National Air Toxics Trends Stations (NATTS) Methods Overview

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September 9, 2003

Presentation Outline

- 6 “Priority” and 18 “Core” Hazardous Air Pollutants (HAPs) for NATTS
- Methods used to measure these HAPs
- Method issues
- Status of research to address issues

Priority and Core HAPs

- 6 most important HAPs based on risk
  - Benzene
  - 1,3-Butadiene
  - Acrolein
  - Formaldehyde
  - Hexavalent Chromium: Cr (VI)
  - Arsenic
- 18 Additional core HAPs (subset of 33 UATS HAPs) requested if possible

Priority and Core HAPs

- **Volatile Organic Compounds (VOCs)**
  - ✓ **Benzene**
  - ✓ **1,3-Butadiene**
  - Carbon tetrachloride
  - Chloroform
  - 1,2-Dibromoethane
  - 1,3-Dichloropropane
  - 1,2-Dichloropropane
  - 1,2-Dichloroethane

- **VOCs (cont'd)**
  - Ethylene oxide
  - Methylene chloride
  - 1,1,2,2-Tetrachloroethane
  - Tetrachloroethylene
  - Trichloroethylene
  - Vinyl chloride

Priority and Core HAPs

- Metals
  - ✓ **Arsenic**
  - Beryllium
  - Cadmium
  - Total Chromium
  - ✓ **Cr (VI)**
  - Lead
  - Manganese
  - Nickel
- Carbonyls
  - Acetaldehyde
  - ✓ **Formaldehyde**
  - ✓ **Acrolein**

NATTS Methods

- **TO-15**, "Determination of VOCs in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)"
  - Whole air sample collection in SUMMA canisters with GC/MS analysis and moisture management
- **IO-3.1**, "Selection, Preparation and Extraction of Filter Material"
  - High volume sample collection on quartz filter media with acid filter extraction (TSP)
- **IO-3.5**, "Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)"

NATTS Methods

- **Adaptation of CARB Cr (VI) method**
  - Sodium bicarbonate impregnated cellulose filters with Ion Chromatography analysis
- **TO-11A**, "Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High-performance Liquid Chromatography (HPLC)“
  - Collection on dinitrophenylhydrazine (DNPH)-coated silica-gel sorbent with HPLC-UV analysis

Priority HAPs Method Issues

- Acrolein
  - Method stability and recovery
- Cr (VI)
  - Method sensitivity and background contamination
- 1,3-Butadiene
  - Method stability and sensitivity

Method Issues and Research

- Acrolein
  - TO-11a not suitable due to stability and poor recovery
  - ORD exploring dansylhydrazine (DNSH)-coated sorbent with HPLC-fluorescence
    - Finalized laboratory method
    - Plan to begin field studies in fall
    - Provide preliminary lab results at Methods Workshop October 7-9, 2003; Las Vegas

Method Issues and Research

- DNHS Acrolein Method Goals
  - Stability
    - Current stability on cartridge (stability defined as ratio of day x to day 0):
      - Below 0.9 after ~ 5 days when refrigerated
      - Below 0.9 after ~ 1 day at room temperature
    - Goal: Minimum on cartridge stability ratio of 0.9 at 10 days
  - Recovery
    - Current acrolein recovery ~ 60%
    - Goal: increase recovery to minimum of 85%

Method Issues and Research

- Hexavalent chromium
  - Method sensitivity: several observations <MDL
  - More data from additional sites needed to further characterize issue
  - Method research needed to improve sensitivity

Table 11.1. Sample sizes for hexavalent chromium and chromium TSP concentrations.

State	Pollutant	Observations Above MDL	Observations Below MDL w/ Values	Observations Below MDL w/ Missing Values
CA	HEXAVALENT CHROMIUM	17	159	2
CA	CHROMIUM TSP	56	0	119
MI	HEXAVALENT CHROMIUM	17	123	46
MI	CHROMIUM TSP	613	0	0

From LADCO/Battelle Draft Air Toxics Monitoring Data Analysis Report, July 3, 2003

Method Issues and Research

- **Hexavalent chromium**
  - Potential for background contamination and need to improve filter blank levels
  - Need more data at more locations to characterize extent of the issue

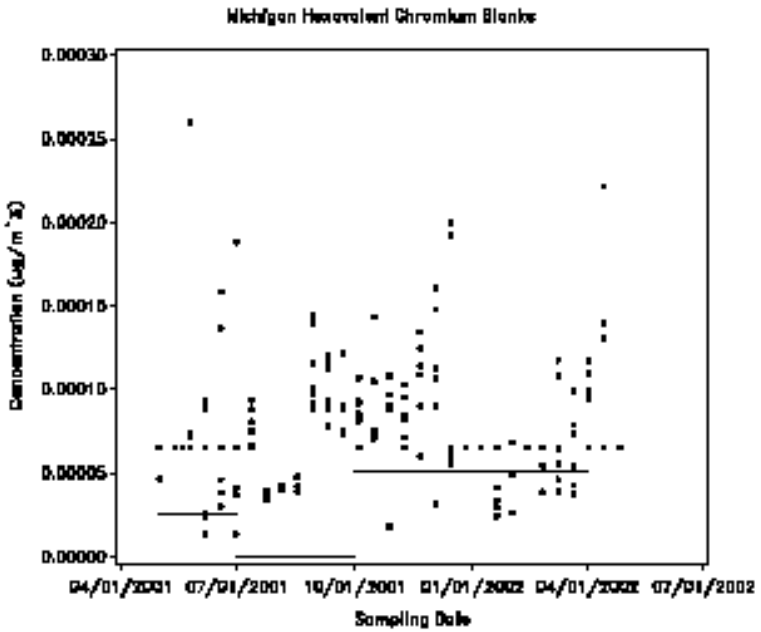

Figure 11.1. Plot of Michigan hexavalent chromium concentrations with quarterly blank averages (horizontal bars).

From LADCO/Battelle Draft Air Toxics Monitoring Data Analysis Report, July 3, 2003

Method Issues and Research

- 1,3-Butadiene
  - 31% of values below MDL and 28% not quantified

Table 5.1. Distribution of data by category for VOCs.

Observations--VOCs (Replicates Only)					
Pollutant	**Total**	**> LCL**	**MDL - LCL**	**< MDL**	**Not Quantified**
1,1,2,2-TETRACHLOROETHANE	628	0.0%	1.3%	3.5%	95.2%
1,2-DIBROMOETHANE	628	0.0%	1.4%	2.7%	95.9%
1,2-DICHLOROETHANE	628	0.0%	0.2%	13.4%	86.5%
1,2-DICHLOROPROPANE	628	0.0%	0.3%	4.5%	95.2%
1,3-BUTADIENE	778	8.7%	32.3%	31.1%	27.9%
ACRYLONITRILE	628	4.3%	13.5%	6.7%	75.5%
BENZENE	776	95.5%	3.5%	0.0%	1.0%
CARBON TETRACHLORIDE	628	19.7%	56.4%	21.5%	2.4%
CHLOROFORM	628	11.8%	16.9%	12.9%	58.4%
CIS 1,3-DICHLOROPROPENE	628	0.0%	0.3%	2.1%	97.6%
ETHYLENE OXIDE	80	18.8%	63.8%	17.5%	0.0%
METHYLENE CHLORIDE	628	46.3%	34.6%	12.4%	6.7%
TETRACHLOROETHYLENE	628	12.6%	16.6%	29.0%	41.9%
TRANS 1,3-DICHLOROPROPENE	628	0.0%	0.0%	2.2%	97.8%
TRICHLOROETHYLENE	628	7.6%	4.1%	11.1%	77.1%
VINYL CHLORIDE	628	0.0%	0.0%	4.9%	95.1%

From LADCO/Battelle Draft Air Toxics Monitoring Data Analysis Report, July 3, 2003

Summary

- 6 Priority HAPs to be measured
- Remaining 18 Core HAPs measurements *wanted*
- Method issues exist for 3 of 6 Priority HAPs
- Work currently in progress on Acrolein
  - Measurement with TO-11a not recommended
- More characterization needed for Cr (VI)
- Research needed by ORD to improve sensitivity and stability for 1,3-Butadiene
- Methods Workshop October 7-9; Las Vegas