# ASSESSMENT OF TRENDS IN QUALITY ASSURANCE RESULTS FOR THE NATIONAL AIR TOXICS TRENDS STATIONS NETWORK DURING THE PERIOD 2005-2007

## Final

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# FOREWORD

This report was prepared by RTI International, under Work Assignment 00-05, Task 10, and Work Assignment 01-06, Task 2, for EPA contract EP-D-08-047. Substantial contributions to the acquisition of the laboratory method detection limits and parameter occurrence codes were provided by Dennis Mikel and Mike Jones of U.S.EPA.

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## 1.0 INTRODUCTION

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

The National Air Toxics Trends Station (NATTS) network was established to create a database of air quality data toward assessment of progress in reducing ambient concentrations of air toxics and concomitant exposure-associated risk. Presently, the NATTS network consists of 27 stations in the contiguous 48 states, with Los Angeles and Rubidoux, CA added in 2007 and Richmond, VA and Portland OR added in 2008. To ensure the quality of the data collected under the NATTS network, the U.S. EPA has implemented a Quality System comprised of two primary components: 1.) Technical Systems Audits (TSAs) and 2.) Instrument Performance Audits (IPAs) for both the network stations and the associated sample analysis laboratories. As an integral part of the Quality System, EPA has also instituted quarterly analysis of proficiency testing samples to provide quantitative assessment of laboratory performance and to ensure that sampling and analysis techniques are consistent with precision, bias, and method detection limits specified by the NATTS measurement quality objectives (MQOs). Please note that in 2007/2008, two new instruments/techniques were phased into the NATTS: Hexavalent Chromium and Polycyclic Aromatic Hydrocarbons. Due to this phase in, the QA data for these compounds are not included in this report.

Completion of sample and data collection for the NATTS program over the inclusive period of 2005 through 2007 affords the opportunity to examine changes in collection site and laboratory performance during that time period. The AQS database, as well as each of the yearly summary reports, contains a rich assessment of completeness, precision, bias and method detection limit results for a particular year and affords the opportunity to search for trends in that data since the inception of the NATTS program. The results of these tabulations and trends analyses will provide a “report card” that summarizes how the NATTS locations and their associated laboratories have been doing over the past three years and if adoption of new procedures has led to improvements in detection, higher data capture, and so on. For this effort, the following approach to exploring these trends was used:

- Tabulated completeness and precision data for selected volatile organic compounds were compiled directly from the AQS database for each of the calendar years: 2005, 2006, and 2007. Similarly, bias data were extracted from the original proficiency testing analysis reports for the same time period. Method detection limit data were captured directly from the respective annual reports[1,2,3] and augmented with original data from the laboratories themselves, where available. All data were assembled using an appropriate data management tool into datasets compatible with subsequent data summaries and quantitative analyses.
- Summaries of each of the major quality assessments (completeness, precision, bias, and MDLs) were created in tabular and graphical formats.

Subjective comparisons between years was facilitated through graphical displays of data summaries. Where supported by the data, formal tests of hypotheses and longitudinal data analyses of trends in the data quality parameters were performed using the individual original data. These data were acquired so that variance estimates could be computed for each site and laboratory. The following questions are of particular interest in this regard:

- Overall and for each NATTS monitoring site, has there been a change in data completeness over time and, if so, is it improving or deteriorating?
- Overall and for each monitoring location and chemical analysis laboratory combination, is there a discernable trend in the precision of replicate sample collections and analyses for selected analytes, over time? Was the proportion of sites exceeding the measurement quality objectives different between years?
- For laboratories participating in the proficiency testing program over multiple years, was there an improvement (i.e., decrease) in bias associated with chemical measurements over time?
- For each chemical analyte and analysis laboratory, are method detection limits exhibiting any change over time?

The results of these analyses are presented in this three year QA data trends report. Complete descriptions of sites, analytes of interest, measurement quality objectives and statistical measurements are presented in the 2007 NATTS QA Report[1]. Only NATTS sites participating in all three years were included in the analysis dataset, although in some cases results for specific analytes may be available for only one or two years.

Where possible, all data analyses were performed in SAS, version 9.2. Exhaustive compilation of laboratory bias and MDL results, by laboratory, was performed using Microsoft Excel. Trends analyses across years were performed using the SAS MIXED procedure, accounting for the correlation between measurements at the same site and/or laboratory over time. As an example, completeness trends were examined, by site and analyte, with a model which included percent completeness as an outcome and year as the explanatory variable. For this model, the slope estimates reported in Table 4 may be interpreted as the amount of change in percent completeness, for a given analyte and site, for each unit change in year. In simple terms, this parameter estimate is analogous to the slope of a curve of Percent Completeness plotted against Time. The amount of variability or “scatter” in the Percent Completeness measurements is reflected in the standard error, adjusted for the number of data points. Finally, the p-value is the statistical probability that the parameter estimate (i.e., slope) might be equal to zero. By way of example, a p-value of 0.02 would indicate that there was a 2% probability that the actual slope was equal to zero or, conversely, a 98% probability that the slope was not equal to zero. A slope of zero for this example would indicate that when the degree of change in percent completeness with year is examined in light of the variability in the data, no trend, either increasing or decreasing, can be concluded, based on the available data.

## 2.0 DATA COMPILATION AND ANALYSIS DATASET ASSEMBLY

Data for completeness and replicate (i.e., analytical, duplicate and collocated) precision assessments were extracted directly from the Air Quality Systems (AQS) database for samples collected during the period January 1, 2005 through December 31, 2007. NATTS site and parameter (i.e., chemical analyte) codes were identical to those employed for the 2007 QA Report[2]. Parameter occurrence codes (POCs) which identified primary, duplicate and collocated samples collected at each NATTS site were assumed to be unchanged across the three-year period.

Completeness, analytical precision, and overall precision were computed for benzene, 1,3-butadiene, carbon tetrachloride, acrolein, formaldehyde, acetaldehyde, arsenic, cadmium, and lead as previously described[1], with the variable, YEAR, created to facilitate analysis between years. Laboratory bias data for the three year intervals were obtained from U.S. EPA in spreadsheet format and carefully examined for correctness of associations between specific laboratories and NATTS monitoring sites. Only laboratory data associated with NATTS sites were retained for analysis; data for sites mentioned in Section 1 were excluded because they were not affiliated with the NATTS network until 2007 or 2008.

Table 1 presents the 22 NATTS sites which participated in the NATTS program for the three years of interest to this report. Similarly, Table 2 illustrates the pollutants of interest for the NATTS program. Measurement quality objectives for each analyte and year, presented in Table 3, were established by the U.S. EPA to promote the highest quality of data and were the benchmarks of performance against which NATTS sites and laboratories were measured. All acrolein results presented in this report should be viewed with consideration for the fact that some laboratories were still developing analytical proficiency for this compound during the 2005 through 2007 performance period.

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

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

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

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

## Table 3. NATTS Measurement Quality Objectives by Analyte and Year.

| Analyte | Completeness | Precision (Coefficient of Variation) | Laboratory Bias | MDL[a] 2005 | MDL[a] 2006 | MDL[a] 2007 |
|---|---|---|---|---|---|---|
| benzene[c] | > 85 % | < 15 % | < 25 % | 0.044 µg/m$^3$ | 0.016 µg/m$^3$ | 0.016 µg/m$^3$ |
| 1,3-butadiene[c] | > 85 % | < 15 % | < 25 % | 0.020 µg/m$^3$ | 0.013 µg/m$^3$ | 0.013 µg/m$^3$ |
| formaldehyde[c] | > 85 % | < 15 % | < 25 % | 0.014 µg/m$^3$ | 0.0074 µg/m$^3$ | 0.0074 µg/m$^3$ |
| acrolein | > 85 % | < 15 % | < 25 % | --[b] | --[b] | --[b] |
| acetaldehyde | > 85 % | < 15 % | < 25 % | --[b] | --[b] | --[b] |
| carbon tetrachloride | > 85 % | < 15 % | < 25 % | --[b] | --[b] | --[b] |
| arsenic[c] | > 85 % | < 15 % | < 25 % | 0.046 ng/m$^3$ | 0.217 ng/m$^3$ | 0.217 ng/m$^3$ |
| cadmium | > 85 % | < 15 % | < 25 % | --[b] | --[b] | --[b] |
| lead | > 85 % | < 15 % | < 25 % | --[b] | --[b] | --[b] |

[a] Method detection limit.

[b] MDL measurement quality objective not specified for this analyte and year.

[c] Data Quality Objectives and subsequent MQOs were created for these compounds at the beginning of this program.

# 3.0 DATA ANALYSIS AND RESULTS

## 3.1 Completeness

Completeness assessments for each of the three years were computed from the primary parameter occurrence code and were based on a maximum of 60 data collections (i.e., 1 day in 6) during the year. These data are presented in Figures 1-9 for the nine representative compounds. Missing values reflect sites for which data were not reported for a particular analyte. In the case of Seattle, completeness statistics were adjusted for the fact that this site was relocated in 2006 and, therefore, non-operational for nearly six months. With the exception of acrolein during 2005 and 2006, the completeness statistics for all sites and analytes was remarkably high and exceeded the measurement quality objective in nearly every instance. However, because of the difficulty in analyzing for acrolein and the limited number of sites attempting this measurement, acrolein completeness for sites where it is reported is somewhat lower for 2005 and 2006 but improves dramatically during 2007. With the exception of the Phoenix, AZ site, all NATTS locations which provided results for acrolein exceeded the measurement quality objective of 85% completeness for 2007. Overall, completeness statistics for formaldehyde and acetaldehyde exceeded the MQO for most sites and years, with Mayville, WI and Northbrook, IL as notable exceptions for specific years. Notable exceptions included Dearborn, MI (2005), Mayville, WI(2007) and Northbrook, IL (2005). No aldehyde data were reported for Mayville, WI in 2005. Despite a challenging chemical analysis, arsenic completeness statistics (Figure 2) exceeded, or nearly exceeded, the MQO for every site at which metals were measured, for each of the three years. Metals were not reported for Bronx, NY (2006), Phoenix, AZ (2005), Rochester, NY (2005, 2006), Harrison County, TX(2005, 2006, 2007), and Underhill, VT (2005, 2006, 2007) sites. Similarly, Figures 1 and 2 show completeness statistics for benzene and 1,3-butadiene, respectively, to be above the MQO at each site and for each year with no notable trend. No measurements were compiled for either of the VOCs at the Washington, DC site because the parameter occurrence codes (POCs) recorded in the 2006 NATTS QA Report were inconsistent with the POCs for primary samples resident in the AQS database for both 2005 and 2006. Figure 10 illustrates that all NATTS sites met or exceeded the MQO for completeness for all analytes except for acrolein during 2005, which showed a dramatic increase from 2005 to 2007. With this notable exception, no clear evidence for a trend in completeness exists for any site although some variability between years is indicated for some sites.

Lastly, the proportion of sites achieving at least 85% completeness (Figure 11) for each of the three years shows that, again with the exception of acrolein in 2005, at least 90% of sites met or exceeded the 85% completeness threshold for each of the three years. While 2006 seemed to exhibit the best completeness statistic, no clear trend with year is apparent.

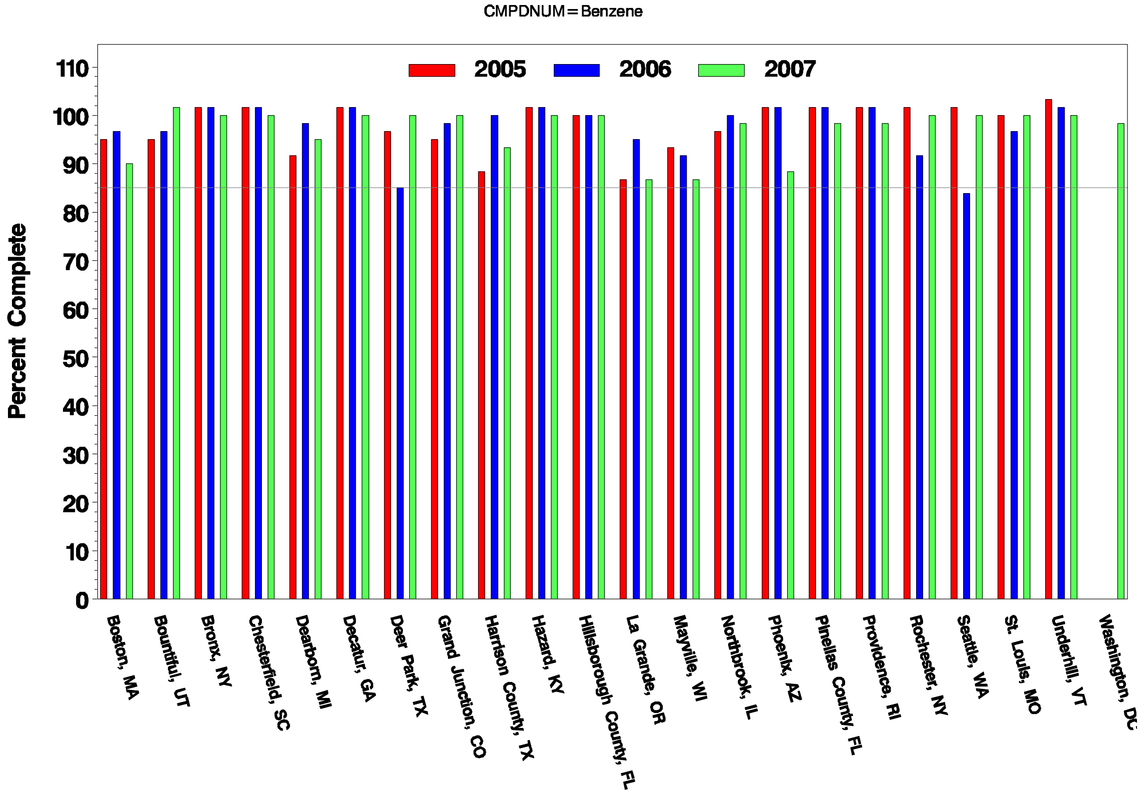


Figure 1. Completeness for Benzene at NATTS Sample Collection Sites

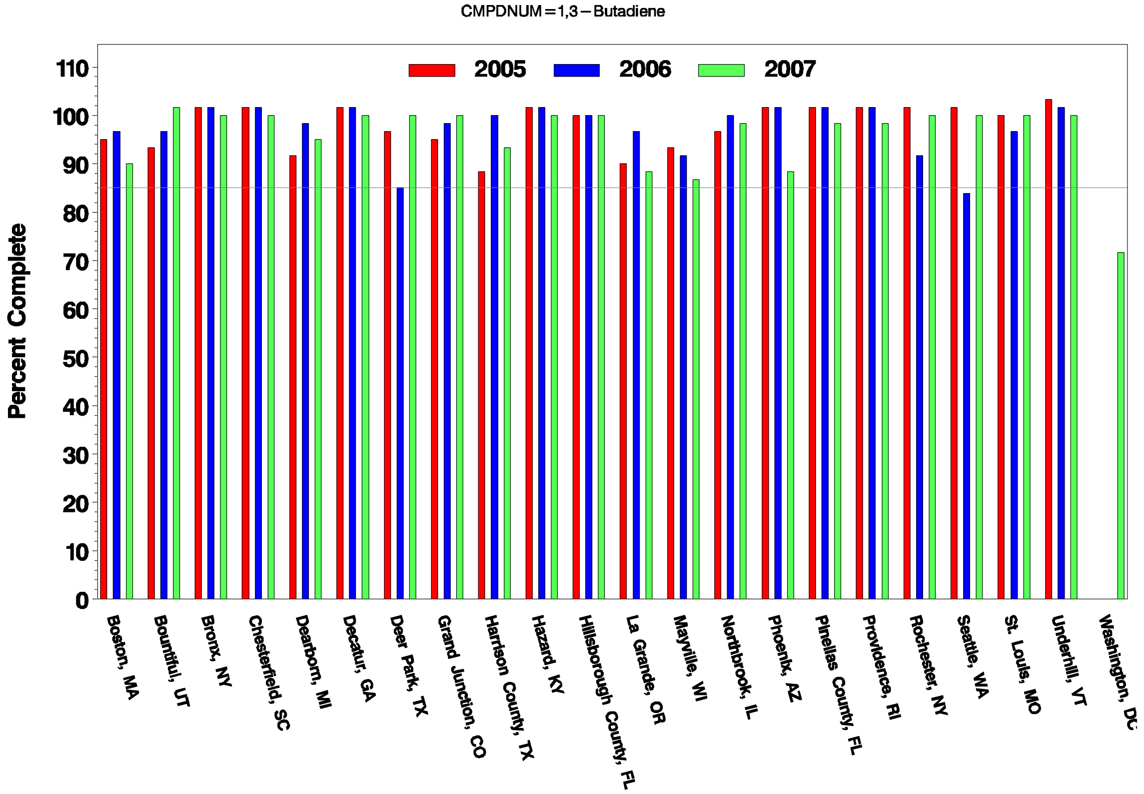


Figure 2. Completeness for 1,3-Butadiene at NATTS Sample Collection Sites.

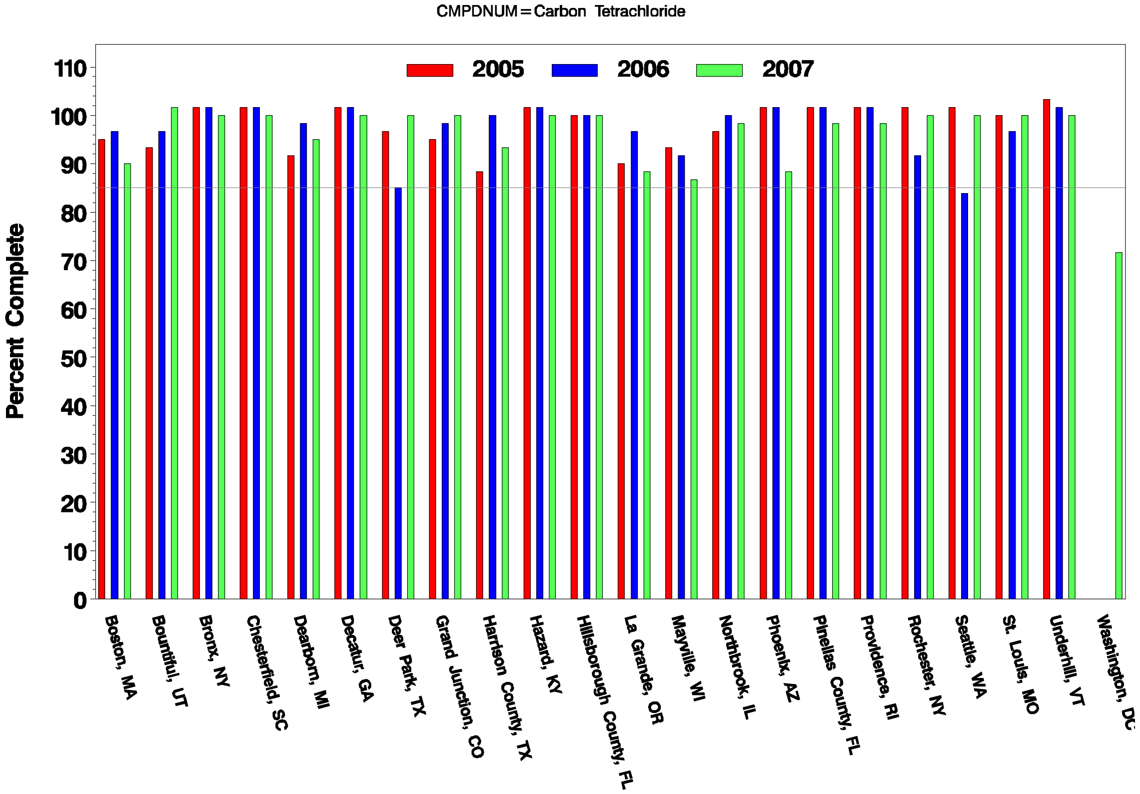


Figure 3. Completeness for Carbon Tetrachloride at NATTS Sample Collection Sites.

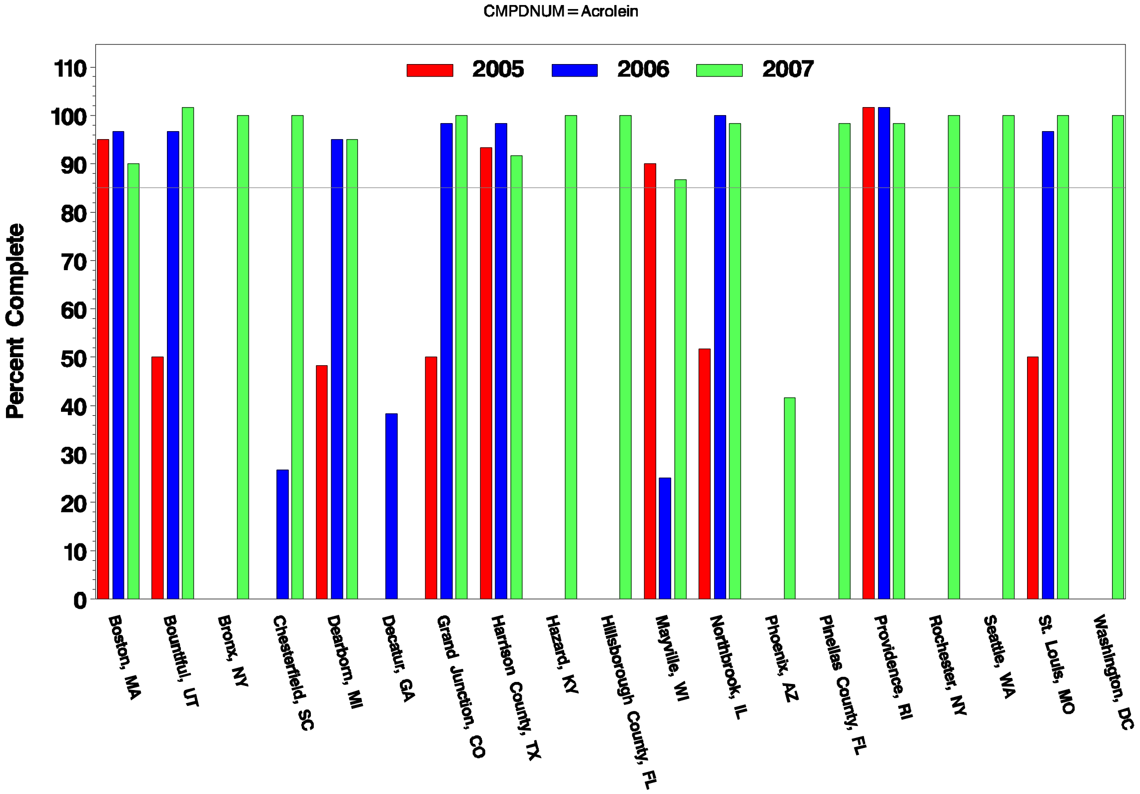


Figure 4. Completeness for Acrolein at NATTS Sample Collection Sites (data not available for Deer Park, TX; LaGrande, OR; Underhill, VT sites).

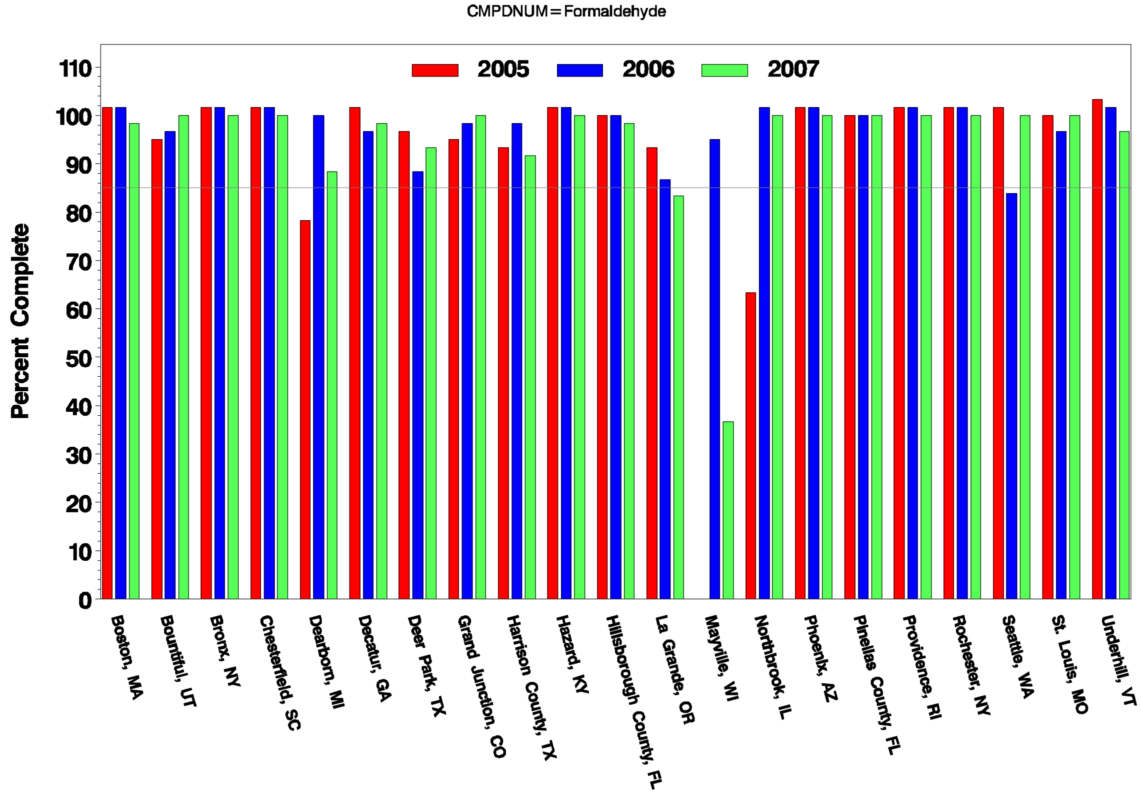


Figure 5. Completeness for Formaldehyde at NATTS Sample Collection Sites (data not available for Washington D.C. site).

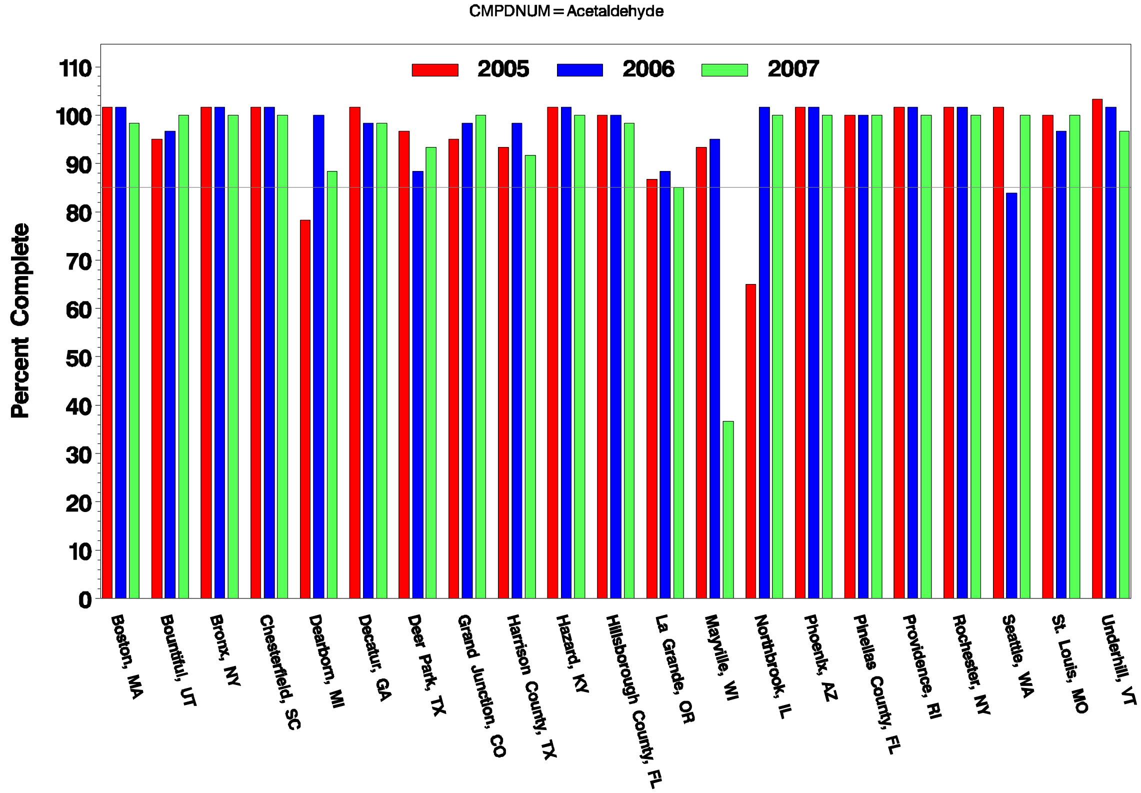


Figure 6. Completeness for Acetaldehyde at NATTS Sample Collection Sites (data not available for Washington D.C. site).

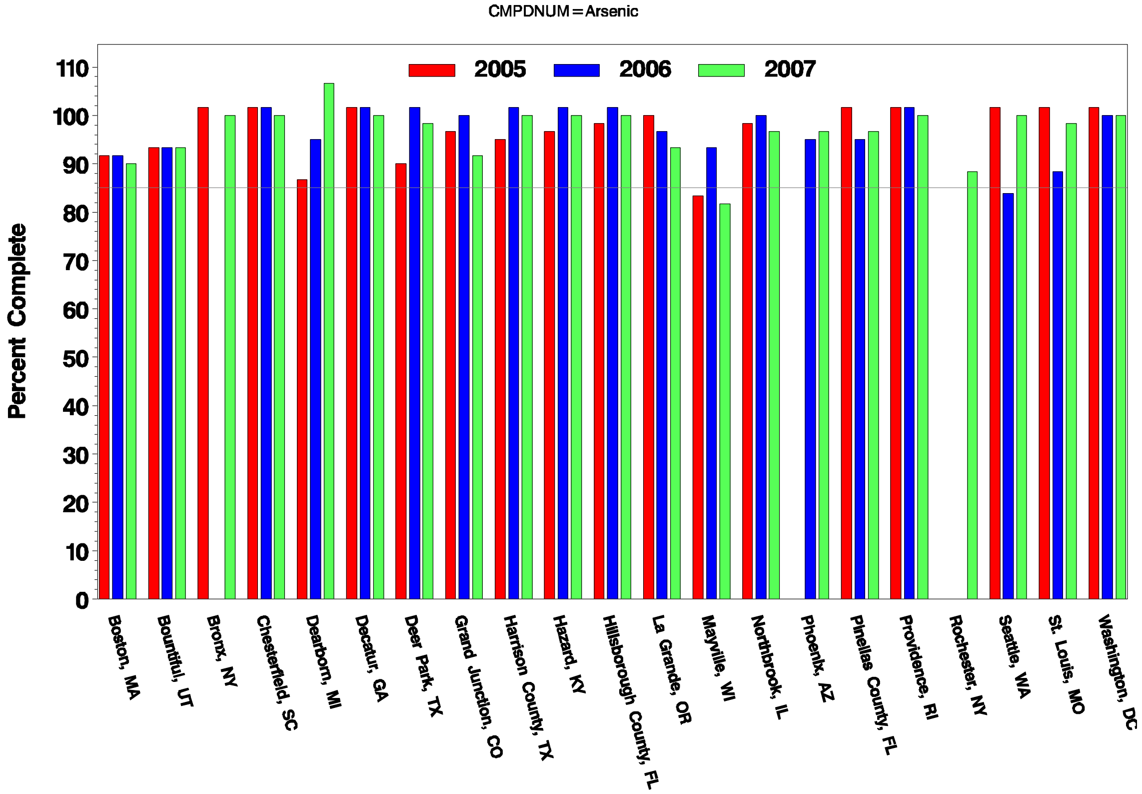


**Figure 7. Completeness for Arsenic at NATTS Sample Collection Sites (data not available for Underhill, VT site).**

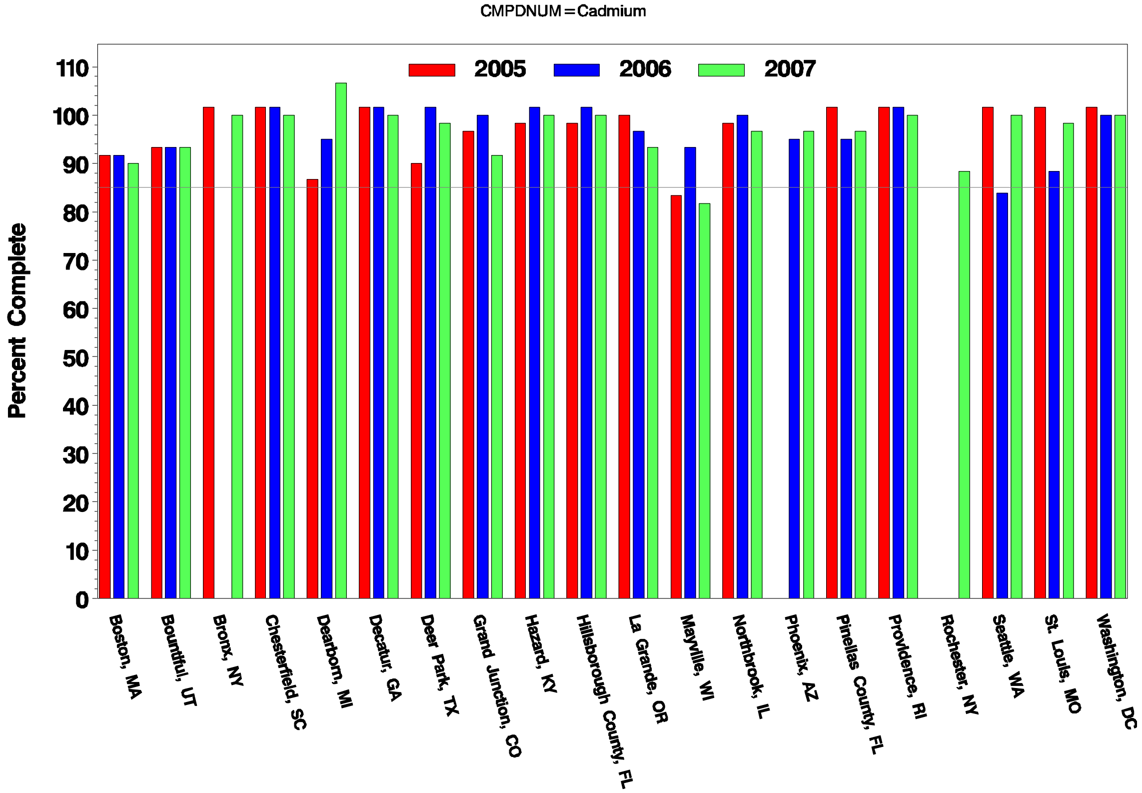


**Figure 8. Completeness for Cadmium at NATTS Sample Collection Sites (data not available for Underhill, VT; Harrison County, TX sites).**

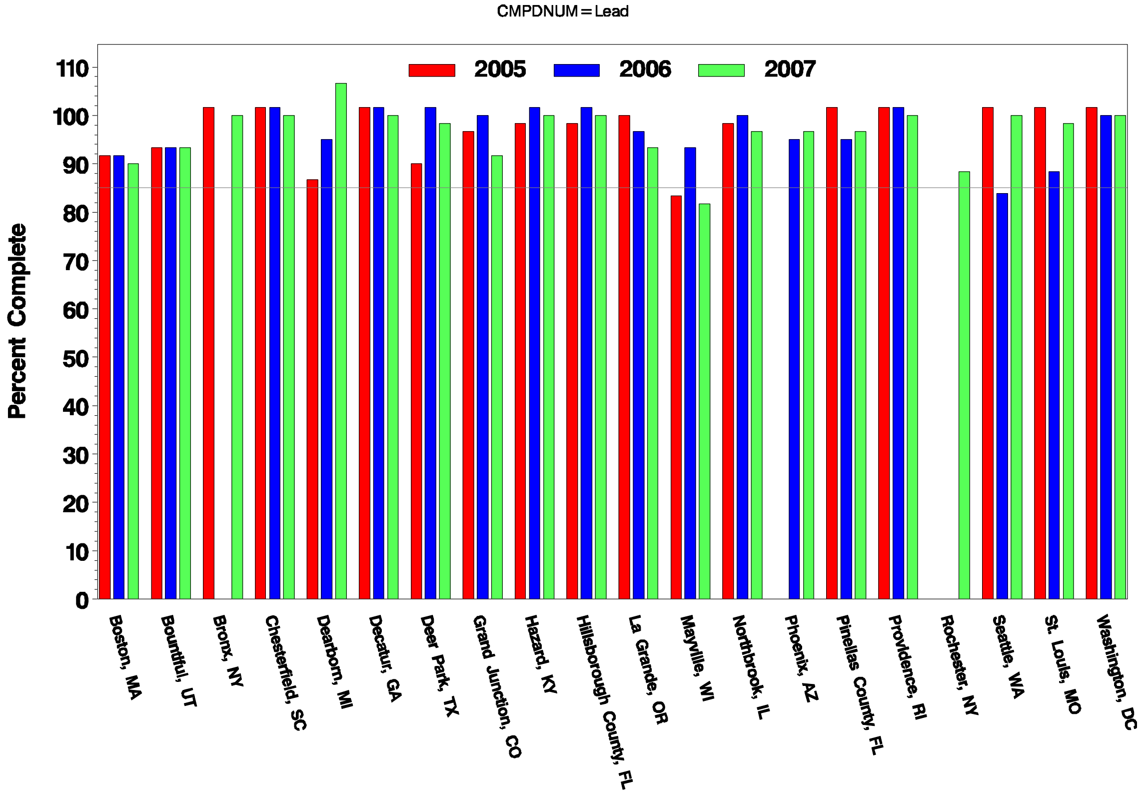


**Figure 9. Completeness for Lead at NATTS Sample Collection Sites (data not available for Underhill, VT; Harrison County, TX sites).**

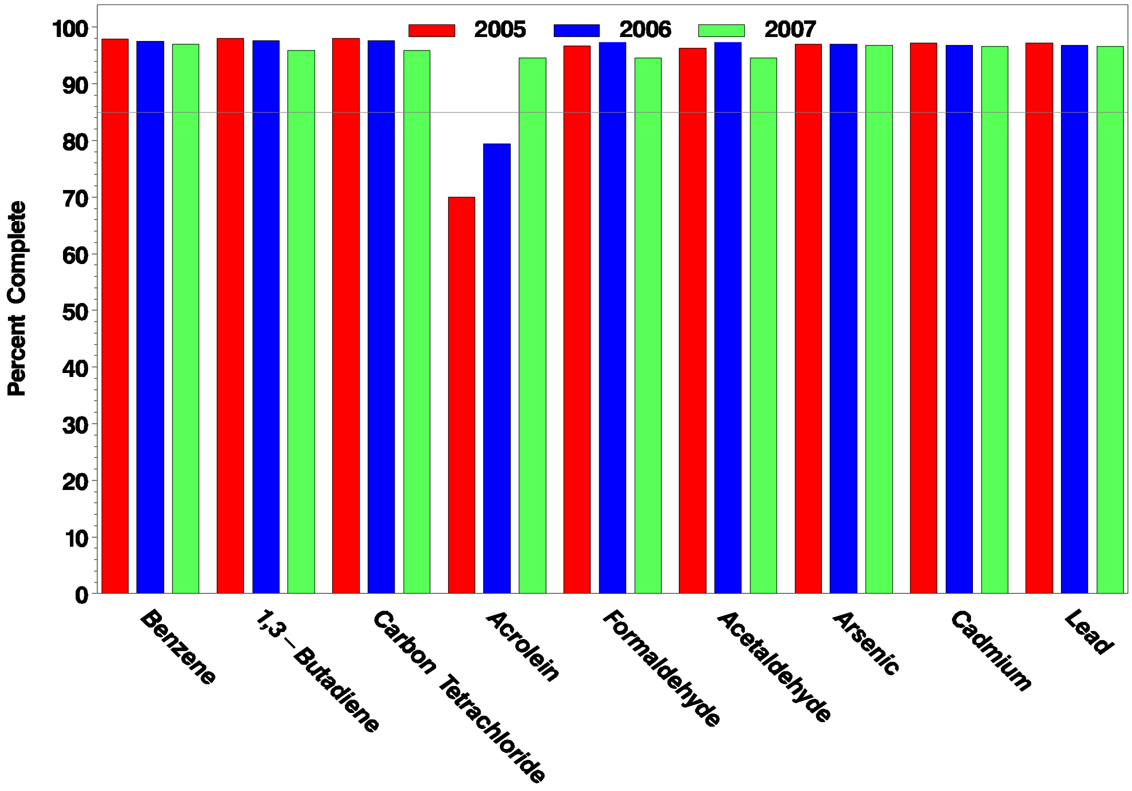


**Figure 10. Percent Completeness Across All Reporting NATTS Sites Across Years 2005-2007.**

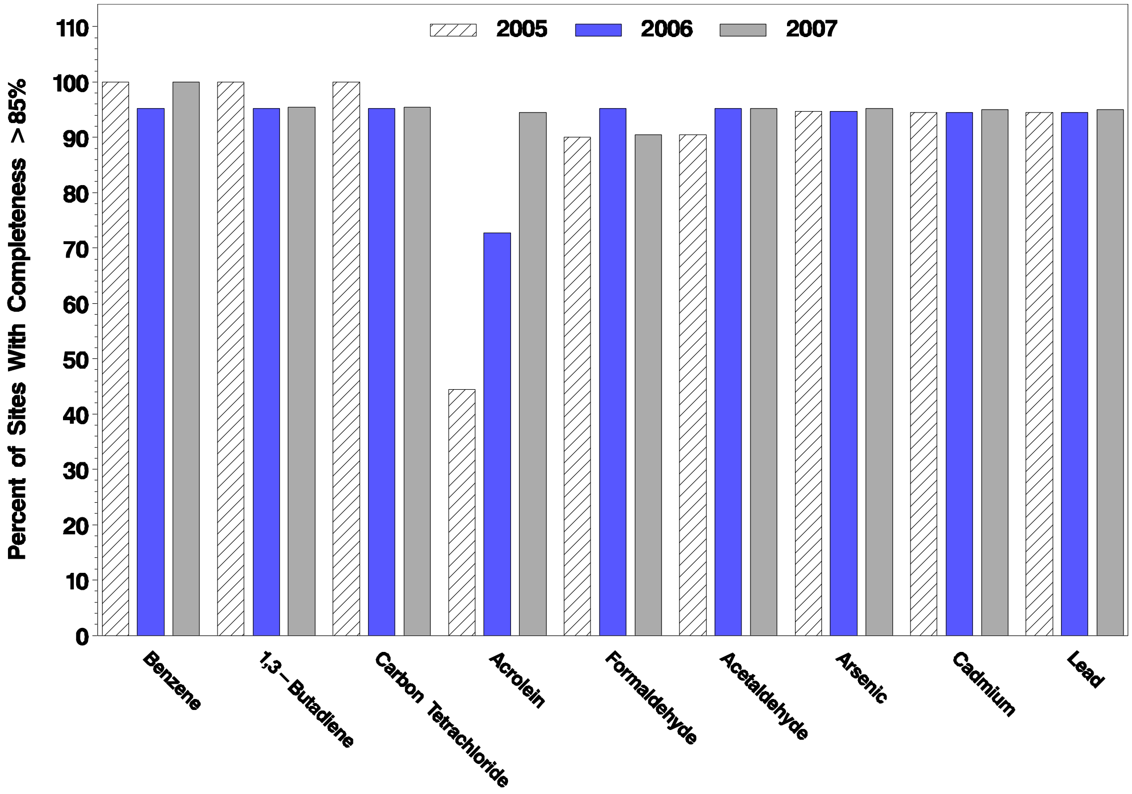


**Figure 11. Percent of Reporting NATTS Sites Meeting the Completeness Measurement Quality Objectives for 2005 through 2007.**

Trends analysis results across all sites and for each analyte are shown in Figure 12 and Table 4. Two interesting features are apparent in Figure 12: 1.) the variability in the mean completeness for a given analyte appears to be decreasing with time and 2.) completeness for acrolein is improving significantly. This latter observation is corroborated by the slope (12.03) and probability that this slope could actually be equal to zero (p=0.0170) for acrolein. With acrolein as an exception, the magnitude of the standard error in the slope relative to the magnitude of the slope itself, suggests a very high degree of variability in the data. No other trends were observed in the plot and no statistically significant trends (i.e., $p<=0.05$) were found for any of the individual site and analyte combinations.

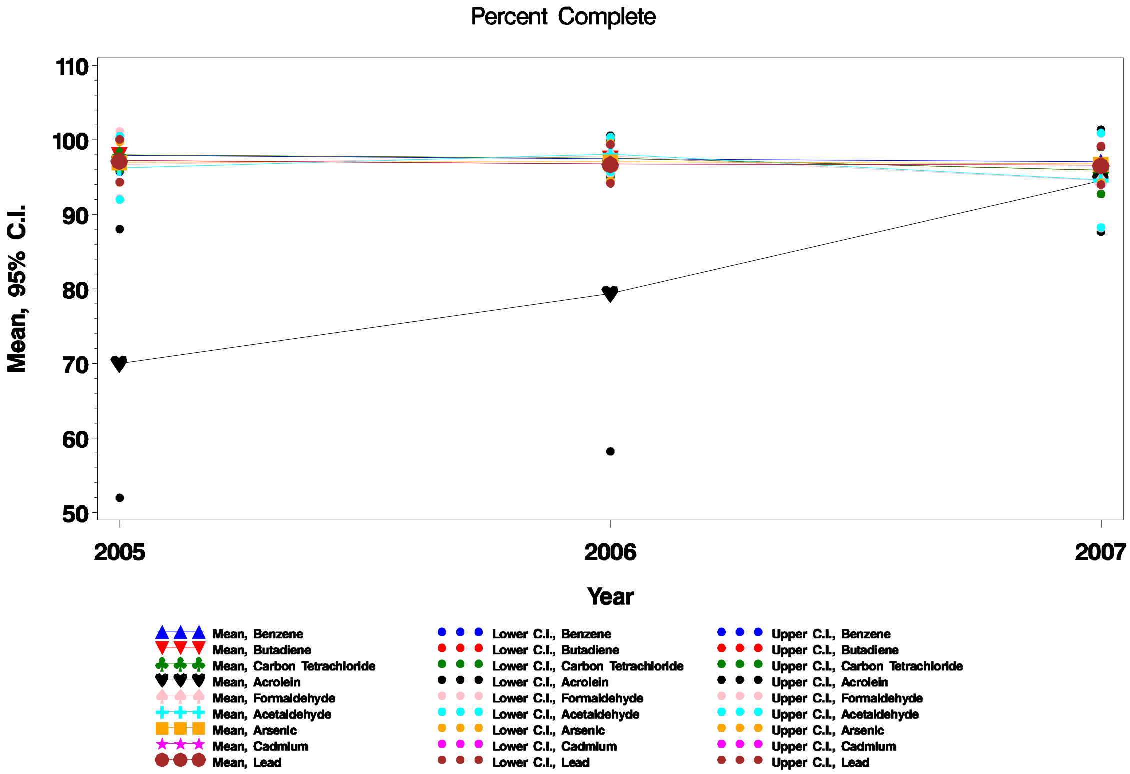


**Figure 12. Change in Average Completeness with Time Across All NATTS Sites.**

**Table 4. Modeled Parameter Estimates and Significance Levels for Completeness with Time - All NATTS Sites.**

| Analyte Abbreviation | Time Effect | Slope[a] | Standard Error[b] | N[c] | P-value[d] |
|---|---|---|---|---|---|
| ACET | YEAR | -0.8333 | 1.4483 | 63 | 0.5682 |
| ACRO | YEAR | 12.0335 | 4.7358 | 38 | 0.0170 |
| AS | YEAR | -0.06858 | 0.7398 | 59 | 0.9266 |
| BENZ | YEAR | -0.4539 | 0.6499 | 64 | 0.4887 |
| BUTA | YEAR | -0.8164 | 0.7125 | 64 | 0.2610 |
| CD | YEAR | -0.2440 | 0.7644 | 56 | 0.7515 |
| CTET | YEAR | -0.8164 | 0.7125 | 64 | 0.2610 |
| FORM | YEAR | -0.8719 | 1.4768 | 62 | 0.5588 |
| PB | YEAR | -0.2440 | 0.7644 | 56 | 0.7515 |

[a] The slope of the regression line for percent completeness vs. time.
[b] Reflects the amount of variability in the slope.
[c] Number of data points included in the regression.
[d] Probability that the slope is statistically equal to zero, values less than 0.05 reflect significance.

## 3.2 Analytical Precision

Analytical precision was computed from replicate chemical analyses performed on the same sample and was reported by NATTS collection site, rather than analytical laboratory, to allow direct comparison with overall precision discussed below in Section 3.3. To facilitate this presentation, linkages between collection sites and specific analytical laboratories were established for each analyte group and year. Analytical precision data, presented in detail in Appendix A and summarized in Figures 13-18, show relatively good precision (i.e., less than the MQO of 15%) with sporadic spikes of poorer precision. All instances of missing results for specific years and collection sites exclusively reflect the absence of precision data for those cases. No analytical precision data are shown for the metals analytes since replicate analyses these compounds were reported only in 2007. Cases where agreement between replicate analyses exceeded the MQO may reflect single extreme values, as was found to be true for benzene and the carbonyl compounds (i.e., formaldehyde and acetaldehyde) at specific sites in 2007. Although a detailed investigation of all such cases would be needed to verify this suggestion, extreme values were observed in some data included in the 2007 QA Report. Not surprisingly, precision estimates for acrolein tend to exceed the MQO more often than for other analytes although the precision is remarkably good for many years and sites considering the difficulty in analyzing air samples for this compound. Figure 19 shows the average analytical precision for each analyte across NATTS sites with 1,3-butadiene and possibly carbon tetrachloride showing improvement (i.e., lowering) in precision. Acrolein and the two carbonyl compounds, formaldehyde and acetaldehyde, show a deterioration of precision with time. Average analytical precision estimates, computed across sites for most analytes and years, were well within the MQO of 15%. Despite the absence of a discernable trend with time, appreciable variability is apparent (Figure 20) for the percent of sites meeting the MQO for analytical precision, particularly for 1,3-butadiene and acrolein. It is again noteworthy that both of these analytes pose challenges to analytical chemistry procedures. Nevertheless, the proportion of sites achieving the MQO for precision tended to be 80% or better, with acrolein and 1,3-butadiene noted as exceptions. As noted previously, precision data for arsenic, cadmium and lead were reported only for 2007 and are, therefore, not included in the results presented by site.

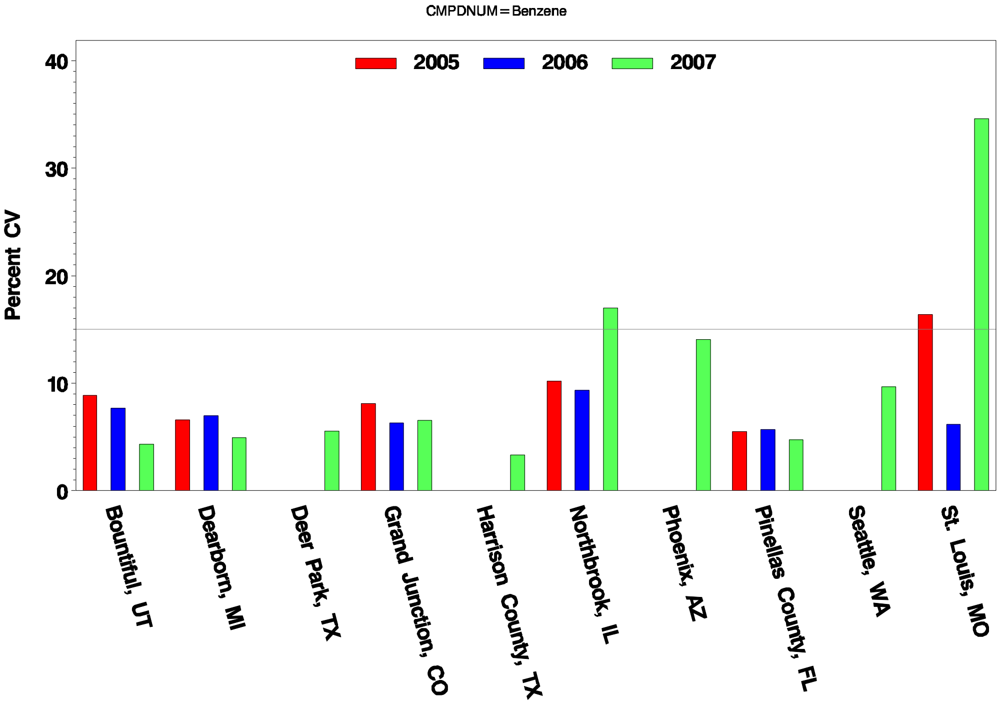


**Figure 13. Analytical Precision for Benzene at NATTS Sites (duplicate analysis data unavailable for sites not shown).**

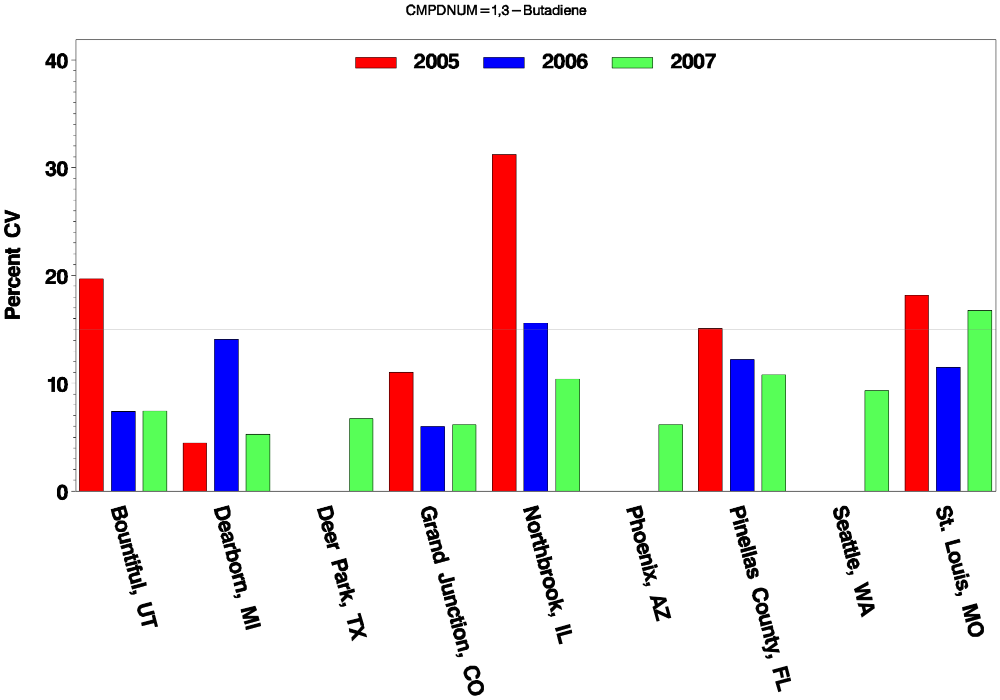


Figure 14. Analytical Precision for 1,3-Butadiene at NATTS Sites (duplicate analysis data unavailable for sites not shown).

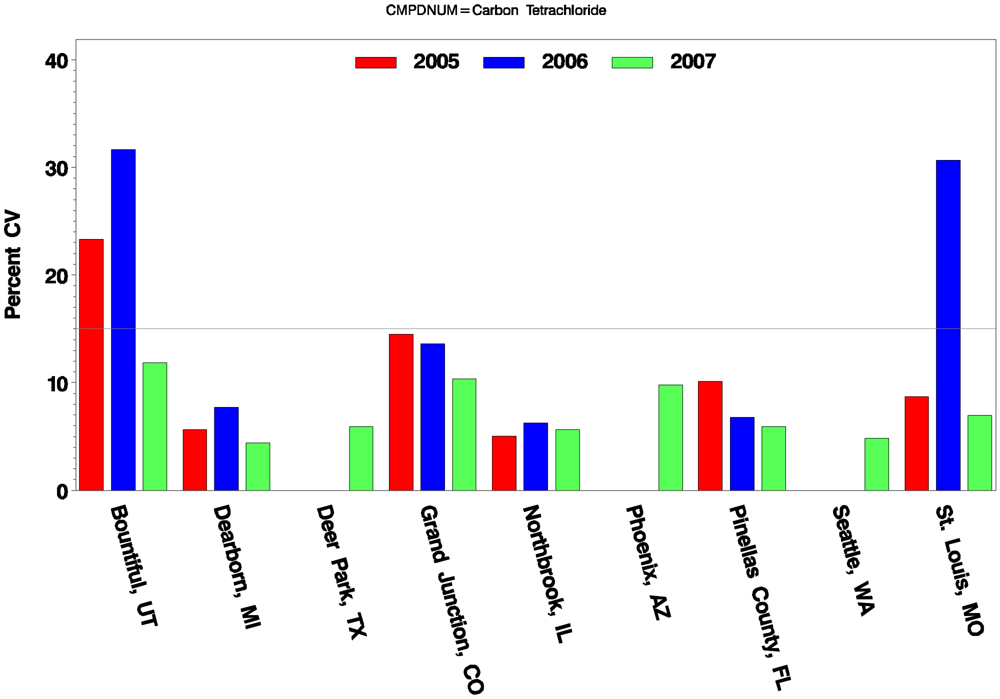


Figure 15. Analytical Precision for Carbon Tetrachloride at NATTS Sites (duplicate analysis data unavailable for sites not shown).

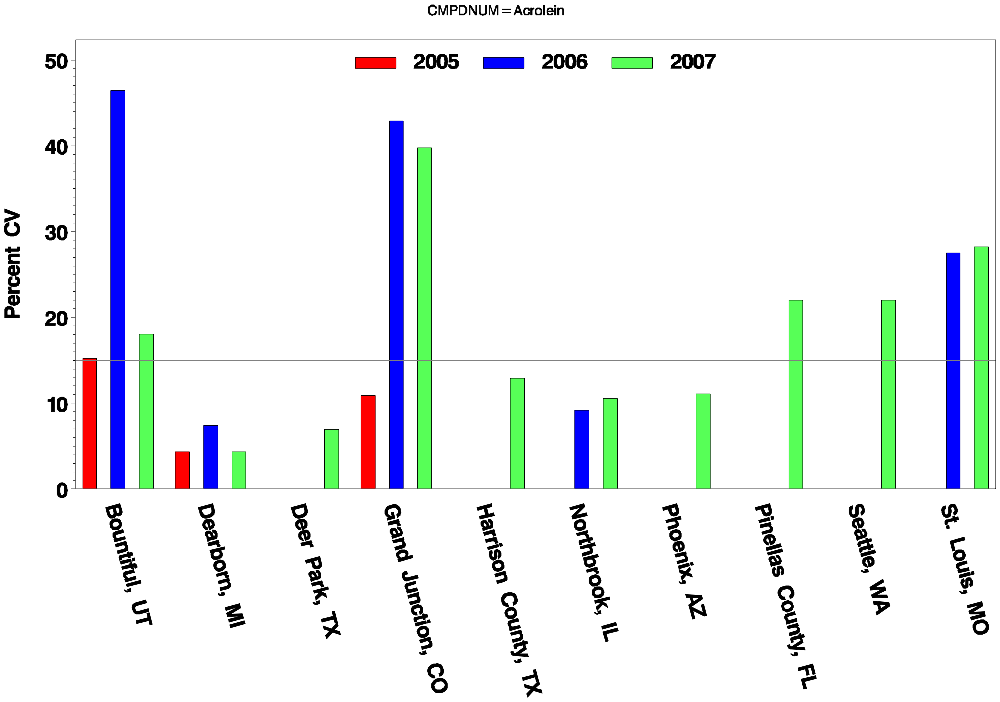


Figure 16. Analytical Precision for Acrolein at NATTS Sites (duplicate analysis data unavailable for sites not shown).

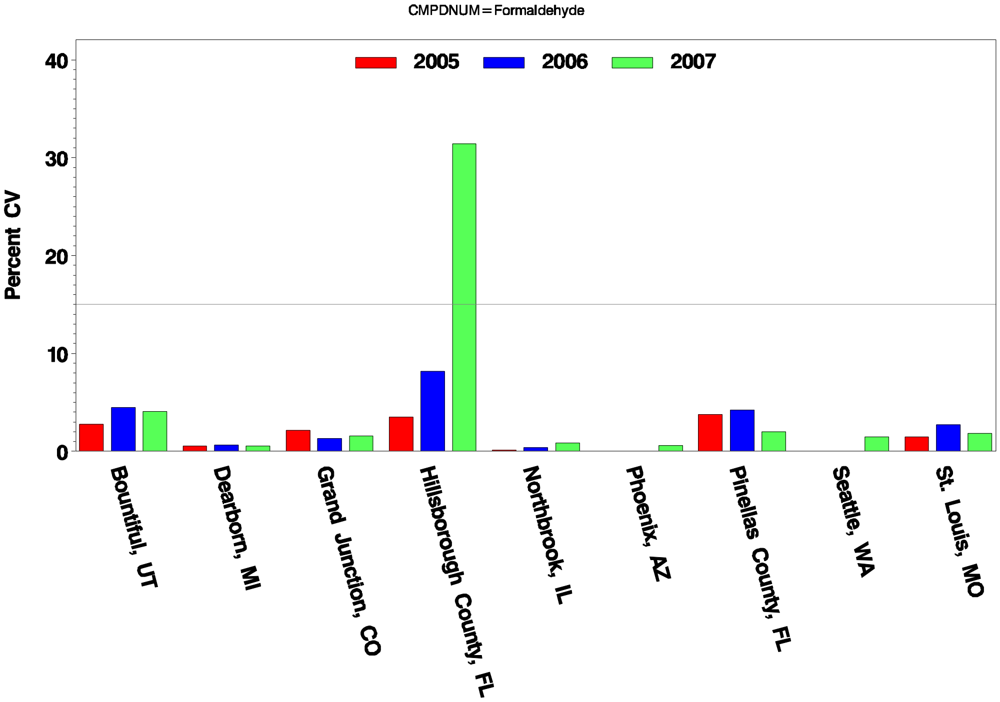


Figure 17. Analytical Precision for Formaldehyde at NATTS Sites (duplicate analysis data unavailable for sites not shown).

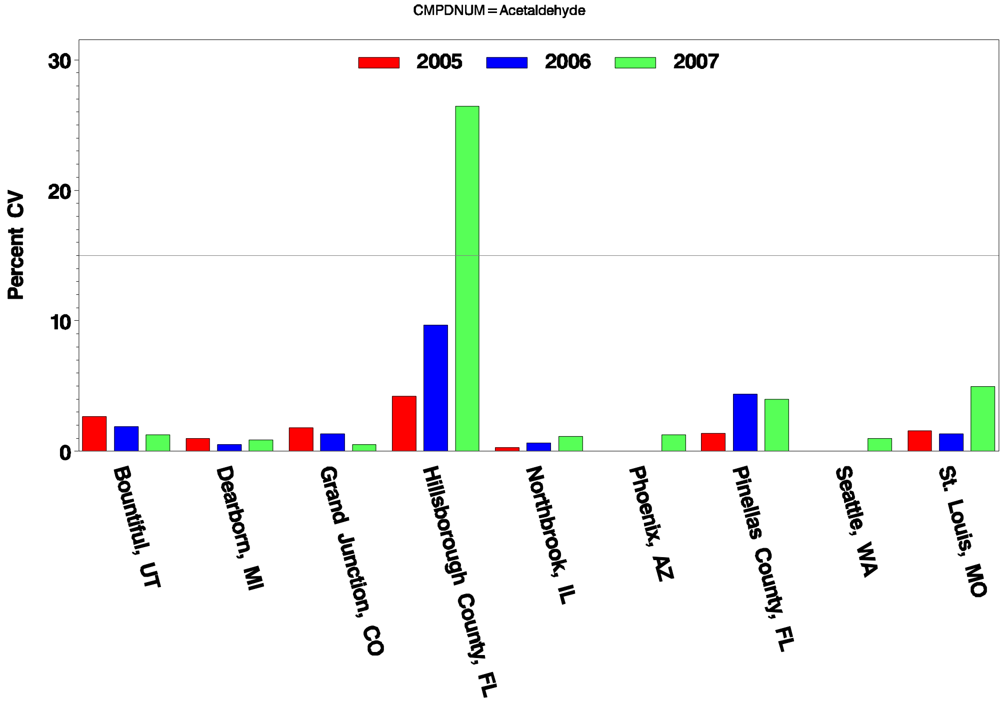


Figure 18. Analytical Precision for Acetaldehyde at NATTS Sites (duplicate analysis data unavailable for sites not shown).

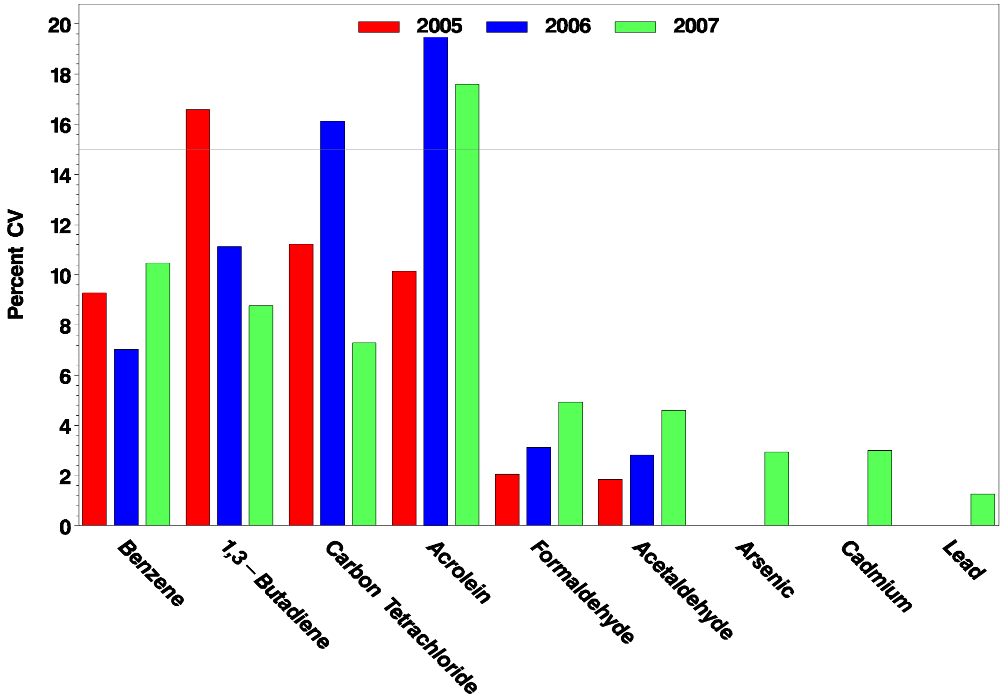


Figure 19. Analytical Precision for Reporting NATTS Laboratories Across Years 2005-2007

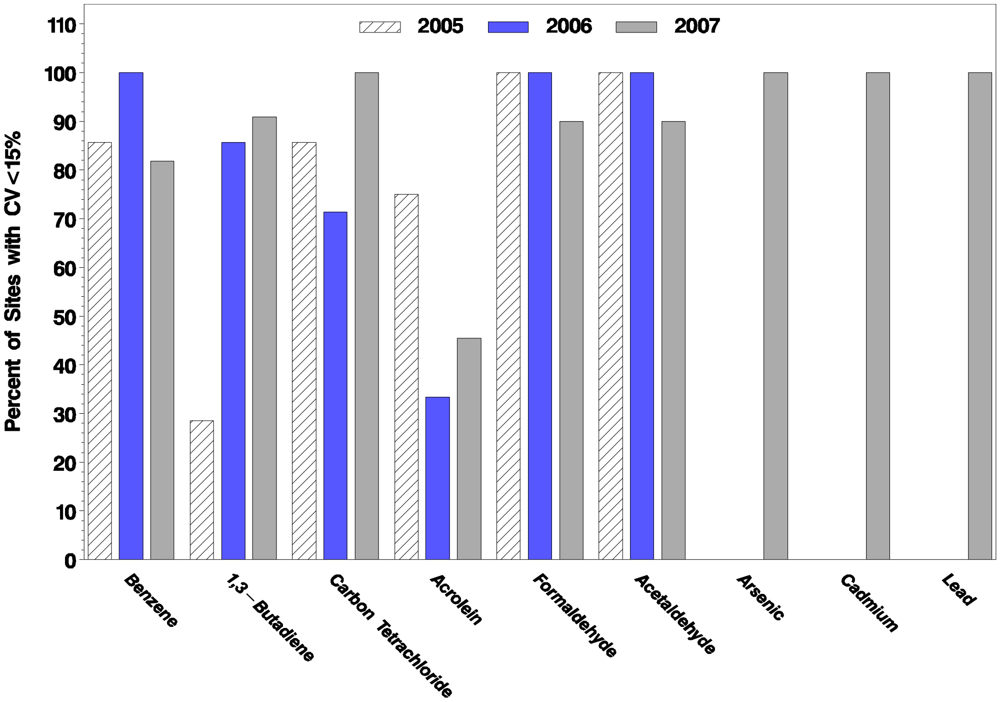


**Figure 20. Percent of Reporting NATTS Sites Meeting the Precision Measurement Quality Objectives for 2005 through 2007.**

Examination of the quantitative results for improvement in analytical precision with time shows appreciable scatter in the data but does reveal a possible effect for 1,3-butadiene (red markers, Figure 21). The slope estimates, expressed as the change in percent CV per day, and their corresponding probabilities of being equal to zero (i.e. p-values) in Table 5 confirm this observation although the slopes are very small and their associated variability (i.e., standard errors) relatively large. On average, the percent CV appeared to decrease by approximately 4% across the three year period. Although arsenic data are only available for 2007 and therefore must be interpreted cautiously, an improvement in %CV for this shorter period is observed. Based on the slope estimates for the individual sites (Table 6) which exhibit a statistically significant change in analytical precision with time (i.e., p-value ≤0.05), all except acetaldehyde at the St. Louis site show a decrease (i.e., improvement) in %CV. Precision for acrolein at the Phoenix, AZ site improved the most dramatically to the extent of approximately 20% during 2007, possibly reflecting improvements in laboratory proficiencies with this difficult analyte.

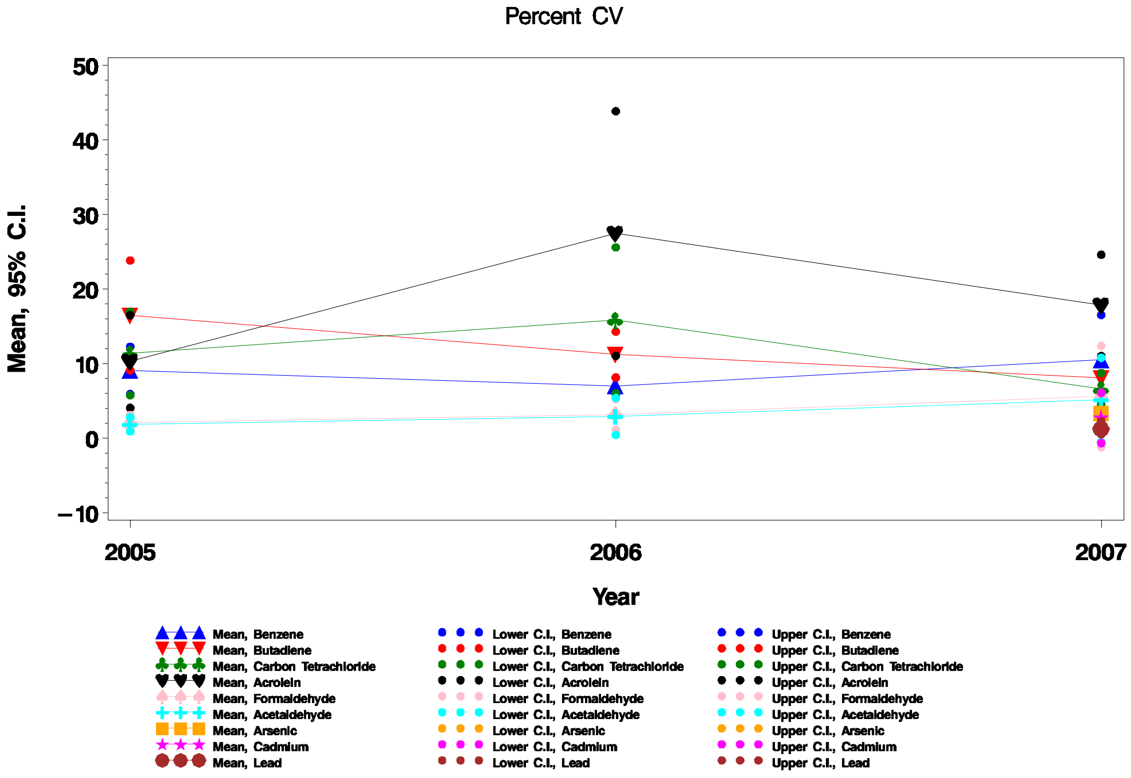


**Figure 21. Change in Average Analytical Precision with Time Across All NATTS Sites.**

## Table 5. Modeled Parameter Estimates and Significance Levels for Analytical Precision with Time - All NATTS Sites.

| Analyte Abbreviation | Time Effect | Slope[a] | Standard Error[b] | N[c] | P-value[d] |
|---|---|---|---|---|---|
| ACET | DATE | 0.000012 | 0.000021 | 318 | 0.5793 |
| ACRO | DATE | -0.00011 | 0.000103 | 269 | 0.2951 |
| AS | DATE | -0.00004 | 0.000013 | 81 | 0.0075 |
| BENZ | DATE | 0.000020 | 0.000017 | 573 | 0.2247 |
| BUTA | DATE | -0.00004 | 0.000013 | 506 | 0.0042 |
| CD | DATE | -2.47E-6 | 1.248E-6 | 81 | 0.0516 |
| CTET | DATE | -0.00004 | 0.000019 | 495 | 0.0581 |
| FORM | DATE | 0.000038 | 0.000022 | 318 | 0.0845 |
| PB | DATE | 2.992E-6 | 2.507E-6 | 81 | 0.2362 |

[a] The slope of the regression line for percent C.V. vs. time.
[b] Reflects the amount of variability in the slope.
[c] Number of data points included in the regression.
[d] Probability that the slope is statistically equal to zero, values less than 0.05 reflect significance.

**Table 6. Modeled Parameter Estimates and Significance Levels for Analytical Precision with Time - Sites and Analytes Exhibiting Significant Change.**

| Analyte Abbreviation | Site Effect | Time Effect | Slope[a] | Standard Error[b] | N[c] | P-value[d] |
|---|---|---|---|---|---|---|
| ACET | St. Louis, MO | DATE | 7.389E-6 | 3.482E-6 | 36 | 0.0412 |
| ACRO | Phoenix, AZ | DATE | -0.00055 | 0.000155 | 6 | 0.0240 |
| AS | Boston, MA | DATE | -0.00005 | 0.000019 | 56 | 0.0059 |
| BENZ | Bountiful, UT | DATE | -0.00001 | 7.137E-6 | 80 | 0.0455 |
| BUTA | Bountiful, UT | DATE | -0.00009 | 0.000031 | 60 | 0.0063 |
| BUTA | Pinellas County, FL | DATE | -0.00003 | 0.000013 | 264 | 0.0333 |
| CD | Boston, MA | DATE | -2.65E-6 | 1.193E-6 | 56 | 0.0304 |
| CTET | Pinellas County, FL | DATE | -0.00002 | 5.632E-6 | 264 | 0.0003 |

[a] The slope of the regression line for percent C.V. vs. time.
[b] Reflects the amount of variability in the slope.
[c] Number of data points included in the regression.
[d] Probability that the slope is statistically equal to zero, values less than 0.05 reflect significance.

## 3.3 Overall Precision

Overall precision incorporates the variability of all replicate (i.e., collocated and/or duplicate) sampling along with the variability inherent in the analytical methodology (i.e., analytical precision). Collocated samples represent identical and independent, proximate sample collections from different air sampling streams. Similarly, duplicate samples are replicate collections to independent samplers from a common air sampling stream. For the precision assessment presented in this report, these sample types are treated equivalently. In essence, overall precision measures the total variability associated with a given sample. Figures 22-30 show the overall precision for each of the target analytes at sites where replicate sampling was performed. Collection sites not shown for a particular analyte reflect the absence of either collocated or duplicate sampling at that site. Similarly, missing results for a particular year reflect unreported replicate results for that specific year. Detailed scatter plots are provided in Appendix B. As expected, variability is significantly higher for collocated and duplicate sample results than for replicate analyses on the same sample. With obvious scatter in the data between years, no analyte/site combination exhibits a clear graphical trend with time. Furthermore, sites which tended to show overall precision above the MQO threshold tended to remain above that threshold in all three years. The converse also seemed to be true, in that sites which tended to show overall precision within the MQO tended to continue in that behavior across time. When overall precision is examined across sites (Figure 31), however, acrolein precision appears to be improving with each successive year, although still markedly above the 15% MQO benchmark. Over all sites, as shown in Figure 32, arsenic seems to be the only analyte, and only in 2005, achieving overall precision within the measurement quality objective with nearly 100% of replicate collections agreeing to within 15%. Although somewhat less consistently, lead precision values show that approximately 90 and 80% of sites met the MQO for 2005 and 2007, respectively. The proportion of sites and analytes attaining the MQO ranges for all other years was generally between 30 and 60%. No trend is apparent in the graphical representation of the overall precision data.

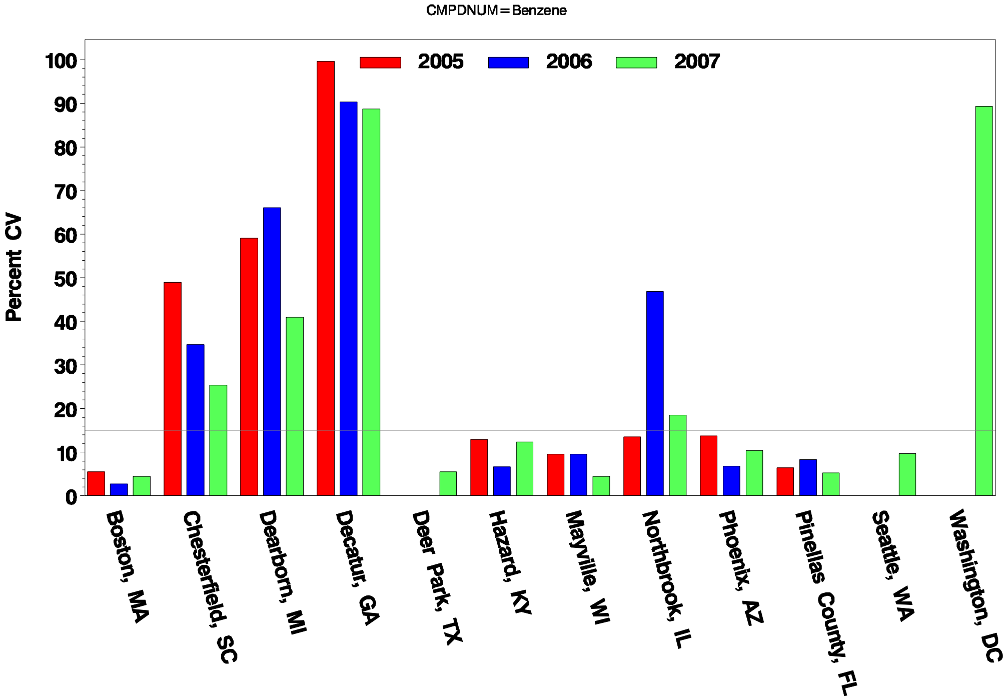


Figure 22. Overall Sample Precision for Benzene at NATTS Sites (replicate sample collection data unavailable for sites not shown).

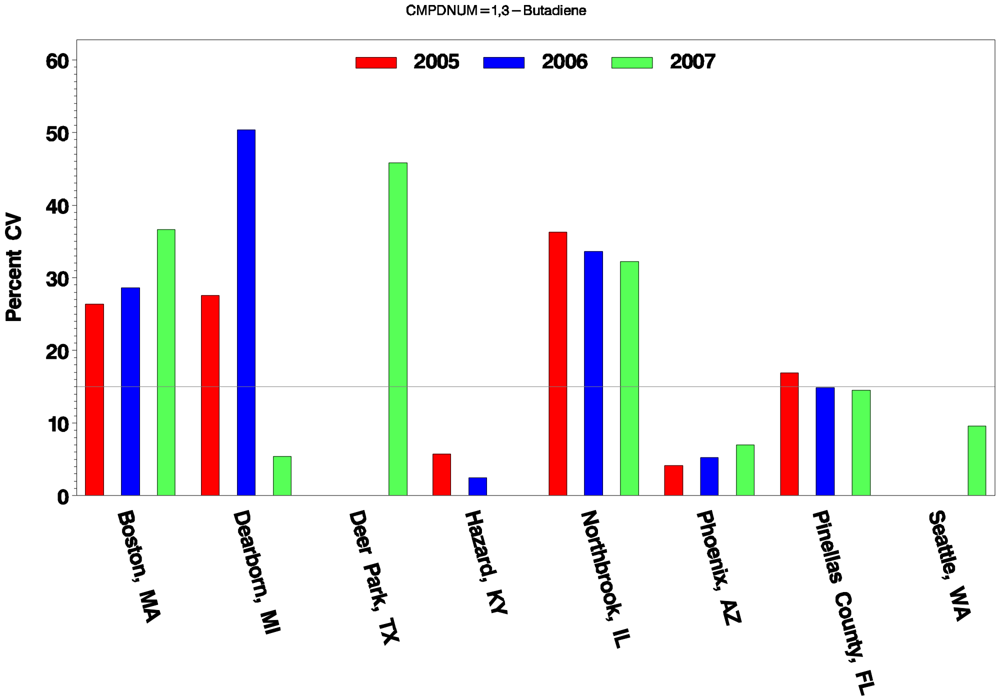


Figure 23. Overall Sample Precision for 1,3-Butadiene at NATTS Sites (replicate sample collection data unavailable for sites not shown).

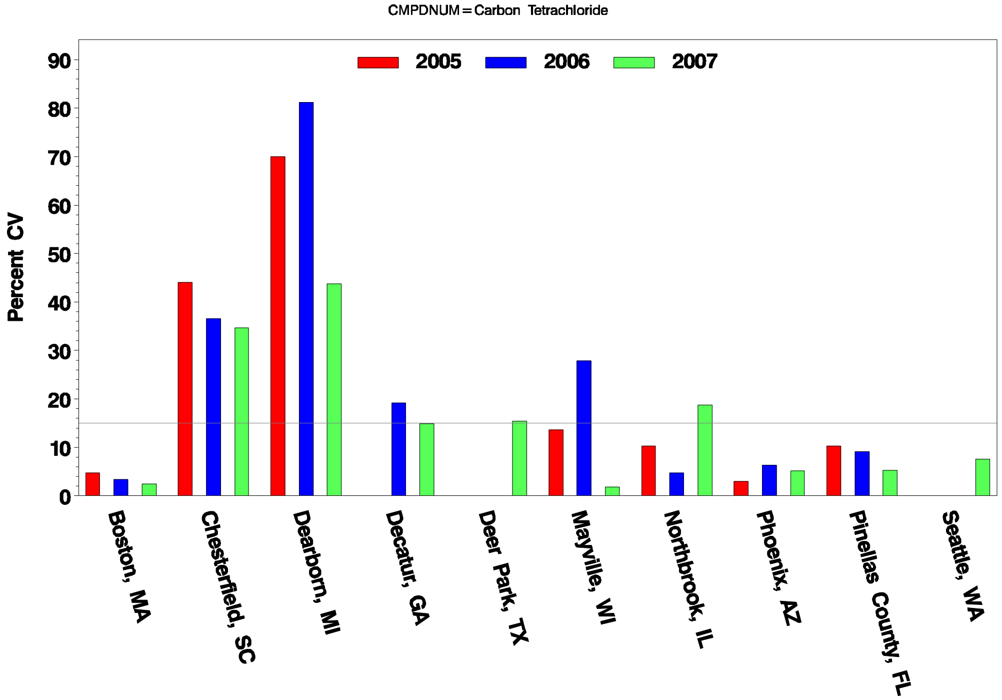


Figure 24. Overall Sample Precision for Carbon Tetrachloride at NATTS Sites (replicate sample collection data unavailable for sites not shown).

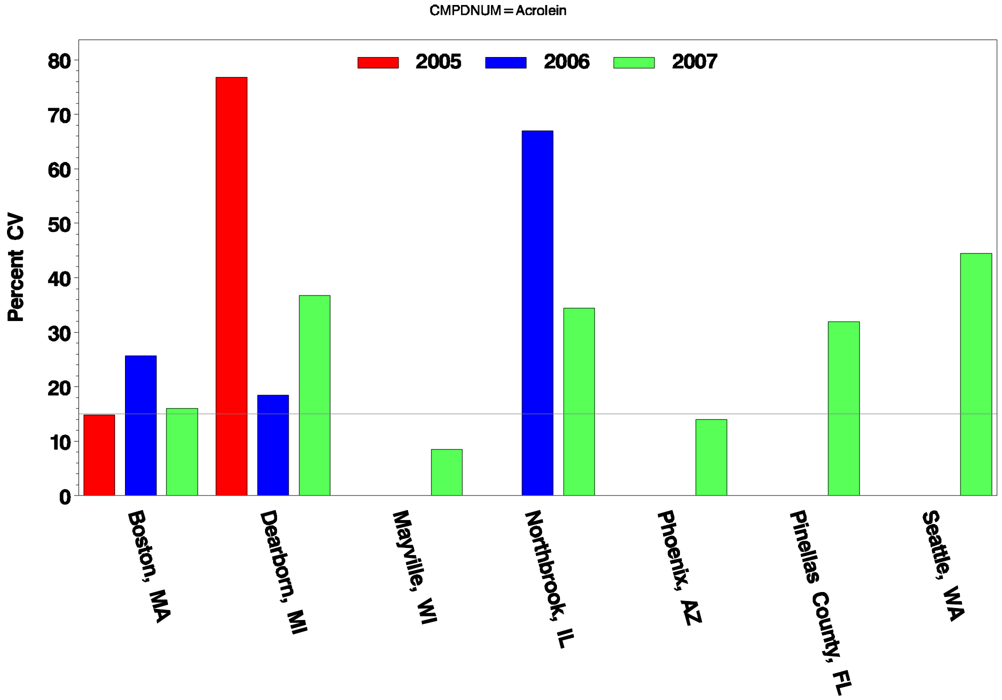


Figure 25. Overall Sample Precision for Acrolein at NATTS Sites (replicate sample collection data unavailable for sites not shown).

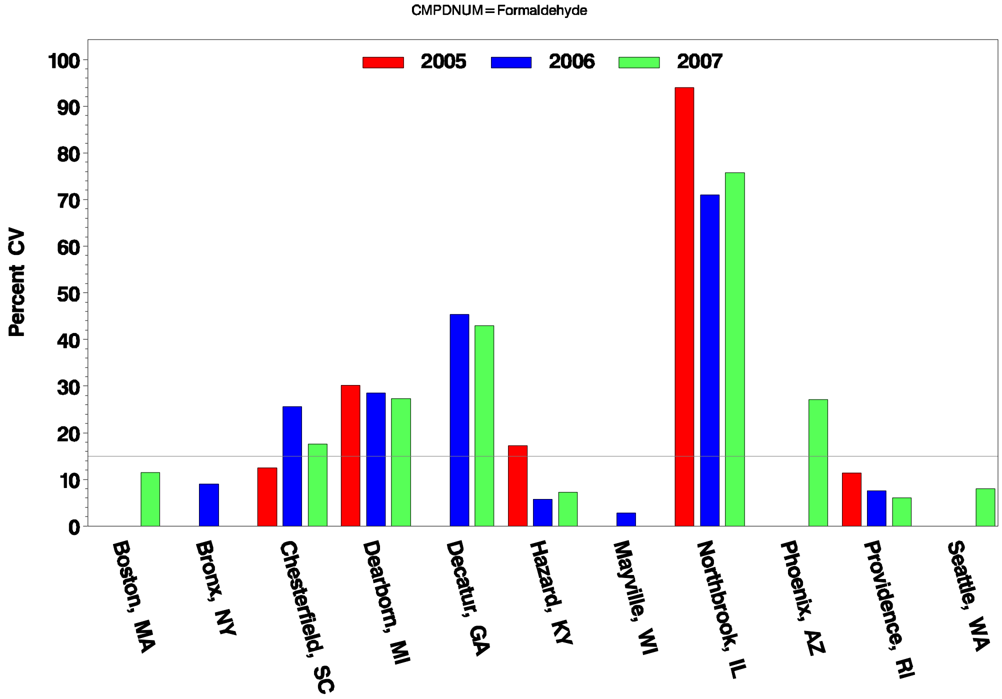


**Figure 26. Overall Sample Precision for Formaldehyde at NATTS Sites (replicate sample collection data unavailable for sites not shown).**

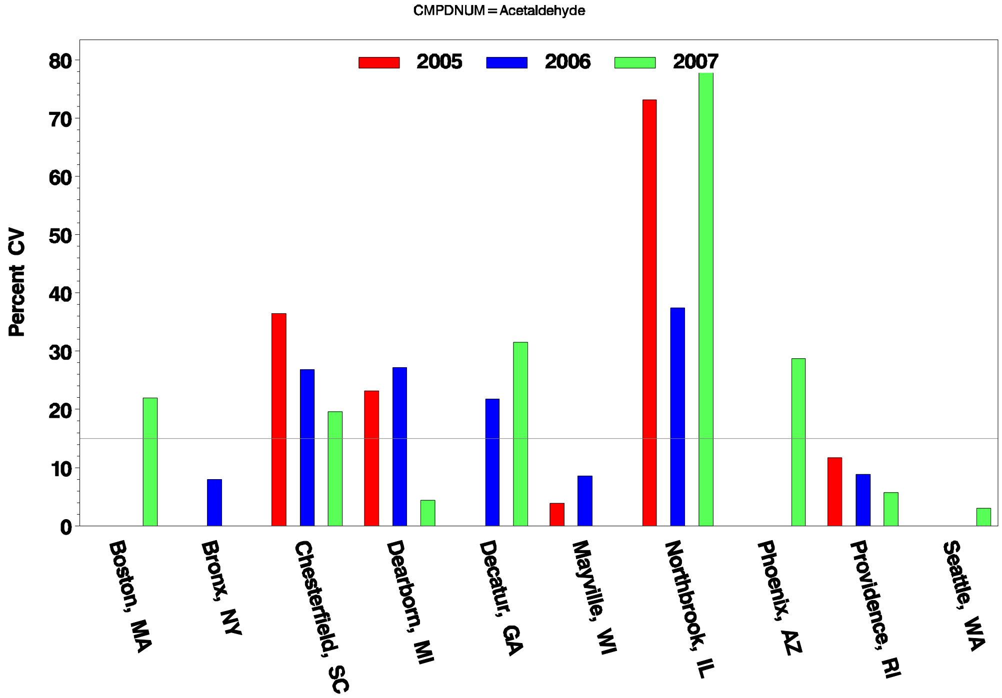


**Figure 27. Overall Sample Precision for Acetaldehyde at NATTS Sites (replicate sample collection data unavailable for sites not shown).**

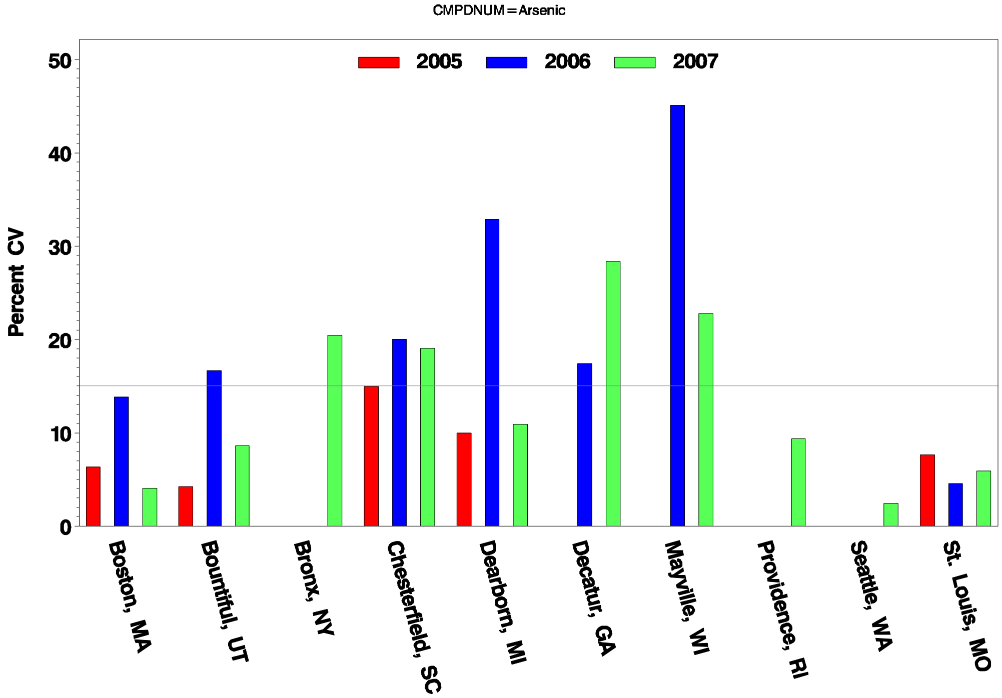


Figure 28. Overall Sample Precision for Arsenic at NATTS Sites (replicate sample collection data unavailable for sites not shown).

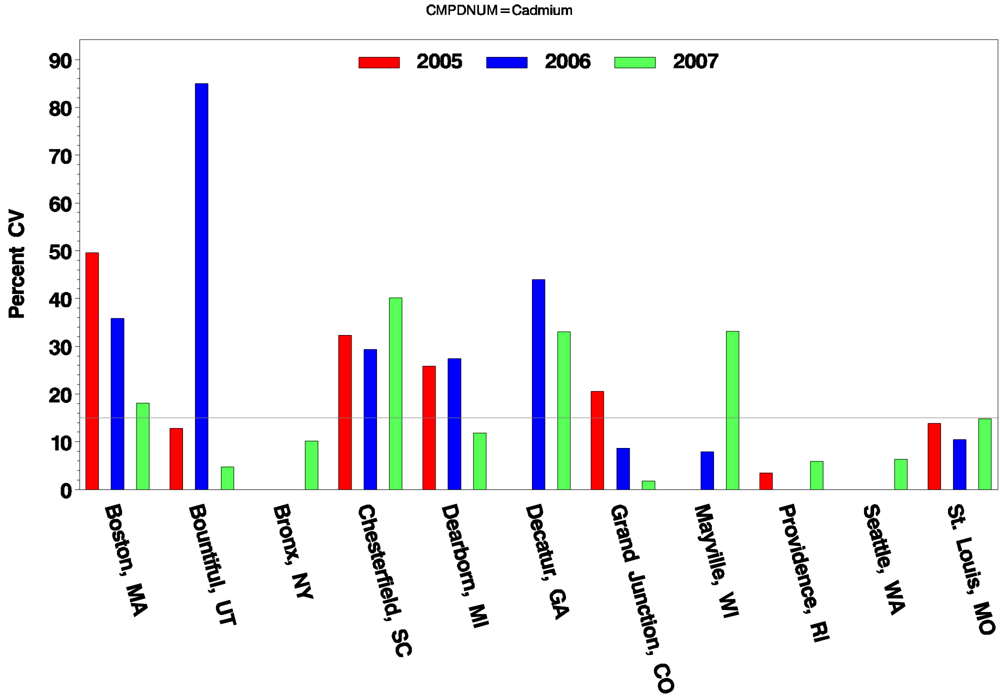


Figure 29. Overall Sample Precision for Cadmium at NATTS Sites (replicate sample collection data unavailable for sites not shown).

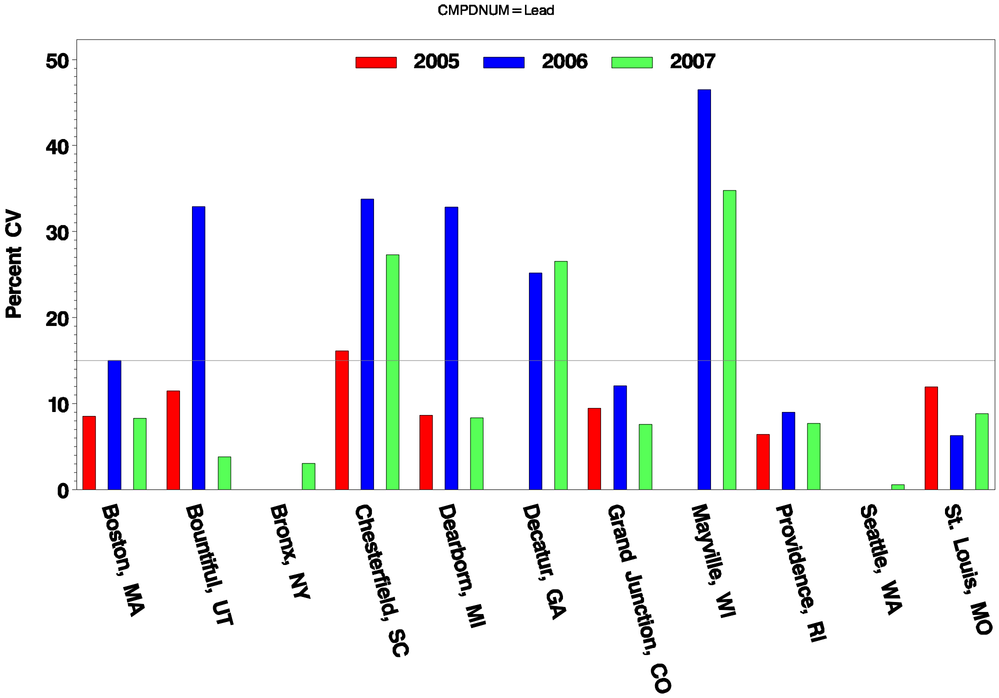


Figure 30. Overall Sample Precision for Lead at NATTS Sites (replicate sample collection data unavailable for sites not shown).

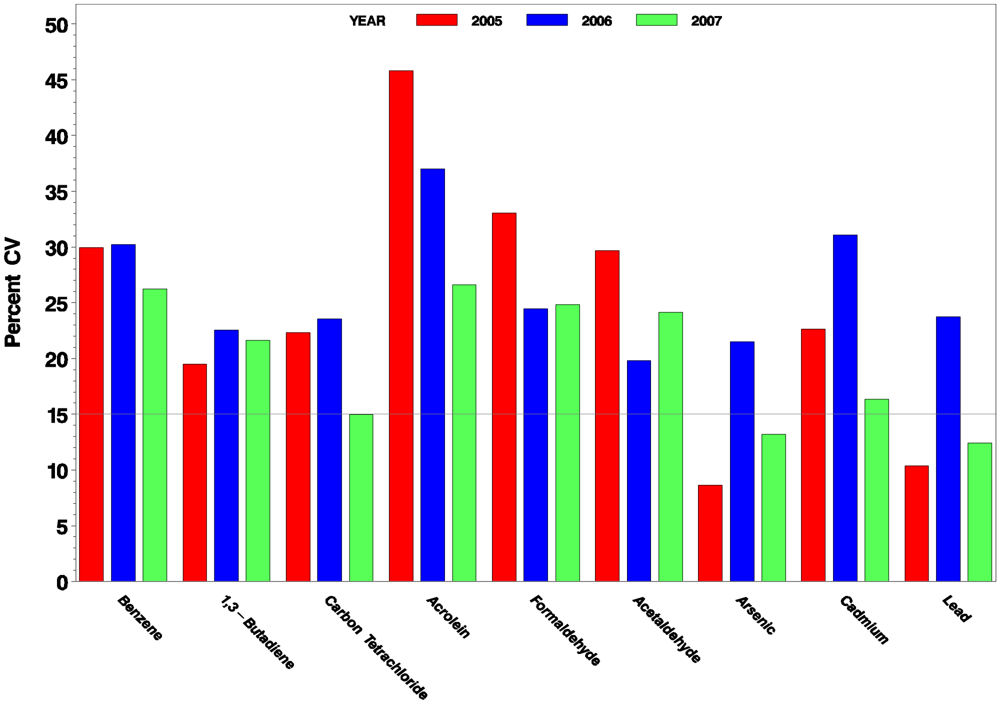


Figure 31. Overall Precision for Reporting NATTS Laboratories Across Years 2005-2007.

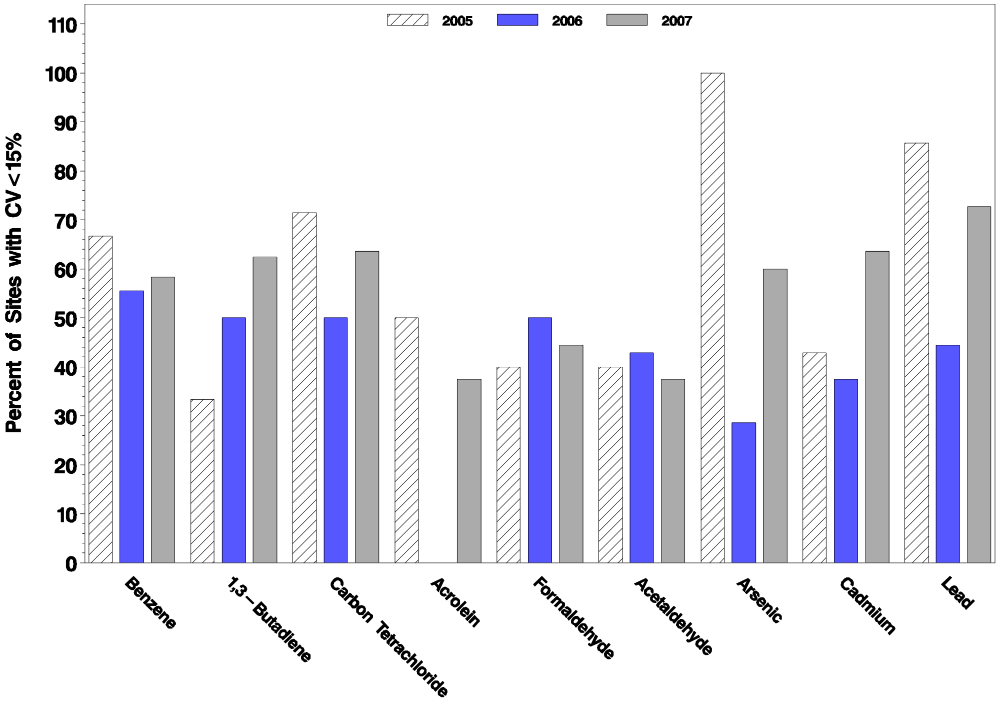


**Figure 32. Percent of Reporting NATTS Sites Meeting the Overall Precision Measurement Quality Objective.**

Trend plots for overall precision, shown in Figure 33 for all analytes across sites, reveal no obvious trend for any analyte. However, examination of the slopes and probability values in Table 7 for the quantitative analyses, show that the %CV for both benzene and cadmium may be decreasing with time when all sites are considered together. Overall precision for benzene (p=0.0325) is improving by 0.20 %CV units over the three-year period; cadmium (p=0.0115) by 0.16 %CV units for the same time interval. Considering the magnitude of the %CV measurements, these are very small incremental decreases, particularly in light of the relatively high variability of the slopes shown in the standard error. Table 8 shows that most site/analyte combinations exhibiting a statistically significant change over the three-year period also show a decrease in %CV. Based on the magnitude of the slope estimates for each site-analyte combination, the most notable of these improvements in precision were observed for acetaldehyde at the Phoenix, AZ site and acrolein at the Pinellas County, FL site. Acetaldehyde at the Seattle site and cadmium at the Mayville site show an increase in %CV with time.

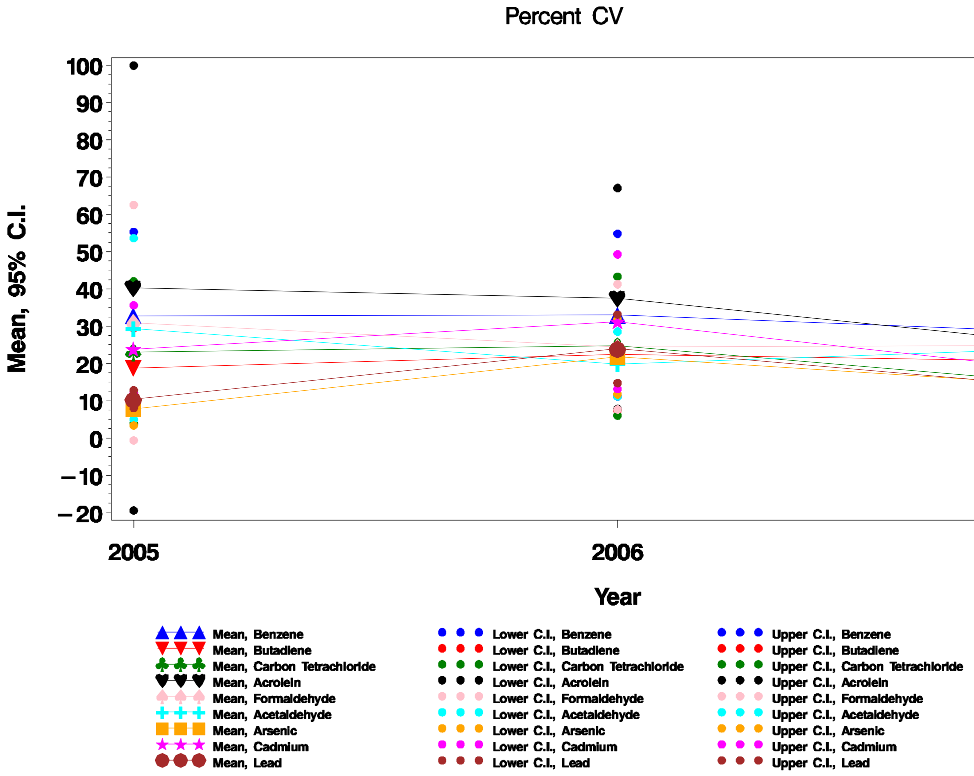


**Figure 33. Change in Average Overall Precision with Time Over All NATTS Sites.**

**Table 7. Modeled Parameter Estimates and Significance Levels for Overall Precision with Time - All NATTS Sites.**

| Analyte Abbreviation | Time Effect | Slope[a] | Standard Error[b] | N[c] | P-value[d] |
|---|---|---|---|---|---|
| ACET | DATE | -0.00011 | 0.000062 | 494 | 0.0691 |
| ACRO | DATE | -0.00031 | 0.000191 | 108 | 0.1108 |
| AS | DATE | 0.000034 | 0.000046 | 544 | 0.4555 |
| BENZ | DATE | -0.00018 | 0.000083 | 791 | 0.0325 |
| BUTA | DATE | 0.000021 | 0.000094 | 326 | 0.8250 |
| CD | DATE | -0.00015 | 0.000058 | 564 | 0.0115 |
| CTET | DATE | -0.00006 | 0.000063 | 377 | 0.3449 |
| FORM | DATE | -0.00005 | 0.000045 | 585 | 0.2406 |
| PB | DATE | 0.000035 | 0.000036 | 748 | 0.3301 |

[a] The slope of the regression line for percent C.V. vs. time.
[b] Reflects the amount of variability in the slope.
[c] Number of data points included in the regression.
[d] Probability that the slope is statistically equal to zero, values less than 0.05 reflect significance.

**Table 8. Modeled Parameter Estimates and Significance Levels for Overall Precision with Time - Sites and Analytes Exhibiting Significant Change.**

| Analyte Abbreviation | Site Effect | Time Effect | Slope[a] | Standard Error[b] | N[c] | P-value[d] |
|---|---|---|---|---|---|---|
| ACET | Chesterfield, SC | DATE | -0.00034 | 0.000085 | 152 | 0.0001 |
| ACET | Phoenix, AZ | DATE | -0.00215 | 0.000845 | 28 | 0.0173 |
| ACET | Seattle, WA | DATE | 0.000012 | 3.42E-6 | 7 | 0.0175 |
| ACRO | Pinellas County, FL | DATE | -0.00160 | 0.000603 | 37 | 0.0122 |
| BENZ | Decatur, GA | DATE | -0.00050 | 0.000227 | 227 | 0.0280 |
| CD | Boston, MA | DATE | -0.00060 | 0.000145 | 87 | <.0001 |
| CD | Mayville, WI | DATE | 0.000670 | 0.000246 | 10 | 0.0260 |
| CTET | Boston, MA | DATE | -4.51E-6 | 1.968E-6 | 27 | 0.0307 |
| CTET | Pinellas County, FL | DATE | -0.00003 | 9.445E-6 | 98 | 0.0093 |

[a] The slope of the regression line for percent C.V. vs. time.
[b] Reflects the amount of variability in the slope.
[c] Number of data points included in the regression.
[d] Probability that the slope is statistically equal to zero, values less than 0.05 reflect significance.

## 3.4 Laboratory Bias

Independent proficiency testing (PT) samples are prepared for each analyte of interest and distributed to NATTS laboratories for assessment of accuracy of analysis. Reported results are compared to actual loaded amounts and reflected as bias[1], with a positive bias indicative of a measured amount greater than the loaded reference value. Figure 34 illustrates the summarized results of this comparison, across time, for the nine analytes of interest. The most obvious feature of this display is the extreme variability in percent difference across years, with no consistent bias apparent across time. The proportion of laboratories which attained the MQO for bias of ±25%, shown in Figure 35, reveals that, overall, laboratories were showing consistently high accuracy in their reported measurements. Only acrolein in 2006 and 2007 and the metal analytes in 2005 showed a high percentage of bias results outside the acceptable MQO.

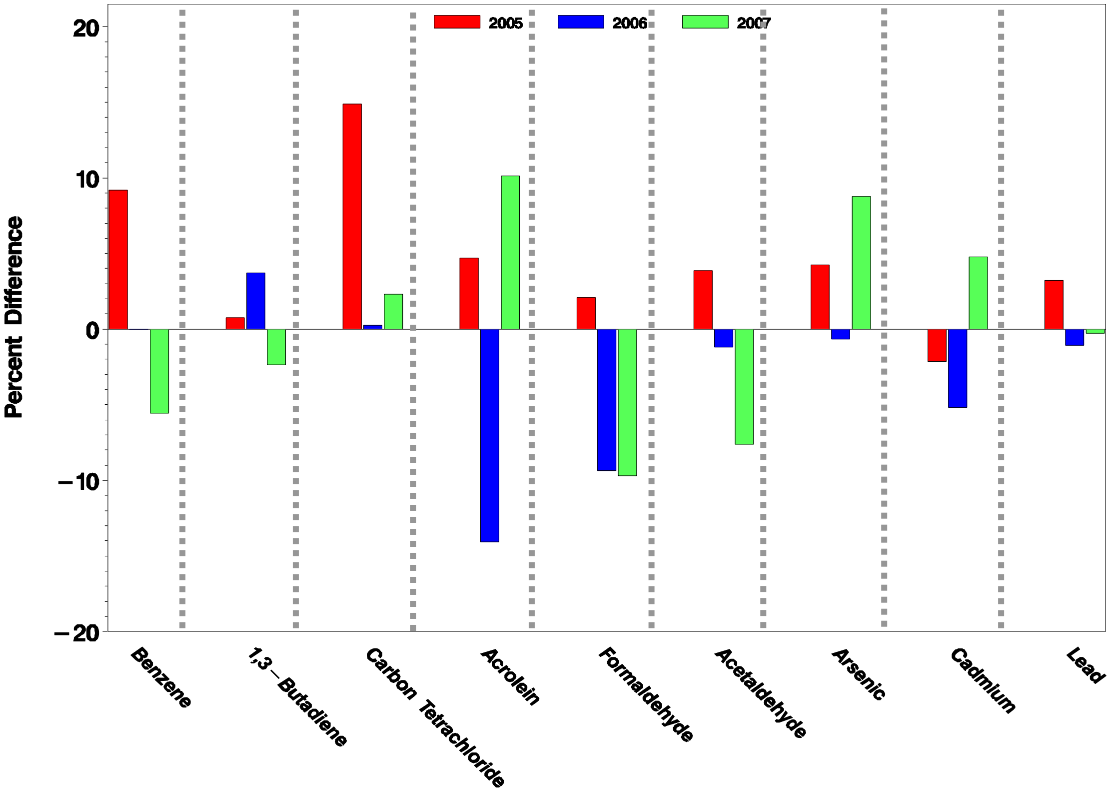


Figure 34. Summary of Laboratory Bias Across All Reporting NATTS Sites.

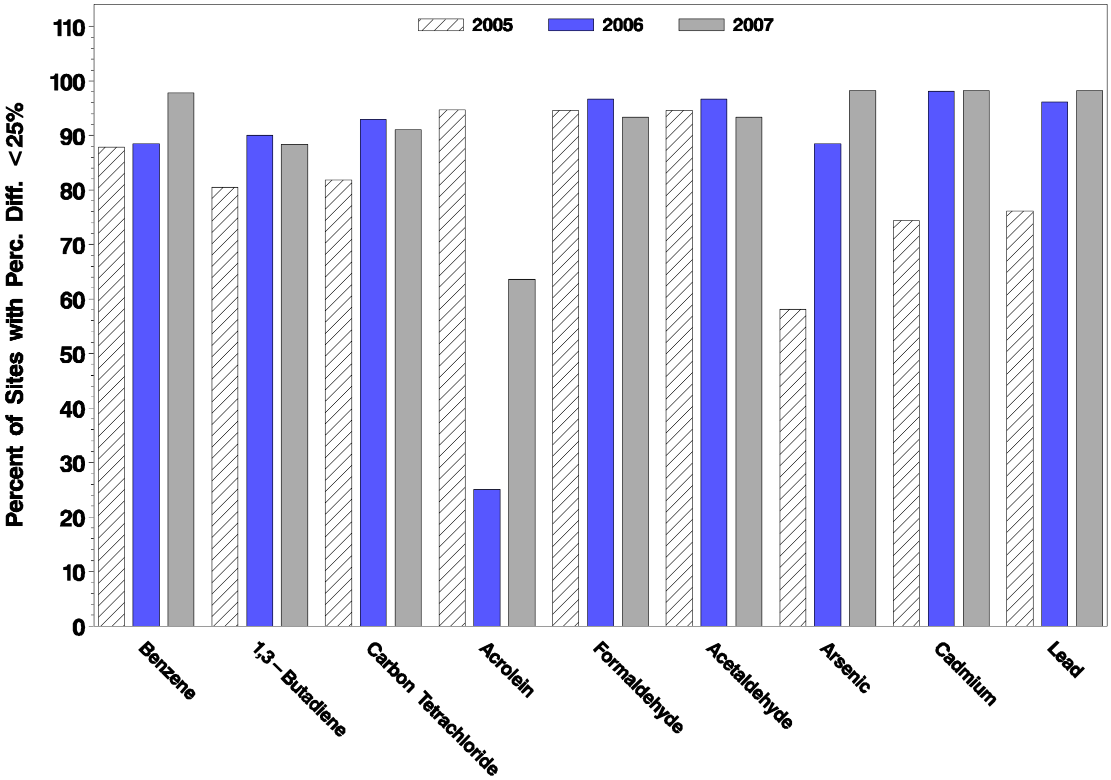


Figure 35. Percent of Reporting NATTS Sites Meeting the Overall Laboratory Bias Measurement Quality Objective.

Trends analyses were performed on the absolute value of the percent difference to avoid spurious trends resulting from positive to negative biases over time. Figure 36 illustrates the effect of time on the average percent difference for each analyte. On first inspection, a high degree of scatter is noted in the data; however, at least one analyte, arsenic, appears to be showing a decrease in mean percent difference over time. The quantitative results, shown in Table 9, confirm this visual assessment and also show a pronounced and statistically significant decrease in bias for carbon tetrachloride, cadmium and lead, as expressed by the parameter estimate and p-value. Results for individual sites, shown in Table 10, reveal a number of site/analyte combinations with significantly decreasing bias across time (i.e., negative slopes with p-values <0.05). Interestingly, three cases show an increase in bias with time which points again to the high degree of variability in much of these data.

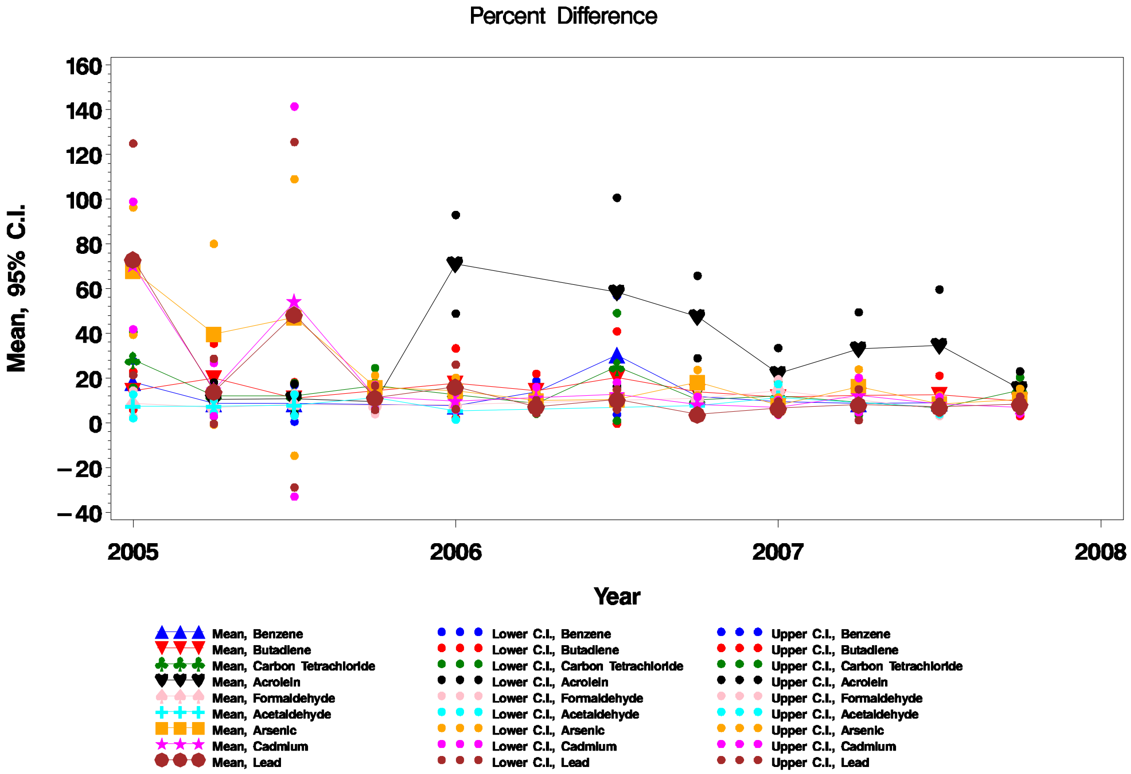


**Figure 36. Change in Average Laboratory with Time Over All NATTS Sites.**

## Table 9. Modeled Parameter Estimates and Significance Levels for Laboratory Bias with Time - All NATTS Sites.

| Analyte Abbreviation | Time Effect | Slope[a] | Standard Error[b] | N[c] | P-value[d] |
|---|---|---|---|---|---|
| ACET | YEAR | 0.3719 | 0.6951 | 101 | 0.5938 |
| ACRO | YEAR | 4.4603 | 3.7664 | 116 | 0.2387 |
| AS | YEAR | -14.6966 | 3.2042 | 140 | <.0001 |
| BENZ | YEAR | -1.2769 | 1.8746 | 136 | 0.4969 |
| BUTA | YEAR | -1.9098 | 1.7004 | 150 | 0.2632 |
| CD | YEAR | -13.2718 | 3.7323 | 140 | 0.0005 |
| CTET | YEAR | -3.1651 | 1.4456 | 159 | 0.0300 |
| FORM | YEAR | 0.8885 | 0.7677 | 102 | 0.2499 |
| PB | YEAR | -13.0897 | 3.5461 | 139 | 0.0003 |

[a] The slope of the regression line for percent difference vs. time.
[b] Reflects the amount of variability in the slope.
[c] Number of data points included in the regression.
[d] Probability that the slope is statistically equal to zero, values less than 0.05 reflect significance.

## Table 10. Modeled Parameter Estimates and Significance Levels for Laboratory Bias with Time - Sites and Analytes Exhibiting Significant Change.

| Analyte Abbreviation | Site Effect | Time Effect | Slope[a] | Standard Error[b] | N[c] | P-value[d] |
|---|---|---|---|---|---|---|
| ACET | Providence, RI | YEAR | -3.4677 | 1.2886 | 6 | 0.0360 |
| ACRO | Northbrook, IL | YEAR | -21.9421 | 6.9918 | 4 | 0.0349 |
| AS | Grand Junction, CO | YEAR | -9.3650 | 4.1121 | 19 | 0.0345 |
| AS | Hazard, KY | YEAR | -18.7451 | 7.6731 | 10 | 0.0347 |
| AS | Dearborn, MI | YEAR | -8.8486 | 4.0990 | 22 | 0.0420 |
| BENZ | Decatur, GA | YEAR | 3.8236 | 1.5440 | 8 | 0.0383 |
| BUTA | San Jose, Ca | YEAR | -19.1716 | 6.1070 | 6 | 0.0201 |
| BUTA | Decatur, GA | YEAR | 4.4553 | 1.9000 | 9 | 0.0437 |
| BUTA | Underhill, VT | YEAR | 10.0288 | 4.1035 | 8 | 0.0403 |
| CTET | Dearborn, MI | YEAR | -5.2437 | 2.0514 | 10 | 0.0286 |

[a] The slope of the regression line for percent difference vs. time.
[b] Reflects the amount of variability in the slope.
[c] Number of data points included in the regression.
[d] Probability that the slope is statistically equal to zero, values less than 0.05 reflect significance.

## 3.5 Method Detection Limits

Unlike the completeness, precision, and bias data presented in earlier sections of this report, method detection limit data are summarized only for benzene, 1,3-butadiene, formaldehyde, and arsenic since measurement quality objectives were available for the three years of interest only for this abbreviated compound list. As discussed at some length in the 2007 QA Report[1], the consistency of the method detection limit data provided by the NATTS laboratories appeared to be somewhat lower than desired. Different laboratories might have different computational methods for determining their MDLs. For this reason, both qualitative and quantitative analyses of these results must be interpreted with extreme caution. In that light, Figures 37-41 illustrate the extreme variability in MDLs between sites and also between years. In addition, there are numerous cases where method detection limits were reported to be exactly the same (e.g., LaGrande, OR) for the three years of interest in this report. With the possible exception of arsenic (Figure 40), no visual trends in MDLs are apparent across years. The proportion of sites meeting the MQO, shown in Figure 42, was typically less than 40% and often was zero, although there is, at least subjectively, a sense that the percent of sites achieving the MDL measurement quality objective is increasing with time. Despite the highly scattered results displayed in Figure 43, statistically significant decreases with time for average MDLs across sites, shown in Table 11, were observed only for arsenic (p-value=0.0330). Based on the probability values computed for each of the slopes, no individual sites showed a significant change in MDL with year.

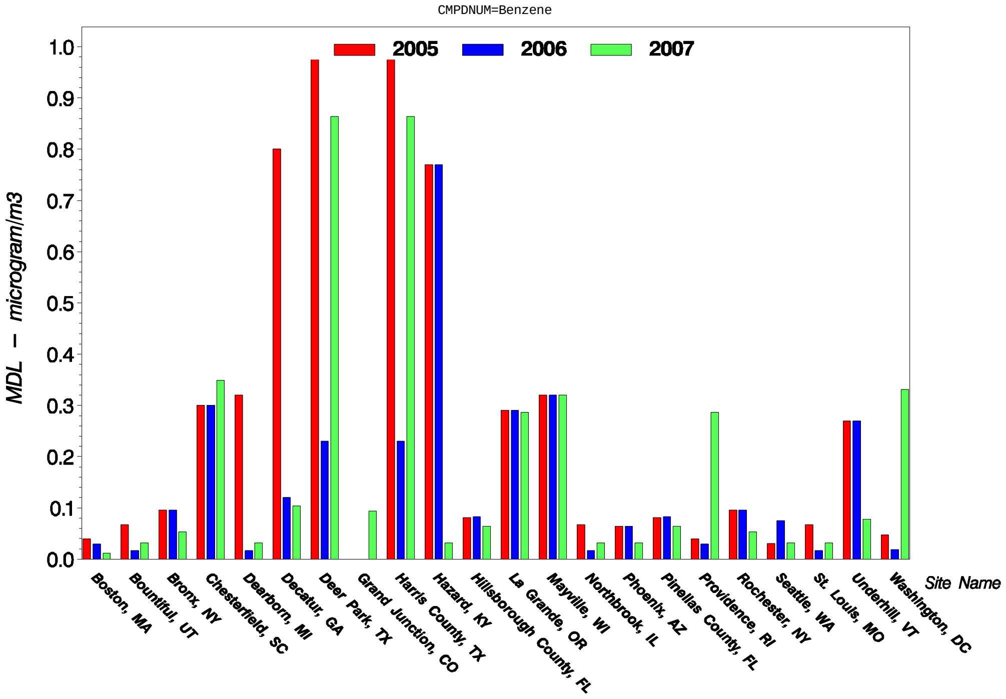


**Figure 37. Method Detection Limits for Benzene at NATTS Sites.**

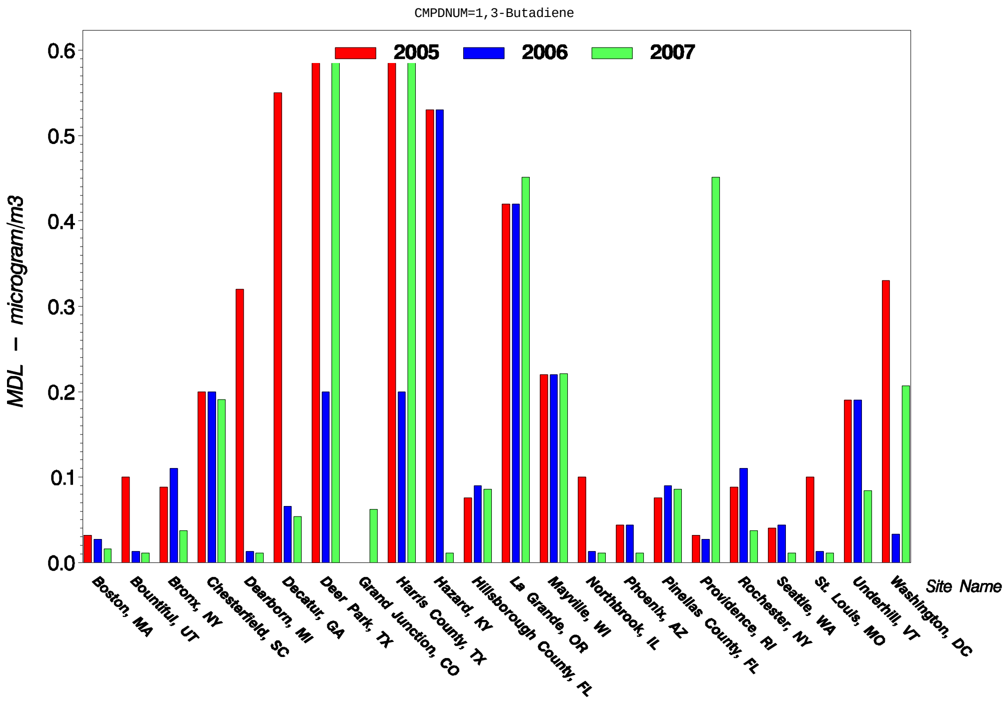


Figure 38. Method Detection Limits for 1,3-Butadiene at NATTS Sites.

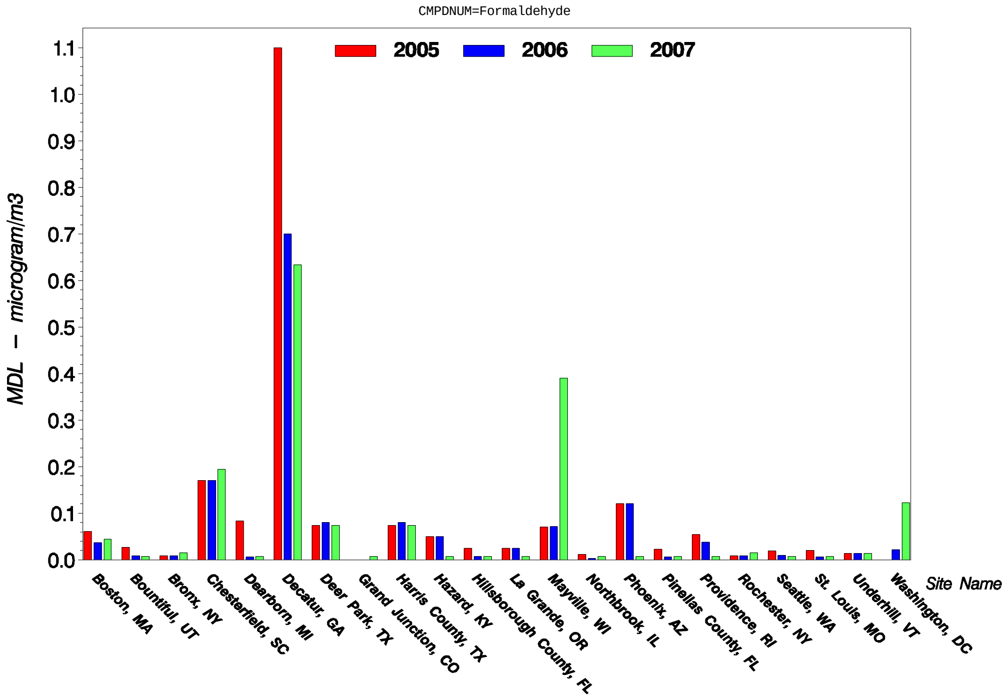


Figure 39. Method Detection Limits for Formaldehyde at NATTS Sites.

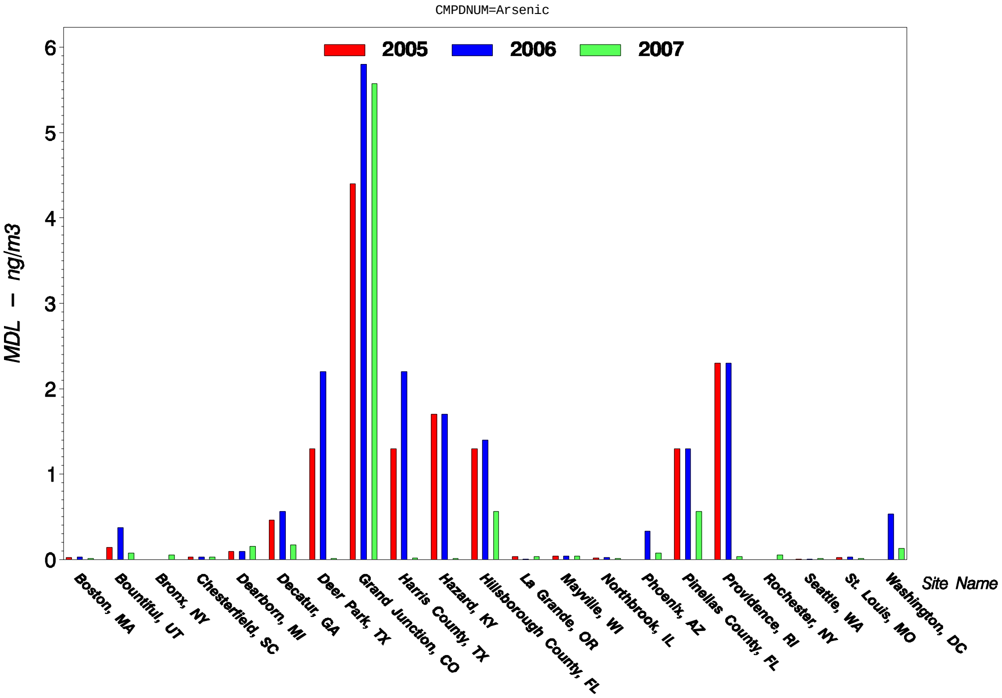


Figure 40. Method Detection Limits for Arsenic at NATTS Sites (data not available for Underhill, VT site).

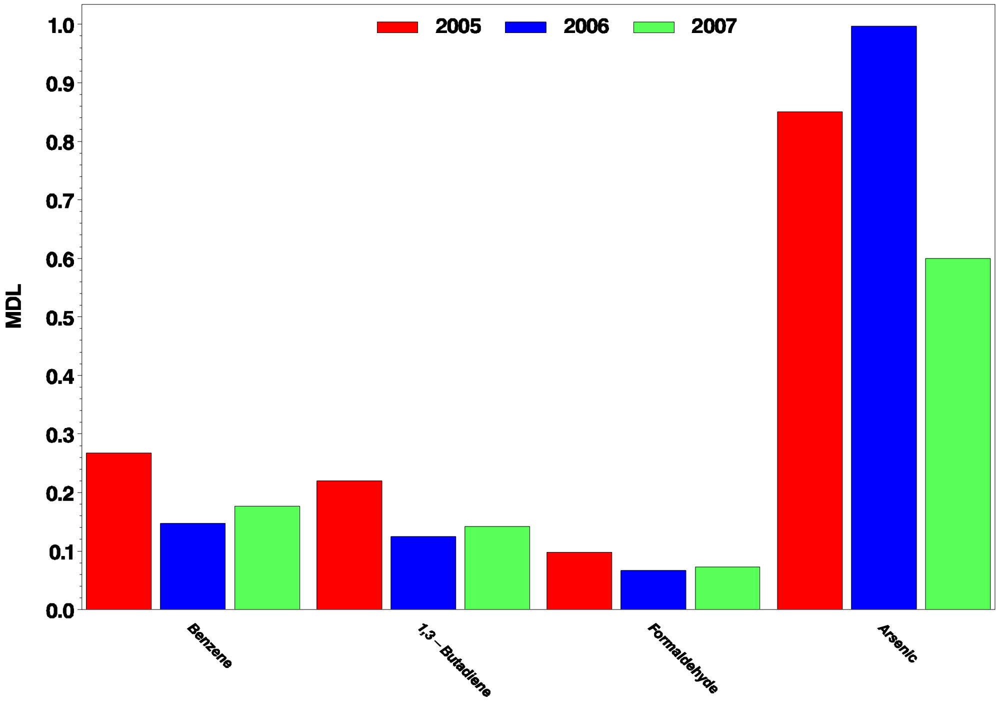


Figure 41. Summary of Method Detection Limits Across All Reporting NATTS Sites (MDL units: arsenic=ng/m$^3$, all other analytes=µg/m$^3$)

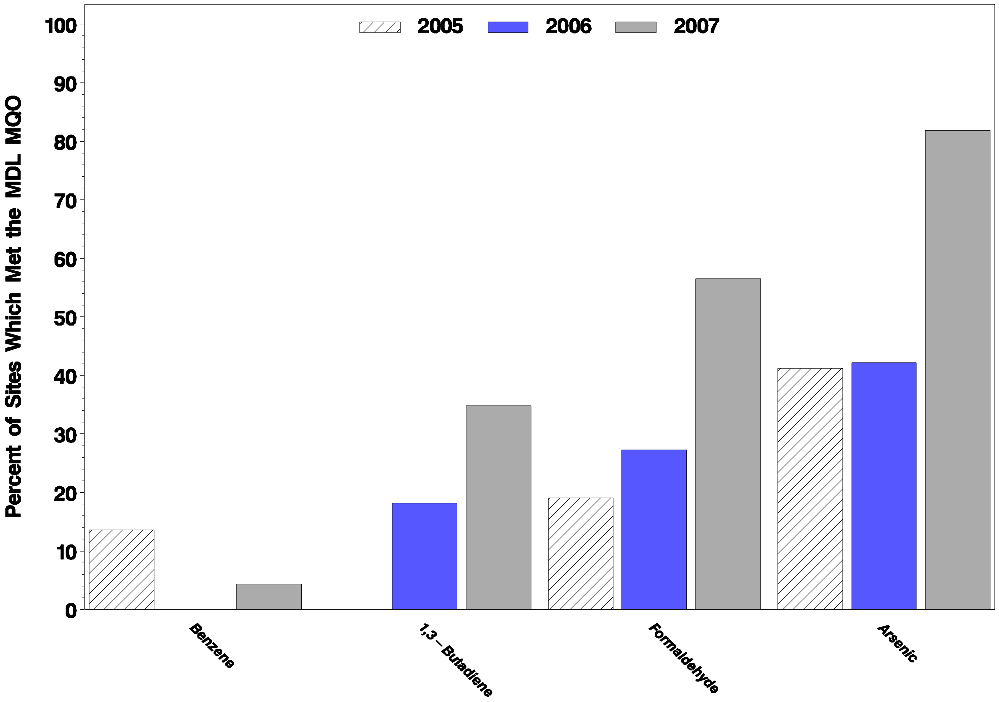


Figure 42. Percent of Reporting NATTS Sites Meeting the Overall MDL Measurement Quality Objective (missing values reflect zero percentages).

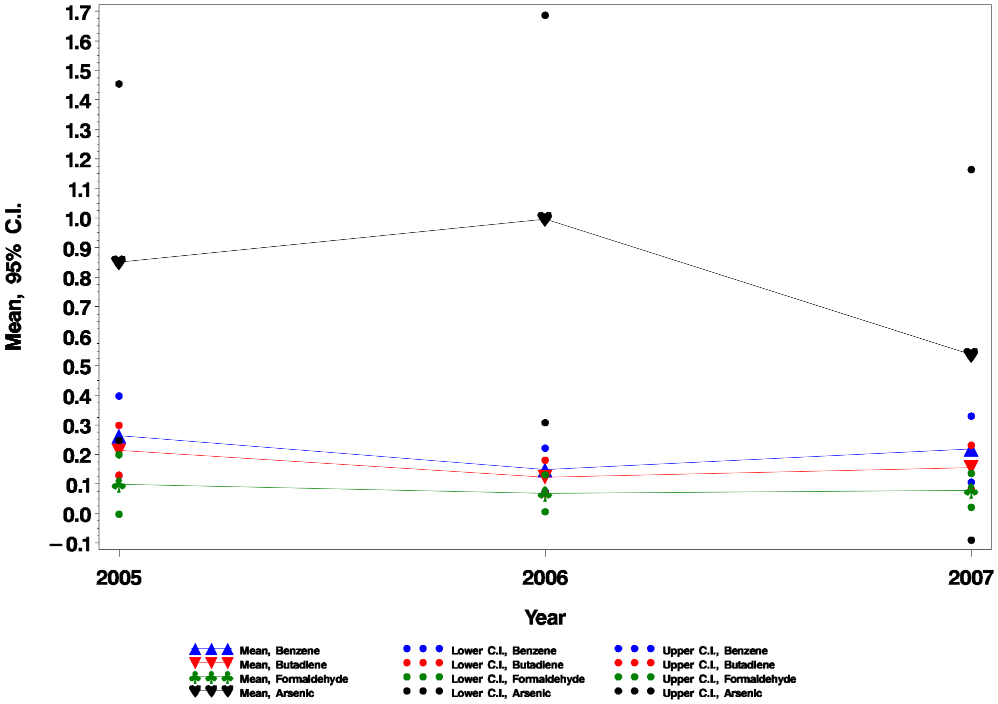


Figure 43. Change in Average MDL with Time Across All NATTS Sites.

# Table 11. Modeled Parameter Estimates and Significance Levels for MDLs with Time - All NATTS Sites.

| Analyte Abbreviation | Time Effect | Slope[a] | Standard Error[b] | N[c] | P-value[d] |
|---|---|---|---|---|---|
| AS | YEAR | -0.2075 | 0.09353 | 35.4 | 0.0330 |
| BENZ | YEAR | -0.02207 | 0.02979 | 48.7 | 0.4623 |
| BUTA | YEAR | -0.02861 | 0.01940 | 48.6 | 0.1467 |
| FORM | YEAR | -0.00999 | 0.01035 | 45.5 | 0.3393 |

[a] The slope of the regression line for percent difference vs. time.
[b] Reflects the amount of variability in the slope.
[c] Number of data points included in the regression.
[d] Probability that the slope is statistically equal to zero, values less than 0.05 reflect significance.

# 4.0 SUMMARY AND CONCLUSIONS

*Completeness* – Overall, the completeness statistics were very high and exceeded the measurement quality objective of 85% at nearly every site and for every analyte during the three-year period from 2005-2007. This was profoundly apparent in the 90% of sites which achieved at least the MQO for each of the three years. The sole exception, acrolein, while exhibiting less than the MQO for reporting sites in 2005/2006, showed substantial improvement in 2007, exceeding the MQO for all sites but one. This improvement is entirely consistent with the attainment of analytical proficiency by laboratories measuring acrolein during the first two years. No clear evidence for a trend in completeness exists for any site although some variability between years is indicated for some sites. While 2006 seemed to exhibit the best overall completeness statistic, no clear trend with year is apparent; however, the variability in the mean for a given year and analyte appears to be much greater in 2005 than for subsequent years. Only acrolein shows a statistically significant change in completeness with time; no significant changes were detected for any other analyte.

*Analytical Precision* – In general, precision was found to be well within the MQO of 15% CV but with sporadic incidences of poorer precision. Precision estimates for acrolein tended to exceed the MQO more often than other analytes although the precision was remarkably good for many years and sites. When the data were examined by site, 1,3-butadiene and possibly carbon tetrachloride showed evidence of improvement (i.e., lowering) in precision, while results for acrolein, formaldehyde and acetaldehyde, suggested a deterioration of precision with time. As for the individual sites, average analytical precision estimates across sites for most analytes and years were well within the MQO of 15%. Despite the absence of a discernable trend with time, appreciable variability was apparent (Figure 20) for the percent of sites meeting the MQO for analytical precision, particularly for 1,3-butadiene and acrolein. Nevertheless, the proportion of sites achieving the MQO for precision tended to be 80% or better, with acrolein and 1,3-butadiene noted as exceptions. Improvement in analytical precision with time was visually noted for 1,3-butadiene and confirmed by modeling, although the effect was very small, amounting to approximately a 4% decrease in the percent CV across the three year period. Very modest but statistically significant decreases in % CV were observed for Phoenix, AZ, Boston, MA, Bountiful, UT, and Pinellas County, FL, for specific analytes.

*Overall Precision* – In general, variability in %CV among sites and analytes was found to be significantly greater for collocated and duplicate sample results than for results from replicate analyses performed on the same sample. Consistent with this observation, the proportion of sites and analytes achieving the MQO tended to be lower for overall precision estimates than for analytical precision. Furthermore, sites which tended to show overall precision above the MQO threshold also tended to remain above that threshold in all three years while sites whose overall precision measurements fell within the MQO continued to maintain similar %CVs across time. Over all sites, arsenic, and only in 2005, was observed to have consistently attained overall precision within the measurement quality objective. With the additional exception of lead, the proportion of sites and analytes attaining the MQO for all years was generally between 30 and 60%. Statistically significant trends in %CV for both benzene and cadmium are observed when all sites are considered together. Similar significant findings are shown for several analyte/site combinations, most notably for acetaldehyde at the Phoenix, AZ site and acrolein at the Pinellas County, FL site.

*Laboratory Bias* – The laboratory proficiency testing results, overall, showed consistently very high accuracy. The data also reveal appreciable and “random” variability in percent difference across years. MQO objectives were widely achieved with only acrolein and the metal analytes exhibiting a high proportion of bias results outside the acceptable MQO. Trends analyses with all sites considered together show a pronounced and statistically significant decrease in bias for carbon tetrachloride, cadmium and lead. Results for individual sites reveal seven site/analyte combinations with significantly decreasing bias across time and three site/analyte combinations with increasing bias across time.

*Method Detection Limits* – Perhaps due to differences in computational approaches used by different laboratories, the consistency of the method detection limit data across sites appeared to be somewhat lower than desired with typically less than 40% of labs meeting the MQO. In deference to the highly scattered results, statistically significant decreases in average MDL over time for were observed for arsenic. No individual sites showed a significant change in MDL with year.

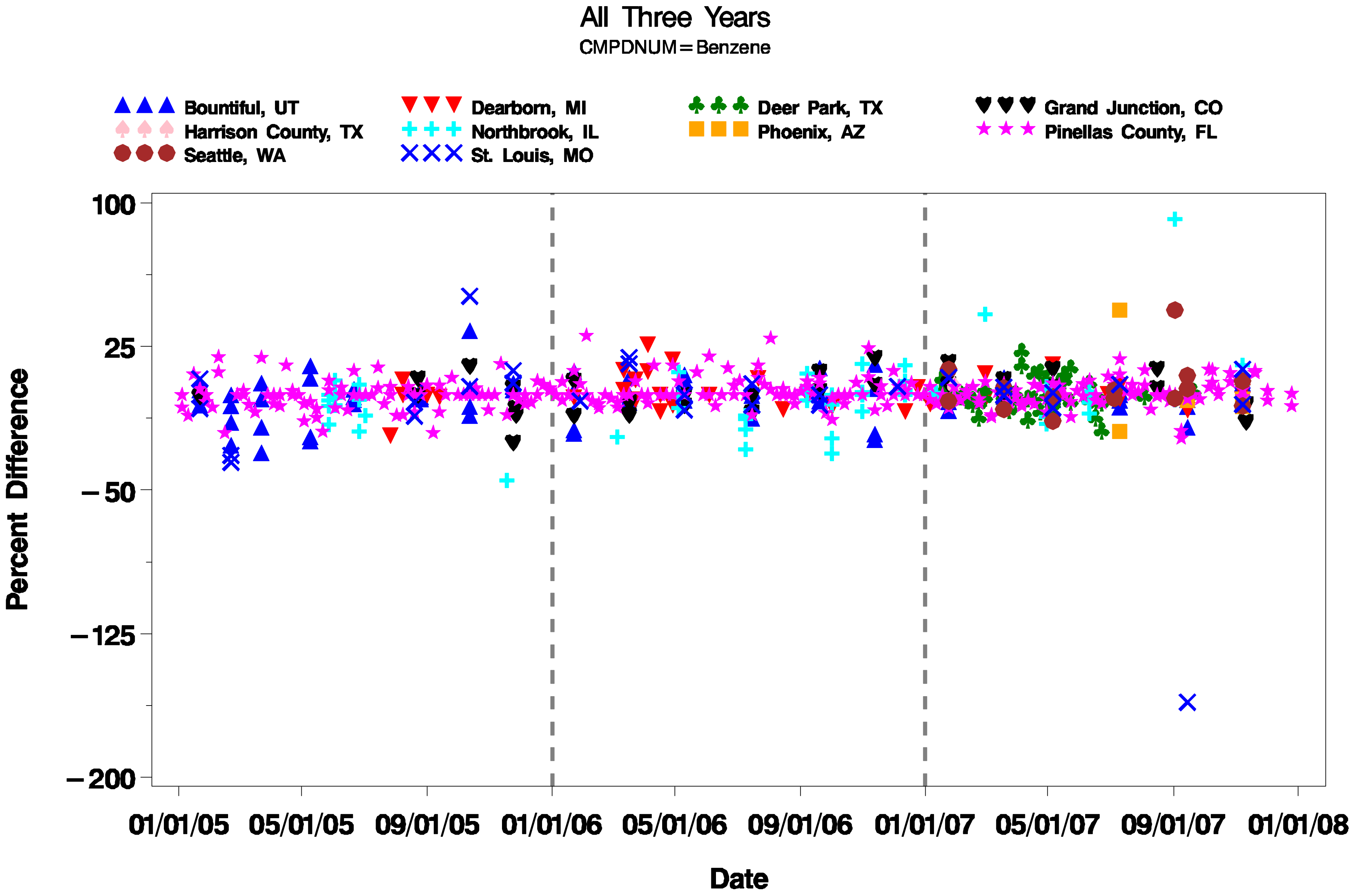
# 5.0 REFERENCES

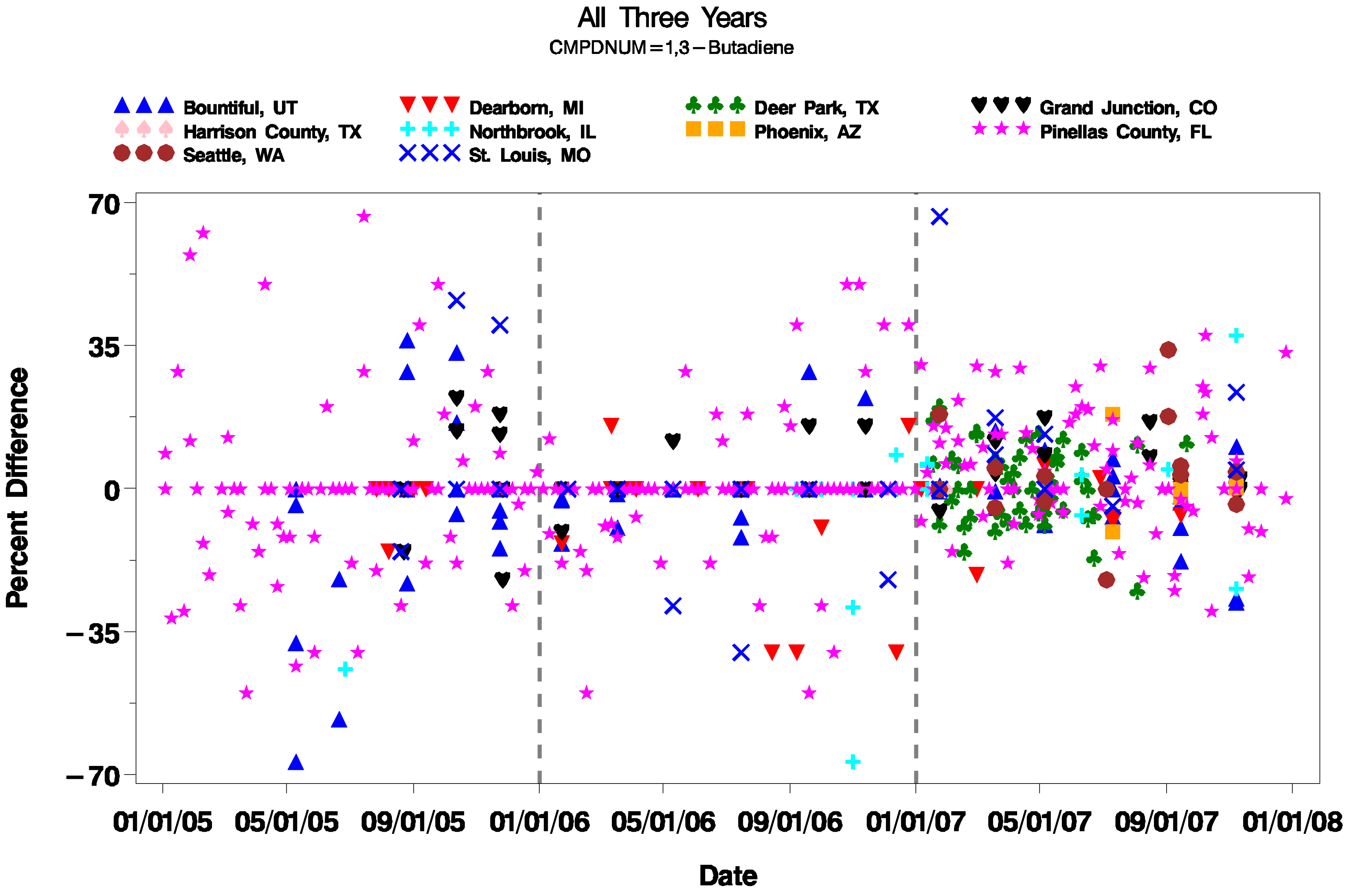
1. "National Air Toxics Trends Stations Quality Assurance Annual Report – Calendar Year 2007" prepared by RTI International for U.S.EPA, 2008.
2. "National Air Toxics Trends Stations Quality Assurance Annual Report – Calendar Year 2006" prepared by Battelle Memorial Institute for U.S.EPA, 2007.
3. "National Air Toxics Trends Stations Quality Assurance Annual Report – Calendar Year 2005" prepared by Battelle Memorial Institute for U.S.EPA, 2006.

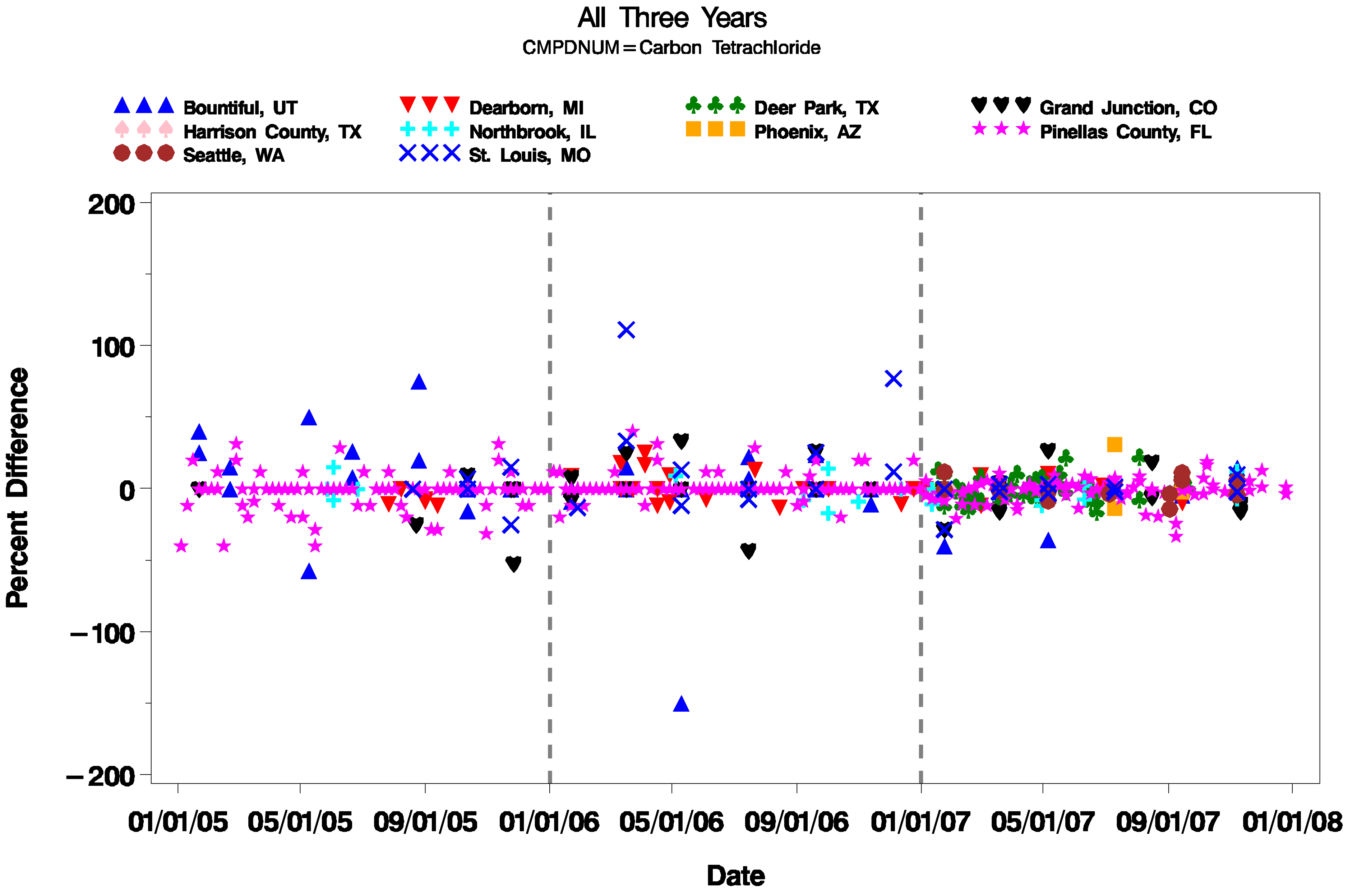
# Appendix A

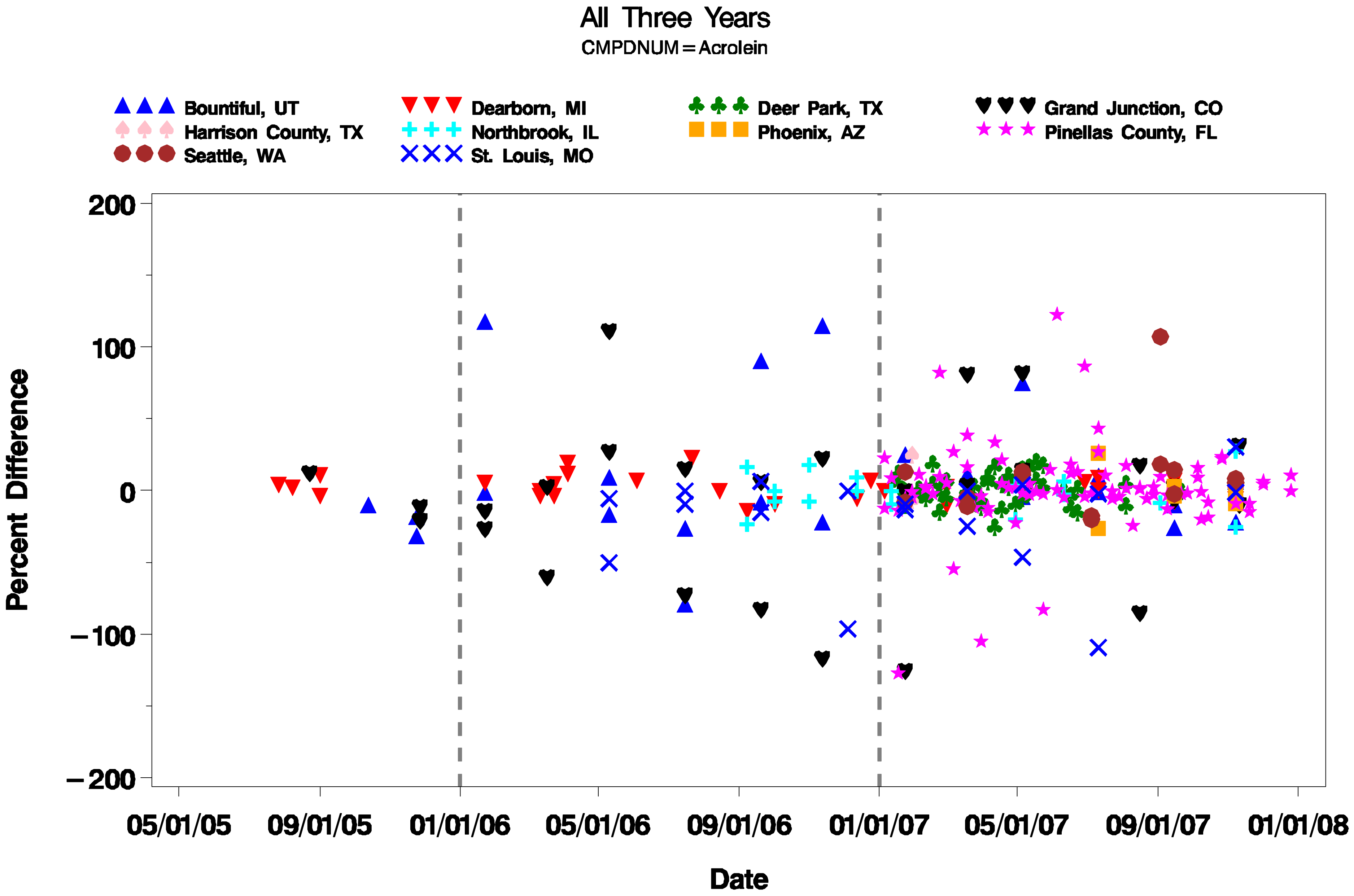
## Analytical Precision Plots for Selected Analytes by NATTS Site

(replicate sample analysis data unavailable for sites not shown)


All Three Years
CMPDNUM=Benzene
▲▲▲ Bountiful, UT
♠♠♠ Harrison County, TX
●●● Seattle, WA
▼▼▼ Dearborn, MI
+++ Northbrook, IL
××× St. Louis, MO
♣♣♣ Deer Park, TX
■■■ Phoenix, AZ
♥♥♥ Grand Junction, CO
★★★ Pinellas County, FL
Percent Difference
100
25
−50
−125
−200
01/01/05
05/01/05
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date

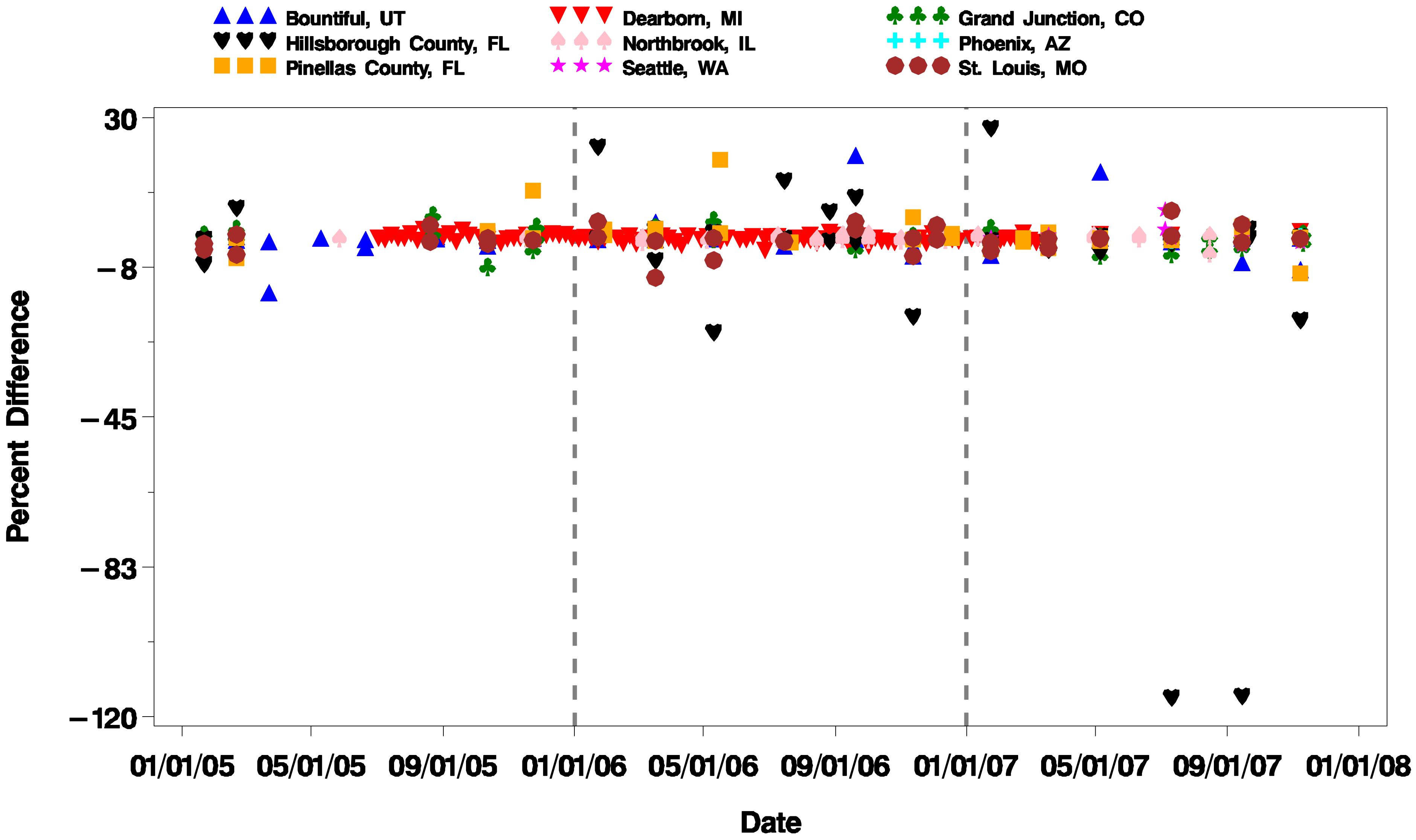

All Three Years
CMPDNUM=1,3−Butadiene
Bountiful, UT
Dearborn, MI
Deer Park, TX
Grand Junction, CO
Harrison County, TX
Northbrook, IL
Phoenix, AZ
Pinellas County, FL
Seattle, WA
St. Louis, MO
Percent Difference
70
35
0
−35
−70
01/01/05
05/01/05
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date

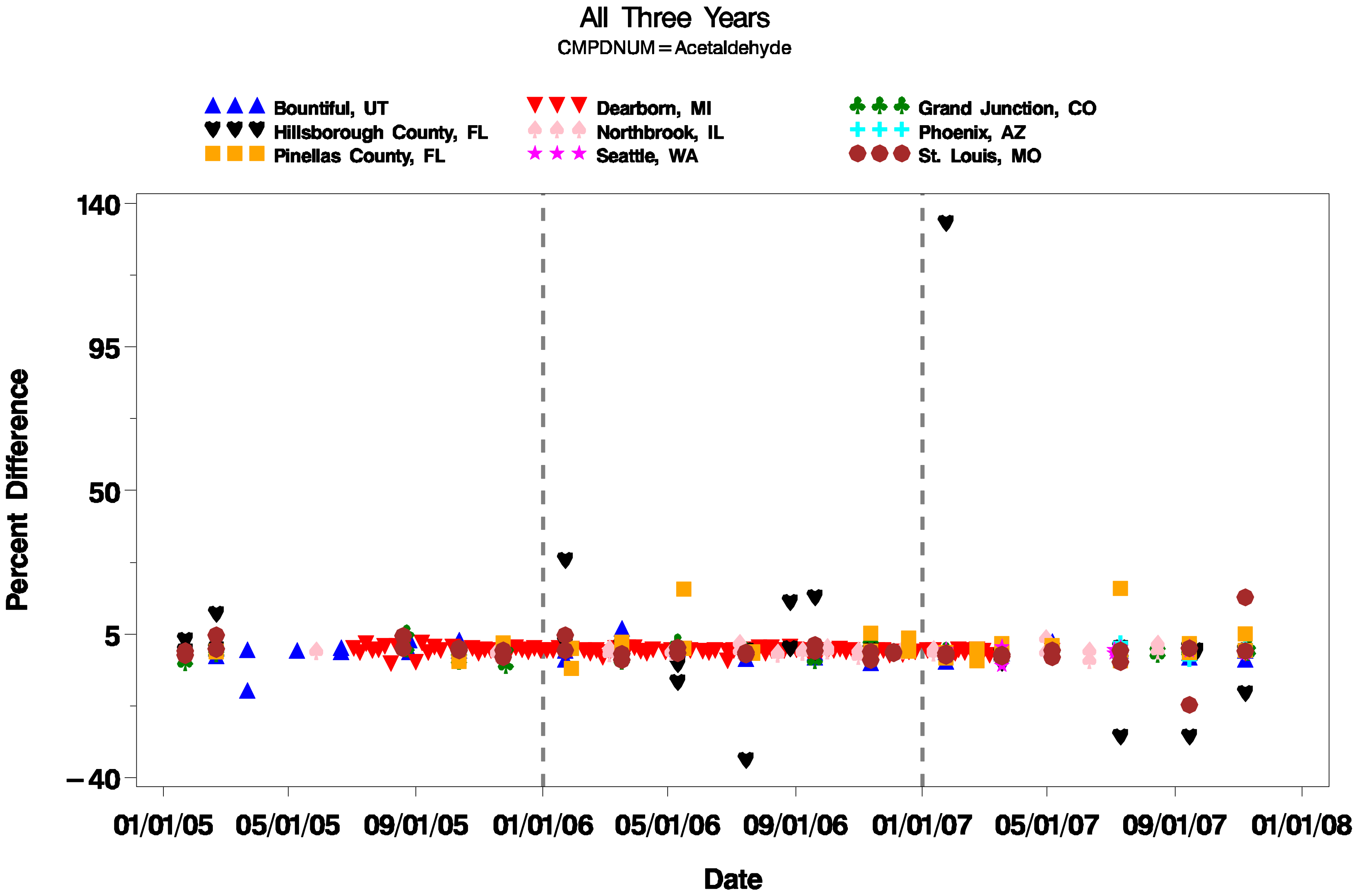

All Three Years
CMPDNUM=Carbon Tetrachloride
Bountiful, UT
Dearborn, MI
Deer Park, TX
Grand Junction, CO
Harrison County, TX
Northbrook, IL
Phoenix, AZ
Pinellas County, FL
Seattle, WA
St. Louis, MO
Percent Difference
200
100
0
−100
−200
01/01/05
05/01/05
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date


All Three Years
CMPDNUM=Acrolein
Bountiful, UT
Dearborn, MI
Deer Park, TX
Grand Junction, CO
Harrison County, TX
Northbrook, IL
Phoenix, AZ
Pinellas County, FL
Seattle, WA
St. Louis, MO
Percent Difference
200
100
0
−100
−200
05/01/05
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date

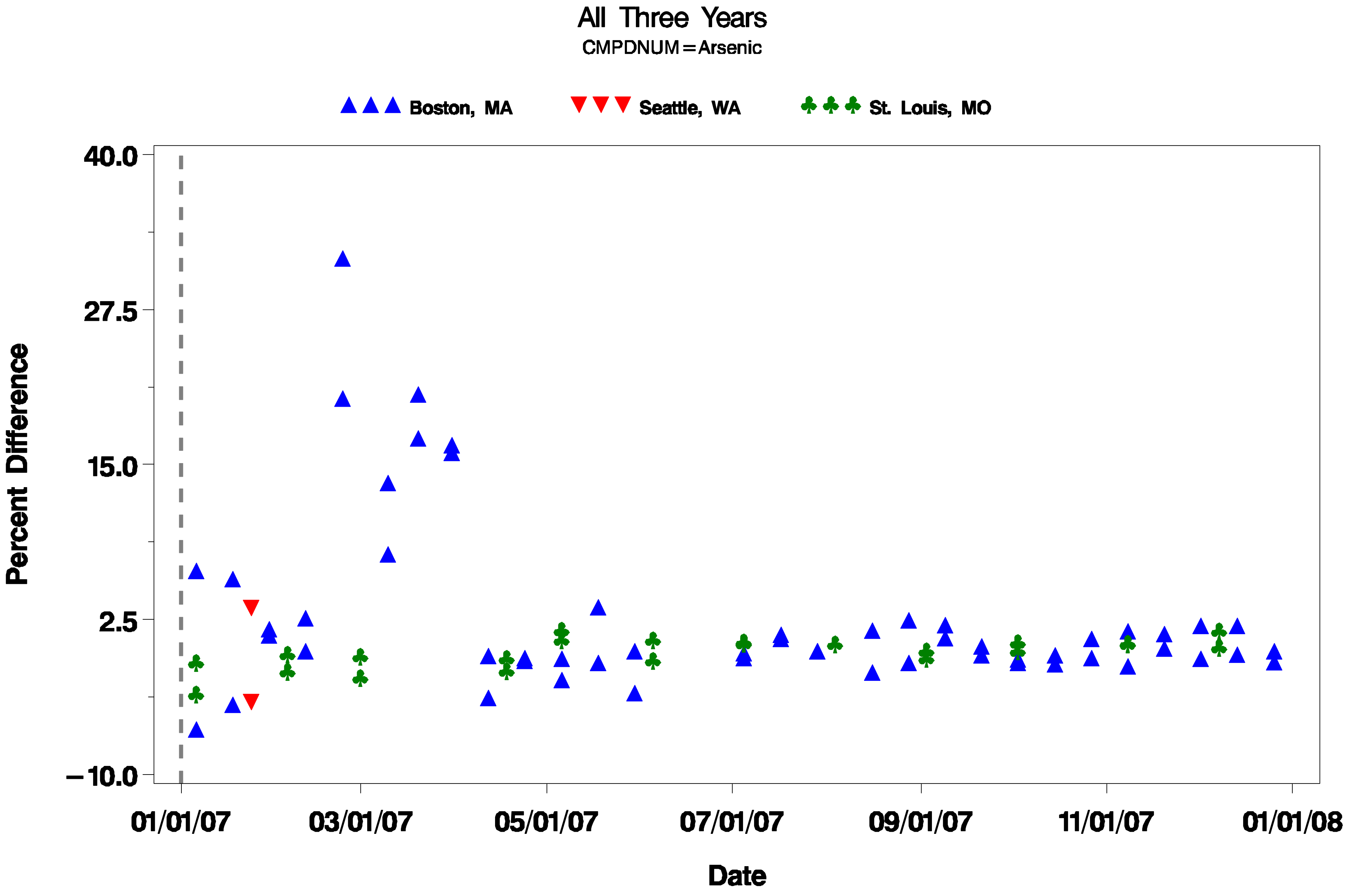
All Three Years

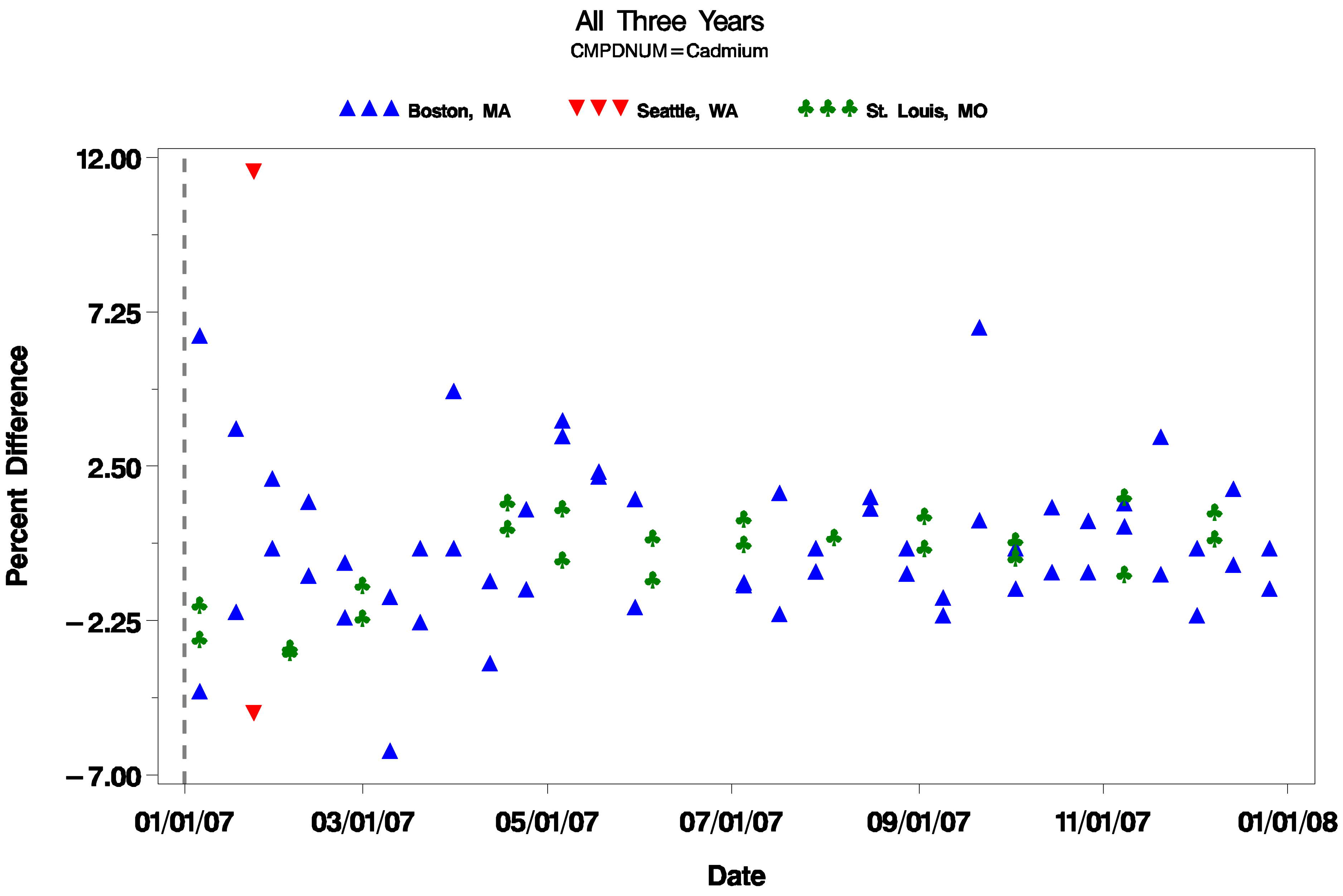
CMPDNUM=Formaldehyde

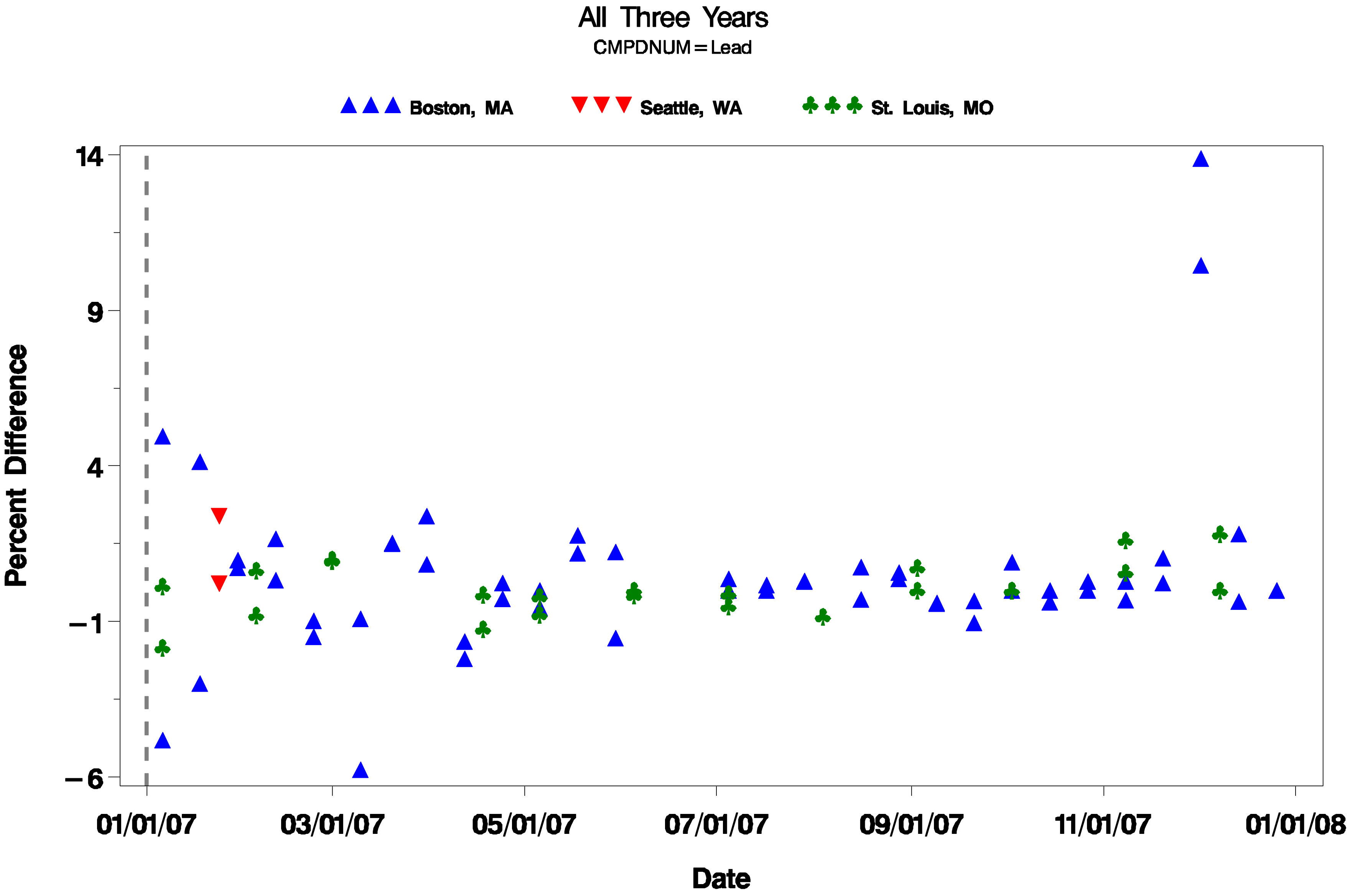




All Three Years
CMPDNUM=Acetaldehyde
▲▲▲ Bountiful, UT
♥♥♥ Hillsborough County, FL
■■■ Pinellas County, FL
▼▼▼ Dearborn, MI
♠♠♠ Northbrook, IL
★★★ Seattle, WA
♣♣♣ Grand Junction, CO
+++ Phoenix, AZ
●●● St. Louis, MO
140
95
50
5
−40
Percent Difference
01/01/05
05/01/05
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date


All Three Years
CMPDNUM=Arsenic
▲▲▲ Boston, MA
▼▼▼ Seattle, WA
♣♣♣ St. Louis, MO
40.0
27.5
15.0
2.5
−10.0
Percent Difference
01/01/07
03/01/07
05/01/07
07/01/07
09/01/07
11/01/07
01/01/08
Date


All Three Years
CMPDNUM=Cadmium
▲▲▲ Boston, MA
▼▼▼ Seattle, WA
♣♣♣ St. Louis, MO
12.00
7.25
2.50
−2.25
−7.00
Percent Difference
01/01/07
03/01/07
05/01/07
07/01/07
09/01/07
11/01/07
01/01/08
Date

All Three Years
CMPDNUM=Lead
Boston, MA
Seattle, WA
St. Louis, MO
14
9
4
−1
−6
Percent Difference
01/01/07
03/01/07
05/01/07
07/01/07
09/01/07
11/01/07
01/01/08
Date

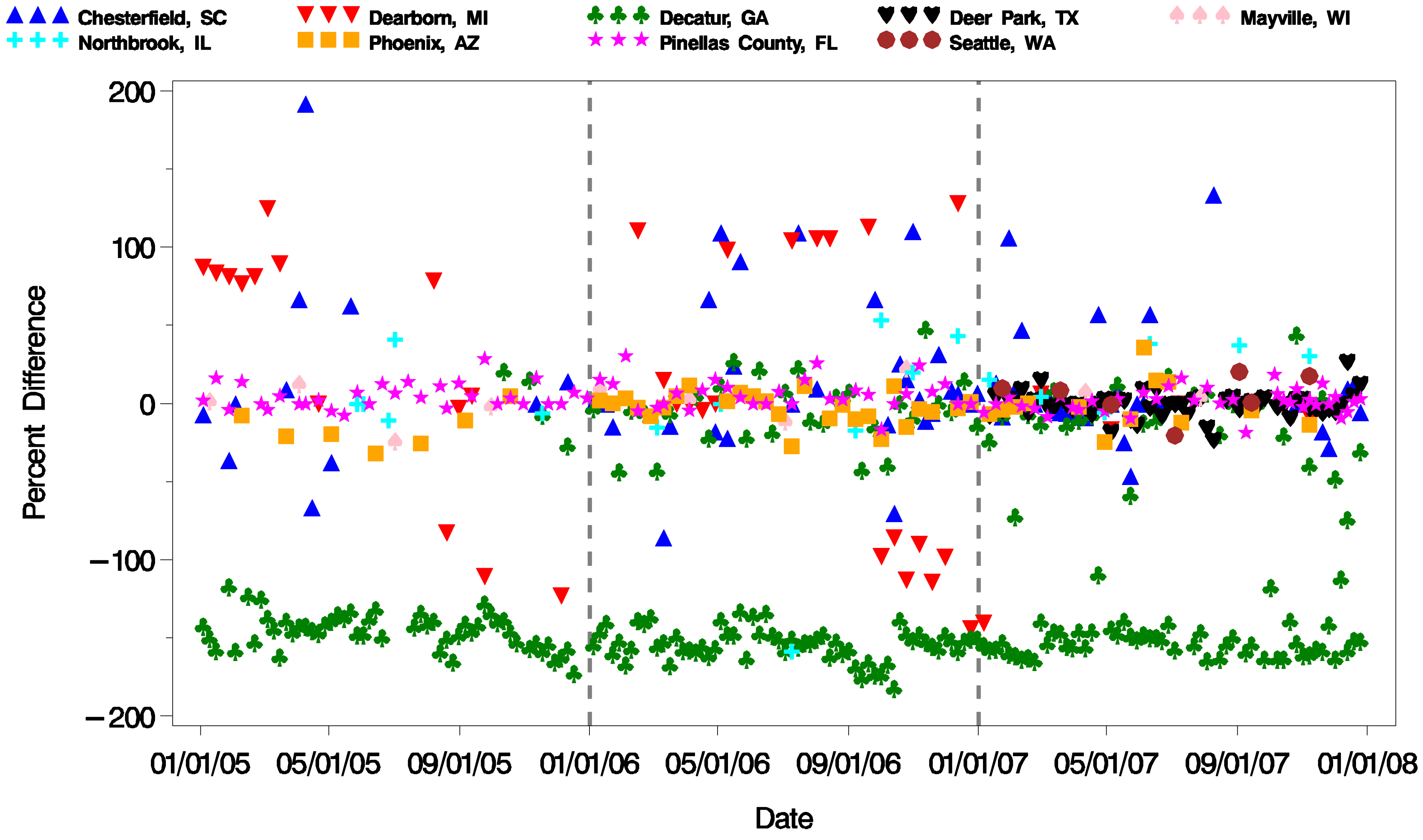
# Appendix B

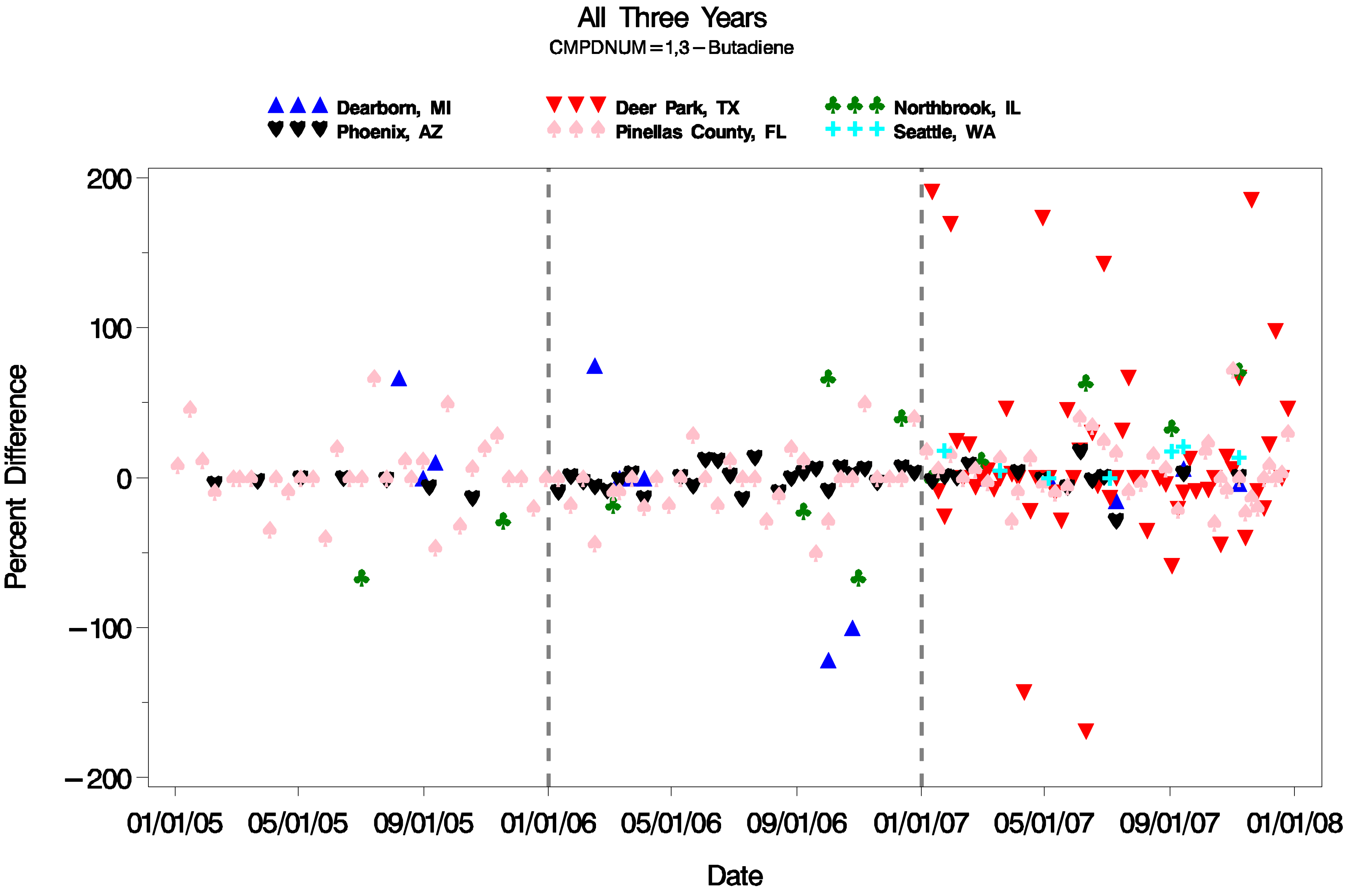
## Overall Precision Plots for Selected Analytes by NATTS Site

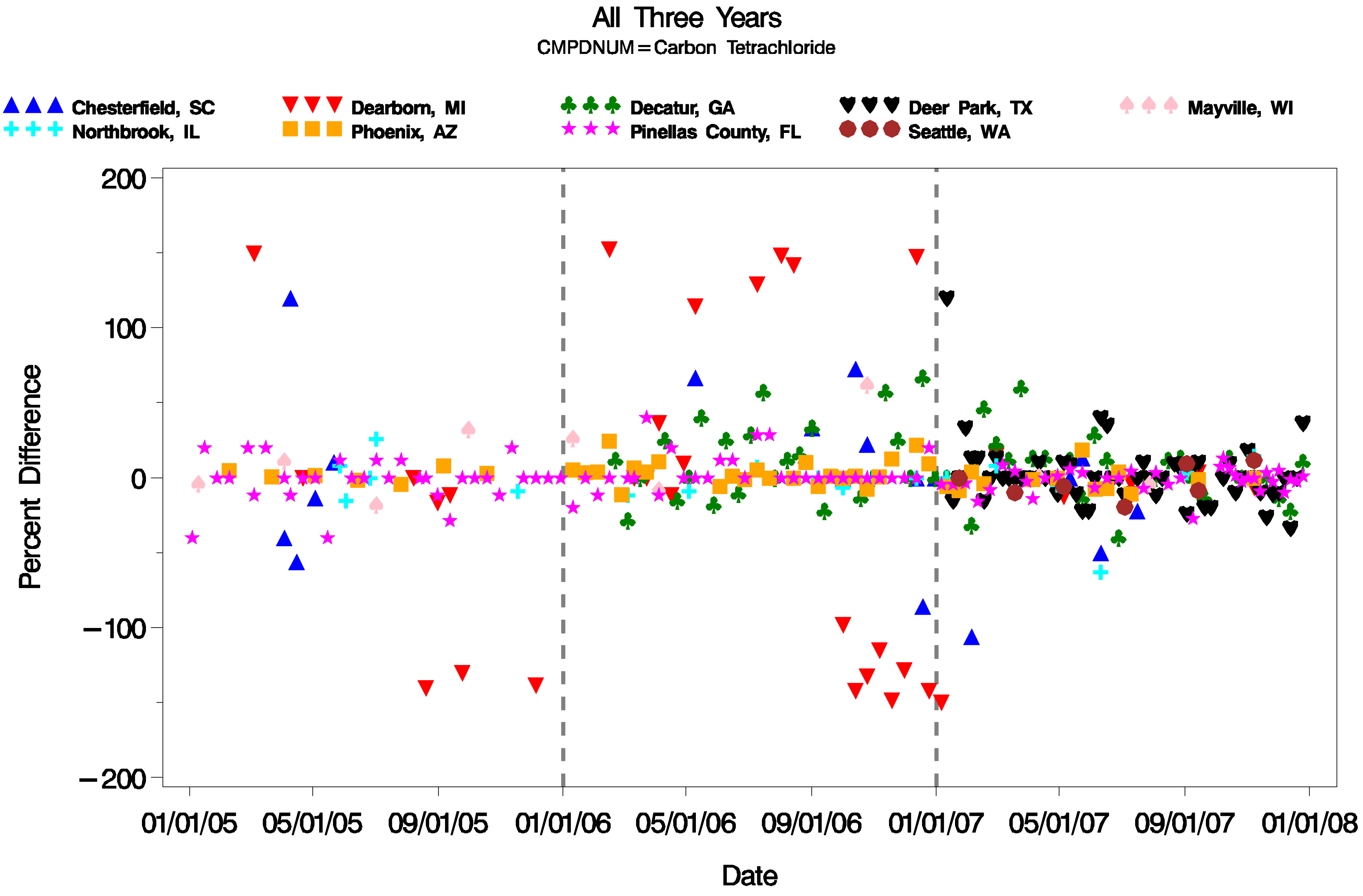
(replicate sample collection data unavailable for sites not shown)

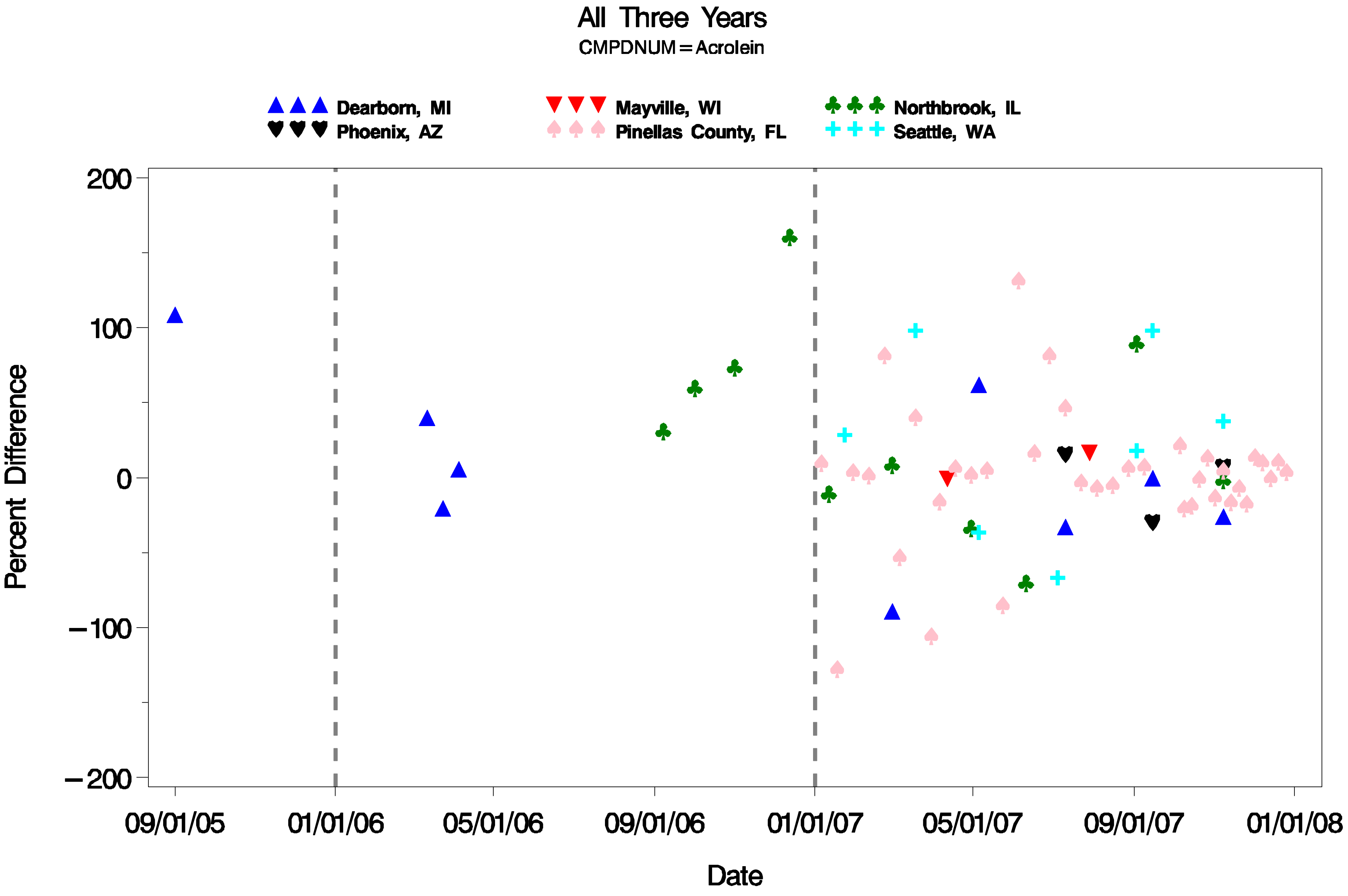
## All Three Years

CMPDNUM=Benzene

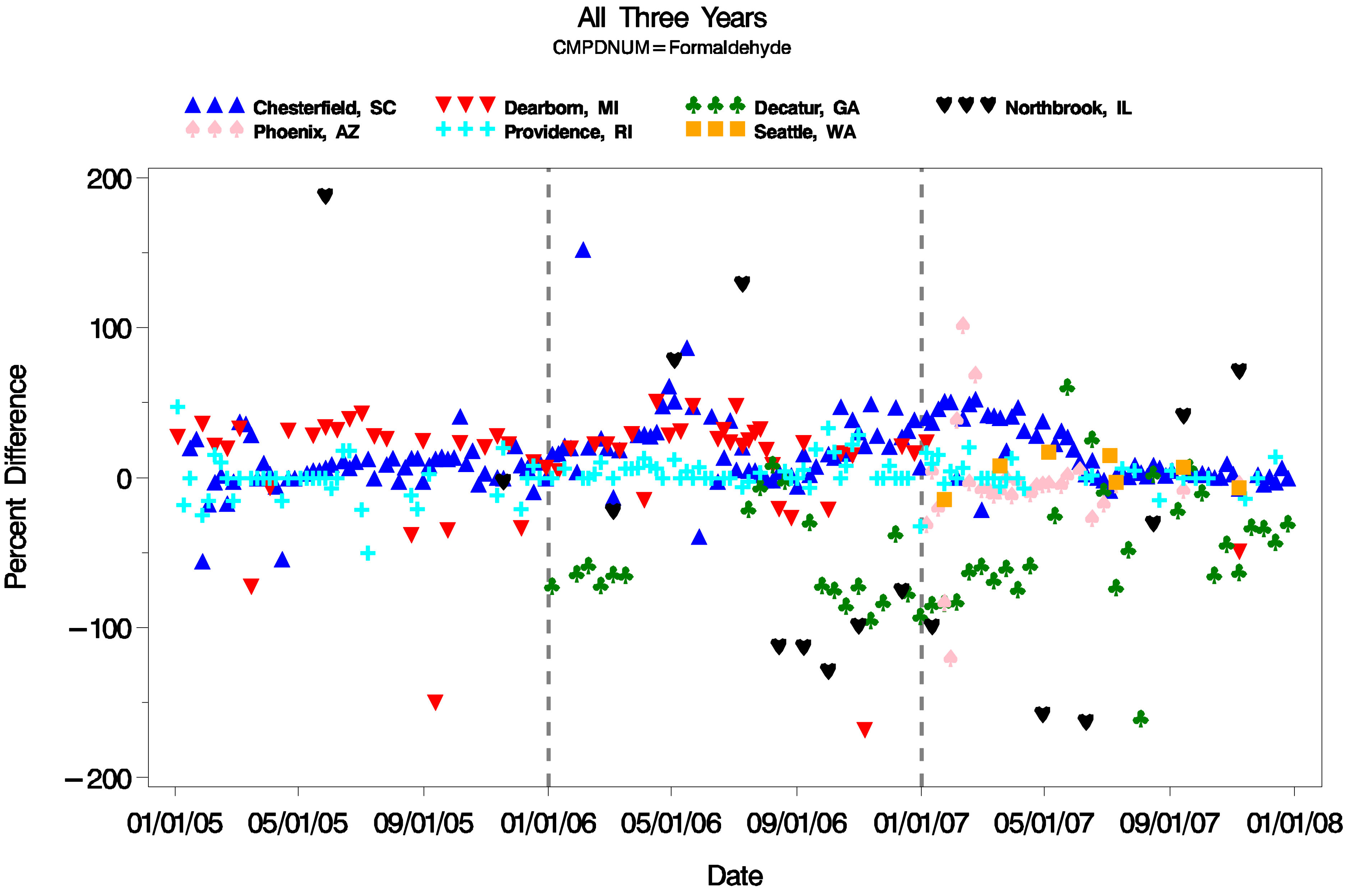



All Three Years
CMPDNUM=1,3−Butadiene
▲▲▲ Dearborn, MI
▼▼▼ Deer Park, TX
♣♣♣ Northbrook, IL
♥♥♥ Phoenix, AZ
♠♠♠ Pinellas County, FL
+++ Seattle, WA
200
100
0
−100
−200
Percent Difference
01/01/05
05/01/05
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date

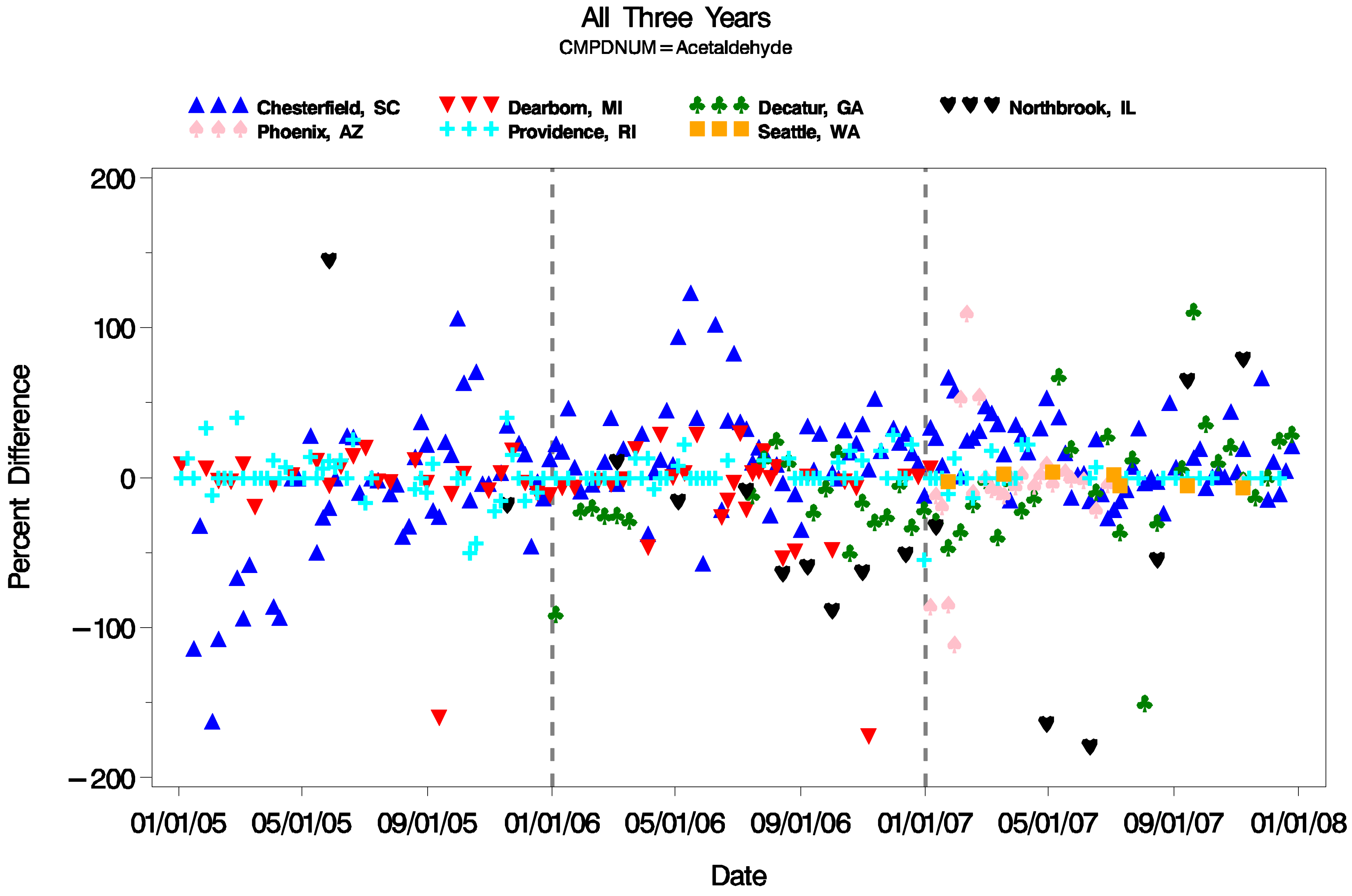

All Three Years
CMPDNUM=Carbon Tetrachloride
Chesterfield, SC
Dearborn, MI
Decatur, GA
Deer Park, TX
Mayville, WI
Northbrook, IL
Phoenix, AZ
Pinellas County, FL
Seattle, WA
Percent Difference
200
100
0
−100
−200
01/01/05
05/01/05
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date



All Three Years
CMPDNUM=Acrolein
Dearborn, MI
Mayville, WI
Northbrook, IL
Phoenix, AZ
Pinellas County, FL
Seattle, WA
200
100
0
−100
−200
Percent Difference
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date

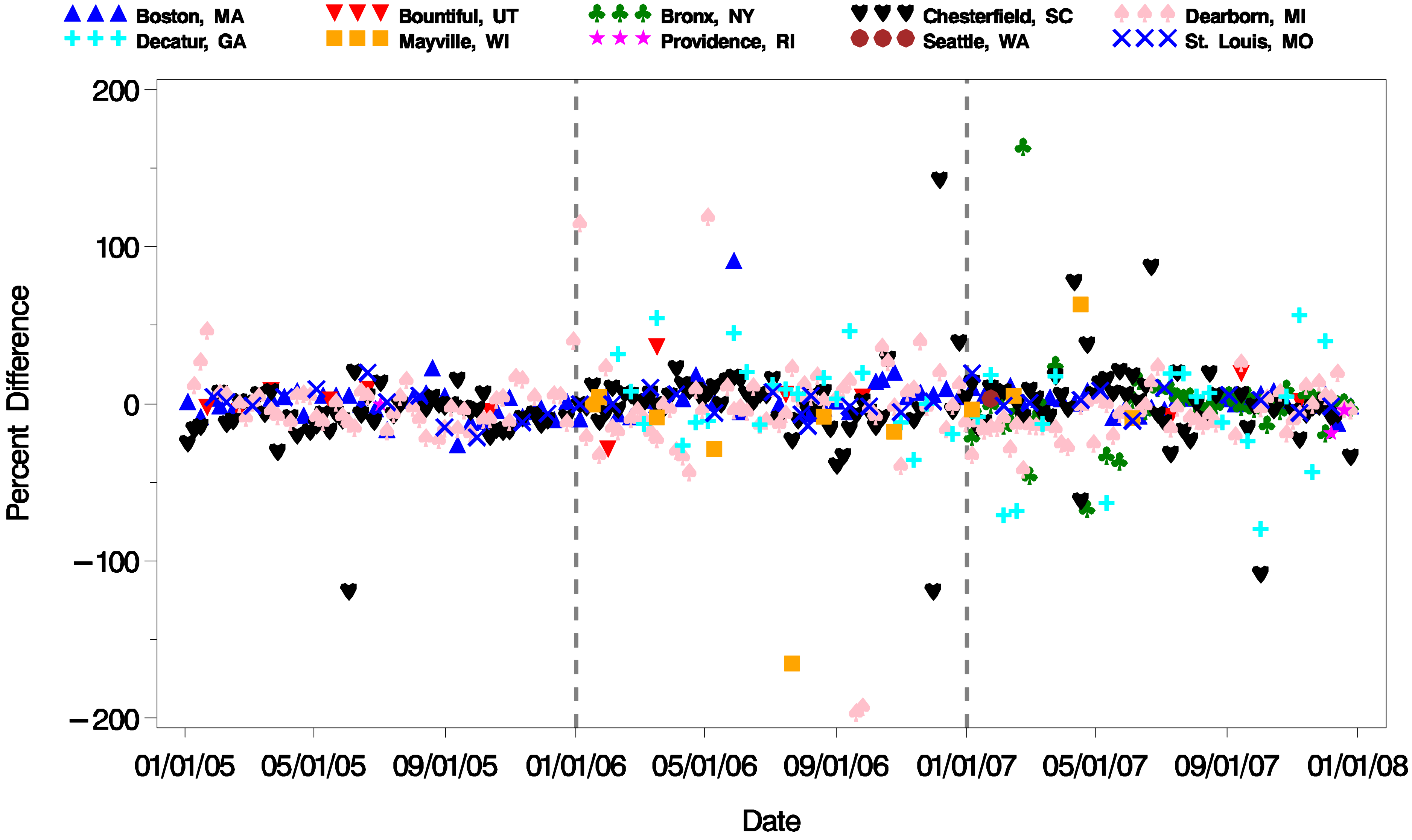


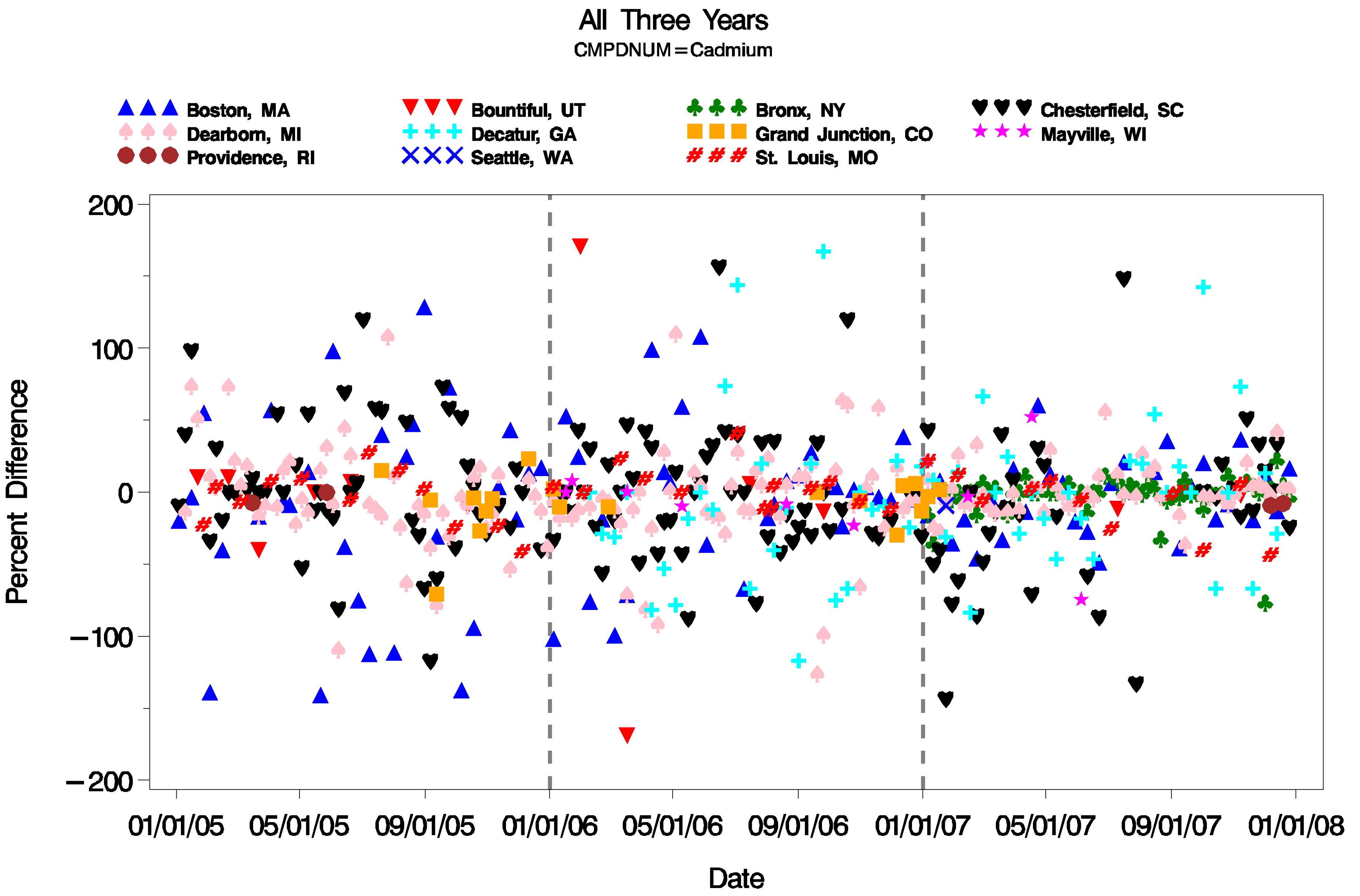
All Three Years
CMPDNUM=Formaldehyde
▲▲▲ Chesterfield, SC
▼▼▼ Dearborn, MI
♣♣♣ Decatur, GA
♥♥♥ Northbrook, IL
♠♠♠ Phoenix, AZ
+++ Providence, RI
■■■ Seattle, WA
200
100
0
−100
−200
Percent Difference
01/01/05
05/01/05
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date


All Three Years
CMPDNUM=Acetaldehyde
▲ Chesterfield, SC
▼ Dearborn, MI
♣ Decatur, GA
♥ Northbrook, IL
♠ Phoenix, AZ
+ Providence, RI
■ Seattle, WA
Percent Difference
200
100
0
−100
−200
01/01/05
05/01/05
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date

# All Three Years

CMPDNUM=Arsenic




All Three Years
CMPDNUM=Cadmium
▲▲▲ Boston, MA
▼▼▼ Bountiful, UT
♣♣♣ Bronx, NY
♥♥♥ Chesterfield, SC
♠♠♠ Dearborn, MI
+++ Decatur, GA
■■■ Grand Junction, CO
★★★ Mayville, WI
●●● Providence, RI
××× Seattle, WA
### St. Louis, MO
Percent Difference
200
100
0
−100
−200
01/01/05
05/01/05
09/01/05
01/01/06
05/01/06
09/01/06
01/01/07
05/01/07
09/01/07
01/01/08
Date

## All Three Years

CMPDNUM=Lead