Outline

- An Effective QA Program

- The NATTS Program QA Indicators
  - Evolution of the NATTS Program and Compounds
  - Data Quality Objectives
  - Measurement Quality Objectives

- Meeting our Stated Objectives
  - Precision
  - Bias
  - Completeness
  - Detectability

- Other Effectiveness Indicators
- Proficiency Testing (PT) Expansion
- Summary/Recommendations
Presentation Objective

For a QA Program to be effective it must:

- Meet the stated objectives;
- Successfully implement quality improvements;
- Identify method issues or problems;
- Be cost effective, and;
- Deliver this information in a timely manner!
**Evolution of the NATTS Compound List**

<table>
<thead>
<tr>
<th>UATS</th>
<th>Concept Paper</th>
<th>NATA</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>“Dirty Thirty”</strong></td>
<td><strong>“Core 18”</strong></td>
<td><strong>“6 NATTS”</strong></td>
</tr>
<tr>
<td>acrylonitrile, benzene, 1,3-butadiene, carbon tetrachloride, chloroform, 1,2 dibromomethane, 1,3-dichloropropene, 1,2-dichloropropane, ethylene dichloride, ethylene oxide, dichloromethane, tetrachloroethane, tetrachloroethylene, vinyl chloride, arsenic, beryllium, cadmium, chromium, lead, mercury, manganese, nickel, acetaldehyde, formaldehyde acrolein, 2,2,7,8 tetrachlorobenzo-p-dioxin, coke oven emissions, hexachlorobenzene, hydrazine, polycyclic organic matter, polychloronated biphenyls, quinoline</td>
<td>benzene, 1,3-butadiene, carbon tetrachloride, chloroform, 1,2-dichloropropene, dichloromethane, tetrachloroethylene, vinyl chloride, arsenic, beryllium, cadmium, chromium, lead, mercury, manganese, nickel, formaldehyde, acetaldehyde, acrolein</td>
<td>benzene, acrolein, 1,3 butadiene, arsenic, formaldehyde, hexavalent chromium</td>
</tr>
</tbody>
</table>

**CAA 1990**

188 HAPs

Blue – EPA method

Black – no EPA method
NATTS Sites - 2006

• Urban Sites
  - E. Providence, RI
  - Boston (Roxbury), MA
  - New York, NY
  - Rochester, NY
  - Washington, DC
  - Decatur, GA
  - Tampa, FL
  - Detroit, MI
  - Chicago, IL
  - Houston (Deer Park), TX
  - St. Louis, MO
  - Bountiful, UT
  - San Jose, CA
  - Phoenix, AZ
  - Seattle WA

• Rural Sites
  - Underhill, VT
  - Hazard, KY
  - Chesterfield, SC
  - Mayville, WI
  - Grand Junction, CO
  - La Grande, OR
  - Harrison County, TX

Urban Sites

Rural Sites

Map of the United States showing locations of NATTS Sites in 2006.
NATTS QA Objective

Data Quality Objectives (DQOs) are tied to the GPRA goal of reduction of Air Toxics by 75% (1993 levels) by 2010:

“To be able to detect a 15% difference (trend) between two successive 3-year annual mean concentrations within acceptable levels of decision error.”

To meet these DQOs we need:

- 1-in-6 day sampling frequency with at least an 85% quarterly completeness;
- precision controlled to a Coefficient of Variance (CV) of no more than 15%;
- detectability based on 2001 Pilot Study Minimum Detection Limits (MDLs);
- bias for the data set of less than 25%.

These are our Measurement Quality Objectives (MQOs)!
DQOs and Parameters

- Initially, six compounds had DQOs calculated
  - benzene, 1,3-butadiene: VOCs
  - formaldehyde, acrolein: Aldehydes
  - arsenic, chromium: Metals
    - chromium was replaced with hexavalent chromium;
    - acrolein – issues with method - new method developed;
  - Bottom line: There are now 4 compounds with DQOs
    - Chromium and acrolein DQOs are not valid!
### NATTS QA Program

#### Measurement Quality Objectives (MQOs)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Precision (CV)</th>
<th>Bias (Lab)</th>
<th>Detectability</th>
<th>Completeness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>&lt; 15%</td>
<td>&lt; 25%</td>
<td>0.046 ng/m³</td>
<td>&gt; 85%</td>
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<tr>
<td>Benzene</td>
<td>&lt; 15%</td>
<td>&lt; 25%</td>
<td>0.044 ug/m³</td>
<td>&gt; 85%</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>&lt; 15%</td>
<td>&lt; 25%</td>
<td>0.020 ug/m³</td>
<td>&gt; 85%</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>&lt; 15%</td>
<td>&lt; 25%</td>
<td>0.014 ug/m³</td>
<td>&gt; 85%</td>
</tr>
</tbody>
</table>
Meeting Objectives: Precision Results 2004 - 2006

NATTS DQO Compounds - Precision

% CV

Benzene
1,3 Butadiene
Formaldehyde
Arsenic

Three Year Average:
Benzene: 18%
1,3 Butadiene 12%
Formaldehyde: 10%
Arsenic: 12%

No. of collocated sites

<table>
<thead>
<tr>
<th></th>
<th>'04</th>
<th>'05</th>
<th>'06</th>
</tr>
</thead>
<tbody>
<tr>
<td>vocs</td>
<td>7</td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td>aldehydes</td>
<td>5</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>metals</td>
<td>1</td>
<td>2</td>
<td>8</td>
</tr>
</tbody>
</table>
Meeting Objectives: Bias from PT Analysis

NATTS Bias Comparison 2004-2006 All Data

- acetaldehyde
- formaldehyde
- Carbonyl Mean
- Benzene
- 1,3 Butadiene
- PERC
- 1122TCE
- Vinyl Chloride
- TCE
- Chloroform
- Carb Tet
- VOC Mean
- Arsenic
- Benzo(a)pyrene
- Cadmium
- Manganese
- Nickel
- Lead
- Metals Mean
Meeting Objectives: Data Completeness 2004 – 2006

- Benzene
- 1,3 Butadiene
- Formaldehyde
- Arsenic
Meeting Objectives: Mean MDLs 2004 - 2006

MDLs '04 - 06 DQOs and RBCs

Benzene 1,3 BD Formaldehyde Arsenic

ug/m³/(ng/m³ for Arsenic)

Mean MDL 2004
DQO MDL
RBC 1/10-6
Mean MDL 2005
Mean MDL 2006
Identifying Problems: MDLs Reported 2006 VOCs/Carbonyls
Identifying Problems: DQO compounds 2004 – 2006

DQO Compounds - Method Detection Limits

- Benzene
- 1,3 Butadiene
- Formaldehyde
- Arsenic

Years:
- 2004
- 2005
- 2006

(ug/m3 - ng/m3)
Identifying Problems: Technical System Audits

• All stations and most labs audited (DRI, Reno Nevada still to be audited)

• Most common problems found:
  • QAPPs and SOPs needing to be updated;
  • No system in place for QAPP/SOP review and updating;
  • Field Blanks were not collected at a number of sites.

• Overall, the most labs are doing an excellent job!
Identifying Problems: Acrolein by DNPH - 3rd Qtr ‘04
Identifying Problems: Acrolein TO-15 3rd Qtr 07
Quality Improvement: Averages by Quarter - Metal PTs

Mean of % Differences - Metals

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Changed Filter medium from Teflon to Quartz

Decreased concentration from 6 ng/filter to 3 ng/filter
Quality Improvement: VOCS

Study Number: 200601-V

- Target Value = 4.55 ppbv
- Mean = 4.57 ppbv (0.5 %)
- Median 4.65 ppbv (2.2 %)
- STD = 0.405 ppbv (8.9 %)

Study Number: 200602-V

- Target Value = 0.7 ppbv
- Mean = 0.62 ppbv (-12.1 %)
- Median 0.60 ppbv (-13.7 %)
- STD = 0.20 ppbv (28.4 %)
Quality Improvements: Metals

Target Value = 6.73 ng/filter
Mean = 15.1 ng/filter (223.6 %)
Median 6.9 ng/filter (2.7 %)
STD = 45.7 ng/filter (679.0 %)

Target Value = 2.51 ng/filter
Mean = 2.42 ng/filter (-3.6 %)
Median 2.40 ng/filter (-4.4 %)
STD = 0.31 ng/filter (12.1 %)
QA Program Cost Effectiveness

<table>
<thead>
<tr>
<th>Year</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of NATTS Funds</td>
<td>14%</td>
<td>10%</td>
<td>9%</td>
</tr>
</tbody>
</table>

QA Support Contract Costs

- TSAs/QA Annual Report
- PT
- Total
PT Program and Expansion

- Shortly after PT program started, we began to get requests from Non-NATTS labs for PT samples;
- In 2006, we expanded the program to include Non-NATTS lab;
- The EPA Regional Labs (6) requested inclusion;
- The PT program is flexible, i.e., a non-NATTS lab can buy-in for any number of samples.
### PT Program Expansion: Number of Lab Participating

<table>
<thead>
<tr>
<th></th>
<th>Startup (2004)</th>
<th>Currently</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyls</td>
<td>17</td>
<td>24</td>
</tr>
<tr>
<td>Metals</td>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>VOC</td>
<td>15</td>
<td>29*</td>
</tr>
<tr>
<td>Total</td>
<td>47</td>
<td>72*</td>
</tr>
</tbody>
</table>

* Six of these labs are EPA Regional labs (Regions 1,3,4,5,6 and 9)

This is a 53% increase
All Voluntary!!
PT Program Expansion

There is an estimated 417 Air Toxics Stations in US (2006)

For 77% (322) of these sites, are supported by labs analyzing OAQPS PT Samples

Our goal, 100% of all Air Toxics labs analyzing PT samples.

- AT Stations using PT Program
- AT Station not using PT Program
Summary: Is the Program Able to Meet the DQOs?

Short Answer: Yes and No.

- The mean data completeness is below the required 85% for the 3rd year in a row, with the exception of the VOCs. Improvement has been seen in this area;

- The detectability for the 4 DQO compounds does not meet the MDLs stated in the DQOs, although there are improvement;

- The CV data from the collocated/duplicate data illustrates that we are meeting CV of less than 15% with the exception of Benzene;

- The laboratories are meeting the 25% Bias requirement.
Yes, the NATTS QA program is very successful:

- The QA program can detect problems and issues;
  - Acrolein by DNPH and TO-15 have issues
  - Extraction of metals from Teflon filters is a problem

- The QA program illustrates there has been improvements;
  - Improvements have been seen across the board

- The QA program has been shown to be cost effective;
  - Costs have gone down three years in a row

- PT program has undergone 53% growth!

- We understand the realistic quality of HAPS data!
Summary/Recommendations

- Recommend working NATTS agencies to report data in a more timely manner and increase data completeness;
- Recommend that we work together to get all Air Toxics labs analyzing PT samples at least once per year;
- Recommend we continues our task force to see how to lower MDLs.