

# Background

What are air toxics and why are they important?

# Background

## *What's Covered in This Section?*

- Air toxics overview
- Health risks from air toxics; terminology
- Air toxics emissions
- Physical properties
- Formation, destruction, and transport of air toxics
- History of sampling; objectives of air toxics and other monitoring programs
- Air toxics sampling and analysis
- Critical issues for data interpretation

# Air Toxics

## Overview

- **What are air toxics?**
  - Air toxics are gaseous, aerosol, or particle pollutants present in the air in varying concentrations with characteristics such as toxicity or persistence that can be hazardous to human, plant, or animal life.
  - The terms “air toxics” and “hazardous air pollutants” (HAPs) are used interchangeably in this document.
  - Air toxics include the following general categories of compounds: volatile and semi-volatile organic compounds (VOCs, SVOCs), polycyclic aromatic hydrocarbons (PAHs), heavy metals, and carbonyl compounds.
- **What are the health and environmental effects of toxic air pollutants?**
  - People exposed to toxic air pollutants at sufficient concentrations and durations may have an increased chance of getting cancer or experiencing other serious health effects.
  - Both high values and annual means of air toxics concentrations are of interest because some air toxics have both episodic, short-term health effects and chronic, long-term health effects.
  - Other health effects can include damage to the immune system, as well as neurological, reproductive (e.g., reduced fertility), developmental, respiratory, and other health problems.
  - Some toxic air pollutants, such as mercury, can deposit onto soils or surface waters where they are taken up by plants and ingested by animals and are eventually magnified up through the food chain.
  - Animals may experience health problems if exposed to sufficient quantities of air toxics over time.
- **How are people exposed to air toxics?**
  - Breathing contaminated air.
  - Eating contaminated food products, such as fish from contaminated waters; meat, milk, or eggs from animals that feed on contaminated plants; and fruits and vegetables grown in contaminated soil on which air toxics have been deposited.
  - Drinking water contaminated by toxic air pollutants.
  - Ingesting contaminated soil.
  - Touching contaminated soil, dust, or water.
  - Accumulating some persistent toxic air pollutants in body tissues after toxic air pollutants have entered the body. Predators typically accumulate even greater pollutant concentrations than their contaminated prey. 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.

# 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. Animal experiments and human studies provide information about a substance's level of hazard. Scientists use the results of such studies to estimate the likelihood of illness at different levels of exposure.
- Exposure to toxic air pollutants can increase your health risks. For example, if you live near a factory that releases cancer-causing chemicals and inhale contaminated air, your risk of getting cancer may increase. Breathing air toxics could also increase your risk of noncancer effects such as emphysema, asthma, or reproductive disorders.
- Ambient concentrations of air toxics are compared to health related concentrations derived from scientific assessments conducted by the EPA and other environmental agencies. These levels of concern provide a frame of reference to put air toxics concentrations into perspective.



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

# Air Toxics Emissions

## *What Are the Sources of Air Toxics?*

- Air toxics are both directly emitted by sources and formed in the atmosphere. In emission inventory terminology, emissions are grouped as point (major), area, and mobile sources. The following 3 definitions describe how these terms are used in the emission inventory.
- **Major sources** include chemical plants, steel mills, oil refineries, and hazardous waste incinerators for which there is a specific location provided in the inventory. Pollutants can be released when equipment leaks, when material is transferred from one area to another, or when waste is given off from a facility through smoke stacks.
- **Area sources** are made up of many smaller sources releasing pollutants to the outdoor air in a defined area. Examples include neighborhood dry cleaners, small metal plating operations, gas stations, and woodstoves. These sources may not be identified in the inventory by a specific location.
- **Mobile sources** include highway vehicles, trains, marine vessels, aircraft, and non-road equipment (such as construction equipment).
- Routine releases, such as those from industry, cars, landfills, or incinerators, may follow regular patterns and happen continuously over time. Other releases may be routine but intermittent, such as when a plant's production is performed in batches. Accidental releases can occur during an explosion, equipment failure, or a transportation accident. The timing and amount released during accidental releases are difficult to estimate.
- Natural sources – Some air toxics are also released from natural sources such as volcanoes or fires, typically in the inventory these would be included in area source emissions.



# Air Toxics Emissions

## *Source Type Characteristics*

Understanding the emission source type of a particular air toxic can help the analyst begin to develop a conceptual model of concentration patterns and gradients that might be expected.

- Major source emissions, for example, are a localized source of toxics. Steep concentration gradients of primarily emitted toxics around point sources are typical, especially if there are no other nearby sources of the pollutants.
- Area source emissions are typically well-distributed emissions sources because there are multiple sources in an area. Area source emissions can lead to relatively homogeneous concentrations of toxics on the urban scale. However, if a monitor is placed close to any source type, gradients may be observed.
- Mobile source air toxics exhibit both point source and area source characteristics. Very close to a roadway or near a construction site, mobile source air toxics may be seen in higher concentrations. A few hundred meters away from the roadway, for example, concentrations typically fall to more normal average urban-scale levels.

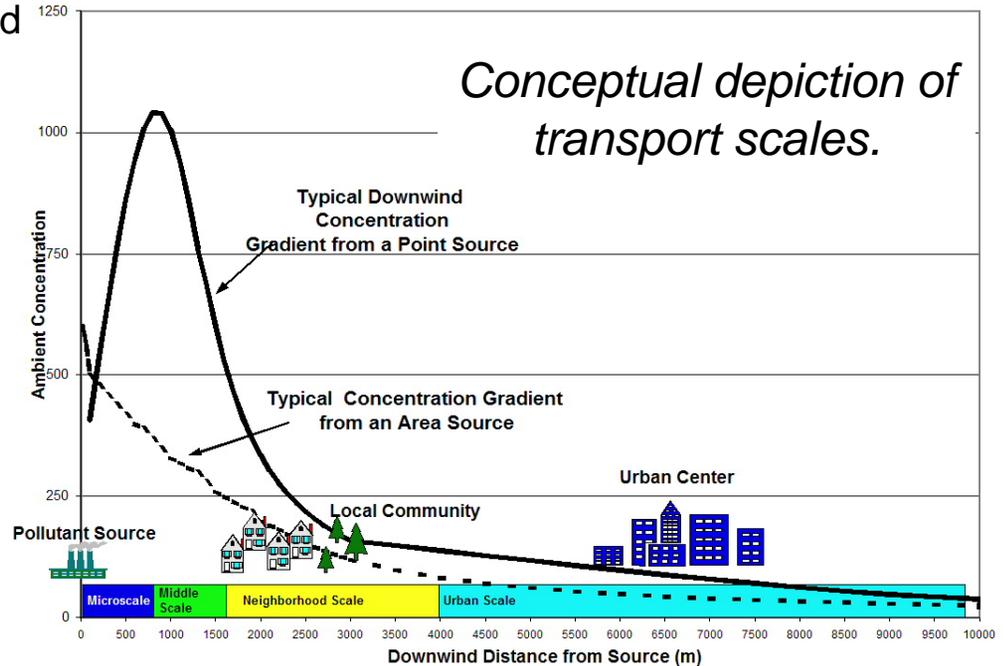


# Physical Properties

- Physical properties of air toxics span the entire range of pollutants present in the atmosphere.
  - Air toxics are present in the atmosphere as particles and gases and in semi-volatile form.
  - Air toxics can be both primary (directly emitted) and secondary (formed in the atmosphere) in origin.
  - Air toxics are mostly emitted from anthropogenic sources, but include some biogenic sources.
  - Some air toxics have very short atmospheric lifetimes while others remain in the atmosphere for decades.
- Some air toxics such as 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.
- Preliminary investigation of the linkage between criteria pollutants and air toxics showed a correlation of acetaldehyde and formaldehyde with ozone but that correlation was likely because of similar photochemical production mechanisms, rather than source similarities (i.e., not a causal association) and most air toxics did not correlate well with ozone, PM<sub>2.5</sub>, or other air toxics (<http://www.epa.gov/ttn/amtic/files/ambient/airtox/2005%20workshop/explore.pdf>).

# Formation, Destruction, Transport *(1 of 2)*

- Some air pollution problems are limited to the local area where pollution is emitted. Other air quality problems spread to cover cities or regions of the country. Emissions of some pollutants from anywhere on earth can contribute to a global problem. While some pollutants can be neatly characterized as contributors to local, regional, or global problems, many pollutants are important on multiple spatial scales. Explaining the factors that control the spatial extent of a pollutant requires understanding the emissions, transport, and chemistry of a pollutant.



- Concentrations of primarily emitted pollutants are almost always highest very close to their emissions source (for primary pollutants). The figure illustrates the typical drop-off in concentrations from an emissions source as distance increases from the source. Pollution concentrations start very high, but are diluted by the atmosphere in the first few hundred feet from a source as they are transported and dispersed.

# Formation, Destruction, Transport *(2 of 2)*

- Concentrations of pollutants that are secondarily formed in the atmosphere are often highest downwind of the source of precursor compounds. Chemical or physical rates of formation determine how far the precursor pollutants travel before they begin forming secondary pollutants such as formaldehyde. Factors such as wind speed and temperature will also influence where these secondary pollutants are formed, relative to where they were originally emitted. Generally, pollutants that are secondarily formed do not have steep concentration gradients near the original precursor emissions source.
- The distance that a particular air pollutant emitted from a source may travel is determined by atmospheric chemistry (pollutant lifetimes and formation and removal processes), meteorology (air mass movement and precipitation), and topography (mountains and valleys that affect air movement). The longer a pollutant stays in the atmosphere, the farther it can be transported. Some air toxics are removed quickly by chemical reactions (e.g., 1,3-butadiene) or physical processes, (e.g., heavy larger particles deposit to the ground quickly). These short-lived pollutants can only travel short distances from where they are emitted (10s to 100s of miles). Other pollutants react more slowly and can travel large distances from where they are formed or emitted (e.g., toxic metals in PM<sub>2.5</sub>). These pollutants may be more regionally homogenous. Finally, some unreactive pollutants can remain in the atmosphere for months, years, or decades and spread across the Earth (e.g., carbon tetrachloride).

# Residence Time

## *Overview*

- 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; these 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. Some air toxics and their residence times are listed in the appendix to this section.

# History of Sampling

- Air toxics measurements have been collected across the country since the 1960s as part of various programs and measurement studies.
- National monitoring efforts have included programs specific to air toxics:
  - National Air Toxics Trends Stations (NATTS)
  - Urban Air Toxics Monitoring Program (UATMP)
- Some ambient monitoring networks are designed for other purposes but also provide air toxics data:
  - Photochemical Assessment Monitoring Station (PAMS) program
  - Chemical Speciation Network (CSN) which includes the Speciation Trends Network (STN)
  - Interagency Monitoring of Protected Visual Environments (IMPROVE)
- State and local agencies have also operated long-running monitoring operations and special studies to understand air toxics in their communities.

# NATTS Sampling Overview

- NATTS sampling began in 2003 with 23 sites; the first complete year of data was 2004.
- There are currently 27 national air toxics trends sites: 21 urban and 6 rural.
- Most stations are collocated with PM<sub>2.5</sub> speciation samplers, and some also include PAMS measurements.
- The principle objective of the NATTS network is to provide long-term monitoring data across representative areas of the country for certain priority HAPs (e.g., benzene, formaldehyde, 1,3-butadiene, acrolein, and hexavalent chromium) in order to establish national trends for these and other HAPs.
- Recently, the list of pollutants monitored at NATTS sites was expanded to include polycyclic aromatic hydrocarbons (PAHs), of which naphthalene is the most prevalent.
- All sites follow QA programs for sampling and siting.
- Periodic refinement of pollutants and/or sampling may be made (e.g., EPA plans to re-evaluate the program every six years).



- More information can be found on the NATTS web site:  
<http://www.epa.gov/ttn/amtic/natts.html>

# NATTS Sampling

## *Objectives*

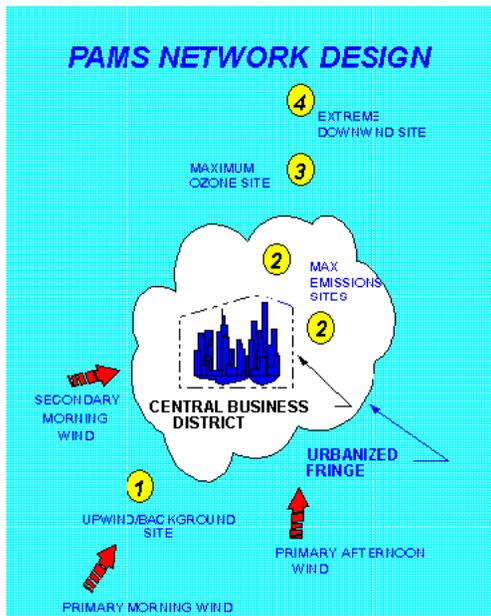
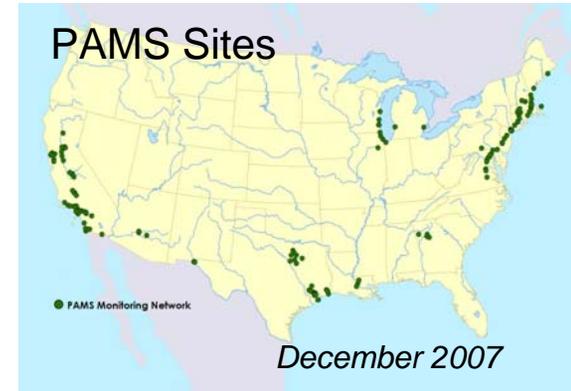
The primary objectives of NATTS monitoring include

- Providing air toxics data of sufficient quality to identify trends, characterize ambient concentrations in representative areas, and evaluate air quality models.
- Providing tools and guidance that enable consistent, high certainty measurements.
- Using these consistent measurements to facilitate measuring progress towards national emission and risk reduction goals.
- Considering all NATTS sites to be NCORE level 2 sites, thereby providing rich data sets to address multi-pollutant issues. NCORE level 2 sites are “backbone” sites providing consistent, long-term data for multiple pollutant types.



# PAMS Sampling

- The goal of the PAMS network is to help assess ozone control programs by
  - identifying key constituents and parameters
  - tracking trends
  - characterizing transport
  - assisting in forecasting episodes
  - assisting in improving emission inventories
- Toxic VOCs sampled by the PAMS network include benzene, formaldehyde, xylenes, toluene, ethylbenzene, styrene, and acetaldehyde.
- PAMS sites collect subdaily measurements at the same sites that are useful in assessing diurnal trends.
- More information can be found on the PAMS web site at <http://www.epa.gov/ttn/amtic/pamsmain.html>.



Analysis Objectives	PAMS Site Type			
	I (Upwind)	II (Max. Emissions)	III (Max. Ozone)	IV (Downwind)
Corroborate precursor EI		✓		
Assess changes in emissions; corroborate reductions		✓		
Assess ozone & precursor trends		✓		
Provide input to models; evaluate models	✓	✓	✓	✓
Evaluate population exposure		✓	✓	
Other analyses:				
biogenics	✓		✓	✓
transport	✓		✓	✓
source apportionment		✓		
diurnal patterns		✓		
day-of-week		✓		
episode vs. non-episode		✓	✓	

# CSN Sampling

- The Chemical Speciation Network is a companion network to the mass-based Federal Reference Method (FRM) network implemented in support of the PM<sub>2.5</sub> National Ambient Air Quality Standards (NAAQS).
- The purpose of the CSN is to provide nationally consistent speciated PM<sub>2.5</sub> data for the assessment of trends at representative sites in urban areas across the country.
- As part of a routine monitoring program, the CSN quantifies mass concentrations and PM<sub>2.5</sub> constituents, including numerous trace elements, ions (sulfate, nitrate, sodium, potassium, ammonium), elemental carbon, and organic carbon.
- CSN data are available via AQS.
- Prior to 2007, the carbon (especially EC) measurements from this network differed from IMPROVE. A phased in change in methodology is underway (<http://www.epa.gov/ttn/amtic/specurg3000.html>).



*Circa 2005*

U.S. Environmental Protection Agency (2007f)

# IMPROVE Sampling

- Interagency Monitoring of Protected Visual Environments (IMPROVE) program provides  $PM_{2.5}$  speciated and mass measurements in 156 Class I areas (national parks and wilderness areas). Speciated  $PM_{2.5}$  metals are the only toxics measured in this network.
- Data are available in AQS.
- IMPROVE data can also be accessed via the internet from the VIEWS\* web site.
  - Raw data and various aggregates can be obtained in a variety of output formats (ASCII, HTML, XLS etc.).
  - All data from the inception of the IMPROVE network in 1988 are currently available.
- User-input mapping and plotting tools are available to visualize trends, spatial patterns, back trajectories and metadata (i.e., site locations).
- IMPROVE also provides site photos and local topographical maps which are very useful for data analyses.
- To download data or get more information see <http://vista.cira.colostate.edu/views/>

IMPROVE Site Locations



\*VIEWS: Visibility Exchange Web System

# Local-Scale Monitoring Projects

- EPA began programs to fund local-scale monitoring projects beginning in the 2004 fiscal year.
- The goal of local monitoring is to provide more flexibility to address middle- and neighborhood-scale (0.5 km to 4 km) issues that are not handled well by national networks, given the diversity of toxics issues across the nation.
- Specific objectives include identifying and profiling air toxics sources, developing and assessing emerging measurement methods, characterizing the degree and extent of local air toxics problems, and tracking progress of air toxics reduction activities.
- Projects are selected through an open competition process. Grant topics, funding levels, and number of awards are set for each grant cycle – for more information, see <http://www.epa.gov/ttn/amtic/local.html>.
- Local scale monitoring is typically only conducted from 1-2 years.

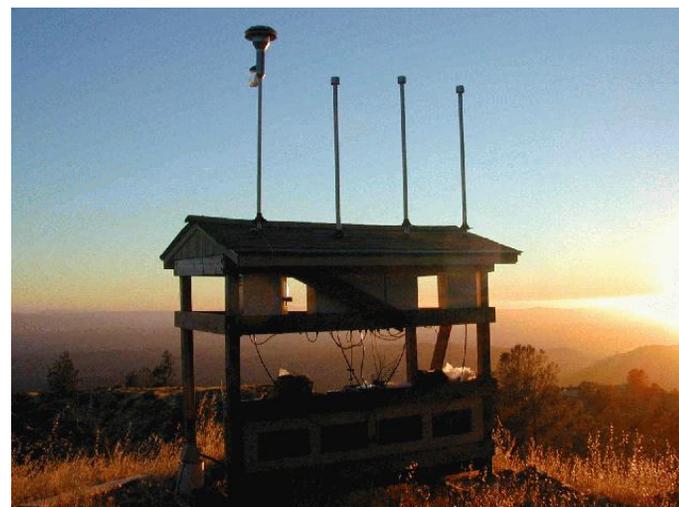
U.S. Environmental Protection Agency (2006c).

# Air Toxics Sampling and Analysis (1 of 2)

- Because air toxics are present in the atmosphere in gaseous, particulate, and semi-volatile form, no single measurement technique is adequate. Differences in chemical and physical properties further complicate collection; the choice of measurement technique depends on the objectives of data collection, including the chemical species of interest, funds available, and desired detection limit
- EPA offers seventeen approved sampling and analysis methods for toxic gases; among the most commonly used methods are the following:
  - Compendium method TO-11A. Used to measure formaldehyde and other carbonyl compounds. Previous methods include TO-5 which had lower sensitivity and reproducibility and was more labor-intensive. Method TO-11A uses coated dinitrophenylhydrazine (DNPH) cartridges to collect the samples and analyzes them using high performance liquid chromatography (HPLC).
  - Compendium method TO-13A. Used to measure Polycyclic Aromatic Hydrocarbon (PAH) compounds. This method allows for a variety of sampling media; an effective choice is the combination of polyurethane foam (PUF) and XAD-2 ®. Samples are analyzed by high resolution gas chromatography/mass spectrometry (GC/MS).
  - Compendium method TO-15. Created to target 97 compounds on the list of 187 hazardous air pollutants. The method uses specially prepared canisters analyzed by high resolution gas chromatography/mass spectrometry (GC/MS).

# Air Toxics Sampling and Analysis (2 of 2)

- EPA-approved methods for collection and analysis of suspended particulate matter are documented in the “Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air.”
  - Chapters 1 and 2 address mass measurement only; while important to the criteria air pollutant program, these chapters are not of particular importance to the air toxics ambient monitoring program:
    - Chapter IO-1, Continuous Measurement of PM<sub>10</sub> Suspended Particulate Matter (SPM) in Ambient Air
    - Chapter IO-2, Integrated Sampling of Suspended Particulate Matter (SPM) in Ambient Air
  - Chapter IO-3, Chemical Species Analysis of Filter-Collected Suspended Particulate Matter (SPM), is of considerable importance to the air toxics ambient monitoring program
    - Several different methods for speciated particulate analyses are available
      - Each have advantages and disadvantages depending on the target analytes and desired minimum detection limits.
      - For Hazardous Air Pollutant (HAP) metals, IO-3.5 (Inductively Coupled Plasma / Mass Spectrometry (ICP/MS)) offers the lowest detection limits.
- Detailed information about these monitoring methods is available at: <http://www.epa.gov/ttn/amtic/airtox.html>.



# Differences Among Sampling Networks

- When using data from different sampling networks, it is important to consider
  - The multiple sampling networks from which data were drawn for these analyses vary in their objectives and sampling and analytical methods. *Data may not always be comparable.*
  - Sampling, analysis, method detection limits, objectives, site characteristics, etc. have changed over time. *Care is needed in interpreting temporal and spatial trends.*
- Analysts need to gather, and understand, all metadata prior to conducting analyses.

# Critical Issues for Interpretation

## Issues to consider when planning and performing data analysis

- Data quality. Information from collection and chemical analysis such as standard operating procedures, audits, accuracy and precision, and data validation provide insight into sample and collection biases and errors. This information is necessary for data validation. Metadata such as precision and accuracy are required for other analyses (e.g., receptor modeling).
- Data quantity. The number of species and amount of data above detection give insight into what analyses can be performed and provide a starting point for planning data analysis.
- Sampling duration. Duration provides information about analysis possibilities, for example, 24-hr data cannot be used to investigate diurnal patterns. This information may also be necessary for calculating completeness criteria when aggregating data.
- Sampling frequency. Frequency information provides further insight into what analyses will be possible; for example, one year of 1-in-6 day data may not be sufficient to investigate day-of-week tendencies. Sample frequency will also be necessary to calculate data completeness and to aggregate data.
- Complementary data. Additional data for criteria pollutants, speciated PM, and non-toxic hydrocarbons and meteorological data can be useful in a variety of analyses such as data validation, understanding transport, and source identification.

# Sampling Design

- To develop a sampling design or monitoring plan, the following should be considered:
  - Monitoring objectives including consideration of geophysical setting, meteorology, types and characteristics of sources, and existing monitoring programs.
  - Data quality objectives needed to answer questions to be asked of the data (i.e., how precisely or accurately do the questions need to be answered?).
  - Options for what, when, where, how frequently, and for how long to monitor; these are related to the selection of appropriate monitoring equipment and laboratory analyses.
  - Data quality assurance and validation approach including collocated data requirements, QA programs for analytical laboratories, and data validation guidelines for ambient data.
  - Options for data analysis and exploration including available tools, data analyses, data needs, and training needs.
- Sampling design for the national air toxics monitoring program is thoroughly discussed by Battelle and available here: <http://www.ladco.org/toxics.html> (Phase I report).

# Resources

## *Monitoring Networks*

- NATTS: <http://www.epa.gov/ttn/amtic/natts.html>
- UATMP: <http://www.epa.gov/ttn/amtic/uatm.html>
- PAMS: <http://www.epa.gov/ttn/amtic/pamsmain.html>
- CSN: <http://www.epa.gov/ttn/amtic/speciepg.htm>
- IMPROVE: A source of speciated PM<sub>2.5</sub> data  
<http://vista.cira.colostate.edu/views/>
- Local scale monitoring programs:  
<http://www.epa.gov/ttn/amtic/local.html>

# Appendix

## *Residence Times*

- Approximate atmospheric residence times for some air toxics are listed here.
- These values were found at <http://www.scorecard.org/chemical-profiles/>. To find the atmospheric persistence of other air toxics, enter the pollutant's name in the chemical profile. Once the pollutant page is available, select "links" and the entry for "CalEPA Air Resources Board Toxic Air Contaminant Summary". A summary of physical properties is provided including atmospheric persistence.

Species	Lifetime by reaction with OH
Carbon Tetrachloride	decades
Chloroform	months
Tetrachloroethylene	months
Methylene Chloride	months
Benzene	84 hrs
1,2-Dichloropropane	weeks*
Trichloroethylene	84 hrs
Acrylonitrile	2.4 days
Ethylbenzene	2 days
Vinyl Chloride	27 hrs
Formaldehyde	26 hrs
Acrolein	17 hrs
Naphthalene	16 hrs
Acetaldehyde	12 hrs
1,3-Butadiene	2.8 hrs
Arsenic and other toxic metal compounds	N/A**

\* Wet deposition is also a sink

\*\* Lifetime is dependant on particle deposition and is typically days to weeks. Deposition time is primarily determined by the size of the particles.

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