

NATIONAL AIR TOXICS TRENDS STATIONS QUALITY ASSURANCE ANNUAL REPORT CALENDER YEAR 2005

FINAL

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

FORWARD

In the fall of 2006, Battelle Inc. prepared a final technical report under Contract No. 68-D-02-061 Work Assignment 4-01, Task 11. The report was prepared for Margaret Dougherty, Project Officer and Candace Sorrell, Work Assignment Manager of the Air Quality Assessment Division (AQAD) within the Office of Air Quality Planning and Standards (OAQPS) in Research Triangle Park, North Carolina. The report was written by Ian C. MacGregor and Laura L. Aume of Battelle. That report was incorporated into this final report.

Additional work on this report was provided by AQAD staff.

TABLE OF CONTENTS

| | | Page |
|------------|--|------|
| 1.0 INTROD | OUCTION | 1 |
| 2.0 NATTS | QUALITY ASSURANCE DATA FOR CALENDAR YEAR 2005 | 2 |
| 2.1 | | |
| 2.2 | Measurement Quality Objectives | |
| 2.3 | Precision of NATTS Data | |
| 2.3.1 | J | |
| 2.3.2 | | |
| 2.4 2.5 | Laboratory Bias Data from Performance Evaluation Samples from Alion | |
| 2.6 | Method Detection Limit Data | |
| 3.0 SUMMA | .RY | 26 |
| 4.0 REFERE | NCES | 27 |
| | LIST OF TABLES | |
| Table 1. | The 23 NATTS sites with EPA region numbers and AQS site codes | 2 |
| Table 2. | The 23 HAPS and their AQS compound codes | 3 |
| Table 3. | Measurement Quality Objectives for the NATTS program | 4 |
| Table 4. | Sources of data for the evaluation of MQOs for the NATTS program | 4 |
| Table 5. | Percent completeness of the 2005 AQS data set by site for four HAPs | 6 |
| Table 6. | Analytical precision given as % CV determined from 2005 AQS data | 8 |
| Table 7. | Overall precision given as % CV determined from the 2005 AQS data | 10 |
| Table 8. | Cross-reference between laboratory codes and affiliated NATTS sites | 12 |
| Table 9. | Participation in PT program by quarter for CY2005 | 15 |
| Table 10. | Flow audit results from 2005 Instrument Performance Audits. | 16 |
| Table 11. | Laboratories performing analyses for the three different compound types for each of the NATTS sites in 2005. | 19 |
| Table 12. | Abbreviations and full names of laboratories performing analyses of NATTS samples | 19 |
| Table 13. | Method detection limits by site for the year 2005 for the 23 HAPs. | 21 |
| Table 14. | Mean and median CY2005 MDLs across all NATTS laboratories for four compounds. | 26 |

LIST OF FIGURES

| Figure 1. | Box and whisker plot of the completeness data for 2005 for 23 NATTS sites and for four compounds. | |
|------------|---|----|
| Figure 2. | Overall precision data for 2005 from AQS by NATTS site. | 11 |
| Figure 3. | Laboratory bias boxplot for benzene PT data from CY2005. | 13 |
| Figure 4. | Laboratory bias boxplot for 1,3-butadiene PT data from CY2005 | 13 |
| Figure 5. | Laboratory bias boxplot for formaldehyde PT data from CY2005. | 14 |
| Figure 6. | Laboratory bias boxplot for arsenic PT data from CY2005. | 14 |
| Figure 7. | Comparison of Mean Differences for the PT Program | 15 |
| Figure 8. | Summary of Instrument Performance Audit sorted by sampling method. | 18 |
| Figure 9. | Box and whisker plot of the VOC and carbonyl MDLs across all the NATTS sites | 24 |
| Figure 10. | Box and whisker plot of the metals MDLs across all the NATTS sites | 24 |
| Figure 11. | Plot of the VOC and carbonyl MDLs for all of the NATTS sites. | 25 |
| Figure 12. | Plot of the metals MDLs for all of the NATTS sites. | 25 |

Final Report on NATTS Quality Assurance Annual Report For Calendar Year 2005

1.0 INTRODUCTION

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

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

This report describes and summarizes the quality assurance (QA) data generated by the NATTS program for calendar year (CY) 2005. 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 PM₁₀ arsenic. These four pollutants were selected as principle pollutants of interest by virtue of associated health risk, frequency of occurrence at measurable concentrations, and the fact that they represent the three main categories of HAPs routinely measured in the NATTS program (VOCs, carbonyls, and PM10 metals). EPA staff believe that if the program can meet the Data Quality Objectives (DQOs) for these four compounds, the additional 19 compounds of concern will have similar quality since the other 19 compounds would be collected and analyzed using the same field and laboratory equipment.

Entries into AQS also include results from replicate analyses of a given sample and from collocated samplers. Data were retrieved from AQS, and analytical and overall sampling

precision were calculated for as many of the 23 applicable compounds and for as many of the 23 NATTS sites as had such data posted to AQS.

Data from the analysis of PT samples for many of the 23 compounds are also presented. From the PT data, laboratory bias was calculated. Field bias data is determined by calculating the differences between actual and measured sampler flow readings for each of the three different sampler types (volatile organic compounds (VOCs), carbonyls, and PM₁₀ metals), are presented for primary and collocated samplers (where available) at the ten sites visited during the IPAs conducted in CY 2005. Finally, information regarding MDLs was solicited from all the NATTS State and Local agencies and affiliated laboratories for the 23 compounds of interest. Taken together, the combination of the QA data summarizes the activities of the NATTS QS for CY 2005.

2.0 NATTS QUALITY ASSURANCE DATA FOR CALENDAR YEAR 2005

Table 1 illustrates 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.

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 | 36-055-1001 |
| 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, FL | Urban | 12-057-3002 |
| IV | Pinellas Cty, FL | Urban | 12-103-0026 |
| V | Dearborn, MI | Urban | 26-163-0033 |
| V | Mayville, WI | Rural | 55-027-0007 |
| V | Northbrook, IL | Urban | 17-031-4201 |
| VI | Deer Park, TX | Urban | 48-201-1039 |
| VI | Harrison County, TX | Rural | 48-203-0002 |
| VII | St. Louis, MO | Urban | 29-510-0085 |
| VIII | Bountiful, UT | Urban | 49-011-0004 |
| VIII | Grand Junction, CO | Rural | 08-077-0017, -0018 |
| IX | Phoenix, AZ | Urban | 04-013-9997 |
| IX | San Jose, CA | Urban | 06-085-0005 |
| X | La Grande, OR | Rural | 41-061-0119 |
| X | Seattle, WA | Urban | 53-033-0080 |

Though city and state are typically used as the site identifier, the county name is used in three instances: the two Florida sites on either side of Tampa Bay, and the rural Vermont site near Underhill. The Grand Junction, Colorado, site has two separate codes, one for VOCs and carbonyls (-0018), the other for the metals (-0017), since the organics and metals samplers are present at two separate physical locations at the sampling site. The 23 hazardous air pollutants measured in the NATTS program are compounds that have been identified by EPA as being cancer and non-cancer risk drivers. The compounds of interest are given in Table 2. These include 14 VOCs, two carbonyls, and seven PM₁₀ metals. Also included in Table 2 are the unique AQS identification codes for each compound that are utilized in the tables and graphs throughout this report. Please note that the Compound Number in the right hand column is an arbitrary number assigned in this report. These numbers are utilized throughout this report in various graphs and tables.

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

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

2.1 Measurement Quality Objectives

Several different Measurement Quality Objectives (MQOs) have been established for the NATTS network in order to ensure that only data of the highest quality are collected by the NATTS network. The stated 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" [2]. MQOs for the four compounds of primary importance to the NATTS QS program (benzene, 1,3-butadiene, formaldehyde, and PM₁₀ arsenic) are summarized below in Table 3.

| Table 3. | Measurement Quality | Objectives for the | e NATTS program. |
|----------|----------------------------|--------------------|------------------|
|----------|----------------------------|--------------------|------------------|

| Compound | Completeness | Precision (Coefficient of Variation) | Laboratory Bias | Method Detection Limit (MDL) |
|---------------|--------------|--|-----------------|---------------------------------|
| benzene | > 85 % | < 15 % | < 25 % | $0.044 \mu g/m^3$ |
| 1,3-butadiene | > 85 % | < 15 % | < 25 % | $0.020 \ \mu g/m^3$ |
| formaldehyde | > 85 % | < 15 % | < 25 % | $0.014 \ \mu g/m^3$ |
| arsenic | > 85 % | < 15 % | < 25 % | 0.046 ng/m ³ |

The MQOs require that (1) sampling occurs every sixth day and is successful 85 percent of the time; (2) precision as measured by the coefficient of variation (CV) be controlled to less than 15 percent; and that (3) that laboratory (measurement) bias be less than 25 percent. Furthermore, actual MDLs are compared to those listed here that were used to determine the DQOs as outlined in the NATTS Technical Assistance Document (TAD) [2].

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

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

| MQO | Data Source |
|-------------------------------------|------------------------------|
| Completeness | Air Quality System (AQS) |
| Analytical and Overall Precision | AQS |
| Bias - Laboratory | Proficiency Testing |
| Bias - Field | Audits of sampler flow-rates |
| MDL | Laboratories |

The AQS database contains data that is used to assess data completeness, and to estimate precision from results of replicate analyses and collocated sampling. Field bias was evaluated by measurement of sampler flow rates during on-site IPAs. Finally, MDL data were solicited from the individual laboratories.

2.2 Completeness of NATTS Data

The AQS database was accessed and the raw data records for calendar year 2005 were retrieved for the 23 NATTS sites using the site codes given in Table 1. Please note that the AQS data was accessed on July 5, 2006. Therefore the completeness statistics only represent the completeness of this data on or before that date. Any NATTS data submitted later than July 5, 2006 would be reflected in the statistics or summary. Results of the 2005 AQS completeness assessment are presented in Table 5. The presence of 61 concentration values in the database indicates 100 percent completeness for a 1 in 6 day sampling frequency. Zero values in the database indicate a valid data point and are thus counted toward total dataset completeness. Moreover, transactions where non-detects were indicated with the appropriate qualifier code were counted as complete. However, if the appropriate data field were empty, if no data were found, or if one of several "null codes" were found, then the sampling event was determined to be incomplete and data were understood to be missing. In these instances, the total completeness percentage decreased accordingly.

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

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

The mean completeness values across all of the NATTS laboratories were 77 percent, 77 percent, 72 percent, and 52 percent for benzene, 1,3-butadiene, formaldehyde, and arsenic, respectively. The median completeness values were higher: 90 percent, 89 percent, 92 percent, and 87 percent for benzene, 1,3-butadiene, formaldehyde, and arsenic, respectively.

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

Table 5. Percent completeness of the 2005 AQS data set by site for four HAPs.

| | Completeness of Compound by AQS number and by name, % | | | | | | |
|-----------------------|---|---------------|--------------|---------|--|--|--|
| | 45201 | 43218 | 43502 | 82103 | | | |
| Site Identifier | benzene | 1,3-butadiene | formaldehyde | Arsenic | | | |
| Boston-Roxbury, MA 89 | | 89 | 62 | 77 | | | |
| Chittenden Cty, VT | 87 | 87 | 97 | No data | | | |
| Providence, RI | 92 | 92 | 89 | 98 | | | |
| Bronx, NY | 97 | 97 | 100 | No data | | | |
| Rochester, NY | No data | No data | No data | No data | | | |
| Washington, DC | 98 | 98 | No data | No data | | | |
| Chesterfield, SC | 100 | 100 | 95 | No data | | | |
| Decatur, GA | 90 | 89 | 95 | 90 | | | |
| Hazard, KY | 100 | 100 | 97 | 95 | | | |
| Hillsborough Cty, FL | 97 | 97 | 97 | 97 | | | |
| Pinellas Cty, FL | 100 | 100 | 98 | 100 | | | |
| Dearborn, MI | 39 | 39 | 61 | 89 | | | |
| Mayville, WI | No data | No data | No data | No data | | | |
| Northbrook, IL | 84 | 84 | 77 | No data | | | |
| Deer Park, TX | 97 | 97 | 95 | 87 | | | |
| Harrison County, TX | 95 | 95 | 92 | 93 | | | |
| St. Louis, MO | 95 | 95 | 95 | 100 | | | |
| Bountiful, UT | 87 | 87 | 87 | 93 | | | |
| Grand Junction, CO | 85 | 85 | 90 | 87 | | | |
| Phoenix, AZ | No data | No data | No data | No data | | | |
| San Jose, CA | 51 | 51 | 46 | No data | | | |
| La Grande, OR | 89 | 89 | 92 | 98 | | | |
| Seattle, WA | 98 | 98 | 92 | No data | | | |
| Mean | 77 | 77 | 72 | 52 | | | |
| Median | 90 | 89 | 92 | 87 | | | |

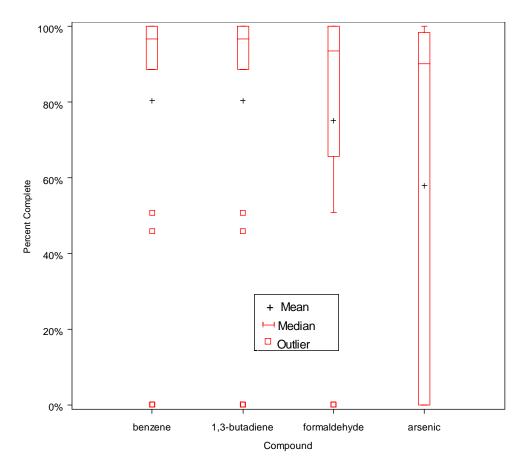


Figure 1. Box and whisker plot of the completeness data for 2005 for 23 NATTS sites and for four compounds.

2.3 Precision of NATTS Data

The precision was assessed for as many of the 23 compounds as were available in AQS. These are illustrated in Tables 6 and 7. Replicate and collocated data transactions were retrieved from AQS². AQS data can have three separate transactions with Precision IDs of 1, 2, or 3. Concentration data from the collocated sampler are given in the transaction with Precision ID 1 or POC 1. Concentration information from the primary sampler that is analyzed twice, (i.e., primary replicate data) are labeled with Precision ID 2 or POC 2. Collocated sampler replicate data are given in the transaction with Precision ID 3 or POC 3. The <u>analytical precision</u> is derived from the replicate pairs of data from the primary sampler (POC 2) **and** the replicate pairs of data from the collocated sampler (POC 3). The <u>overall precision</u> was determined from the collocated and primary sampler non-replicate data pairs (POC 1 and data with no POC code indicated).

Overall precision may also be calculated from AQS using primary and collocated raw data "RD" transactions, which are distinguished using different POCs. However, for the assessment of precision described in this report, only precision transactions in the AQS database – those labeled with "RP" – were used.

2.3.1 Analytical Precision Results

The following calculations used are from the Code of Federal Regulations, (CFR) Title 40 Chapter 58 [3]. The precision estimate is expressed in the form of the percent coefficient of variation (% CV). A smaller % CV indicates a more precise measurement. To assess the analytical precision, the % CV was calculated in the following manner:

$$\%CV = 100 \cdot \sqrt{\frac{\sum_{i=1}^{n} \left[\frac{(p_i - r_i)}{0.5 \cdot (p_i + r_i)} \right]^2 + \sum_{j=1}^{m} \left[\frac{(c_j - cr_j)}{0.5 \cdot (c_j + cr_j)} \right]^2}}{2 \cdot (n+m)}$$
(Eq. 2.2.1)

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 6. Analytical precision given as % CV determined from 2005 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. The data in parentheses are the number of pairs that were used in the calculation of the CV.

| | Compound Number | | | | | | | | |
|----------------------|-----------------|----------|----------|----------|---------|----------|--|--|--|
| Site Identifier | 1 | 2 | 3 | 4 | 7 | 8 | | | |
| Grand Junction, CO | 8% (10) | 11% (6) | 14% (10) | 8% (2) | | 6% (8) | | | |
| Pinellas Cty, FL | 6% (91) | 14% (86) | 10% (91) | 13% (61) | 0% (10) | 16% (88) | | | |
| Northbrook, IL | 6% (12) | | 5% (6) | 11% (5) | | 18% (6) | | | |
| St. Louis, MO | 16% (10) | 17% (4) | 9% (6) | 0%(1) | | 27% (8) | | | |
| Bountiful, UT | 9% (32) | 13% (6) | 20% (12) | 0%(1) | | 12% (11) | | | |
| Mean | 9% | 14% | 12% | 7% | 0% | 16% | | | |
| | | • | Compound | Number | | | | | |
| Site Identifier | 10 | 11 | 14 | 15 | 16 | | | | |
| Grand Junction, CO | 7% (6) | | | 2% (12) | 2% (12) | | | | |
| Hillsborough Cty, FL | | | | 4% (4) | 4% (4) | | | | |
| Pinellas Cty, FL | 12% (82) | 14% (8) | 0%(1) | 4% (6) | 1% (6) | | | | |
| Northbrook, IL | 0% (1) | | | 0% (4) | 0% (4) | | | | |
| St. Louis, MO | 39% (2) | | | 1% (10) | 2% (10) | | | | |
| Bountiful, UT | 8% (8) | | | 3% (13) | 3% (13) | | | | |
| Mean | 13% | 14% | 0% | 2% | 2% | | | | |

2.3.2 Overall Precision Results

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

$$\%CV = 100 \cdot \sqrt{\frac{\sum_{i=1}^{n} \left[\frac{(p_i - c_i)}{0.5 \cdot (p_i + c_i)} \right]^2}{2 \cdot n}}$$
 (Eq. 2.2.2)

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 either zero or less than the MDL assigned for that compound in AQS. If no MDL was given and non-zero precision data were present, the precision data were included in the % CV calculation. Values in parentheses indicate the number of records used in the precision calculation.

Precision data available in AQS varied widely by compound and by site. However, the precision data, when available, shows that MQOs are being attained. The mean analytical precision values for benzene (5 sites, 155 records), 1,3-butadiene (4 sites, 102 records), and formaldehyde (6 sites, 49 records) are 9 percent, 14 percent, and 2 percent, respectively. Moreover, the overall precision estimates for benzene (4 sites, 58 records), 1,3-butadiene (4 sites, 39 records), formaldehyde (5 sites, 23 records), and arsenic (2 sites, 64 records) are 7 percent, 9 percent, 4 percent, and 11 percent, respectively. These overall precision data are depicted graphically in Figure 2. Reporting of precision data to AQS continues to remain sparse: only five stations out of 23 reported data for either replicate analyses of a single sample or analyses of collocated samples. Thus, across the entire NATTS network, using the coefficients of variations estimated using PT data, benzene, 1,3-butadiene, formaldehyde and arsenic meet the MQO criteria that CVs must be less than 15 percent.

Table 7. Overall precision given as % CV determined from the 2005 AQS data. Only those sites and compounds for which data were available are shown. HAPs are given by abbreviated codes. Data in parenthesis are the number of pairs used to make the CV calculation.

| | Compound Number | | | | | | | | |
|----------------------|-----------------|----------|----------|----------|------------|----------|----------|----------|--------|
| Site Identifier | 1 | 2 | 3 | 4 | 7 | 8 | 10 | 11 | 14 |
| Grand Junction, CO | 8% (6) | 7% (4) | 14% (6) | 8% (1) | | 6% (5) | 7% (3) | | |
| Pinellas Cty, FL | 6% (31) | 16% (30) | 10% (31) | 13% (22) | 0% (4) | 17% (30) | 10% (30) | 0% (3) | 0% (1) |
| St. Louis, MO | 8% (5) | 10% (2) | 11% (3) | 0% (1) | | 17% (4) | 8% (1) | | |
| Bountiful, UT | 6% (16) | 3% (3) | 21% (6) | | | 8% (6) | 0% (5) | | |
| Mean | 7% | 9% | 14% | 7% | 0% | 12% | 6% | 0% | 0% |
| | | • | | Cor | npound Num | ber | | | |
| Site Identifier | 15 | 16 | 17 | 18 | 19 | 21 | 21 | 23 | |
| Grand Junction, CO | 3% (6) | 2% (6) | | | | | | | |
| Hillsborough Cty, FL | 7% (2) | 3% (2) | 18% (59) | 8% (59) | 18% (59) | 23% (59) | 10% (59) | 21% (59) | |
| Pinellas Cty, FL | 5% (3) | 2% (3) | | | | | | | |
| St. Louis, MO | 1% (5) | 2% (5) | | | | | | | |
| Bountiful, UT | 4% (7) | 4% (7) | 4% (5) | 0% (2) | 15% (4) | 11% (6) | 7% (5) | 47% (6) | |
| Mean | 4% | 2% | 11% | 4% | 17% | 17% | 9% | 34% | |

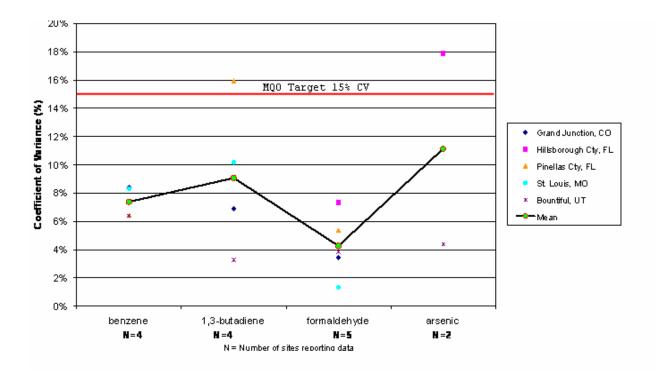


Figure 2. Overall precision data for 2005 from AQS by NATTS site. Shown are both the mean precision across sites reporting data and the goal precision of 15 percent.

2.4 Laboratory Bias Data from Performance Evaluation Samples from Alion

Alion Science Inc. is under contract (Contract No. 68-D03-006) to the U.S. EPA to conduct quarterly PT audits of the NATTS laboratories. Alion provided to Battelle the results of the calendar year 2005 PT audits for inclusion in the present work. Spiked samples containing known amounts of the HAPs of interest were forwarded to each laboratory that was performing analyses for a NATTS site and that chose to participate in a given PT study. Participating laboratories forwarded their results to Alion, after which reports were prepared comparing the values measured by the laboratory to the stated value. For calendar year 2005, four separate VOC, carbonyl, and metals PT studies were conducted such that one of each of the three sample types (canister, DNPH cartridge, or spiked filter) was sent out for analysis on a quarterly basis.

Table 8. Cross-reference between laboratory codes and affiliated NATTS sites.

| Laboratory Code | NATTS Site(s) |
|-----------------|---------------------------------|
| 01-01 | Providence, RI |
| 01-02 | Chittenden Cty, VT |
| 01-03 | Boston-Roxbury, MA |
| 01-04 | EPA Region 1 Laboratory* |
| 02-01 | Bronx & Rochester, NY |
| 03-01 | Washington, DC |
| 04-01 | Hillsborough & Pinellas Cty, FL |
| 04-02 | Chesterfield, SC |
| 04-03 | Hazard, KY |
| 04-04 | Decatur, GA |
| 05-01 | Dearborn, MI |
| 05-02 | Northbrook, IL |
| 05-03 | Mayville, WI |
| 06-01 | Deer Park & Harrison Cty, TX |
| 07-01 | St. Louis, MO |
| 08-01 | Bountiful, UT |
| 09-01 | San Jose, CA |
| 09-02 | Phoenix, AZ |
| 10-01 | Seattle, WA |
| 10-02 | La Grande, OR |
| 11-01 | ERG** |

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

Given in Figures 3 through 6 are boxplots summarizing laboratory bias results for all the participating laboratories for the four compounds of interest: benzene, 1,3-butadiene, formaldehyde, and arsenic. The dashed line in these figures represents the goal bias of 25 percent. In Figures 3 through 6, the laboratories are identified by numbers assigned by Alion; a cross-reference between NATTS site and laboratory code is provided in Table 8.

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

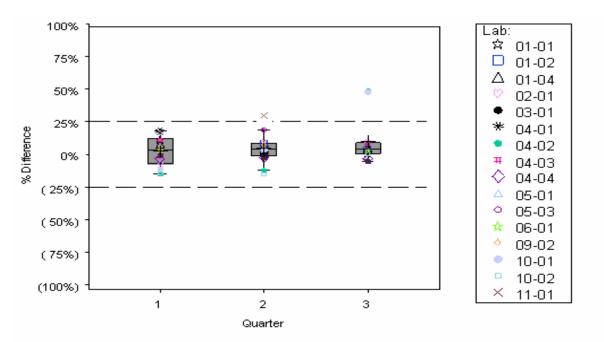


Figure 3. Laboratory bias boxplot for benzene PT data from CY2005. Benzene was not present in the 4th quarter PT sample.

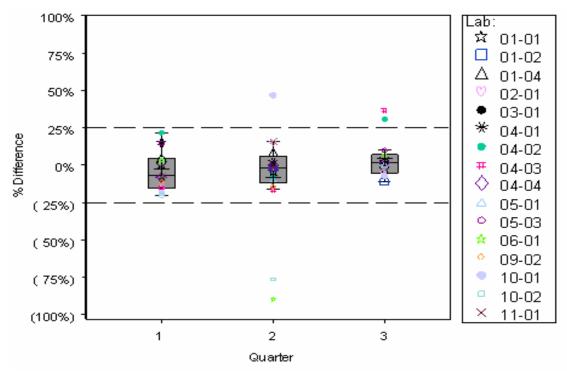


Figure 4. Laboratory bias boxplot for 1,3-butadiene PT data from CY2005. 1,3-butadiene was not present in the 4th quarter PT sample.

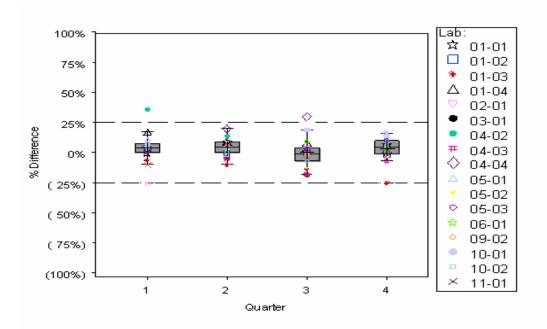


Figure 5. Laboratory bias boxplot for formaldehyde PT data from CY2005.

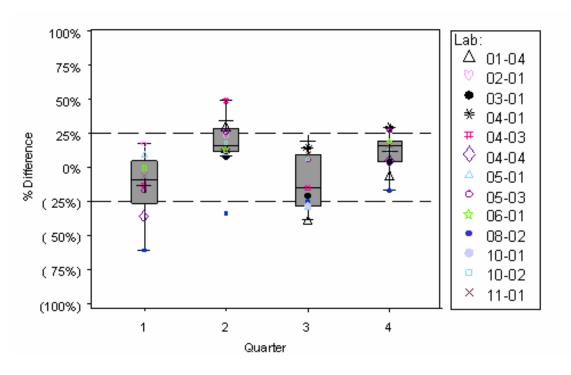


Figure 6. Laboratory bias boxplot for arsenic PT data from CY2005.

Table 9. Participation in PT program by quarter for CY2005.

| Compound Class | Quarter, CY2005 | | | | | |
|----------------|-----------------|------|------|-----|--|--|
| Compound Class | 1 | 2 | 3 | 4 | | |
| VOCs | 88% | 94% | 76% | 88% | | |
| Carbonyls | 100% | 100% | 100% | 94% | | |
| Metals | 59% | 71% | 65% | 65% | | |

Participation in the PT program remains high. For the VOCs and carbonyls, the percent participation is 87% and 99%, respectively. However, participation of the laboratories that perform metals analysis is lower at 65%. The PT program results for CY2005 demonstrate that across all laboratories performing analyses for the NATTS network of sites, laboratory bias is within the acceptable tolerance limit of ± 25 percent. Of the four compounds for which MOOs are established, results are in general excellent for benzene, 1,3-butadiene, and formaldehyde, but arsenic appears to be more problematic. Alion noted that many laboratories returned results for both arsenic and beryllium beyond the acceptable bias range when compared to the assigned "true" value, but performed well against the mean calculated across all laboratories reporting data. [4] It was determined that a possible cause of the problem was the filter media. When the program was begun, it was decided by both the EPA and the participating laboratories that Teflon filters would be used as the PT media. However, this was problematic from the beginning of the program. After consultation between Alion, EPA and the NATTS agencies, it was decided that quartz filters, which are used in the PM₁₀ samplers, would be a better alternative by which the PT metals would be delivered. Figure 7 illustrates the dramatic change in the mean differences for all of the metals once the PT filter media was changed from Teflon to quartz.

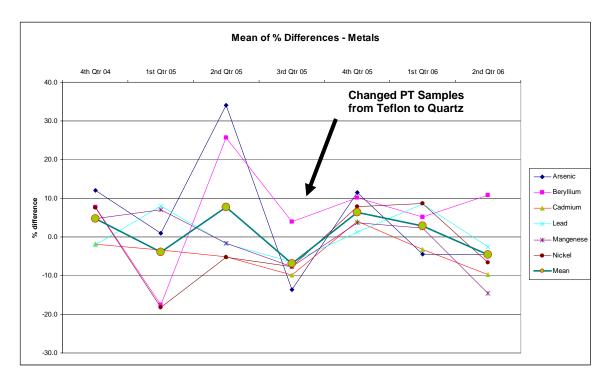


Figure 7. Comparison of Mean Differences for the PT program

2.5. Field Bias Data from Flow Audits Performed During IPAs

Ten NATTS field sites were audited during calendar year 2005. The IPA maintains its focus on the sampling that occurs at the NATTS station. Flow rates through all three sampler types are confirmed using certified flow, temperature, and pressure instruments. 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):

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

The results from the flow audits conducted at ten NATTS sites during calendar year 2005 are shown in Table 10. 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. The percent difference (field bias) as defined above is given in column 5.

Table 13. Flow audit results from 2005 Instrument Performance Audits.

| Site Identifier | Method | Monitor | Channel | Percent Difference |
|---------------------|-----------------------------|------------|---------|-----------------------|
| | Canister | Primary | 1 | 2.0 |
| | Carbonyl | Primary | 1 | 4.1 |
| Detroit, MI | Carbonyl | Primary | 2 | 4.8 |
| | PM10 | Primary | NA | -3.7 |
| | PM10 | Collocated | NA | 3.3 |
| | Canister | Primary | 1 | 17.1 |
| | Canister | Collocated | 1 | 6.8 |
| Charterfald CC | Carbonyl | Primary | 1 | -7.4 |
| Chesterfield, SC | Carbonyl | Collocated | 1 | 3.8 |
| | PM10 | Primary | NA | 35.7 |
| | PM10 | Collocated | NA | 7.7 |
| Deer Park, TX | Carbonyl | Primary | 1 | -1.5 |
| | Carbonyl | Primary | 2 | -1.1 |
| (Houston TV) | Carbonyl | Primary | 3 | -0.1 |
| (Houston, TX) | PM10 | Primary | NA | 1.5 |
| | PM10 | Collocated | NA | 3.0 |
| Harrison County, TX | arrison County, TX Carbonyl | | 1 | -0.3 |
| (Karnack, TX) | Carbonyl | Primary | 2 | 2.6 |
| | PM10 | Primary | NA | -2.9 |

| Site Identifier | Method | Monitor | Channel | Percent Difference |
|-----------------|----------|------------|---------|-----------------------|
| | Canister | Primary | 1 | -24.1 |
| | Canister | Primary | 2 | -15.6 |
| | Carbonyl | Primary | 1 | 1.8 |
| Mayville, WI | Carbonyl | Primary | 2 | 1.5 |
| | PM10 | Primary | NA | -5.1 |
| | Canister | Primary | 1 | -8.8 |
| La Grande, OR | Carbonyl | Primary | 1 | -1.0 |
| | PM10 | Primary | NA | -3.6 |
| | Carbonyl | Primary | 1 | -4.5 |
| St. Louis, MO | Carbonyl | Primary | 2 | -5.3 |
| St. Louis, MO | PM10 | Primary | NA | -2.6 |
| | PM10 | Collocated | NA | -3.2 |
| | Canister | Primary | 1 | -0.3 |
| | Canister | Collocated | 1 | -2.3 |
| Seattle, WA | Carbonyl | Primary | 1 | 10.7 |
| Seattle, WA | Carbonyl | Primary | 2 | 7.1 |
| | PM10 | Primary | NA | 1.3 |
| | PM10 | Collocated | NA | 1.3 |
| | Canister | Primary | 1 | -3.8 |
| | Canister | Collocated | 1 | -0.9 |
| Northbrook, IL | Carbonyl | Primary | 1 | -2.2 |
| | Carbonyl | Collocated | 1 | -2.4 |
| | PM10 | Primary | NA | -1.5 |
| | Canister | Primary | 1 | -7.6 |
| Phoenix, AZ | Canister | Collocated | 1 | 5.8 |
| FIIOCIIIX, AL | Carbonyl | Primary | 1 | -2.7 |
| | Carbonyl | Collocated | 1 | -2.8 |

A summary of the IPA flow results is given in Figure 8. On the ordinate is given the absolute percent difference in flow rate (the % difference of the field bias in Table 10, column 5). All but one of the 20 carbonyl flow rates provided by the field sampling crew were within ± 10 percent of the audit flow rate. Nine of the 12 canister sampler flow audits were within ± 10 percent, two had bias less than 20 percent, but one showed a bias of 24 percent. All but one of the 13 metals sampler results are within ± 10 percent. Overall, only approximately 11 percent of all the audits (5 out of 46) demonstrated a bias greater than 10 percent.

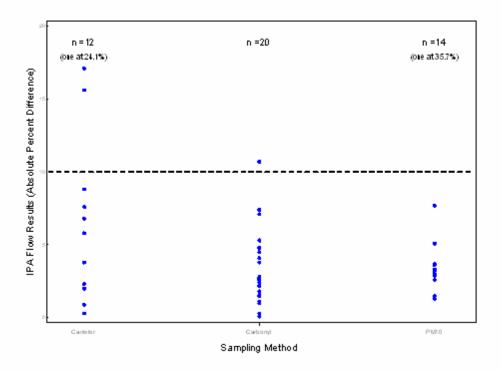


Figure 8. Summary of Instrument Performance Audit flow results sorted by sampling method.

2.6 Method Detection Limit Data

MDL data were requested from the points-of-contact at all 23 NATTS field sites for all three sample types: VOCs, carbonyls, and metals. Different information was requested depending on the sample type, but the fundamental objective for each was the same; i.e., to calculate the overall sampling and analytical MDL for each of the 23 HAPS listed in Table 2. This process was facilitated through a series of e-mail exchanges 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 13. The marker "N/A" indicates where MDL information was unavailable because such compounds are not presently being analyzed at a particular laboratory whereas "NR" indicates that no data were received. Mean MDLs across all laboratories reporting data are also given in Table 13.

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. However, in some cases, only overall MDL information was received and reported. Shown in Table 11 are the laboratories that performed the analyses of the different sample types for the 23 NATTS sites for calendar year 2005.

Table 11. Laboratories performing analyses for the three different compound types for each of the NATTS sites in 2005. (See Table 13 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 | None |
| Rochester, NY | NYSDEC | NYSDEC | None |
| Washington, DC | MDDE | PAMSL | WVDEP |
| Chesterfield, SC | SCDHEC | SCDHEC | SCDHEC |
| Decatur, GA | GADNR | GADNR | GADNR |
| Hazard, KY | KYDES | KYDES | KYDES |
| Hillsborough Cty, FL | PCDEM | ERG | EPCHC |
| Pinellas Cty, FL | PCDEM | ERG | EPCHC |
| Dearborn, MI | MDEQ/ERG | MDEQ | MDEQ |
| Mayville, WI | WSLH | WSLH | WSLH |
| Northbrook, IL | ERG | ERG | ERG |
| Deer Park, TX | TCEQ | TCEQ | TCEQ |
| Harrison County, TX | TCEQ | TCEQ | TCEQ |
| St. Louis, MO | ERG | ERG | ERG |
| Bountiful, UT | ERG | ERG | ERG |
| Grand Junction, CO | ERG | ERG | CDHE |
| Phoenix, AZ | SDAPCD | SDAPCD | None |
| San Jose, CA | CARB | CARB | None |
| La Grande, OR | ODEQ | ODEQ | ODEQ |
| Seattle, WA | WSU | WSU | RJLCLS |

Table 12. Abbreviations and full names of laboratories performing analyses of NATTS samples.

| Laboratory Abbreviation | Full Name of Analytical Laboratory |
|----------------------------|--|
| 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 |
| 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 |
| SCDHEC | South Carolina Department of Health and Environmental Control |
| SDAPCD | San Diego Air Pollution Control Division |
| TCEQ | Texas Commission on Environmental Quality |
| VTDEC | Vermont Department of Environmental Conservation |
| WSLH | Wisconsin State Laboratory of Hygiene |
| 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 sub-atmospheric 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 = 5.3 psig (pounds per square inch gauge), then the dilution factor is 20 psia/10 psia = 2. Hence, in this instance, the overall MDL is twice that of the analytical MDL.

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 $\mu g/mL$, V_E the extraction volume in mL, t the average sampling time in minutes, and t is the average volumetric flow rate through the carbonyl cartridge in t minutes.

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

where O_{MDL} is the compound-specific overall MDL in $\mu g/m^3$.

Table 13. (MDLs by site for the year 2005 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 $\Box g/m^3$ and ng/m^3 , respectively.

| Site Identifier | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Boston-Roxbury, MA | 3.9E-02 | 3.2E-02 | 2.5E-01 | 9.8E-02 | 9.6E-02 | 7.1E-02 | 8.8E-02 | 7.7E-02 | 3.4E-01 | 1.2E-01 | 1.1E-01 | 6.0E-02 |
| Chittenden Cty, VT | 2.7E-01 | 1.9E-01 | 7.5E-01 | 3.7E-01 | 6.1E-01 | 3.1E-01 | 3.5E-01 | 3.1E-01 | 2.3E-01 | 7.1E-01 | 4.1E-01 | 2.0E-01 |
| Providence, RI | 3.9E-02 | 3.2E-02 | 2.5E-01 | 9.8E-02 | 9.6E-02 | 7.1E-02 | 8.8E-02 | 7.7E-02 | 3.4E-01 | 1.2E-01 | 1.1E-01 | 6.0E-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 | 4.7E-02 | 3.3E-01 | 2.8E-01 | 1.4E-01 | 2.7E-01 | 1.5E-01 | 9.9E-02 | 1.6E-01 | 1.6E-01 | 1.1E-01 | 8.6E-02 | 1.1E-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 | 7.7E-01 | 5.3E-01 | 1.5E+00 | 1.2E+00 | 1.8E+00 | 1.1E+00 | 9.6E-01 | 8.2E-01 | 1.6E+00 | 1.6E+00 | 1.3E+00 | 6.0E-01 |
| Hillsbrgh Cty, FL | 8.1E-02 | 7.6E-02 | 1.8E-01 | 1.4E-01 | 2.2E-01 | 1.5E-01 | 7.1E-02 | 1.5E-01 | 2.1E-01 | 1.2E-01 | 1.3E-01 | 1.1E-01 |
| Pinellas Cty, FL | 8.1E-02 | 7.6E-02 | 1.8E-01 | 1.4E-01 | 2.2E-01 | 1.5E-01 | 7.1E-02 | 1.5E-01 | 2.1E-01 | 1.2E-01 | 1.3E-01 | 1.1E-01 |
| Dearborn, MI | 3.2E-01 | 3.2E-01 | 7.3E-01 | 5.5E-01 | 6.8E-01 | 5.3E-01 | 4.8E-01 | 1.5E+00 | 1.1E+00 | 5.3E-01 | 8.9E-01 | 3.8E-01 |
| Mayville, WI | 3.2E-01 | 2.2E-01 | 7.5E-01 | 4.9E-01 | N/A | 4.6E-01 | 4.0E-01 | 3.5E-01 | 6.9E-01 | 6.8E-01 | 5.4E-01 | 2.6E-01 |
| Northbrook, IL | 6.7E-02 | 1.0E-01 | 2.5E-01 | 1.4E-01 | 2.5E-01 | 1.3E-01 | 1.1E-01 | 1.4E-01 | 2.5E-01 | 1.7E-01 | 2.2E-01 | 1.0E-01 |
| 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 | 6.7E-02 | 1.0E-01 | 2.5E-01 | 1.4E-01 | 2.5E-01 | 1.3E-01 | 1.1E-01 | 1.4E-01 | 2.5E-01 | 1.7E-01 | 2.2E-01 | 1.0E-01 |
| Bountiful, UT | 6.7E-02 | 1.0E-01 | 2.5E-01 | 1.4E-01 | 2.5E-01 | 1.3E-01 | 1.1E-01 | 1.4E-01 | 2.5E-01 | 1.7E-01 | 2.2E-01 | 1.0E-01 |
| Grand Junction, CO | 6.7E-02 | 1.0E-01 | 2.5E-01 | 1.4E-01 | 2.5E-01 | 1.3E-01 | 1.1E-01 | 1.4E-01 | 2.5E-01 | 1.7E-01 | 2.2E-01 | 1.0E-01 |
| Phoenix, AZ | 6.4E-02 | 4.4E-02 | 1.3E-01 | 9.8E-02 | 1.5E-01 | 9.2E-02 | 8.1E-02 | 6.9E-02 | 1.4E-01 | 1.4E-01 | 1.1E-01 | 5.1E-02 |
| San Jose, CA | 1.6E-01 | 8.8E-02 | 1.3E-01 | 9.8E-02 | 7.7E-02 | N/A | 8.1E-01 | 3.5E-01 | N/A | 6.8E-02 | 1.1E-01 | N/A |
| La Grande, OR | 2.9E-01 | 4.2E-01 | 3.0E-01 | 4.5E-01 | 4.6E-01 | 4.1E-01 | 5.1E-01 | 2.6E-01 | 4.5E-01 | 4.0E-01 | 4.7E-01 | 1.6E-01 |
| Seattle, WA | 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 |
| Mean | 2.6E-01 | 2.1E-01 | 6.1E-01 | 3.7E-01 | 5.6E-01 | 3.6E-01 | 4.0E-01 | 5.9E-01 | 5.7E-01 | 5.0E-01 | 4.6E-01 | 2.1E-01 |

Table 13. (Continued).

| Site Identifier | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 |
|---------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Boston-Roxbury, MA | 5.3E-02 | 9.4E-02 | 6.1E-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 | 3.3E-01 | 3.2E-01 | 1.4E-02 | 3.1E-02 | 1.4E+00 | 3.0E-02 | 1.4E-01 | 1.7E+00 | 3.4E-01 | N/A | 8.5E-01 |
| Providence, RI | 5.3E-02 | 9.4E-02 | 5.4E-02 | 3.1E-01 | 2.3E+00 | 1.1E+00 | 5.5E-01 | 1.1E+00 | 1.1E+00 | N/A | 1.1E+00 |
| Bronx, NY | 1.8E-01 | 1.8E-01 | 8.6E-03 | 7.2E-03 | N/A |
| Rochester, NY | 1.8E-01 | 1.8E-01 | 8.6E-03 | 7.2E-03 | N/A |
| Washington, DC | 1.5E-01 | 2.1E-01 | NR |
| Chesterfield, SC | 5.0E-01 | 5.0E-01 | 1.7E-01 | 1.7E-01 | 3.1E-02 | 1.5E-03 | 1.1E-03 | 2.7E-03 | 2.3E-03 | N/A | 2.8E-03 |
| Decatur, GA | 1.1E+00 | 1.1E+00 | 1.1E+00 | 1.1E+00 | 4.6E-01 | 5.2E-02 | 2.6E-02 | 1.0E-01 | 1.5E-01 | N/A | 2.1E-01 |
| Hazard, KY | 1.1E+00 | 1.1E+00 | 5.0E-02 | 6.8E-02 | 1.7E+00 | 8.3E-01 | 8.3E-01 | 8.3E-01 | 8.3E-01 | N/A | 8.3E-01 |
| Hillsbrgh Cty, FL | 1.1E-01 | 1.1E-01 | 2.5E-02 | 2.2E-02 | 1.3E+00 | 3.6E-02 | 1.7E-01 | 7.8E-01 | 2.1E-01 | N/A | 1.7E+00 |
| Pinellas Cty, FL | 1.1E-01 | 1.1E-01 | 2.3E-02 | 2.0E-02 | 1.3E+00 | 3.5E-02 | 1.6E-01 | 7.5E-01 | 2.0E-01 | N/A | 1.6E+00 |
| Dearborn, MI | 6.1E-01 | 6.4E-01 | 8.4E-02 | 8.0E-02 | 9.3E-02 | 9.2E-02 | 9.2E-02 | 1.3E-01 | 1.9E-01 | N/A | 1.3E-01 |
| Mayville, WI | 5.4E-01 | 5.4E-01 | 7.0E-02 | 8.0E-02 | 4.1E-02 | N/A | 1.6E-02 | 6.1E-03 | 2.2E-02 | N/A | 1.4E-01 |
| Northbrook, IL | 1.1E-01 | 1.8E-01 | 1.2E-02 | 1.0E-02 | 1.9E-02 | 2.5E-02 | 2.0E-02 | 1.4E+00 | 1.8E-01 | 1.6E-01 | 1.9E-01 |
| Deer Park, TX | 9.1E-01 | 9.1E-01 | 7.4E-02 | 1.5E-01 | 1.3E+00 | N/A | N/A | N/A | N/A | N/A | N/A |
| Harrison County, TX | 9.1E-01 | 9.1E-01 | 7.4E-02 | 1.5E-01 | 1.3E+00 | N/A | N/A | N/A | N/A | N/A | N/A |
| St. Louis, MO | 1.1E-01 | 1.8E-01 | 2.0E-02 | 1.8E-02 | 2.1E-02 | 2.9E-02 | 2.2E-02 | 1.5E+00 | 2.0E-01 | 1.9E-01 | 2.2E-01 |
| Bountiful, UT | 1.1E-01 | 1.8E-01 | 2.7E-02 | 2.4E-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 | 1.1E-01 | 1.8E-01 | 2.4E-02 | 2.1E-02 | 4.4E+00 | 1.5E+00 | 5.2E-01 | 5.4E-01 | 7.4E-01 | N/A | 1.1E+00 |
| Phoenix, AZ | 9.1E-02 | 9.1E-02 | 1.2E-01 | 1.8E-01 | N/A |
| San Jose, CA | 4.5E-01 | 4.5E-01 | 9.9E-02 | 9.9E-02 | N/A |
| La Grande, OR | 4.2E-01 | 3.7E-02 | 2.5E-02 | 3.4E-02 | 3.3E-02 | 3.3E-03 | 3.3E-02 | 3.3E-01 | 3.3E-01 | N/A | 3.3E-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 | N/A | 8.4E-02 |
| Mean | 3.7E-01 | 3.7E-01 | 1.0E-01 | 1.2E-01 | 8.8E-01 | 2.6E-01 | 1.7E-01 | 7.0E-01 | 3.1E-01 | 2.1E-01 | 6.1E-01 |

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, f the average sampling time in minutes, and f the average volumetric flow rate through the metals sampler in m^3/min , then

$$O_{MDL} = \frac{A_{MDL} \cdot V_D}{f \cdot t \cdot F}$$
 (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 9 and 10 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 "+" symbols indicate the mean MDL for each compound and the horizontal line "—" in the box represents the median. The upper and lower ends of the boxes represent the upper and lower quartiles; thus, the height of the box is the interquartile range. The upper whisker shows the maximum value less than the sum of the upper quartile value plus 1.5 times the interquartile range. Similarly, the lower whisker depicts the minimum value above the lower quartile minus 1.5 times the interquartile range. The squares show "outliers" that represent individual laboratories' MDL values greater than 1.5 times the interquartile range from the upper or lower quartile. Note the log scale on the ordinate of both plots. See Table 2 for the cross-reference between compound number, name, and AQS compound code.

The MDL data for individual laboratories, in addition to the mean across all laboratories reporting data, are presented graphically in Figures 11 and 12.

As shown in Table 13, across all laboratories, the mean and median MDL for benzene, 1,3-butadiene, formaldehyde, and arsenic all exceed the MDLs given in the NATTS TAD [2], which were chosen to be "reasonably attainable maximum(s)" for use in DQO simulations.

Although referred to as overall sampling and analytical 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.

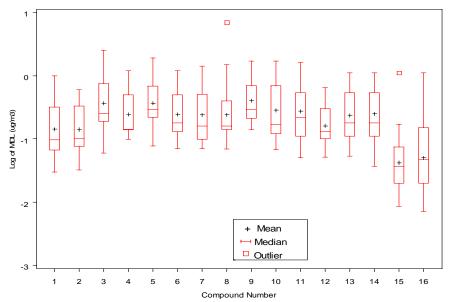


Figure 9. Box and whisker plot of the VOC and carbonyl MDLs across all the NATTS sites.

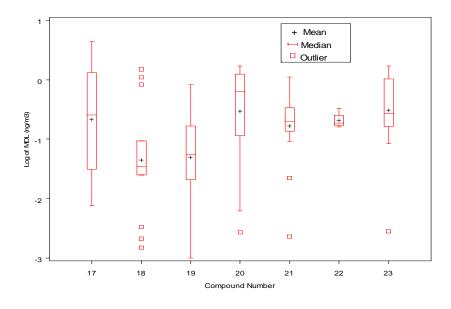


Figure 10. Box and whisker plot of the metals MDLs across all of the NATTS sites.

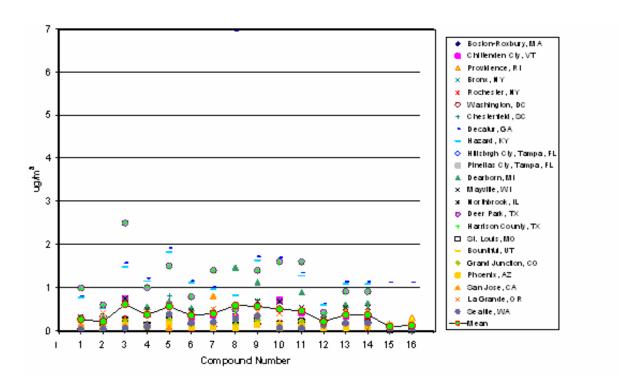


Figure 11. Plot of the VOC and carbonyl MDLs for all of the NATTS sites.

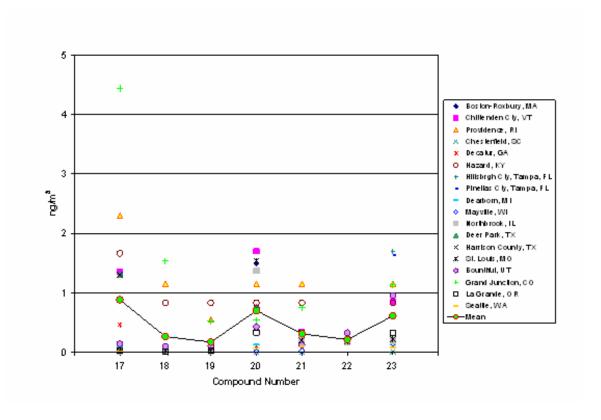


Figure 12. Plot of the metals MDLs for all of the NATTS sites.

Table 14. Mean and median CY2005 MDLs across all NATTS laboratories for four compounds. Compare with detectability requirements given in Table 3.

| MDL | Compound | | | | | | | | | |
|--------|----------------------------|----------------------------------|---------------------------------|----------------------------|--|--|--|--|--|--|
| WIDL | Benzene, μg/m ³ | 1,3-butadiene, μg/m ³ | formaldehyde, μg/m ³ | arsenic, ng/m ³ | | | | | | |
| Mean | 0.263 | 0.215 | 0.100 | 0.881 | | | | | | |
| Median | 0.096 | 0.102 | 0.038 | 0.304 | | | | | | |
| MQO | 0.044 | 0.020 | 0.014 | 0.046 | | | | | | |

3.0 SUMMARY

For calendar year 2005, across the entire NATTS network, and for the four target compounds (benzene, 1,3-butadiene, formaldehyde, and arsenic):

- Mean completeness of AQS data was less than the goal of 85 percent but median completeness was greater than 85 percent.
- Overall sampling and analytical precision met the MQO goal of a CV less than 15 percent. However, only very little precision data are available in AQS.
- Mean laboratory bias met the MQO of less than 25 percent for all compounds except arsenic, and then only during the second quarter of CY2005. Problems with PT sample may have been the cause. The program moved to using quartz filters instead of Teflon and the results illustrated a dramatic improvement.
- Flow rates measured during Instrument Performance Audits at NATTS field sites demonstrated that field bias is in general acceptably low. Only 11 percent of the flow rates showed greater than 10 percent bias.
- Mean MDLs were roughly an order of magnitude greater than those given in the NATTS TAD and used to develop NATTS DQOs. Median MDLs were approximately 2 to 6 times greater.

4.0 REFERENCES

- [1] "Final Draft, July 2004, National Monitoring Strategy, Air Toxics Component." Available at http://www.epa.gov/ttn/amtic/files/ambient/airtox/atstrat804.pdf; accessed July 31, 2006.
- [2] "Draft Technical Assistance Document for the National Ambient Air Toxics Trends and Assessment Program." http://www.epa.gov/ttn/amtic/files/ambient/airtox/drafttad.pdf. Accessed August 24, 2006.
- [3] Federal Register Proposed Rule Vol. 71, No. 10. January 17, 2006, p 2788.
- [4] Caviston, K. (2005). "National Air Toxics Trends Stations (NATTS) Proficiency Testing Program 200502 Data Report (2nd Quarter)." Available at http://www.epa.gov/ttn/amtic/files/ambient/airtox/datareport05.pdf; accessed July 31, 2006.