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Office of Air Quality
Planning and Standards
Research Triangle Park, NC 27711

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April 2002

Air Toxics Pilot Study Laboratory Intercomparison

Quality Assurance Report

Acknowledgments

This report is the product of the EPA Office of Air Quality Planning and Standards. The following individuals are acknowledged for their contributions.

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Contributions

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Figures

Executive Summary

A laboratory "round robin" intercomparison was conducted by the US Environmental Protection Agency (EPA) during the National Air Toxics Pilot Study (NATPS). Volatile Organic Compounds (VOCs) and elemental metallic compounds were collected and distributed to the laboratories that participated in the study. The data were sent to EPA's Office of Air Quality, Planning and Standards (OAQPS). The results were tabulated and statistically analyzed. The following statements can be made about the results of the intercomparison:

- For the VOCs, an issue has been identified concerning the identification and reporting of compounds. EPA will need to establish clear guidelines on what and how compounds are identified and reported.
- 1,3-butadiene values reported on the west coast were significantly different from the values reported on the east coast. Stability of this compound may be a factor. However, several laboratories did not report any values for this compound, therefore more data are needed from across the nation to discern whether this is a problem.
- Most of the compounds that were statistically analyzed were within 2 standard deviations of the mean.
- The Hillsborough County laboratory reported a beryllium value approximately 100 times the mean of the other values. It is believed that there may have been contamination or a dilution error with this metals sample.

Background

To address the concerns about the prevalence of air toxics emissions and to meet EPA's strategic goals, a national air toxics program has been designed to characterize, prioritize, and equitably address the impacts of Hazardous Air Pollutants (HAPs) on the public health and environment. The national air toxics program seeks to address air toxics problems through a combination of activities and authorities, including regulatory approaches and voluntary partnerships. One of the key activities is the National Air Toxics Assessment (NATA). NATA activities will help EPA identify areas of concern, characterize human health and ecosystem risks and track progress of trends.

As outlined in the air toxics monitoring "Concept Paper[1]," the role of ambient monitoring is to support NATA activities includes:

- characterization of ambient concentrations and deposition in representative monitoring areas;
- provide data to support and evaluate dispersion and deposition models; and
- establish trends and evaluate the effectiveness of HAP reduction strategies.

The Concept Paper identifies 18 "core" compounds that have been identified through the NATA as being of particular risk to the health the nations. These are: Benzene, 1,3-butadiene, carbon tetrachloride, chloroform, 1,2-dichloropropane, dichloromethane, tetrachloroethylene, trichloroethylene, vinyl chloride, beryllium, cadmium, chromium, lead, manganese, nickel, acetaldehyde, formaldehyde and arsenic. Arsenic was not included in this intercomparison due to the difficulty of analysis. Continued method development research is required for arsenic.

To help further our understanding of monitoring the core HAPS, EPA embarked on the NATPS in CY 2001. This initial pilot monitoring together with data analysis of existing measurements was needed to provided information on spatial and temporal variability of ambient air toxics. This information will aid in providing state and local air agencies important information about their particular network needs. The pilot monitoring program will also provide very useful information to help the EPA design a long-term national air toxics monitoring network.

In order to provide consistency in the data set generated by the NATPS, a laboratory work group was formed to discuss the details regarding procedures to be used for measurements. This group of laboratory, State and local, Regional and EPA representatives recommended in early 2001 to create a "round robin " interlaboratory program that would provide Performance Evaluation samples (PEs) to the laboratories that are involved in the NATPS.

The purpose of this document is to discuss the procedures used and the results of the interlaboratory comparison.

Procedures

For the Volatile Organic Compounds, (VOCs) the California Air Resources Board (CARB) collected ambient air samples in SUMMA™ passivated 6 liter canisters from the following laboratories: Bay Area Air Quality Management District (BAAQMD), State of Michigan Department of Environmental Quality (MDEQ), Pinellas County Air Quality Division (PCAQD), Maryland Department of Environmental Laboratory (MDEL), Rhode Island Department of Health (RIDOH), Eastern Research Group (ERG), New Mexico Department of Health (NMDOH), South Coast Air Quality Management District (SCAQMD) and Washington State University Laboratory (WSU). The canisters arrived at CARB cleaned and evacuated. CARB filled each canister with an urban ambient sample, from Azusa California, analyzed their own canister and shipped the rest of the canisters to the participating laboratories. The analysis of the canisters was performed by Toxic Organic Method TO-14A or 15[2]. The results were then sent to CARB, who culminated the data. The data were sent to each laboratory and to OAQPS. The results are discussed in the next section. Please note that BAAQMD was not part of the NATPS, however, this agency did participate in the CARB-VOC intercomparison. The results were forwarded to OAQPS, therefore the BAAQMD results are included here for comparison.

For the elemental metallic compounds, the SCAQMD collected collocated Fine Particle - 10 micron or less (PM_{10}) samples. The filter media (quartz) was cut into 1" by 4" strips that were sent directly to OAQPS. The OAQPS Quality Assurance Manager (QAM) for the National Air Toxics Program divided up the filter strips and sent them to all of the laboratories that were performing metals analysis. These laboratories were: Hillsborough County Environmental Protection Commission (HCEPC), Research Triangle Institute (RTI) through the State of Rhode Island and ERG, MDEQ, Energy Northwest through the State of Washington, NMDOH and the State of West Virginia. Analysis results were sent directly to OAQPS QAM. These laboratories analyzed the samples using Inductively Coupled Plasma (ICP) method Inorganic Compendium IO-3.5[3].

There are two aldehyde compounds, acrolein and formaldehyde, that were not included in the intercomparison study. Methods for delivery and capture of these compounds are still under development and were not included in this study.

The statistical analysis was performed by calculating the mean value for each compound, then calculating the standard error (i.e., standard deviation). In order to see distribution of the data, one and two standard errors were calculated about the mean. The resulting data and the error bars are illustrated in Figures 4 - 19.

Results and Findings

VOCs

For the VOCs, the QAM decided to examine the data recovery for the sample. Figure 1 and 2 illustrate that a discrepancy exists on what laboratories report. Figure 1 illustrates that some of the laboratories reported as high as 83.3% (Rhode Island) of the total number of compounds reported, while some laboratories only reported 26.6% (New Mexico). Figure 3 also bears out this trend. This graph illustrates that only 2 laboratories reported 17 compounds. Figure 2 shows that for most of the compounds, only 2 laboratories reported those. A simple calculation shows that 40% of all compounds were only reported by two laboratories. There may be several reasons for this pattern:

- A laboratory may get a peak in their chromatogram, but the GC operator may not be able to identify the peak;
- A laboratory may get a peak in a their chromatogram, but not report it because it is not required to do so;
- A laboratory may not have the correct mix of standards to identify every peak;
- A laboratory may be unwilling to report a value that is below or near their Method Detection Limit (MDL).

This bring to the surface the issue of reporting of values. There must be standardization across the network a target list of compounds, the calibration standards used by all of the laboratories, identification techniques and reporting standards. The EPA must work with the S/L/T agencies that are in the air toxic network on these issues.

The laboratories that participated in the intercomparison reported 9 of the 9 VOCs that were requested. Vinyl chloride was reported by only one laboratory, and this values was below their MDL. All other laboratories reported vinyl chloride as below their MDL or not detected. All other requested VOCs were analyzed statistically. The QAM calculated the standard error for each compound. The standard error was then plotted against the values and the mean. For most of the compounds, the values were within 2 standard deviations of the mean. However, there are several exceptions (please see figures 4 - 12):

- For 1,3-butadiene, the WSU result was outside of 2 standard deviations about the mean. In addition, the CARB result was near the mean. The four laboratories in the eastern part of the country reported levels much lower than CARB or WSU. This discrepancy

may be due to stability of 1,3-butadiene in canisters. This should be investigated further.

- Among the Pilot laboratories, the values reported for Benzene, Carbon Tetrachloride, Tetrachloroethylene, Trichloroethylene and chloroform were all within 2 standard deviations about the mean.
- For dichloromethane, the SCAQMD reported value was outside of 2 standard deviations. For 1,2-dichloropropane, only two laboratories reported for this compound, both values at 0.01 ppb-v. Since these values were the same, the standard error is zero.

Metals

Metallic compounds were collected on quartz filters using collocated PM_{10} samplers. Each laboratory that performed metals analysis during the pilot study was sent 2 sample strips. OAQPS did not receive results from the West Virginia or New Mexico laboratories. The same statistical test was performed for the metals as for the VOCs. All other labs reported values. Figures 13 - 19 illustrate the results:

- For beryllium, the HCEPC reported a value that was an order of magnitude 100 higher (275 ng/strip) than the average of the other laboratories (2.59 ng/strip). The QAM believes there was a dilution error or the filter strip was contaminated. All other samples ranged from 5 ng/strip to 0.95 ng/strip.
- For cadmium, all of the reported values were within 1 standard deviation. HCEPC did not report a value for cadmium.
- For chromium, manganese and nickel, all reported values were within 2 standard deviations of the mean. For lead, HCEPC value was outside of the 2 standard deviations limit.
- Recovery and analysis for chromium has been reported in the literature as being problematic[4]. Reference 4 reports that the recovery of Chromium from Standard Reference Material 1648 as being 23%. It would be expected that this metal may be problematic for the laboratories to extract, recover and analyze and the statistical analysis would show large variability. However, as Figure 15 illustrates, this does not appear to be a problem. All values were within 2 standard deviations. Three of the laboratories reported values that were very close (i.e., 389.3, 391.0 and 368.0 ng/strip). Two laboratories reported values of 300.0 and 300.5 ng/strip. It appears that all of the laboratories are getting consistent recoveries through their extraction procedures and comparable analysis for chromium.

Graphs

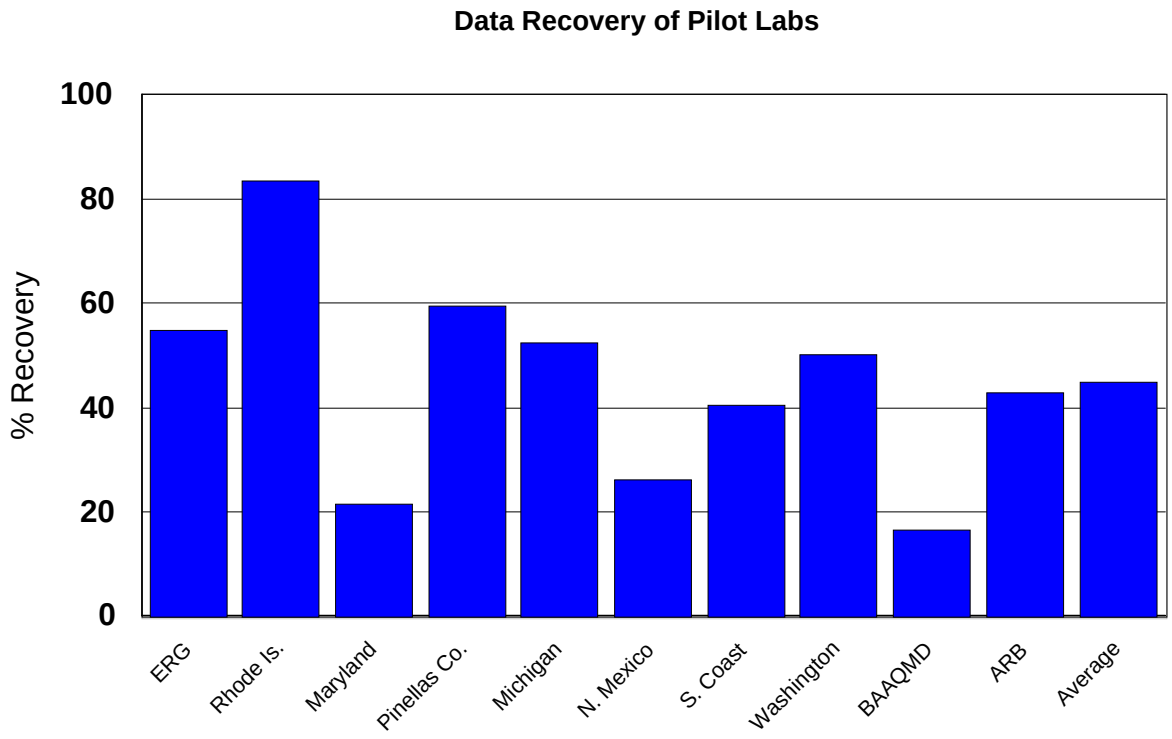


Figure 1

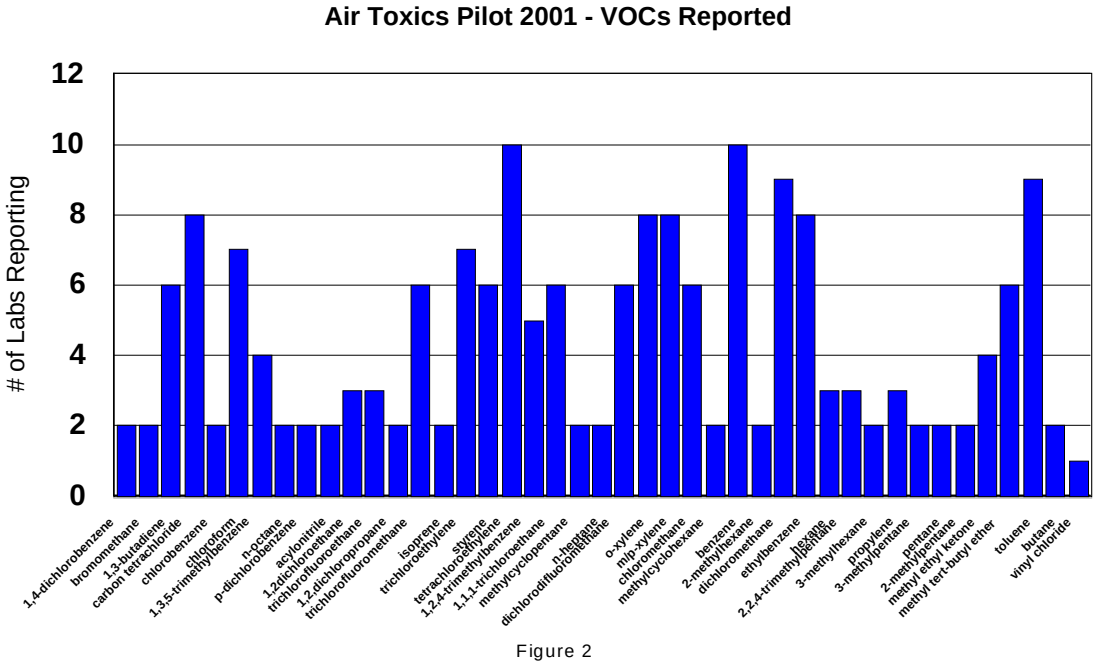


Figure 2

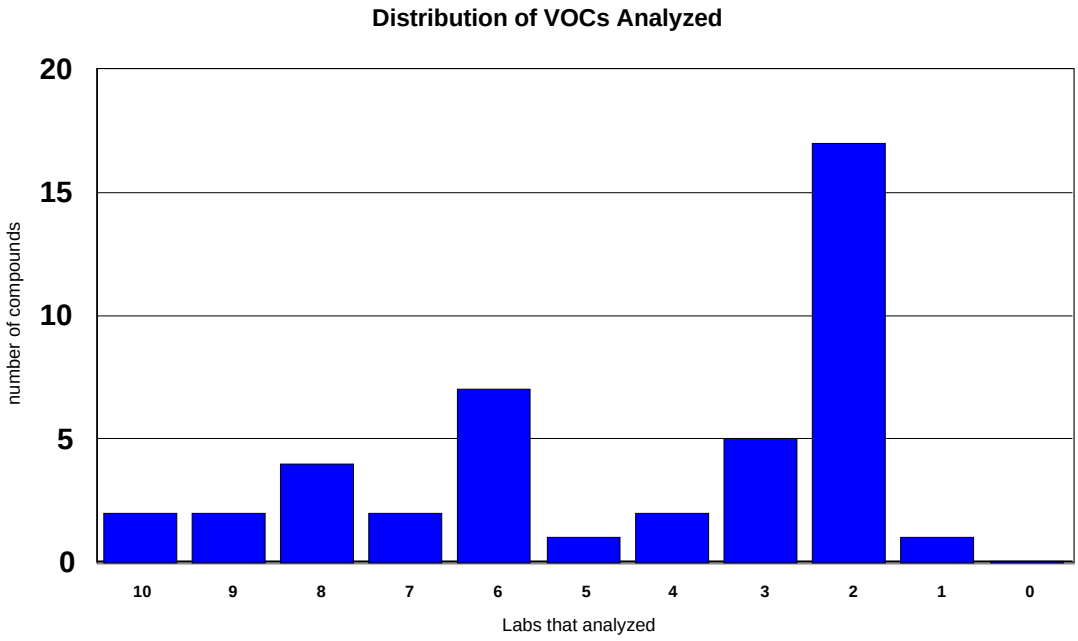


Figure 3

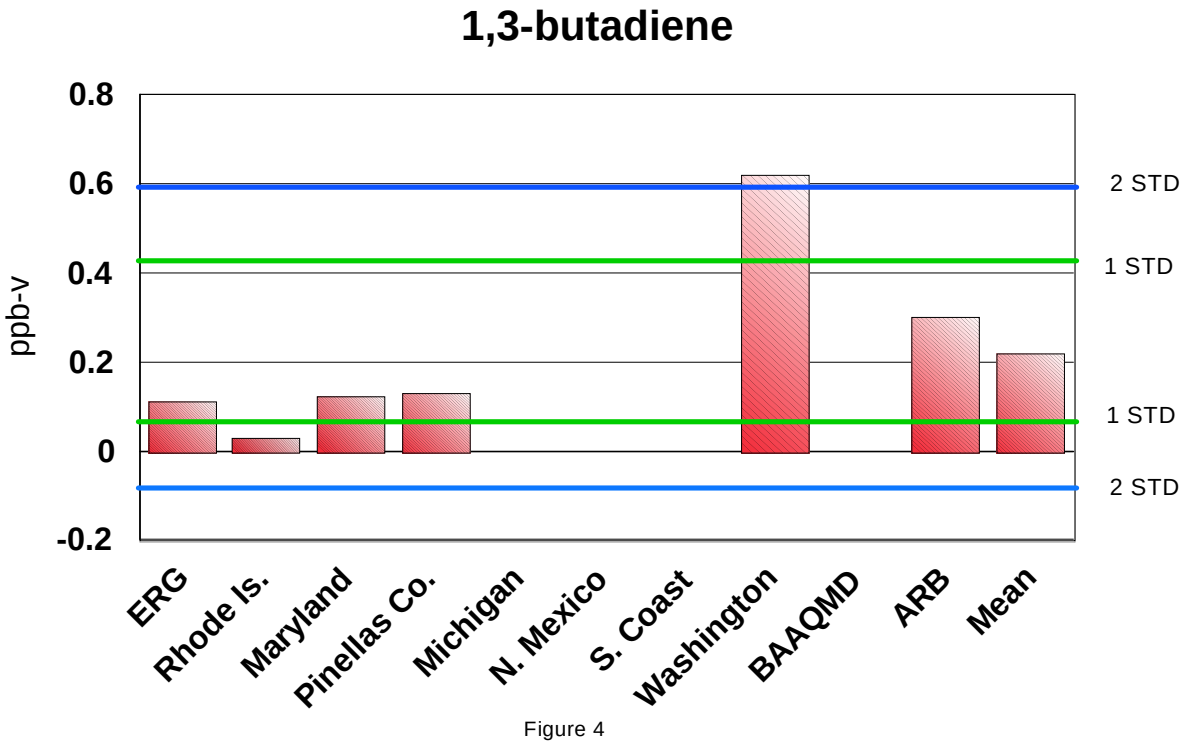


Figure 4

Carbon Tetrachloride

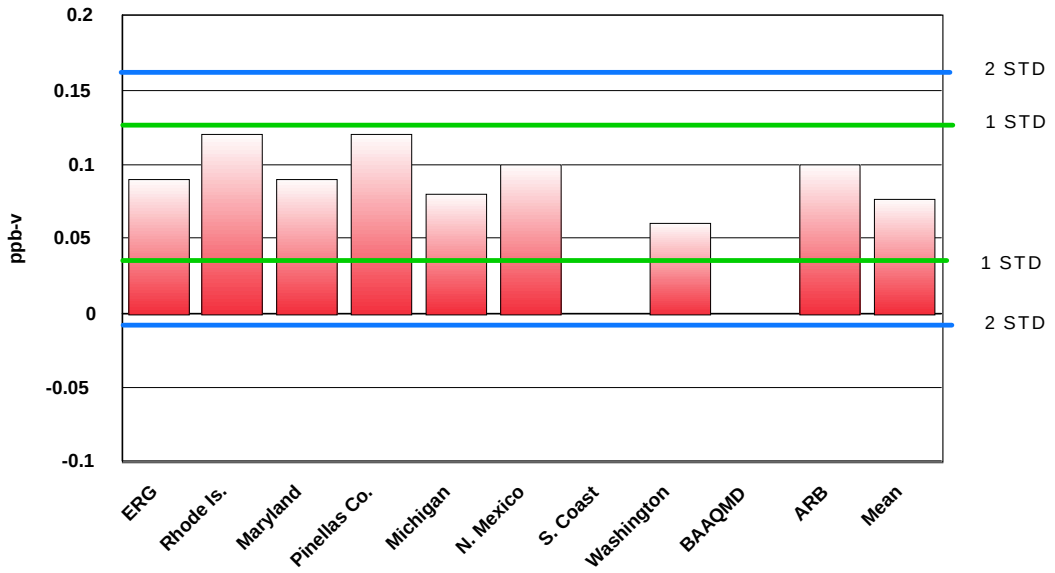


Figure 5

Tetrachloroethylene (PCE)

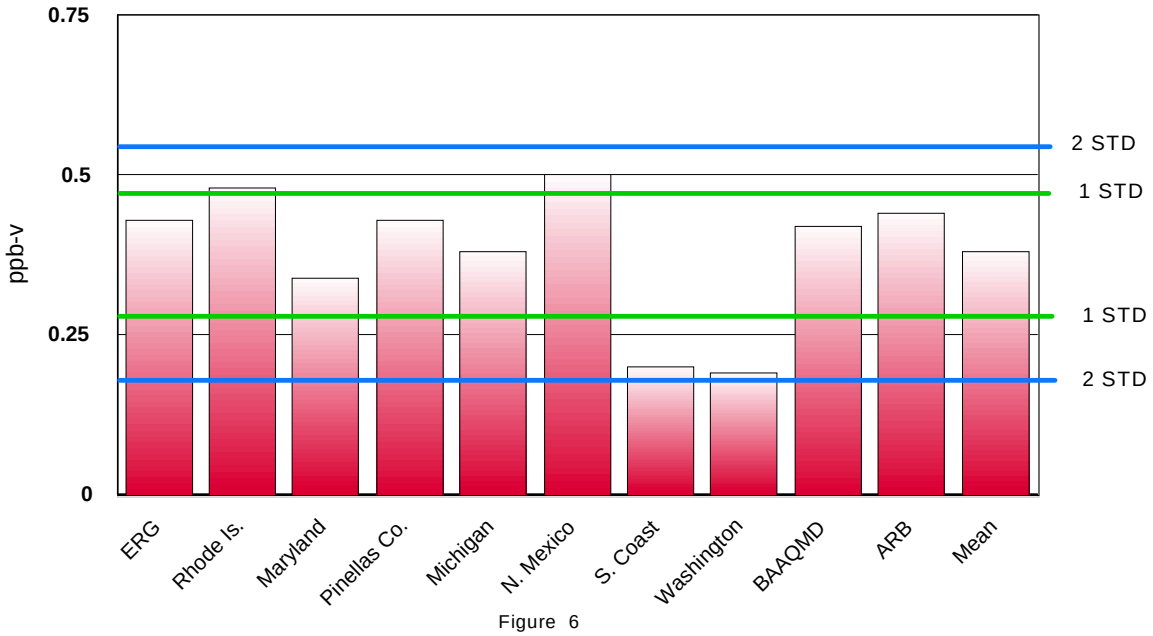
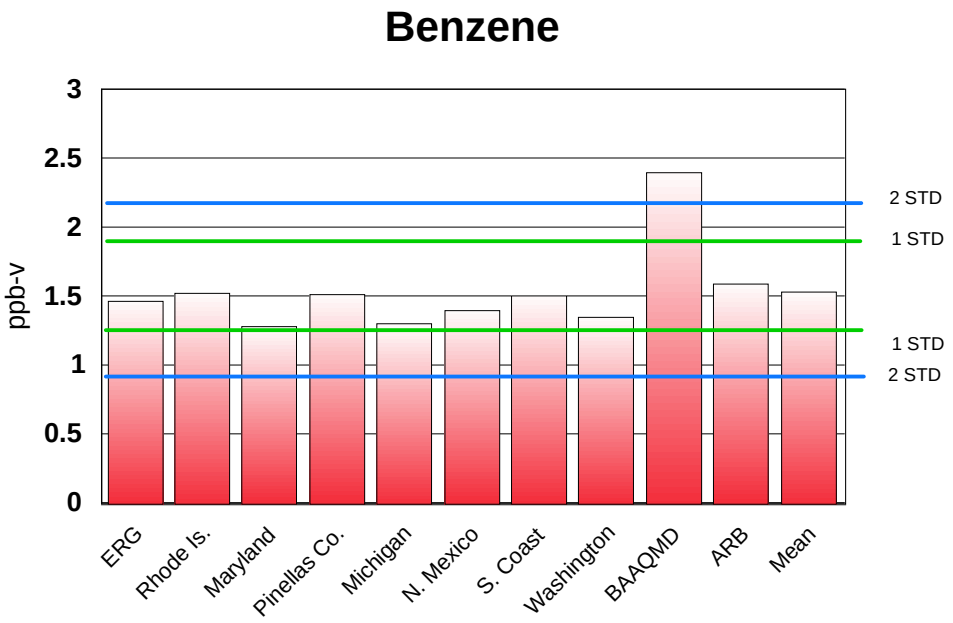


Figure 6



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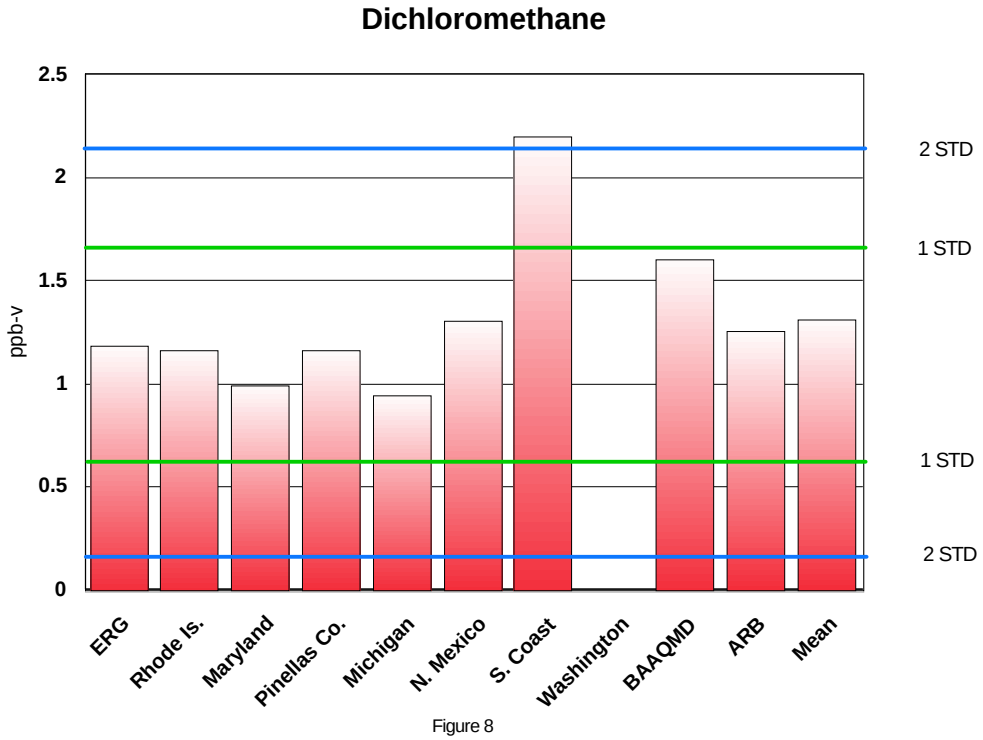

Figure 8

Chloroform

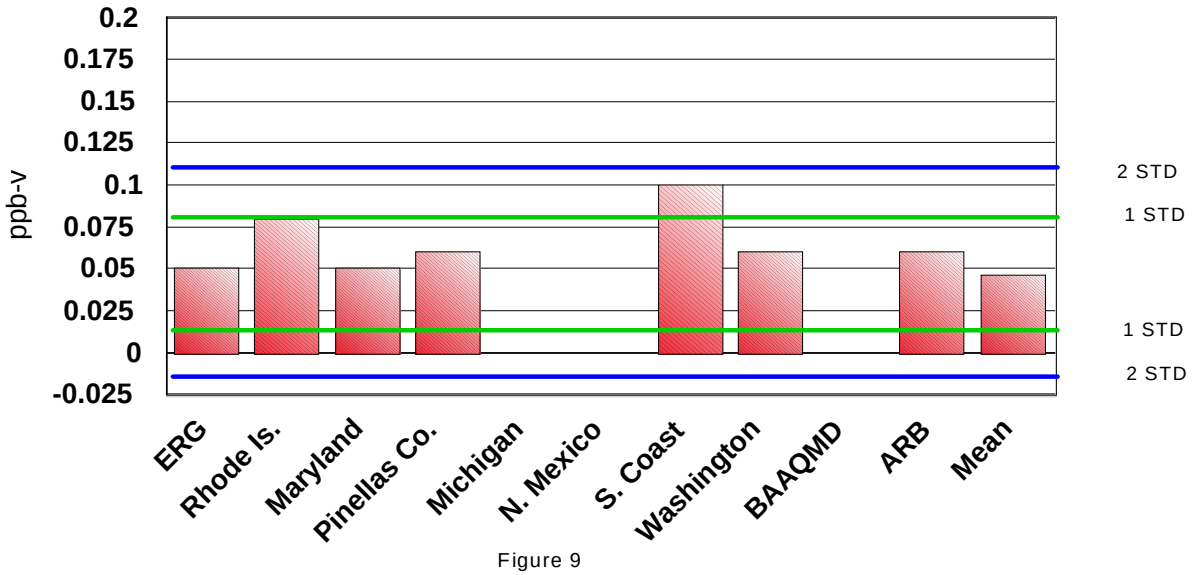

Figure 9

1,2 dichloropropane

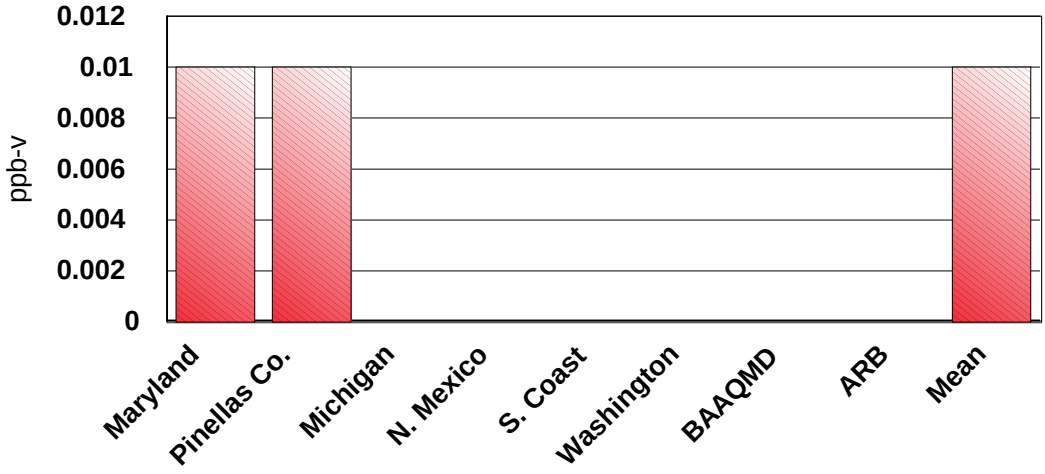

Figure 10

Note: Since both reported values are the same, the Standard deviation is zero.

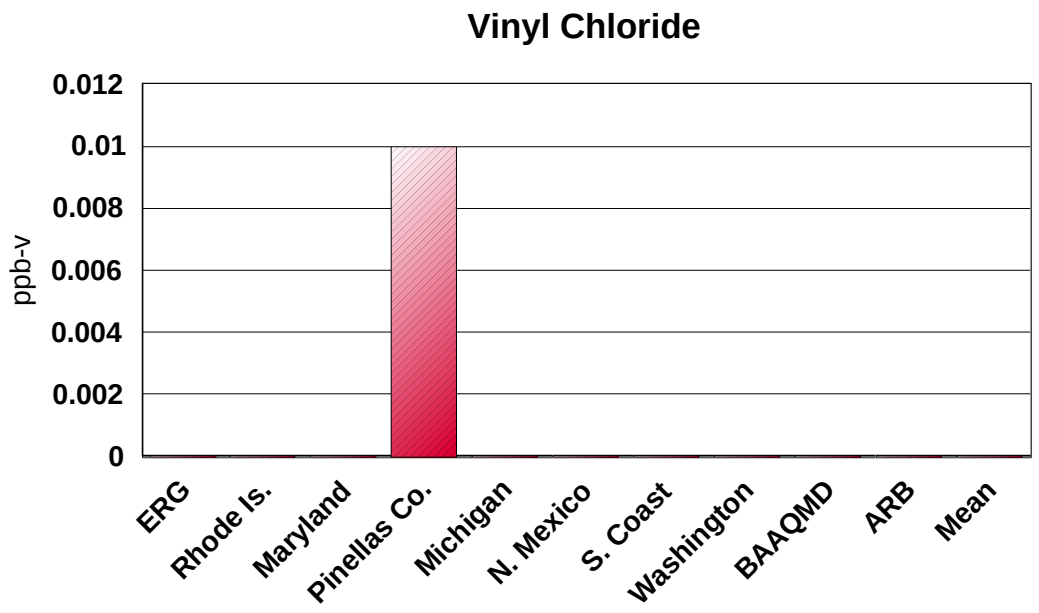

Figure 11

Note: Only one lab reported a value, therefore, the standard error is zero.

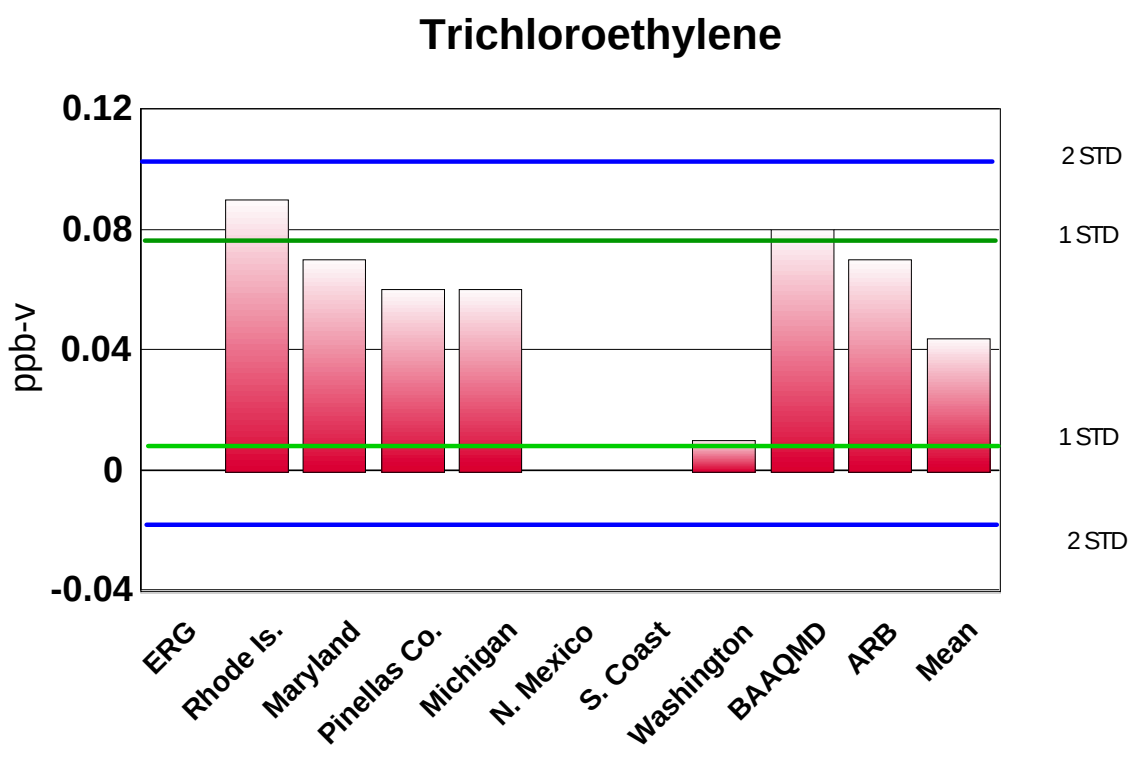

Figure 12

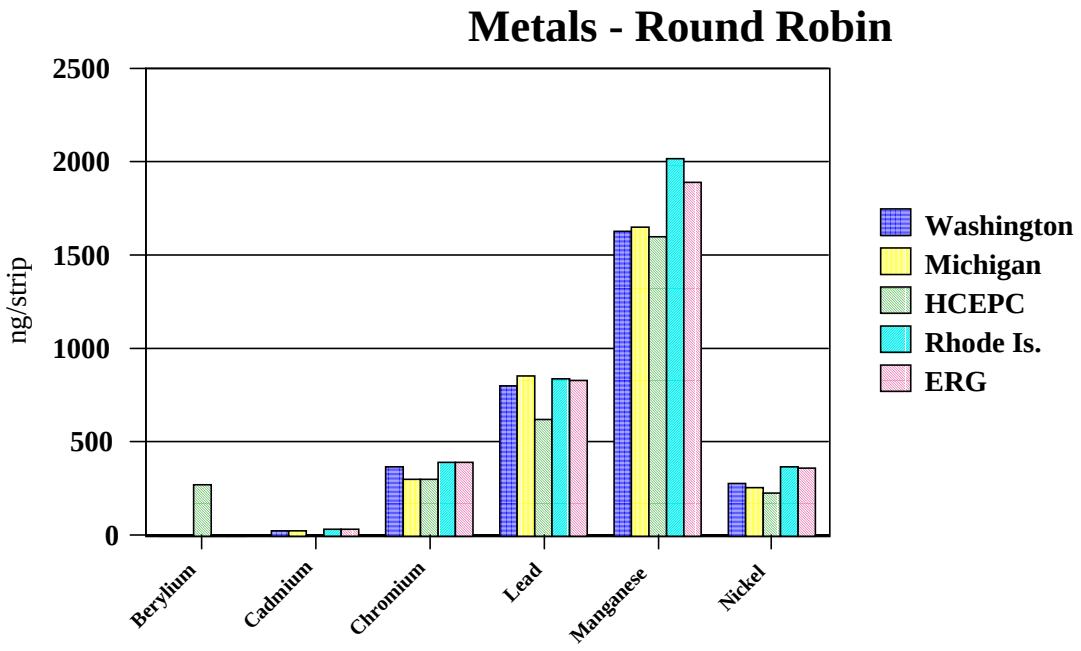

Figure 13

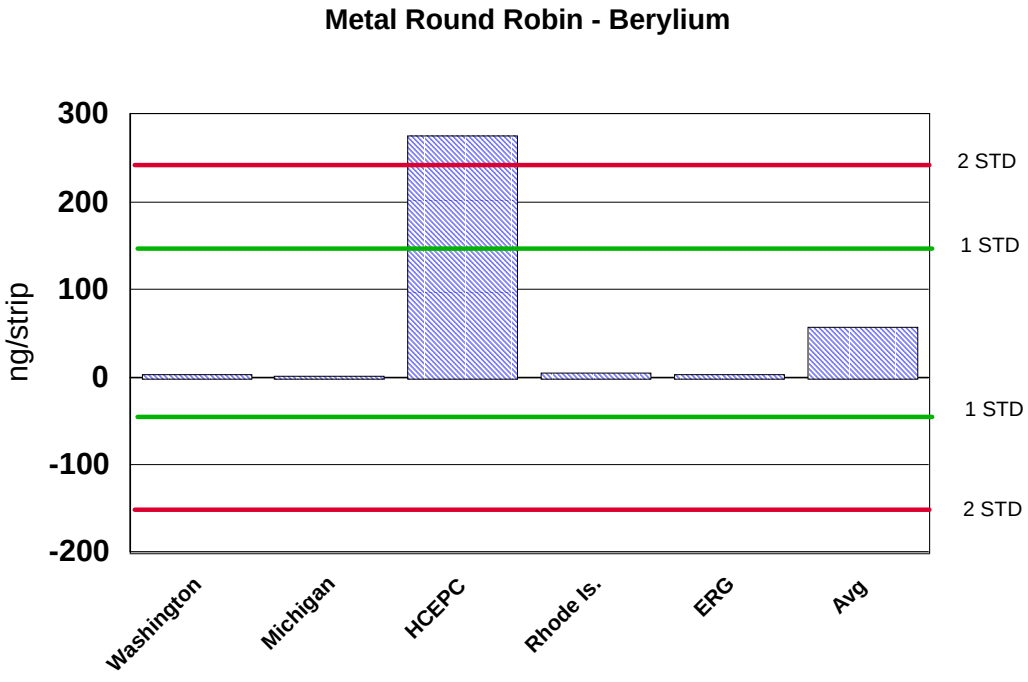

Figure 14

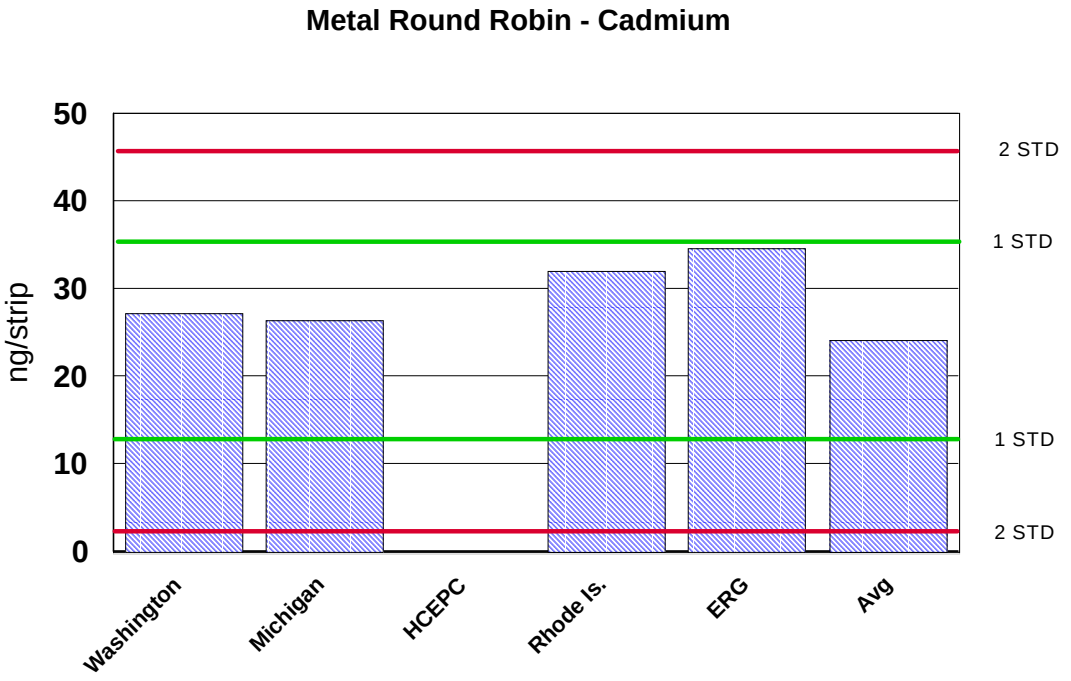

Figure 15

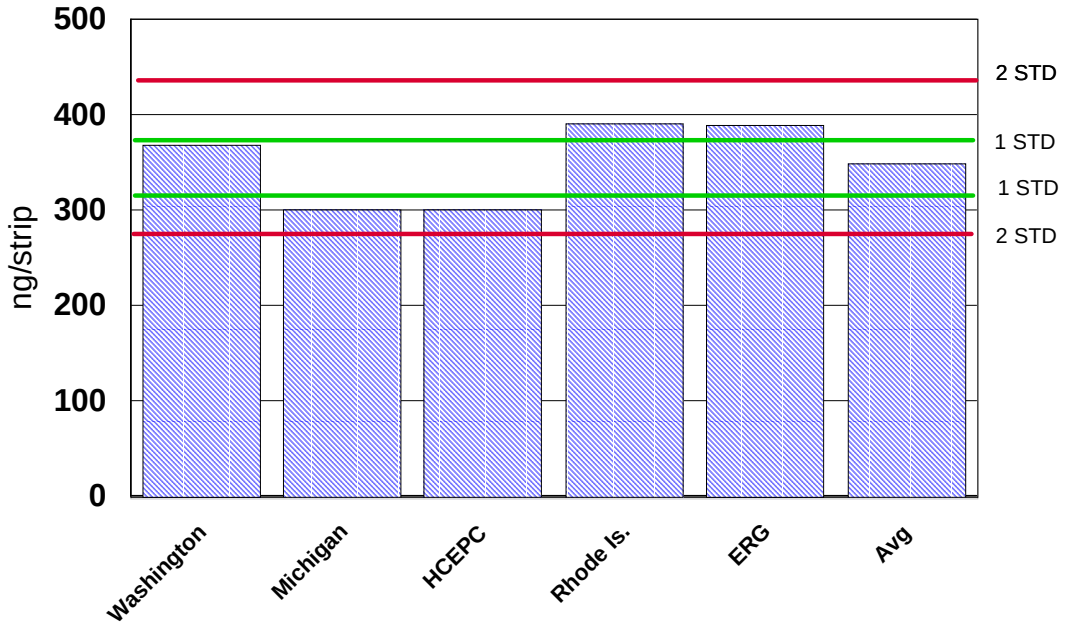

Figure 16

Metal Round Robin - Lead

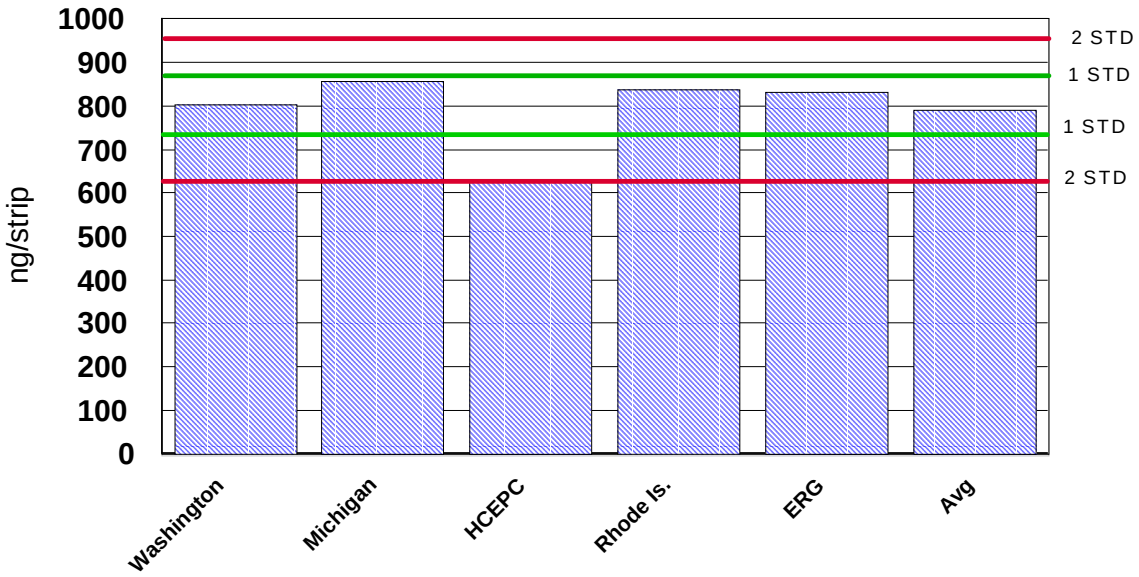

Figure 17

Metal Round Robin - Manganese

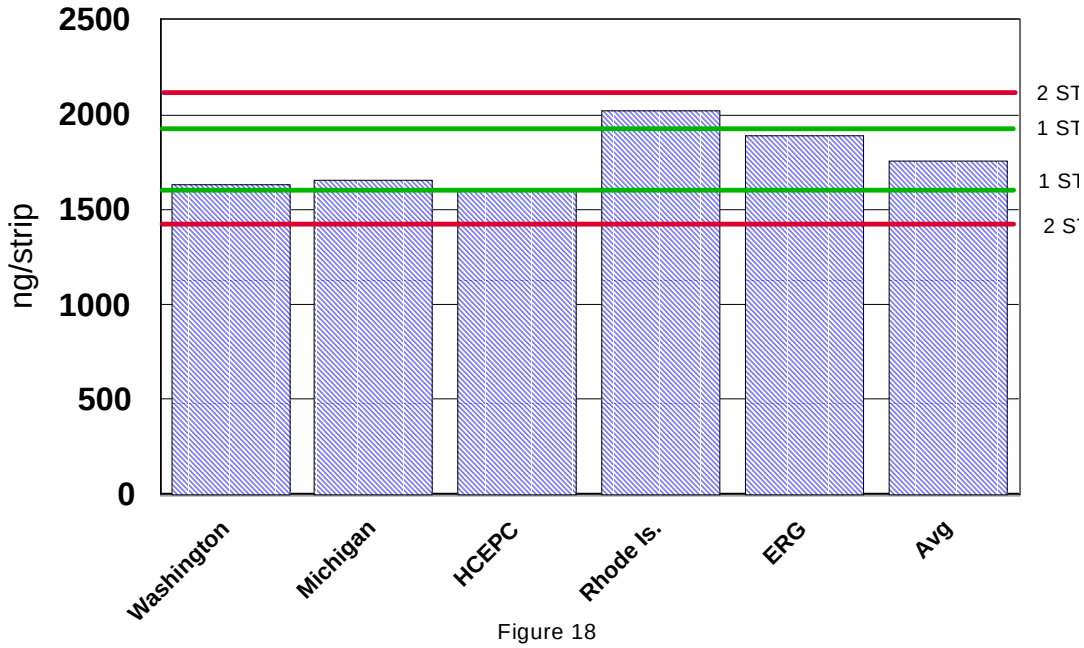

Figure 18

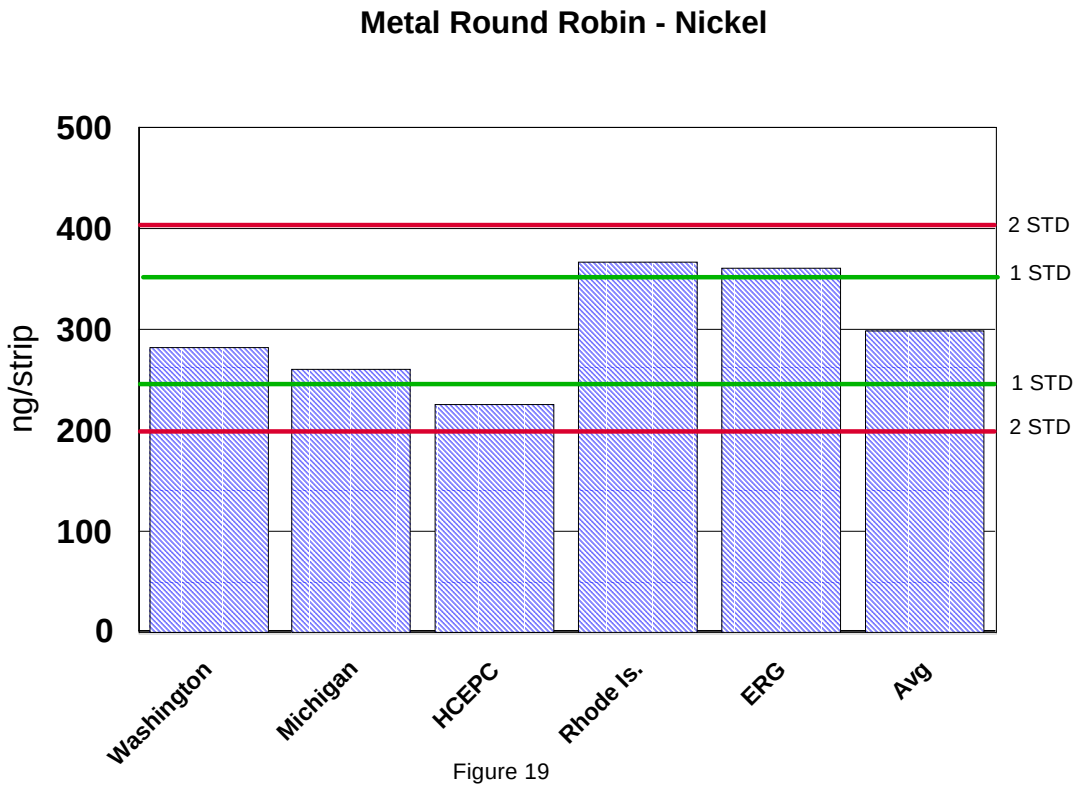
Metal Round Robin - Nickel
500
400
300
200
100
0
ng/strip
2 STD
1 STD
1 STD
2 STD
Washington
Michigan
HCEPC
Rhode Is.
ERG
Avg

Figure 19

References

1. Air Toxics Monitoring Concept Paper" (Draft), February 29, 2000. This file can be found at the following EPA Internet site: http://www.epa.gov/ttn/amtic/airtxfil.html.

2. Compendium Method for Determination of Toxics Organic Compounds in Air, United States Environmental Protection Agency Section TO-14A and TO-15A, January 1999. This document can be found on the following Internet address: http://www.epa.gov/ttn/amtic/airtox.html.

3. Compendium Method for Determination of Inorganic Compounds in Air, United States Environmental Protection Agency Section TO-14A and TO-15A, June 1999. This document can be found on the following Internet address: http://www.epa.gov/ttn/amtic/inorg.html

4. Harper, Sharon, Walling, Joseph F., Holland, David and Pranger, Louis J. , "Simplex Optimization of Multielement Ultrasonic Extraction of Atmospheric Particles" Analytical Chemistry Volume 55, Number 9, August 1983.

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16. ABSTRACT

The Air Toxics Pilot Study Laboratory Intercomparison Quality Assurance Report compares the results of two Performance Evaluation (PE) studies that were conducted for the Air Toxics Pilot studies. Blind ambient air toxics samples were sent to 10 laboratories that participated in the CY01 Air Toxics Pilot Study. The laboratories analyzed the samples and forwarded their results to EPA. EPA Air Toxics QA Manager statistically analyzed the results and provided comments and suggestions for the improvements for a national air toxics program.

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