How to Create a Successful Air Toxics Monitoring Project

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Agenda

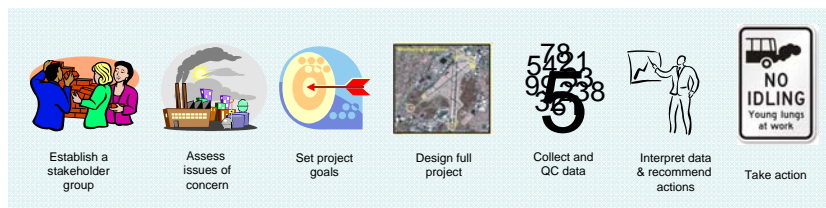| Schedule	Topic
10:00-10:15	Introductions
10:15-12:00	1. Overview of successful air toxics monitoring projects (45 min.) 2. Getting started/Setting project goals (30 min.) 3. Monitoring strategy and design (part 1, 30 min.)
12:00-1:00	Lunch (on your own)
1:00-3:00	3. Monitoring strategy and design (part 2, 60 min.) Discussion (30 min.) 4. Collect and QC data (30 min.)
3:00-3:15	Break
3:15-5:00	5. Data analysis and interpretation (50 min.) 6. Taking action (20 min.) 7. Summary (30 min.) Wrap up

Disclaimer

The information and procedures set forth here are intended as a technical resource to those planning to monitor for air toxics. This document does not constitute rulemaking by the Agency and cannot be relied on to create a substantive or procedural right enforceable by any party in litigation with the United States. As indicated by the use of non-mandatory language such as "may" and "should," it provides recommendations and does not impose any legally binding requirements. In the event of a conflict between the discussion in this document and any Federal statute or regulation, this document would not be controlling. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products. This is a living document and may be revised periodically.

The Environmental Protection Agency welcomes public input on this document at any time. Comments should be sent to Barbara Driscoll (driscoll.barbara@epa.gov).
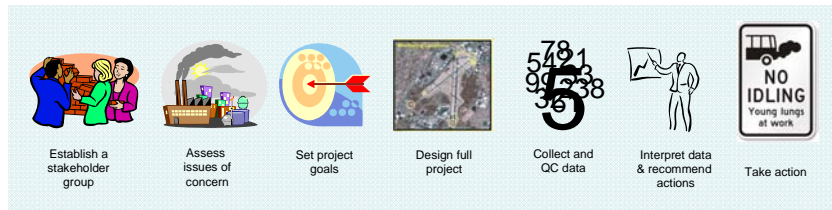

Overview of Air Toxics Monitoring Projects

- What makes a project successful?
- Introduction to air toxics
- Project topic areas
- What is already known about air toxics on a national and community scale?

| Establish a stakeholder group | Assess issues of concern | Set project goals | Design full project | Collect and QC data | Interpret data & recommend actions | Take action |

What Makes a Project Successful?

- Project's goals were met!
  - Well thought out
  - Thorough planning
  - Communication during the entire process

- Project resulted in action to reduce pollution or exposure.
  - Stakeholders engaged early
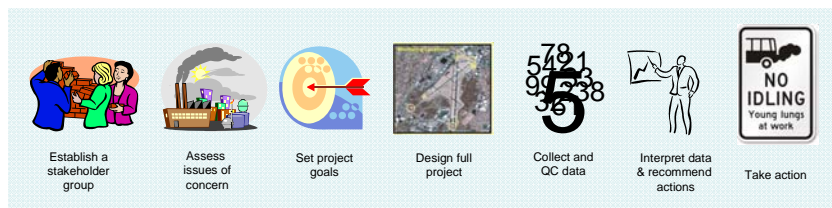 - Mitigation strategies built into the plan

| Establish a stakeholder group | Assess issues of concern | Set project goals | Design full project | Collect and QC data | Interpret data & recommend actions | Take action |

What Makes a Project Successful? (cont.)

- Characterizing local air toxics issues that are the same as or different from national-scale issues.
- Communicating results and disseminating information to all team members through all phases.

All steps in the process are important.

| Establish a stakeholder group | Assess issues of concern | Set project goals | Design full project | Collect and QC data | Interpret data & recommend actions | Take action |

What Makes a Project Successful? (cont.)

- Other successful project characteristics
  - Plan early and reassess often
  - Look at data quickly, adjust plans accordingly, and be flexible
  - Collect the data needed to answer your questions and meet your goals

What Are Air Toxics?

- The 1990 Clean Air Act defines 188 hazardous air pollutants (HAPs).
  - The terms "HAPs" and "air toxics" are used interchangeably.
- Air toxics are those pollutants known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects.
  - EPA is working with state, local, and Tribal governments to reduce the release of air toxics into the environment.

What Are the Health and Environmental Effects of Air Toxics?

Exposure to air toxics at sufficient concentrations and durations may increase a person's chance of health problems, including

- cancer
- damage to the immune system
- neurological damage
- developmental problems
- respiratory problems
- reproductive problems (e.g., reduced fertility)

Both high values and annual means of air toxics concentrations are of interest because some air toxics have both acute, short-term health effects and chronic, long-term health effects.

Some air toxics, such as mercury, can deposit onto soils or surface waters, where they are taken up by plants and ingested by animals—and eventually magnified up through the food chain.

U.S. Environmental Protection Agency (2007c, g)

How Are People Exposed to Air Toxics?

- **Breathing** contaminated air.
- **Eating** contaminated food products (e.g., fish from contaminated waters; meat, milk, or eggs from animals that feed on contaminated plants; and fruits and vegetables grown in contaminated soil).
- **Drinking** water contaminated by air toxics.
- **Ingesting** contaminated soil.
- **Touching** contaminated soil, dust, or water.
- **Accumulating** some persistent air toxics in body tissues after the air toxics have entered the body. As a result, people and other animals at the top of the food chain who eat contaminated fish or meat are exposed to concentrations that are much higher than the concentrations in the water, air, or soil.

U.S. Environmental Protection Agency (2007c, g)

Health Risks from Air Toxics

Simply put, health risks are a measure of the chance that you will experience health problems.

Health risk = Hazard x Exposure

- Health risk is the probability that exposure to a hazardous substance will make you sick.
- Exposure to toxic air pollutants can increase your health risks.
- Ambient concentrations of air toxics are compared to chronic exposure risk levels derived from scientific assessments conducted by the EPA and other environmental agencies.

U.S. Environmental Protection Agency (2007a, b)

What Are the Sources of Air Toxics?

Air toxics are both directly emitted by sources and formed in the atmosphere.

- **Major sources** include chemical plants, steel mills, oil refineries, and hazardous waste incinerators for which the inventory provides a specific location.

- **Area sources** are made up of many smaller sources releasing pollutants to the outdoor air in a defined area.

- **Mobile sources** include highway vehicles, trains, marine vessels, and non-road equipment (such as construction equipment).

- **Natural sources** – Some air toxics are released from natural sources such as volcanoes or fires; in the inventory, these would typically be included in area source emissions.

Some Air Toxics and Their Sources

Semivolatile organic compounds (SVOCs)
such as naphthalene (petroleum refining
and fossil fuel and wood combustion)

**Arsenic, mercury, chromium,
and lead compounds**
(e.g., metal processing operations)

Perchloroethylene
(emitted from some dry
cleaning facilities)

Benzene
(found in gasoline)

Methylene chloride
(solvent and paint stripper)

Air Toxics With Greatest Risks Nationally

Air Toxic	Sources
Acrolein	Mobile sources, combustion, open burning
Arsenic	Combustion, non-ferrous metal production, iron and steel, incineration, mobile sources
Benzene	Mobile sources, combustion, oil and gas production/distribution, petroleum refining/distribution
1,3-butadiene	Mobile sources, chemical manufacturing, petroleum refining/distribution
Chlorine	Primary magnesium refining, incineration, combustion
Chromium, hexavalent	Electroplating, non-ferrous metal production, iron and steel, mobile sources
Coke oven emissions	Iron and steel
Diesel exhaust	Mobile sources
Formaldehyde	Mobile sources, combustion, plywood, pulp and paper, oil and gas production/distribution
Hydrogen chloride	Combustion, incineration
Manganese	Iron and steel, non-ferrous metal production, combustion
Perchloroethylene	Dry cleaning, solvent use
Polycyclic organic matter (POM)	Mobile sources, open burning, combustion, incineration

From inhalation. Taken from Wayland, 2011
http://www.epa.gov/ttn/amtic/files/ambient/airtox/2011workshop/day2ChetWaylandAirToxicsStrategy.pdf

Emissions Source Type Characteristics

Understand emission source types of air toxics to help develop a conceptual model of concentration patterns and gradients that might be expected.

- **Major source emissions**, for example, are a localized source of toxics and may show steep concentration gradients.
- **Area source emissions** are typically well-distributed emissions sources because there are multiple sources in an area.
- **Mobile source air toxics** exhibit both point source and area source characteristics.

Physical Properties

- Physical properties of air toxics span the entire range of pollutants present in the atmosphere
  - As particles and gases and in semi-volatile form
  - As both primary (directly emitted) and secondary (formed in the atmosphere) pollutants
  - From mostly anthropogenic sources, but include some biogenic sources
  - Have a wide range of atmospheric lifetimes
- Some air toxics such as volatile organic compounds (VOCs, e.g., benzene and toluene) are precursors to ozone and particulate matter (PM); and other toxics (such as heavy metals) are components of PM.

Formation, Destruction, Transport

Conceptual depiction of transport scales

While some pollutants can be neatly characterized as contributors to local, regional, or global problems, many pollutants are important on multiple spatial scales.
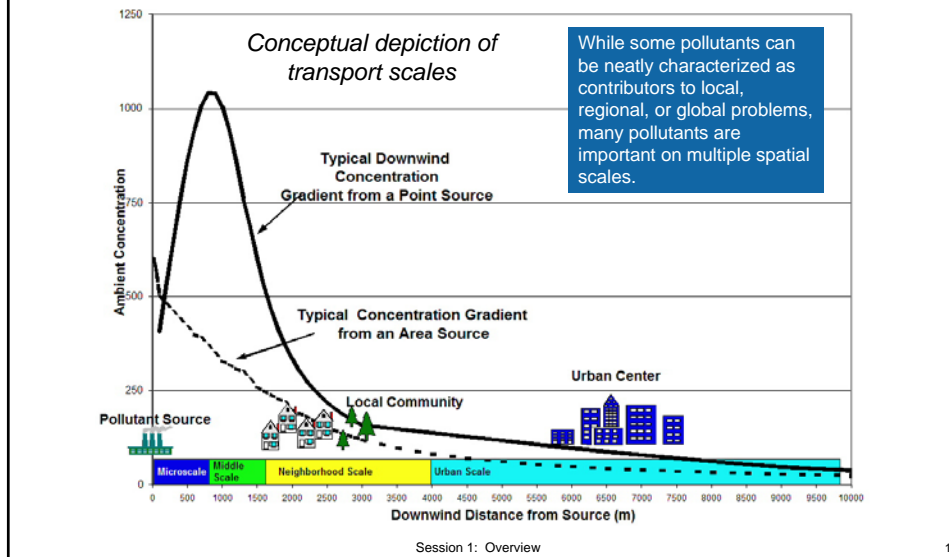
Formation, Destruction, Transport (cont.)

- Concentrations of pollutants that are secondarily formed in the atmosphere
  - are often highest downwind of the source of precursor compounds
  - generally do not have steep concentration gradients near the original precursor emissions source
- Transport distance is determined by
  - atmospheric chemistry (pollutant lifetimes and formation and removal processes)
  - meteorology (air mass movement and precipitation)
  - topography (mountains and valleys that affect air movement)
- Short-lived pollutants can travel only short distances from where they are emitted. Longer-lived pollutants can travel large distances from where they are formed or emitted (e.g., toxic metals in $PM_{2.5}$) and may be more regionally homogenous.
- Some unreactive pollutants can remain in the atmosphere for months, years, or decades and spread across the Earth (e.g., carbon tetrachloride).

Residence Time

- Residence time is a pollutant-specific measure of the average lifetime of a molecule in the atmosphere.
- It is dependent on chemical and physical removal pathways that include
  - *Chemical:* reaction with hydroxyl radical (OH), photolysis
  - *Physical:* wet or dry deposition
- Why is it important to understand residence times?
  - Residence times can provide insight into the spatial and temporal variability of air toxics.
  - Longer residence times result in less spatial variability (e.g., carbon tetrachloride).
  - Conversely, short residence times should result in steep gradients in concentrations near sources and temporal patterns that are dependent on emissions schedules.
- Residence times are not characterized well for all air toxics.

Key Things You Need to Know About Air Toxics

- EPA has sponsored many phases of national level investigations of air toxics.

- There have also been many community-scale air toxics projects.

- Many summaries of results are available: http://www.epa.gov/ttn/amtic/airtoxpg.html

So, what is already known about air toxics at the national and community scale?

Measuring Air Toxics Is Expensive and Complicated

Compared to criteria pollutants:

- Fewer samples achieved (60 vs. 8,400)
- More capital costs ($25,000 vs. $15,000)
- Recurring annual costs ($20,000 vs. $2,000)
- More species (30 vs. 1)
- QA/QC more expensive, complicated, and time-consuming
- Multiple methods needed to capture VOCs, polycyclic aromatic hydrocarbons (PAHs), metals, and carbonyls (FRM vs. TO-3, 11, 14, 15, etc.)
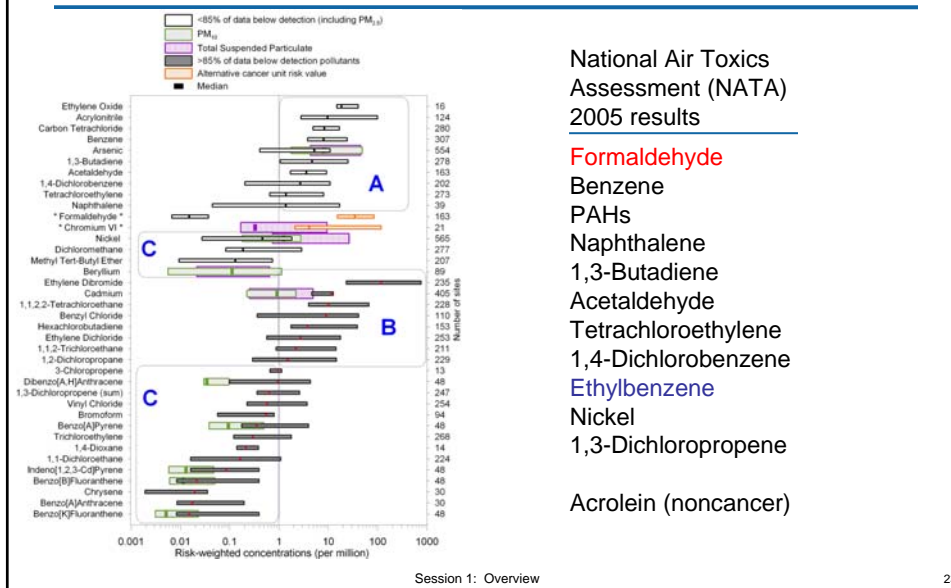

Most Air Toxics Aren't Monitored Routinely

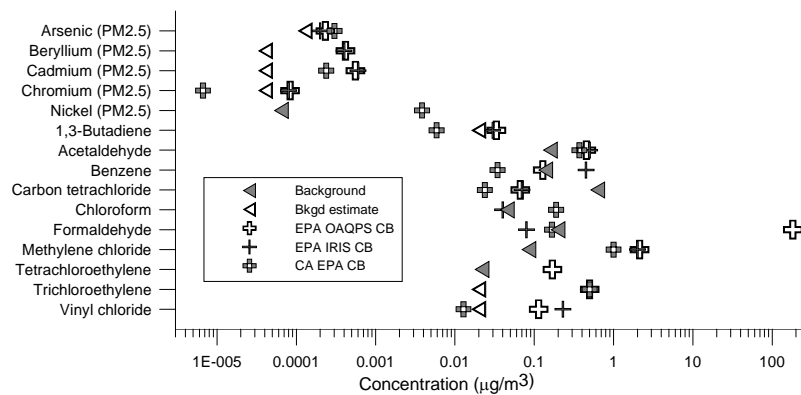|					
1,1,2,2-Tetrachloroethane	**Cobalt (Tsp)**	**Vinyl Chloride**	Mercury (Pm10) Stp	*Acrylamide*	*Hydrochloric acid*
1,1,2-Trichloroethane	**Cobalt Pm2.5 Lc**	1,2-Dibromo-3-Chloropropane	Mercury (Vapor)	*Acrylic acid*	*Hydrogen fluoride*
1,1-Dichloroethane	**Dichloromethane**	1,3-Dichloropropene(Total)	Mercury Pm10 Lc	*Asbestos*	*Hydrogen sulfide*
1,1-Dichloroethylene	**Ethyl Acrylate**	1,4-Dioxane	Methanol	*Benzidine*	*Hydroquinone*
1,2,4-Trichlorobenzene	**Ethylbenzene**	2,4,5-Trichlorophenol	Methoxychlor	*Benzotrichloride*	*Maleic anhydride*
1,2-Dichloropropane	**Ethylene Dibromide**	2,4,6-Trichlorophenol	M-Xylene	*beta-Propiolactone*	*m-Cresol*
1,3-Butadiene	**Ethylene Dichloride**	2,4-Dinitrophenol	Nickel (Coarse Particulate)	*Bis(chloromethyl)ether*	*Methyl hydrazine*
1,4-Dichlorobenzene	**Formaldehyde**	2,4-Dinitrotoluene	Nickel Pm10 Lc	*Calcium cyanamide*	*Methyl iodide (Iodomethane)*
2,2,4-Trimethylpentane	**Hexachlorobutadiene**	3-Chloropropene	Nitrobenzene	*Captan*	*Methyl isocyanate*
Acetaldehyde	**Isopropylbenzene**	4,6-Dinitro-2-Methylphenol	O-Cresol	*Carbaryl*	*Methylene diphenyl diisocyanate*
Acetonitrile	**Lead (Pm10) Stp**	4-Nitrophenol	P-Cresol	*Carbonyl sulfide*	*N,N-Diethyl aniline*
Acrolein	**Lead (Tsp)**	Aniline	Pentachlorophenol	*Catechol*	*N-Nitrosodimethylamine*
Acrylonitrile	**Lead Pm2.5 Lc**	Antimony (Pm10) Stp	Phenol	*Chloramben*	*N-Nitrosomorpholine*
Antimony (Tsp)	**M/P-Xylene**	Antimony Pm10 Lc	Phosphorus (Tsp)	*Chlordane*	*N-Nitroso-N-methylurea*
Antimony Pm2.5 Lc	**Manganese (Pm10) Stp**	Arsenic Pm10 Lc	Phosphorus Pm10 Lc	*Chloroacetic acid*	*o-Anisidine*
Arsenic (Pm10) Stp	**Manganese (Tsp)**	Beryllium Pm10 Lc	P-Xylene	*Chlorobenzilate*	*o-Toluidine*
Arsenic (Tsp)	**Manganese Pm2.5 Lc**	Biphenyl	Selenium Pm10 Lc	*Chloromethyl methyl ether*	*Parathion*
Arsenic Pm2.5 Lc	**Mercury (Tsp)**	Bis (2-Chloroethyl)Ether	Xylene(S)	*Coke Oven Emissions*	*Pentachloronitrobenzene*
Benzene	**Mercury Pm2.5 Lc**	Bis(2-Ethylhexyl)Phthalate	*1,1-Dimethyl hydrazine*	*Cresols/Cresylic acid*	*Phosgene*
Benzyl Chloride	**Methyl Chloroform**	Cadmium Pm10 Lc	*1,2-Diphenylhydrazine*	*Cyanide Compounds*	*Phosphine*
Beryllium (Pm10) Stp	**Methyl Isobutyl Ketone**	Caprolactam	*1,2-Epoxybutane*	*DDE*	*Phthalic anhydride*
Beryllium (Tsp)	**Methyl Methacrylate**	Chlorine (Tsp)	*1,2-Propylenimine*	*Diazomethane*	*Polychlorinated biphenyls*
Bromoform	**Methyl Tert-Butyl Ether**	Chlorine Pm10 Lc	*1,3-Propane sultone*	*Dichlorvos*	*Polycyclic Organic Matter*
Bromomethane	**Naphthalene**	Chromium (Coarse Particulate)	*2,3,7,8-Tetrachlorodibenzo-p-dioxin*	*Diethanolamine*	*p-Phenylenediamine*
Cadmium (Pm10) Stp	**N-Hexane**	Chromium Pm10 Lc	*2,4-D, salts and esters*	*Diethyl sulfate*	*Propoxur (Baygon)*
Cadmium (Tsp)	**Nickel (Pm10) Stp**	Cobalt Pm10 Lc	*2,4-Toluene diamine*	*Dimethyl aminoazobenzene*	*Propylene oxide*
Cadmium Pm2.5 Lc	**Nickel (Tsp)**	Dibenzofurans	*2,4-Toluene diisocyanate*	*Dimethyl carbamoyl chloride*	*Quinoline*
Carbon Disulfide	**Nickel Pm2.5 Lc**	Dimethyl Phthalate	*2-Acetylaminofluorene*	*Dimethyl formamide*	*Quinone*
Carbon Tetrachloride	**O-Xylene**	Di-N-Butyl Phthalate	*2-Chloroacetophenone*	*Dimethyl sulfate*	*Radionuclides (including radon)*
Chlorine Pm2.5 Lc	**Phosphorus Pm2.5 Lc**	Ethylene Oxide	*2-Nitropropane*	*Epichlorohydrin*	*Styrene oxide*
Chlorobenzene	**Propionaldehyde**	Heptachlor	*3,3-Dichlorobenzidene*	*Ethyl carbamate (Urethane)*	*Titanium tetrachloride*
Chloroethane	**Selenium (Pm10) Stp**	Hexachlorobenzene	*3,3-Dimethoxybenzidine*	*Ethylene glycol*	*Toxaphene*
Chloroform	**Selenium (Tsp)**	Hexachlorocyclopentadiene	*3,3'-Dimethyl benzidine*	*Ethylene imine (Aziridine)*	*Triethylamine*
Chloromethane	**Selenium Pm2.5 Lc**	Hexachloroethane	*4,4-Methylene bis(2-chloroaniline)*	*Ethylene thiourea*	*Trifluralin*
Chloroprene	**Styrene**	Isophorone	*4,4-Methylenedianiline*	*Fine mineral fibers*	*Vinyl bromide*
Chromium (Pm10) Stp	**Tetrachloroethylene**	Lead Pm10 Lc	*4-Aminobiphenyl*	*Glycol ethers*	
Chromium (Tsp)	**Toluene**	Lindane	*4-Nitrobiphenyl*	*Hexamethylene-1,6-diisocyanate*	
Chromium Pm2.5 Lc	**Trichloroethylene**	Manganese (Coarse Particulate)	*Acetamide*	*Hexamethylphosphoramide*	
Cobalt (Pm10) Stp	**Vinyl Acetate**	Manganese Pm10 Lc	*Acetophenone*	*Hydrazine*	

Abundance of data: > 20 monitoring sites with sufficient data to create a valid annual average between 2003-2005, up to 434 sites
Little data: < 20 monitoring sites with sufficient data to create a valid annual average between 2003-2005, between 1-17 sites
No Data: No valid annual averages between 2003 and 2005

From: http://www.epa.gov/ttn/atw/188polls.html

Air Toxics of Most Concern Nationally

National Air Toxics
Assessment (NATA)
2005 results

Formaldehyde
Benzene
PAHs
Naphthalene
1,3-Butadiene
Acetaldehyde
Tetrachloroethylene
1,4-Dichlorobenzene
Ethylbenzene
Nickel
1,3-Dichloropropene
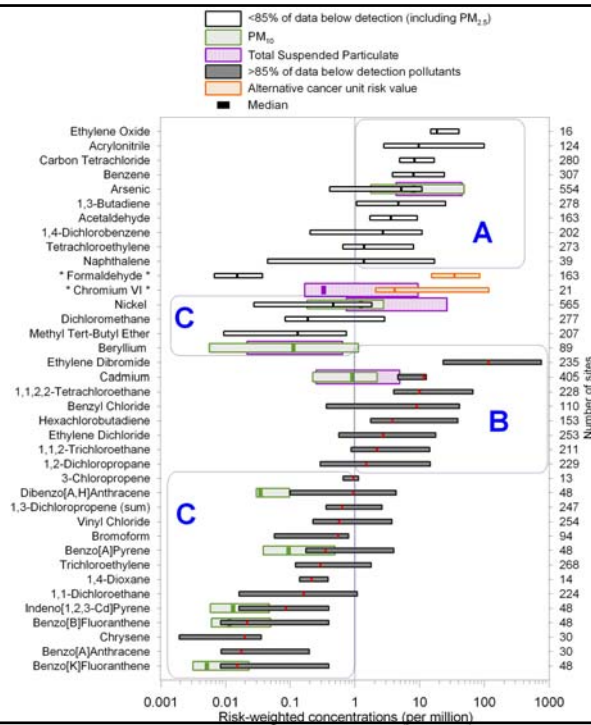
Acrolein (noncancer)

Background Levels Can Be Above Levels of Concern (e.g., Benzene, Carbon Tetrachloride)
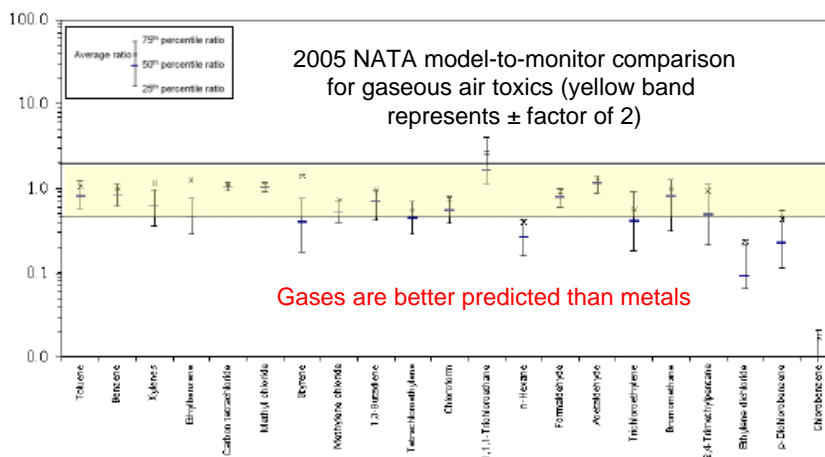

Background concentrations (filled triangles) and estimated upper-limits (open triangles) compared to 10^{-6} cancer benchmark (CB) concentrations from EPA OAQPS, EPA IRIS, and California EPA (McCarthy et al., 2006).

Slide 1

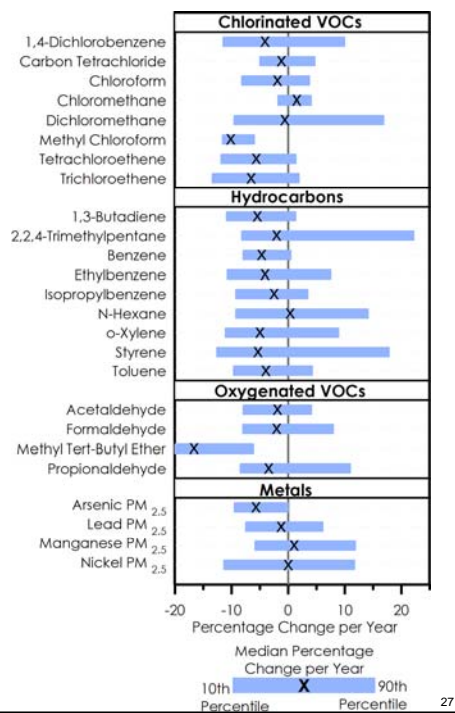Monitoring Methods Often Have MDLs Too High to Characterize Risk

Legend:
- <85% of data below detection (including $PM_{2.5}$)
- PM_{10}
- Total Suspended Particulate
- >85% of data below detection pollutants
- Alternative cancer unit risk value
- Median

Pollutant	Number of sites
Ethylene Oxide	16
Acrylonitrile	124
Carbon Tetrachloride	280
Benzene	307
Arsenic	554
1,3-Butadiene	163
Acetaldehyde	163
1,4-Dichlorobenzene	202
Tetrachloroethylene	273
Naphthalene	39
* Formaldehyde *	163
* Chromium VI *	21
Nickel	565
Dichloromethane	277
Methyl Tert-Butyl Ether	207
Beryllium	89
Ethylene Dibromide	235
Cadmium	405
1,1,2,2-Tetrachloroethane	228
Benzyl Chloride	110
Hexachlorobutadiene	153
Ethylene Dichloride	253
1,1,2-Trichloroethane	211
1,2-Dichloropropane	229
3-Chloropropene	13
Dibenzo[A,H]Anthracene	48
1,3-Dichloropropene (sum)	247
Vinyl Chloride	254
Bromoform	94
Benzo[A]Pyrene	48
Trichloroethylene	268
1,4-Dioxane	14
1,1-Dichloroethane	224
Indeno[1,2,3-Cd]Pyrene	48
Benzo[B]Fluoranthene	48
Chrysene	30
Benzo[A]Anthracene	30
Benzo[K]Fluoranthene	48

Regions labeled A, B, C

X-axis: Risk-weighted concentrations (per million) — 0.001, 0.01, 0.1, 1, 10, 100, 1000

McCarthy et al. (2007)

Slide 2

Models (NATA 2005) Show Favorable Comparison to Monitoring Data

Legend:
- Average ratio
- 75th percentile ratio
- 50th percentile ratio
- 25th percentile ratio

2005 NATA model-to-monitor comparison for gaseous air toxics (yellow band represents ± factor of 2)

Gases are better predicted than metals

Y-axis: 0.0, 0.1, 1.0, 10.0, 100.0

X-axis labels: Toluene, Benzene, Xylenes, Ethylbenzene, Carbon tetrachloride, Methyl chloride, Styrene, Methylene chloride, 1,3-Butadiene, Tetrachloroethylene, Chloroform, 1,1,1-Trichloroethane, n-Hexane, Formaldehyde, Acetaldehyde, Trichloroethylene, Bromomethane, 2,2,4-Trimethylpentane, Ethylene dichloride, o-Dichlorobenzene, Chlorobenzene

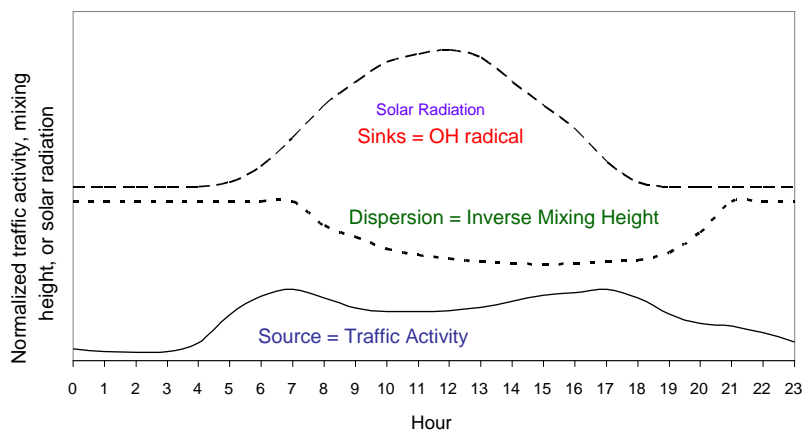Model-to-Monitor Comparisons of Gaseous HAPs (>100 Monitors)

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Many Air Toxics Concentrations Are Declining over Time
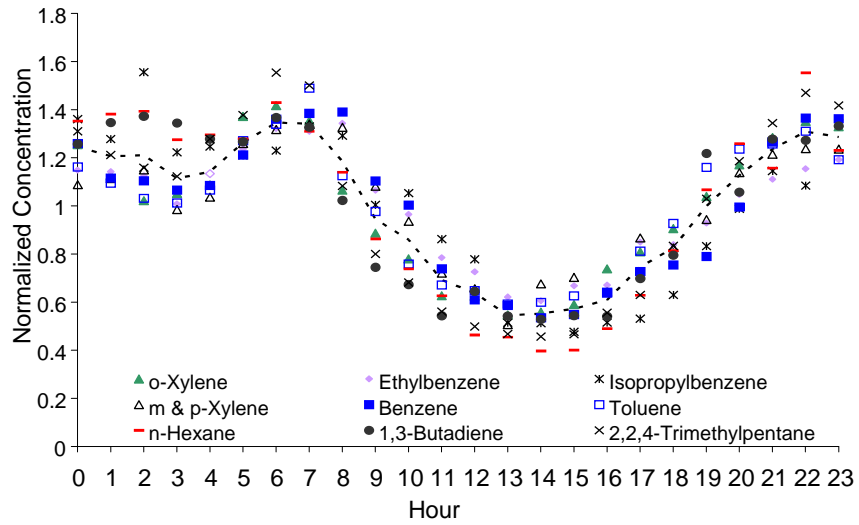

Temporal Variability Can Be Used to Identify Likely Emissions Sources

Concentrations = (Sources − Sinks + Transport)/Dispersion

Solar Radiation
Sinks = OH radical

Dispersion = Inverse Mixing Height

Source = Traffic Activity

Normalized traffic activity, mixing height, or solar radiation

Hour

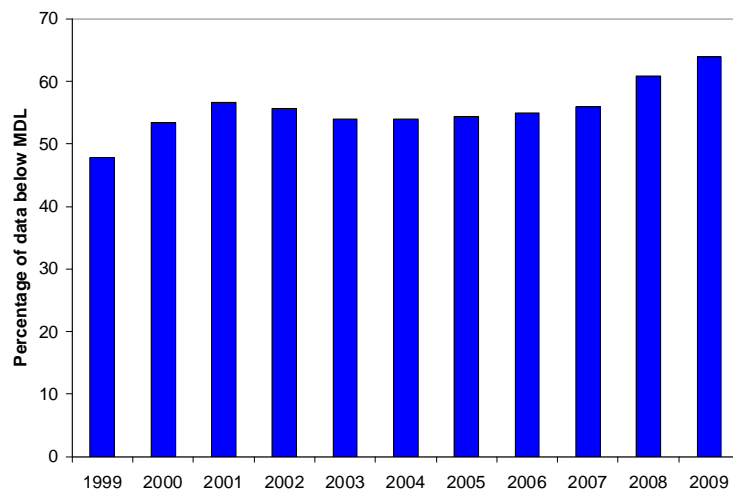**Temporal Variability Can Be Used to Identify Likely Emissions Sources** (cont.)

Most Air Toxics Concentrations Are Below MDLs

Key Things You Need to Know About Air Toxics

- EPA has sponsored many phases of national level investigations of air toxics.
- There have also been many community-scale air toxics projects.
- Many summaries of results are available: http://www.epa.gov/ttn/amtic/airtoxpg.html

> So, what is already known about air toxics at the national and community scale?

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3:15-5:00	5. Data analysis and interpretation (50 min.) 6. Taking action (20 min.) 7. Summary (30 min.) Wrap up