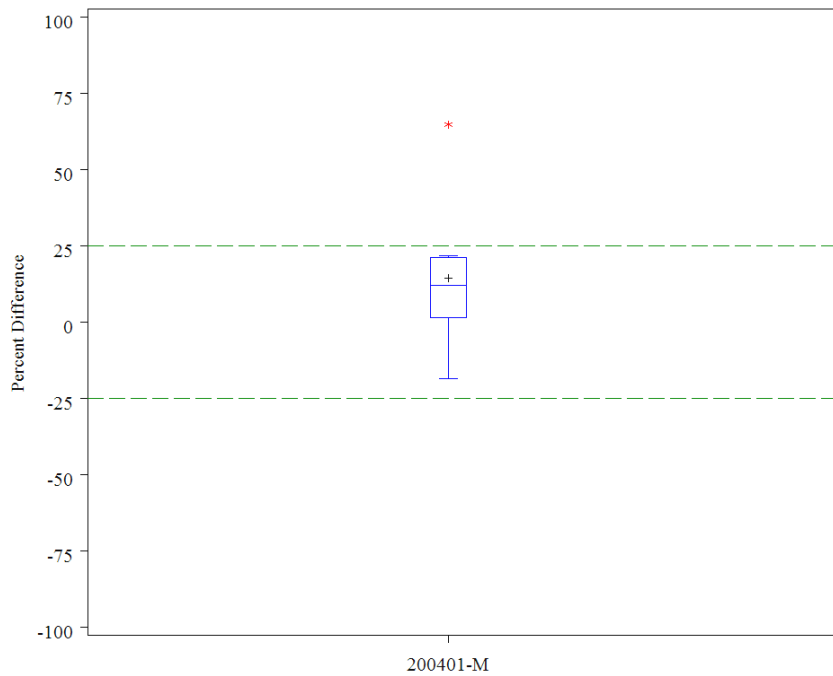**Figure A-22. Box and whisker plot of laboratory bias data for nickel.**

Figure A-23. Box and whisker plot of laboratory bias data for chromium.