# Introduction to Air Toxics

## Student Workbook

## APTI Course 400

**Authors**

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**Developed by**:

Lake Michigan Air Directors Association Consortium (LADCO)

July 27, 2009 (Updated: October, 2024)

### Course 400

# Introduction to Air Toxics

### October 7 – 10, 2024

## AGENDA

| LOCATION | INSTRUCTORS |
|---|---|
| *On-Line* Presentation | William Franek; Ph.D., P.E., DEE |
| CenSARA | Lou DeRose; J.D., M.S., P.E. |

| DAY & TIME | SUBJECT | SPEAKER |
|---|---|---|
| ***Monday, Oct. 7*** **(Central Time)** | | |
| 9:00 | Introduction | W. Franek |
| 9:15 | History of Air Toxic Regulation | L. DeRose |
| 10:15 | Regulation of Air Toxics | L. DeRose |
| 10:45 | BREAK | |
| 11:00 | Regulation of Air Toxics (cont.) | L. DeRose |
| 12:00 | Air Toxics: Chemicals, Sources & Emission Inventories | W. Franek |
| 1:15 | ADJOURN | |
| ***Tuesday, Oct. 8*** | | |
| 9:00 | Air Toxics: Chemicals, Sources & Emission Inventories (cont.) | W. Franek |
| 9:15 | Introduction to Risk Assessment | W. Franek |
| 10:30 | BREAK | |
| 10:45 | Dispersion, Transport, Fate & Modeling of Air Toxics | W. Franek |
| 11:45 | Exposure Assessment | W. Franek |
| 1:15 | ADJOURN | |
| ***Wednesday, Oct. 9*** | | |
| 9:00 | Exposure Assessment (cont.) | W. Franek |
| 9:15 | Hazardous Identification and Dose Response | L. DeRose |
| 10:15 | Risk Characterization | L. DeRose |
| 10:45 | BREAK | |
| 11:00 | Risk Characterization (cont.) | L. DeRose |
| 11:30 | *Toxic Trials* (film) | |
| 12:30 | Ambient Monitoring for HAP's | W. Franek |
| 1:15 | ADJOURN | |
| ***Thursday, Oct. 10*** | | |
| 9:00 | Ambient Monitoring for HAP's (cont.) | W. Franek |
| 9:15 | Source Sampling for HAP's | W. Franek |
| 10:30 | BREAK | |
| 10:45 | Controls of HAPs for Stationary Sources | W. Franek |
| 1:15 | ADJOURN | |

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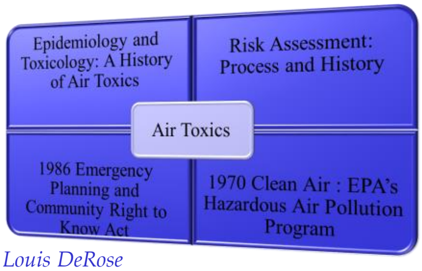
# Chapter One
## *Air Toxics: A Legislative History*



Epidemiology and Toxicology: A History of Air Toxics

Risk Assessment: Process and History

Air Toxics

1986 Emergency Planning and Community Right to Know Act

1970 Clean Air : EPA's Hazardous Air Pollution Program

*By: Louis DeRose*

## Epidemiology and Toxicology

- **Epidemiology**: Seeks to answers the question? What is causing this person (or these people) to experience this particular harmful effect?
  - Try to establish a *relationship* between an "exposure" and a "harm."
- **Toxicology**: Begins with a known or suspected cause of the adverse health effects & seeks to discover the *relationship* between the amount taken in (dose) & the degree of effect (response).
  - Paracelsus (1493-1541) noted that all things are poisons and the amount we are exposed to determines whether the substance is harmful or not.

## Epidemiology

- *Adverse effects are observed & their causes sought*.
- Early Romans: exposure to lead fumes caused health injuries.
  - Used "crude ores" to make swords, etc.
  - Knew fumes from certain "ores" causes injury
- 1775: Percival Pott noted scrotal cancer in chimney sweeps (from arsenic in soot).
  - Did not know composition of soot, but he was first to establish "cause & effect" (soot with cancer).
- 1854: John Snow traced London's cholera outbreak to the use of a contaminated well.

## London's 1854 Cholera Outbreak

- Cholera: is caused by a bacteria (from human excrement) that lines the small intestine, & causes the body to expel water at a high rate (normally the intestines absorb & expel water at about the same rate).
  - *Die of dehydration*: all major organs fail – blood has less water causing it to thicken & heart to pump faster & eventually fail – kidneys also fail.
  - Worst case: you lose 30% of body weight in a few hours.
  - *Cure: water given intravenously* – in1832 Dr. Latta's approach only differed from modern treatment in terms of quantity of water – Latta's remedy was lost in a swarming mass of proposed cholera cures.

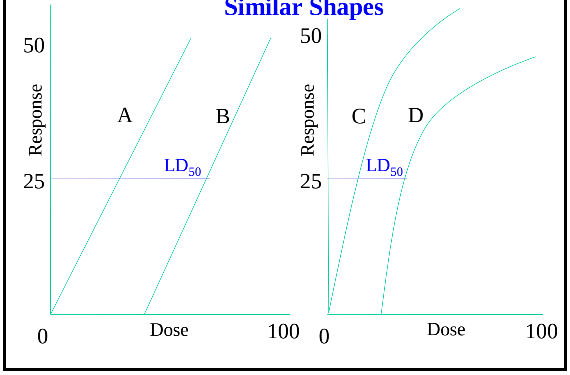
## London's 1854 Cholera Outbreak

- Late 1840's: Dr. Snow was trying to show that "cholera" was a waterborne agent & had to be ingested (others thought it was an airborne disease).
- London (around 1850) greatly expanded city sewage system (eliminated 30,000 cesspools over 6 yrs. & caused the "Thames" to become a sewer).
  - Later found out cesspool waste water pipe leaked into well.
- 1854: 750 died in 2 weeks that lived within 250 yards of the Broad St. well (Snow's "ghost" map) before they removed the pump handle.

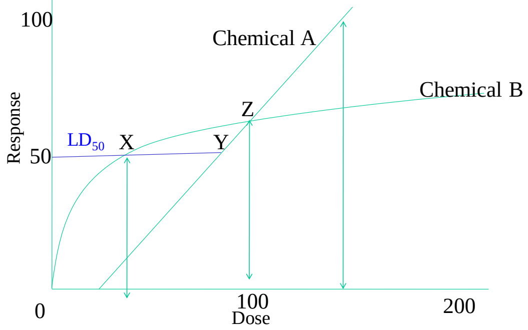
## Toxicology

- Toxicology actually means "study of poisons"
- Middle ages: a poisoner: well respected & paid
- 1927: J.W. Trevan studied chemical warfare chemicals (poison gas) & developed the first toxicology test that used $LD_{50}$:
  - Used a small group of animals & measured the amount that could kill half quickly (*acute effect*)
  - $LD_{50}$: dose that is lethal to half the population
    - i.e. measure # of deaths after 14 days at varying exposures
  - $LD_{50}$ used to compare toxic potency of different compounds

## Examples of Dose-Response Curves with Similar Shapes



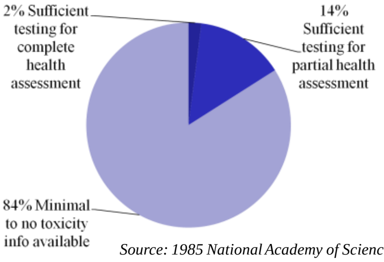
## Examples of Dose-Response Curves with Dissimilar Shapes



## Toxicology

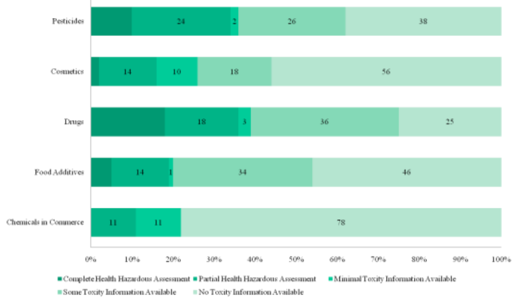
- During the past 125 years, scientists created over a 100,000 compounds that do not occur in nature.
  - After WWII, development of new chemicals accelerated
  - Vast majority of chemicals have no toxicity information

## Over 5 Million Chemicals: Americans Potentially Exposed to About 70,000 of Them



*Source: 1985 National Academy of Science Report*

## Availability of Health-Hazard Data for Six Categories of Chemicals

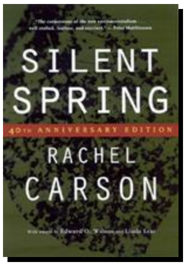


Data from a 1984 National Resource Council Document

## History of Toxic Regulations

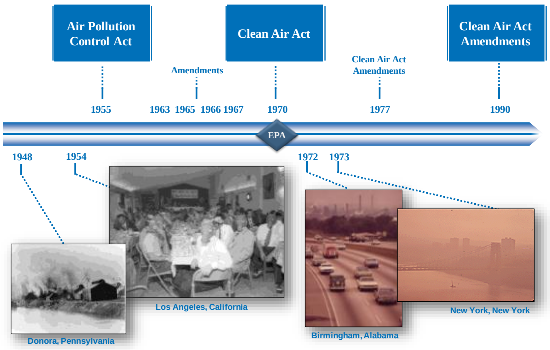
- **1906 Pure Food and Drug Act**: For preventing the manufacture of adulterated or harmful foods, drugs, & medicines. ("animal testing" was not yet developed.)
- **1938 Food and Drug Act** passed as a result of 100 people dying of acute kidney failure after ingesting the new antibiotic "sulfanilamide" made with "diethylene glycol."
  - By 1940, FDA tested new chemicals that entered in the food & drug supply. Used animal testing to develop a new 100 to 1 safety factor (the NOEL was divided by 100 to find safe level).
    - For carcinogens: if the test animal got cancer, the toxic substance was totally banned. (at any level)
- **1958 Food & Drug Act Amendment**: Added "**Delaney Clause**" which prohibited food additives that caused cancer in man or animal (no safe levels – zero tolerance).

## 1962: Toxic Awareness



The book described the effects of DDT on animals, & increased public awareness to environmental issues.

## Air Pollution Control – History



## 1970 Clean Air Act

- **National Ambient Air Quality Standards (NAAQS)** §108 & 109
  - Criteria Pollutants: "Those which create or contribute to air pollution which may reasonably be anticipated to endanger public health or welfare."
  - Standard: *Adequate* margin of safety
- **New Source Performance Standards (NSPS)** Section 111
  - New Sources of Pollution: "Those stationary sources that cause or contribute significantly to air pollution which may reasonably be anticipated to endanger public health or welfare."
  - Standard: Cost and technological feasibility may be considered
- **National Emission Standards for Hazardous Air Pollution (NESHAP)** Section 112
  - Hazardous Air Pollutants: "Those air pollutants that may reasonably be anticipated to result in an increase in mortality or an increase in serious irreversible or incapacitating reversible illness."
  - Standard: *Ample* margin of safety

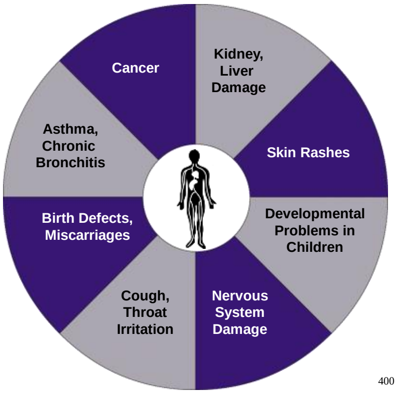
## Introduction to "Air Toxics"

- Air toxics, also called ***hazardous air pollutants*** (HAPs): it was not until EPCRA (1986) that the term "**toxic**" was specifically applied to air pollution.
- The 1970 CAA defined ***hazardous air pollutants*** as "*chemicals which may reasonably be anticipated to cause adverse effects*." EPA construed this to mainly **focus on carcinogens**.

## Some Human Carcinogenic Sites of Toxicity for 1970-1989 HAPs

| Chemical (HAP) | Carcinogenic Site(s) |
|---|---|
| Arsenic | Lungs, bladder, liver |
| Asbestos | Lungs |
| Benzene | Bone marrow |
| Beryllium | Lungs |
| Radionuclides | Bone marrow, lungs |
| Vinyl chloride | Liver |
| Coke oven emissions | Lung, kidney |

*Mercury*: the only 1970-1989 HAP that is a *non-carcinogen*.



## 1970 CAAA Air Toxics Program Required EPA to:

- List chemicals they decide are hazardous:
  - Arsenic, asbestos, beryllium, mercury, benzene, vinyl chloride, radionuclides and coke oven emissions
- Set an emission limitation (NESHAP) in 1 year (after listing) with "ample margin of safety" protection.
  - 1976: EPA originally set NESHAP by:
    - 1st *Does it cause cancer?* Yes, then "shut it down."
    - If shutting it down is impractical, then (2nd ) take action to *reduce risk by considering cost & technical feasibility.*
- *NRDC v EPA* (1987): vinyl chloride case
  - NRDC contended: use zero emission when no safe level can be determined
  - Held: use 2 step process
  - Health based standard

## Ample Margin of Safety

### 1st Step

**Determine what is "safe"**

- **"Safe" is not necessarily risk free**
- **Base decision on what is "safe" only on human health – no costs or technical feasibility are considered.**
- **Will always be marked with uncertainty**

**SAFE**

## Ample Margin of Safety

### 2nd Step

**Determine "ample margin of safety"**

- **Once you determine what a 'safe' emission level is, set the regulation to allow less emissions (costs can be considered)**
- **This will provide an "ample margin," beyond what is "safe"**

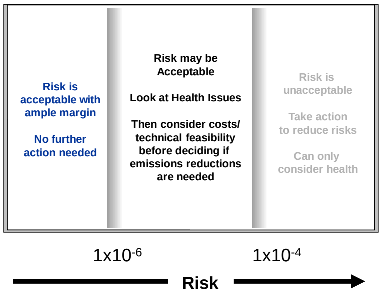
**SAFE**

**REALLY SAFE!**

## 1989: EPA New "Risk Policy"

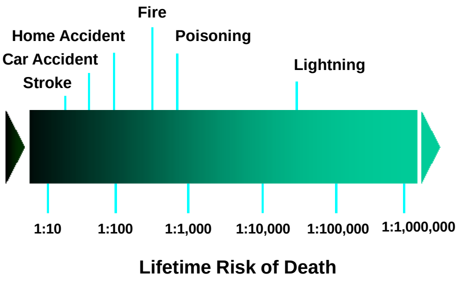
- Acceptable risk ranges from 1 x $10^{-4}$ to 1 x $10^{-6}$
- What is safe: "maximum individual risk" (MIR) should not be greater than 1 in 10,000.
  - MIR: estimated risk that a person living near a plant would have if he were exposed to the maximum (highest average annual) pollutant concentration for 70 years.
- With an "ample margin of safety:" To protect the greatest number of persons possible to an "individual lifetime risk" (ILR) should be no greater than 1 in a million *plus* consider costs, economic impact, technical feasibility, etc.
  - ILR: same as MIR except use the average annual pollution concentration

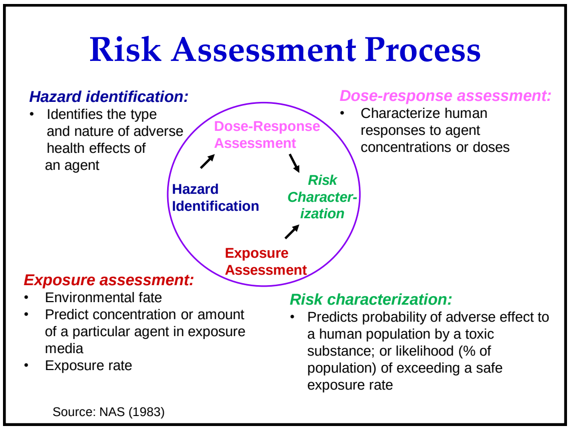
## Benzene NESHAP Risk Ranges



| Risk is acceptable with ample margin<br>No further action needed | Risk may be Acceptable<br>Look at Health Issues<br>Then consider costs/ technical feasibility before deciding if emissions reductions are needed | Risk is unacceptable<br>Take action to reduce risks<br>Can only consider health |
|---|---|---|

## Putting Risks in Perspective





## Risk Assessment Process

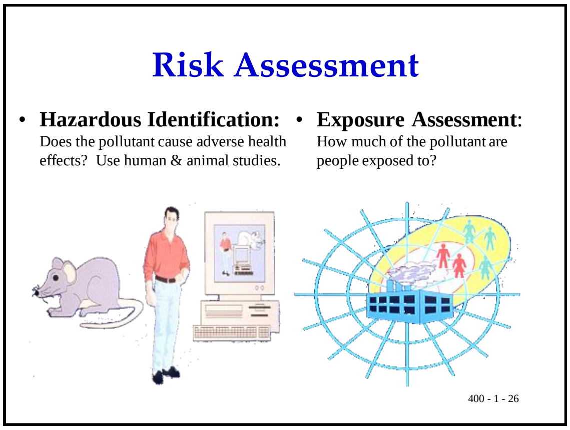
***Hazard identification:***
- Identifies the type and nature of adverse health effects of an agent

***Dose-response assessment:***
- Characterize human responses to agent concentrations or doses

***Exposure assessment:***
- Environmental fate
- Predict concentration or amount of a particular agent in exposure media
- Exposure rate

***Risk characterization:***
- Predicts probability of adverse effect to a human population by a toxic substance; or likelihood (% of population) of exceeding a safe exposure rate

Source: NAS (1983)



## Risk Assessment

- **Hazardous Identification:** Does the pollutant cause adverse health effects? Use human & animal studies.
- **Exposure Assessment:** How much of the pollutant are people exposed to?

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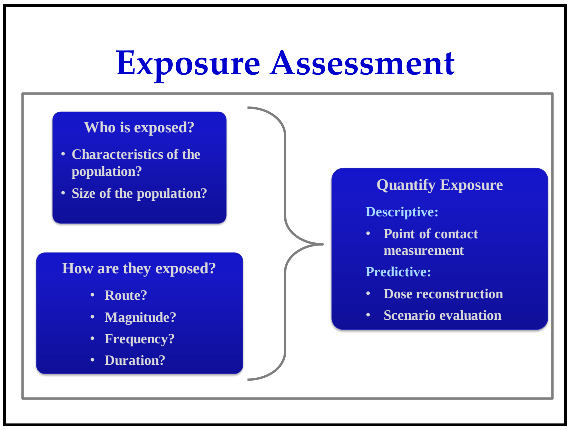


## Exposure Assessment

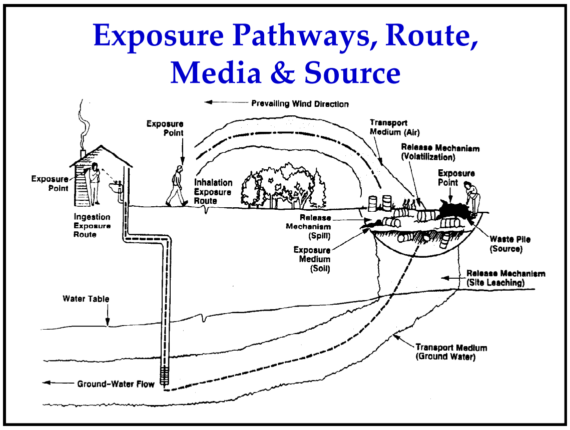
**Who is exposed?**
- Characteristics of the population?
- Size of the population?

**How are they exposed?**
- Route?
- Magnitude?
- Frequency?
- Duration?

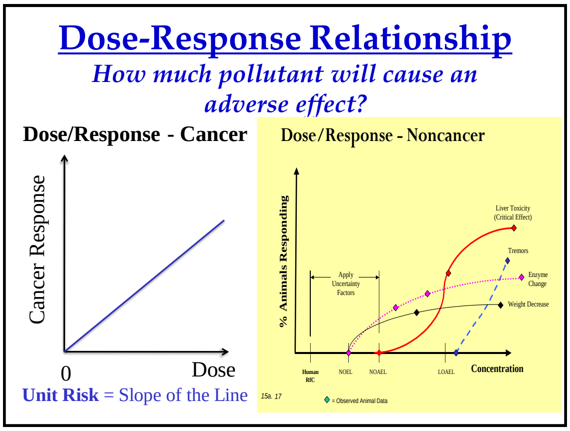
**Quantify Exposure**

Descriptive:
- Point of contact measurement

Predictive:
- Dose reconstruction
- Scenario evaluation



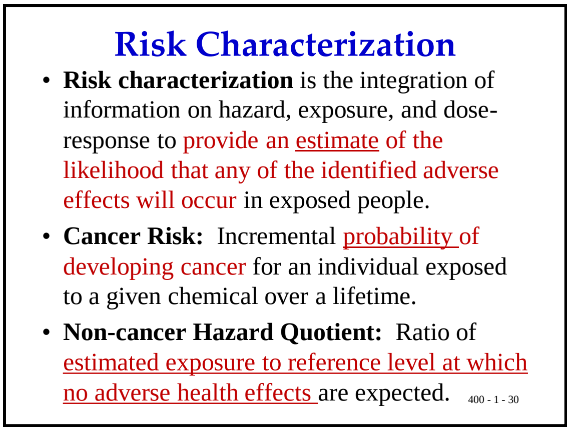
## Exposure Pathways, Route, Media & Source



## Dose-Response Relationship

*How much pollutant will cause an adverse effect?*

**Unit Risk** = Slope of the Line



## Risk Characterization

- **Risk characterization** is the integration of information on hazard, exposure, and dose-response to provide an estimate of the likelihood that any of the identified adverse effects will occur in exposed people.
- **Cancer Risk:** Incremental probability of developing cancer for an individual exposed to a given chemical over a lifetime.
- **Non-cancer Hazard Quotient:** Ratio of estimated exposure to reference level at which no adverse health effects are expected.

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## Risk Characterization: Quantitative Results

**Cancer**

$$\text{Cancer Risk (Inhalation)} = \text{Lifetime Average Exposure Concentration} \left(\frac{\mu g}{m^3}\right) \times \text{Inhalation Unit Risk} \left(\frac{\text{Extra Risk}}{\mu g/m^3}\right)$$

$$\text{Cancer Risk (Oral)} = \text{LADD} \left(\frac{mg}{kg-day}\right) \times \text{Oral Slope Factor} \left(\frac{mg}{kg-day}\right)^{-1}$$

**LADD**: lifetime average daily dose

**Noncancer Effects**

$$\text{Hazard Quotient (HQ) (Inhalation)} = \frac{\text{EC} \left(\frac{\mu g}{m^3}\right)}{\text{RfC} \left(\frac{\mu g}{m^3}\right)}$$

$$\text{Hazard Quotient (HQ) (Oral)} = \frac{\text{ADD} \left(\frac{mg}{kg-day}\right)}{\text{RfD} \left(\frac{mg}{kg-day}\right)}$$

**EC:** exposure concentration

**ADD:** average daily dose (from exposure assessment)

**RfD:** reference dose (or)
**RfC:** reference concentration

## Uncertainties in Risk Assessment

- **Too few human or animal studies** of the health effects of chemicals
- **Interspecies adjustment** i.e.
  - Metabolism & absorption rates
  - Size, life span & exposure route
- **Extrapolation from high to low doses**

## Risk Assessment

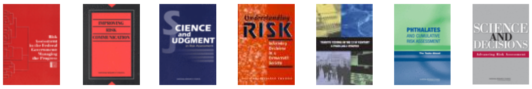
- Winston Churchill said, "*democracy was the worst form of government, except for all the others.*"
- Joseph Rodricks paraphrases this in his 2007 book *Calculated Risks*, "*Risk assessment is the worst basis for making public health decisions, except for all the others.*"

## Brief History of Human Health Risk Assessment at EPA

- 1975: First EPA risk assessment:
  - *Quantitative Risk Assessment for Community Exposure to Vinyl Chloride*
- 1976: EPA published: *Interim Procedures and Guidelines for Health Risk and Economic Impact Assessments of Suspected Carcinogens*
  - This was not a formal guidelines or policy, but were the beginnings of such guidelines.

## Brief History of Human Health Risk Assessment at EPA

- **National Research Council** (NRC) publications on risk assessment
  - 1983: *Managing the Process* – the "Red Book"
  - 1989: *Improving Risk Communication*
  - 1994: *Science and Judgment* – the "Blue Book"
  - 1996: *Understanding Risk*
  - 2007: *Toxicity Testing in the 21st Century*
  - 2008: *Phthalates and Cumulative Risk Assessment*
  - 2009: *Science and Decisions* – the "Silver Book"



## Three Fundamental Books

The Red Book

1983: First time 4 step RA process identified

The Blue Book

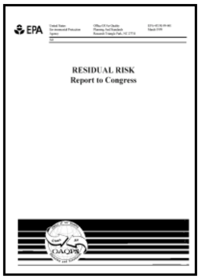
1994: Reviewed EPA's RA methods

The White Book

1997: Focuses on risk management & policy

## Residual Risk Report to Congress (March, 1999)

- The 1990 CAAA section 112(f)(1) required EPA to report to Congress on methods for calculating residual risks remaining after implementation of MACT.
- The Report does not specify a particular method for conducting risk assessment.
- The Report describes the framework EPA will use in its residual risk determinations: one being a screening process utilized a 3- tiered approach to risk assessment.


EPA

RESIDUAL RISK
Report to Congress

## EPA's Risk Assessment Guideline Documents

- EPA has developed a series of **guideline documents** concerning risk assessment that provides guidance & support to risk assessors.
- Many risk assessment documents are available; including the **Integrated Risk Information System (IRIS):** IRIS contains information for more than 540 chemicals.)
- EPA's "Risk Assessment Portal" https://www.epa.gov/risk/risk-assessment-guidelines

## Air Toxics Risk Assessment Library

- EPA has developed methods and guidance for conducting facility-specific and community-scale air toxics assessments in the following manuals called the "Air Toxics Risk Assessment Library:"
- Web site: https://www.epa.gov/fera/risk-assessment-and-modeling-air-toxics-risk-assessment-reference-library
- Volume 1: Technical Resource Manual
- Volume 2: Facility-specific Assessment
- Volume 3: Community-Level Assessment
- Community Screening How-To Manual

## Accidental Releases of HAP

- In 1984, 30 tons of methyl isocyanate accidentally released at Union Carbide's plant near Bhopal India: 2,500 killed & 17,000 disabled
- A subsequent release from a Western Virginia facility sent 100 people to the hospital.
- **Result**: (1) states started toxic air programs; & (2) Congress passed Emergency Planning & Community Right to Know Act (EPCRA).
  - allows EPA to compile the Toxic Release Inventory (TRI) database

## 1986: Emergency Planning & Community Right to Know Act (EPCRA)

- *Emergency Planning*
  - Local governments are to prepare chemical emergency release plans.
- *Emergency Release Notification*
  - Facilities must immediately report accidental releases of "hazardous substances."
- *Community Right-to-Know Requirements*
  - Facilities make their Material & Safety Data Sheets (MSDS) available to the public.
- *Toxic Release Inventory*

## Emergency Planning: Sections 301-303

- Establishes state & local emergency planning bodies.
- Local body to **prepare *emergency response plan.***
- State governments are required to oversee & coordinate local planning efforts.
- Facilities that maintain an "**extremely hazardous chemical**" over a "*threshold planning quantity*" amount must cooperate in emergency plan preparation.

## List of 356 "Extremely Hazardous Substances" (EHSs)

- EHSs are listed in 40 CFR Part 355 appendix A
- Each chemical will list a:
  - *Reportable Quantity* (RQ) (between 1 & 10,000 pounds)
  - *Threshold Planning Quantity* (TPQ) (also between 1 & 10,000 pounds)
- Example: Acrolein
  - RQ = 1 pound
  - TPQ = 500 pounds

## Emergency Release Notification: Section 304

- **Facilities must *immediately* report *accidental releases*** (in quantities > corresponding "*reportable quantities*") to state & local officials:
  - of "*Extremely Hazardous Substances*" (EHSs) chemicals and
  - "*hazardous substances*" defined under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).
- Information about accidental chemical releases must be available to the public.

## Community Right-to-Know Requirements: Sections 311 & 312

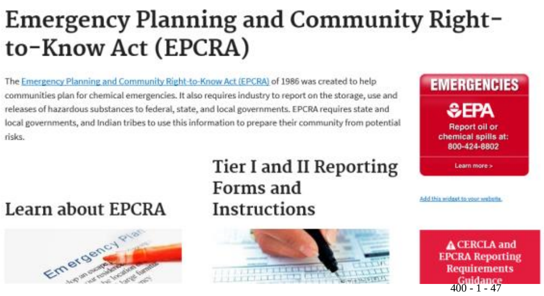
- Section 311: **facility submits list of their *MSDS chemicals*** (all chemicals under OSHA) present at site *over threshold amount* to state & local officials.
  - Describe properties & health effects of these chemicals.
- Section 312: **facility submits *chemical inventory annually*** (of all hazardous chemicals present at site).
- All information must be available to the public.

## EPCRA Chemicals & Reporting Thresholds

| | **Section 302** | **Section 304** | **Section 311/312** | **Section 313** |
|---|---|---|---|---|
| **Chemicals Covered** | 356 extremely hazardous chemicals | > 1,000 substances | 500,000 products | 650 toxic chemicals & categories |
| **Thresholds** | Threshold Planning Quantity (TPQ) 1-10,000 pounds on site at any one time | Reportable quantity, 1- 50,000 pounds, released in a 24-hour period | TPQ or 500 pounds for Section 302 chemicals; 10,000 pounds on site at any one time for other chemicals | 25,000 pounds/yr manufactured or processed; 10,000 pounds/yr used; certain persistent bio-accumulative toxics have lower thresholds |
| **Reporting Requirements** | One time notification to the state emergency response commissions (SERC) | Each time a release above reportable quantities occur, report to SERC & local emergency planning commission (LEPC) | 311: one time report to SERC & LEPC, & fire department<br>312: Annually to all of the above | Annually to EPA and the State |

## EPA's EPCRA Web Page

- https://www.epa.gov/epcra



Emergency Planning and Community Right-to-Know Act (EPCRA)

The Emergency Planning and Community Right-to-Know Act (EPCRA) of 1986 was created to help communities plan for chemical emergencies. It also requires industry to report on the storage, use and releases of hazardous substances to federal, state, and local governments. EPCRA requires state and local governments, and Indian tribes to use this information to prepare their community from potential risks.

Learn about EPCRA

Tier I and II Reporting Forms and Instructions

## Toxic Release Inventory (Section 313)

- Applicable facilities must ***report annually*** the amount of toxic chemicals ***released*** to the environment ***each year***.
- **Applicable facilities**:
  - Are a designated facility (by SIC codes);
  - Has at least 10 full time employees, and
  - Uses 10,000 lbs/yr or manufactures or processes 25,000 lbs/yr of a listed toxic chemical (650 chemicals), or 0.1 gm/yr of dioxin, or 10 or 100 tons of other PBT (persistent, bio-accumulative toxins) chemicals.

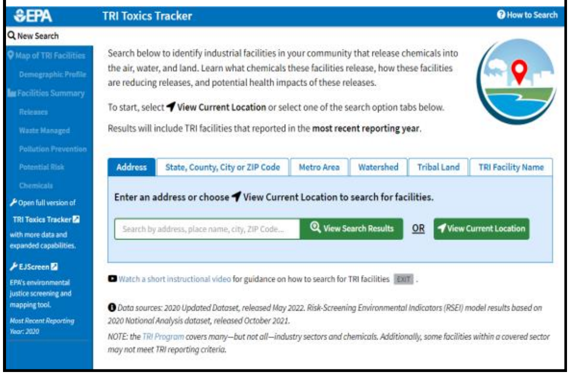
## Toxic Release Inventory (Section 313)

- Facilities report using a *Toxic Chemical Release Inventory Form* for each of the 650 Toxic Release Inventory (TRI) chemicals at their facility.
- The facilities must report the amount of each listed chemical:
  - *Disposed of or released* to the environment at facility;
  - *Recycled, burned* for energy recovery, or *treated at facility;* and/or
  - *Sent to other locations* for recycling, energy recovery, treatment, disposal or other release.

## Toxic Release Inventory δ 313

- This reporting created the **toxic release inventory** (TRI) & is available to the public.
  - First, 1988 TRI: 2.4 billion lbs toxic chemicals released to air.
  - 1989 EPA risk assessment: 2,700 cancer cases occur each year as a result of air exposure to EPCRA toxic pollutants.
- http://www.epa.gov/tri/
- EPA's **TRI Toxics Tracker** is where you can access nationwide TRI data from the past 10 years and easily explore by geography, facility, industry, chemical, or specific data elements.
- https://edap.epa.gov/public/extensions/TRIToxicsTracker/TRIToxicsTracker.html#continue

## TRI Toxic Tracker



with more data and expanded capabilities.

EPA's environmental justice screening and mapping tool.

*Most Recent Reporting Year: 2020*

Search below to identify industrial facilities in your community that release chemicals into the air, water, and land. Learn what chemicals these facilities release, how these facilities are reducing releases, and potential health impacts of these releases.

To start, select **View Current Location** or select one of the search option tabs below.

Results will include TRI facilities that reported in the **most recent reporting year**.

Enter an address or choose View Current Location to search for facilities.

Watch a short instructional video for guidance on how to search for TRI facilities EXIT .

*Data sources: 2020 Updated Dataset, released May 2022. Risk-Screening Environmental Indicators (RSEI) model results based on 2020 National Analysis dataset, released October 2021.*

*NOTE: the TRI Program covers many—but not all—industry sectors and chemicals. Additionally, some facilities within a covered sector may not meet TRI reporting criteria.*

# Chapter Two
# *Regulation of Air Toxics*

*By: Louis DeRose*

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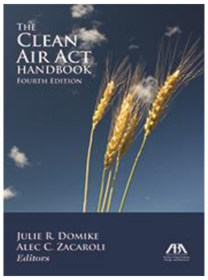
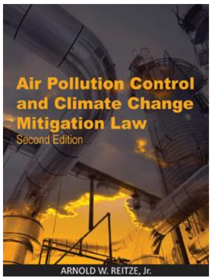
# Air Toxics Regulation Reference Books





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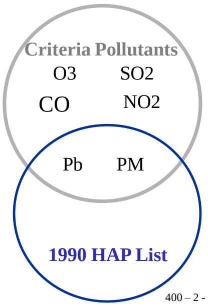
# Overlap Between HAPs and Criteria Pollutants

- PMs is comprised of many chemicals, some which may be HAPs:
  - i.e., trace metals or hazardous organic matter
- Lead Compounds: (HAP) Lead: Criteria Pollutant
- Many HAPs are VOC
  - Ozone formation



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# The Clean Air Act Amendments (CAAA) of 1990

- The 1970 CAA required <u>EPA to list</u> a HAP and required “ample margin of safety” protection (*health-based* standard)
- The 1990 CAAA:
  - *Lists the HAP* and
  - Required a *technology-based* control standard

1990

---

# 1990 CAAA: HAPs (Section 112)

- Congress originally listed <u>189 substances</u> as HAPs (this list does <u>not</u> include “Hydrogen Sulfide” which was added by clerical error & removed in 1991).
  - EPA can add or delete (delist)
  - Caprolactam (<u>delisted</u> June 1996)
  - Methyl Ethyl Ketone (MEK) (<u>delisted</u> Dec. 2005)
  - 1-Bromopropane <u>added to list</u> Feb 4, 2022 (FR Jan 5, 2022).
- EPA required to list <u>source categories</u> that emit one or more of §112 listed HAPs
  - 174 *major* and 8 *area* source categories
  - EPA can add or delete

---

# EPA HAP Web Site: https://www.epa.gov/haps

## Hazardous Air Pollutants

Hazardous air pollutants are those known to cause cancer and other serious health impacts. The Clean Air Act requires the EPA to regulate toxic air pollutants, also known as air toxics, from categories of industrial facilities in two phases.

### About Hazardous Air Pollutants

- What are Hazardous Air Pollutants?
- Health and Environmental Effects
- Sources and Exposure
- Reducing Emissions

### Urban Air Toxics

- Urban Air Toxics Home
- About Urban Air Toxics
- Integrated Urban Air Toxics Strategy

### National Air Toxics Assessments (NATA)

- NATA Overview
- Current NATA Home
- Previous NATA Versions

### Controlling Air Pollution from Stationary Sources

- Stationary Sources of Air Pollution
- Air Toxics Website
- Rules and Implementation

**Related Information**

- Air Quality Data and Tools
- Clean Air Act
- Criteria Air Pollutants
- Permitting Under the Clean Air Act
- Technical Air Pollution Resources
- Visibility and Haze
- Voluntary Programs for Improving Air Quality

## 1990 CAAA: HAP Emission Standards (Section 112)

- EPA to establish a control *technology-based* emission standard (MACT) for each “major” source category (and for an “area” source category if EPA feels it is warranted)
  - 25% in 2 yrs; 50% in 7 yrs; all remaining MACTs in 10 years (by 2000).
  - EPA passed all MACTs (96) by September, 2004
- Residual Risk program
  - 8 yrs. after MACT: EPA required to pass *health-based* emission standards if necessary (based on a EPA conducted risk assessment).

## Major Source under HAP

- Major source is any stationary source or group of stationary sources that are contiguous & under common control that has the potential to emit considering controls *at least*:
  - 10 tons/yr of a listed HAP, or
  - 25 tons/yr of a combination of listed HAPs
- All HAP major sources must meet MACT

## Area Sources

- An area source is any stationary source of HAPs that is not a major source
- Under δ112(d)(5), an (unaffected) area source *may* be regulated by a less stringent requirement: (GACT) “*generally available control technology*”
  - No floor analysis & no residual risk standard required

## HAP Major Source

- Source: (same as NSPS) small as an emission unit or as large as the entire facility
  - Does not have to have the same “standard industrial classification” (SIC) code (industrial category)
  - *Fugitive emissions* must be included
- Contiguous: same as in NSR & PSD programs
- Common Control: same ownership
- Potential to emit: maximum design capacity of the source after pollution controls & restrictions on hours of operation or type & amount of material combusted or processed
  - Limitations must be “*federally enforceable*” (EPA interprets this as “practical enforceability” of state emission limits.)

## Example: Major Source Determination

- Larry’s Printing Co., Curly’s Chemical Co., and Moe’s Wood Furniture Co. are owned by Lou’s Recreational Products Co. and are located in the same industrial complex, but separated by a street and a railroad track.
- Same ownership?
- Contiguous?
- Different SIC Codes

## Calculate PTE

- Printing Co:
  - Wash solvent: 2 *tons toluene/yr*
  - Fountain solution: *1 ton ethylene glycol/yr*
- Chemical Co:
  - Reactor controlled by a scrubber (90%):
    - 60 tons styrene/yr = uncontrolled
    - *6 tons styrene/yr* = after federal enforceable scrubber
    - *2 tons styrene/yr* = fugitive emissions
  - Storage tanks: *4 tons toluene/yr*
- Wood Furniture Co - coating line:
    - 9 tons toluene/yr = maximum emission running 24/7
    - *3 tons toluene/yr* = limit hrs of operation: one shift (fed enforceable)

# Total HAP Emissions

| HAP | Facility | Emission Unit | PTE (tons/yr) | Major (tons/yr) |
|---|---|---|---|---|
| Styrene | Chemical Co. | Reactor | 6.0 | |
| Styrene | Chemical Co. | Fugitive emissions | 2.0 | |
| Total styrene | | | 8.0 | < 10 |
| Toluene | Printing Co. | Wash solvent | 2.0 | |
| Toluene | Chemical Co. | Storage tank | 4.0 | |
| Toluene | Furniture Co. | Coating line | 3.0 | |
| Total toluene | | | 9.0 | < 10 |
| Ethylene glycol | Printing Co. | Fountain solution | 1.0 | |
| Total Eth. glycol | | | 1.0 | < 10 |
| Total HAP | | | 18.0 | < 25 |

# Major Source Can Become an Area Source

- **Oct. 1, 2020: EPA “final rule”** ***It allows a major source to become an area source if it reduces total HAP emissions below the required amount*****.**
  - *Below the major source threshold of* 10 tons/yr. for a single HAP or 25 tons/yr. combined HAPs.
- **Sept. 21, 2023: EPA “proposed rule”** sources reclassifying from major source status to area source status must satisfy the following criteria:
  - Must be *federally enforceable*,
  - Permit *must contain safeguards to prevent emission increases* after reclassification, and
  - Becomes *effective once a permit has been issued*.

# Two Types of Area Sources: *Affected & Unaffected*

- “Applicability provisions” of each MACT will state if the source is subject to the MACT rule
- Affected *area* source: *subject to MACT* in its source category (i.e. dry cleaner & chromium electroplating MACTs)
- Unaffected *area* source: *not subject to MACT* in its source category (i.e. petroleum refinery)
  - An “unaffected area source” can become subject to MACT if its emissions increases to “major source” thresholds (i.e. 10 tons/yr. individual HAP or 25 tons/yr. total HAPs)

# NESHAP Guidelines

- MACT, Residual Risk and Area Source control standards are all commonly called NESHAPs.
  - The reason: NESHAPs regulate both area sources and major sources of HAPs (MACTs only regulate major sources).
  - i.e., Dry Cleaning NESHAP regulates both area & major sources (part MACT) .
  - i.e., Petroleum Refinery NESHAP is all MACT because it regulates only major sources.
- All NESHAPs passed under the 1990 CAAA §112 program are codified at *40 CFR Part 63*.
- All NESHAPs passed prior to the 1990 CAAA §112 program are codified at *40 CFR Part 61*.

# EPA NESHAP Web Site

- This is a link to control regulations for all HAP major and area sources (MACTs & GACTs):
- https://www.epa.gov/stationary-sources-air-pollution/national-emission-standards-hazardous-air-pollutants-neshap-8

# Rules and Implementation: NESHAP

- Rule Summary
- Rule History (Federal Register)
  - Proposed and Final Rules
- Additional Resources
  - Fact Sheets
  - Background Information Documents
  - Implementation Documents
  - Risk Assessment Information
- Compliance Information
  - Implementation Guide
  - Compliance Timetable etc.

## Maximum Achievable Control Technology (MACT)

- Technology-based & costs considered
- All HAP major sources are required to meet MACT: (done in your Title V permit)
- **New** sources
  - *Comply immediately* (upon startup) &
  - Use technology-based control standard based on *best controlled similar sources* (the "MACT floor")
- **Existing** sources
  - *3 years to comply* after promulgation of rule &
  - Use technology-based control standard based on *best controlled 12% of existing sources*

## Dry Cleaning NESHAP (1993)
## 40 CFR 63 Subpart M

| Requirement | Small Area Source | Large Area Source | Major Source |
|---|---|---|---|
| **Applicability**<br>Dry Cleaning Facilities with:<br>1. Only Dry-to-Dry Machines<br>2. Only Transfer Machines<br>3. Both Dry-to-Dry and Transfer Machines | Consuming <:<br>140 gallons PCE/yr.<br>200 gallons PCE/yr.<br>140 gallons PCE/yr. | Consuming equal to or between PCE/yr):<br>140 – 2,100 gallons<br>200 – 1,000 gallons<br>140 – 1,800 gallons | Consuming >:<br>2,100 gallons PCE/yr.<br>1,800 gallons PCE/yr.<br>1,800 gallons PCE/yr. |
| **Process Vent Controls**:<br>Existing Facilities | None | Refrigerated condenser (or equivalent)<br>Carbon adsorbers installed on existing machines before 9/22/93 can remain | |
| New Facilities | Refrigerated condenser (or equivalent) | | Refrigerated condenser and small carbon adsorber (or equivalent) |
| **Fugitive Controls:**<br>Existing Facilities | - Leak detection/repair<br>- Store all PCE solvent & waste in sealed containers | | Transfer machine systems are contained inside a room enclosure |
| New Facilities | - Leak detection/repair<br>- Store PCE solvent & waste in sealed containers<br>- No new transfer machine systems allowed | | |

| Requirement | Small Area Source | Large Area Source | Major Source |
|---|---|---|---|
| **Monitoring:** | New: Same as large area source<br>Existing: None | Refrigerated condenser (RC): Measure the RC outlet temperature at the end of the cycle on dry-to-dry machines or dryer. (Must be <45 degrees F.) Measure the RC inlet & outlet temperature difference on a washer. (Must be >20 degrees F.)<br>Carbon adsorber (CA): Measure the PCE concentration out of the CA with a colorimetric detector tube. (Must be < 100ppm) | |
| **Operation & Maintenance:** | Operate and maintain dry cleaning systems according to manufacturer's specifications and recommendations. | | |
| **Records:** | Each facility must maintain records of PCE purchases and the calculation of yearly PCE consumption each month, along with dated records of all monitoring and leak detection and repair activities. The last 5 years of records must be kept. | | |
| **Reporting & Compliance**:<br>Existing Facilities | Each facility must submit an initial report by 12/20/1993 and compliance report by 1/19/1994. Large Area and Major facilities must comply with process controls by 9/23/1996 and must submit additional compliance report 10/22/96 | | |
| New Facilities | All other new facilities must comply upon start-up with all requirements and submit a compliance report within 30 days from the date the dry cleaner must be in compliance. | | |

## Residual Risk for Dry Cleaners (2006)

- The residual risk standard strengthened air toxic requirements for dry cleaning facilities and is incorporated in the Dry Cleaning NESHAP (40 CFR 63 Subpart M).
  - Required the elimination of all transfer machines (considered the highest-emitting type of dry cleaning equipment), and
  - Required the elimination of all PCE dry-cleaning machines at residential buildings by December 21, 2020.

## 1990 CAAA
## Residual Risk Program

- 6 years after 1990 CAAA, EPA must evaluate *methods* available to evaluate remaining risks from major sources after application of a MACT.
  - Result: 1999 "Residual Risk Report to Congress"
- No more than *8 years after MACT*, EPA must pass a residual risk standard (if necessary).
  - Protect with an "ample margin of safety"
- CAA δ112(d)(5) provides that *residual risk review is not required for area sources* which are subject to GACT standards.

## Risk & Technology Review (RTR)

- EPA must conduct a risk & technology review on MACTs every 8 years.
  - **Technology review**: to determine if there are *new developments in practices or control technologies* that may be appropriate to incorporate into the standards.
  - **Risk review**: conduct a "risk assessment" for any remaining risks and then protect public health with an "ample margin safety." (health-based standard)
  - /risk-and-technology-review-national-emissions-sthttps://www.epa.gov/stationary-sources-air-pollutionandards-hazardous

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  - **Risk review**: conduct a "*risk assessment*" for any remaining risks and then protect public health with an "ample margin safety." (health-based standard)
  - CAA does not limit *EPA's discretion to conduct another risk review* should EPA consider that such review is warranted.
  - /risk-and-technology-review-national-emissions-sthttps://www.epa.gov/stationary-sources-air-pollutionandards-hazardous

## Residual Risks

- For cancer risks > $10^{-4}$, EPA will set a residual risk standard (health based).
- For cancer risks < $10^{-6}$ EPA will not set a residual risk standard.
- For cancer risks in between $10^{-6}$ & $10^{-4}$, EPA will consider costs, technical feasibility, location of people near facility, etc. in deciding on whether to set a residual risk standard.
- For non-cancer risks, EPA will look at target organ hazard info. in deciding on whether to issue a residual risk standard.

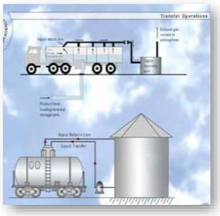
## General Provisions for NESHAP

- (40 C.F.R. Part 63 Subpart A) "general provisions" used to eliminate the need to repeat general information and requirements for each emission standard. They cover:
  - Applicability determinations (i.e. new v. existing)
  - Construction and reconstruction (modification)
  - Compliance extensions & compliance dates
  - Operation & maintenance requirements
  - Methods for determining compliance
  - Procedures for testing, monitoring, malfunctions, reporting, & recordkeeping
- If conflict between general provisions and specific requirements, use specific requirements

## NESHAP Organization

- Applicability determination & Definitions
- Emission standards
  - Process equipment, storage tanks, & wastewater etc.
- Work practice standards: i.e.,
  - Equipment leak detection & repair, operation & maintenance plan, & inspections of control devices, ductwork & monitoring equipment etc.
- Test methods and compliance procedures
  - Initial test for compliance determination
- Monitoring requirements i.e.,
  - Pressure drop across control device, process feed rates, installation of a stack monitor, etc.
- Recordkeeping & Reporting

## Gasoline Distribution Facilities MACT (40 CFR 63 Subpart R)



## Gasoline Distribution Facilities MACT

- §63.420 - **Applicability**: Applies to *Bulk Gasoline Terminals (BGT)* or *Pipeline Breakout Stations (PBS)* that are a major source. The BGT and the PBS are the "affected sources" for this MACT.
  - BGT & PBS are then "screen tested" for applicability.
- §63.421 – **Definitions**: PBS means any facility along a pipeline containing *storage vessels* used … to store gasoline from the pipeline… and continue transport…
- §63.422 – **Standards:** *loading racks* **–** [this MACT regulates the *loading racks* (emission units) from only the BGT affected source]
  - Meet the NSPS for Bulk Gasoline Terminals &
  - Install a vapor collection system with emissions < 10 mg VOC/liter gasoline

## Gasoline Distribution Facilities MACT

- §63.423 – **Standards:** *storage vessels* – [this MACT regulates the storage vessels (emission units) from both affected sources: PBS & BGT]. The standards apply only to gasoline storage vessels having a capacity ≥ 75 $m^3$ (19,813 gallons) and storing gasoline.
  - New sources (built after 2/8/94): Subject to all control provisions under NSPS subpart Kb (§60.110(b))
  - Existing sources: Install Kb floating deck rim seals or a control device on all storage vessels: and install Kb deck fitting on all external floating roof tanks

## Gasoline Distribution Facilities MACT

- §63.424 **Standards**: *Equipment leaks* - equipment leaks from all gasoline equipment (during loading) (for both BGT and PBS) shall perform a monthly *leak inspection (& repair)* of all equipment.
- §63.425 **Test methods**: any storage vessels or loading racks that have installed a vapor processing system must perform *tests* as required under NSPS for Bulk Gasoline Terminals §60.503 (i.e., methods 21,25A, 25B).
- §63.427 **Continuous monitoring (CM)**: CM system required for 4 specified control devices.
- §63.428 **Reporting and Recordkeeping**

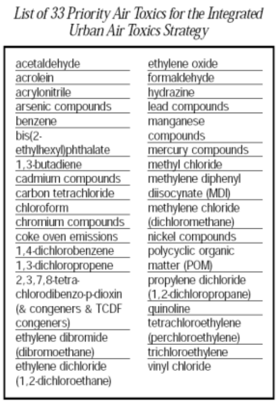
## Novel Concepts in NESHAP (MACT):

### 1990 CAAA: EPA to look at wide variety of emission reduction mechanism to be included in a MACT

- Can dictate the kinds of raw material used or the design of the production unit to minimize emissions
  - Dry cleaners: banned transfer machines on new sources
- Can use emission averaging (i.e. HON)
  - Over-control one emission point in order to under-control another emission point covered by the same MACT
- Use the predominant MACT concept
  - If facility covered by multiple categorical MACTS, may choose predominant MACT (i.e. multiple coating MACTS)
- Incorporate pollution prevention concepts
  - i.e. EPA can prohibit a particular HAP: i.e. (cooling tower MACT) prohibited the use of *chromium* based water treatment chemicals in cooling towers

## Urban Area Source Standards

- 1990 CAAA 112(k)(3)(B) *overlapped* 112(c)(3): *both required the regulation of HAPs from **urban area sources:***
  - *112(k)(3)(B)* required EPA:
    - to list at least 30 HAPs (EPA identified 33 HAP) that causes the greatest threat to public health from *urban area sources* &
    - to list their area source categories (EPA identified 70)
  - *112(c)(3)* required EPA to pass control standards for these source categories by 2000 (after litigation all were finally passed by 2011)



*List of 33 Priority Air Toxics for the Integrated Urban Air Toxics Strategy*

acetaldehyde
acrolein
acrylonitrile
arsenic compounds
benzene
bis(2-ethylhexyl)phthalate
1,3-butadiene
cadmium compounds
carbon tetrachloride
chloroform
chromium compounds
coke oven emissions
1,4-dichlorobenzene
1,3-dichloropropene
2,3,7,8-tetra-chlorodibenzo-p-dioxin (& congeners & TCDF congeners)
ethylene dibromide (dibromoethane)
ethylene dichloride (1,2-dichloroethane)
ethylene oxide
formaldehyde
hydrazine
lead compounds
manganese compounds
mercury compounds
methyl chloride
methylene diphenyl diisocynate (MDI)
methylene chloride (dichloromethane)
nickel compounds
polycyclic organic matter (POM)
propylene dichloride (1,2-dichloropropane)
quinoline
tetrachloroethylene (perchloroethylene)
trichloroethylene
vinyl chloride

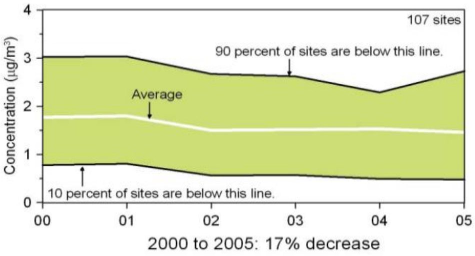
## 33 Urban HAP

From the188 listed HAPs, EPA identified 30 that pose the greatest potential health threat in urban areas. These HAPs are referred to as the 30 urban air toxics. EPA also identified an additional three HAPs, but these HAPs are not generally emitted by area sources and, as such, were not included as part of the 30 urban air toxics. The three additional HAPs are coke oven emissions, 1,2-dibromoethane and carbon tetrachloride.

## Integrated Urban Air Toxics Strategy

- EPA developed the 1999 Integrated Urban Air Toxics Strategy (Strategy) to address the CAA sect. 112(c)(3) & 112(k)(3) overlapping requirements.
- The Strategy regulates 33 HAP in *urban* settings by looking at significant *stationary and mobile sources*. The strategy goals are:
  - 75% reduction in cancer caused from stationary sources
  - Reduce HAP public health risk from area sources
  - Address disproportionate impacts of HAP across urban areas
- https://www.epa.gov/urban-air-toxics/integrated-urban-air-toxics-strategy

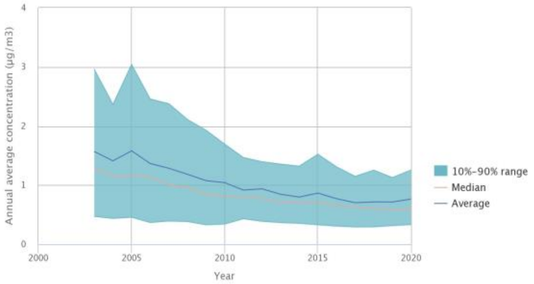
## Ambient Benzene, Nationwide, 2000-2005 (data taken from 107 urban monitoring sites)



2000 to 2005: 17% decrease

Benzene, the most widely monitored toxic air pollutant, is the most significant HAP for which cancer risks can be estimated (**contributes 25% of the average individual cancer risk in 1999 assessment**).

## Ambient Benzene Concentrations, Nationwide, 2003-2020



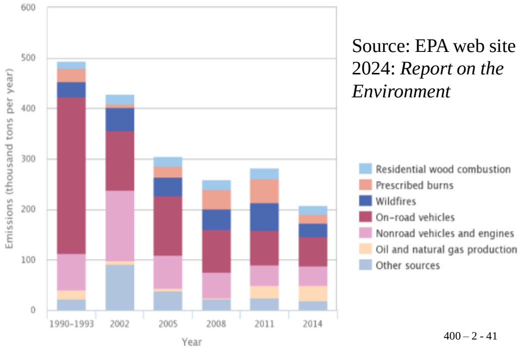
**Coverage:** 133 monitoring sites nationwide (out of a total of 198 sites measuring benzene in 2020) that have sufficient data to assess trends since 2003.

Source: EPA web site 2024: *Report on the Environment*

## 2018 ABA Air Quality Report: Benzene

- **Benzene content in gasoline** is limited by regulation (40 C.F.R. § 80.1230).
- In 2008, EPA created a rule specifically **targeting benzene emissions from gas stations,** which included an extensive discussion of EPA's rationale for controlling benzene (F.R. Jan. 10, 2008).
- EPA data going back to 1990 show that the **emissions of benzene in the US decreased by about 85 percent in the following two decades**, largely due to controlling the amount of benzene in gasoline.
- Today, our major sources of outdoor exposure to benzene are about evenly split between cars, non-road emissions (e.g., lawnmowers), wildfires, and prescribed burns.

## Benzene Emissions 1990 to 2014



Source: EPA web site 2024: *Report on the Environment*

## Mobile Sources

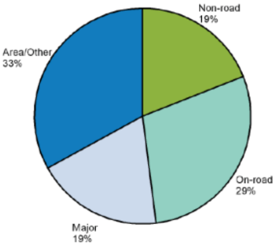
- **On-road** - Vehicles found on roads and highways (e.g., cars, trucks, buses)
- **Non-road** - Mobile sources not found on roads and highways
  - Lawn mower engines, construction vehicles, farm machinery, etc.
  - Aircraft
  - Locomotives
  - Commercial marine vessels
- **EPA web-site** for On-road & off-road air regulations



# Mobile Sources

- About 50% of air toxics are from mobile sources
- Much of the historical focus of mobile source emissions reduction has been on on-road cars, trucks & their fuel (under CAA Title II).
- Non-road engines are also sources of air toxics & are coming under increasing focus
- EPA uses Integrated Urban Air Toxics Strategy plus MSAT rule to regulate HAP from mobile sources.

U.S. HAP Emissions by Source: 2002



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## The 1990 CAAA §202(l) Addressed Toxic Pollutants from Mobile Sources for the First Time

- Section 202(l) directed EPA to set HAP standards from motor vehicles and their fuels:
  - 2001: ***Mobile Source Air Toxic* (MSAT) *Rule***
    - EPA identified 21 mobile source HAP; &
    - Established toxic emission performance standards for gasoline refineries.
  - 2007: Final rule to reduce mobile source air toxics:
    - By 2015 refineries: lower benzene in gas to 0.62% (in 2007 it was 1.06%).
    - Reducing NMHC exhaust standards from cars when operating cold, etc.

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# 21 Mobile Source Air Toxics Listed in 2001 MSAT Rule

- acetaldehyde
- acrolein
- arsenic compounds
- benzene
- 1,3-butadiene
- chromium compounds
- diesel particulate matter and diesel exhaust organic gases (DPM + DEOG)
- dioxin/furans
- ethyl benzene
- formaldehyde
- n-hexane
- lead compounds
- manganese compounds
- mercury compounds
- methyl tertiary butyl ether (MTBE)
- naphthalene
- nickel compounds
- polycyclic organic matter (POM)
- styrene
- toluene
- xylene

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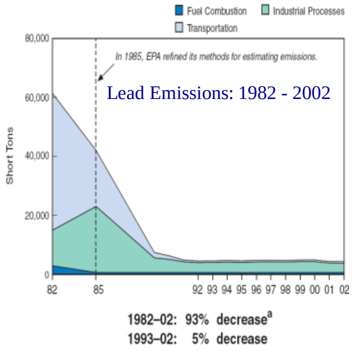
# Mobile Sources: Leaded-Gas Regs

- 1973: EPA banned lead in cars with catalytic converters.
- 1977: EPA began a phase down of the average lead content in all gasoline.
- 1990 CAAA: banned the sale of leaded gas for use in all motor vehicles by Dec 1995.



Lead Emissions: 1982 - 2002

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## Mobile Sources: Diesel Exhaust

- *EPA (1999 Report)*: Diesel exhaust a "*likely human carcinogen*"
- In 2001, EPA passed a Diesel Rule for regulating on-road (highway) diesel engines & fuels.
  - PM & NOx emissions limits took effect in 2007 model
  - *Also* regulates the sulfur content of fuel (because sulfur can damage control devices & increase PM emissions).
- In 2004, EPA passed the Clean Air Non-road Diesel Rule that regulated non-road engines starting in 2007.
  - Low sulfur (500 ppm) fuel was phased in for non-road, locomotive, and marine diesel fuel from 2007-2014

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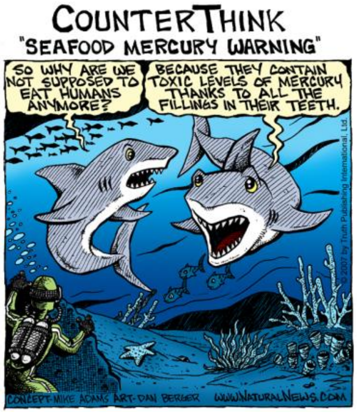


## Coal Fired Electric Power Plants

- 1990 CAAA required EPA to <u>study</u> & report on <u>mercury</u> emissions & its sources, possible controls & impacts. The *1997 Mercury Report*:
  - Primary mercury source is <u>coal fired utilities</u> &
  - Control technology is in research stage.
- 1990 CAAA required EPA to <u>study</u> & report on <u>HAP from power plants</u>. The *1998 & 1999 EPA reports*:
  - Mercury from coal fired utilities is the HAP of greatest concern to public health. Others that need further study are dioxins, arsenic & nickel.
- In 2000 (F.R.), the <u>EPA added EGUs</u> to the <u>δ112(c)</u> list of major HAP source categories. (EGUs were not on EPA's original list.)

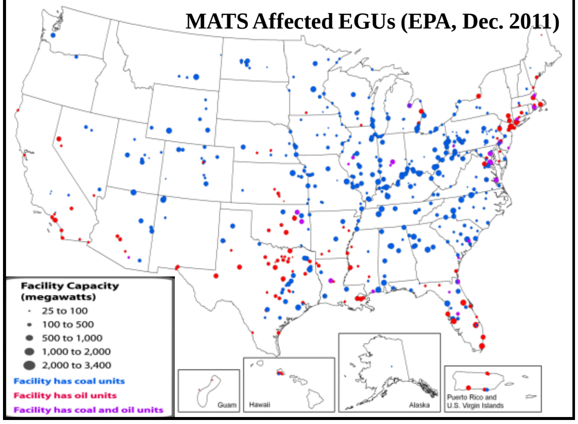
## Mercury Emissions from Power Plants

- In 2002, Bush <u>proposed</u> "*<u>Clear Skies Initiative</u>*" that called for 70% reduction in mercury emissions from power plants by 2018. (statute never passed)
- 2005: EPA passed the *Clean Air Mercury Rule* (CAMR)
  - Required <u>coal-fired power plants</u> to reduce <u>mercury</u> emissions by 70% by establishing a <u>"cap & trade"</u> program (as a NSPS).
  - The Rule took EGUs off the <u>δ112(c) list</u> & regulated them under NSPS (<u>δ111(d)</u>) & said that <u>MACT approach not necessary</u>.
- In 2008, Ct. **vacated** CAMR & said EPA cannot delist EGUs because it did not follow δ112(c)(a) delisting procedures. EPA must establish a δ112 mercury MACT for power plants & can't substitute a NSPS for it.

## Mercury Emissions from Power Plants

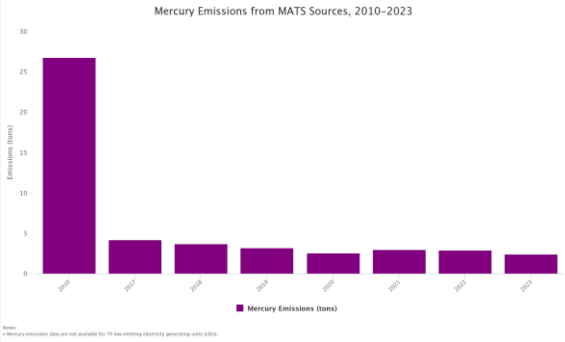
- On Feb 6, 2012, EPA passed a <u>coal &/or oil fired power plant</u> mercury MACT (called <u>MATS</u> – Mercury Air Toxic Standard)
  - <u>Applies</u> to EGUs larger than 25 megawatts (MW) that burn coal or oil for the purpose of generating electricity (600 power plants).
  - Will <u>reduce</u> emissions of <u>mercury</u> & other HAPs:
    - Heavy metals (mercury, arsenic, chromium, & nickel) & acid HAP gases HCl & HF, and
    - Organic HAP such as formaldehyde and dioxins/furans from coal- and oil-fired power plants.

**MATS Affected EGUs (EPA, Dec. 2011)**



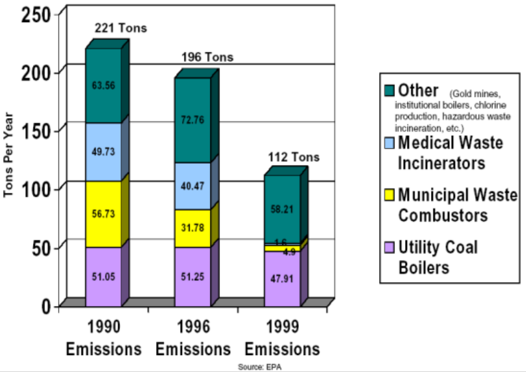
## Mercury Emissions from Power Plants

- **In 2016**, EPA finds that the <u>cost of compliance with MATS is reasonable</u> to satisfy the *2015 SCOTUS requirement*.
  - <u>Costs</u> = $10 billion/yr.
  - <u>Benefits</u> = $6 billion/yr. from mercury reductions only;
  - <u>Co-benefits</u> = $60 billion/yr. from reductions of non-HAPs
- **May 22, 2020**: <u>EPA rejects the value of co-benefits,</u> therefore the *costs* of such regulation grossly outweigh the HAP benefits.
- **Feb 15, 2023**: EPA <u>final rule</u>: This action <u>revokes the above 2020 rule</u>. (EPA's <u>will use the previous, 2016, cost analysis.)</u>
- **April 25, 2024**: EPA <u>final rule</u>:
  - That lignite-fired EGUs meet the same mercury emission standard as EGUs firing other coal-fired power plants, &
  - To further limit the emission of non-mercury HAP metals from existing coal-fired power plants (PM as a surrogate & CEMs required).



Source: EPA 2024 *Power Sector Programs Progress Report*

## Mercury Emissions Have Dropped 45% Since 1990



Source: EPA

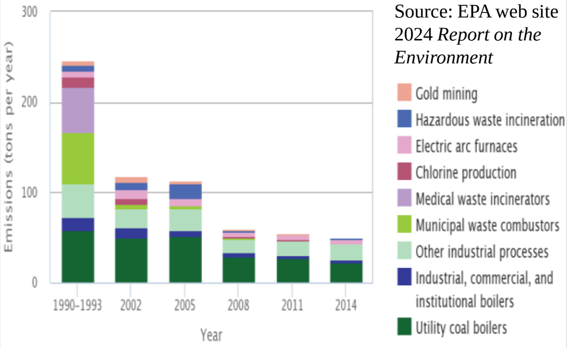
## Solid Waste Combustion: CAA δ129

- δ129 was added (1990 CAAA) & required EPA to pass <u>NSPS</u> for new & existing <u>solid waste combustion units</u>.
  - *Municipal waste combustion units* (MWC)
  - *Hospital/medical/infectious waste incinerators*
  - Commercial & industrial solid waste incinerators
  - Other solid waste incinerators (small, residential, agricultural & construction waste, wood waste, crematories, & contaminated soil treatment waste)
- δ129 limits emissions of particulate matter, carbon monoxide, dioxins/furans, sulfur dioxide, nitrogen oxides, hydrogen chloride, lead, **mercury**, and cadmium
- δ129 <u>does not regulate</u> incineration of <u>hazardous waste</u>.

## Recent Mercury Regulations

- <u>August 2010</u>: EPA issued final NESHAP requiring reductions of mercury emission from **cement plants** (*third-largest source* of mercury air emissions in the U.S.)
- <u>Dec 2010</u>: EPA issued final NESHAP for **gold ore processing & production** facilities (*sixth-largest source* of mercury air emission in the U.S.)

## Anthropogenic Mercury Emissions in the U.S. by Stationary Source Category: 1990 - 2014



Source: EPA web site 2024 *Report on the Environment*

## Prevention of Accidental Releases: CAA §112(r)

- <u>Purpose</u>: prevent disastrous accidental releases
- <u>Facilities</u> that store or handle ***extremely hazardous substances*** over a "threshold limit" must submit a ***risk management plan*** for each hazardous substance used
  - EPA lists 100 substances w/threshold limit: [40 CFR 68.130] 1994
- <u>Risk management plan</u> (RMP) due 1999 (5 yr. updates):
  - Hazardous assessment
    - Hazardous effects & facility's history of releases for the last 5 years
  - Program to prevent accidental releases
  - Emergency response program (in case of an accidental release)
- Dec 2019: Final Rule relaxing some RMP requirements
- RMP Information | Emergency Management | US EPA

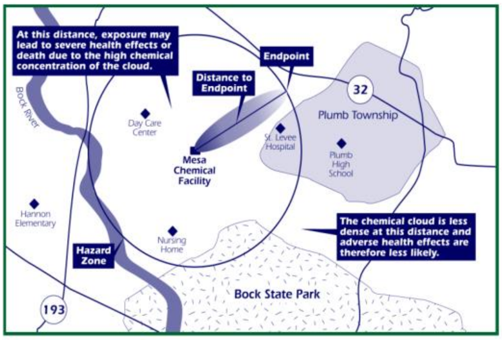


**Figure 3:** This is a typical map found in an RMP, showing hazardous areas, vulnerable populations, and sensitive environments. This map shows the endpoint, distance to endpoint, and the hazard zone for one possible scenario. The hazard zone is a circle because wind variability could cause the toxic cloud or fire

## General Duty Clause

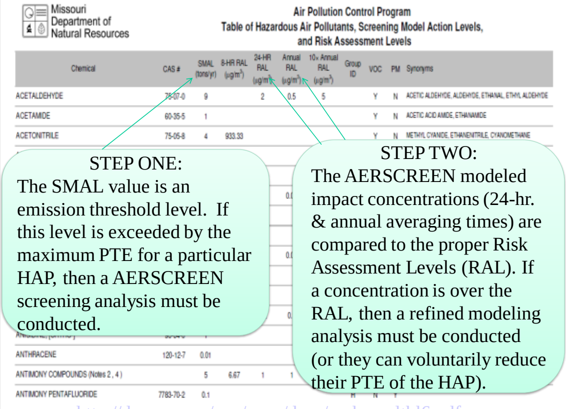
- CAAA of 1990, Congress enacted δ112(r)(1), also known as the ***General Duty Clause*** (GDC), which makes the owners and operators of facilities that have **regulated substances (40 CFR 68.130) and other extremely hazardous substances** responsible for ensuring that their chemicals are managed safely.
  - **Maintain a safe facility** to *prevent accidental releases, and minimize the consequences of accidental releases* that occur.
  - "**Extremely hazardous substances**" are not defined in Section 112(r). They are not limited to the list of regulated substances under Section 112(r) nor the extremely hazardous substances under EPCRA.
- In 2010, BP paid a $15 million civil penalty for GDC violations from explosions at its Texas City Refinery.

## State Programs

- CAA §112(l) allows state & local, air toxics programs to be implemented rather than other applicable §112 standards.
- Delegation in 3 ways:
  - EPA may delegate to state authority to implement fed HAP program.
  - States may substitute a state rule that is no less stringent for an EPA industry-specific rule.
  - States may substitute an approved state air toxic program that is no less stringent than fed program.

## Some State HAP Programs Could Enhance Fed HAP Program

- State programs vary in the number of toxics covered:
  - i.e. California and Oregon listing as many as 600 additional toxics over EPA HAPs, and Washington listing over 400 toxics.
- Also, the methodology for determining health impacts of a given pollutant may vary from state to state. Different states are responding in different ways, resulting in a patchwork of air thresholds and permitting requirements.
- In some states, if a HAP PTE exceeds a state's HAP threshold level, a screening analysis is required. If this fails, further reviews that includes a health impact assessment are required.



Missouri Department of Natural Resources

Air Pollution Control Program
Table of Hazardous Air Pollutants, Screening Model Action Levels, and Risk Assessment Levels

| Chemical | CAS # | SMAL (tons/yr) | 8-HR RAL (µg/m³) | 24-HR RAL (µg/m³) | Annual RAL (µg/m³) | 10x Annual RAL (µg/m³) | Group ID | VOC | PM | Synonyms |
|---|---|---|---|---|---|---|---|---|---|---|
| ACETALDEHYDE | 75-07-0 | 9 | | 2 | 0.5 | 5 | | Y | N | ACETIC ALDEHYDE, ALDEHYDE, ETHANAL, ETHYL ALDEHYDE |
| ACETAMIDE | 60-35-5 | 1 | | | | | | Y | N | ACETIC ACID AMIDE, ETHANAMIDE |
| ACETONITRILE | 75-05-8 | 4 | 933.33 | | | | | Y | N | METHYL CYANIDE, ETHANENITRILE, CYANOMETHANE |
| ANTHRACENE | 120-12-7 | 0.01 | | | | | | | | |
| ANTIMONY COMPOUNDS (Notes 2, 4) | | 5 | 6.67 | 1 | 1 | | | | | |
| ANTIMONY PENTAFLUORIDE | 7783-70-2 | 0.1 | | | | | | | | |

STEP ONE:
The SMAL value is an emission threshold level. If this level is exceeded by the maximum PTE for a particular HAP, then a AERSCREEN screening analysis must be conducted.

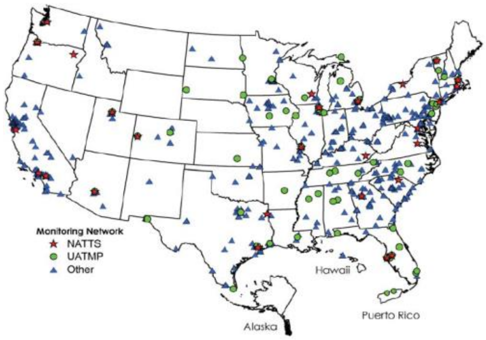
STEP TWO:
The AERSCREEN modeled impact concentrations (24-hr. & annual averaging times) are compared to the proper Risk Assessment Levels (RAL). If a concentration is over the RAL, then a refined modeling analysis must be conducted (or they can voluntarily reduce their PTE of the HAP).

http://dnr.mo.gov/env/apcp/docs/cp-hapraltbl6.pdf

## HAP Air Monitoring Network

- EPA does not maintain an extensive air monitoring network for HAP, as they do for criteria pollutants, but have established:
  - 27 (17 urban) National Air Toxic Trends Stations (NATTS). These are monitoring sites that focus on high-risk HAP such as benzene, formaldehyde, 1,3 butadiene, acrolein & chromium.
  - About 300 state HAP monitoring sites under the Urban Air Toxics Monitoring Program (UATMP).

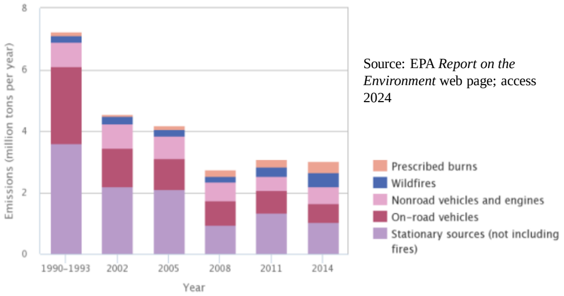
## HAP Monitoring Sites: 2007



## National Emission Inventory (NEI)

- NEI *tracks both HAP & criteria pollutants*.
  - https://www.epa.gov/air-emissions-inventories
- EPA uses the NEI to estimate and track national emissions trends for the188 HAPs.
  - NEI data available to EPA modelers for use in the *National Air Toxics Assessment (NATA) & AirToxScreen.*
  - NEI data will be used in *residual risk and technology assessments* conducted by EPA.

## Air Toxic Emissions in the U.S. by Source Category, 1990-2014



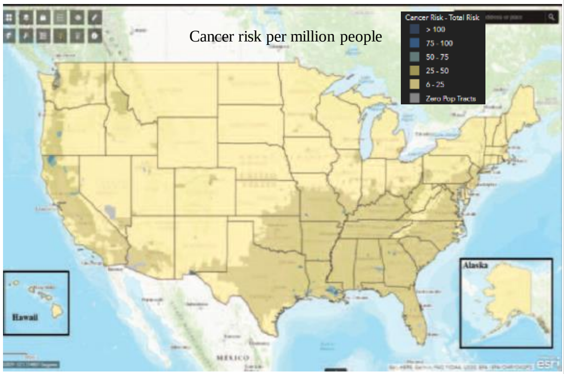
Source: EPA *Report on the Environment* web page; access 2024

Note: 2008 year not representative because emission inventory data not calculated like the other years.

## National Air Toxic Assessment (NATA)

- The **National-Scale Air Toxic Assessment** (NATA), is a nationwide modeling study of ambient levels, inhalation exposures, and health risks associated with air toxic emissions.
- NATA is a screening tool to prioritize pollutants, emission sources and locations of interest for further study in order to gain a better understanding of risks.
- NATA assessment is based on data from the most recent NEI.
- https://www.epa.gov/national-air-toxics-assessment

## 2014 National Air Toxic Assessment of Cancer Risk



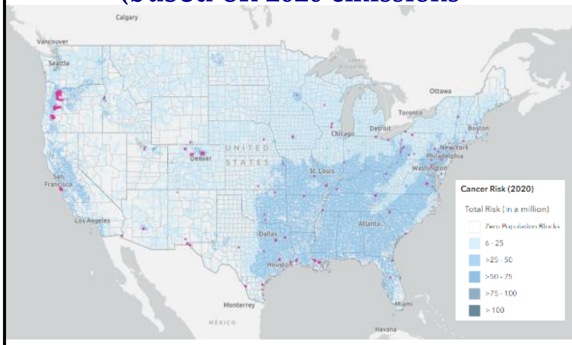
Cancer risk per million people

Source: EPA2014; https://gispub.epa.gov/NATA/(accessed June 23, 2020).

## AirToxScreen

- **AirToxScreen** is replacing the National Air Toxics Assessment (NATA). EPA's last NATA was released in August 2018 using 2014 emissions data. NATA, and its successor, AirToxScreen, are EPA screening tools, used to identify which pollutants, emission sources, and places states may wish to study further to better understand any possible risks to public health from air toxics.
- NATA was released every 3 to 4 years, where the AirToxScreen assessment is released annually.
- https://www.epa.gov/AirToxScreen/airtoxscreen-overview

## AirToxScreen Mapping Tool (based on 2020 emissions)



## 2014 NATA: Formaldehyde

- The U.S. EPA 2014 NATA has identified formaldehyde as the hazardous air pollutant that contributes more than half of the U.S. average estimate of incremental cancer risk and roughly one third of the respiratory effects hazard quotient, making it the leading air toxic that is regulated under Section 112 of the CAA .

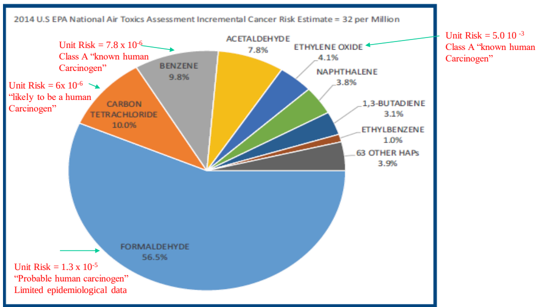


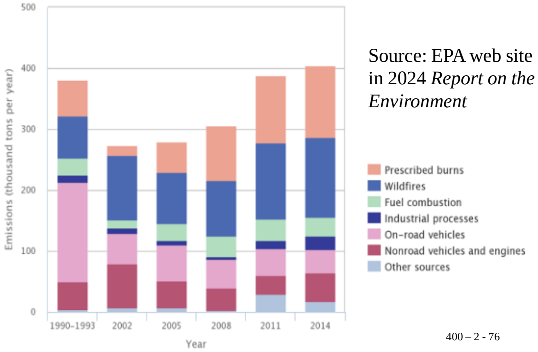
**Figure 2.** HAP Attribution to the 2014 NATA U.S. Average Incremental Cancer Risk Estimate of 32 per million.

Source: AWMA EM Magazine January 2019

## Formaldehyde

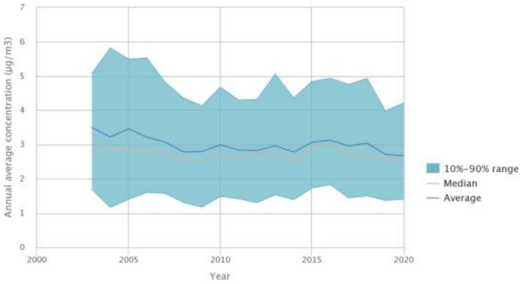
- In 2017, the majority of stationary source formaldehyde emissions are from landfills (64%).
- Landfill gas to energy emissions engines: one 1.6 MW engine can emit 8.7 tons/yr. of formaldehyde, and if engine is *poorly maintained* it can emit over 10 tons/yr. (making it a major source of HAPs).

## Formaldehyde Emissions 1990 to 2014



Source: EPA web site in 2024 *Report on the Environment*

## Ambient Formaldehyde Concentrations in the U.S. 2003 to 2020

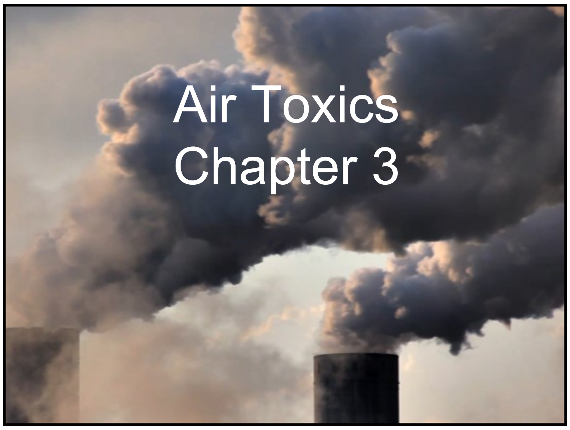


**Coverage:** 59 monitoring sites nationwide (out of a total of 73 sites measuring formaldehyde in 2020) that have sufficient data to assess trends since 2003.

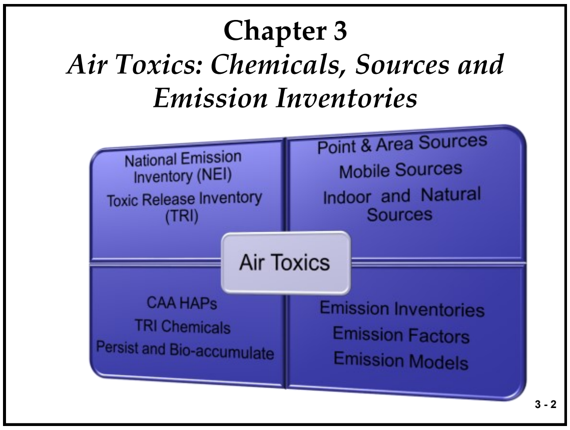
Source: EPA web site in 2024 *Report on the Environment*

## Ethylene Oxide (EtO)

- The latest National Air Toxics Assessment, identified EtO as a potential concern in several areas.
- After a *risk assessment* on the Miscellaneous Organic Chemical Manufacturing MACT, EPA passed a *residual risk rule (August 2020)* that requires additional controls on their equipment that emit ethylene oxide.
- On April 5, 2024, EPA passed a *residual rule* for commercial sterilizers (90 sterilizers in the US):
  - EPA strengthened the standards by using air pollution controls to obtain over 90% reduction in EtO emissions from commercial sterilizers nationwide.
    - New standards for sterilization vents (and other vents) and for EtO emissions from room air, etc.



Air Toxics
Chapter 3



## Chapter 3

*Air Toxics: Chemicals, Sources and Emission Inventories*

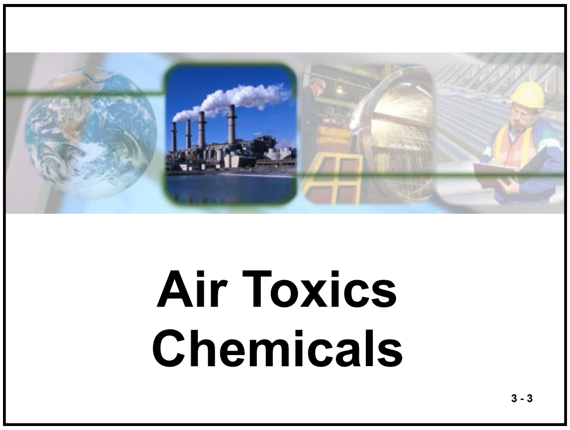
National Emission Inventory (NEI)
Toxic Release Inventory (TRI)

Point & Area Sources
Mobile Sources
Indoor and Natural Sources

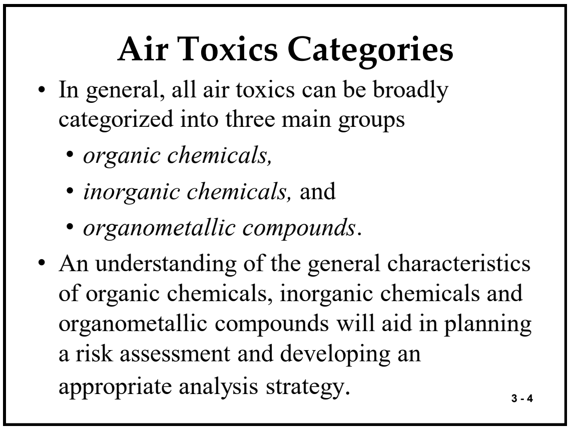
Air Toxics

CAA HAPs
TRI Chemicals
Persist and Bio-accumulate

Emission Inventories
Emission Factors
Emission Models

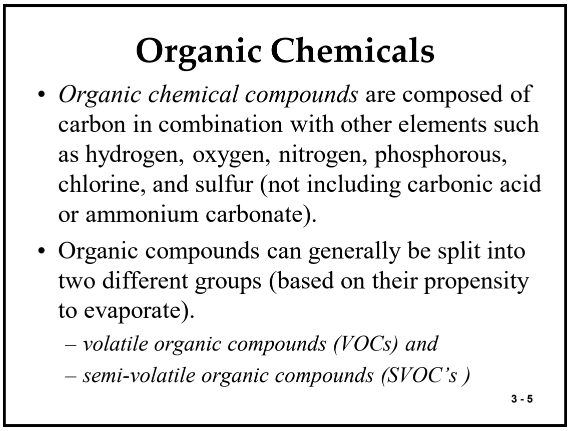


## Air Toxics Chemicals



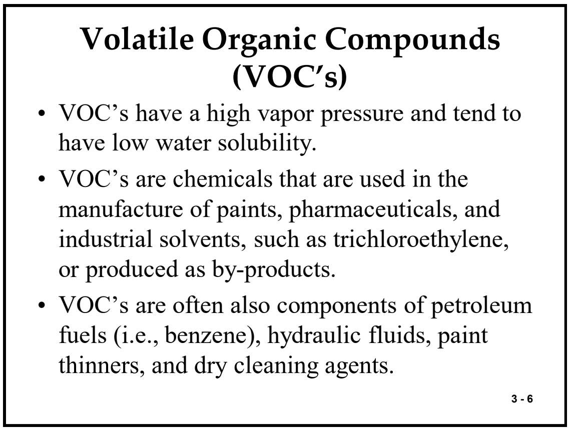
## Air Toxics Categories

- In general, all air toxics can be broadly categorized into three main groups
  - *organic chemicals,*
  - *inorganic chemicals,* and
  - *organometallic compounds*.
- An understanding of the general characteristics of organic chemicals, inorganic chemicals and organometallic compounds will aid in planning a risk assessment and developing an appropriate analysis strategy.



## Organic Chemicals

- *Organic chemical compounds* are composed of carbon in combination with other elements such as hydrogen, oxygen, nitrogen, phosphorous, chlorine, and sulfur (not including carbonic acid or ammonium carbonate).
- Organic compounds can generally be split into two different groups (based on their propensity to evaporate).
  - *volatile organic compounds (VOCs) and*
  - *semi-volatile organic compounds (SVOC's )*



## Volatile Organic Compounds (VOC's)

- VOC's have a high vapor pressure and tend to have low water solubility.
- VOC's are chemicals that are used in the manufacture of paints, pharmaceuticals, and industrial solvents, such as trichloroethylene, or produced as by-products.
- VOC's are often also components of petroleum fuels (i.e., benzene), hydraulic fluids, paint thinners, and dry cleaning agents.

## Semi-Volatile Organic Compounds (SVOCs )

- SVOCs are organic chemicals that have a lower vapor pressure than VOCs.
  - Therefore, SVOCs have a lower propensity to evaporate from the liquid or solid form (compared to VOCs).
- Examples of SVOCs include most organic pesticides (e.g., chlordane), and certain components of petroleum, such as polycyclic aromatic hydrocarbons.

## Inorganic Chemicals

- The *inorganic chemicals group* includes all substances that do not contain carbon and includes a wide array of substances such as:
  - Metals (i.e., mercury, lead, and cadmium) and their various salts (e.g., mercury chloride);
  - Halogens (i.e., chlorine and bromine);Inorganic bases (e.g., ammonia); and
  - Inorganic acids (e.g., hydrogen chloride, sulfuric acid).

## Organometallic Compounds

- The *organometallic compounds group* is comprised of compounds that are both organic and metallic in nature.
- Example: Alkyl lead compounds were added to gasoline to enhance its properties "Alkyl" refers to the organic portion of a compound which is attached to the inorganic metal lead. The result is a so-called "organometallic" material, a hybrid of both metallic and organic.

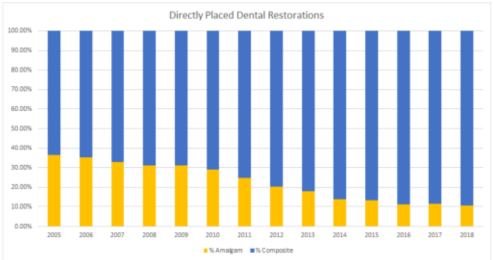
## Toxic Chemical Legislation and Programs

- Clean Air Act list of 188 HAP's
- Clean Air Act Section 112 (k) 33 Urban HAP's
- Persistent Bio-accumulative Toxics (PBT's)
- Long-Range Trans-boundary Air Pollution (LRTAP) Persistent Organic Pollutants (POPs) and heavy metals
- TRI Chemicals
- EPCRA Chemicals
- State and local agency lists

## Minamata Convention on Mercury

- A global United Nations treaty to control the use and trade of heavy metal mercury signed in 2013.
- It is the world's first legally binding agreement on the toxic substance.
- The treaty envisages the phasing out a myriad of products containing mercury, the manufacture, import and export many products, including mercury thermometers, by 2020.
- It also gives governments 15 years to end all mercury mining.
- Dental fillings which use mercury amalgam are also regulated under the convention, and their use must be phased down through a number of measures.

## Minamata Convention Conference of Parties 4 Statement American Dental Association and International Association for Dental Research April 2020



ADA_and_IADR_DentalAmalgam.pdf (mercuryconvention.org)

## HAP Groups in the CAA

- Polycyclic organic matter (POM) & naphthalene
- Dioxins and furans
- Metals (Lead, Arsenic (including arsine), Chromium, Mercury, etc. Compounds)
- Cyanide compounds
- Glycol Ethers
- Xylenes
- Cresols

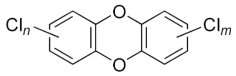
https://www3.epa.gov/airtoxics/agghapsmemo3.pdf

## Polycyclic Organic Matter (POM)

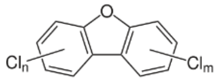
- "Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100° C"
- Examples include polycyclic aromatic hydrocarbons (PAHs), chrysene, benzo(a)pyrene, and naphthalene
- Naphthalene is unique in that it is listed as a separate HAP on the 188 list

## Dioxins and Furans PCDE Background

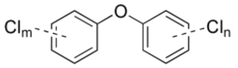
Compound Structures



Chlorinated dibenz(p)dioxin

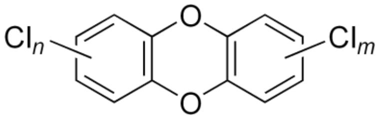


Chlorinated dibenzofuran



Chlorinated diphenyl ether

## Polychlorinated dibenzo(p)Dioxin



12 carbon atoms (~12 amu)

2 oxygen atoms (~32 amu)

Up to 8 positions where chlorine atoms can be substituted

Base mass with no chlorine = 184 amu

Multiple chlorine atoms add mass in increments of ~35 or 37 amu

## Dioxin-Furan Formation

- PCDD and PCDF
  - Stable & persistent
  - Combustion generated
- Toxicity
  - Very low levels are of concern
- PIC formation
  - Mostly from Cl aromatics, but . . .
  - Some organic fragments required
- Sources
  - Transformer fires, bad incinerators, forest fires
- Elimination

## Sources of Dioxins and Dioxin-like Compounds (DLC's) in the Environment

- DLCs are unintended byproducts of combustion, except for the dioxin-like PCBs.
- Combustion processes forming dioxins include waste incineration (e.g., municipal solid waste, sewage sludge, medical waste, and hazardous waste), burning of various fuels (e.g., coal, wood, and petroleum products), other high-temperature sources (e.g., cement kilns), and poor or uncontrolled combustion sources (e.g., forest fires, volcanic eruptions, building fires, and residential wood burning)

## Other Sources of DLC’s

- Metals Smelting and Refining
- There are several types of primary and secondary metal smelting and refining operations, including iron ore sintering, steel production, and scrap metal recovery.
- Such operations use both ferrous and nonferrous metals.

## Other Sources of DLC’s

- Secondary smelting and refining of nonferrous metals such as aluminum, copper, lead, and zinc may result in formation of DLCs, due to combustion of organic impurities (e.g., plastic, paints, and solvents) in the metals and chlorine-containing chemicals (e.g., sodium chloride and potassium chloride) used in the smelting process (Aittola et al., 1992; EPA, 1987, 1997, as cited in EPA, 2000).

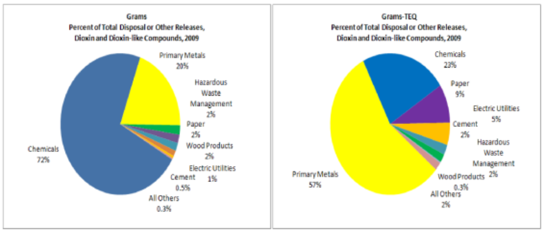
## Dioxins and Furans

- Dibenzofurans and 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) are listed on the 188 list
- EPA inventories all dioxins and furans
- Dioxins occur in the environment in complex mixtures of 210 congeners and have different toxicities
- Compounds can be grouped by 2,3,7,8 TCDD for Toxic Equivalents (TEQs)
- TEQs are multipliers for some dioxin and furan congeners to get to a common basis of toxicity
- For some air quality models, dioxins will require more refined inventory (not sufficient to report TEQs)

http://www.epa.gov/tri/lawsandregs/teq/teqpfinalrule.html

**http://www.greenfacts.org/en/dioxins/toolboxes/teq-explanations.htm**

## Summary Statistics – Persistent and Bioaccumulative and Toxic chemicals (PBTs)



Releases of dioxin and dioxin-like compounds
– Difference between dioxin grams and dioxin TEQs by sector (http://www.epa.gov/tri/lawsandregs/teq/teqpfinalrule.html)
– Total disposal or other releases in 2009 about 32,000 g
– Dioxin in grams decreased 18% from 2008 to 2009

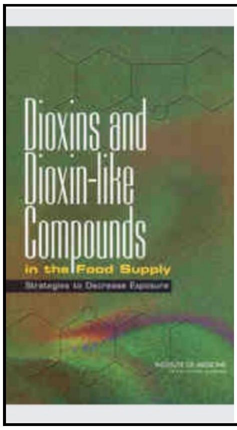
## Toxic Equivalent Factors (TEF) for the 17 "toxic" congeners

| Dioxins | Factor (TEF) | | Factor (TEF) |
|---|---|---|---|
| 2,3,7,8-TCDD | 1 | 2,3,7,8-TCDF | 0.1 |
| | | 2,3,4,7,8-PeCDF | 0.5 |
| 1,2,3,7,8-PeCDD | 0.5 | 1,2,3,7,8-PeCDF | 0.05 |
| 1,2,3,4,7,8-HxCDD )<br>1,2,3,6,7,8-HxCDD )<br>1,2,3,7,8,9-HxCDD ) | 0.1 | 1,2,3,4,7,8-HxCDF<br>1,2,3,7,8,9-HxCDF<br>1,2,3,6,7,8-HxCDF<br>2,3,4,6,7,8-HxCDF | 0.1 |
| 1,2,3,4,6,7,8-HpCDD | 0.01 | 1,2,3,4,6,7,8-HpCDF) | 0.01 |
| | | 1,2,3,4,7,8,9-HpCDF) | 0.01 |
| OCDD | 0.001 | OCDF | 0.001 |

| | |
|---|---|
| 2,3,7,8-Tetrachlorodibenzo-p-Dioxin | 1 |
| 1,2,3,7,8-Pentachlorodibenzo-p-Dioxin | 0.5 |
| 2,3,4,7,8-Pentachlorodibenzofuran | 0.5 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | 0.1 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-Dioxin | 0.1 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 0.1 |
| 1,2,3,7,8,9-Hexachlorodibenzo-p-Dioxin | 0.1 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | 0.1 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-Dioxin | 0.1 |
| 2,3,7,8-Tetrachlorodibenzofuran | 0.1 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | 0.1 |
| 1,2,3,7,8-Pentachlorodibenzofuran | 0.05 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-Dioxin | 0.01 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran | 0.01 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | 0.01 |
| Octachlorodibenzofuran | 0.001 |
| Octachlorodibenzo-p-Dioxin | 0.001 |

## How TEQs Are Calculated

- In order to calculate a TEQ, a toxic equivalent factor (TEF) is assigned to each member of the dioxin and dioxin-like compounds category. The TEF is the ratio of the toxicity of one of the compounds in this category to the toxicity of the two most toxic compounds in the category, which are each assigned a TEF of 1: 2,3,7,8-tetrachlorodibenzo-p-dioxin (commonly referred to as dioxin) and 1,2,3,7,8-pentachlorodibenzo-p-dioxin. TEFs that have been established through international agreements currently range from 1 to 0.0001.
- A TEQ is calculated by multiplying the actual grams weight of each dioxin and dioxin-like compound by its corresponding TEF (e.g., 10 grams X 0.1 TEF = 1 gram TEQ) and then summing the results. The number that results from this calculation is referred to as grams TEQ.
- For example, consider the following 60g mixture:
  10g of compound A, with a TEF of 1
  20g of compound B, with a TEF of 0.5
  30g of compound C, with a TEF of 0.2.
- The TEQ of this mixture would be:
  (10g x 1) + (20g x 0.5) + (30g x 0.2) = 26g TEQ,
- In other words, this mixture of 60g of various compounds would be as toxic as 26g of either of the two most toxic compounds.



**Further Reading:**

**http://nap.edu/10763**

## Air Toxic Metals

☐ Antimony Compounds
☐ Arsenic Compounds
☐ Beryllium Compounds
☐ Cadmium Compounds
☐ Chromium Compounds
☐ Hexavalent and trivalent (non-toxic)
☐ Cobalt Compounds
☐ Lead Compounds
☐ Organic and inorganic
☐ Manganese Compounds
☐ Mercury Compounds
Particulate, gaseous elemental, and gaseous divalent
☐ Nickel Compounds
☐ Nickel subsulfide and other nickel compounds
☐ Selenium

## Cyanide Compounds

- Includes: Hydrogen cyanide, Zinc cyanide, Potassium ferrocyanide, etc.
- NATA Methodology: "Convert" (mass adjustment) all cyanides to hydrogen cyanide equivalents and group as "cyanide compounds"

  Example: To quantify how much hydrogen cyanide emissions would result from silver cyanide (AgCN):
  Molecular Weight of AgCN is 133.8857
  Molecular Weight of HCN is 27.0256
  Factor = 27.0256/133.8857= 0.2019
  Equivalent emissions of HCN = AgCN Emissions * 0.2019

## Glycol Ethers

- "Includes moni-and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol…Polymers are excluded from the glycol category."
- Over 50 individual compounds in NEI pollutant code look up table
- https://deq.nc.gov/about/divisions/air-quality/air-quality-rules/haps-taps

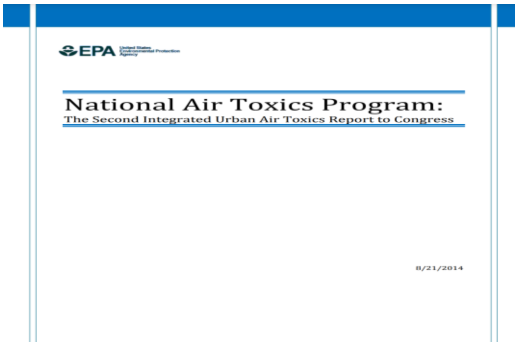
## Xylenes and Cresols

- Xylenes: mixture of o-,m- and p- isomers
- Cresols: mixture of o-,m- and p- isomers, cresylic acid

**Note: NATA, not currently using the isomers.**

# 33 Urban HAPs

Acetaldehyde
Acrolein
Acrylonitrile
Arsenic compounds
Benzene
Beryllium compounds
1, 3-Butadiene
Cadmium compounds
Carbon tetrachloride
Chloroform
Chromium compounds
Coke oven emissions
1, 3-Dichloropropene
Diesel particulate matter
Ethylene dibromide
Ethylene dichloride
Ethylene oxide
Formaldehyde
Hexachlorobenzene
Hydrazine
Lead compounds
Manganese compounds
Mercury compounds
Methylene chloride
Nickel compounds
Perchloroethylene
Polychlorinated biphenyls (PCBs)
Polycyclic organic matter (POM)*
Propylene dichloride
Quinoline
* 1, 1, 2, 2-Tetrachloroethane
Trichloroethylene
Vinyl chloride


EPA United States Environmental Protection Agency

National Air Toxics Program:
The Second Integrated Urban Air Toxics Report to Congress

8/21/2014

The Second Integrated Urban Air Toxics Report to Congress (epa.gov)

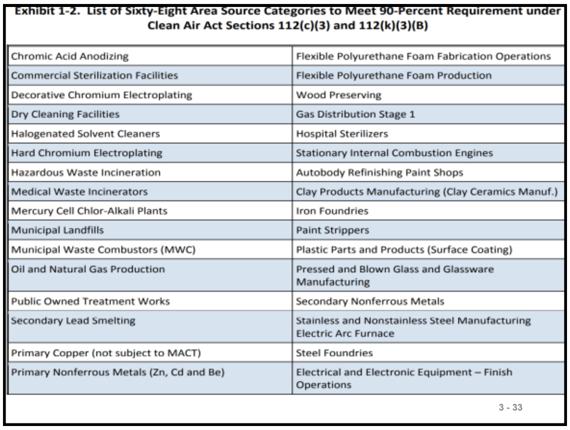


**Exhibit 1-2. List of Sixty-Eight Area Source Categories to Meet 90-Percent Requirement under Clean Air Act Sections 112(c)(3) and 112(k)(3)(B)**

| | |
|---|---|
| Chromic Acid Anodizing | Flexible Polyurethane Foam Fabrication Operations |
| Commercial Sterilization Facilities | Flexible Polyurethane Foam Production |
| Decorative Chromium Electroplating | Wood Preserving |
| Dry Cleaning Facilities | Gas Distribution Stage 1 |
| Halogenated Solvent Cleaners | Hospital Sterilizers |
| Hard Chromium Electroplating | Stationary Internal Combustion Engines |
| Hazardous Waste Incineration | Autobody Refinishing Paint Shops |
| Medical Waste Incinerators | Clay Products Manufacturing (Clay Ceramics Manuf.) |
| Mercury Cell Chlor-Alkali Plants | Iron Foundries |
| Municipal Landfills | Paint Strippers |
| Municipal Waste Combustors (MWC) | Plastic Parts and Products (Surface Coating) |
| Oil and Natural Gas Production | Pressed and Blown Glass and Glassware Manufacturing |
| Public Owned Treatment Works | Secondary Nonferrous Metals |
| Secondary Lead Smelting | Stainless and Nonstainless Steel Manufacturing Electric Arc Furnace |
| Primary Copper (not subject to MACT) | Steel Foundries |
| Primary Nonferrous Metals (Zn, Cd and Be) | Electrical and Electronic Equipment – Finish Operations |

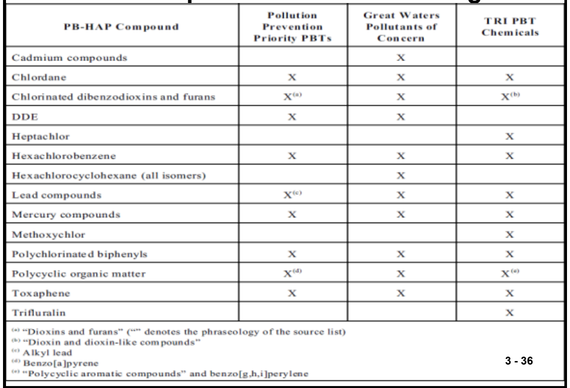

**Exhibit 1-2. List of Sixty-Eight Area Source Categories to Meet 90-Percent Requirement under Clean Air Act Sections 112(c)(3) and 112(k)(3)(B)**

| | |
|---|---|
| Polyvinyl Chloride and Copolymers Production | Heating Equipment, Except Electric |
| Secondary Copper Smelting | Industrial Machinery and Equipment – Finish Operations |
| Acrylic Fibers/Modacrylic Fibers Production | Iron and Steel Forging |
| Carbon Black Production | Fabricated Metal Products |
| Chemical Manufacturing: Chromium Compounds | Fabricated Plate Work |
| Lead Acid Battery Manufacturing | Fabricated Structural Metal Manufacturing |
| Pharmaceutical Production | Plastic Materials and Resins Manufacturing |
| Synthetic Rubber Manufacturing | Copper Foundries |
| Nonferrous Foundries | Aluminum Foundries |
| Asphalt Processing and Asphalt Roofing Manufacturing | Paints and Allied Products Manufacturing |
| Chemical Preparations | Prepared Feeds Materials |
| Portland Cement | Sewage Sludge Incineration |
| Industrial Boilers Fired by Coal, Wood and Oil | Institutional/Commercial Boilers Fired by Coal, Wood and Oil |
| Plating and Polishing | Primary Metal Products Manufacturing |
| Valves and Pipe Fittings | Ferroalloys Production: Ferromanganese & Silicomanganese |
| Agricultural Chemicals and Pesticides Manufacturing | Cyclic Crude and Intermediate Production |
| Industrial Inorganic Chemical Manufacturing | Industrial Organic Chemical Manufacturing |
| Inorganic Pigments Manufacturing | Miscellaneous Organic NESHAP |

# Persistent Bio-accumulative Toxics (PBTs)

- Alkyl-lead
  Cadmium
  Dioxins
  Furans
  Mercury compounds
  Octachlorostyrene
  Polychlorinated biphenyls (PCBs)
  Aldrin/Dieldrin
  Chlordane
  DDT, DDD, DDE
  Hexachlorobenzene
  Mirex
  Toxaphene

# PB-HAP Compounds and USEPA Programs

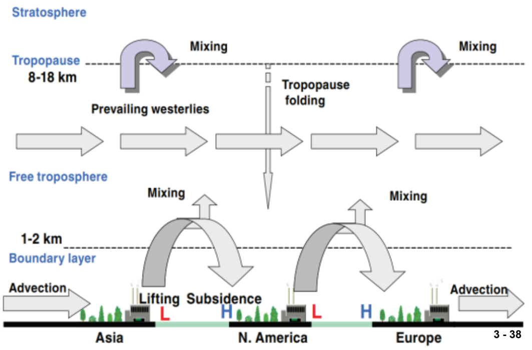

| PB-HAP Compound | Pollution Prevention Priority PBTs | Great Waters Pollutants of Concern | TRI PBT Chemicals |
|---|---|---|---|
| Cadmium compounds | | X | |
| Chlordane | X | X | X |
| Chlorinated dibenzodioxins and furans | X[a] | X | X[b] |
| DDE | X | X | |
| Heptachlor | | | X |
| Hexachlorobenzene | X | X | X |
| Hexachlorocyclohexane (all isomers) | | X | |
| Lead compounds | X[c] | X | X |
| Mercury compounds | X | X | X |
| Methoxychlor | | | X |
| Polychlorinated biphenyls | X | X | X |
| Polycyclic organic matter | X[d] | X | X[e] |
| Toxaphene | X | X | X |
| Trifluralin | | | X |

[a] "Dioxins and furans" ("" denotes the phraseology of the source list)
[b] "Dioxin and dioxin-like compounds"
[c] Alkyl lead
[d] Benzo[a]pyrene
[e] "Polycyclic aromatic compounds" and benzo[g,h,i]perylene

## Long-Range Trans-Boundary Air Pollution (LRTAP)

- The United States signed protocols on Persistent Organic Pollutants (POPs) and heavy metals pursuant to the LRTAP Convention in June 1998 at a ministerial meeting in Aarhus, Denmark. *Sixteen POPs and three metals are regulated*.
- http://www.epa.gov/international/toxics/brochure.html
- http://www.unece.org/env/lrtap/
- http://www.akaction.org/Publications/POPs/Contaminants_in_Alaska.pdf

## Schematic of the dominant dynamical processes involved in long-range midlatitude pollution transport.



## LRTAP Chemicals

- Aldrin
- polychlorinated biphenyls (PCBs)
- cadmium
- Dichlorodiphenyltrichloroethane (DDT)
- Chlordane
- lindanedioxins (polychlorinated dibenzo-p-dioxins)
- dieldrin
- furans (polychlorinated dibenzofurans)
- Endrin
- polycyclic aromatic hydrocarbons
- hexachlorobenzene
- hexabromobiphenyl
- kepone (chlordecone)
- mirex
- Toxaphene
- Hexachlorobenzene
- Heptachlor
- Lead
- mercury

GLOBAL SOURCES OF LOCAL POLLUTION

An Assessment of Long-Range Transport of Key Air Pollutants to and from the United States

NATIONAL RESEARCH COUNCIL

Global Sources of Local Pollution: An Assessment of Long-Range Transport of Key Air Pollutants to and from the United States |The National Academies Press

## Emerging Contaminants PFOA's & PFOS's

List of PFAS analytes and acronyms.

| | |
|---|---|
| PFBA = Perfluorobutanoic acid | PFOS = Perfluorooctanesulfonic acid |
| PFPeA = Perfluoropentanoic acid | PFNS = Perfluorononanesulfonic acid |
| PFHxA = Perfluorohexanoic acid | PFDS = Perfluorodecanesulfonic acid |
| PFHpA = Perfluoroheptanoic acid | PFDoS = Perfluorododecanesulfonic acid |
| PFOA = Perfluorooctanoic acid | PFOSA = Perfluorooctanesulfonamide |
| PFNA = Perfluorononanoic acid | N-MeFOSA = N-Methylperfluorooctanesulfonamide |
| PFDA = Perfluorodecanoic acid | N-EtFOSA = N-Ethylperfluorooctanesulfonamide |
| PFUnA = Perfluoroundecanoic acid | N-MeFOSAA = N-Methylperfluorooctanesulfonamidoacetic acid |
| PFDoA = Perfluorododecanoic acid | N-EtFOSAA = N-Ethylperfluorooctanesulfonamidoacetic acid |
| PFTrDA = Perfluorotridecanoic acid | N-MeFOSE = N-Methylperfluorooctanesulfonamidoethanol |
| FTeDA = Perfluorotetradecanoic acid | N-EtFOSE = N-Ethylperfluorooctanesulfonamidoethanol |
| PFBS = Perfluorobutanesulfonic acid | 4:2 FTS = 4:2 Fluorotelomer sulfonate |
| PFPeS = Perfluoropentanesulfonic acid | 6:2 FTS = 6:2 Fluorotelomer sulfonate |
| PFHxS = Perfluorohexanesulfonic acid | P8:2 FTS = 8:2 Fluorotelomer sulfonate |
| PFHpS = Perfluoroheptanesulfonic acid | |

EPA United States Environmental Protection Agency

**Technical Fact Sheet – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)**
November 2017

TECHNICAL FACT SHEET – PFOS and PFOA

**At a Glance**

- Manmade chemicals not naturally found in the environment.
- Fluorinated compounds that repel oil and water.
- Used in a variety of industrial and consumer products, such as carpet and clothing treatments and firefighting foams.
- Extremely persistent in the environment.
- Known to bioaccumulate in humans and wildlife.
- Readily absorbed after oral exposure. Accumulate primarily in the blood serum, kidney and liver.
- Toxicological studies on animals indicate potential developmental, reproductive and systemic effects.
- Health-based advisories or screening levels have been developed by EPA and state agencies.
- EPA has not issued a Maximum Contaminant Level (MCL) for drinking water.
- Standard analytical methods use high-performance liquid chromatography coupled with tandem mass spectrometry.
- Resistant to most chemical and microbial conventional treatment technologies. Most common groundwater treatment method is extraction and filtration through granular activated carbon filters.

**Introduction**

This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Federal Facilities Restoration and Reuse Office (FFRRO), provides a summary of two contaminants of emerging concern, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), including physical and chemical properties; environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information. This fact sheet is intended for use by site managers who may address these chemicals at cleanup sites or in drinking water supplies and for those in a position to consider whether these chemicals should be added to the analytical suite for site investigations.

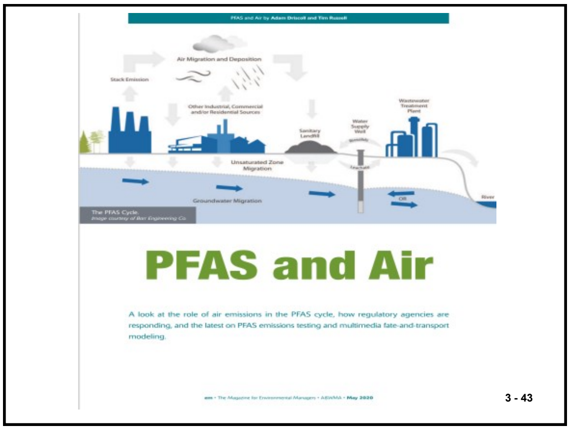
PFOS and PFOA are part of a larger group of chemicals called per- and polyfluoroalkyl substances (PFASs). PFASs, which are highly fluorinated aliphatic molecules, have been released to the environment through industrial manufacturing and through use and disposal of PFAS-containing products (Liu and Mejia Avendano 2013). PFOS and PFOA are the most widely studied of the PFAS chemicals. PFOS and PFOA are persistent in the environment and resistant to typical environmental degradation processes. As a result, they are widely distributed across all trophic levels and are found in soil, air and groundwater at sites across the United States. The toxicity, mobility and bioaccumulation potential of PFOS and PFOA result in potential adverse effects on the environment and human health.

**What are PFOS and PFOA?**

- They are human-made compounds that do not occur naturally in the environment (ATSDR 2015; EPA 2009b).
- PFOS and PFOA are fully fluorinated, organic compounds. They are the two PFASs that have been produced in the largest amounts within the United States (ATSDR 2015; EFSA 2008).
- PFOS and PFOA are part of a subset of PFASs known as perfluorinated alkyl acids (PFAAs).

**Disclaimer**: The U.S. EPA prepared this fact sheet using the most recent publicly-available scientific information; additional information can be obtained from the source documents. This fact sheet is not intended to be used as a primary source of information and is not intended, nor can it be relied on, to create any rights enforceable by any party in litigation with the United States. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

United States Environmental Protection Agency | Office of Land and Emergency Management (5106P) | EPA 505-F-17-001 November 2017



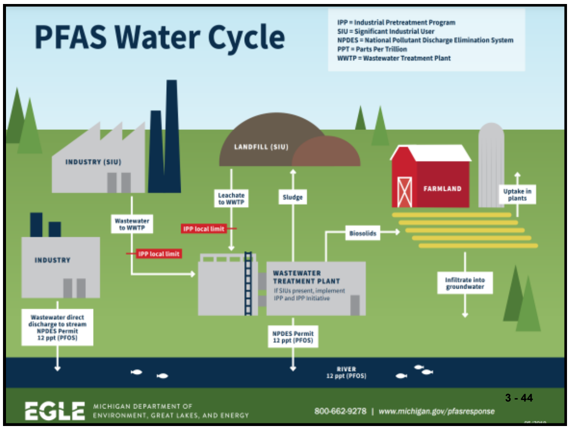
PFAS and Air by **Adam Driscoll and Tim Russell**

The PFAS Cycle.
*Image courtesy of Barr Engineering Co.*

# PFAS and Air

A look at the role of air emissions in the PFAS cycle, how regulatory agencies are responding, and the latest on PFAS emissions testing and multimedia fate-and-transport modeling.

**em** • The Magazine for Environmental Managers • A&WMA • **May 2020**

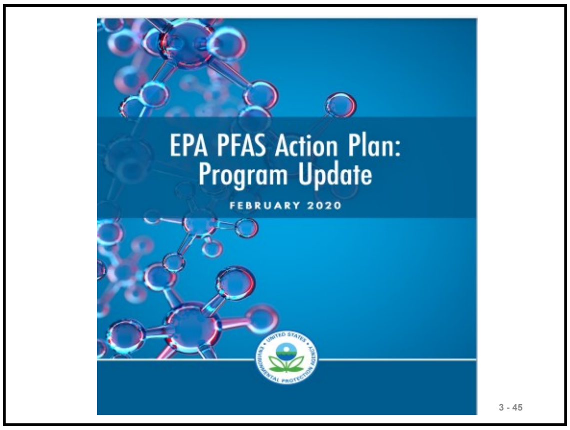


# PFAS Water Cycle

IPP = Industrial Pretreatment Program
SIU = Significant Industrial User
NPDES = National Pollutant Discharge Elimination System
PPT = Parts Per Trillion
WWTP = Wastewater Treatment Plant

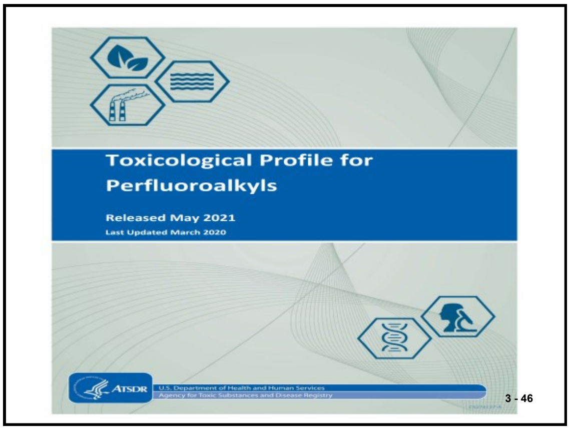
EGLE MICHIGAN DEPARTMENT OF ENVIRONMENT, GREAT LAKES, AND ENERGY

800-662-9278 | www.michigan.gov/pfasresponse



# EPA PFAS Action Plan: Program Update

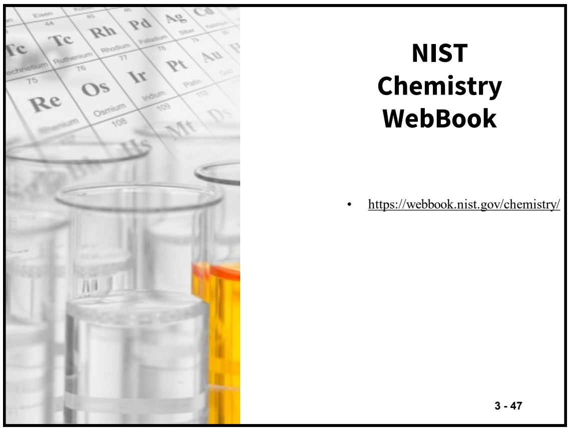
FEBRUARY 2020



# Toxicological Profile for Perfluoroalkyls

Released May 2021
Last Updated March 2020

ATSDR U.S. Department of Health and Human Services
Agency for Toxic Substances and Disease Registry



# NIST Chemistry WebBook

- https://webbook.nist.gov/chemistry/

Emergency Planning and Community Right-to-Know Act (EPCRA) | US EPA

Reporting Year 2019

Emergency Planning + Community RIGHT-TO-KNOW Act (EPCRA) Section 313

EPA

*Toxics Release Inventory Reporting Requirements*

TRI

# TRI Emissions and Thresholds

https://www.epa.gov/toxics-release-inventory-tri-program/tri-data-and-tools

## Emergency Planning and Community Right-to-Know Act (EPCRA)

The Emergency Planning and Community Right-to-Know Act (EPCRA) of 1986 was created to help communities plan for chemical emergencies. It also requires industry to report on the storage, use and releases of hazardous substances to federal, state, and local governments. EPCRA requires state and local governments, and Indian tribes to use this information to prepare for and protect their communities from potential risks.

### Learn about EPCRA

- What is EPCRA?
- Amendments to EPCRA: America's Water Infrastructure Act
- EPCRA (Non-Section 313) Regulatory Amendments and Guidance
- Frequent Questions and EPCRA Call Center
- EPCRA Regional Contacts

### Tier I and II Reporting Forms and Instructions

- Tier2 Submit™ Software
- Tier II Forms and Instructions
- Physical and Health Hazards Cross-Walk
- Tier I Forms and Instructions
- State Tier II Reporting Requirements and Procedures

### Emergency Planning in My Area

- Local Emergency Planning Committees
- State Emergency Response Commissions
- How to Better Prepare Your Community for a Chemical Emergency: A Guide for State, Tribal and Local Agencies
- Chemical Emergency Preparedness and Prevention on Tribal Lands

### Emergency Release Notification

- State Contact Information for Emergency Release Notification
- EPCRA Section 304 Release Notification Requirements
- CERCLA Section 103 Release Notification Requirements
- Continuous Release Reporting

### EPCRA Training

- Training for States, Tribes, LEPCs, Local Planners and Responders (Non-Section 313)
- Workshops in New England
- 2019 Tier2 Submit™ Tutorial

### Trade Secrecy under EPCRA

- Trade Secret Forms and Instructions

**EMERGENCIES**

EPA

Report oil or chemical spills at: 800-424-8802

Learn more »

Add this widget to your website.

**⚠ CERCLA and EPCRA Reporting Requirements**

On June 4, 2019, EPA Administrator Wheeler signed a final rule to amend the emergency release notification regulations under EPCRA. This amendment adds a reporting exemption for air emissions from animal waste at farms. For more information, please see: CERCLA and EPCRA Reporting Requirements for Air Releases of Hazardous Substances from Animal Waste at Farms.

**Most Requested Documents**

- Consolidated List of Lists
- EPCRA Tier II Form Instructions
- EPCRA Tier II Form
- EPCRA Fact Sheet
- EPCRA Guide for Oil and Gas Operations
- Hazardous Chemical Reporting Advisory: Facilities Operating in the Plastics Industry

https://www.epa.gov/epcra

## Toxics Release Inventory (TRI) Program

- TRI Program Home
- What is TRI?
  - Covered Chemicals
  - Covered Industry Sectors
- Find, Understand & Use TRI
  - TRI Data & Tools
  - TRI National Analysis
  - Data Quality
  - What You Can Do
- Reporting for Facilities
  - Enforcement
  - GuideME
  - Laws & Regulatory Activities
  - Pollution Prevention
    - TRI P2 Resources
  - TRI-MEweb
- TRI Site Map

### TRI Data and Tools

The Toxics Release Inventory (TRI) Program tracks the industrial management of toxic chemicals that may pose a threat to human health and the environment. The data facilities submit to EPA are available here in multiple ways. For information about the steps EPA takes to optimize the quality of TRI data, see the TRI Data Quality webpage.

NOTICE: In early 2019, EPA learned that two TRI queries available in EPA's Envirofacts database regarding off-site transfers of nonmetallic chemicals to Publicly Owned Treatment Works (POTWs) had not been updated with more accurate default assumptions regarding POTW treatment efficiencies. EPA updated the two queries within days of the discovery. Prior to the updates, between July 15, 2015, and March 20, 2019, it is possible that TRI data users accessing the 2014-2017 TRI datasets through Envirofacts queries that specifically related to off-site transfers to POTWs could have received data based on the previous default assumptions regarding POTW treatment efficiencies. Searches done during this time may be redone to make sure the results reflect the current default assumptions for non-metals sent off site to POTWs. For more information, please see the EPA Office of Inspector General's webpage about the issue.

TRI Explorer: Access the most commonly requested TRI information. Search by chemical or facility releases, waste management, or waste transfers.

RSEI: The Risk-Screening Environmental Indicators (RSEI) model produces scores based on potential relative risk that can be compared for different locations. These scores can help establish priorities for further investigation.

TRI Pollution Prevention (P2) Tool: Find and compare information about how companies manage chemical waste and work to reduce chemical releases into the environment.

Envirofacts: Find all publicly available TRI data in a searchable, downloadable format. Multiple search options available.

myRTK: Find summary-level facility information, including chemical releases, pollution prevention activities, and compliance history. Provided in English and Spanish.

TRI National Analysis website: An annual snapshot of TRI data. Maps, charts, and tables highlight national-level data, while factsheets detail specific geographic areas.

### More Ways to Get TRI Data and Help Using TRI

Download data from TRI reporting forms for any reporting year since 1987. Recommended for users with extensive knowledge of TRI data.

- Basic Data Files: Frequently requested data elements. National, federal, tribal and state-level data files grouped by reporting year.
- Basic Plus Data Files: National-level data files containing all data elements reported on the Reporting Form R, grouped by reporting year.
- Dioxin, Dioxin-Like Compounds and TEQ Data Files: Dioxin mass quantity data reported on Reporting Form R Schedule 1, with associated Toxic Equivalency data elements. National-level data files by current reporting year.

# Why was the Toxics Release Inventory created?

**Bhopal, India** **December 1984**

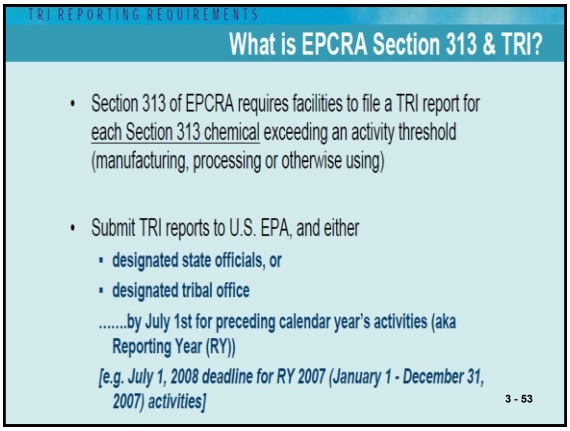
- Methyl isocyanate gas was released at a Union Carbide chemical plant.
- Thousands died the first night, thousands more since.
- Survivors continue to suffer with permanent disabilities.

- **Institute, West Virginia** **August 1985**

- Chemical release at a similar facility in the U.S.
- More than 100 people hospitalized.

Bhopal memorial for those killed and disabled by the 1984 toxic gas release

- These events led to increased concern about local preparedness for chemical emergencies and the availability of information on hazardous substances.
- The passage of the Emergency Planning and Community Right-to-Know Act in 1986 was part of the United States' response.



TRI REPORTING REQUIREMENTS

## What is EPCRA Section 313 & TRI?

- Section 313 of EPCRA requires facilities to file a TRI report for each Section 313 chemical exceeding an activity threshold (manufacturing, processing or otherwise using)
- Submit TRI reports to U.S. EPA, and either
  - **designated state officials, or**
  - **designated tribal office**

  .......by July 1st for preceding calendar year's activities (aka Reporting Year (RY))

  *[e.g. July 1, 2008 deadline for RY 2007 (January 1 - December 31, 2007) activities]*

# EPCRA Chemicals

The "Title III List of Lists" is the key to EPCRA and is available from:

https://www.epa.gov/toxics-release-inventory-tri-program/tri-listed-chemicals

– The current TRI toxic chemical list contains 595 individually listed chemicals and 33 chemical categories

United States
Environmental Protection
Agency

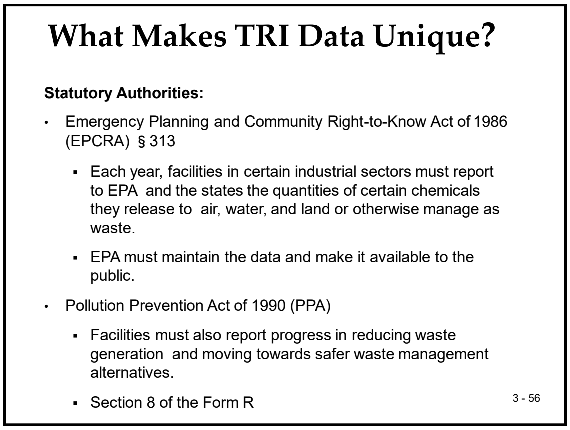
Office of Land
and
Emergency Management

EPA 550-B-21-001
April 2022
www.epa.gov/epcra

LIST OF LISTS

Consolidated List of Chemicals
Subject to the Emergency Planning and
Community Right-To-Know Act (EPCRA),
Comprehensive Environmental Response,
Compensation and Liability Act (CERCLA), and
Section 112(r) of the Clean Air Act (CAA)

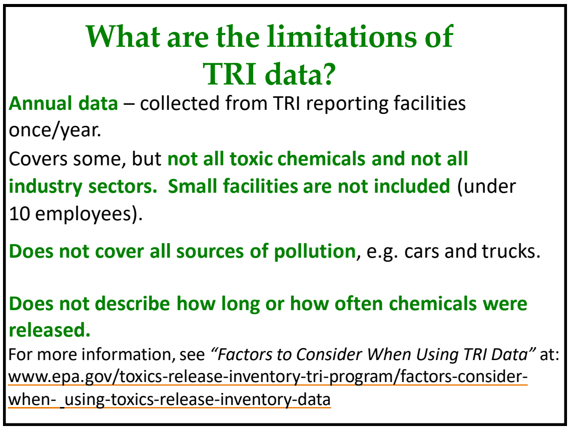
- EPCRA Section 302 Extremely Hazardous Substances
- CERCLA Hazardous Substances
- EPCRA Section 313 Toxic Chemicals
- CAA 112(r) Regulated Chemicals for Accidental Release Prevention



## What Makes TRI Data Unique?

**Statutory Authorities:**

- Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) § 313
  - Each year, facilities in certain industrial sectors must report to EPA and the states the quantities of certain chemicals they release to air, water, and land or otherwise manage as waste.
  - EPA must maintain the data and make it available to the public.
- Pollution Prevention Act of 1990 (PPA)
  - Facilities must also report progress in reducing waste generation and moving towards safer waste management alternatives.
  - Section 8 of the Form R



## What are the limitations of TRI data?

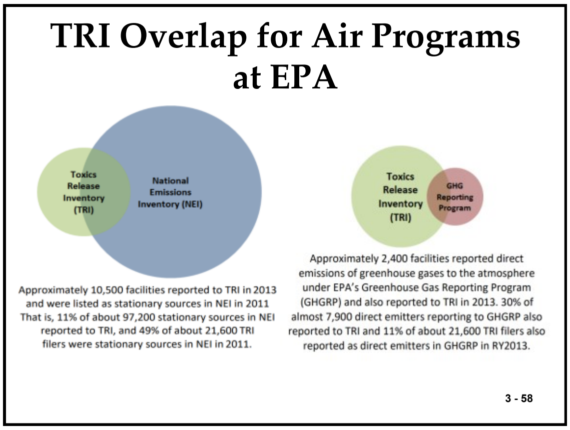
**Annual data** – collected from TRI reporting facilities once/year.

Covers some, but **not all toxic chemicals and not all industry sectors. Small facilities are not included** (under 10 employees).

**Does not cover all sources of pollution**, e.g. cars and trucks.

**Does not describe how long or how often chemicals were released.**

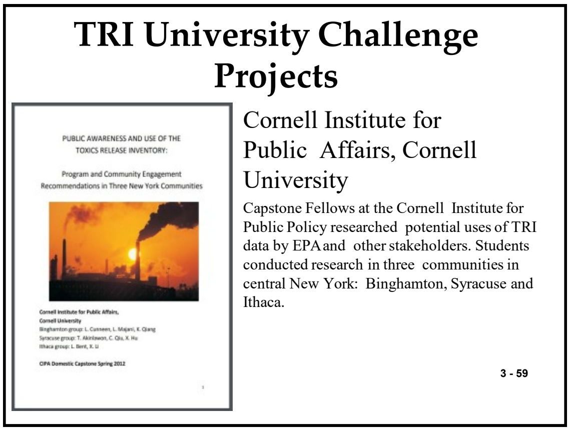
For more information, see *"Factors to Consider When Using TRI Data"* at: www.epa.gov/toxics-release-inventory-tri-program/factors-consider-when- using-toxics-release-inventory-data



## TRI Overlap for Air Programs at EPA

Approximately 10,500 facilities reported to TRI in 2013 and were listed as stationary sources in NEI in 2011 That is, 11% of about 97,200 stationary sources in NEI reported to TRI, and 49% of about 21,600 TRI filers were stationary sources in NEI in 2011.

Approximately 2,400 facilities reported direct emissions of greenhouse gases to the atmosphere under EPA's Greenhouse Gas Reporting Program (GHGRP) and also reported to TRI in 2013. 30% of almost 7,900 direct emitters reporting to GHGRP also reported to TRI and 11% of about 21,600 TRI filers also reported as direct emitters in GHGRP in RY2013.



## TRI University Challenge Projects

PUBLIC AWARENESS AND USE OF THE TOXICS RELEASE INVENTORY:

Program and Community Engagement Recommendations in Three New York Communities

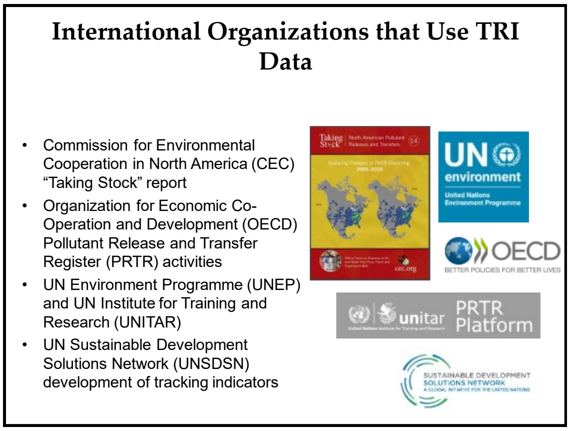
Cornell Institute for Public Affairs,
Cornell University
Binghamton group: L. Cunneen, L. Majani, K. Qiang
Syracuse group: T. Akinlawon, C. Qiu, X. Hu
Ithaca group: L. Bent, X. Li

CIPA Domestic Capstone Spring 2012

1

Cornell Institute for Public Affairs, Cornell University

Capstone Fellows at the Cornell Institute for Public Policy researched potential uses of TRI data by EPA and other stakeholders. Students conducted research in three communities in central New York: Binghamton, Syracuse and Ithaca.

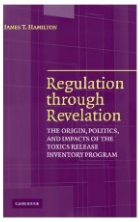


## International Organizations that Use TRI Data

- Commission for Environmental Cooperation in North America (CEC) "Taking Stock" report
- Organization for Economic Co-Operation and Development (OECD) Pollutant Release and Transfer Register (PRTR) activities
- UN Environment Programme (UNEP) and UN Institute for Training and Research (UNITAR)
- UN Sustainable Development Solutions Network (UNSDSN) development of tracking indicators

# Research about TRI

Researchers have looked at the TRI program as a subject unto itself to investigate the impact of information disclosure as a means to achieve environmental policy outcomes.



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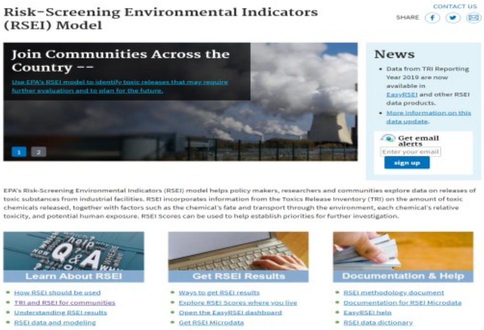
# Risk-Screening Environmental Indicators and TRI Data



Risk-Screening Environmental Indicators (RSEI) Model

CONTACT US

SHARE

Join Communities Across the Country --

Use EPA's RSEI model to identify toxic releases that may require further evaluation and to plan for the future.

News

- Data from TRI Reporting Year 2019 are now available in EasyRSEI and other RSEI data products.
- More information on this data update.

Get email alerts

Enter your email

sign up

EPA's Risk-Screening Environmental Indicators (RSEI) model helps policy makers, researchers and communities explore data on releases of toxic substances from industrial facilities. RSEI incorporates information from the Toxics Release Inventory (TRI) on the amount of toxic chemicals released, together with factors such as the chemical's fate and transport through the environment, each chemical's relative toxicity, and potential human exposure. RSEI Scores can be used to help establish priorities for further investigation.

Learn About RSEI
- How RSEI should be used
- TRI and RSEI for communities
- Understanding RSEI results
- RSEI data and modeling

Get RSEI Results
- Ways to get RSEI results
- Explore RSEI Scores where you live
- Open the EasyRSEI dashboard
- Get RSEI Microdata

Documentation & Help
- RSEI methodology document
- Documentation for RSEI Microdata
- EasyRSEI help
- RSEI data dictionary

Risk-Screening Environmental Indicators (RSEI) Model | US EPA

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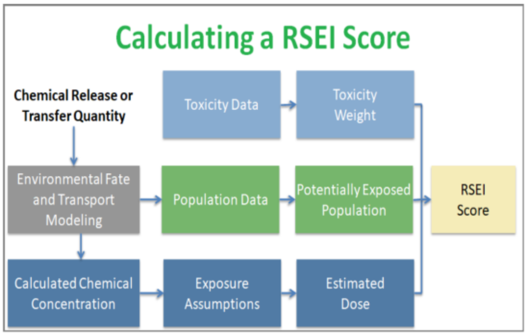
# What is a RSEI Score?



Calculating a RSEI Score

Chemical Release or Transfer Quantity

Toxicity Data

Toxicity Weight

Environmental Fate and Transport Modeling

Population Data

Potentially Exposed Population

RSEI Score

Calculated Chemical Concentration

Exposure Assumptions

Estimated Dose

---

# RESI Video

EPA

Understanding RSEI Results

RSEI Informational Video

May 2022

Risk-Screening Environmental Indicators Model

Office of Pollution Prevention and Toxics

Understanding RSEI Results | US EPA

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# State Agency's Air Toxics Definitions/LIST

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# Example of State Air Toxics Regulations:

Guidelines For the Control of Toxic Ambient Air Contaminants
http://www.dec.ny.gov/chemical/30681.html

http://www.dec.ny.gov/docs/air_pdf/dar1.pdf

Kansas Department of Health & Environment Web site
www.kdheks.gov/environment/

TCEQ Toxicology - Texas Commission on Environmental Quality - www.tceq.texas.gov

## Chemical Air Toxics Lists: Overlap and Differences

- With the Clean Air Act (HAPs), the Emergency Planning and Community Right to Know Act (TRI chemicals), or a specific EPA initiative (i.e., LRTAP chemicals): there is not always consistency among these various lists in either the naming of chemicals or the meaning of the names.
- The various lists of chemicals do not always treat groups of chemicals in the same manner.

## Chemical Air Toxics Lists: Overlap and Differences

- Keep overlaps and differences in mind since they can have important legal, policy, and other practical implications when studying air toxics impact.
- Differences among chemical “lists” are based mostly on legal and regulatory considerations, not necessarily on toxicological properties.
- Some regulatory listings are comprised of multiple chemicals (e.g., polycyclic organic matter or POM), while toxicity data may exist only for the individual chemicals that make up the listing.
- Example: “Glycol ethers” are defined differently for the TRI and as HAPs

## Issues to Consider With HAP’s

- Important to use CAS#s
- Keep in mind toxicology varies by chemical
  - Carcinogen
  - Non-carcinogen

HAP Groups in CAA and Diesel PM

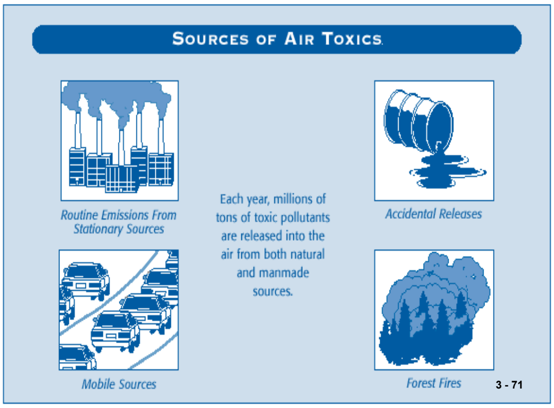
Chemical Abstract Service (CAS#s)

http://www.epa.gov/ttn/chief/nif/index.html#ver3

EPA Office of Environmental Information

Substance Registry System www.epa.gov/srs

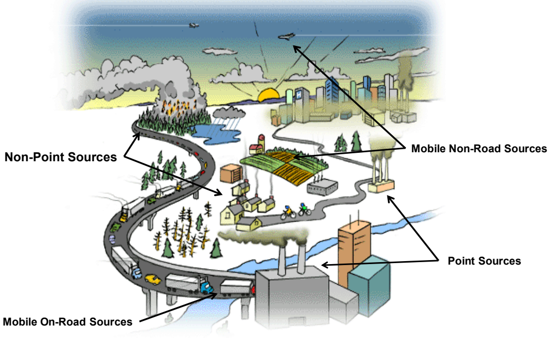
## Sources of Air Toxics



SOURCES OF AIR TOXICS

Each year, millions of tons of toxic pollutants are released into the air from both natural and manmade sources.

## Potential Sources Everywhere -- Where to Start???



Sustaining the Environment and Resources for Canadians
Environment Canada

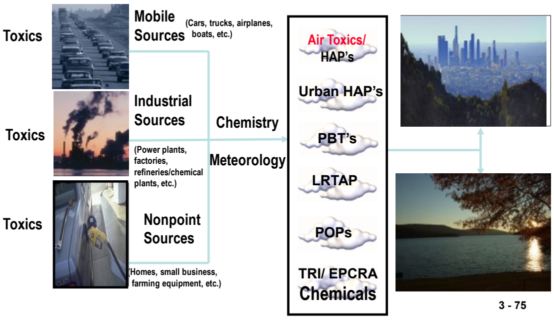
## Major Air Toxic Source Types

- Point sources;
- Nonpoint sources;
- On-road mobile sources;
- Non-road mobile sources;
- Indoor sources;
- Natural sources; and
- Exempt sources.

## Terminology Related to Groupings of Source Types

| Source Type | Definition in CAA | Reported Type in NEI |
|---|---|---|
| Point Source - Major | Point Source - Major | Point Source |
| Point Source - Area | Point Source - Area | Point Source if location coordinates reported<br>Area Source if location coordinates not reported |
| Nonpoint Source | Nonpoint Source | Area |
| Mobile Source-On road | Mobile Source-On road | Modeled |
| Mobile Source-Non road | Mobile Source-Non road | Modeled or Estimated |
| Indoor | Not Defined | Not Reported |
| Natural | Not Defined | Not Reported |
| Exempt | Not Defined | Not Report |

## Air Toxic Sources and Regulated Air Toxics



Toxics — Mobile Sources (Cars, trucks, airplanes, boats, etc.)

Toxics — Industrial Sources (Power plants, factories, refineries/chemical plants, etc.)

Toxics — Nonpoint Sources (Homes, small business, farming equipment, etc.)

Chemistry

Meteorology

Air Toxics/ HAP's

Urban HAP's

PBT's

LRTAP

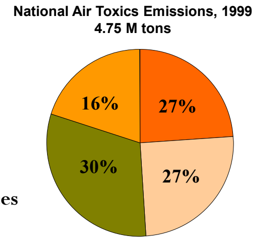
POPs

TRI/ EPCRA Chemicals

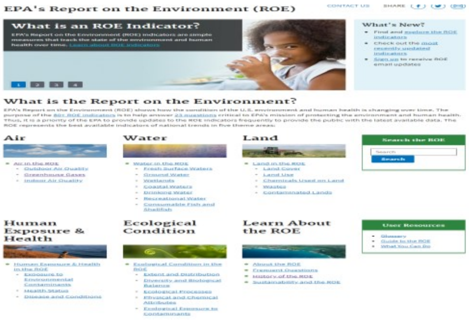
## Types of HAP's Sources

EPA divides ambient emission sources into four main groups:

- 🟥 Major sources
- ⬜ Area source and other sources
- 🟩 On-road mobile sources
- 🟧 Non-road mobile sources



## Report on the Environment Air Toxics Emissions



EPA's Report on the Environment (ROE)

CONTACT US SHARE

What is an ROE Indicator?

EPA's Report on the Environment (ROE) indicators are simple measures that track the state of the environment and human health over time. Learn about ROE indicators

What's New?

- Find and explore the ROE indicators
- Check out the most recently updated indicators
- Sign up to receive ROE email updates

What is the Report on the Environment?

EPA's Report on the Environment (ROE) shows how the condition of the U.S. environment and human health is changing over time. The purpose of the 80+ ROE indicators is to help answer 23 questions critical to EPA's mission of protecting the environment and human health. Thus, it is a priority of the EPA to provide updates to the ROE indicators frequently to provide the public with the latest available data. The ROE represents the best available indicators of national trends in five theme areas:

Air

- Air in the ROE
  - Outdoor Air Quality
  - Greenhouse Gases
  - Indoor Air Quality

Water

- Water in the ROE
  - Fresh Surface Waters
  - Ground Water
  - Wetlands
  - Coastal Waters
  - Drinking Water
  - Recreational Water
  - Consumable Fish and Shellfish

Land

- Land in the ROE
  - Land Cover
  - Land Use
  - Chemicals Used on Land
  - Wastes
  - Contaminated Lands

Search the ROE

Human Exposure & Health

- Human Exposure & Health in the ROE
  - Exposure to Environmental Contaminants
  - Health Status
  - Disease and Conditions

Ecological Condition

- Ecological Condition in the ROE
  - Extent and Distribution
  - Diversity and Biological Balance
  - Ecological Processes
  - Physical and Chemical Attributes
  - Ecological Exposure to Contaminants

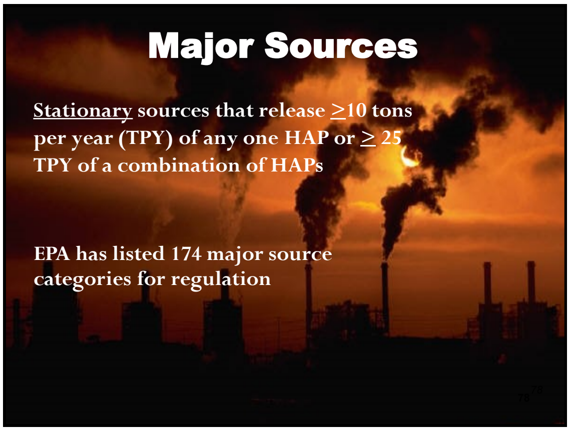
Learn About the ROE

- About the ROE
- Frequent Questions
- History of the ROE
- Sustainability and the ROE

User Resources

- Glossary
- Guide to the ROE
- What You Can Do

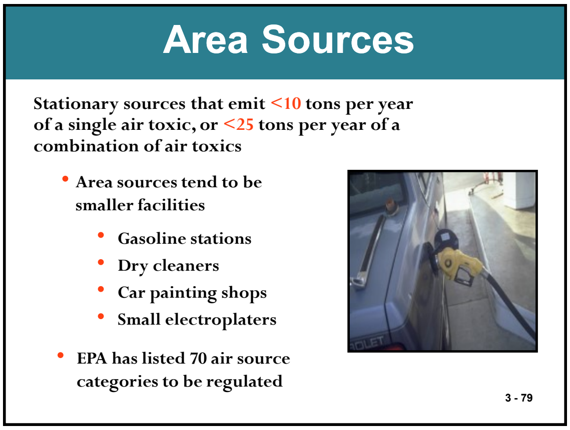
https://www.epa.gov/report-environment



## Major Sources

Stationary sources that release ≥10 tons per year (TPY) of any one HAP or ≥ 25 TPY of a combination of HAPs

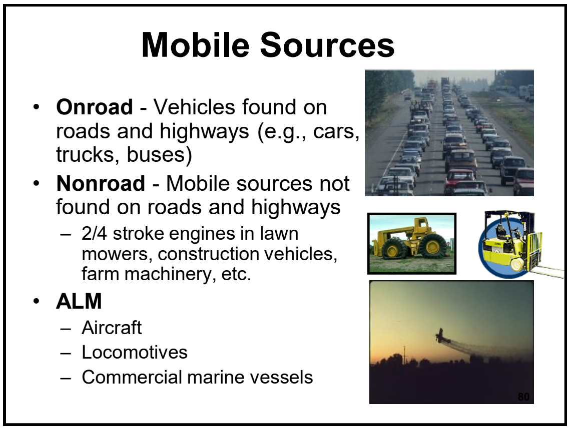
EPA has listed 174 major source categories for regulation



## Area Sources

Stationary sources that emit <10 tons per year of a single air toxic, or <25 tons per year of a combination of air toxics

- Area sources tend to be smaller facilities
  - Gasoline stations
  - Dry cleaners
  - Car painting shops
  - Small electroplaters
- EPA has listed 70 air source categories to be regulated



## Mobile Sources

- **Onroad** - Vehicles found on roads and highways (e.g., cars, trucks, buses)
- **Nonroad** - Mobile sources not found on roads and highways
  - 2/4 stroke engines in lawn mowers, construction vehicles, farm machinery, etc.
- **ALM**
  - Aircraft
  - Locomotives
  - Commercial marine vessels

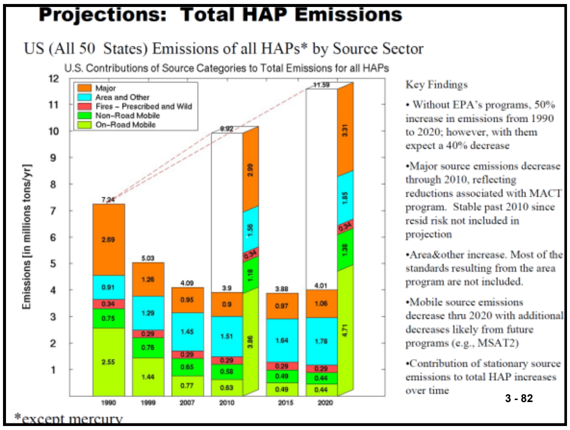
## Mobile Sources

Much of the historical focus of mobile source emissions reduction has been on on-road cars, trucks, and their fuels

Non-road engines are also significant sources of air toxics and are coming under increasing focus

The main Air Toxics released by both on- and off-road sources:

- Diesel particulate matter and diesel exhaust organic gases
- 20 volatile organic compounds and metals



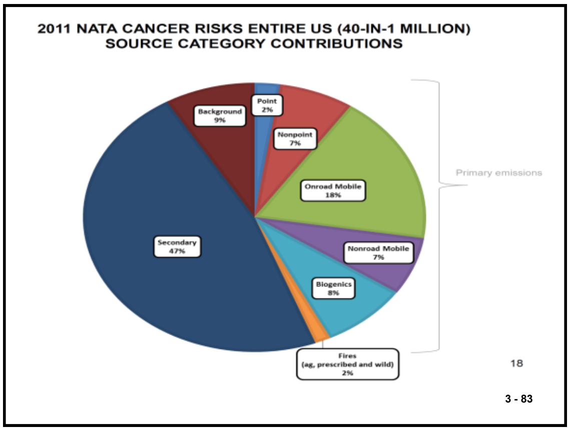
## Projections: Total HAP Emissions

US (All 50 States) Emissions of all HAPs* by Source Sector

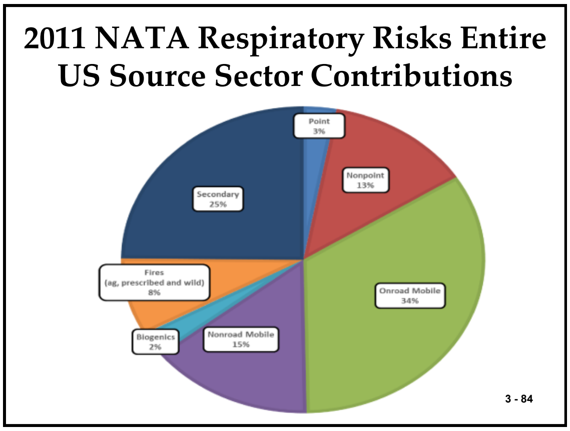
Key Findings

- Without EPA's programs, 50% increase in emissions from 1990 to 2020; however, with them expect a 40% decrease
- Major source emissions decrease through 2010, reflecting reductions associated with MACT program. Stable past 2010 since resid risk not included in projection
- Area&other increase. Most of the standards resulting from the area program are not included.
- Mobile source emissions decrease thru 2020 with additional decreases likely from future programs (e.g., MSAT2)
- Contribution of stationary source emissions to total HAP increases over time

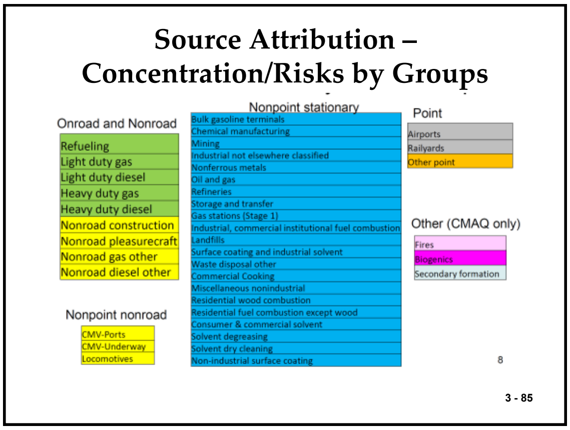
*except mercury



## 2011 NATA CANCER RISKS ENTIRE US (40-IN-1 MILLION) SOURCE CATEGORY CONTRIBUTIONS



## 2011 NATA Respiratory Risks Entire US Source Sector Contributions



## Source Attribution – Concentration/Risks by Groups

Onroad and Nonroad

- 🟩 Refueling
- 🟩 Light duty gas
- 🟩 Light duty diesel
- 🟩 Heavy duty gas
- 🟩 Heavy duty diesel
- 🟨 Nonroad construction
- 🟨 Nonroad pleasurecraft
- 🟨 Nonroad gas other
- 🟨 Nonroad diesel other

Nonpoint nonroad

- 🟨 CMV-Ports
- 🟨 CMV-Underway
- 🟨 Locomotives

Nonpoint stationary

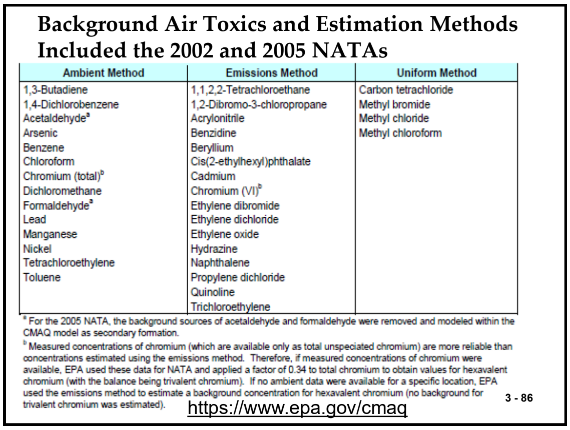
- Bulk gasoline terminals
- Chemical manufacturing
- Mining
- Industrial not elsewhere classified
- Nonferrous metals
- Oil and gas
- Refineries
- Storage and transfer
- Gas stations (Stage 1)
- Industrial, commercial institutional fuel combustion
- Landfills
- Surface coating and industrial solvent
- Waste disposal other
- Commercial Cooking
- Miscellaneous nonindustrial
- Residential wood combustion
- Residential fuel combustion except wood
- Consumer & commercial solvent
- Solvent degreasing
- Solvent dry cleaning
- Non-industrial surface coating

Point

- Airports
- Railyards
- Other point

Other (CMAQ only)

- Fires
- Biogenics
- Secondary formation



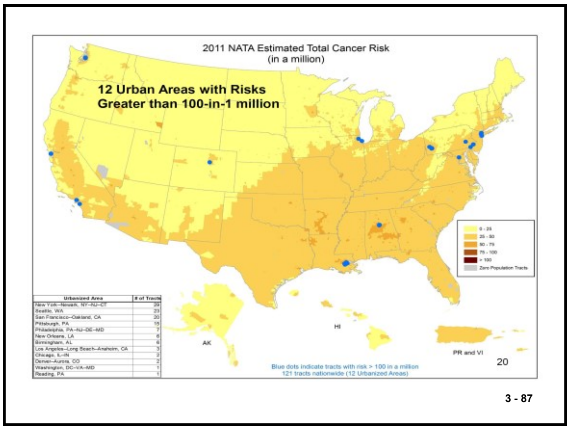
## Background Air Toxics and Estimation Methods Included the 2002 and 2005 NATAs

| Ambient Method | Emissions Method | Uniform Method |
|---|---|---|
| 1,3-Butadiene | 1,1,2,2-Tetrachloroethane | Carbon tetrachloride |
| 1,4-Dichlorobenzene | 1,2-Dibromo-3-chloropropane | Methyl bromide |
| Acetaldehyde[a] | Acrylonitrile | Methyl chloride |
| Arsenic | Benzidine | Methyl chloroform |
| Benzene | Beryllium | |
| Chloroform | Cis(2-ethylhexyl)phthalate | |
| Chromium (total)[b] | Cadmium | |
| Dichloromethane | Chromium (VI)[b] | |
| Formaldehyde[a] | Ethylene dibromide | |
| Lead | Ethylene dichloride | |
| Manganese | Ethylene oxide | |
| Nickel | Hydrazine | |
| Tetrachloroethylene | Naphthalene | |
| Toluene | Propylene dichloride | |
| | Quinoline | |
| | Trichloroethylene | |

[a] For the 2005 NATA, the background sources of acetaldehyde and formaldehyde were removed and modeled within the CMAQ model as secondary formation.

[b] Measured concentrations of chromium (which are available only as total unspeciated chromium) are more reliable than concentrations estimated using the emissions method. Therefore, if measured concentrations of chromium were available, EPA used these data for NATA and applied a factor of 0.34 to total chromium to obtain values for hexavalent chromium (with the balance being trivalent chromium). If no ambient data were available for a specific location, EPA used the emissions method to estimate a background concentration for hexavalent chromium (no background for trivalent chromium was estimated).

https://www.epa.gov/cmaq

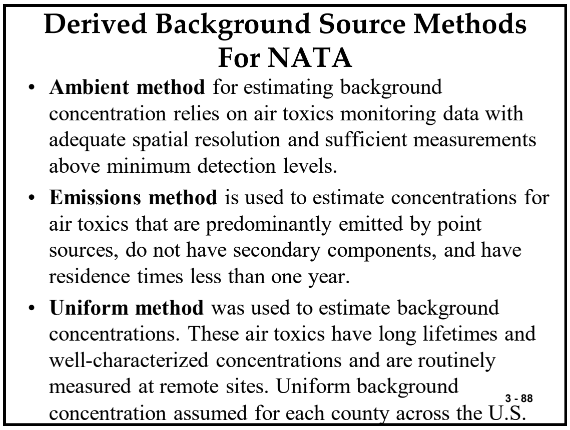


2011 NATA Estimated Total Cancer Risk
(in a million)

12 Urban Areas with Risks Greater than 100-in-1 million

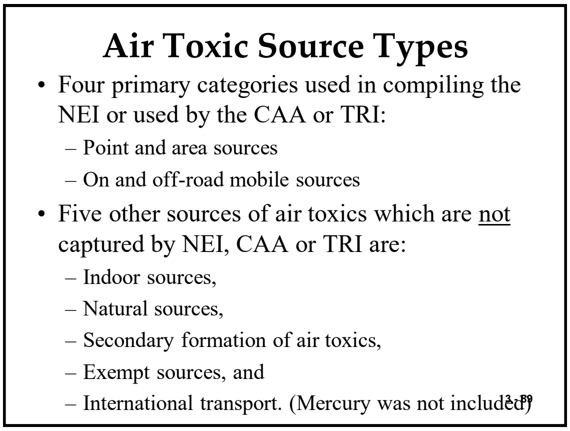
| Urbanized Area | # of Tracts |
|---|---|
| New York–Newark, NY–NJ–CT | 29 |
| Seattle, WA | 23 |
| San Francisco–Oakland, CA | 20 |
| Pittsburgh, PA | 15 |
| Philadelphia, PA–NJ–DE–MD | 7 |
| New Orleans, LA | 6 |
| Birmingham, AL | 6 |
| Los Angeles–Long Beach–Anaheim, CA | 3 |
| Chicago, IL–IN | 2 |
| Denver–Aurora, CO | 2 |
| Washington, DC–VA–MD | 1 |
| Reading, PA | 1 |

Blue dots indicate tracts with risk > 100 in a million
121 tracts nationwide (12 Urbanized Areas)



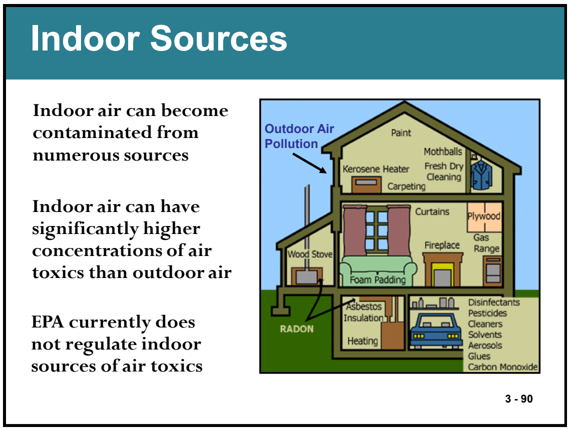
## Derived Background Source Methods For NATA

- **Ambient method** for estimating background concentration relies on air toxics monitoring data with adequate spatial resolution and sufficient measurements above minimum detection levels.
- **Emissions method** is used to estimate concentrations for air toxics that are predominantly emitted by point sources, do not have secondary components, and have residence times less than one year.
- **Uniform method** was used to estimate background concentrations. These air toxics have long lifetimes and well-characterized concentrations and are routinely measured at remote sites. Uniform background concentration assumed for each county across the U.S.



## Air Toxic Source Types

- Four primary categories used in compiling the NEI or used by the CAA or TRI:
  - Point and area sources
  - On and off-road mobile sources
- Five other sources of air toxics which are not captured by NEI, CAA or TRI are:
  - Indoor sources,
  - Natural sources,
  - Secondary formation of air toxics,
  - Exempt sources, and
  - International transport. (Mercury was not included)



## Indoor Sources

**Indoor air can become contaminated from numerous sources**

**Indoor air can have significantly higher concentrations of air toxics than outdoor air**

**EPA currently does not regulate indoor sources of air toxics**

## Natural Sources

Many HAPs are found in nature or are produced through natural events

- Forest fires
- Volcanic eruptions
- Natural cycling of mercury
- Windblown entrainment of metallic containing dusts (e.g., arsenic)
- Atmospheric production of formaldehyde and other chemicals from naturally occurring volatile organic compounds, etc.

## Categories of Natural Sources

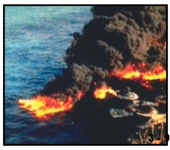
| Category | Example or Emissions | Sources |
|---|---|---|
| Geologic | • Sulfuric, hydrofluoric and hydrochloric acids<br>• Radon<br>• Nitrogen oxides | • Volcanic gases<br>• Radioactive decay of rock<br>• Soils, lightning |
| Biogenic | • Ammonia<br>• Methane<br>• VOCs | • Animals wastes<br>• Animal wastes, plant decay<br>• Vegetation |
| Marine | • Di-methyl sulfide, ammonia, chlorides, sulfates, alkyl halides, nitrous oxides | • Sea spray released by breaking waves |

*Source: International Fertilizer Industry Association. 2001. Food and Agriculture Organization of the* United Nations. *Global estimates of gaseous emissions of NH3, NO and N2O from agricultural land. ISBN 92-5-104698-1. Available at:* www.fao.org/DOCREP/004/Y2780E/y2780e01.htm.

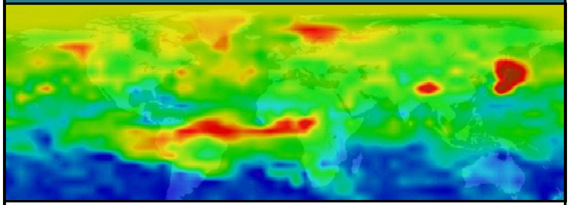
## Other Types of Sources

There are a number of other important sources of air toxics that aren't so easy to categorize or count

- Barrel burning (a significant source of dioxin)
- Accidents

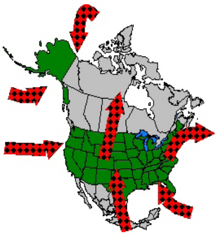


## Other Types of Sources

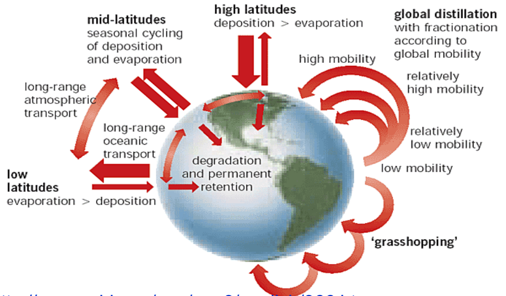


- Long-range transport of air pollutants (Hg) (PCB's) (Pesticides)
  http://www.epa.gov/airnow/2007conference/monday/eagan.ppt#265,1,Saharan
- Dust Event Impacts on Florida Particulate Concentrations
- Historical background concentrations ($CCl_4$)

The adjacent figure illustrates the mean wind flow at 1500 meters of altitude during the months of June, July and August from 1985 to 1996. Although these patterns can be disrupted by climatologically events such as El Niño, it is clear that "persistent organic pollutants," POP's released in the southern areas of this hemisphere can impact areas of the *U.S. Studies have shown that long range transport from many regions of the globe is a significant source of POP chemicals to the Great Lakes* and that mitigation efforts are going to be needed both in the U.S. and globally to address potential sources. The study of Central American sources has shown that this region is a potential contributor to POP's contamination in the Great Lakes, due to the fact that these chemicals degrade very slowly, and there still exist areas of high contamination and stockpiles of these chemicals that are no longer in use in Central America.



## Migration Transport of Persistent Pollutants from Long Range Transport



http://www.grida.no/geo/geo3/english/366.htm
http://literacynet.org/polar/pop/html/project-pops.html

# Emission Inventories

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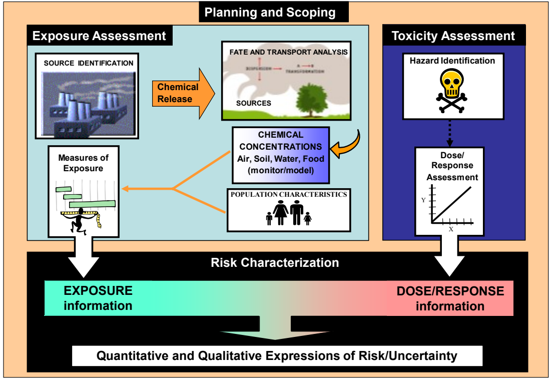
## The Detailed Air Toxics Risk Assessment Process



Planning and Scoping

Exposure Assessment

SOURCE IDENTIFICATION

Chemical Release

FATE AND TRANSPORT ANALYSIS

SOURCES

CHEMICAL CONCENTRATIONS Air, Soil, Water, Food (monitor/model)

POPULATION CHARACTERISTICS

Measures of Exposure

Toxicity Assessment

Hazard Identification

Dose/ Response Assessment

Risk Characterization

EXPOSURE information

DOSE/RESPONSE information

Quantitative and Qualitative Expressions of Risk/Uncertainty

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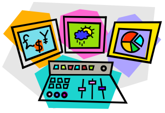
## Data on Emissions



- When performing an air toxics study, the NEI and TRI are excellent places to start identifying sources and source characteristics
- The NEI may provide sufficient information to perform the risk assessment
- Sometimes it is necessary to obtain additional source specific information from SLT Air Authority permit files

---

## Data on Emissions

EPA tracks emissions of the 188 HAPs in the National Emissions Inventory (NEI)*

- Includes major, area, mobile, and some natural sources (e.g., forest fires)
- Updated every 3 years (1999 most recent)
- Compilation of State, local, and tribal (SLT) inventories, with data gaps filled in by EPA using a variety of methods (e.g., emission factors)

*The NEI also contains information on releases of criteria pollutants

---

## Data on Emissions

The NEI is a "modeling inventory"

- Provides detailed information on specific source characteristics (e.g., stack location, height, emission rates and temperature, etc.)

Includes both "point" and "non-point" sources

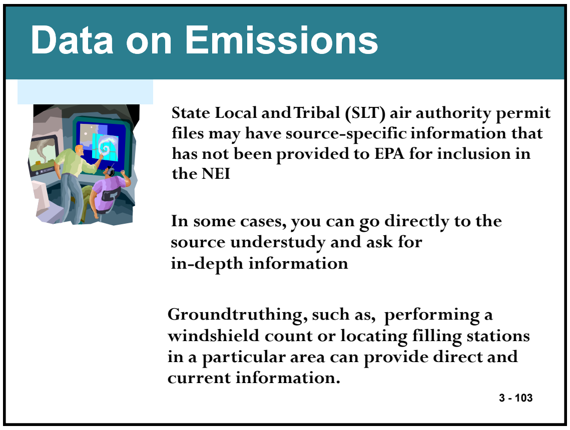
- Point sources – you know the point on the map where the source is (major and some area sources)
- Non-point sources – for some area sources, the NEI provides only an aggregate amount of release for a geographic area (e.g., total tons per year of PERC from all drycleaners in a county)

---

## Data on Emissions

Toxics Release Inventory (TRI) provides emissions estimates

- Includes ~650 chemicals from medium to large stationary sources
- Provides air releases as both fugitive and stack
- Useful for initial phase of identifying sources in a study area
  - Large number of covered chemicals
  - Ease of data access
- Not a modeling inventory (does not include specific source characteristics)
- Updated every year (2006 most recent)

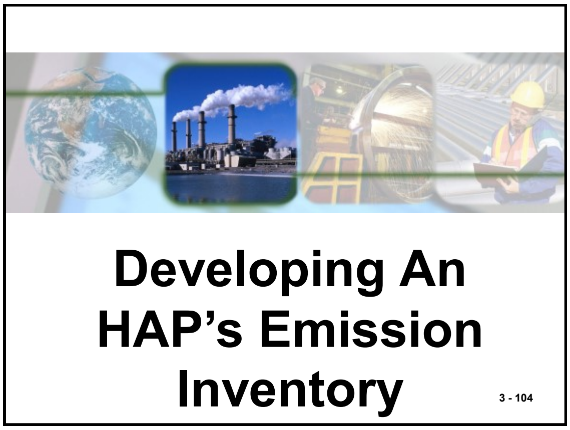


## Data on Emissions

State Local and Tribal (SLT) air authority permit files may have source-specific information that has not been provided to EPA for inclusion in the NEI

In some cases, you can go directly to the source understudy and ask for in-depth information

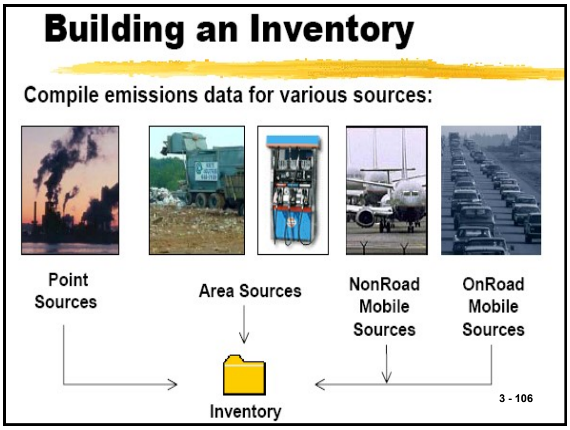
Groundtruthing, such as, performing a windshield count or locating filling stations in a particular area can provide direct and current information.



## Developing An HAP's Emission Inventory

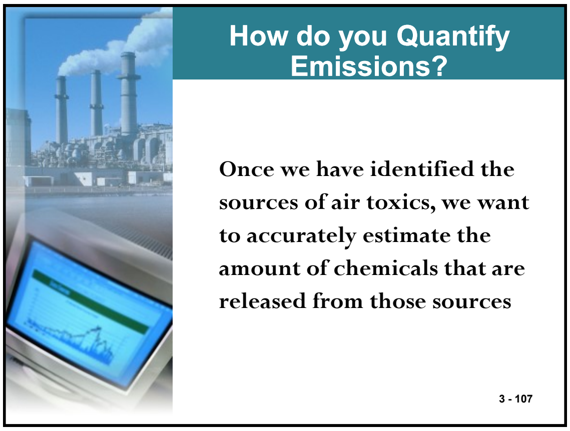
## Eight Steps for Developing an Emission Inventory

- (1) planning;
- (2) gathering information;
- (3) estimating emissions;
- (4) compiling data into a database;
- (5) data augmentation;
- (6) quality control/quality assurance;
- (7) documentation; and
- (8) access to data.
- The emissions inventory process is described in detail in Chapter 7 of EPA's "*Air Toxics Risk Assessment Reference Library, Volume I Technical Resource Manual.*"



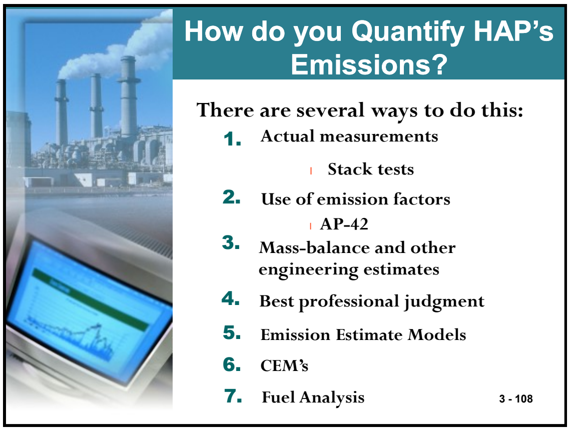
## Building an Inventory

Compile emissions data for various sources:



## How do you Quantify Emissions?

Once we have identified the sources of air toxics, we want to accurately estimate the amount of chemicals that are released from those sources

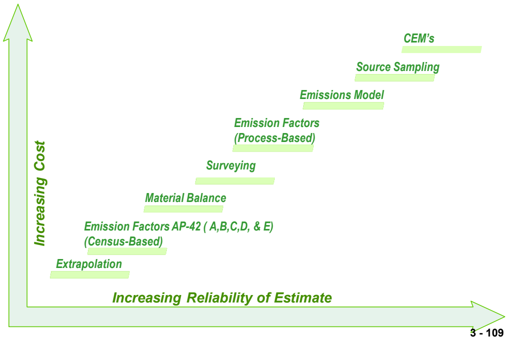


## How do you Quantify HAP's Emissions?

There are several ways to do this:

1. Actual measurements
    - Stack tests
2. Use of emission factors
    - AP-42
3. Mass-balance and other engineering estimates
4. Best professional judgment
5. Emission Estimate Models
6. CEM's
7. Fuel Analysis

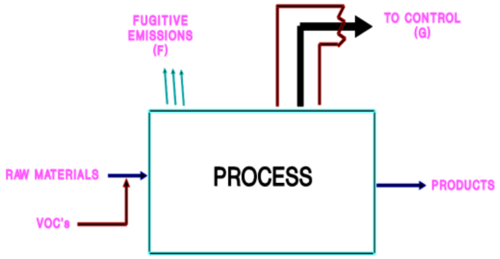
## Emission Estimation Techniques



## Process Emissions

- Process Emissions are emissions from sources where an enclosure, collection system, ducting system, and/or stack (with or without an emission control device) is in place for a process.
- Process emissions represent emissions from process equipment (other than leaks) where the emissions can be captured and directed through a controlled or uncontrolled stack for release into the atmosphere.

## Simplified process/emissions diagram

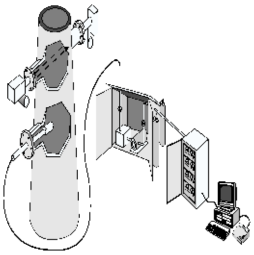


http://www.epa.gov/ttn/atw/coat/common/coatingscalc.html

Surface Coatings of Large Appliances; Printing, Coating, and Dyeing of Fabrics and Other Textiles; and Surface Coating of Metal Furniture Residual Risk and Technology Reviews | US EPA

## Estimation Methods: Continuous Emission Monitoring (CEM) System

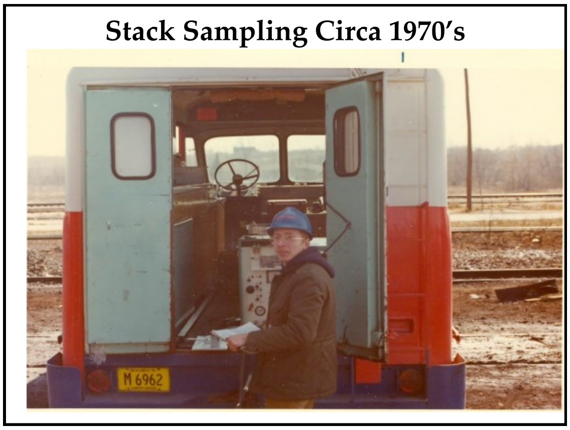
- Sampling is continuous
- CEMs measure and record actual emissions during the time period the monitor is operating and the data produced can be used to estimate emissions for different operating periods.
- CEMs can be required by permit conditions for some pollutants



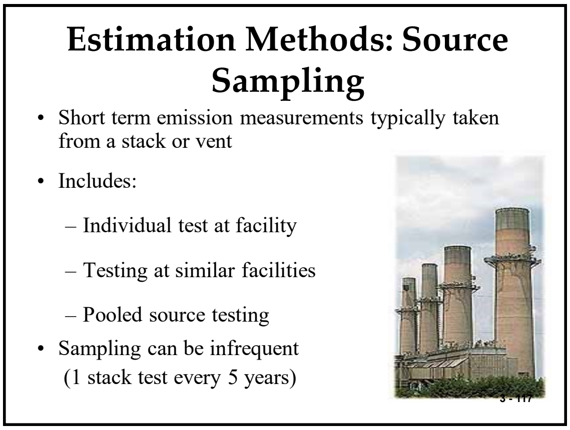
## Source Test

- Source tests are short-term emission measurements taken at a stack or vent.
- Due to the substantial time and equipment involved, a source test requires more resources than an emission factor or material balance emission estimate.
- Typically, a source test uses two instruments:
  - one to collect the pollutant in the emission stream and
  - one to measure the emission stream flow rate.
- The essential difference between a source test and CEM is the duration of time over which measurements are conducted. A source test is conducted over a discrete, finite period of time, while CEM is continuous.

## Stack Sampling Circa 1970's



## Stack Sampling Circa 1970's



## Estimation Methods: Source Sampling

- Short term emission measurements typically taken from a stack or vent
- Includes:
  - Individual test at facility
  - Testing at similar facilities
  - Pooled source testing
- Sampling can be infrequent (1 stack test every 5 years)

## Estimation Methods: Source Sampling

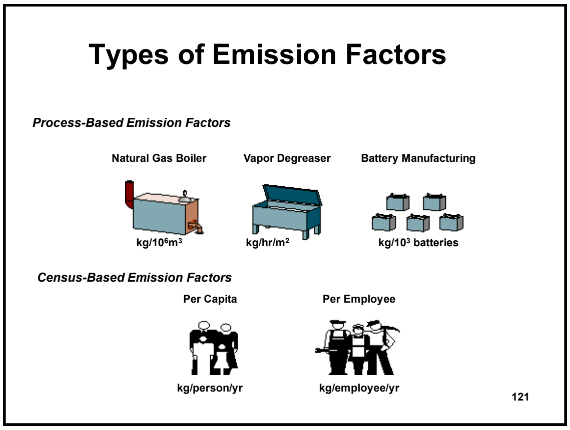
- Emission rates generally reported as concentrations which must be converted to mass units for use in emission inventories.
- Summarize emissions for each pollutant in terms of:
  - Mass loading rate
  - Emission factor
  - Flue gas concentration
- Results depend upon air pollution control device performance and design.
- Screening measurements can be indicators of emissions, potential compliance issues.

## Emission Factors

- Emission factors allow the development of generalized estimates of typical emissions from source categories or individual sources within a category.
- Emission factors, used extensively in point source inventories, estimate the rate at which a pollutant is released to the atmosphere as a result of some process activity.

## Emission Factors

- Definition: a ratio that relates the quantity of a pollutant released to a unit of activity
- Allow development of generalized estimates of typical emissions from source categories or individual sources within a category
- Estimates the rate at which a pollutant is released to the atmosphere as a result of some process



## Types of Emission Factors

*Process-Based Emission Factors*

Natural Gas Boiler — $kg/10^6m^3$

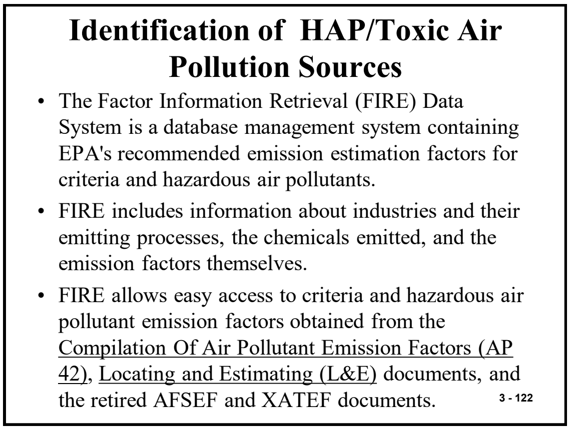
Vapor Degreaser — $kg/hr/m^2$

Battery Manufacturing — $kg/10^3$ batteries

*Census-Based Emission Factors*

Per Capita — kg/person/yr

Per Employee — kg/employee/yr



## Identification of HAP/Toxic Air Pollution Sources

- The Factor Information Retrieval (FIRE) Data System is a database management system containing EPA's recommended emission estimation factors for criteria and hazardous air pollutants.
- FIRE includes information about industries and their emitting processes, the chemicals emitted, and the emission factors themselves.
- FIRE allows easy access to criteria and hazardous air pollutant emission factors obtained from the Compilation Of Air Pollutant Emission Factors (AP 42), Locating and Estimating (L&E) documents, and the retired AFSEF and XATEF documents.

## *http://www.epa.gov/ttn/chief*

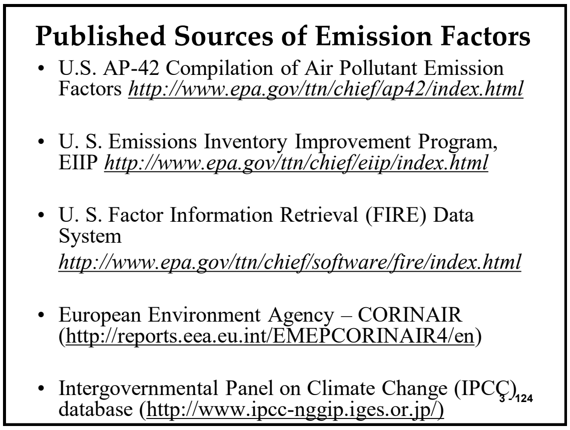
**Emissions Inventories**

Emissions Inventories are the basis for numerous efforts including trends analysis, regional, and local scale air quality modeling, regulatory impact assessments, and human exposure modeling.**Emissions Factors**

The Emissions Factors & Policy Applications Center (EFPAC) provides information about existing emission factors, the revision of existing factors and the development of new factors from stationary point and non point sources. **Emissions Modeling**

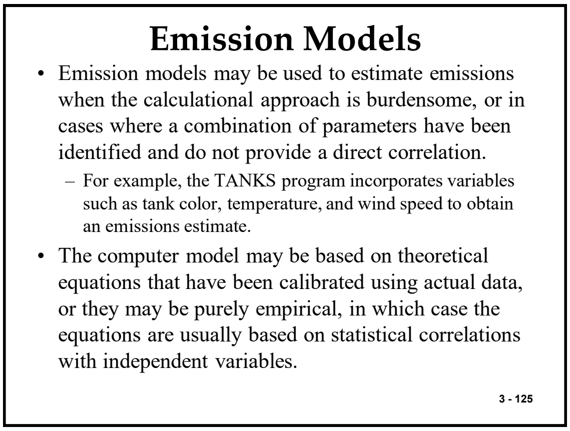
The Emissions Modeling Clearinghouse (EMCH) has been designed to support and promote emission modeling activities both internal and external to the EPA. Through this site the EPA intends to distribute emissions model input formatted inventories based on the latest versions of its National Emission Inventory databases.**Emissions Monitoring Knowledge Base**

EPA's Monitoring Knowledge Base Site provides information about monitoring techniques for air pollution control. The monitoring information is presented by industry type and by control technique.



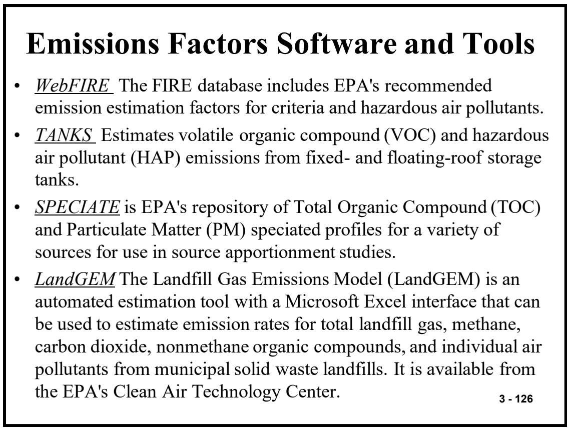
## Published Sources of Emission Factors

- U.S. AP-42 Compilation of Air Pollutant Emission Factors *http://www.epa.gov/ttn/chief/ap42/index.html*
- U. S. Emissions Inventory Improvement Program, EIIP *http://www.epa.gov/ttn/chief/eiip/index.html*
- U. S. Factor Information Retrieval (FIRE) Data System *http://www.epa.gov/ttn/chief/software/fire/index.html*
- European Environment Agency – CORINAIR (http://reports.eea.eu.int/EMEPCORINAIR4/en)
- Intergovernmental Panel on Climate Change (IPCC) database (http://www.ipcc-nggip.iges.or.jp/)



## Emission Models

- Emission models may be used to estimate emissions when the calculational approach is burdensome, or in cases where a combination of parameters have been identified and do not provide a direct correlation.
  - For example, the TANKS program incorporates variables such as tank color, temperature, and wind speed to obtain an emissions estimate.
- The computer model may be based on theoretical equations that have been calibrated using actual data, or they may be purely empirical, in which case the equations are usually based on statistical correlations with independent variables.



## Emissions Factors Software and Tools

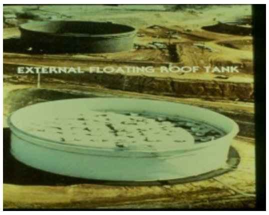
- *WebFIRE* The FIRE database includes EPA's recommended emission estimation factors for criteria and hazardous air pollutants.
- *TANKS* Estimates volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions from fixed- and floating-roof storage tanks.
- *SPECIATE* is EPA's repository of Total Organic Compound (TOC) and Particulate Matter (PM) speciated profiles for a variety of sources for use in source apportionment studies.
- *LandGEM* The Landfill Gas Emissions Model (LandGEM) is an automated estimation tool with a Microsoft Excel interface that can be used to estimate emission rates for total landfill gas, methane, carbon dioxide, nonmethane organic compounds, and individual air pollutants from municipal solid waste landfills. It is available from the EPA's Clean Air Technology Center.

## Emissions Factors Software and Tools

- *WATER9*, a wastewater treatment model, consists of analytical expressions for estimating air emissions of individual waste constituents in wastewater collection, storage, treatment, and disposal facilities; a database listing many of the organic compounds; and procedures for obtaining reports of constituent fates, including air emissions and treatment effectiveness. *PM Calculator* After receiving numerous inquiries regarding the removal of the PM Calculator, EPA has reposted the software. The software is, however, is no longer supported by EPA.
- **http://www.epa.gov/ttn/chief/efpac/efsoftware.html**

## Estimating HAP's Emissions From Storage Tanks

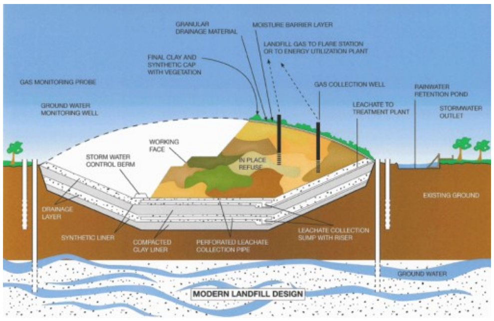
**http://www.epa.gov/ttn/chief/software/tanks/index.html#new**

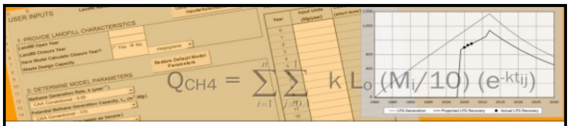


## What is Tanks?

- *TANKS* is a Windows-based computer software program that estimates volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions from fixed- and floating-roof storage tanks.
- *TANKS* is based on the emission estimation procedures from Chapter 7 of EPA's Compilation Air Pollution Emission Factors (AP-42). The user's manual explains the many features and options of *TANKS*. The program includes on-line help for every screen.

## LandGEM Model





$$Q_{CH4} = \sum_{i=1}^{n} \sum_{j=0.1}^{1} k L_o (M_i/10)(e^{-kt_{ij}})$$

- EPA's Landfill Gas Emissions Model (LandGEM) is a Microsoft Excelbased software application that uses a first-order decay rate equation to calculate estimates for methane and LFG generation. LandGEM is the most widely used LFG model and is the industry standard for regulatory and non-regulatory applications in the United States. LandGEM uses the first-order decay equation below to estimate methane generation. Landfill gas (LFG) modeling is the practice of forecasting gas generation and recovery based on past and future waste disposal histories and estimates of gas collection system (GCS) efficiency.

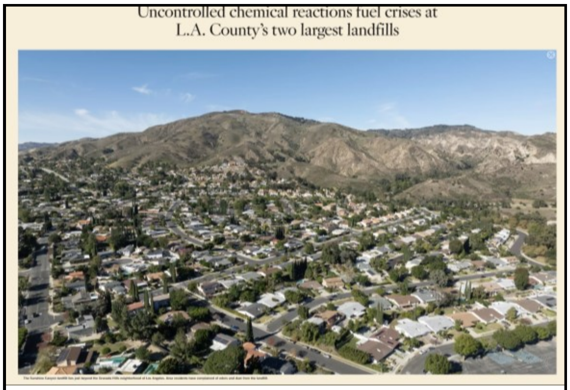
## Sample Output from the LandGEM Model

- **Model Parameters**
  Lo : 100.00 m^3 / Mg
  k : 0.0400 1/yr
  NMOC : 595.00 ppmv
  Methane : 50.0000 % volume
  Carbon Dioxide : 50.0000 % volume
  Air Pollutant : Vinyl Chloride (HAP/VOC)
  Molecular Wt = 62.50 Concentration = 7.340000 ppmV
  ==============================================
  **Landfill Parameters**
  Landfill type : Co-Disposal
  Year Opened : 1969 Current Year : 1999 Closure Year: 1980
  Capacity : 792000 Mg
  Average Acceptance Rate Required from
  Current Year to Closure Year : 0.00 Mg/year

## LandGEM Model Results:

### Vinyl Chloride (HAP/VOC) Emission Rate

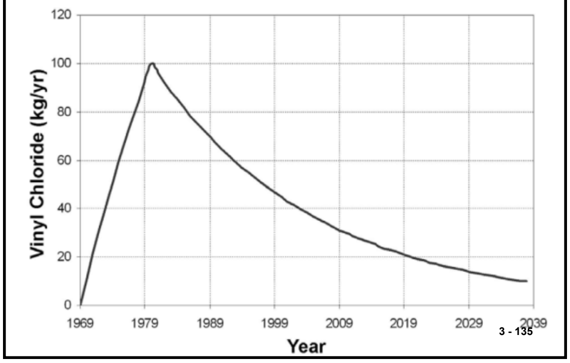
| Year | Refuse In Place (Mg) | (Mg/yr) | (Cubic m/yr) |
|---|---|---|---|
| 1970 | 7.200E+04 | 1.099E-02 | 4.228E+00 |
| 1971 | 1.440E+05 | 2.155E-02 | 8.290E+00 |
| 1972 | 2.160E+05 | 3.170E-02 | 1.219E+01 |
| 1973 | 2.880E+05 | 4.144E-02 | 1.594E+01 |
| 1974 | 3.600E+05 | 5.081E-02 | 1.955E+01 |
| 1975 | 4.320E+05 | 5.981E-02 | 2.301E+01 |
| 1976 | 5.040E+05 | 6.845E-02 | 2.633E+01 |
| 1977 | 5.760E+05 | 7.676E-02 | 2.953E+01 |
| 1978 | 6.480E+05 | 8.474E-02 | 3.260E+01 |
| 1979 | 7.200E+05 | 9.241E-02 | 3.555E+01 |
| 1980 | 7.920E+05 | 9.977E-02 | 3.838E+01 |
| 1981 | 7.920E+05 | 9.586E-02 | 3.688E+01 |
| 1982 | 7.920E+05 | 9.210E-02 | 3.543E+01 |
| 1998 | 7.920E+05 | 4.857E-02 | 1.868E+01 |
| 1999 | 7.920E+05 | 4.666E-02 | 1.795E+01 |
| 2000 | 7.920E+05 | 4.483E-02 | 1.725E+01 |
| . . . . | | | |
| . . . . | | | |
| 2266 | 7.920E+05 | 1.073E-06 | 4.128E-04 |
| 2267 | 7.920E+05 | 1.031E-06 | 3.967E-04 |
| 2268 | 7.920E+05 | 9.907E-07 | 3.811E-04 |



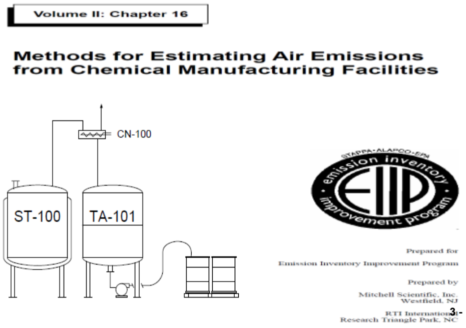
Uncontrolled chemical reactions fuel crises at
L.A. County's two largest landfills

Toxic chemical reactions fuel crises at L.A. County landfills - Los Angeles Times (latimes.com)

## Example Compounds Of Principal Concern Emission Estimates Produced by LandGEM



## Methods for Estimating Air Emissions from Chemical Manufacturing Facilities



Volume II: Chapter 16

Methods for Estimating Air Emissions from Chemical Manufacturing Facilities

Prepared for
Emission Inventory Improvement Program

Prepared by
Mitchell Scientific, Inc.
Westfield, NJ

RTI International
Research Triangle Park, NC

## Air Emissions from Chemical Manufacturing Facilities

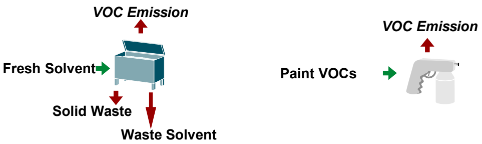
- This guideline document describes the procedures and recommended approaches for estimating emissions from batch chemical manufacturing operations.
- The majority of emissions that occur from batch chemical manufacturing operations are from volatile organic solvents that evaporate during manufacturing. Particulate matter emissions may also occur from the handling of solid powders that are used in manufacturing.
- The air emission sources for chemical manufacturing operations; have been identified as follows:
  ☐ Process operations ☐ Storage tanks ☐ Equipment leaks
  ☐ Wastewater collection and treatment ☐ Cleaning
  ☐ Solvent recovery ☐ Spills

## Estimation Methods: Material Balance

- Approach considers all inputs of a material and all possible fates for the material after passing through the process, including direct air emissions, fugitive air emissions, solid and liquid waste streams, and residual product content
  - Uses measurements of various components of a process to determine air emissions:

    Air emissions = Input – liquid emissions – solid wastes – products – by products – recycled material
- Commonly used to estimate emissions from solvent usage based on contents of various solvents
  - Solvent degreasing operations
  - Surface coating operations

## Examples of Material Balances



Assume waste solvent is sent to a reprocessor and solid waste is sent to a treatment facility

Assume all solvents in paint are evaporated

## Estimation Methods: Engineering Judgment (Extrapolation)

- Last resort to be used only if none of the methods described can be used to generate accurate emission estimates
- Provides an "order of magnitude" estimate with significant uncertainty
- Scaling emissions estimates to create another inventory using scaling parameters
  - Production quantity
  - Material throughput
  - Land area
  - Number of employees
  - Population

## Chapter 3 Questions

- 1. True or False; Does TRI data reveal whether or to what degree the public is exposed to listed chemicals?

## Chapter 3 Questions

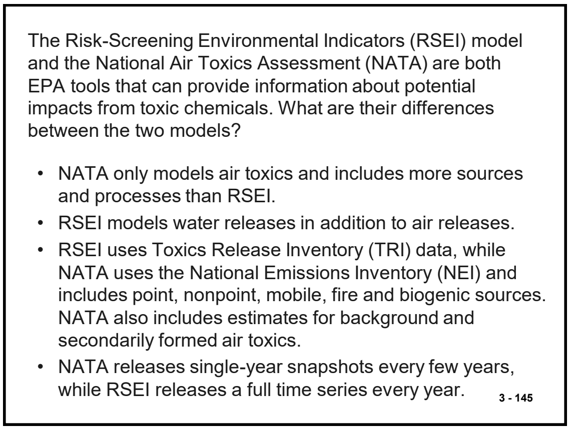
- 1. Answer False: TRI provides information about releases of toxic chemicals from facilities throughout the United States; however, TRI data do not reveal whether or to what degree the public is exposed to listed chemicals. TRI data can, in conjunction with other information, be used as a starting point in evaluating such exposures and the risks posed by such exposures.

## Chapter 3 Questions

- 2. True or false. TRI provides all the information necessary on the quantity of a toxic chemical that is being released from a facility and all the information necessary to answer questions about health risks.

## Chapter 3 Questions

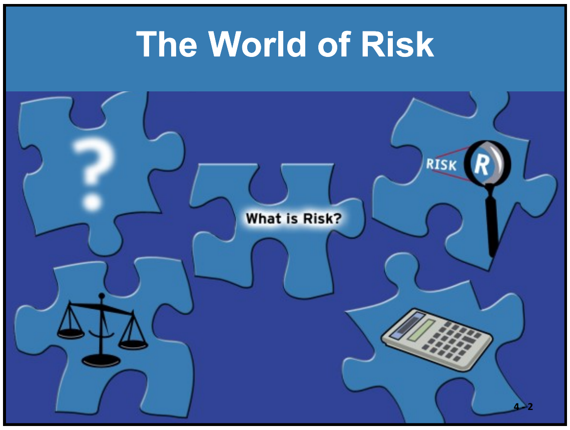
- 2. Answer False: TRI provides useful information on the quantity of a toxic chemical that is being released from a facility. However, it does not provide all the information necessary to answer questions about health risks.



The Risk-Screening Environmental Indicators (RSEI) model and the National Air Toxics Assessment (NATA) are both EPA tools that can provide information about potential impacts from toxic chemicals. What are their differences between the two models?

- NATA only models air toxics and includes more sources and processes than RSEI.
- RSEI models water releases in addition to air releases.
- RSEI uses Toxics Release Inventory (TRI) data, while NATA uses the National Emissions Inventory (NEI) and includes point, nonpoint, mobile, fire and biogenic sources. NATA also includes estimates for background and secondarily formed air toxics.
- NATA releases single-year snapshots every few years, while RSEI releases a full time series every year.

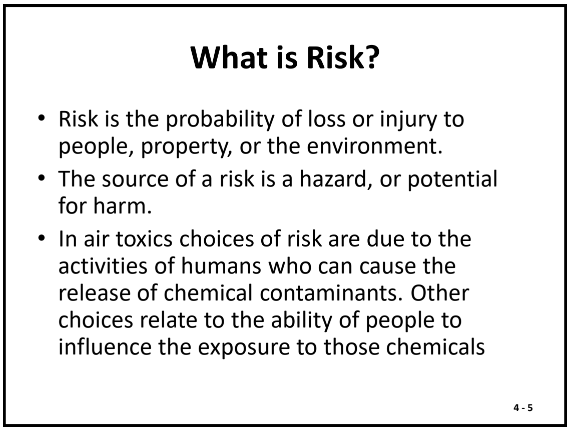
## Introduction to Air Toxics Risk Assessment



## The World of Risk

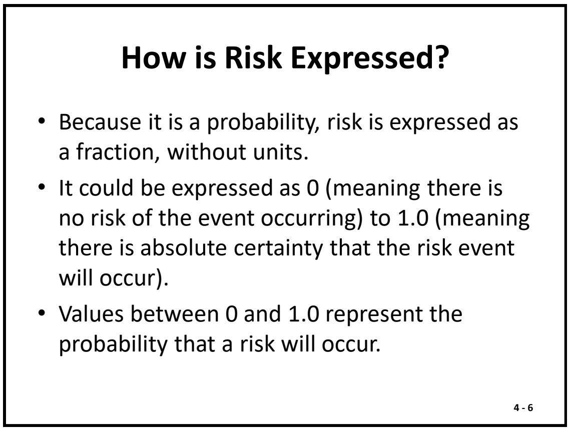
## A Walk Through Risk on Youtube

http://www.youtube.com/watch?v=A_-9d-ihXGU



## What is Risk?

- Risk is the probability of loss or injury to people, property, or the environment.
- The source of a risk is a hazard, or potential for harm.
- In air toxics choices of risk are due to the activities of humans who can cause the release of chemical contaminants. Other choices relate to the ability of people to influence the exposure to those chemicals



## How is Risk Expressed?

- Because it is a probability, risk is expressed as a fraction, without units.
- It could be expressed as 0 (meaning there is no risk of the event occurring) to 1.0 (meaning there is absolute certainty that the risk event will occur).
- Values between 0 and 1.0 represent the probability that a risk will occur.

## Risk

- A simple mathematical formula can show the basis for human health risk assessment.
- Potential for Injury or Disease (i.e., the "Risk") = ƒ (metric of exposure, metric of toxicity)
  - Specifically, the likelihood that injury or disease may occur from exposure to air toxics can be described as a function of two separate, but related, things – an estimate of exposure to a chemical and an estimate of the toxic properties of the chemical:

## Example Risk Estimation

- If approximately 50,000 deaths occur from automobile accidents each year in the U.S., how many fatalities may could occur in a city with a population of 2 million during the coming 3-day weekend.
- Starting with an estimated U.S population of 275,000,000, the fatality rate can be approximated by the deaths divided by the population.

  $F = 50{,}000$ deaths /year/ $2.75 \times 10^{8}$ persons
  $F = 2 \times 10^{-4}$ death/persons-year
  $F = 1.82$ death/person-year
  $F_p = 2 \times 10^{-4}$ death/person-year $\times\ 2 \times 10^{6}$ persons $\times\ 3$ days/365 days/year
  $F_p = 3.3$ deaths/ 3 day weekend

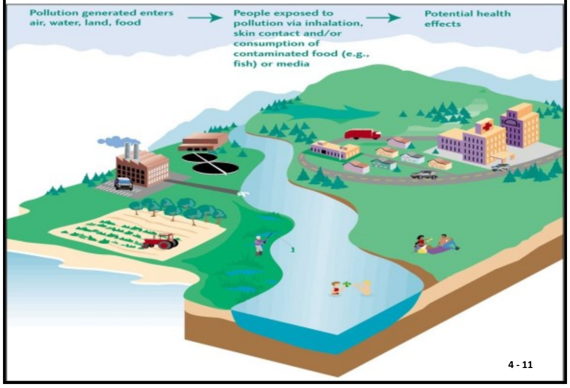
**Environmental Agencies are working to ensure that people and the environment are protected from <u>significant risk</u>…**

**In this class, we are going to study the process EPA uses to evaluate the risks posed to human health from <u>toxic air pollutants</u> and their control or abatement.**

## Human Exposure to Air Toxics

- People are exposed to toxic air pollutants in many ways that can pose health risks, such as by:
- Breathing contaminated air.
- Eating contaminated food products, such as fish from contaminated waters; meat, milk, or eggs from animals that fed 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. Young children are especially vulnerable because they often ingest soil from their hands or from objects they place in their mouths.
- Touching (making skin contact with) contaminated soil, dust, or water (for example, during recreational use of contaminated water bodies).

## Pathway from Pollution to Exposure to Potential Health Effects



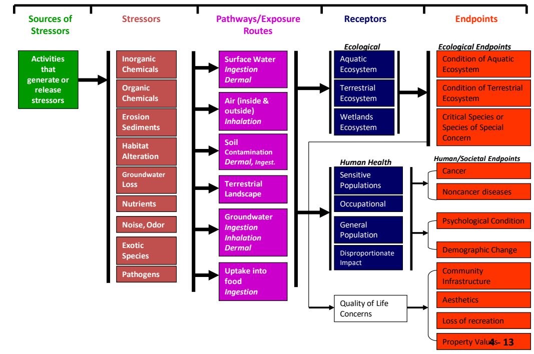
## Environmental Risk

**Human health can be at risk from many different things in the environment:**

- ***Biological Agents***
- ***Physical stresses***
- ***Psychological stresses***
- ***Etc.***

**Some of these risks are voluntary (smoking cigarettes), while some can be seen as involuntary (breathing polluted air).**

## Example of how stresses on people and the environment may lead to negative outcomes



Sources of Stressors
Stressors
Pathways/Exposure Routes
Receptors
Endpoints

Activities that generate or release stressors

Inorganic Chemicals
Organic Chemicals
Erosion Sediments
Habitat Alteration
Groundwater Loss
Nutrients
Noise, Odor
Exotic Species
Pathogens

Surface Water *Ingestion* *Dermal*
Air (inside & outside) *Inhalation*
Soil Contamination *Dermal, Ingest.*
Terrestrial Landscape
Groundwater *Ingestion* *Inhalation* *Dermal*
Uptake into food *Ingestion*

*Ecological*
Aquatic Ecosystem
Terrestrial Ecosystem
Wetlands Ecosystem

*Human Health*
Sensitive Populations
Occupational
General Population
Disproportionate Impact

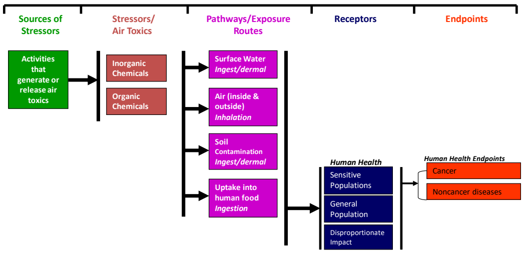
Quality of Life Concerns

*Ecological Endpoints*
Condition of Aquatic Ecosystem
Condition of Terrestrial Ecosystem
Critical Species or Species of Special Concern

*Human/Societal Endpoints*
Cancer
Noncancer diseases
Psychological Condition
Demographic Change
Community Infrastructure
Aesthetics
Loss of recreation
Property Values

---

## Example of how *Air Toxics Releases* may result in adverse human health outcomes



Sources of Stressors
Stressors/ Air Toxics
Pathways/Exposure Routes
Receptors
Endpoints

Activities that generate or release air toxics

Inorganic Chemicals
Organic Chemicals

Surface Water *Ingest/dermal*
Air (inside & outside) *Inhalation*
Soil Contamination *Ingest/dermal*
Uptake into human food *Ingestion*

*Human Health*
Sensitive Populations
General Population
Disproportionate Impact

*Human Health Endpoints*
Cancer
Noncancer diseases

---

## The flow diagram is very detailed and a visualization of pathways and endpoints could be beneficial!

**Redraw this conceptual model with *pictures* of what we think may be happening in the real world when dangerous chemicals are released to the air…**

---

## Conceptual Model

- The conceptual model that follows illustrates how air toxics risk assessments usually focuses, at a minimum, on the inhalation of contaminated air.
- However, for a small subset of air toxics, the risk assessment also may need to address ingestion of or dermal contact with soils, water, or food that have become contaminated with chemicals that have deposited out of the air.

---

## Conceptual Model

- Starting at the upper left hand side of this diagram, air toxics are released from one or more sources (i.e. factories, cars/trucks, small businesses, forest fires) to the air and begin to disperse by the wind away from the point of release.
- Once released, the chemical may remain airborne; convert into a different substance; and/or deposit out of the air onto soils, water, or plants.
- People may be exposed to air toxics by breathing contaminated air (inhalation) or through ingestion of chemicals that can accumulate in soils, sediments, and foods (the latter process is called bioaccumulation)

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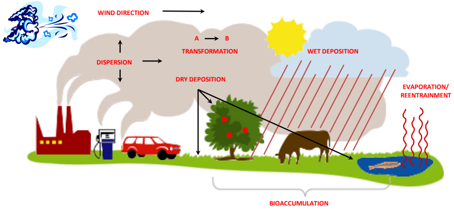
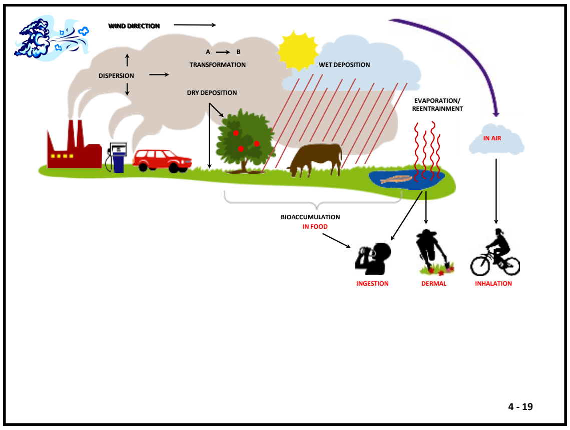
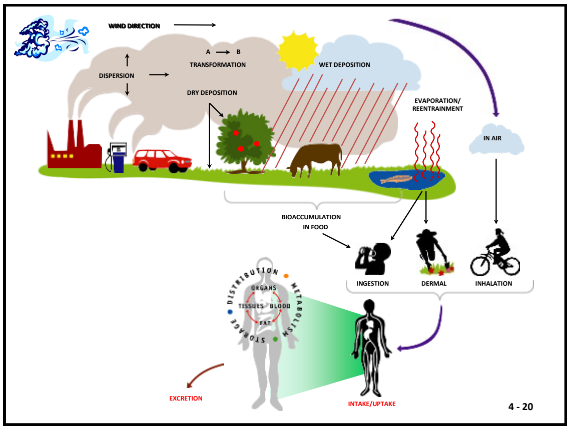
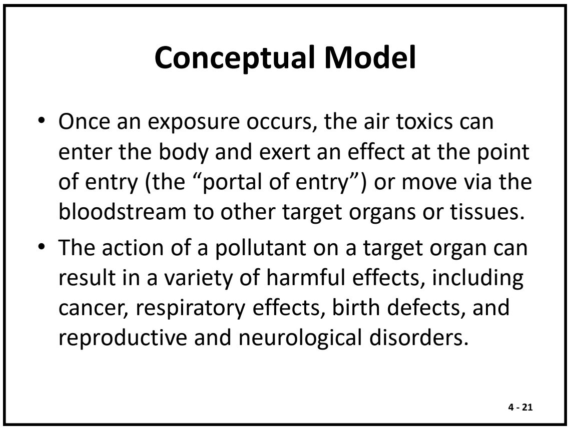


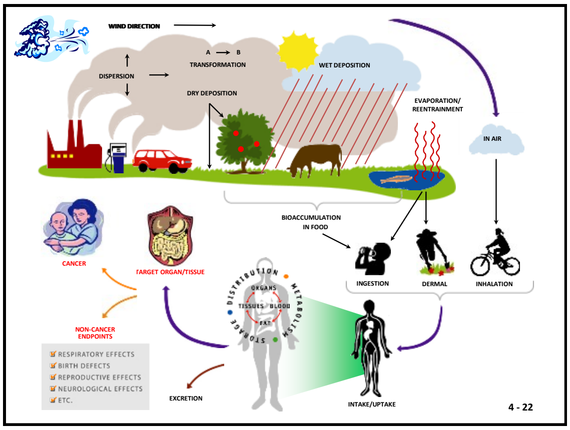


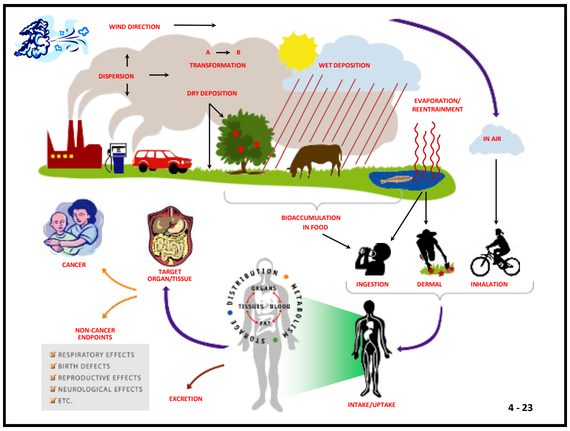


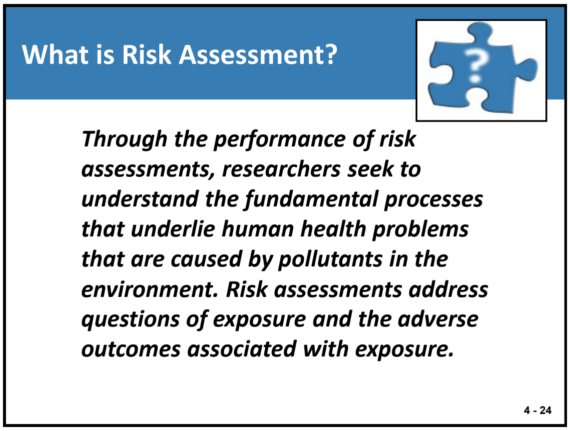


## Conceptual Model

- Once an exposure occurs, the air toxics can enter the body and exert an effect at the point of entry (the “portal of entry”) or move via the bloodstream to other target organs or tissues.
- The action of a pollutant on a target organ can result in a variety of harmful effects, including cancer, respiratory effects, birth defects, and reproductive and neurological disorders.







## What is Risk Assessment?

***Through the performance of risk assessments, researchers seek to understand the fundamental processes that underlie human health problems that are caused by pollutants in the environment. Risk assessments address questions of exposure and the adverse outcomes associated with exposure.***

## What is Risk Assessment?

One possible definition…

***Human health risk assessment is the process of using the factual base of information to define the health effects of exposure of individuals or populations to hazardous materials and situations.***

***Adapted from NAS, 1983***

## What is Risk Assessment?

*Basic Questions for the Risk Assessment Process:*

- *Who is exposed to the environmental pollutants?*
- *What pollutants are they exposed to?*
- *How are they exposed?*
- *How toxic are the agents they are exposed to?*
- *What is the likelihood that harm will occur?*

## What is Risk Assessment?

**Risk assessment is a process for organizing and analyzing information to determine if an environmental chemical or other agent might cause harm to exposed persons and ecosystems. The risk assessment process consists of four primary steps: hazard assessment, dose-response assessment, exposure assessment, and risk characterization. The steps are interrelated, but all include a consideration of all relevant information and a detailed discussion of the strengths and weaknesses of that information.**

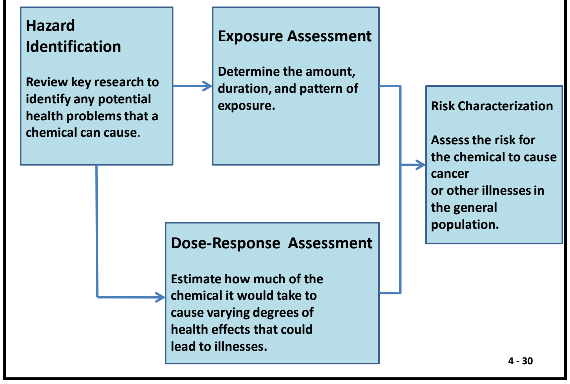
## What is Risk Assessment?

**The current cancer guidelines revision effort emphasizes full characterization of all information, the expanded role of mode-of-action information (key events and processes, starting with the interaction of an agent with a cell, through functional and anatomical changes, resulting in cancer or other health endpoints), the use all information to design a dose-response approach, and a two-step process for dose-response**

## Four-Step, Risk Assessment Process

- In addition to a conceptual model, there is a need for a defined process to quantify relationships among the conceptual model components in order to generate numeric risk estimates. Risk assessment is that process.
- The 1983 National Resource Commission (NRC) report, "*Risk Assessment in the Federal Government: Managing the Process,*" defined risk assessment as a process in which information is analyzed to determine if an environmental hazard might cause harm to exposed persons and ecosystems.
- The NRC report also described the following four-step paradigm for risk assessment process that continues to serve as EPA's model for human health risk assessments:

## The 4 – Step Risk Assessment Process



**Hazard Identification**

**Review key research to identify any potential health problems that a chemical can cause.**

**Exposure Assessment**

**Determine the amount, duration, and pattern of exposure.**

**Dose-Response Assessment**

**Estimate how much of the chemical it would take to cause varying degrees of health effects that could lead to illnesses.**

**Risk Characterization**

**Assess the risk for the chemical to cause cancer or other illnesses in the general population.**

## Hazard Identification

- The first step in a risk assessment is to determine whether the pollutants of concern can be causally linked to the health effects in question (cancer and/or non-cancer).
- Factors such as the route of exposure, the type and quality of the effects, the biological plausibility of findings, the consistency of findings across studies, and the potential for bioaccumulation all contribute to the strength of the hazard identification statement.

## Dose-Response Assessment

- This step is the quantitative characterization of the relationship between the concentration, exposure, or dose of a pollutant and the resultant health effects.
- When adequate data exist, the typical end product of the dose-response assessment for non-cancer effects is the identification of a sub-threshold dose or exposure level that humans could experience daily for a lifetime without appreciable probability of ill effect.
  - For cancer, the typical goal of this step is estimation of a full dose-response curve for low exposures.

## Exposure Assessment

- EPA's current *"Guidelines for Exposure Assessment"*, published in 2019, provide the framework for this step. An exposure assessment for air toxics has four major components: (1) emissions characterization; (2) environmental fate and transport analysis; (3) characterization of the study population; and (4) exposure characterization for both inhalation and non-inhalation pathways

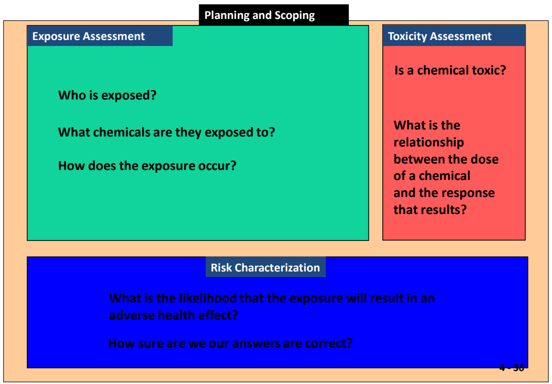
## Risk Characterization

- This step is where all the information from the previous steps is integrated to describe the outcome of the analysis, and where the uncertainty and variability in the results are described.
- EPA's 1995 *"Guidance for Risk Characterization"* is the foundation for this step of the process.

## Framework for Risk Assessment

- The USEPA has developed a general framework for risk assessment for a human health risk assessment as shown on the following slide.
- It includes the following four components (or steps):
  - 1. Planning and scoping (data evaluation);
  - 2. Exposure assessment analysis;
  - 3. Toxicity assessment analysis; and
  - 4. Risk characterization

**The General Air Toxics Risk Assessment Process**



**Planning and Scoping**

**Exposure Assessment**

Who is exposed?

What chemicals are they exposed to?

How does the exposure occur?

**Toxicity Assessment**

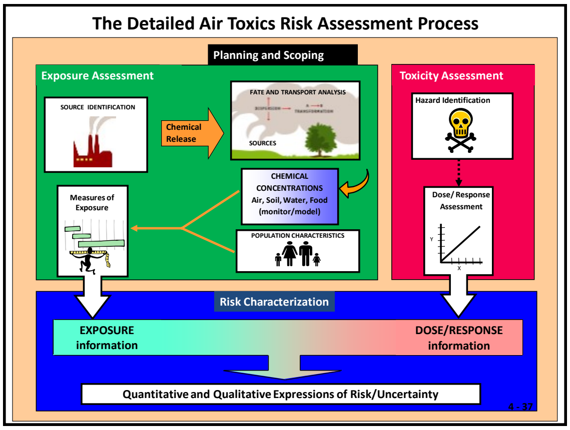
Is a chemical toxic?

What is the relationship between the dose of a chemical and the response that results?

**Risk Characterization**

What is the likelihood that the exposure will result in an adverse health effect?

How sure are we our answers are correct?



## The Detailed Air Toxics Risk Assessment Process

Planning and Scoping

Exposure Assessment

SOURCE IDENTIFICATION

Chemical Release

FATE AND TRANSPORT ANALYSIS

SOURCES

CHEMICAL CONCENTRATIONS Air, Soil, Water, Food (monitor/model)

POPULATION CHARACTERISTICS

Measures of Exposure

Toxicity Assessment

Hazard Identification

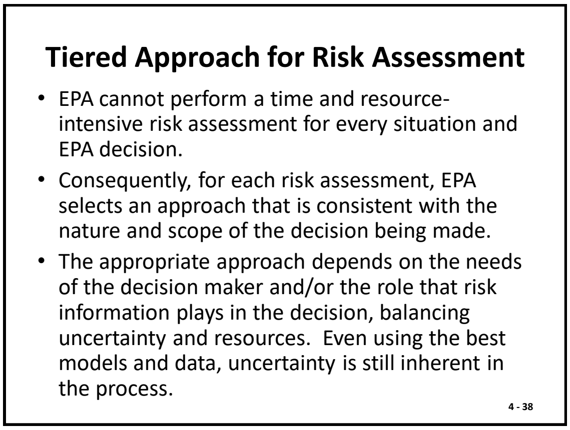
Dose/ Response Assessment

Risk Characterization

EXPOSURE information

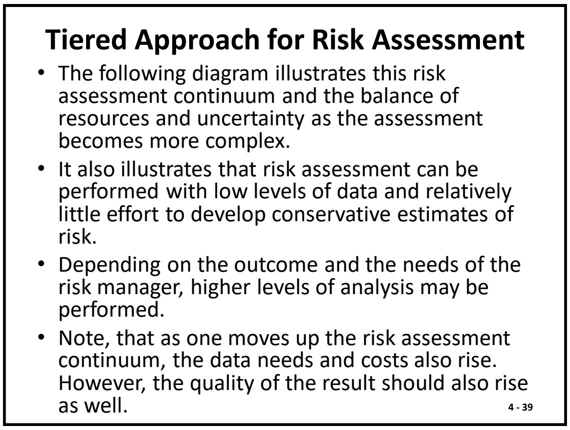
DOSE/RESPONSE information

Quantitative and Qualitative Expressions of Risk/Uncertainty



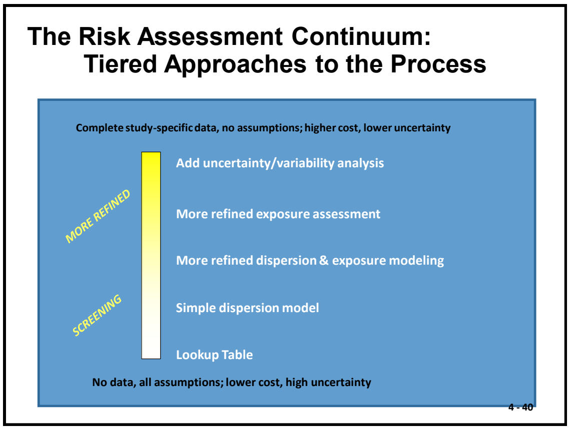
## Tiered Approach for Risk Assessment

- EPA cannot perform a time and resource-intensive risk assessment for every situation and EPA decision.
- Consequently, for each risk assessment, EPA selects an approach that is consistent with the nature and scope of the decision being made.
- The appropriate approach depends on the needs of the decision maker and/or the role that risk information plays in the decision, balancing uncertainty and resources. Even using the best models and data, uncertainty is still inherent in the process.



## Tiered Approach for Risk Assessment

- The following diagram illustrates this risk assessment continuum and the balance of resources and uncertainty as the assessment becomes more complex.
- It also illustrates that risk assessment can be performed with low levels of data and relatively little effort to develop conservative estimates of risk.
- Depending on the outcome and the needs of the risk manager, higher levels of analysis may be performed.
- Note, that as one moves up the risk assessment continuum, the data needs and costs also rise. However, the quality of the result should also rise as well.



## The Risk Assessment Continuum: Tiered Approaches to the Process

Complete study-specific data, no assumptions; higher cost, lower uncertainty

Add uncertainty/variability analysis

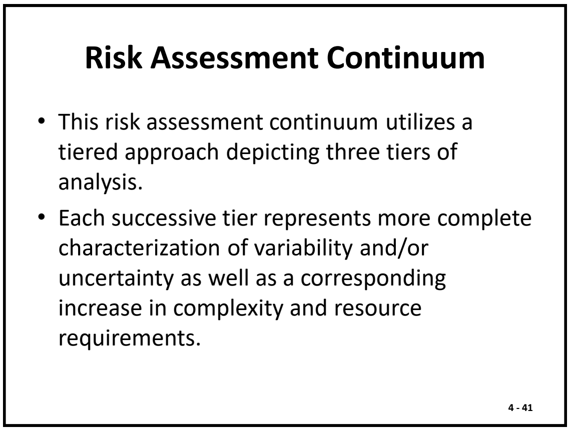
More refined exposure assessment

More refined dispersion & exposure modeling

Simple dispersion model

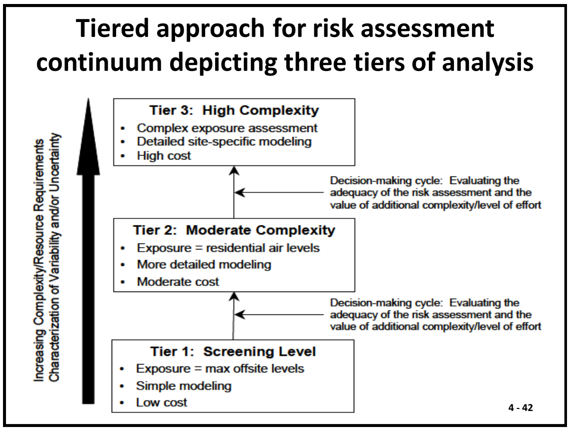
Lookup Table

No data, all assumptions; lower cost, high uncertainty



## Risk Assessment Continuum

- This risk assessment continuum utilizes a tiered approach depicting three tiers of analysis.
- Each successive tier represents more complete characterization of variability and/or uncertainty as well as a corresponding increase in complexity and resource requirements.



## Tiered approach for risk assessment continuum depicting three tiers of analysis

**Tier 3: High Complexity**
- Complex exposure assessment
- Detailed site-specific modeling
- High cost

Decision-making cycle: Evaluating the adequacy of the risk assessment and the value of additional complexity/level of effort

**Tier 2: Moderate Complexity**
- Exposure = residential air levels
- More detailed modeling
- Moderate cost

Decision-making cycle: Evaluating the adequacy of the risk assessment and the value of additional complexity/level of effort

**Tier 1: Screening Level**
- Exposure = max offsite levels
- Simple modeling
- Low cost

## Tier 1

- **Tier 1** is represented as a relatively simple, screening-level analysis using conservative exposure assumptions (e.g., receptors are located in the area with the highest estimated concentrations) and relatively simple modeling (e.g., a model that requires few inputs, most of which can be “generic,” yet conservative).

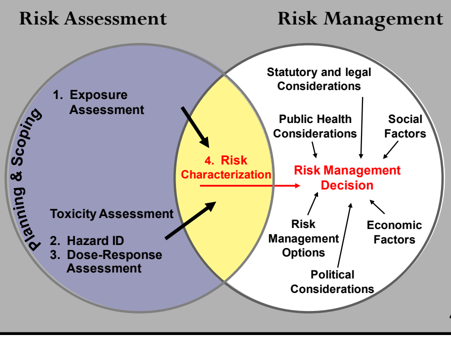
## Tier 2 & Tier 3

- **Tier 2** is represented as an intermediate-level analysis using more realistic exposure assumptions (e.g., use of actual receptor locations) and more detailed modeling (e.g., a model that requires additional site-specific inputs).
- **Tier 3** is represented as an advanced analysis using probabilistic techniques such as Monte Carlo analysis

## Risk Assessment and Risk Management

- **Risk management** refers to the regulatory and other actions taken to limit or control exposures to a chemical.
- **Risk assessment**, on the other hand, is a tool used to support risk management decisions by providing quantitative and qualitative expressions of risk, along with attendant uncertainties.
  - Specifically, the risk assessment conveys a quantitative and qualitative description of the types of impacts that may occur from exposure to an air toxic, the likelihood that these impacts will occur given existing conditions, and the uncertainties surrounding the analysis.

## The General Four Step Risk Assessment Process



Risk Assessment

Risk Management

Planning & Scoping

1. Exposure Assessment

Toxicity Assessment

2. Hazard ID

3. Dose-Response Assessment

4. Risk Characterization

Statutory and legal Considerations

Public Health Considerations

Social Factors

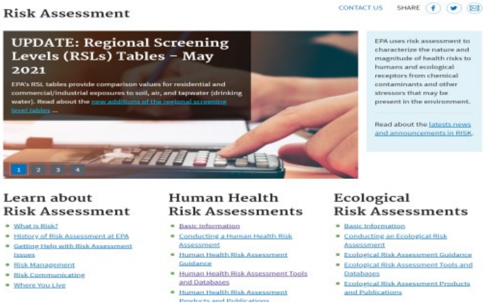
Risk Management Decision

Risk Management Options

Economic Factors

Political Considerations

## Risk Assessment Guidance & Tools



Risk Assessment

CONTACT US SHARE

UPDATE: Regional Screening Levels (RSLs) Tables – May 2021

EPA's RSL tables provide comparison values for residential and commercial/industrial exposures to soil, air, and tapwater (drinking water). Read about the new additions of the regional screening level tables ...

EPA uses risk assessment to characterize the nature and magnitude of health risks to humans and ecological receptors from chemical contaminants and other stressors that may be present in the environment.

Read about the latests news and announcements in RISK.

Learn about Risk Assessment
- What is Risk?
- History of Risk Assessment at EPA
- Getting Help with Risk Assessment Issues
- Risk Management
- Risk Communicating
- Where You Live

Human Health Risk Assessments
- Basic Information
- Conducting a Human Health Risk Assessment
- Human Health Risk Assessment Guidance
- Human Health Risk Assessment Tools and Databases
- Human Health Risk Assessment Products and Publications

Ecological Risk Assessments
- Basic Information
- Conducting an Ecological Risk Assessment
- Ecological Risk Assessment Guidance
- Ecological Risk Assessment Tools and Databases
- Ecological Risk Assessment Products and Publications

Risk Assessment | US EPA

Human Health Risk Assessment | Risk Assessment | US EPA

## Risk Assessment Guidance & Tools

- Risk Assessment | US EPA
- https://www.tceq.texas.gov/assets/public/comm_exec/pubs/rg/rg-263.pdf
- https://www.tceq.texas.gov/toxicology
- http://dnr.mo.gov/env/apcp/docs/cp-hapraltbl6.pdf
- https://www.epa.gov/risk/regional-screening-levels-rsls-equations
- Dose-Response Assessment for Assessing Health Risks Associated With Exposure to Hazardous Air Pollutants | US EPA

## Examples of Risk Assessments National and Local Community

National Air Toxics Assessment

Want more details? Access all NATA results files.

On August 22, 2018, EPA released the most recent update to the National Air Toxics Assessment (NATA). NATA uses emissions data from 2014 to estimate health risks from toxic air pollutants.

Learn more

En español

- Overview
- Limitations
- Glossary of Terms
- Frequent Questions

- 2014 Assessment Results
- 2014 NATA Map
- 2014 Assessment Methods

- Previous versions of NATA
- Other environmental screening tools
- Learn about risk assessment
- Hazardous Air Pollutants website
- Ethylene Oxide website
- Urban Air Toxics website

https://www.epa.gov/national-air-toxics-assessment

## What Is NATA?

Started 1998 as the "Cumulative Exposure Project" with 32 Hazardous Air Pollutants (HAPs).

Today, an in-depth screening and prioritization tool that displays emissions, monitoring, and risk data on a map, including:

- – Sources of 180 "air toxics" emissions
- – Air toxics monitoring data for 2005 to 2013
- – Modeled annual ambient concentrations
- – Estimated cancer risks and respiratory hazard indices
- – From national-scale down to census tracts

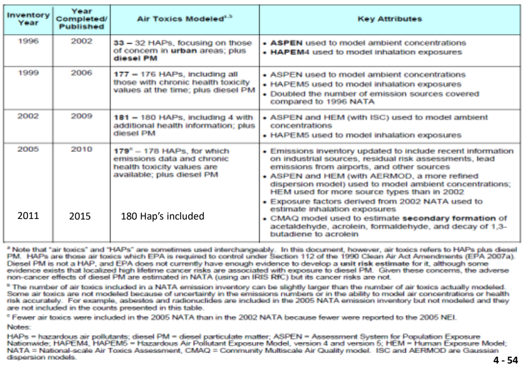
## National-Scale Air Toxics Assessment (NATA)

- Characterization of air toxics across the nation
- Nationwide assessment with *census tract resolution for 177 (for 2014 NATA) air toxics plus diesel PM*
- Emissions, modeled ambient concentrations and estimated *inhalation exposures from outdoor sources*
- *Cancer and non-cancer risk estimates for the 133 air toxics with health data based on chronic exposures*

## NATA's Purpose and Goal

- NATA results are intended to focus resources on air toxics, locations, or populations that are associated with the greatest potential health risks.
- The goal of NATA is to identify those air toxics of greatest potential concern with regard to their contribution to population risk.
- The results are used to set priorities for the collection of additional air toxics information, including emissions and monitoring data.
- NATA was designed to help guide efforts to reduce toxic air pollution and to provide information that can be used to further the already significant emissions reductions achieved in the United States since 1990.

## NATAs EPA Has Conducted to Date



| Inventory Year | Year Completed/ Published | Air Toxics Modeled[a,b] | Key Attributes |
|---|---|---|---|
| 1996 | 2002 | **33 –** 32 HAPs, focusing on those of concern in **urban** areas; plus **diesel PM** | • **ASPEN** used to model ambient concentrations<br>• **HAPEM4** used to model inhalation exposures |
| 1999 | 2006 | **177 –** 176 HAPs, including all those with chronic health toxicity values at the time; plus diesel PM | • ASPEN used to model ambient concentrations<br>• HAPEM5 used to model inhalation exposures<br>• Doubled the number of emission sources covered compared to 1996 NATA |
| 2002 | 2009 | **181 –** 180 HAPs, including 4 with additional health information; plus diesel PM | • ASPEN and HEM (with ISC) used to model ambient concentrations<br>• HAPEM5 used to model inhalation exposures |
| 2005 | 2010 | **179**[c] – 178 HAPs, for which emissions data and chronic health toxicity values are available; plus diesel PM | • Emissions inventory updated to include recent information on industrial sources, residual risk assessments, lead emissions from airports, and other sources<br>• ASPEN and HEM (with AERMOD, a more refined dispersion model) used to model ambient concentrations; HEM used for more source types than in 2002<br>• Exposure factors derived from 2002 NATA used to estimate inhalation exposures<br>• CMAQ model used to estimate **secondary formation** of acetaldehyde, acrolein, formaldehyde, and decay of 1,3-butadiene to acrolein |
| 2011 | 2015 | 180 Hap's included | |

[a] Note that "air toxics" and "HAPs" are sometimes used interchangeably. In this document, however, air toxics refers to HAPs plus diesel PM. HAPs are those air toxics which EPA is required to control under Section 112 of the 1990 Clean Air Act Amendments (EPA 2007a). Diesel PM is not a HAP, and EPA does not currently have enough evidence to develop a **unit risk estimate** for it, although some evidence exists that localized high lifetime cancer risks are associated with exposure to diesel PM. Given these concerns, the adverse non-cancer effects of diesel PM are estimated in NATA (using an IRIS RfC) but its cancer risks are not.

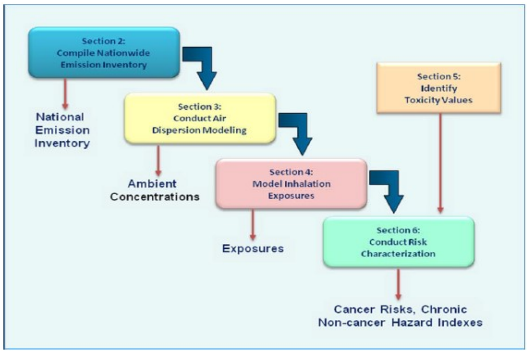
[b] The number of air toxics included in a NATA emission inventory can be slightly larger than the number of air toxics actually modeled. Some air toxics are not modeled because of uncertainty in the emissions numbers or in the ability to model air concentrations or health risk accurately. For example, asbestos and radionuclides are included in the 2005 NATA emission inventory but not modeled and they are not included in the counts presented in this table.

[c] Fewer air toxics were included in the 2005 NATA than in the 2002 NATA because fewer were reported to the 2005 NEI.

Notes:

HAPs = hazardous air pollutants; diesel PM = diesel particulate matter; ASPEN = Assessment System for Population Exposure Nationwide; HAPEM4, HAPEM5 = Hazardous Air Pollutant Exposure Model, version 4 and version 5; HEM = Human Exposure Model; NATA = National-scale Air Toxics Assessment, CMAQ = Community Multiscale Air Quality model. ISC and AERMOD are Gaussian dispersion models.

## The NATA Risk Assessment Process



Section 2:
Compile Nationwide
Emission Inventory

National
Emission
Inventory

Section 3:
Conduct Air
Dispersion Modeling

Ambient
Concentrations

Section 4:
Model Inhalation
Exposures

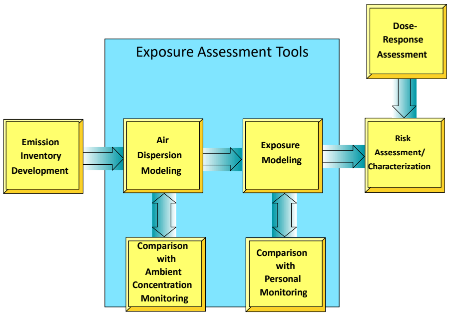
Exposures

Section 5:
Identify
Toxicity Values

Section 6:
Conduct Risk
Characterization

Cancer Risks, Chronic
Non-cancer Hazard Indexes

## Components of the National-Scale Assessment



Exposure Assessment Tools

Emission Inventory Development

Air Dispersion Modeling

Exposure Modeling

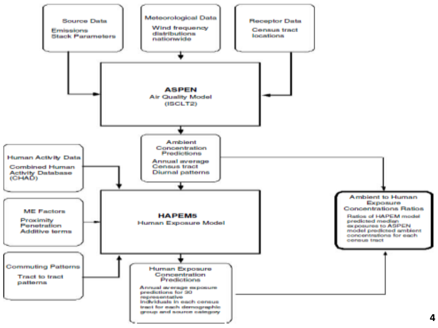
Dose-Response Assessment

Risk Assessment/ Characterization

Comparison with Ambient Concentration Monitoring

Comparison with Personal Monitoring

## Components of air quality and exposure modeling tools used to calculate model predicted exposure to concentration ratios



Source Data
Emissions
Stack Parameters

Meteorological Data
Wind frequency distributions nationwide

Receptor Data
Census tract locations

**ASPEN**
Air Quality Model
(ISCLT2)

Ambient Concentration Predictions
Annual average
Census tract
Diurnal patterns

Human Activity Data
Combined Human Activity Database (CHAD)

ME Factors
Proximity
Penetration
Additive terms

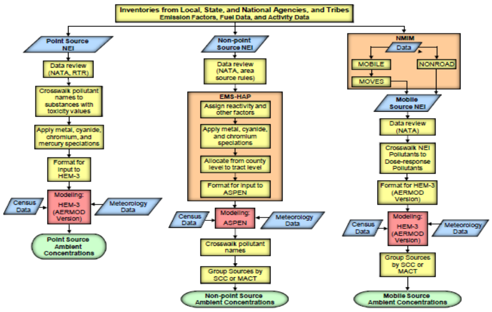
Commuting Patterns
Tract to tract patterns

**HAPEM5**
Human Exposure Model

Human Exposure Concentration Predictions
Annual average exposure predictions for 30 representative individuals in each census tract for each demographic group and source category

Ambient to Human Exposure Concentrations Ratios
Ratios of HAPEM model predicted median exposures to ASPEN model predicted ambient concentrations for each census tract

## The NATA Emissions Inventory and Ambient Concentration Development Processes for Point Sources, Non-point Sources, and Mobile Sources



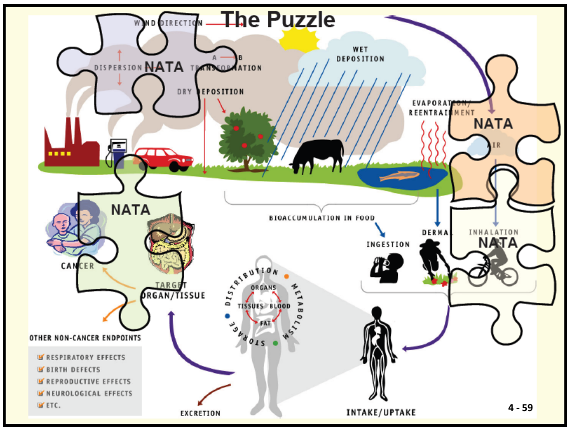
Inventories from Local, State, and National Agencies, and Tribes
Emission Factors, Fuel Data, and Activity Data

Point Source NEI
Data review (NATA, RTR)
Crosswalk pollutant names to substances with toxicity values
Apply metal, cyanide, chromium, and mercury speciations
Format for input to HEM-3
Census Data
Modeling: HEM-3 (AERMOD Version)
Meteorology Data
Point Source Ambient Concentrations

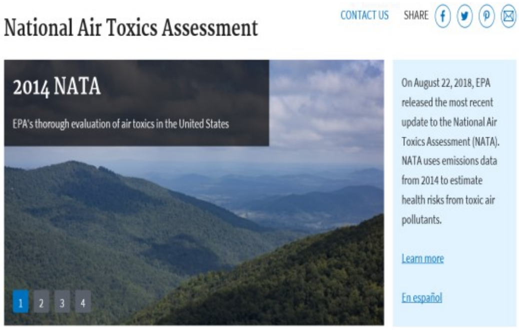
Non-point Source NEI
Data review (NATA, area source rules)
EMS-HAP
Assign reactivity and other factors
Apply metal, cyanide, and chromium speciations
Allocate from county level to tract level
Format for input to ASPEN
Census Data
Modeling: ASPEN
Meteorology Data
Crosswalk pollutant names
Group Sources by SCC or MACT
Non-point Source Ambient Concentrations

NMIM
Data
MOBILE
NONROAD
MOVES
Mobile Source NEI
Data review (NATA)
Crosswalk NEI Pollutants to Dose-response Pollutants
Format for HEM-3 (AERMOD Version)
Census Data
Modeling: HEM-3 (AERMOD Version)
Meteorology Data
Group Sources by SCC or MACT
Mobile Source Ambient Concentrations

## The Puzzle



## NATA Web site



National Air Toxics Assessment

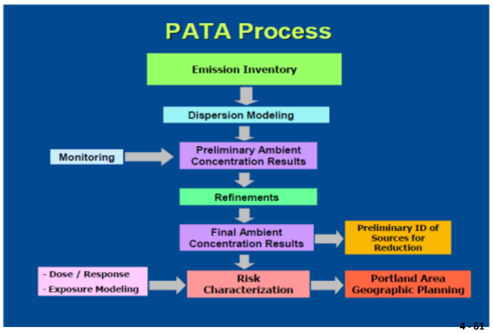
2014 NATA

EPA's thorough evaluation of air toxics in the United States

On August 22, 2018, EPA released the most recent update to the National Air Toxics Assessment (NATA). NATA uses emissions data from 2014 to estimate health risks from toxic air pollutants.

https://www.epa.gov/national-air-toxics-assessment

## Community Example: Portland Air Toxics Assessment



PATA Process

Emission Inventory

Dispersion Modeling

Monitoring

Preliminary Ambient Concentration Results

Refinements

Final Ambient Concentration Results

Preliminary ID of Sources for Reduction

- Dose / Response
- Exposure Modeling

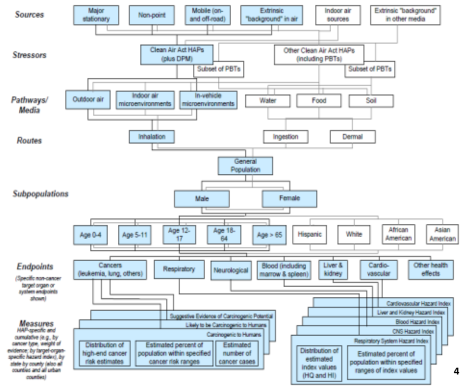
Risk Characterization

Portland Area Geographic Planning

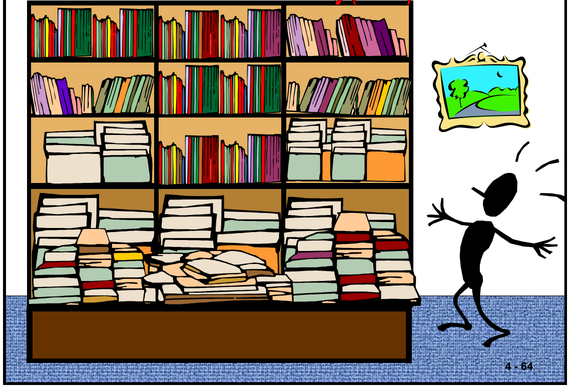
## Portland Air Toxics Assessment Purpose

- The Portland Air Toxics Assessment (PATA) was designed to provide more refined estimates of the most significant air toxics in the Portland area.
- This allows the Department to better characterize the risks from air toxics and better understand local patterns of air toxics exposure and locations with elevated risk.
- By producing more detailed information about the sources of air toxics emissions in Portland, PATA establishes a foundation from which the Department can develop emission reduction strategies and measure changes.
- PATA enables the Department to communicate about air toxics and promote voluntary reductions in Portland in advance of a more prescribed planning process.

## Generalized Conceptual Model for Air Toxics Risk Assessments



## Air Toxics Risk Assessment Library (ATRA)



## Air Toxics Risk Assessment Library (ATRA)

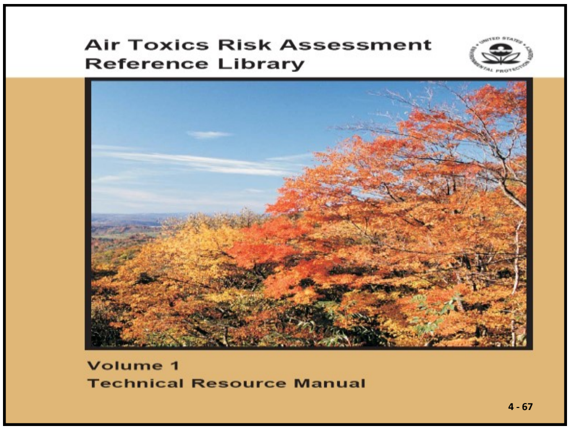
- All Three Volumes are on the Handout CD
- Also found at:

https://www.epa.gov/fera/risk-assessment-and-modeling-air-toxics-risk-assessment-reference-library

## ATRA

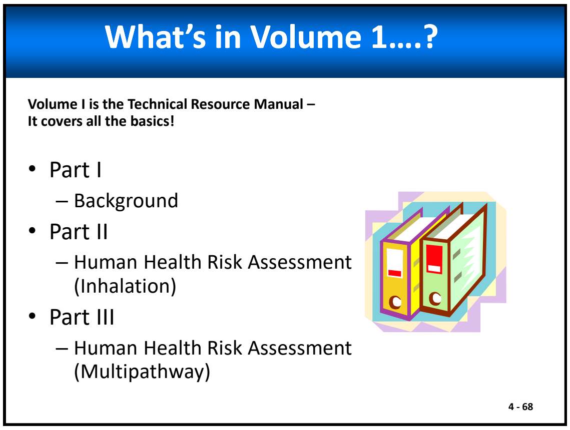
- **Compendium of methods for conducting facility-specific and community-scale assessments**
  - **Volume 1**: Technical Resource Manual
  - **Volume 2**: Facility-specific Assessment
  - **Volume 3**: Community-Level Assessment

**http://www.epa.gov/ttn/fera/risk_atra_main.html**



Air Toxics Risk Assessment
Reference Library

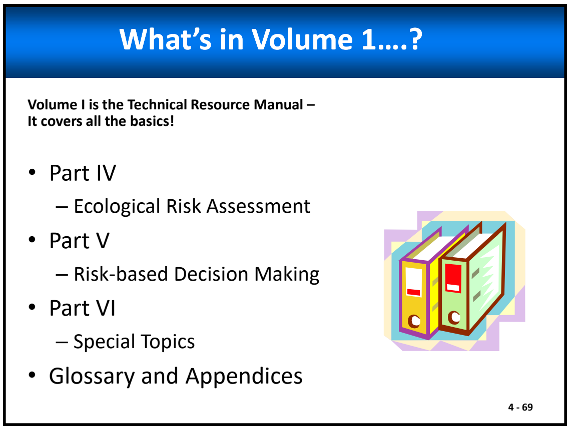
Volume 1
Technical Resource Manual



## What's in Volume 1….?

**Volume I is the Technical Resource Manual –**
**It covers all the basics!**

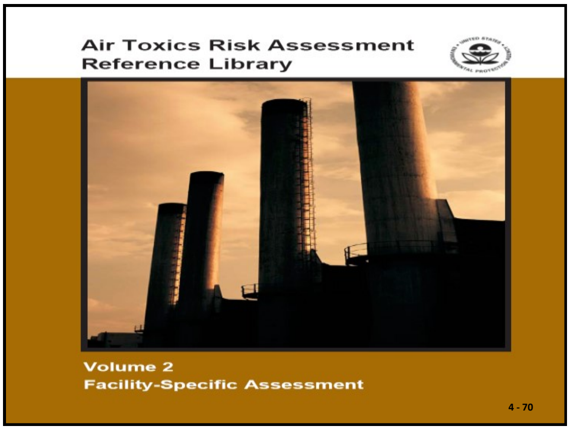
- Part I
  - Background
- Part II
  - Human Health Risk Assessment (Inhalation)
- Part III
  - Human Health Risk Assessment (Multipathway)



## What's in Volume 1….?

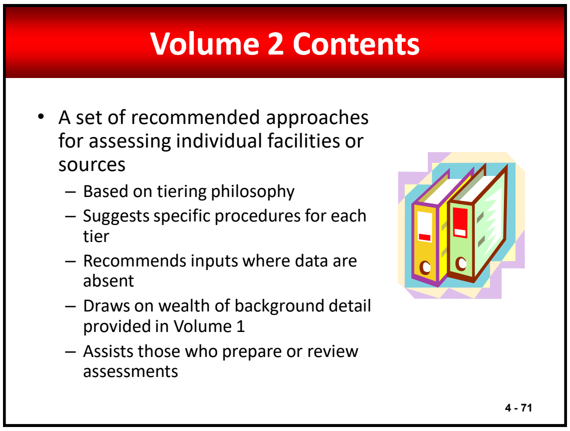
**Volume I is the Technical Resource Manual –**
**It covers all the basics!**

- Part IV
  - Ecological Risk Assessment
- Part V
  - Risk-based Decision Making
- Part VI
  - Special Topics
- Glossary and Appendices



Air Toxics Risk Assessment
Reference Library

Volume 2
Facility-Specific Assessment

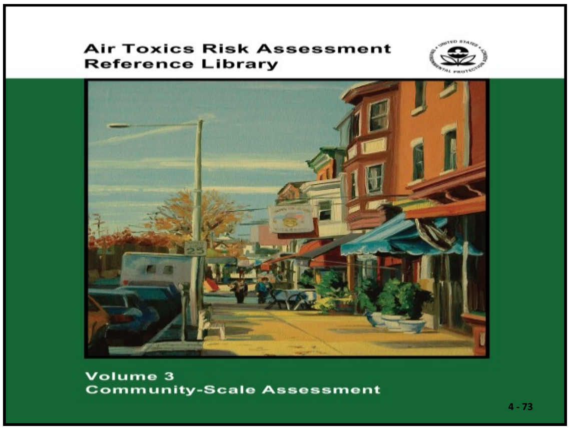


## Volume 2 Contents

- A set of recommended approaches for assessing individual facilities or sources
  - Based on tiering philosophy
  - Suggests specific procedures for each tier
  - Recommends inputs where data are absent
  - Draws on wealth of background detail provided in Volume 1
  - Assists those who prepare or review assessments

## Volume 2 Contains….

- Four major chapters
  - I Background
  - II Overview and introduction
  - III Inhalation risk assessment (human health only)
  - IV Multipathway risk assessment
    - » Sections 1-4 – Human health
    - » Section 5 – Ecological



Air Toxics Risk Assessment
Reference Library

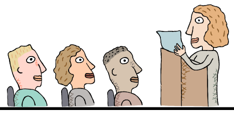
Volume 3
Community-Scale Assessment

## Volume 3

- **Describes to communities how they can evaluate and reduce risks at the local level, including:**
  - Screening level and more detailed analytical approaches, including multi-source air toxics assessments
  - How to balance the need for assessment versus the need for action
  - How to identify and prioritize risk reduction options and measure success
  - How to develop resources
  - Focused information on stakeholder involvement and communicating information in a community-based setting

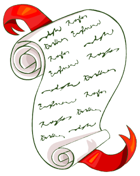
## Volume 3 - Intended Audiences

- The primary audiences are the Federal, State, local, and tribal (S/L/T) air agencies who either conduct, review, or otherwise participate in community-scale air toxics assessments.
- Secondary audiences are the various community stakeholders who wish to participate in the community-scale air toxics evaluation process.



## Contents – Volume 3

- **Part I Background** presents an introduction to this document and the concept behind community-scale air toxics assessments.
- **Part II Human Health Assessment: Inhalation** provides an overview of suggested tools and approaches for conducting a community-scale multisource air toxics inhalation risk assessment.
- **Part III Multimedia Air Toxics Assessment** provides a brief discussion on assessing the impact of air toxics in other media (e.g., mercury deposition with subsequent uptake in food fish).
- **Part IV Other Environmental Risk Factors of Concern to Communities** describes how to put the results of the air toxics assessment in context with other community-scale environmental risk factors and how to identify, prioritize, select, and implement risk reduction approaches for these additional concerns.



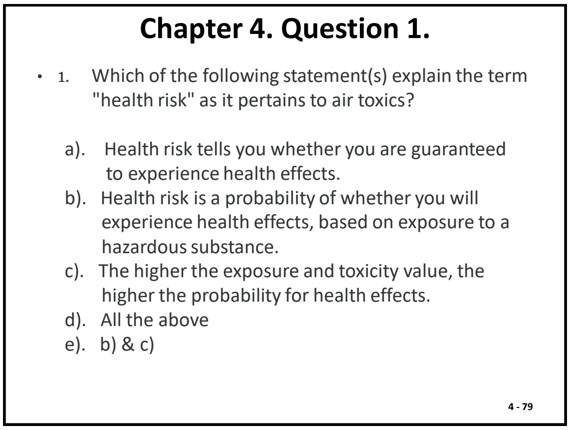
## Community Air Screening How-To Manual

The How To Manual presents and explains a step-by-step process that a community can follow to:

- form a partnership to access technical expertise,
- identify and inventory all local sources of air pollutants,
- review these sources to identify the known hazards that might present a potential health risk to the community, and,
- set priorities and develop a plan for making improvements.
-
- https://www.epa.gov/fera/risk-assessment-and-modeling-air-toxics-risk-assessment-reference-library
- https://www.epa.gov/risk/regional-screening-levels-rsls-equations
- http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/index.htm

## Chapter 4 Questions

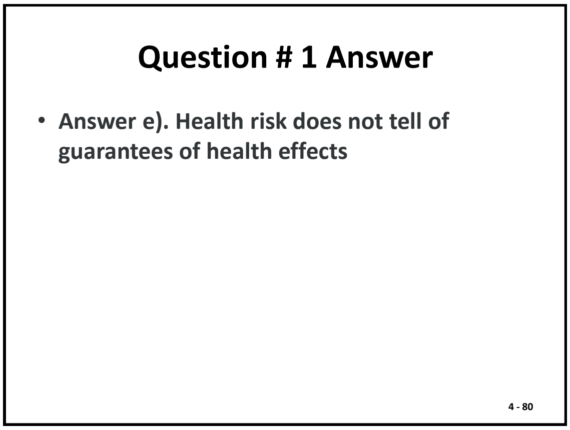
- **Review Questions**



## Chapter 4. Question 1.

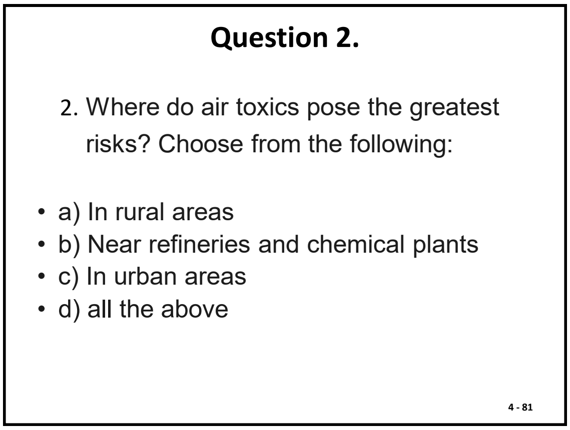
- 1. Which of the following statement(s) explain the term "health risk" as it pertains to air toxics?

  a). Health risk tells you whether you are guaranteed to experience health effects.
  b). Health risk is a probability of whether you will experience health effects, based on exposure to a hazardous substance.
  c). The higher the exposure and toxicity value, the higher the probability for health effects.
  d). All the above
  e). b) & c)



## Question # 1 Answer

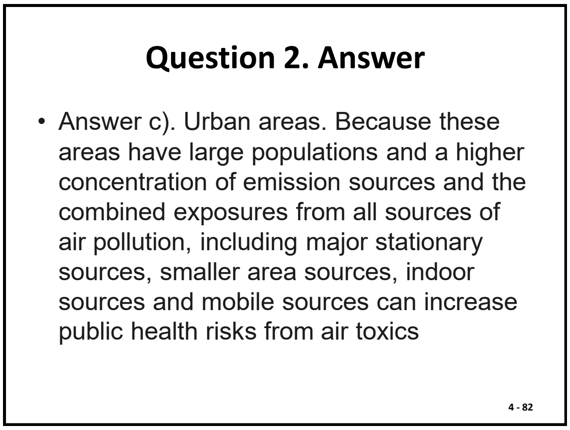
- **Answer e). Health risk does not tell of guarantees of health effects**



## Question 2.

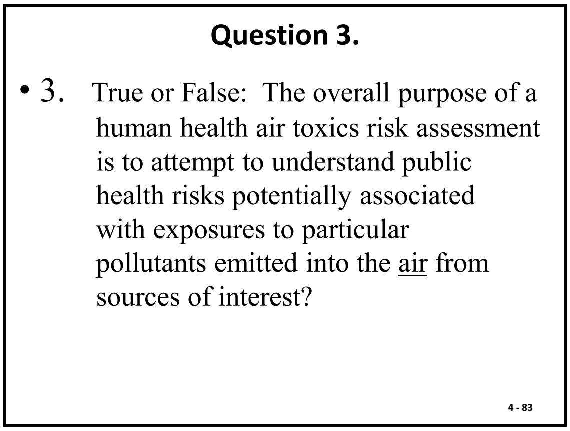
2. Where do air toxics pose the greatest risks? Choose from the following:

- a) In rural areas
- b) Near refineries and chemical plants
- c) In urban areas
- d) all the above



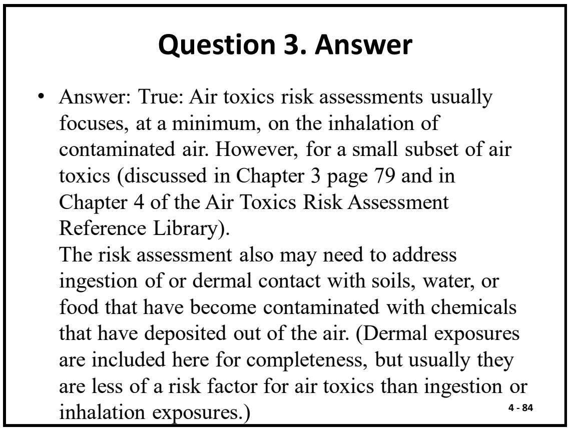
## Question 2. Answer

- Answer c). Urban areas. Because these areas have large populations and a higher concentration of emission sources and the combined exposures from all sources of air pollution, including major stationary sources, smaller area sources, indoor sources and mobile sources can increase public health risks from air toxics



## Question 3.

- 3. True or False: The overall purpose of a human health air toxics risk assessment is to attempt to understand public health risks potentially associated with exposures to particular pollutants emitted into the air from sources of interest?



## Question 3. Answer

- Answer: True: Air toxics risk assessments usually focuses, at a minimum, on the inhalation of contaminated air. However, for a small subset of air toxics (discussed in Chapter 3 page 79 and in Chapter 4 of the Air Toxics Risk Assessment Reference Library).
  The risk assessment also may need to address ingestion of or dermal contact with soils, water, or food that have become contaminated with chemicals that have deposited out of the air. (Dermal exposures are included here for completeness, but usually they are less of a risk factor for air toxics than ingestion or inhalation exposures.)

## Question 4.

- 4. True or False: Do <u>all</u> the listed items below apply to the process for evaluating Risk assessment?
- The sources of air toxics released to the environment;
- How the released chemicals move and change in the environment;
- Who may be exposed to the chemicals and at what levels;
- How exposures may occur;
- The toxic effects of the chemicals in question and how potent; and
- How likely it is that the potentially exposed people will experience harm because of the exposures.

## Question 4. Answer

Answer: True.

- This kind of information can be extremely helpful to decision makers as they try to balance the competing concerns of protecting public health, fostering economic development, and evaluating issues of fairness and equity, among others. Specifically, risk assessment can provide:

## Question 4. Answer (cont.)

- A predictive estimate of the potential health risks posed by air toxics, which may help determine the need for action;
- A basis for determining the levels of chemicals that can be released to the air without posing unacceptable risks to public health and the environment;
- A basis for comparing potential health impacts of various pollution reduction alternatives;
- A consistent process for evaluating and documenting threats to public health and the environment from toxic air pollution; and
- A basis for comparing risks from various exposure scenarios (e.g., the risk from breathing contaminated air compared to the risk from eating contaminated food).

# Environmental Fate & Transport

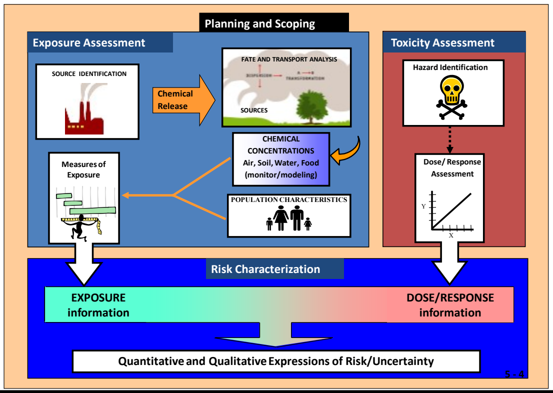
## Dispersion, Transport, and Fate: What's the Difference?

- Dispersion is a term applied to air toxics releases that means to spread or distribute from a source, with (generally) a decrease in concentration with distance from the source. Dispersion is affected by a number of factors including characteristics of the source, the pollutants, and ambient atmospheric conditions.
- Transport is a term that refers to the processes (e.g., winds) that carry or cause pollutants to move from one location to another, especially over some distance.
- Fate of air pollution refers to three things:
  - Where a pollutant ultimately ends up (e.g., air distant from the source, soil, water, fish tissue);
  - How long it persists in the environment; and
  - The chemical reactions which it undergoes.

## Points of Air Toxic Emissions

- Stack or Vent Emissions. These emissions are how most people envision air pollution. Stacks and vents include "smokestacks" that emit combustion products from fuel or waste combustion, as well as vents that carry air toxics away from people or industrial processes.
- Fugitive Emissions. "Fugitive" emissions are uncontrolled air pollutant releases that "escape" from physical, chemical, or industrial processes and activities, and which do not travel through stacks or vents.
  - Examples include dust or vapors that are generated by the transfer of bulk cargo (e.g., coal, gravel, and organic liquids) from one container to another (e.g., from a tank or hopper car to a storage silo, tank, or bin).
  - Another example includes leaks from joints and valves at industrial facilities and evaporative emissions of fuel from mobile sources.

## The Detailed Air Toxics Risk Assessment Process



Planning and Scoping

Exposure Assessment

SOURCE IDENTIFICATION

Chemical Release

FATE AND TRANSPORT ANALYSIS

SOURCES

CHEMICAL CONCENTRATIONS Air, Soil, Water, Food (monitor/modeling)

Measures of Exposure

POPULATION CHARACTERISTICS

Toxicity Assessment

Hazard Identification

Dose/ Response Assessment

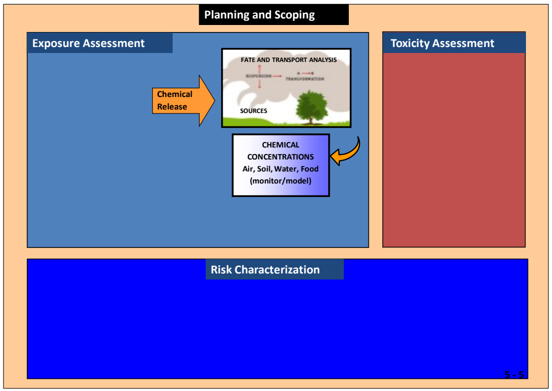
Risk Characterization

EXPOSURE information

DOSE/RESPONSE information

Quantitative and Qualitative Expressions of Risk/Uncertainty

## The Detailed Air Toxics Risk Assessment Process



Planning and Scoping

Exposure Assessment

Chemical Release

FATE AND TRANSPORT ANALYSIS

SOURCES

CHEMICAL CONCENTRATIONS Air, Soil, Water, Food (monitor/model)

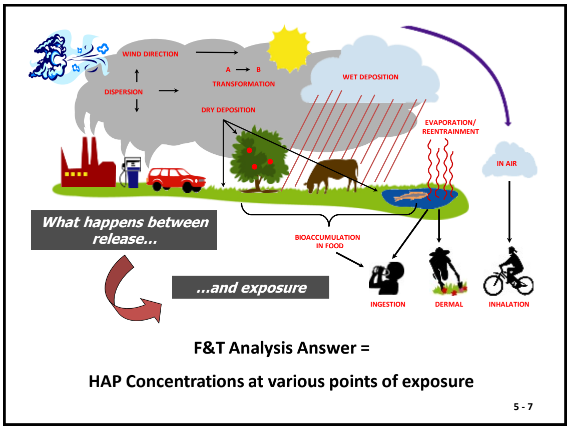
Toxicity Assessment

Risk Characterization

## Fate & Transport Analysis

F & T analysis is the process of understanding how pollutants move through and/or change in the environment

For air toxics risk assessment, F & T analysis evaluates how HAPs released to the air get from the point where a person can contact it

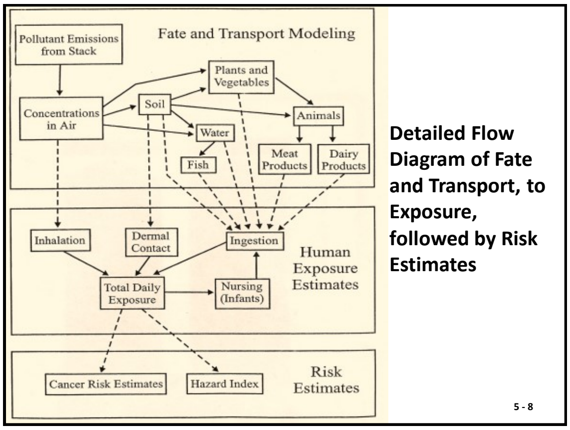


***What happens between release…***

***…and exposure***

**F&T Analysis Answer =**

**HAP Concentrations at various points of exposure**



**Detailed Flow Diagram of Fate and Transport, to Exposure, followed by Risk Estimates**

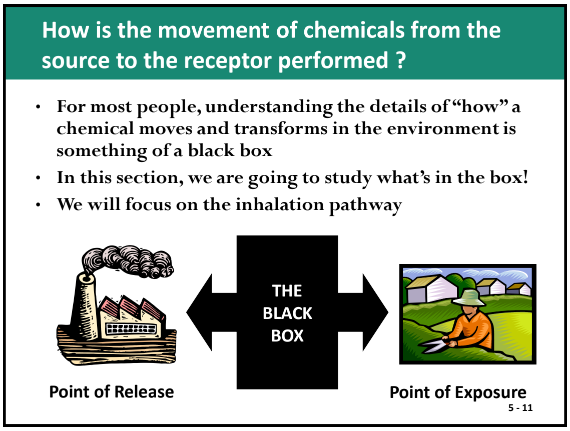
## Source and Atmospheric Effects on Release, Fate & Transport

Several characteristics of sources can affect the movement of air toxics (e.g., source height, gas exit temperature).

Once air toxics are transported beyond the immediate vicinity of the source, atmospheric and meteorological factors (particularly wind speed and direction) will govern the dispersion and transport of air toxics .

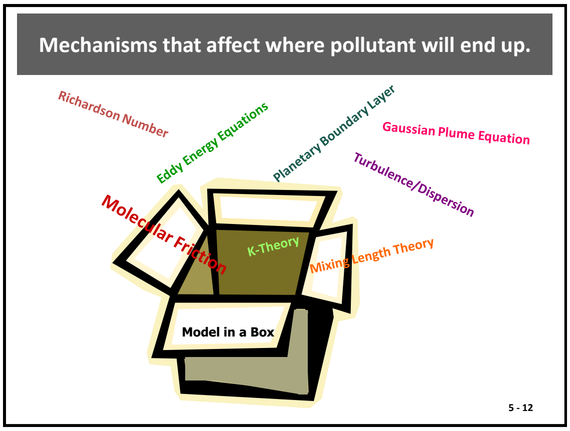
## Mechanisms That Can Govern Air Toxic Releases

- Meteorological principles, terrain characteristics
- Wet and dry deposition rates
- Chemical properties of the HAP (such as aqueous solubility, vapor pressure, air-water partition coefficient (i.e., Henry's Law constant), molecular diffusivity, phase partition coefficient, melting point, and adsorptivity).

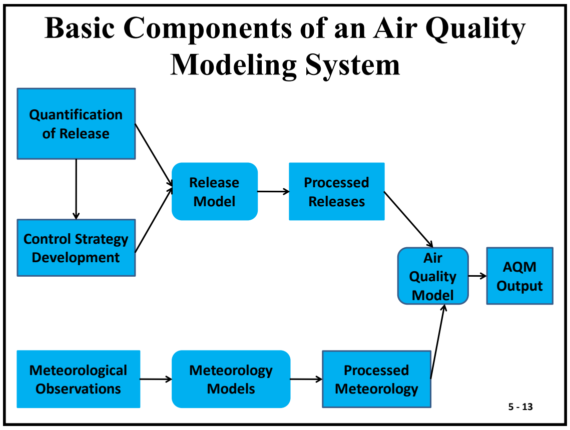


## How is the movement of chemicals from the source to the receptor performed ?

- For most people, understanding the details of "how" a chemical moves and transforms in the environment is something of a black box
- In this section, we are going to study what's in the box!
- We will focus on the inhalation pathway



## Mechanisms that affect where pollutant will end up.



## Basic Components of an Air Quality Modeling System

Quantification of Release

Control Strategy Development

Release Model

Processed Releases

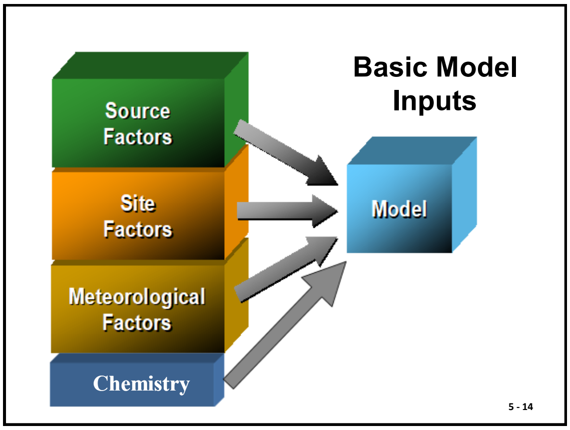
Air Quality Model

AQM Output

Meteorological Observations

Meteorology Models

Processed Meteorology



## Basic Model Inputs

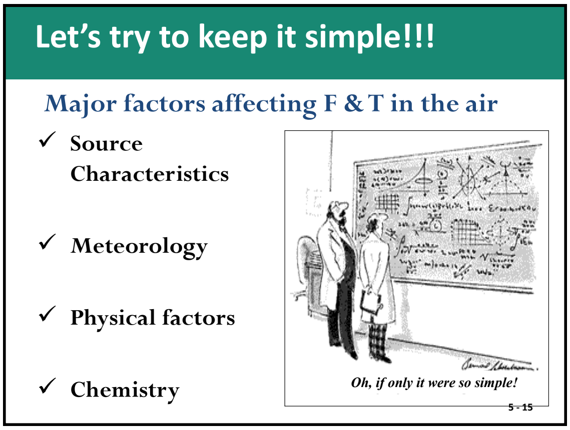
Source Factors

Site Factors

Meteorological Factors

Chemistry

Model

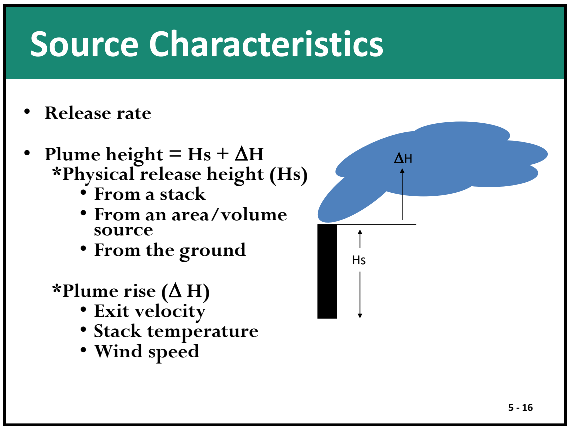


## Let's try to keep it simple!!!

### Major factors affecting F & T in the air

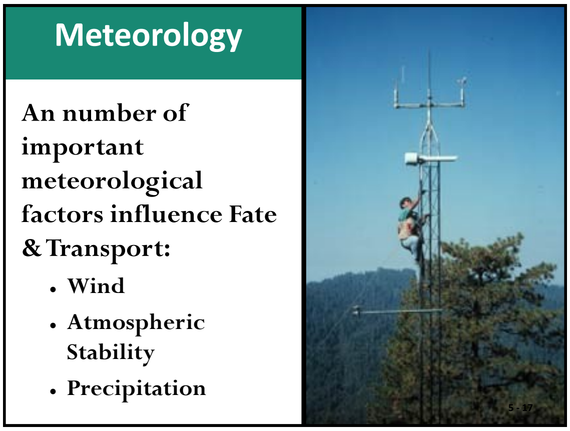
- ✓ Source Characteristics
- ✓ Meteorology
- ✓ Physical factors
- ✓ Chemistry

*Oh, if only it were so simple!*



## Source Characteristics

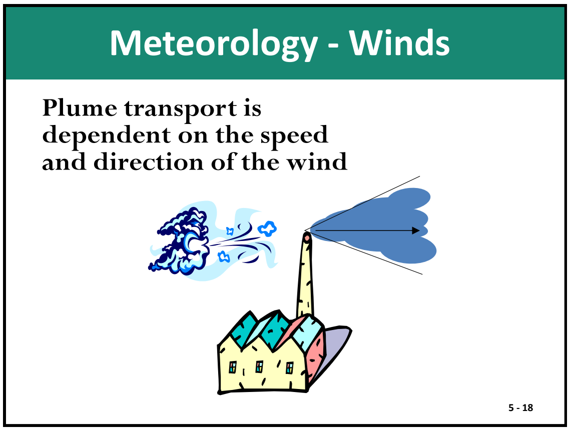
- Release rate
- Plume height = Hs + ΔH
  - *Physical release height (Hs)
    - From a stack
    - From an area/volume source
    - From the ground
  - *Plume rise (Δ H)
    - Exit velocity
    - Stack temperature
    - Wind speed



## Meteorology

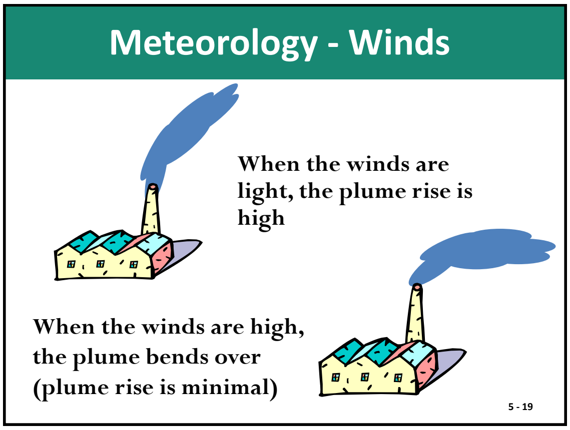
An number of important meteorological factors influence Fate & Transport:

- Wind
- Atmospheric Stability
- Precipitation



## Meteorology - Winds

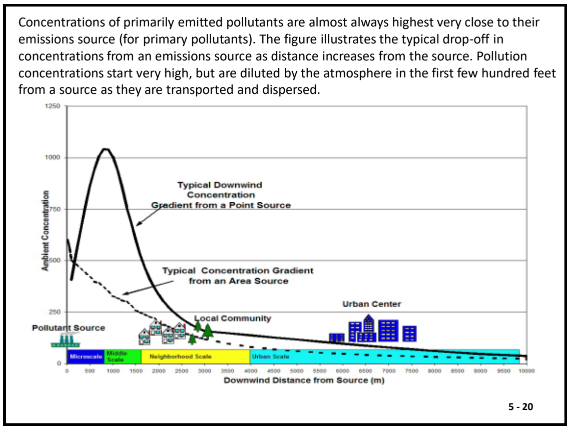
Plume transport is dependent on the speed and direction of the wind



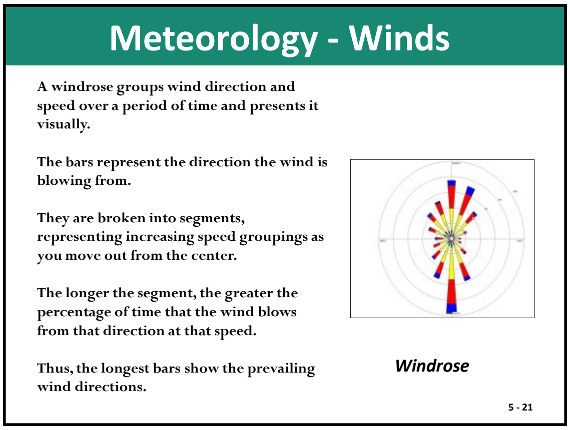
## Meteorology - Winds

When the winds are light, the plume rise is high

When the winds are high, the plume bends over (plume rise is minimal)



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.



## Meteorology - Winds

A windrose groups wind direction and speed over a period of time and presents it visually.

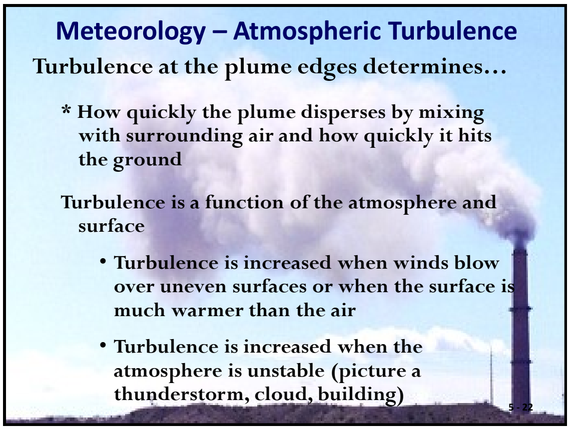
The bars represent the direction the wind is blowing from.

They are broken into segments, representing increasing speed groupings as you move out from the center.

The longer the segment, the greater the percentage of time that the wind blows from that direction at that speed.

Thus, the longest bars show the prevailing wind directions.

*Windrose*



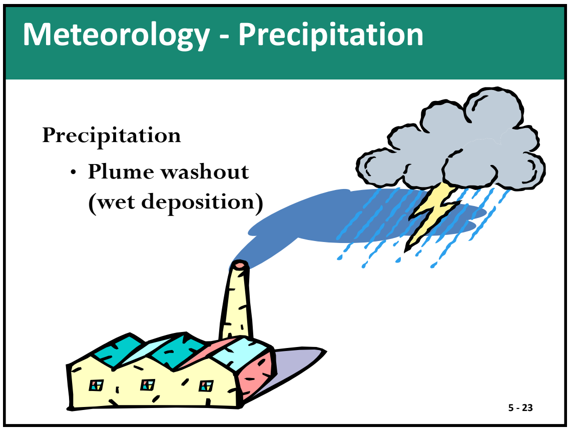
## Meteorology – Atmospheric Turbulence

Turbulence at the plume edges determines…

* How quickly the plume disperses by mixing with surrounding air and how quickly it hits the ground

Turbulence is a function of the atmosphere and surface

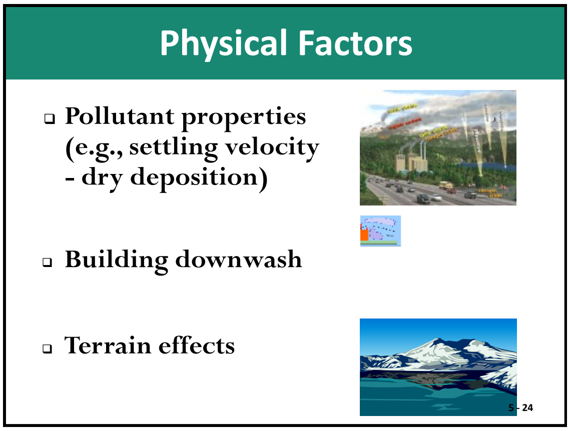
- Turbulence is increased when winds blow over uneven surfaces or when the surface is much warmer than the air
- Turbulence is increased when the atmosphere is unstable (picture a thunderstorm, cloud, building)



## Meteorology - Precipitation

Precipitation

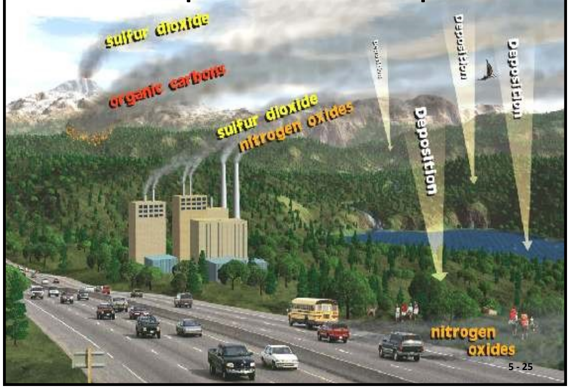
- Plume washout (wet deposition)



## Physical Factors

- ❑ Pollutant properties (e.g., settling velocity - dry deposition)
- ❑ Building downwash
- ❑ Terrain effects

## Pollutant Properties – Particle Deposition



## Pollutant Properties – Physical Form

- The physical form of pollutant releases greatly affects the dispersion, transport and chemical reactions that pollutants undergo.
- *Vapors* (not bound to particles, but existing as single molecules or very small aggregates “dissolved” in air – also called gaseous),
- *Particle-bound* (reversibly absorbed or condensed onto the surface of particles), or *particulate* (irreversibly incorporated into airborne particles).

## Pollutant Properties – Particle Size

- The rate of pollutant removal from the atmosphere to surfaces is dependant upon particle size.
- As the size of particles increases, the rate at which particles fall due to gravity (the settling velocity) increases.
- Thus, fine particles (approximate diameter less than a few microns) may remain suspended in air indefinitely, but particles larger than about 20 microns in diameter settle rapidly and may not transport far from sources of release.

## Approximate Settling Rates for Typical Particles in Air

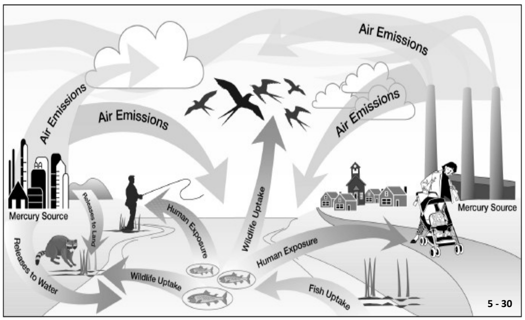
| Equivalent Diameter* (microns) | Settling Rate (cm/sec) |
|---|---|
| 0.01 | 0.00001 |
| 0.1 | 0.0002 |
| 1.0 | 0.01 |
| 10.0 | 0.6 |
| 100 | 40 |

* Diameter of a sphere that is approximately equivalent to a particle’s diameter

## Wet deposition

- *Wet deposition* involves the “washing out” of pollutants from the atmosphere through precipitation events (including rain, snow, and in some cases hail).
- Wet deposition affects both particulate and vapor-phase pollutants. For larger particles and vapor phase pollutants that are soluble in water, precipitation is very efficient at removing pollutants from the air and depositing them on the earth’s surface.
- Wet deposition may be less efficient at removing fine particulates, and has limited effect on the levels of gaseous pollutants with high Henry’s Law constants.

## Mercury is an Important Example of a Toxic Entering the Environment from Source Releases which produce Short and Long Range Transport with Both Dry and Wet Deposition

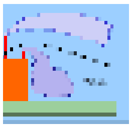


## Mercury Deposition Site Studies

- Wet Hg Deposition Sites: - Steubenville, Ohio
  - Underhill, Vermont
- Dry Hg Deposition Sites: - "Plant A," North Dakota
  - Springfield, Illinois
  - Mount Pleasant, Texas
- Total Hg Deposition: - Bow, New Hampshire

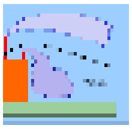
http://www.epa.gov/airtoxics/utility/emis_overview_memo_matsfinal.pdf

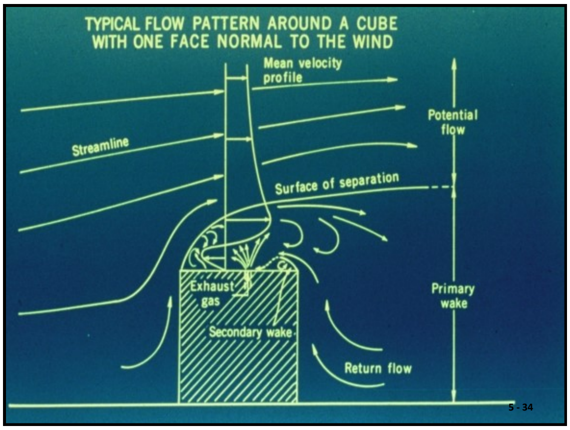
## USEPA Mercury Home Page



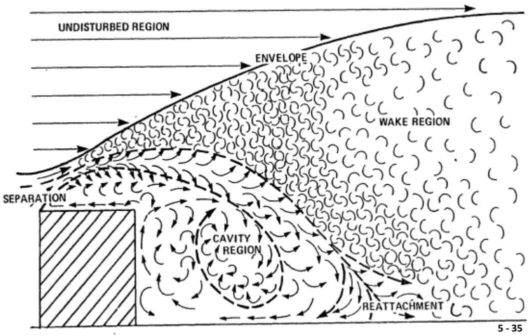
http://www.epa.gov/mercury/index.htm

## Building Downwash

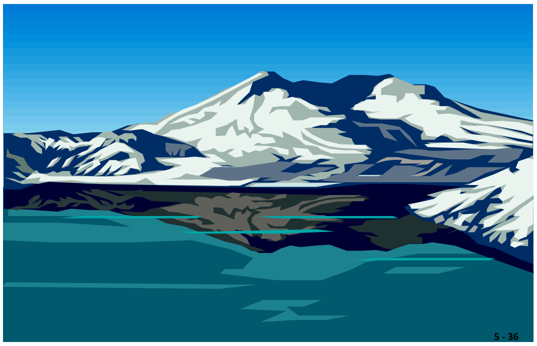


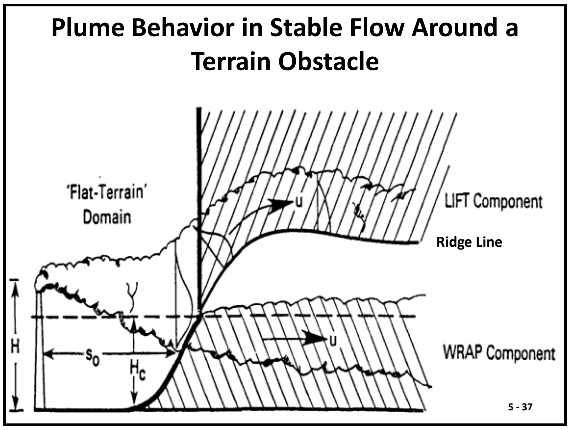


## Envelope and Cavity Regions in the Wake of a Building will Concentrate Released Pollutant Levels Near the Source

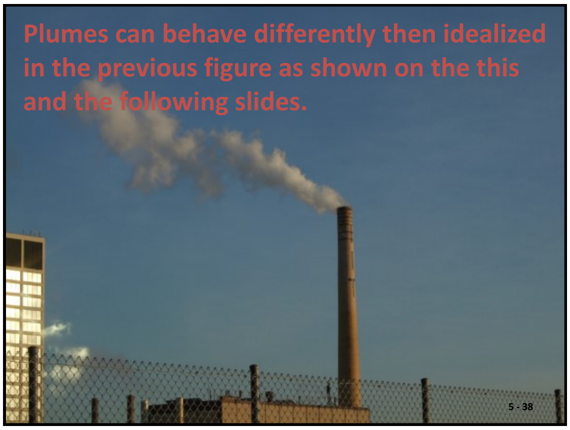


## Terrain effects





## Plume Behavior in Stable Flow Around a Terrain Obstacle

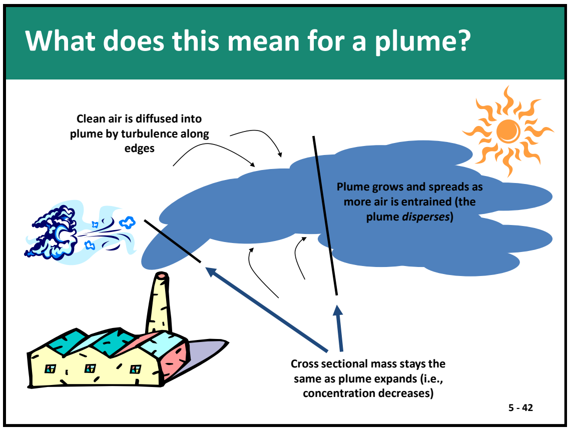


Plumes can behave differently then idealized in the previous figure as shown on the this and the following slides.

Same Day Later Time
Wind Speed Increasing

Same Day Later Time
Wind Speed Increasing More

Same Day Later Time
Wind Speed Increasing Even More

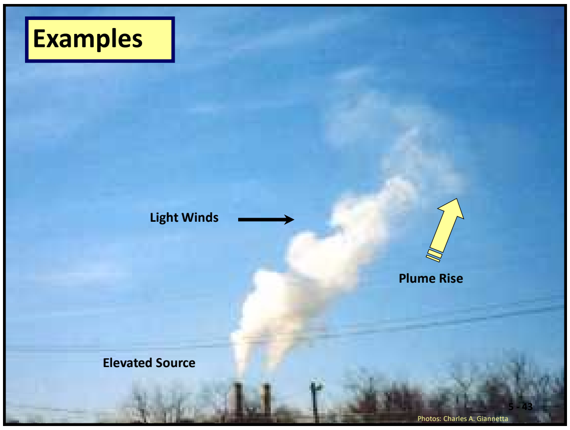


## What does this mean for a plume?

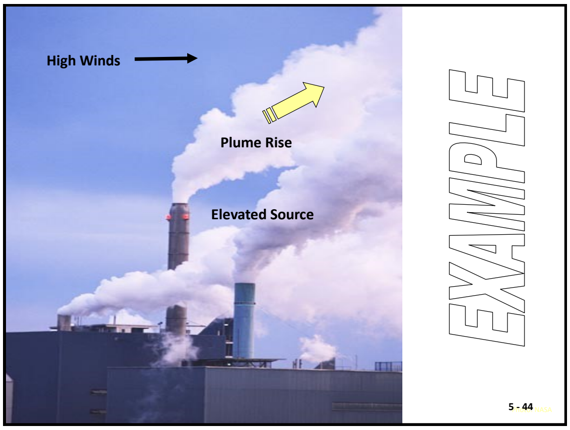
Clean air is diffused into plume by turbulence along edges

Plume grows and spreads as more air is entrained (the plume *disperses*)

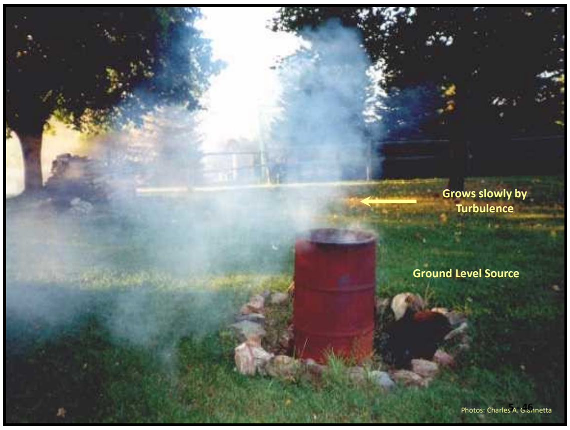
Cross sectional mass stays the same as plume expands (i.e., concentration decreases)



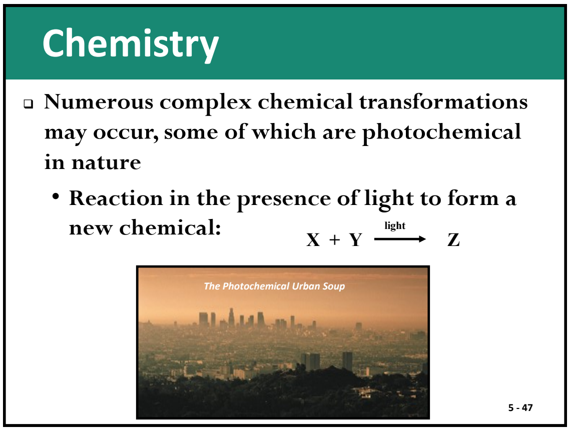
Photos: Charles A. Giannetta



Photos: Charles A. Giannetta



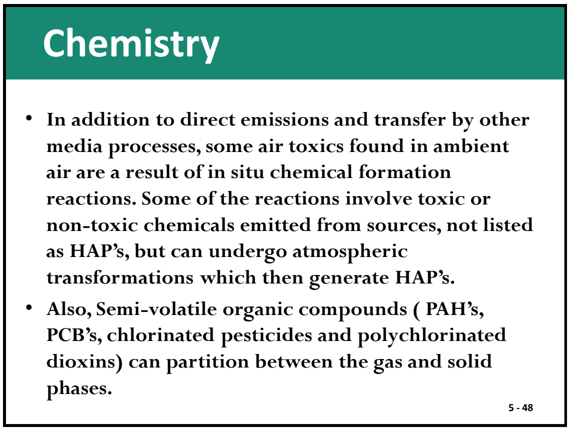
Photos: Charles A. Giannetta



## Chemistry

- Numerous complex chemical transformations may occur, some of which are photochemical in nature
  - Reaction in the presence of light to form a new chemical: $X + Y \xrightarrow{\text{light}} Z$

*The Photochemical Urban Soup*



## Chemistry

- In addition to direct emissions and transfer by other media processes, some air toxics found in ambient air are a result of in situ chemical formation reactions. Some of the reactions involve toxic or non-toxic chemicals emitted from sources, not listed as HAP's, but can undergo atmospheric transformations which then generate HAP's.
- Also, Semi-volatile organic compounds ( PAH's, PCB's, chlorinated pesticides and polychlorinated dioxins) can partition between the gas and solid phases.

## Chemistry

- For what situations would atmospheric transformation reactions of air toxics be important with respect to their emission regulations?
- HAP's that rapidly react to form chemicals not listed as toxic or hazardous could be considered for removal form the list or have reduced regulatory priority.
- The formation of HAP's from other HAP's would still be addressed by removal of the precursor HAP.

## Chemistry - Examples of Secondary Pollutants

| Pollutant | Pollutant Formed From |
|---|---|
| Acetaldehyde | propene, 2-butene |
| acrolein | 1,3-butadiene |
| carbonyl sulfide | carbon disulfide |
| o-cresol | toluene |
| formaldehyde | ethene, propene |
| hydrogen chloride | nitric acid, chlorinated organics |
| methylethyl ketone | butane, branched alkenes |
| N–nitroso-N–methylurea | N–methylurea |
| N–nitrosodiethylamine | dimethylamine |
| N–nitrosomorpholine | morpholine |
| phosgene | chlorinated solvents |
| Propionaldehyde | 1-butene |

Source: Rosenbaum et al., 1998

## Chemistry

- **The formation of greatest concern would be when an unlisted compound from unregulated sources which reacts to form a HAP.**
- **Propylene is an example compound of this scenario, which is not regulated under Title III. It also has emissions of tens of millions of pounds in to the atmosphere from manufacturing industries.**
- **Propylene reacts rapidly in the atmosphere to form acetaldehyde, which in turn quickly produces formaldehyde and peroxyacetyl nitrate (PAN, $CH3C(O)OONO2$). It is a strong phototoxic and irritant and can be linked to mutagenic activity.**

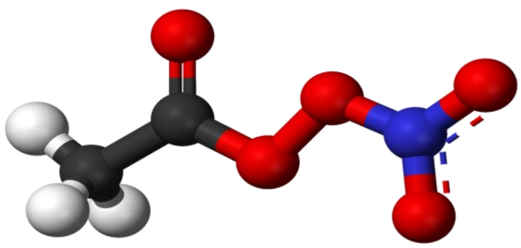
## *Atmospheric Residence Times*

- Approximate atmospheric residence times for some air toxics are listed here.
- These values were found at: scorecard.goodguide.com/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** |

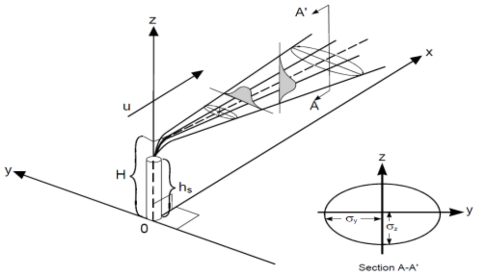
* Wet deposition is also a sink
** Lifetime is dependant on particle deposition and is typically days to weeks. Deposition time is primarily determined by the size of the particles.

## Chemistry



peroxyacetyl nitrate (PAN)

## Schematic Representation of Gaussian Plume for Dispersion Modeling



## Important Factors of the Gaussian Distribution

- The Gaussian distribution determines the size of the plume downwind from the source as represented in the schematic of the Gaussian Plume as shown in the previous figure.
- The plume size is dependent on the stability of the atmosphere and the dispersion of the plume in the horizontal and vertical directions.

## Important Factors of the Gaussian Distribution

- Horizontal and vertical dispersion coefficients ($\sigma_y$ and $\sigma_z$ respectively) are the standard deviation from normal on the Gaussian distribution curve in the y and z directions.
- The coefficients, $\sigma_y$ and $\sigma_z$, are functions of wind speed, cloud cover, and surface heating by the sun.

## Modifications and Assumptions for Application of the Gaussian Distribution

- The Gaussian distribution and plume rise depend on the ground being relatively flat along the path of the plume.
- The topography affects atmospheric wind flow and stability, and therefore, uneven terrain caused by hills, valleys, and mountains will affect the dispersion of the plume so that the Gaussian distribution must be modified.

## Modifications and Assumptions for Application of the Gaussian Distribution

In order for a plume to be modeled using the Gaussian distribution the following assumption must be made:

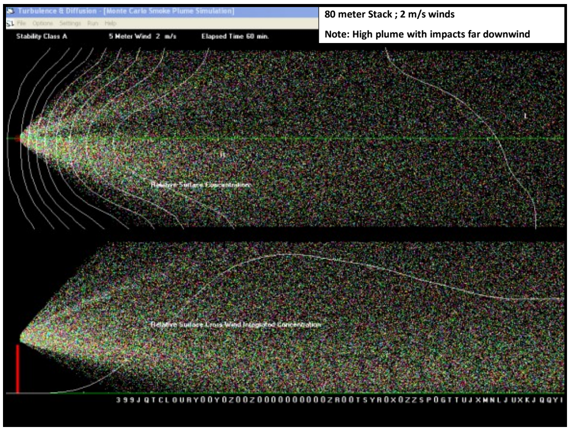
- The plume spread has a normal distribution (i.e. a bell-shaped distribution)
- The emission rate (Q) is constant and continuous.
- Wind speed and direction is uniform.
- Total reflection of the plume takes place at the surface.

## Example

### Fate and Transport

***The Blackadar***
***Monte Carlo***
***Smoke Plume Simulation***

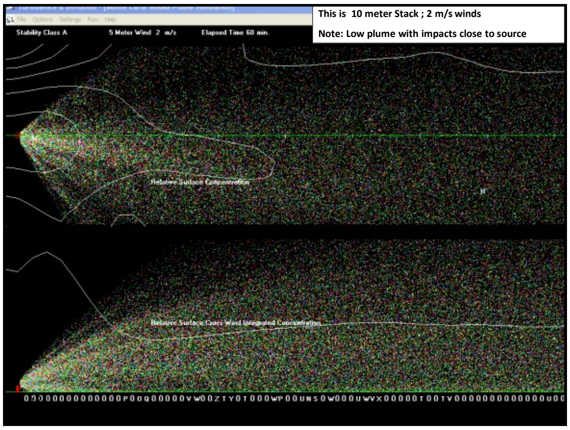
***(Note Stability Class, Stack Height and Wind Speed)***



Stability Class A 5 Meter Wind 2 m/s Elapsed Time 60 min.

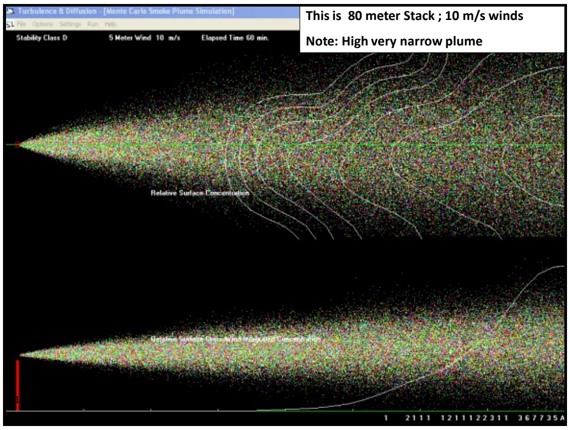
**80 meter Stack ; 2 m/s winds**

**Note: High plume with impacts far downwind**



This is 10 meter Stack ; 2 m/s winds

Note: Low plume with impacts close to source



This is 80 meter Stack ; 10 m/s winds

Note: High very narrow plume

## Smoke Plume from Facility Fire

- At least 1,000 Rockton residents displaced following Chemtool fire (nbc15.com)

## Key to stability categories Affecting Pollutant Dispersion

| Surface wind | Insolation | | | Night | |
|---|---|---|---|---|---|
| Speed (at 10 m) (m/s) | | Moderate | Slight | ≥ 4/8 low cloud cover* | ≤ 3/8 cloud cover |
| < 2 | A | A-B | B | - | - |
| 2-3 | A-B | B | C | E | F |
| 3-5 | B | B-C | C | D | E |
| 5-6 | C | C-D | D | D | D |
| > 6 | C | D | D | D | D |

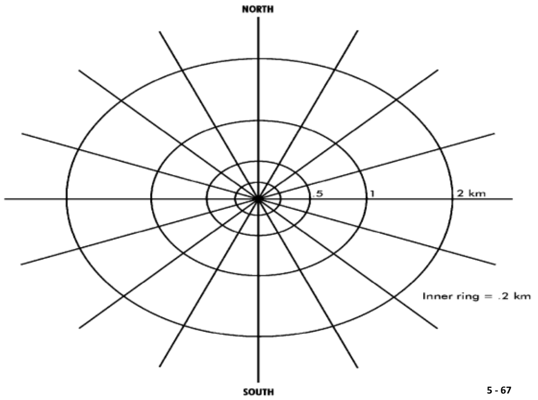
**Stabilities A, B, and C refer to daytime hours with unstable conditions. Stability D is representative of overcast days or nights with neutral conditions. Stabilities E and F refer to nighttime, stable conditions and are based on the amount of cloud cover. Thus, classification A represents conditions of greatest instability, and classification F reflects conditions of greatest stability.**

## Model Calculations of Ambient Concentrations

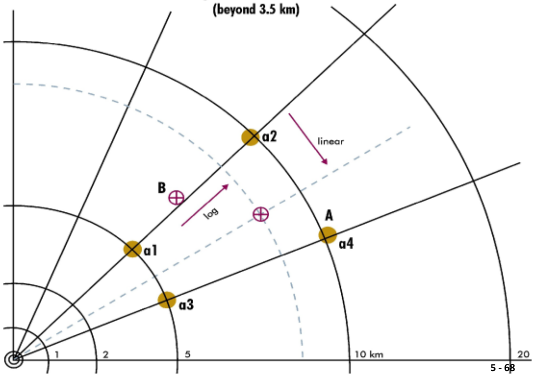
- Many air quality models calculate ambient concentrations at specific exposure points at specified "nodes" using either a polar coordinate grid system (i.e., the intersections of a series of concentric circles and radial lines (next slide) or on a standard Cartesian coordinate system.
    - (Note that the nodes in these types of grids, are simply the points where two lines intersect.) The locations of these nodes often do not fall precisely on the locations of interest for a given risk assessment.
- In cases where the nodes and locations of interest do not align, a process of interpolation is used to estimate the ambient air concentration at the location

## Model Calculations of Ambient Concentrations (cont.)

- For polar grids, a two-step interpolation is used, starting with the modeled concentrations at the nearest locations (e.g., a1, a2, a3, and a4 in the following graph).
- The first interpolation is in the radial direction (i.e., along the two adjacent radial lines [a1,a2] and [a3, a4] in the graph). The concentration is estimated at the intersection of each radial line with the concentric circle hat intersects the receptor location (at the same radial distance from the source as the internal point).



## Interpolation to Centroid (beyond 3.5 km)



## Modeling Exposure Concentrations: Units are Important

- Air toxics exposure concentrations (ECs) should in general be reported as μg/m$^3$.
- Dose-response values often are reported as parts per million (ppm), parts per billion (ppb), or mg/m$^3$.
- In the risk characterization step, ECs are compared to dose-response values, and therefore the units for the EC must match the units for the dose-response values.
- The conversion from mg/m$^3$ to ppm can be expressed as:
- Concentration [ppm] = Concentration [mg/m$^3$] × 24.45 [L/mole] / MW

## Modeling Exposure Concentrations: Units are Important

- The conversion from ppm to mg/m$^3$ is:
- Concentration [mg/m$^3$] = Concentration [ppm] × MW / 24.45 [L/mole],
  - where MW is the molecular weight of the air toxic in g/mole and 24.45 is the volume in liters of one mole of an ideal gas at 1 atmosphere and 25 degrees Celsius. Note also that ppb = 1,000 × ppm and that here, ppm is volume-based. Also, μg/m$^3$ = 1,000 × mg/m$^3$.
- Tip: In the development of the analysis plan, stipulate that all laboratory and modeling results be reported in μg/m$^3$. This will save time and reduce computational errors in the remaining phases of the risk assessment.

## How do we predict Fate & Transport?

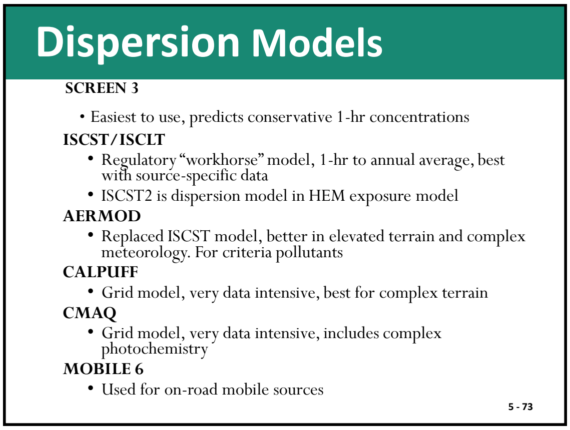
Air Quality Modeling

- Predicts both acute and chronic ambient levels
- Fenceline to national scale
- Can model historical, current, and "what-ifs"
- Also used to:
  - Site monitor locations
  - Show compliance with air Toxic requirements

## Dispersion Models

**EPA models & guidance on SCRAM Website**

http://www.epa.gov/scram001/



# Dispersion Models

**SCREEN 3**

- Easiest to use, predicts conservative 1-hr concentrations

**ISCST/ISCLT**

- Regulatory "workhorse" model, 1-hr to annual average, best with source-specific data
- ISCST2 is dispersion model in HEM exposure model

**AERMOD**

- Replaced ISCST model, better in elevated terrain and complex meteorology. For criteria pollutants

**CALPUFF**

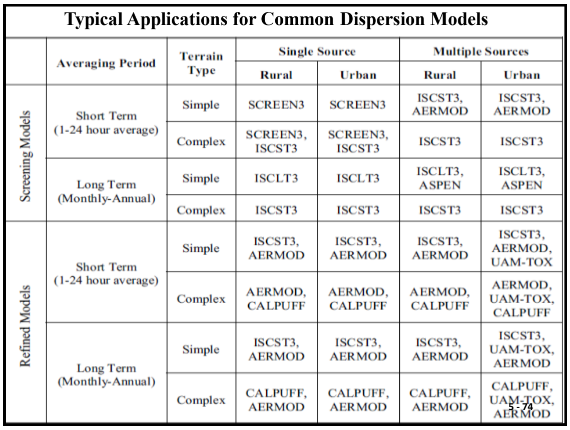
- Grid model, very data intensive, best for complex terrain

**CMAQ**

- Grid model, very data intensive, includes complex photochemistry

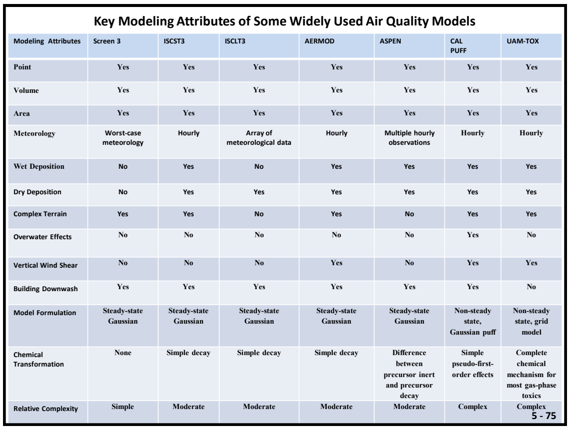
**MOBILE 6**

- Used for on-road mobile sources



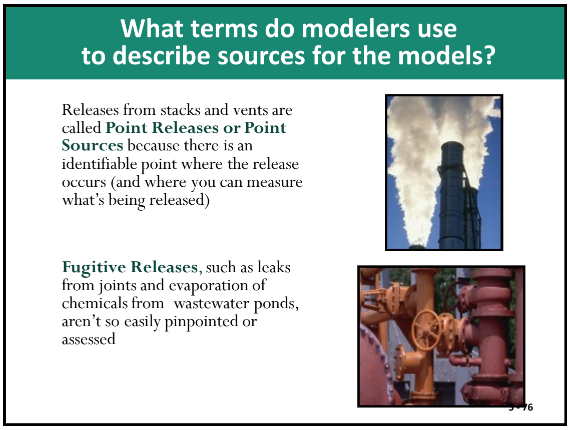
**Typical Applications for Common Dispersion Models**

| | Averaging Period | Terrain Type | Single Source | | Multiple Sources | |
|---|---|---|---|---|---|---|
| | | | Rural | Urban | Rural | Urban |
| Screening Models | Short Term (1-24 hour average) | Simple | SCREEN3 | SCREEN3 | ISCST3, AERMOD | ISCST3, AERMOD |
| | | Complex | SCREEN3, ISCST3 | SCREEN3, ISCST3 | ISCST3 | ISCST3 |
| | Long Term (Monthly-Annual) | Simple | ISCLT3 | ISCLT3 | ISCLT3, ASPEN | ISCLT3, ASPEN |
| | | Complex | ISCST3 | ISCST3 | ISCST3 | ISCST3 |
| Refined Models | Short Term (1-24 hour average) | Simple | ISCST3, AERMOD | ISCST3, AERMOD | ISCST3, AERMOD | ISCST3, AERMOD, UAM-TOX |
| | | Complex | AERMOD, CALPUFF | AERMOD, CALPUFF | AERMOD, CALPUFF | AERMOD, UAM-TOX, CALPUFF |
| | Long Term (Monthly-Annual) | Simple | ISCST3, AERMOD | ISCST3, AERMOD | ISCST3, AERMOD | ISCST3, UAM-TOX, AERMOD |
| | | Complex | CALPUFF, AERMOD | CALPUFF, AERMOD | CALPUFF, AERMOD | CALPUFF, UAM-TOX, AERMOD |



**Key Modeling Attributes of Some Widely Used Air Quality Models**

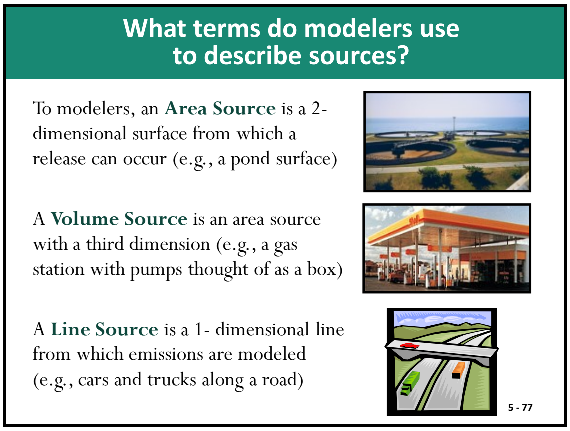
| Modeling Attributes | Screen 3 | ISCST3 | ISCLT3 | AERMOD | ASPEN | CAL PUFF | UAM-TOX |
|---|---|---|---|---|---|---|---|
| Point | Yes | Yes | Yes | Yes | Yes | Yes | Yes |
| Volume | Yes | Yes | Yes | Yes | Yes | Yes | Yes |
| Area | Yes | Yes | Yes | Yes | Yes | Yes | Yes |
| Meteorology | Worst-case meteorology | Hourly | Array of meteorological data | Hourly | Multiple hourly observations | Hourly | Hourly |
| Wet Deposition | No | Yes | No | Yes | Yes | Yes | Yes |
| Dry Deposition | No | Yes | Yes | Yes | Yes | Yes | Yes |
| Complex Terrain | Yes | Yes | No | Yes | No | Yes | Yes |
| Overwater Effects | No | No | No | No | No | Yes | No |
| Vertical Wind Shear | No | No | No | Yes | No | Yes | Yes |
| Building Downwash | Yes | Yes | Yes | Yes | Yes | Yes | No |
| Model Formulation | Steady-state Gaussian | Steady-state Gaussian | Steady-state Gaussian | Steady-state Gaussian | Steady-state Gaussian | Non-steady state, Gaussian puff | Non-steady state, grid model |
| Chemical Transformation | None | Simple decay | Simple decay | Simple decay | Difference between precursor inert and precursor decay | Simple pseudo-first-order effects | Complete chemical mechanism for most gas-phase toxics |
| Relative Complexity | Simple | Moderate | Moderate | Moderate | Moderate | Complex | Complex |



# What terms do modelers use to describe sources for the models?

Releases from stacks and vents are called **Point Releases or Point Sources** because there is an identifiable point where the release occurs (and where you can measure what's being released)

**Fugitive Releases**, such as leaks from joints and evaporation of chemicals from wastewater ponds, aren't so easily pinpointed or assessed

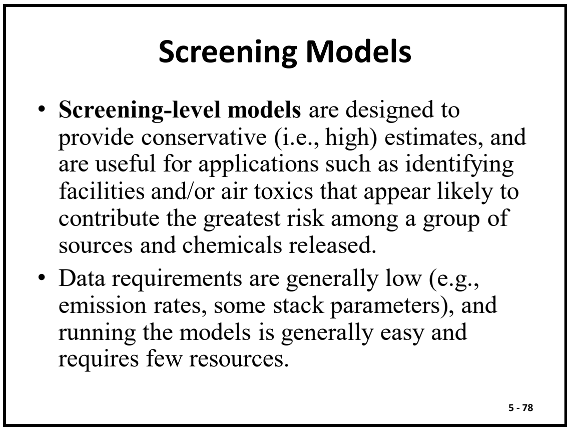


# What terms do modelers use to describe sources?

To modelers, an **Area Source** is a 2-dimensional surface from which a release can occur (e.g., a pond surface)

A **Volume Source** is an area source with a third dimension (e.g., a gas station with pumps thought of as a box)

A **Line Source** is a 1- dimensional line from which emissions are modeled (e.g., cars and trucks along a road)



# Screening Models

- **Screening-level models** are designed to provide conservative (i.e., high) estimates, and are useful for applications such as identifying facilities and/or air toxics that appear likely to contribute the greatest risk among a group of sources and chemicals released.
- Data requirements are generally low (e.g., emission rates, some stack parameters), and running the models is generally easy and requires few resources.

## Screen 3 Dispersion Model

- Screening-level Gaussian dispersion model that estimates an hourly maximum ambient concentration based on an average, constant emission rate (concentration results can be scaled up to annual average using simple conversion factors as specified in EPA guidance; results are not direction- specific (i.e., wind direction is not taken into account).
- Data requirements are relatively low; uses site-specific facility data (e.g., stack height, diameter, flow rate, downwash); does not use site-specific meteorology data.
- Data processing requirements are low; easy to use for quick assessment of a single facility.
- Model does not estimate deposition rates.

## Screen View 3 Freeware Web site

http://www.weblakes.com/lakescr1.html

US EPA Screening Models (Most Recent)

https://www.epa.gov/scram/air-quality-dispersion-modeling-screening-models

## Refined Models

- **Refined models** take into account more complex chemical behavior and a greater degree of site-specific information, generally producing more accurate results. Data requirements are higher (e.g., site-specific meteorology, terrain, chemistry data), and application of more refined models may require expert judgment in developing model inputs and setting model options. Some models can be used both as a screening model and refined model if additional site-specific information is used in the application. The selection of a model for a specific application depends on a number of factors, including:
- The nature of the pollutant (e.g., gaseous, particulate, reactive, inert);
- The meteorological and topographic complexities of the area of concern;
- The complexity of the distribution of sources

## How do we predict F & T?

**Ambient Monitoring**

- ❑ Measures both acute and chronic ambient levels depending upon the monitor
- ❑ Used for:
  - Enforcement issues
  - Development and/or validation of air quality models
  - Identification of emissions inventory gaps

## Ambient Air Toxic Monitoring

AirData - https://www.epa.gov/outdoor-air-quality-data

- Provides access to monitoring data for criteria pollutants and air toxics

Ambient Monitoring Technology Information Center (AMTIC) - http://www.epa.gov/ttn/amtic/

- Information and files on ambient air quality monitoring programs
- Details on monitoring methods
- Documents and articles
- Information on air quality trends and nonattainment areas
- Federal regulations related to ambient air quality monitoring

State websites

## EM Magazine January 2019

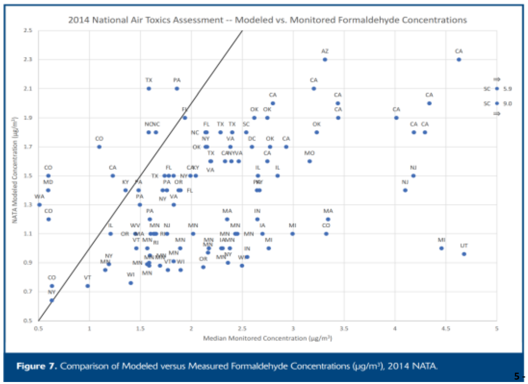
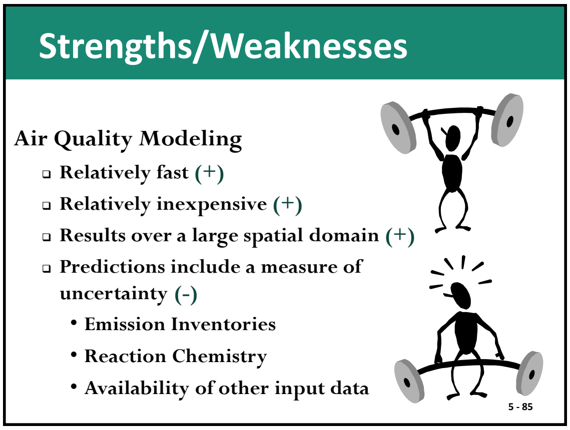


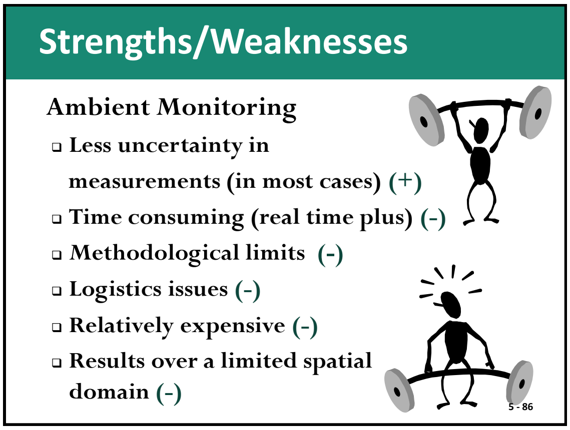
**Figure 7.** Comparison of Modeled versus Measured Formaldehyde Concentrations (µg/m³), 2014 NATA.



## Strengths/Weaknesses

Air Quality Modeling

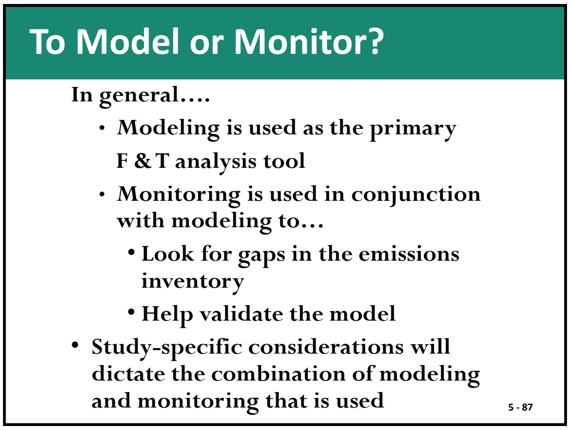
- ❑ Relatively fast (+)
- ❑ Relatively inexpensive (+)
- ❑ Results over a large spatial domain (+)
- ❑ Predictions include a measure of uncertainty (-)
  - Emission Inventories
  - Reaction Chemistry
  - Availability of other input data



## Strengths/Weaknesses

Ambient Monitoring

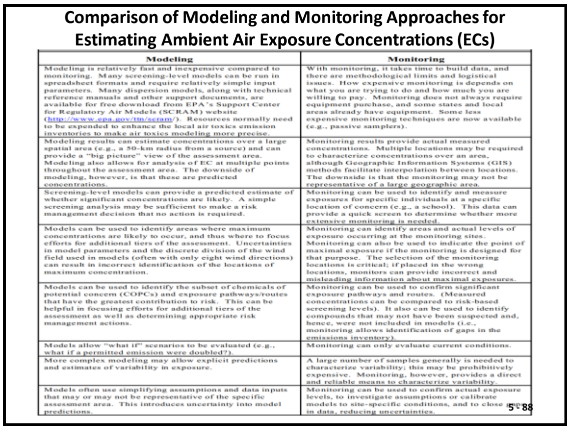
- ❑ Less uncertainty in measurements (in most cases) (+)
- ❑ Time consuming (real time plus) (-)
- ❑ Methodological limits (-)
- ❑ Logistics issues (-)
- ❑ Relatively expensive (-)
- ❑ Results over a limited spatial domain (-)



## To Model or Monitor?

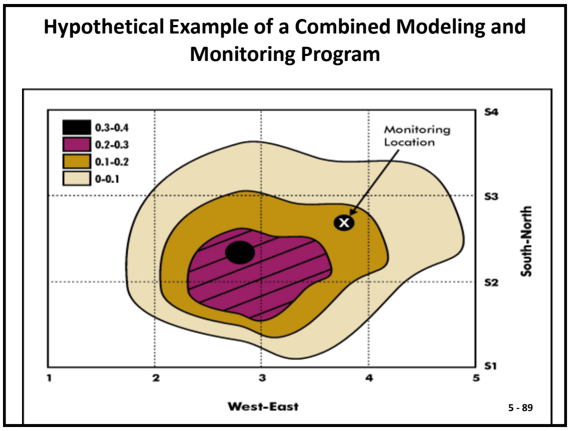
In general….

- Modeling is used as the primary F & T analysis tool
- Monitoring is used in conjunction with modeling to…
  - Look for gaps in the emissions inventory
  - Help validate the model
- Study-specific considerations will dictate the combination of modeling and monitoring that is used

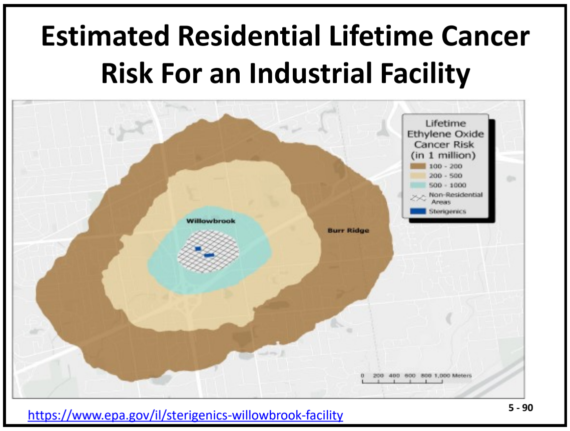


## Comparison of Modeling and Monitoring Approaches for Estimating Ambient Air Exposure Concentrations (ECs)

| Modeling | Monitoring |
|---|---|
| Modeling is relatively fast and inexpensive compared to monitoring. Many screening-level models can be run in spreadsheet formats and require relatively simple input parameters. Many dispersion models, along with technical reference manuals and other support documents, are available for free download from EPA's Support Center for Regulatory Air Models (SCRAM) website (http://www.epa.gov/ttn/scram/). Resources normally need to be expended to enhance the local air toxics emission inventories to make air toxics modeling more precise. | With monitoring, it takes time to build data, and there are methodological limits and logistical issues. How expensive monitoring is depends on what you are trying to do and how much you are willing to pay. Monitoring does not always require equipment purchase, and some states and local areas already have equipment. Some less expensive monitoring techniques are now available (e.g., passive samplers). |
| Modeling results can estimate concentrations over a large spatial area (e.g., a 50-km radius from a source) and can provide a "big picture" view of the assessment area. Modeling also allows for analysis of EC at multiple points throughout the assessment area. The downside of modeling, however, is that these are predicted concentrations. | Monitoring results provide actual measured concentrations. Multiple locations may be required to characterize concentrations over an area, although Geographic Information Systems (GIS) methods facilitate interpolation between locations. The downside is that the monitoring may not be representative of a large geographic area. |
| Screening-level models can provide a predicted estimate of whether significant concentrations are likely. A simple screening analysis may be sufficient to make a risk management decision that no action is required. | Monitoring can be used to identify and measure exposures for specific individuals at a specific location of concern (e.g., a school). This data can provide a quick screen to determine whether more extensive monitoring is needed. |
| Models can be used to identify areas where maximum concentrations are likely to occur, and thus where to focus efforts for additional tiers of the assessment. Uncertainties in model parameters and the discrete division of the wind field used in models (often with only eight wind directions) can result in incorrect identification of the locations of maximum concentration. | Monitoring can identify areas and actual levels of exposure occurring at the monitoring sites. Monitoring can also be used to indicate the point of maximal exposure if the monitoring is designed for that purpose. The selection of the monitoring locations is critical; if placed in the wrong locations, monitors can provide incorrect and misleading information about maximal exposures. |
| Models can be used to identify the subset of chemicals of potential concern (COPCs) and exposure pathways/routes that have the greatest contribution to risk. This can be helpful in focusing efforts for additional tiers of the assessment as well as determining appropriate risk management actions. | Monitoring can be used to confirm significant exposure pathways and routes. (Measured concentrations can be compared to risk-based screening levels). It also can be used to identify compounds that may not have been suspected and, hence, were not included in models (i.e., monitoring allows identification of gaps in the emissions inventory). |
| Models allow "what if" scenarios to be evaluated (e.g., what if a permitted emission were doubled?). | Monitoring can only evaluate current conditions. |
| More complex modeling may allow explicit predictions and estimates of variability in exposure. | A large number of samples generally is needed to characterize variability; this may be prohibitively expensive. Monitoring, however, provides a direct and reliable means to characterize variability. |
| Models often use simplifying assumptions and data inputs that may or may not be representative of the specific assessment area. This introduces uncertainty into model predictions. | Monitoring can be used to confirm actual exposure levels, to investigate assumptions or calibrate models to site-specific conditions, and to close gaps in data, reducing uncertainties. |

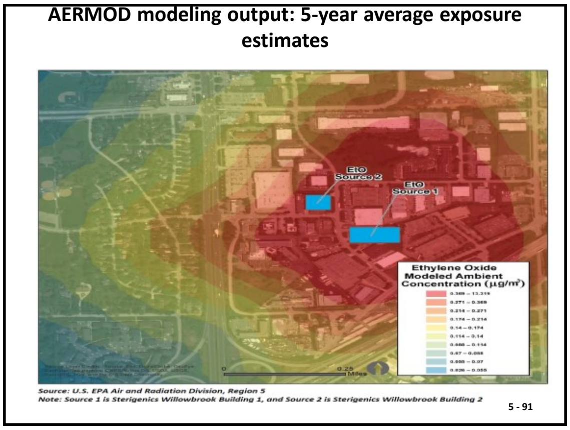


## Hypothetical Example of a Combined Modeling and Monitoring Program



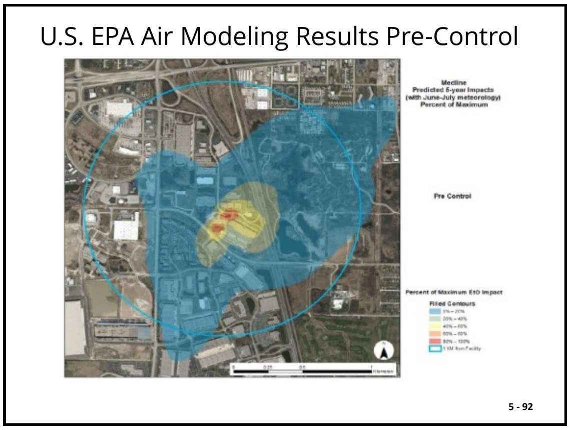
## Estimated Residential Lifetime Cancer Risk For an Industrial Facility

https://www.epa.gov/il/sterigenics-willowbrook-facility

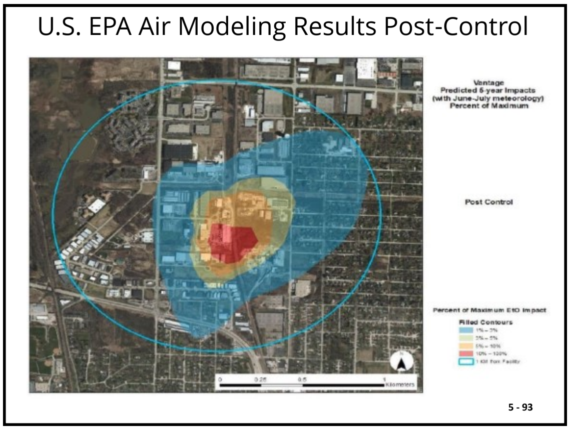


## AERMOD modeling output: 5-year average exposure estimates

*Source: U.S. EPA Air and Radiation Division, Region 5*
*Note: Source 1 is Sterigenics Willowbrook Building 1, and Source 2 is Sterigenics Willowbrook Building 2*



## U.S. EPA Air Modeling Results Pre-Control



## U.S. EPA Air Modeling Results Post-Control

## Modeling Accidental Releases

## Calculating Accidental Release Flow Rates
## From Pressurized Gas Systems

**http://www.air-dispersion.com/feature2.html**

## CAMEO

- CAMEO ® is a system of software applications used widely to plan for and respond to chemical emergencies.
- It is one of the tools developed by EPA's Chemical Emergency Preparedness and Prevention Office (CEPPO) and the National Oceanic and Atmospheric Administration Office of Response and Restoration (NOAA), to assist front-line chemical emergency planners and responders.
- They can use CAMEO to access, store, and evaluate information critical for developing emergency plans.

## CAMEO

- CAMEO supports regulatory compliance by helping users meet the chemical inventory reporting requirements of the Emergency Planning and Community Right-to-Know Act (EPCRA, also known as SARA Title III).
- CAMEO can also be used with a separate software application called LandView ® to display EPA environmental databases and demographic/economic information to support analysis of environmental justice issues.

## CAMEO ® - The Database and Information Management

- CAMEO, contains a chemical database of over 6,000 hazardous chemicals, 80,000 synonyms, and product trade names.
- CAMEO provides a powerful search engine that allows users to find chemicals instantly. Each one is linked to chemical-specific information on fire and explosive hazards, health hazards, firefighting techniques, cleanup procedures, and protective clothing.

## CAMEO ® - The Database and Information Management

- CAMEO also contains basic information on facilities that store chemicals, on the inventory of chemicals at the facility (Tier II) and on emergency planning resources. Additionally, there are templates where users can store EPCRA information.
- CAMEO connects the planner or emergency responder with critical information to identify unknown substances during an incident.

## MARPLOT ® - Mapping Applications for Response, Planning, and Local Operational Tasks

- MARPLOT is the mapping application. It allows users to "see" their data (e.g., roads, facilities, schools, response assets), on computer maps, and print the information on to area maps.
- The areas contaminated by potential or actual chemical release scenarios also can be overlaid on the maps to determine potential impacts.
- The maps are created from the U.S. Bureau of Census TIGER/Line files and can be manipulated quickly to show possible hazard areas.

## ALOHA ® - Areal Locations of Hazardous Atmospheres

- ALOHA is an atmospheric dispersion model used for evaluating releases of hazardous chemical vapors.
- ALOHA allows the user to estimate the downwind dispersion of a chemical cloud based on the toxicological/physical characteristics of the released chemical, atmospheric conditions, and specific circumstances of the release.
- Graphical outputs include a "cloud footprint" that can be plotted on maps with MARPLOT to display the location of other facilities storing hazardous materials and vulnerable locations, such as hospitals and schools for posed hazards.

## NOAA & USEPA Emergency Response Web Sites

**http://response.restoration.noaa.gov/aloha**

**http://response.restoration.noaa.gov/index.php**

**http://www.epa.gov/emergencies/index.htm**

Clean Air Act 112 (r) Risk Management Program (R M P) EPCRA

CHEMICAL EMERGENCY PREVENTION & PLANNING *Newsletter*

October-November 2006 EPA Region 10

*Inside This Issue*

1 Happy Birthday, CAMEO!
2 Off-site Consequence Analysis: Modeling Chemical Spills
4 Emergency Planning: What are LEPCs?
5 EPCRA Corner: Toxics Release Inventory of EPA Region 10/ Understanding TRI Data
6 Safety Alert: Do You Have Storage Pallets That Look Like This?
7 RMP Regulated Facilities: Incident Summaries and Lessons Learned

CHEMICAL EMERGENCY PREVENTION & PLANNING
*Newsletter*
US EPA Region 10, ERU ECL-116
1200 6th Avenue
Seattle, Washington 98101
206.553.1679 • Fax: 206.553.0124
www.epa.gov/r10earth/112r.htm

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For *EPCRA:* Suzanne Powers at powers.suzanne@epa.gov

For *Subscription:* Roger Consolacion at consolacion.rogelio@epa.gov

HAPPY BIRTHDAY, CAMEO!

A Software Product Celebrates 20 Years of Supporting Emergency Responders and Planners Around the World

**CAMEO** (Computer Aided Management of Emergency Operations) is 20 years old this year. It began in 1986 as a collaborative development effort by National Oceanic and Atmospheric Administration (NOAA)'s Office of Response and Restoration (OR&R) and Seattle-area firefighters. OR&R scientists provide scientific support when the U.S. Coast Guard responds to oil spills and chemical accidents, and they have developed many computer tools that they themselves use during hazmat responses. The tools created by OR&R are shared with other responders at no cost. CAMEO is by far their most popular product. Over the past two decades, CAMEO has become the most widely used chemical emergency response and planning tool in the U.S. These days, chances are that your city's fire department uses CAMEO. Since 9/11, CAMEO has experienced a ten-fold increase in use. There have been more than 200,000 downloads of CAMEO in the past three years. Each year, thousands of first responders and emergency planners are trained to use CAMEO in classes led by more than 100 CAMEO-certified instructors.

The earliest versions of CAMEO were designed to support emergency responders, and then it became clear that it can also be used as an emergency preparedness tool. Additional features were incorporated specifically for planners, whose work includes the difficult task of assessing the hazards to communities from chemicals stored at industrial facilities. NOAA and EPA collaborated to develop a database in which users can store information about industrial facilities in their communities, and the chemical inventories maintained at those facilities. Over the years, CAMEO has gained international stature. The United Nations Environment Programme has adopted CAMEO and has provided training in 50 countries. CAMEO has been translated into French and Spanish.

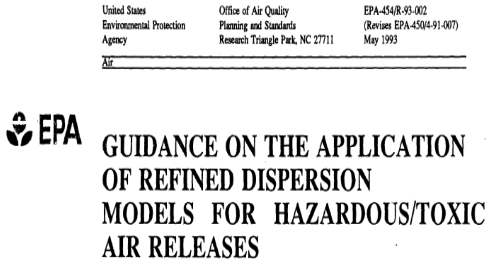
EPA and NOAA developed the web site http://www.epa.gov/ceppo/cameo to facilitate the use of CAMEO and to offer online technical support to users.

https://www.epa.gov/cameo

## Appropriate models for various accidental release scenarios

| Source type | Release Type | | | |
|---|---|---|---|---|
| | Continuous | Finite | Transient | Instantaneous |
| Ground Level | DEGADIS<br>SLAB<br>AFTOX | DEGADIS<br>SLAB<br>AFTOX | DEGADIS | AFTOX |
| Evaporating Liquid Spill | DEGADIS<br>SLAB<br>AFTOX | DEGADIS<br>SLAB<br>AFTOX | | DEGADIS<br>SLAB<br>AFTOX |
| Vertical Jet/ Plume | DEGADIS<br>SLAB<br>INPUFF | DEGADIS<br>SLAB<br>INPUFF | | |
| Horizontal Jet | SLAB | SLAB | | |
| Instantaneous | | | | SLAB |

## Guidance Document on HAP/Toxic Release Dispersion Models



United States Environmental Protection Agency
Office of Air Quality Planning and Standards Research Triangle Park, NC 27711
EPA-454/R-93-002 (Revises EPA-450/4-91-007) May 1993

Air

EPA

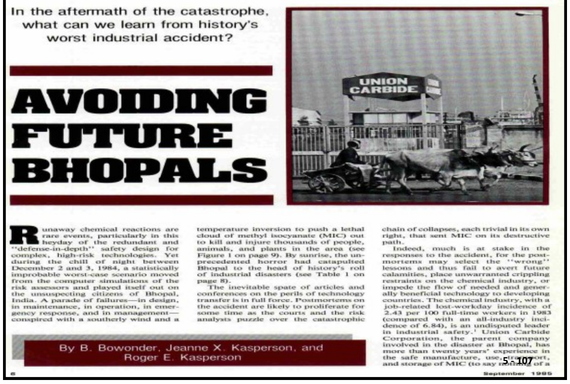
GUIDANCE ON THE APPLICATION OF REFINED DISPERSION MODELS FOR HAZARDOUS/TOXIC AIR RELEASES

## Applying Proper Dispersion Models for Industrial Accidental Releases
## Paper # 726
## Weiping Dai

Trinity Consultants
12801 North Central Expressway, Suite 1200, Dallas, TX 75243
Email: wdai@trinityconsultants.com

**CASE STUDY – APPLYING MODELS PROPERLY**
**Dense Gas Modeling – Ethylene Oxide Release**

## Environment Magazine September 1985



In the aftermath of the catastrophe, what can we learn from history's worst industrial accident?

AVOIDING FUTURE BHOPALS

Runaway chemical reactions are rare events, particularly in this heyday of the redundant and "defense-in-depth" safety design for complex, high-risk technologies. Yet during the chill of night between December 2 and 3, 1984, a statistically improbable worst-case scenario moved from the computer simulations of the risk assessors and played itself out on the unsuspecting citizens of Bhopal, India. A parade of failures—in design, in maintenance, in operation, in emergency response, and in management—conspired with a southerly wind and a temperature inversion to push a lethal cloud of methyl isocyanate (MIC) out to kill and injure thousands of people, animals, and plants in the area (see Figure 1 on page 9). By sunrise, the unprecedented horror had catapulted Bhopal to the head of history's roll of industrial disasters (see Table 1 on page 8).

The inevitable spate of articles and conferences on the perils of technology transfer is in full force. Postmortems on the accident are likely to proliferate for some time as the courts and the risk analysts puzzle over the catastrophic chain of collapses, each trivial in its own right, that sent MIC on its destructive path.

Indeed, much is at stake in the responses to the accident, for the postmortems may select the "wrong" lessons and thus fail to avert future calamities, place unwarranted crippling restraints on the chemical industry, or impede the flow of needed and generally beneficial technology to developing countries. The chemical industry, with a job-related lost-workday incidence of 2.43 per 100 full-time workers in 1983 (compared with an all-industry incidence of 6.84), is an undisputed leader in industrial safety.[1] Union Carbide Corporation, the parent company involved in the disaster at Bhopal, has more than twenty years' experience in the safe manufacture, use, transport, and storage of MIC (to say nothing of a

By B. Bowonder, Jeanne X. Kasperson, and Roger E. Kasperson

8 September 1985

## Chemical Safety Board (CSB) History

The U.S. Chemical Safety Board is authorized by the Clean Air Act Amendments of 1990 and became operational in January 1998. The Senate legislative history states: "The principal role of the new chemical safety board is to investigate accidents to determine the conditions and circumstances which led up to the event and to identify the cause or causes so that similar events might be prevented. Although the Board was created to function independently, it also collaborates in important ways with EPA, OSHA, and other agencies.

http://www.csb.gov

## Mobile Source Air Toxics Modeling – Mobile 6.2 (Replaced with MOVES)

MOBILE6 is a computer model developed by EPA used to predict emissions from on-road motor vehicles.

- MOBILE6.0 – HC, CO, and Nox
- MOBILE6.1 – Add particulates
- MOBILE6.2 – Add toxics
-M6.3/NGM1 – Add greenhouse gases

**http://www.epa.gov/oms/m6.htm**
**http://www.epa.gov/otaq/models/moves/**

## Mobile Source Air Toxics Modeling – Mobile 6.2 (cont.)

- MOBILE6.2 explicitly estimates emissions for the following compounds which dominate risk from mobile sources, based on results of the recent National-Scale Air Toxics Assessment:

1) Benzene
2) 1,3-Butadiene
3) Formaldehyde
4) Acetaldehyde
5) Acrolein
6) MTBE

## Questions

## Chapter 5 Question 1.

- 1. True or False: The fate of an air pollutant is governed both by transport processes and by the characteristics of the pollutant (e.g., its persistence, its ability to undergo reaction, and tendency to accumulate in water or soil, or to concentrate in the food chain).

## Answer for #1

- True: Fate of air pollution refers to three things:
- Where a pollutant ultimately ends up (e.g., air distant from the source, soil, water, fish tissue);
- How long it persists in the environment; and t the chemical reactions which it undergoes.

## Question 2.

- 2. True or False:
- The choice of whether to monitor or model (or both) depends on the goals of the assessment, the exposure setting, other specific project circumstances (e.g., many communities want monitoring as part of a risk assessment), and the assessing entity.

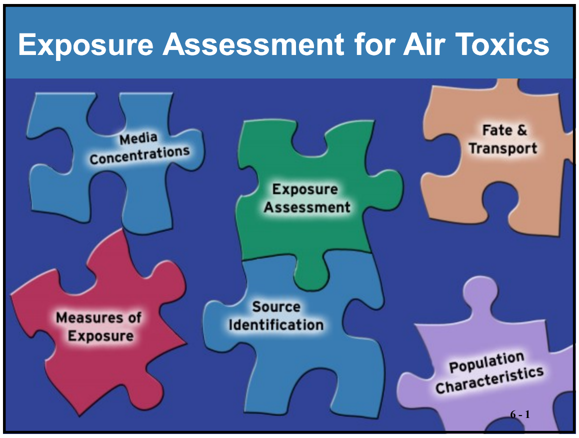
## Answer for Question #2

Answer True:

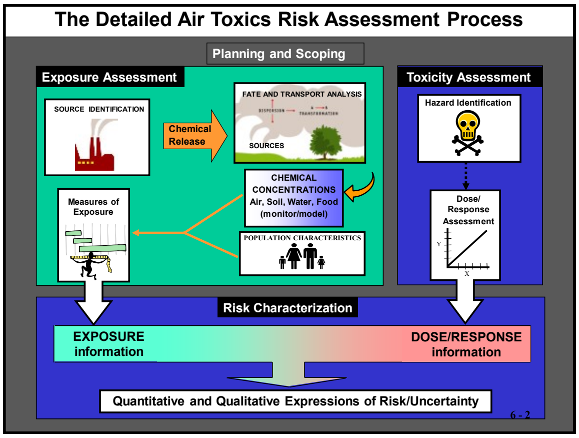
- For example, to understand the exposure an actual individual receives as they move about their daily activities, personal monitoring is the best option because it reflects the pattern of this movement. However, such studies are rarely done outside of research settings. As another example, compliance with a permitted release rate may also require monitoring as the preferred method of measurement. Slide 5-88 and Slide 5-89 provides a brief comparison of modeling versus monitoring.

## Answer for Question #2 (cont.)

- Most air toxics risk assessments that evaluate exposures to populations receiving impacts from one or more sources should generally consider using modeling as their primary tool to evaluate and characterize exposures and risks. In certain instances, assessors may use monitoring as the primary tool to evaluate exposure concentrations for potentially exposed populations. The utility of modeling for neighborhood and larger scale analyses is that it provides a better picture of the variation of exposure conditions over the assessment area domain (i.e., modeling provides spatial resolution) and allows a more straightforward approach to source allocation (i.e., what portion of the risk is caused by each of the modeled sources).



## Exposure Assessment for Air Toxics



## The Detailed Air Toxics Risk Assessment Process

Planning and Scoping

**Exposure Assessment**

SOURCE IDENTIFICATION

Chemical Release

FATE AND TRANSPORT ANALYSIS

CHEMICAL CONCENTRATIONS Air, Soil, Water, Food (monitor/model)

POPULATION CHARACTERISTICS

Measures of Exposure

**Toxicity Assessment**

Hazard Identification

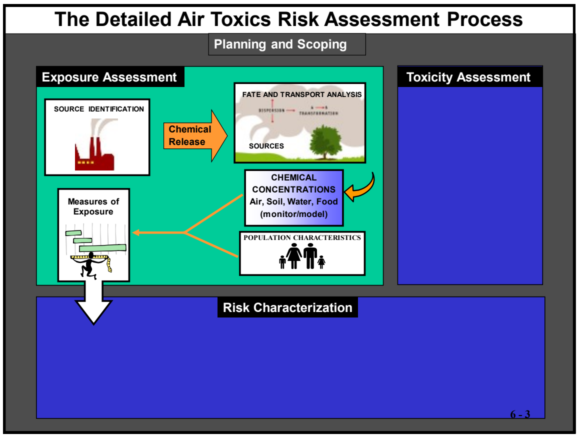
Dose/ Response Assessment

**Risk Characterization**

EXPOSURE information

DOSE/RESPONSE information

Quantitative and Qualitative Expressions of Risk/Uncertainty



## The Detailed Air Toxics Risk Assessment Process

Planning and Scoping

**Exposure Assessment**

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Chemical Release

FATE AND TRANSPORT ANALYSIS

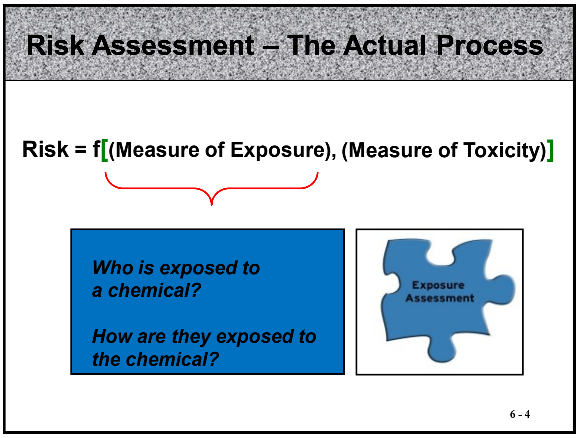
CHEMICAL CONCENTRATIONS Air, Soil, Water, Food (monitor/model)

POPULATION CHARACTERISTICS

Measures of Exposure

**Toxicity Assessment**

**Risk Characterization**

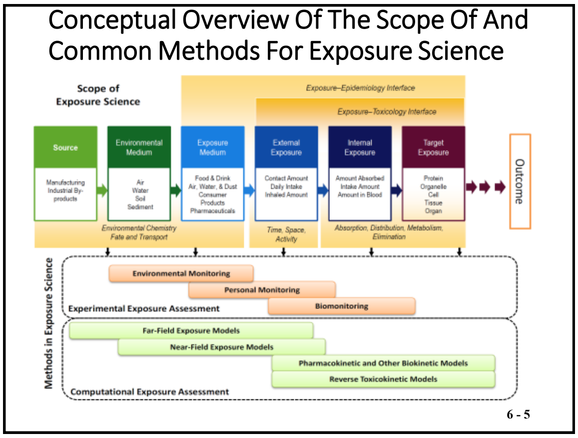


## Risk Assessment – The Actual Process

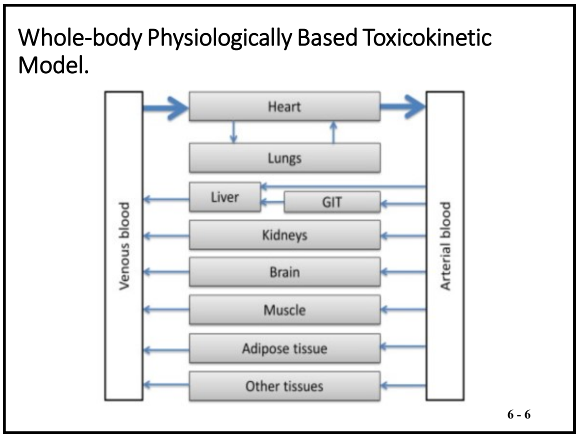
Risk = f[(Measure of Exposure), (Measure of Toxicity)]

*Who is exposed to a chemical?*

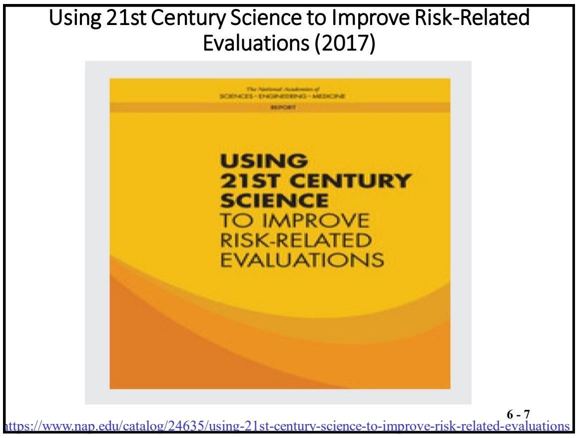
*How are they exposed to the chemical?*



## Conceptual Overview Of The Scope Of And Common Methods For Exposure Science



## Whole-body Physiologically Based Toxicokinetic Model.

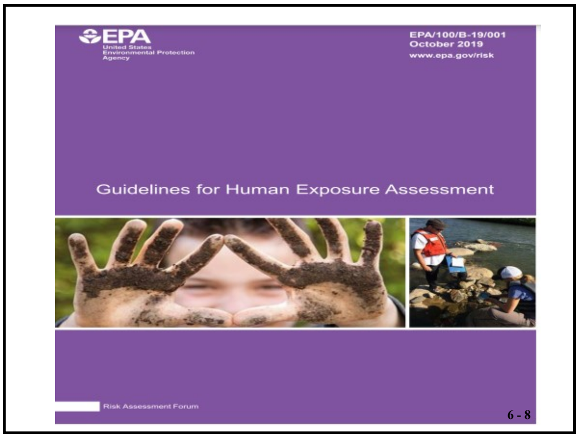


## Using 21st Century Science to Improve Risk-Related Evaluations (2017)

The National Academies of
SCIENCES · ENGINEERING · MEDICINE
REPORT

USING
21ST CENTURY
SCIENCE
TO IMPROVE
RISK-RELATED
EVALUATIONS

ttps://www.nap.edu/catalog/24635/using-21st-century-science-to-improve-risk-related-evaluations

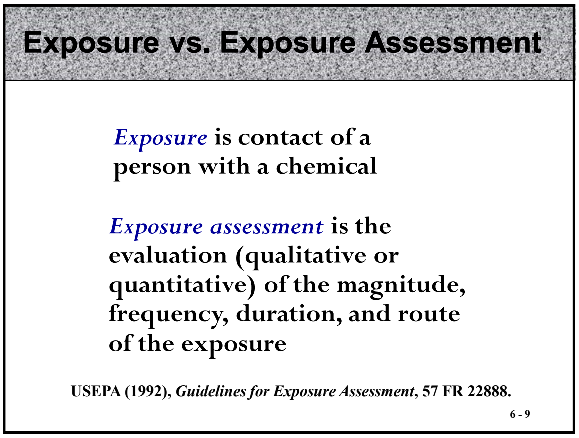


EPA
United States
Environmental Protection
Agency

EPA/100/B-19/001
October 2019
www.epa.gov/risk

Guidelines for Human Exposure Assessment

Risk Assessment Forum

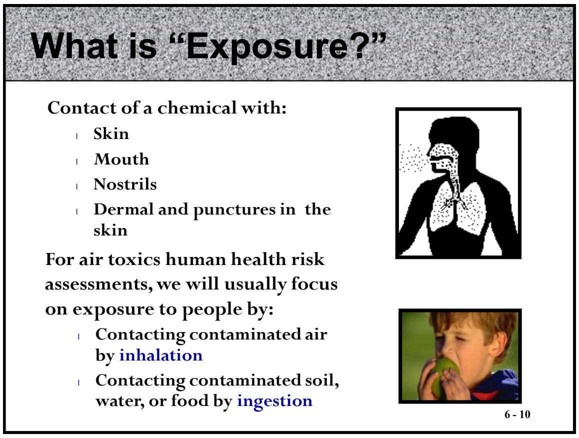


## Exposure vs. Exposure Assessment

*Exposure* is contact of a person with a chemical

*Exposure assessment* is the evaluation (qualitative or quantitative) of the magnitude, frequency, duration, and route of the exposure

USEPA (1992), *Guidelines for Exposure Assessment*, 57 FR 22888.



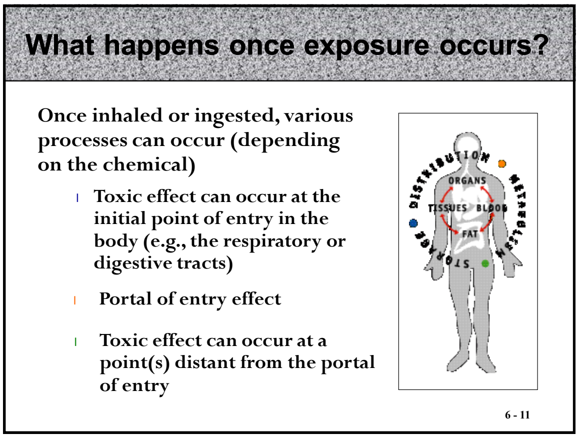
## What is "Exposure?"

Contact of a chemical with:

- Skin
- Mouth
- Nostrils
- Dermal and punctures in the skin

For air toxics human health risk assessments, we will usually focus on exposure to people by:

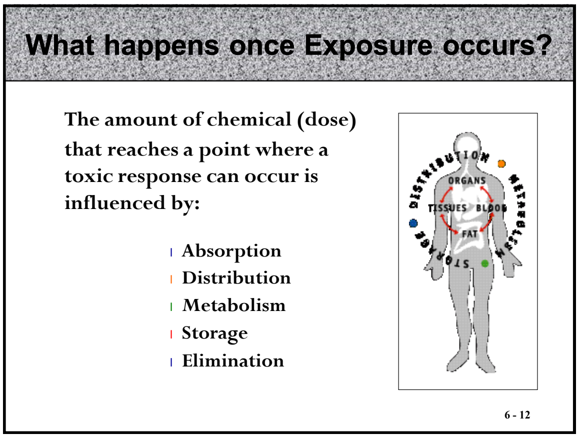
- Contacting contaminated air by inhalation
- Contacting contaminated soil, water, or food by ingestion



## What happens once exposure occurs?

Once inhaled or ingested, various processes can occur (depending on the chemical)

- Toxic effect can occur at the initial point of entry in the body (e.g., the respiratory or digestive tracts)
- Portal of entry effect
- Toxic effect can occur at a point(s) distant from the portal of entry



## What happens once Exposure occurs?

The amount of chemical (dose) that reaches a point where a toxic response can occur is influenced by:

- Absorption
- Distribution
- Metabolism
- Storage
- Elimination

## Different Time Frames

**Chronic Exposure**

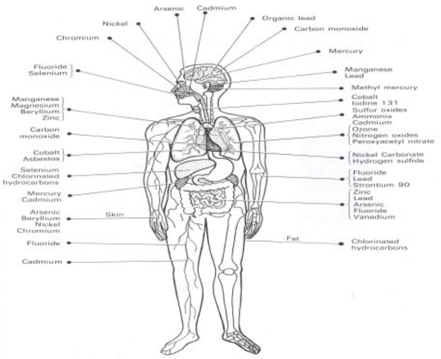
Long term (e.g., years to lifetime) exposure to (usually) relatively low levels of contaminant

Chronic exposure may result in *chronic effects* (cancer, chronic obstructive pulmonary disease, neurological problems, etc.)

**Acute Exposure**

Short term exposure (e.g., minutes, hours, days) to (usually) relative high levels of contaminant

Acute exposure may result in *acute effects* which can range from relatively mild (eye irritation), to extreme (an asthma attack), to fatal



Health Effects of Environmental Pollutants by George L. Waldbott

## Exposure Assessment

- An exposure assessment is generally the most multifaceted and time-consuming part of an air toxics risk assessment.
- The exposure assessment helps identify and evaluate a population receiving exposure to a toxic agent, and describe its composition and size, as well as the type, magnitude, frequency, route and duration of exposure.

## Exposure Assessment

- An exposure assessment is that part of the risk assessment that identifies:
  - Who is potentially exposed to toxic chemicals;
  - What toxics they may be exposed to; and
  - How they may be exposed to those chemicals (amount, pattern, and route).

## Exposure Assessment: 4 Major Components

- **Emission characterization –** a description of the source and a quantification of the rate of emissions of an air toxic from the source.
- **Environmental fate and transport -** how the released air toxics is transported, dispersed, and transformed from the source to the exposed receptor population
- **Characterization of the study population -** the location, behavior, age and other characteristics of the study population
- **Exposure characterization -** the spatial integration of the air toxics concentration with the study population to characterize exposure.

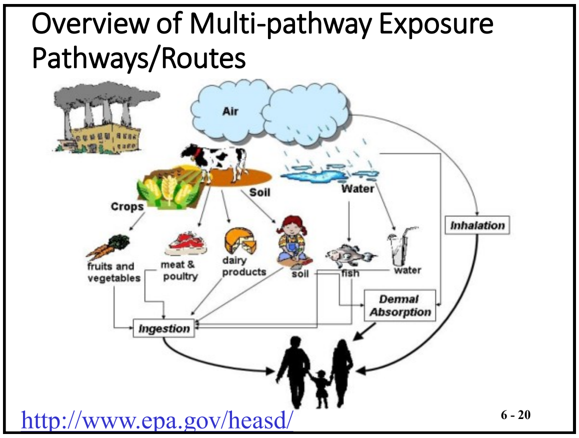
## Exposure Pathway

- Pathway analysis is a concept that is linked strongly to environmental fate and transport.
- The exposure pathway is the course that a toxic chemical takes from its source to the exposed receptor.
- An exposure pathway describes a unique mechanism by which an individual or population is exposed to air toxics at, or originating from, a source or group of sources.

## Exposure Pathway

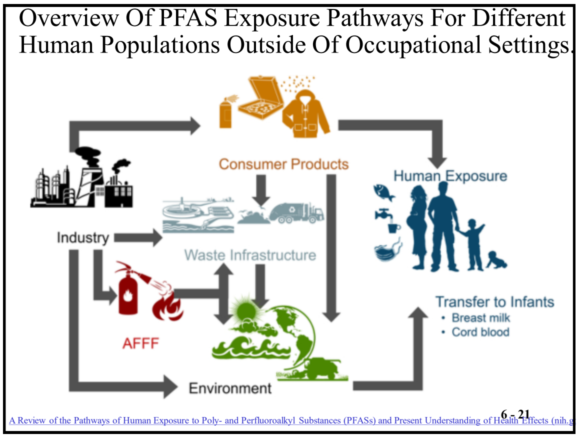
*People may be exposed to air toxics by*:

- breathing contaminated outdoor and/or indoor air (inhalation);
- ingestion (for the small number of air toxics that can accumulate in soils, sediments, and foods – a process called bioaccumulation);
- skin (dermal) contact with deposited air toxics.



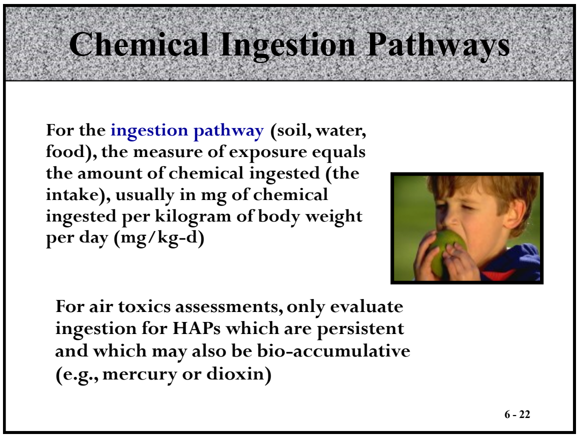
## Overview of Multi-pathway Exposure Pathways/Routes

http://www.epa.gov/heasd/



## Overview Of PFAS Exposure Pathways For Different Human Populations Outside Of Occupational Settings.

A Review of the Pathways of Human Exposure to Poly- and Perfluoroalkyl Substances (PFASs) and Present Understanding of Health Effects (nih.g



## Chemical Ingestion Pathways

For the ingestion pathway (soil, water, food), the measure of exposure equals the amount of chemical ingested (the intake), usually in mg of chemical ingested per kilogram of body weight per day (mg/kg-d)

For air toxics assessments, only evaluate ingestion for HAPs which are persistent and which may also be bio-accumulative (e.g., mercury or dioxin)

## Focus on Ingestion

### Intake Calculation

$$\text{Intake} = \frac{EC \times CR \times EF \times ED}{BW \times AT}$$

Where:

EC = Concentration of a chemical in soil, water, food at the point of exposure

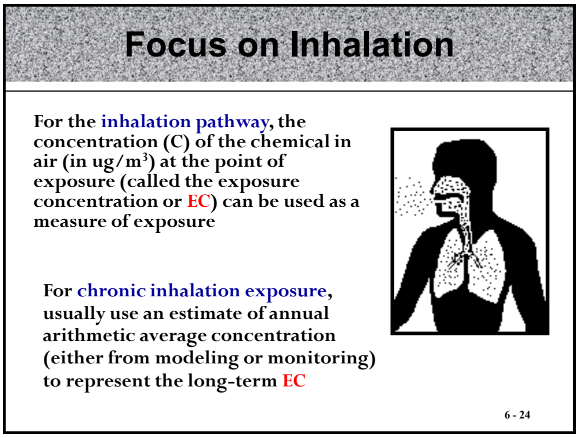
CR = Contact rate with the contaminated medium (i.e., intake rate)

EF = Exposure frequency

ED = Exposure duration

BW = Body weight

AT = Averaging time



## Focus on Inhalation

For the inhalation pathway, the concentration (C) of the chemical in air (in ug/m$^3$) at the point of exposure (called the exposure concentration or EC) can be used as a measure of exposure

For chronic inhalation exposure, usually use an estimate of annual arithmetic average concentration (either from modeling or monitoring) to represent the long-term EC

# Focus on Inhalation

For acute inhalation exposure, usually use a 1-hour or 24-hour arithmetic average to represent the short-term EC (in some cases, a shorter averaging time, like 15 minutes, is used)

In air toxics assessments, always evaluate inhalation as a route of exposure

# But we don't breathe the same thing all the time!

People do different activities in different microenvironments throughout various life stages

- Going to school, work, shopping, etc.
- Going on vacation
- Time spent in the car
- Time spent in the home
- Time working in the yard
- Time away from home on work travel
- Etc.

# Inhalation Exposure Modeling

- Inhalation exposure is characterized by the pollutant concentration in the air (i.e., the exposure concentration) reaching an individual's nostrils and/or mouth (in units of µg/m$^3$).
- Estimates of air concentrations from modeling or monitoring can be used in inhalation exposure modeling.

# Inhalation Exposure Modeling(cont.)

- A common exposure model for inhalation that combines information on microenvironment concentrations and activity patterns calculates a *time-weighted average of all exposures* from the different microenvironments in which a person spends time during the period of interest:
- where:
- ***ECA*** **= the adjusted average inhalation exposure concentration (µg/m$^3$),**
- ***T*** **= total averaging time (T = ∑ tj; years),**
- $C_j$ **= the average concentration for microenvironment *j* (µg/m$^3$), and**
- $t_j$ **= time spent in the microenvironment *j* (years).**

$$\mathbf{EC_A = \frac{1}{T}\left(\sum_j C_j \ x \ t_j\right)}$$

# Example – How to Estimate Exposure Concentrations (EC) for Exposure Modeling

**The following exposure profile has been developed for one year (which represents, for example, the 30 years of "work") for a representative individual within the population of interest:**

| Duration Spent in Each Microenvironment (% year) | Average Concentration of Pollutant A In Each Microenvironment (µg/m$^3$) |
|---|---|
| 10 = outside | 80 |
| 50 = at work | 20 |
| 40 = inside home | 10 |

**The EC for that individual is calculated as:**

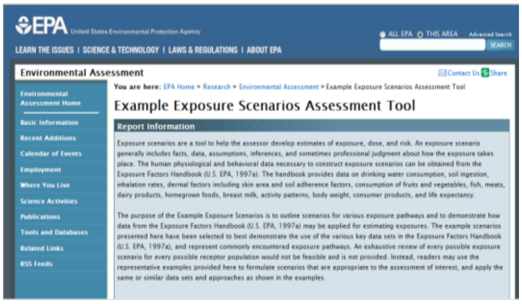
**EC = (0.1 × 80) + (0.5 × 20) + (0.4 × 10) = 22 µg/m$^3$**

April 2004

## EXAMPLE EXPOSURE SCENARIOS

National Center for Environmental Assessment
U.S. Environmental Protection Agency
Washington, DC 20460

## Example Exposure Scenarios Assessment Tool Web site



You are here: EPA Home » Research » Environmental Assessment » Example Exposure Scenarios Assessment Tool

### Example Exposure Scenarios Assessment Tool

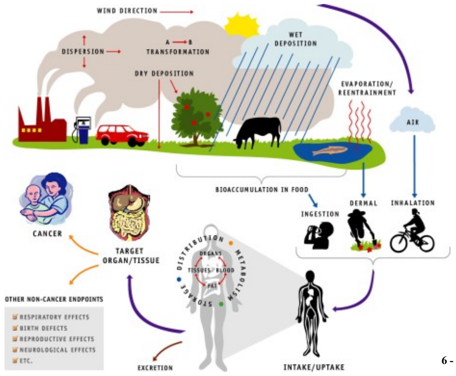
**Report Information**

Exposure scenarios are a tool to help the assessor develop estimates of exposure, dose, and risk. An exposure scenario generally includes facts, data, assumptions, inferences, and sometimes professional judgment about how the exposure takes place. The human physiological and behavioral data necessary to construct exposure scenarios can be obtained from the Exposure Factors Handbook (U.S. EPA, 1997a). The handbook provides data on drinking water consumption, soil ingestion, inhalation rates, dermal factors including skin area and soil adherence factors, consumption of fruits and vegetables, fish, meats, dairy products, homegrown foods, breast milk, activity patterns, body weight, consumer products, and life expectancy.

The purpose of the Example Exposure Scenarios is to outline scenarios for various exposure pathways and to demonstrate how data from the Exposure Factors Handbook (U.S. EPA, 1997a) may be applied for estimating exposures. The example scenarios presented here have been selected to best demonstrate the use of the various key data sets in the Exposure Factors Handbook (U.S. EPA, 1997a), and represent commonly encountered exposure pathways. An exhaustive review of every possible exposure scenario for every possible receptor population would not be feasible and is not provided. Instead, readers may use the representative examples provided here to formulate scenarios that are appropriate to the assessment of interest, and apply the same or similar data sets and approaches as shown in the examples.

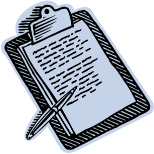
http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=85843

## Exposure and Effects from Air Toxics



## Exposure Assessment for Air Toxics

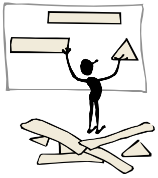
For air toxics, Exposure Assessment is the process we go through to understand:



- Who is potentially exposed to air toxics
- What air toxics they are potentially exposed to
- How the air toxics chemicals get from the point of release to the point of exposure
- How the exposure occurs, possibly through multiple routes

## Air Toxics EA - The Process

*Develop a Study-Specific Conceptual Model*



1. Characterize the exposure setting
   - Physical environment
   - Scale of the study area
   - Important sources and chemicals
   - Potentially exposed populations
2. Identify exposure pathways
   - Fate and transport of chemicals
   - Exposure points and routes

3. Quantify exposure:
   - Use monitoring or fate/transport modeling to estimate the chemical concentrations in air, water, soil, food at the point of contact (the EC)
     - The EC in air is the quantitative measure of exposure for inhalation
     - The EC in water, soil, food is used to calculate intake, the quantitative measure of exposure for ingestion
   - May use exposure modeling to refine the estimate of exposure (e.g., an apparent EC for inhalation)

## Estimating Inhalation Exposure Concentration

- Concentrations in the contaminated air under study vary over space and time, therefore it is important to know where and how long people spend their time in the study area.
- Ambient concentrations of pollutants in air can be estimated geographically and temporally through air quality modeling and monitoring.
- Estimates of exposure via the inhalation route can be adjusted from modeling data to take into account the time they may spend in various microenvironments.

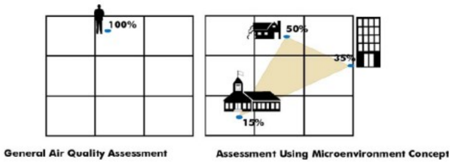
## General Approaches to Derive Exposure Concentrations

**There are two general ways to derive the EC for a given risk assessment:**

- *General Air Quality Assessment* and
- *Exposure Modeling*

Both may incorporate the results of air quality modeling and/or monitoring efforts.

## Two General Approaches to Derive Exposure Concentrations



**In this example, the left side analysis assumes that individuals spend 100 percent of their time at a given location, so the estimate of ambient concentration = EC. The right-hand side illustrates the use of exposure modeling. In this example, the analysis assumes that an individual spends 50 percent of his/her time at home; 15 percent at a school; and 35 percent at an office. The exposure model also takes into consideration that the indoor air concentrations at each location (indoor microenvironment) are different than the corresponding outdoor ambient air concentrations. The EC is the weighted sum of the product of the ambient concentrations at each location and the amount of time spent there.**

## Types of Exposure Time Frames

**Air toxics inhalation exposure assessments usually focus on two of these three different types of possible exposure scenarios:**

- *Chronic exposure* - exposure occurs repeatedly over a long period of time (usually years to lifetime).
- *Sub-chronic exposure* – exposure over a period of time that ranges between acute and chronic exposures.
- *Acute exposure* - exposure occurs over a short period of time (usually minutes, hours, or a day) and usually at relatively high concentrations.

## Common Ways to Estimate Exposure Concentrations

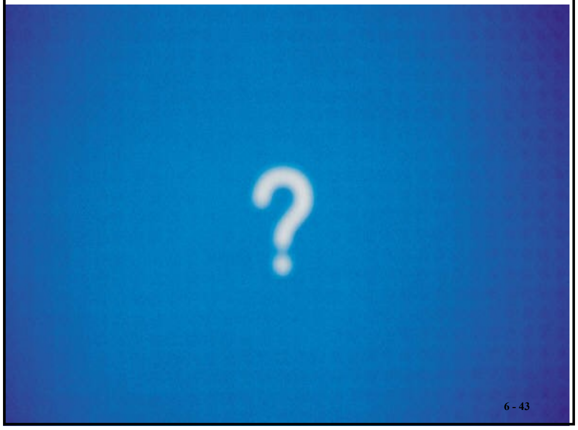
- Risk assessors commonly use several different ways to estimate exposure concentrations.
- Some ways are used primarily for screening-level (Tier 1) assessments; others are used primarily for more refined assessments.

## Common Ways to Estimate Exposure Concentrations(cont.)

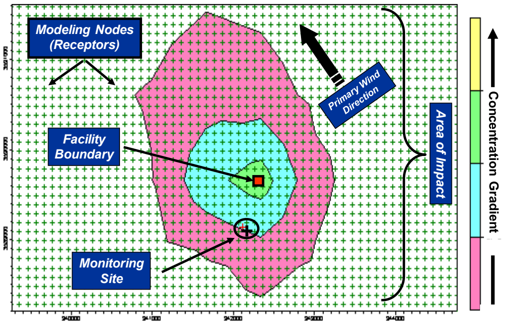
- *Monitoring locations*: Sites where air monitors provide a direct measure of ambient air concentrations at those locations..
- *Point of maximum modeled concentration*: A modeling node where the maximum modeled ambient air concentration occurs and may be called the "*maximum exposed individual (MEI)*."

## Common Ways to Estimate Exposure Concentrations(cont.)

- *Point of maximum modeled concentration at an actual receptor location:* A modeling node where the maximum ambient air concentration occurs for an actual person in the area of impact, usually at an actual residence. This point may be referred to as the point of the "*maximum individual risk (MIR).*"



## Air Dispersion Modeling and/or Air Monitoring

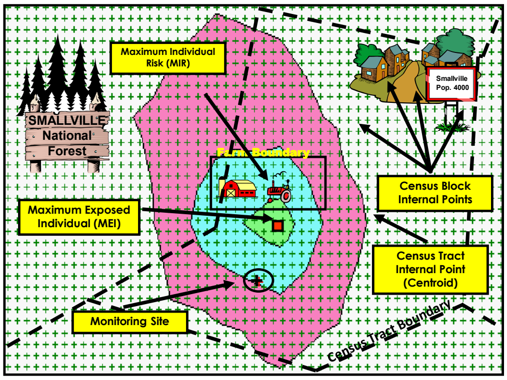


100 meter modeling grid

## Example of a Modeled Volatile Organic HAP Release for an Exposure Concentration(EC)

- For first version of the map (A), it is difficult to say much about exposure since we do not know where the people are in relation to the facility or the area of impact.
- To remedy this, our next step is to obtain demographic data (usually from the Census Bureau) and overlay it on the above map. Performing this analysis and redrawing the map gives map (B).

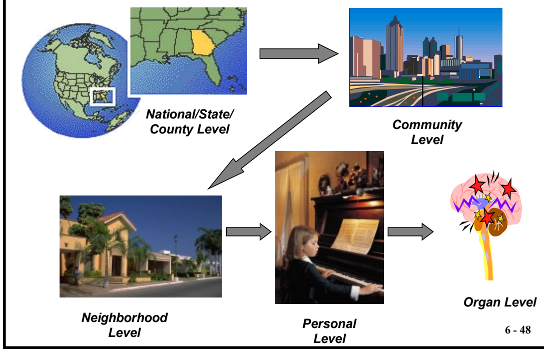
## Which of the many points do we use to represent exposure concentration?



## Example of a Modeled Volatile Organic HAP Release for an Exposure Concentration(EC).

- In map (B), we have included the census tract boundaries (dotted lines) and we also know from study area reconnaissance that there is an uninhabited national forest to the west of the facility, a farmer directly to the north, and a small town in the northeast. Smallville, can be further subdivided into smaller census blocks; but are not shown here to keep the picture simple.)

## Exposure at Different Scales



## Air Toxics Exposure Assessment is Difficult

- MANY air toxics with many different characteristics
  - Difficult to model and monitor
  - Multiple routes of exposure
- Spatial and temporal variability
  - Source dominated
  - "Hot Spots"
- Monitoring issues
  - Costs
  - Measurement methods

## Exposure Models

**General Equation for Calculating the EC for a Specific Cohort***

$EC = \sum EC_i T_i$

Where:

$EC_i$ is the exposure concentration in the microenvironment

$T_i$ is the fraction of time spent in the microenvironment

Combine cohorts to get an apparent exposure concentration that represents a community as a whole

*Volume 1 of the ATRA Library provides the exact equations

- We use exposure models to help make these refined estimates of exposure
- Calculate a refined measure of personal EC
- Reflects activities people do in different microenvironments throughout various life stages
- Often group people and activities by age, sex, ethnicity, etc. (cohorts)

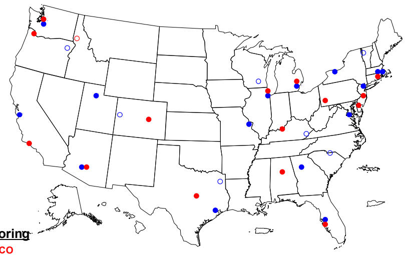
## EPA is Working to Improve Air Toxics Exposure Assessment

- New ambient monitoring program
  - National Air Toxics Trends Sites (NATTS)
- Personal exposure studies
- Enhanced modeling tools
  - Ambient dispersion models
  - Exposure models
- National Air Toxics Assessments (NATA)
- Multimedia Monitoring

## NATTS and Community Monitoring Sites

**NATTS**

Providence RI
Roxbury MA
NY, NY
Washington DC
Decatur (Atlanta), GA
Hazard, KY (Rural)
Detroit, MI
Deer Park (Houston), TX
St. Louis MO
Bountiful UT
Grand Junction, CO (Rural)
San Jose CA
Seattle WA
Chittenden County, VT (Rural)
Rochester, NY
Tampa, FL
Chesterfield, SC (Rural)
Chicago, IL
Mayville WI (Rural)
Harrison County TX (Rural)
Phoenix AZ
La Grande, OR (Rural)



● Urban ○ Rural

**Community Monitoring**

| | |
|---|---|
| Chicago, IL | Denver, CO |
| Birmingham, AL | South Coast, AQMD |
| Warwick, RI | Phoenix, AZ |
| Paterson City, NJ | Portland, OR |
| Wilmington, DE | Spokane, WA |
| Louisville, KY | Nez Perce, ID (Rural) |
| Detroit, MI | Hillsborough Count, FL |
| Austin, TX | Allegheny County, PA |

Community Scale Air Toxics Ambient Monitoring (CSATAM)

Final Reports | Ambient Monitoring Technology Information Center (AMTIC) | US EPA

## Personal Exposure Studies

## EPA Air Toxics Personal Exposure Studies

- EPA Studies
  - Past Studies
    - TEAM
    - NHEXAS
  - Current Studies
    - Detroit Aerosol and Exposure Research Study (DEARS)
- Studies Supported by EPA Funds
  - EPA STAR Program
    - HAP Mixtures: Measuring and Modeling Complex Exposure
    - Human Exposures to Aldehydes Arising from Mobile and Point Sources
  - Mickey Leland National Urban Air Toxics Center
    - Relationship Between Indoor, Outdoor, and Personal Air (RIOPA)
    - Urban Air Toxics Exposure of High School Children
    - VOC Exposure in an Industry-Impacted Community
    - Air Toxics and Asthma in Children
  - Health Effects Institute
    - Hotspots
    - Biomarkers
    - Diesel/PAHs

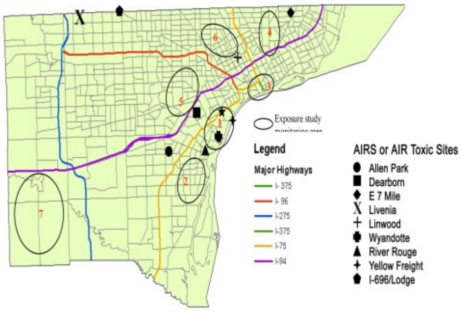
## Detroit Exposure and Aerosol Research Study (DEARS)

- Describe the relationship between concentrations at a central site and residential/personal concentrations
  - Air Toxics and PM constituents
  - Air Toxics and PM from specific sources
- Emphasis placed on understanding impact of:
  - Local sources (mobile and point) on outdoor residential concentrations
  - Housing type and house operation on indoor concentrations
  - Locations and activities on personal exposure

## DEARS Field Monitoring Design

- 3 year study starting in July 2004
- Collect data in 120 homes for 5 days in winter and 5 days in summer (1200 total sampling days- 40 new households each year
- Concurrent (9am to 9 am) monitoring at
  - Central site
  - Residential – outdoors and indoors
  - Personal level
- Survey data
  - Residential characteristics, participant characteristics, time/activity, source usage.

## Seven Monitoring Areas in DEARS



## DEARS Measurements

- Particulate matter
  - Mass
  - Sulfate
  - Metals
  - SVOCs
- EC/OC
- Particle-bound nitrate
- Gases
  - Ozone
  - Nitrogen Dioxide
  - Sulfur Dioxide
- Air Toxics
  - VOCs
  - Carbonyls
- Indoor air exchange rates

## DEARS – Related Research Efforts

- Source Apportionment
- Air Quality and Human Exposure Modeling
- Near Roadway Exposure Study
- Mobile Source Characterization
- Field testing for acrolein and 1,3-butadiene measurement methods
- EPA/NHEERL Toxicity Studies of PM from major sources
- EPA/NHEERL Detroit Children's Health Study
- EPRI Health Studies (with University of Michigan and Michigan State University)

## Community-Based Air Toxics Projects

https://www3.epa.gov/ttnamti1/files/ambient/airtox/CSATAMSummaryReport2009.pdf

http://www.epa.gov/heasd/c-ferst/

https://www3.epa.gov/ttnamti1/local.html

## Air Quality and Exposure Modeling

---

## Enhanced EPA Modeling Tools

- Ambient Dispersion Models
  - Community Multi-scale Air Quality (CMAQ)
- Exposure Models
  - Stochastic Human Exposure and Dose Simulation (SHEDS)
  - Total Risk Integrated Methodology (TRIM)
- Modeling Collaborations

---

## Community Multiscale Air Quality (CMAQ) Model

- Extended the capability of CMAQ to Air Toxics
  - Completed annual (2001 CY) simulation of 20 HAPs
  - Simulations especially relevant for air toxics with significant secondary formation, e.g., formaldehyde, acetaldehyde and acrolein.
- Community-scale modeling
  - Model HAP concentrations at high resolutions and pinpoint risk “hot spots” for HAPs within urban areas.
  - Philadelphia pilot project with EPA Region 3.
- The CMAQ Air Toxics model will provide a tool for developing and evaluating strategies to reduce HAPs, and examining the interactions between control of HAPs, ozone, and PM.

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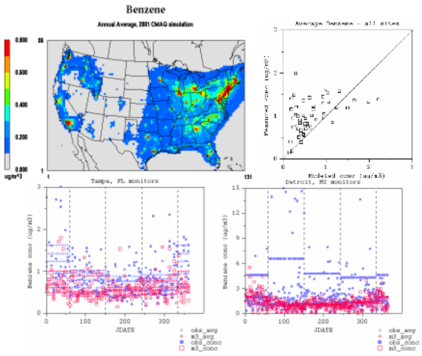
## CMAQ Benzene Results



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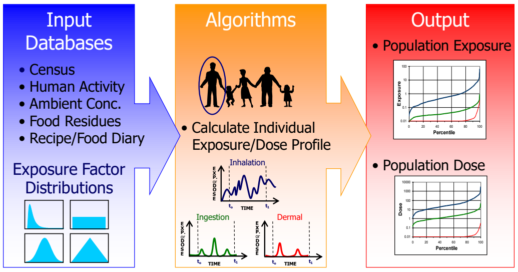
## SHEDS Model Structure



**Input Databases**
- Census
- Human Activity
- Ambient Conc.
- Food Residues
- Recipe/Food Diary

**Exposure Factor Distributions**

**Algorithms**
- Calculate Individual Exposure/Dose Profile

**Output**
- Population Exposure
- Population Dose

---

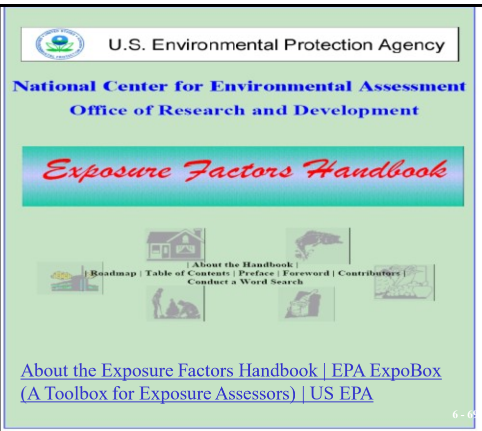
## Stochastic Human Exposure and Dose Simulation (SHEDS) Model

- A model for improving estimates of human exposure and dose to multimedia, multi-pathway pollutants
- SHEDS can:
  - Predict population exposures and dose
  - Characterize variability <u>and</u> uncertainty in exposure and dose estimates
  - Identify important exposure media, routes, pathways, and factors affecting exposures
  - Identify contributions from different sources (single pathway) and different routes and pathways for single (aggregate) or multiple chemicals (cumulative).
  - Prioritize measurement data needs
- Air Toxics applications
  - Benzene
  - Aldehydes
  - Arsenic

## Sources of Data for Human Activity for Exposure Assessments

- Numerous EPA and related databases provide information useful for conducting exposure assessments, including information on activity pattern and demographic information useful for inhalation exposure modeling.
- EPA Consolidated Human Activity Database (CHAD):
- EPA Exposure Factors Handbook:
- EPA Human Exposure Database System (HEDS):
- National Human Exposure Assessment Survey (NHEXAS):
- CDC National Health and Nutrition Examination Survey (NHANES)
- U.S. Census Data:
- LandScan USA

- Consolidated Human Activity Database (CHAD) contains data obtained from pre-existing human activity studies that were collected at city, state, and national levels. CHAD is intended to be an input file for exposure/intake dose modeling and/or statistical analysis. CHAD is a master database providing access to other human activity databases using a consistent format.
- **http://www.epa.gov/chadnet1/**


U.S. Environmental Protection Agency

National Center for Environmental Assessment

Office of Research and Development

*Exposure Factors Handbook*

| About the Handbook |
| Roadmap | Table of Contents | Preface | Foreword | Contributors |
Conduct a Word Search

About the Exposure Factors Handbook | EPA ExpoBox (A Toolbox for Exposure Assessors) | US EPA

HEDS Human Exposure Database System

- **HEDS is the Human Exposure Database System. It is an integrated database system that contains chemical measurements, questionnaire responses, documents, and other information related to EPA research studies of the exposure of people to Environmental contaminants.**
- HEDS - EPA DATABASE SYSTEM FOR PUBLIC ACCESS TO HUMAN EXPOSURE DATA | Science Inventory | US EPA

## Human Exposure Measurements: National Human Exposure Assessment Survey (NHEXAS)

- The National Human Exposure Assessment Survey program was designed to address some of the limitations of single-chemical, and single media exposure route studies.
- The purpose of NHEXAS is to evaluate comprehensive human exposure to multiple chemicals on a community and regional scale.
- NHEXAS will help individuals, communities, states, the EPA, and other organizations understand the greatest health risks from various chemicals and decide whether steps to reduce those risks are needed.
- http://www.epa.gov/heasd/edrb/nhexas.html

## Inhalation Exposure Models

- Important characteristics that vary among the models include:
- Ambient concentrations - Modeling or monitoring estimates
- Exposure concentration time scale
- Spatial scale - Geographic resolution of predictions (i.e., Census tracts, Census blocks, grids)
- Potential size of modeling domain (i.e, neighborhood, county, nation)
- Population activity data

## Comparison of Inhalation Exposure Models

| Model | Population Activity Data | Source of Ambient Concentrations | Spatial Resolution | Framework |
|---|---|---|---|---|
| HEM-3 | None (screening model) | ISCST3<br>AERMOD | Census blocks (additional points can be specified) | Deterministic |
| HAPEM | Micro-environment time/sequence, commuting | External model or monitoring data | Census tract | Stochastic |
| TRIM.Expo (a.k.a. APEX) | Micro-environment time/sequence, commuting | External model or monitoring data | Depends on resolution of air quality and demographic inputs | Stochastic |
| CPIEM | Micro-environment time/sequence, commuting | External model or monitoring data | User-specified for the selection of activity patterns (i.e., state, region) | Stochastic |

## Human Exposure Model (HEM 3)

- The Human Exposure Model (HEM) is used primarily for performing risk assessments for major point sources air toxics.
- The HEM only addresses the inhalation pathway of exposure, and is designed to predict risks associated
- The HEM provides ambient air concentrations, as surrogates for lifetime exposure, for use with unit risk estimates and inhalation reference concentrations to produce estimates of cancer risk and non-cancer hazard, respectively, for the air toxics modeled.

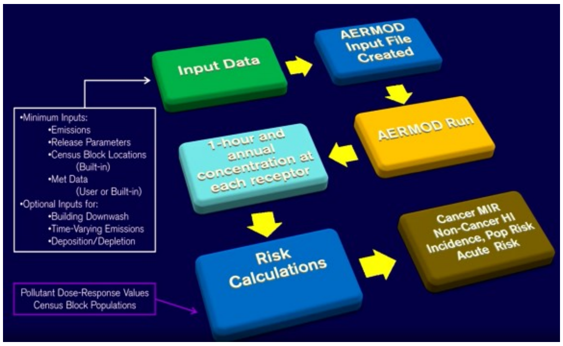
## Human Exposure Model (HEM 3)

**The HEM contains:**

(1) an atmospheric dispersion model, the Industrial Source Complex Model , with included meteorological data: and

(2) U.S. Bureau of Census population data at the Census block level.

## Flow Diagram of the HEM-3 Model



## Human Exposure Modeling - Hazardous Air Pollutant Exposure Model (HAPEM 7)

- The HAPEM 7 model has been designed to estimate inhalation exposure for selected population groups to various air toxics.
- The model makes use of ambient air concentration data, indoor/outdoor microenvironment concentration relationship data, population data, and human activity pattern data to estimate an expected range of inhalation exposure concentrations for groups of individuals.

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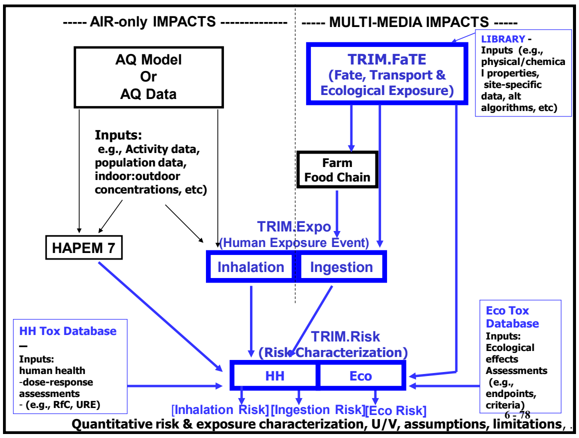


----- AIR-only IMPACTS --------------

----- MULTI-MEDIA IMPACTS -----

AQ Model
Or
AQ Data

**TRIM.FaTE**
**(Fate, Transport & Ecological Exposure)**

**LIBRARY** - Inputs (e.g., physical/chemical properties, site-specific data, alt algorithms, etc)

**Inputs:**
e.g., Activity data, population data, indoor:outdoor concentrations, etc)

Farm Food Chain

HAPEM 7

TRIM.Expo
(Human Exposure Event)

Inhalation | Ingestion

**HH Tox Database** –
Inputs:
human health -dose-response assessments
- (e.g., RfC, URE)

TRIM.Risk
(Risk Characterization)

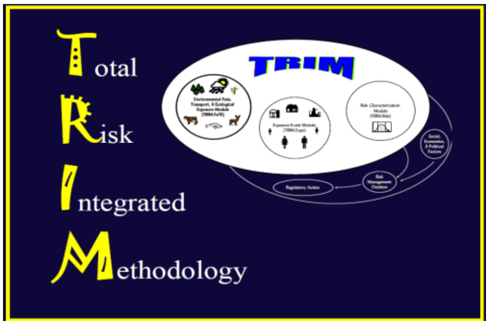
HH | Eco

**Eco Tox Database**
Inputs:
Ecological effects Assessments
(e.g., endpoints, criteria)

[Inhalation Risk] [Ingestion Risk] [Eco Risk]

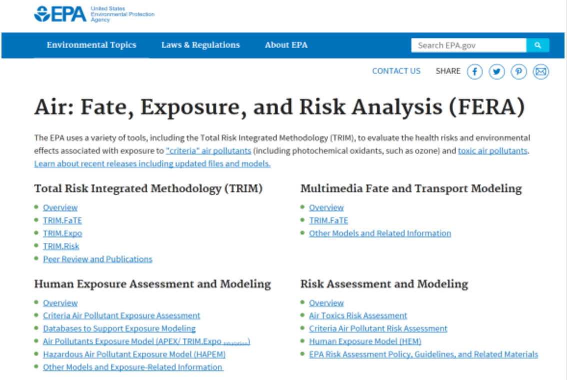
Quantitative risk & exposure characterization, U/V, assumptions, limitations, .

## Total Risk Integrated Methodology



## TRIM Application

- Inhalation Risk Assessments
  - –Residual risk assessments (HAPs) –refined tier
  - –Ozone NAAQS exposure and risk assessment
  - –Lead NAAQS exposure and risk assessment
- Ecological Risk Multimedia Assessments
  - –Residual risk assessments (e.g., Hg, etc)
- Ingestion Risk Assessments
  - –Residual risk multimedia, multipathway assessments (e.g., Hg, dioxins, PAHs)
  - –NAAQS -Lead



### Air: Fate, Exposure, and Risk Analysis (FERA)

The EPA uses a variety of tools, including the Total Risk Integrated Methodology (TRIM), to evaluate the health risks and environmental effects associated with exposure to "criteria" air pollutants (including photochemical oxidants, such as ozone) and toxic air pollutants. Learn about recent releases including updated files and models.

**Total Risk Integrated Methodology (TRIM)**

- Overview
- TRIM.FaTE
- TRIM.Expo
- TRIM.Risk
- Peer Review and Publications

**Multimedia Fate and Transport Modeling**

- Overview
- TRIM.FaTE
- Other Models and Related Information

**Human Exposure Assessment and Modeling**

- Overview
- Criteria Air Pollutant Exposure Assessment
- Databases to Support Exposure Modeling
- Air Pollutants Exposure Model (APEX/ TRIM.Expo inhalation)
- Hazardous Air Pollutant Exposure Model (HAPEM)
- Other Models and Exposure-Related Information

**Risk Assessment and Modeling**

- Overview
- Air Toxics Risk Assessment
- Criteria Air Pollutant Risk Assessment
- Human Exposure Model (HEM)
- EPA Risk Assessment Policy, Guidelines, and Related Materials

Download Fate, Exposure and Risk Models

https://www.epa.gov/fera

## Comparison of Exposure Assessment Tools

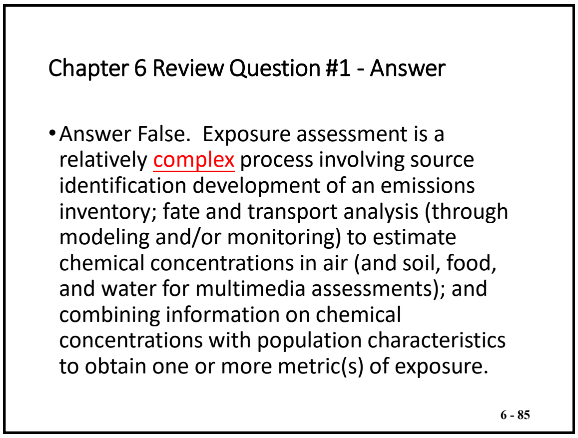
| | PRO | CON |
|---|---|---|
| **Ambient Monitoring** | **-"True" measure of ambient concentration** | **- Spatial and temporal gaps<br>- Costly to monitor everywhere<br>- Surrogate for personal exposure** |
| **Personal Monitoring** | **- "True" measure of personal exposure** | **- Spatial and temporal gaps<br>- Can't monitor everyone all the time (costs and personal inconvenience)** |
| **Ambient Modeling** | **- Good spatial and temporal coverage<br>- Relatively low cost** | **- Uncertainty<br>- Surrogate for personal exposure** |
| **Human Exposure Modeling** | **- Estimates true human exposure<br>- Relatively low cost** | **- Uncertainty** |

**The best approach is to utilize a combination of the above.**

- Questions

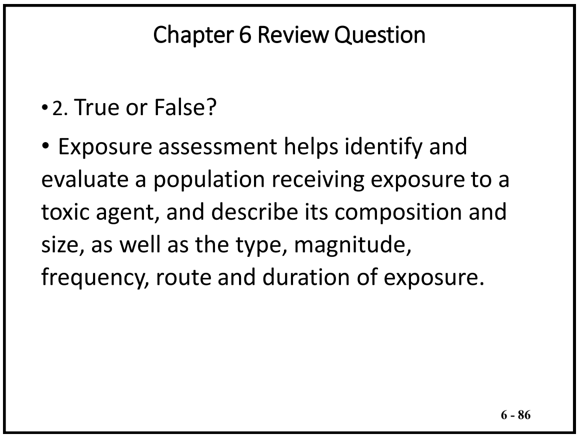
## Chapter 6 Review Questions

- 1. True or False;
- Exposure assessment is a relatively simple process involving source identification; development of an emissions inventory; fate and transport analysis (through modeling and/or monitoring) to estimate chemical concentrations in air (and soil, food, and water for multimedia assessments); and combining information on chemical concentrations with population characteristics to obtain one or more metric(s) of exposure.



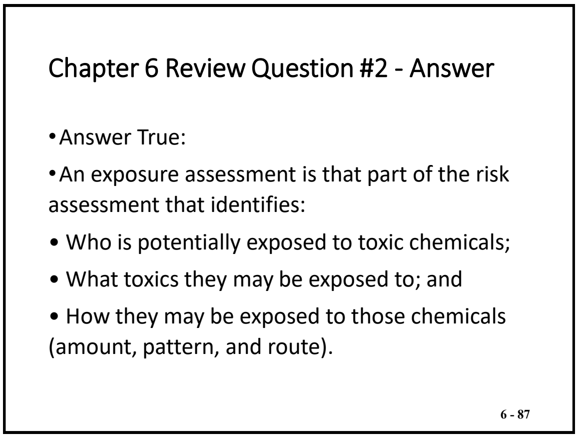
## Chapter 6 Review Question #1 - Answer

- Answer False. Exposure assessment is a relatively complex process involving source identification development of an emissions inventory; fate and transport analysis (through modeling and/or monitoring) to estimate chemical concentrations in air (and soil, food, and water for multimedia assessments); and combining information on chemical concentrations with population characteristics to obtain one or more metric(s) of exposure.



## Chapter 6 Review Question

- 2. True or False?
- Exposure assessment helps identify and evaluate a population receiving exposure to a toxic agent, and describe its composition and size, as well as the type, magnitude, frequency, route and duration of exposure.



## Chapter 6 Review Question #2 - Answer

- Answer True:
- An exposure assessment is that part of the risk assessment that identifies:
- Who is potentially exposed to toxic chemicals;
- What toxics they may be exposed to; and
- How they may be exposed to those chemicals (amount, pattern, and route).

# Chapter Seven
# *Toxicity Assessment of Air Toxics*

Toxicity Assessment

**Hazard Identification:**
-Human & Animal Data
-Weight of Evidence

**Dose Response:**
-Unit Risk
-Reference Concentration

*By: Louis DeRose*

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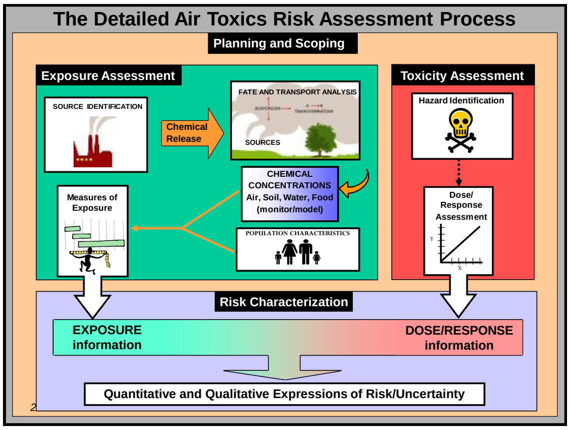
## The Detailed Air Toxics Risk Assessment Process



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## Toxicity Assessment: Two Parts

- **Hazard Identification**:
  - Determines whether exposure to a chemical *can cause adverse health effect* (i.e., cancer, birth defects, etc.) &
  - Looks at the *strength of evidence* & *circumstances* that cause these effects (i.e., long term vs. short term exposure, animal vs. human data, inhalation/ingestion).
- **Dose-response Assessment** establishes a *quantitative relationship* between the *dose* of the contaminant & the incidence of *adverse health effects* (cancer & non-cancer) in the exposed population.
  - Its important to understand how the dose-response data were analyzed & produced (i.e. uncertainties & extrapolations).

---

## Part One: Hazardous Identification

- 1. **Review & analyze toxicity data**: to see if exposure to a chemical can cause particular health effects:
  - What are the affected organs or tissue systems?
  - What is the severity of effects?
  - Who is more sensitive or susceptible?
  - What does the body do to the chemical?
  - What does the chemical do to the body?
  - How does the chemical act to produce an effect?
- 2. **Weigh the evidence**: the strength of the evidence that the chemical causes various toxic effects.

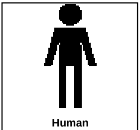
---

## Hazard Identification

### Where do we get our information?

**Data on adverse biologic effects usually generated through…**

- **Epidemiological studies:** study distribution of disease in a specific population of humans
- **Animal Studies** (rats, mice, rabbits, guinea pigs, hamsters, dogs or monkeys)
- **In-vitro assays (test tube studies)** study mutations in genetic material after cell division



Human Epidemiological Studies

Laboratory Animal Experiments

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## Epidemiological Studies

- **Retrospective Studies**: In which groups of individuals are identified based on *past* exposure conditions:
  - Usually occupational i.e. asbestos workers –chronic effect
  - Accidental: i.e. Bhopal –high concentrations with acute effects
- **Prospective Studies**: In which groups of individuals are identified based on *current* exposure and followed into the future to see how exposure affects their outcomes.
- **Advantages**: animal to human extrapolation not necessary
- **Disadvantages**: no control over exposure amount or exposure to other toxins or lifestyle differences
  - Also possible lengthy latency periods

## Animal Studies

- Acute: tests are usually relatively short in duration, but high in concentration.
  - Study effects after exposure for *less than 14 days*
  - Commonly use *Lethal Dose 50 ($LD_{50}$)*
- Sub-chronic:
  - Exposure from about *7 days up to 10% of the animal's lifetime*
  - Commonly use lowest observed adverse effect level *LOAEL*, no observed adverse effect level *NOAEL* or other "critical factors"
- Chronic: tests are usually long in duration, but relatively low in concentration.
  - Study effects (i.e., tumor formation for carcinogens) after exposure *over at least 10% of the animal's lifetime*.
  - Commonly use *LOAEL, NOAEL* or other "critical factors"

## Weight of Evidence: Carcinogens

### WOE Scheme from: EPA's 1986 *Guidelines for Carcinogen Risk Assessment*

**Old (but still around)**

**A** - *Known Human Carcinogen* (sufficient epidemiological)
**B1** - *Probable Human Carcinogen* (limited epidemiological)
**B2** - *Probable Human Carcinogen* (sufficient animal / inadequate or no epidemiological studies)
**C** - *Possible Human Carcinogen* (limited animal / no human)
**D** – Not classifiable as human carcinogen (insufficient data available to see if chemical a carcinogen)
**E** - *No evidence for carcinogenic effects* based on at least two technically adequate animal studies

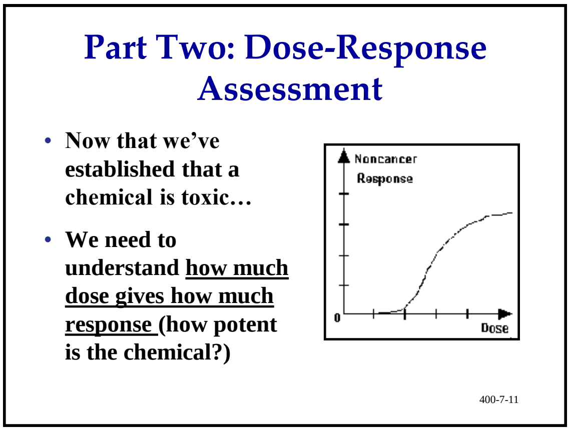
## Weight of Evidence: Carcinogens

### EPA's New WOE Scheme for Carcinogens

**From: EPA's 2005 *Guidelines for Carcinogens Risk Assessment***

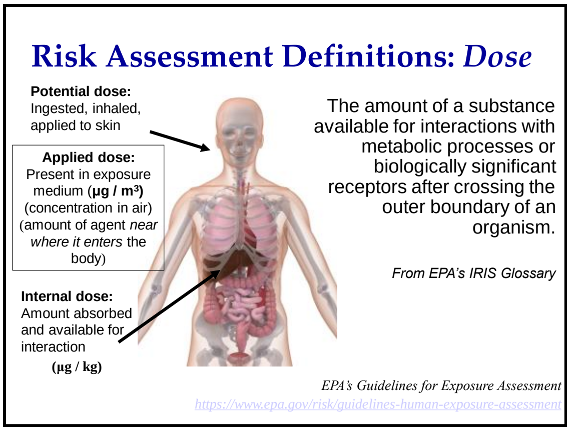
- **Weight of Evidence Narrative**
- **Descriptors for Classifying Human Carcinogenic Potential**
  - **Carcinogenic to humans**
  - **Likely to be carcinogenic**
  - **Suggestive evidence**
  - **Inadequate data**
  - **Not likely**

- ***Carcinogenic to Humans****:* when there is convincing epidemiologic evidence demonstrating causality between human exposure and cancer, or when there is strong epidemiological evidence and extensive animal evidence.
- ***Likely to be Carcinogenic to Humans***: when the available tumor effects are adequate to demonstrate carcinogenic potential to humans, but does not reach the weight-of-evidence for the descriptor "carcinogenic to humans."
- ***Suggestive Evidence of Carcinogenic Potential***: when the evidence from human or animal data is suggestive of carcinogenicity, which raises a concern for carcinogenic effects but is judged not sufficient for a stronger conclusion.
- ***Inadequate Information to Assess Carcinogenic Potential***: when available data are judged inadequate to perform an assessment.
- ***Not Likely to be Carcinogenic to Humans***: when the available data is strong enough to decide that there is no basis for a human hazard.



## Part Two: Dose-Response Assessment

- **Now that we've established that a chemical is toxic…**
- **We need to understand how much dose gives how much response (how potent is the chemical?)**



## Risk Assessment Definitions: *Dose*

**Potential dose:** Ingested, inhaled, applied to skin

**Applied dose:** Present in exposure medium (**µg / m³**) (concentration in air) (amount of agent *near where it enters* the body)

**Internal dose:** Amount absorbed and available for interaction (**µg / kg**)

The amount of a substance available for interactions with metabolic processes or biologically significant receptors after crossing the outer boundary of an organism.

*From EPA's IRIS Glossary*

*EPA's Guidelines for Exposure Assessment*
https://www.epa.gov/risk/guidelines-human-exposure-assessment

# Dose-Response Definitions: *Critical Effect*

- **Critical effect:** "The <u>first adverse effect</u>, or its known precursor, <u>that occurs to the most sensitive species</u> as the dose rate of an agent increases" (U.S. EPA, 2002c).
- <u>Two types</u>: (1) those considered to have a threshold and (2) those for which there may be some risk at any exposure level (non-threshold - carcinogens).

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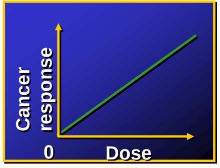
# Dose-Response Assessment

**Cancer Risk**

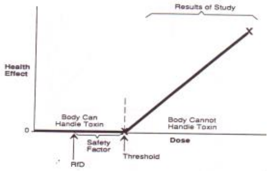
- **Non-threshold: <u>no</u> exposure is without risk**



- **Slope Factors**
  - **Inhalation Unit Risk**
  - **Oral Potency Factor**

**Non-Cancer Hazard**

- **Threshold: Body (liver & kidneys) breaks down many chemicals to less toxic substances**

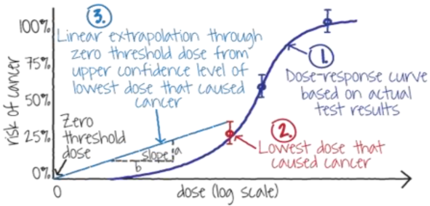


- **Reference Values**
  - **RfC (inhalation)**
  - **RfD (oral)**

---

# Dose-Response Data from Animal Studies

- Dose-response relationships observed from animal studies are often <u>at much higher doses</u> that would be anticipated for humans, so data must be **<u>extrapolated to lower doses</u>**.



***Linearized Multistage Model***

- It <u>assumes linear extrapolation</u> with a <u>zero dose threshold</u> from the upper confidence level of the <u>lowest dose</u> that produced <u>cancer</u> in an animal test or in a human epidemiology study.

---

# Limitations of the Linear, Non-threshold Model for Carcinogens

- In the U.S., carcinogens have <u>historically & currently</u> regulated by using the **<u>non-threshold</u>** <u>*linearized multistage model*)</u>.
  - Designed to <u>overestimate the risk</u> – a conservative approach
- According to the EPA & other agencies, <u>*if cancer evidence suggest a* **threshold** *mechanism, then cancer risks will be assessed differently*</u>.
  - But EPA & other regulatory agencies have **<u>*rarely* *considered the evidence strong enough to use a threshold* mechanism</u>** <u>for carcinogens</u>. (*TRENDS*, Winter 2013)
- EPA *proposed rule* (4/30/2018): Since there is growing evidence of non-linearity…EPA should look at other models.

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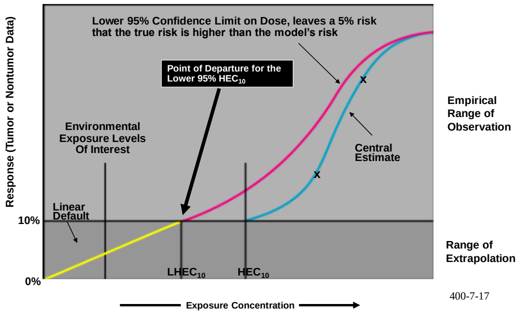
# Dose-Response Extrapolation: Cancer

High to low dose linear extrapolation from POD to 0,0 (non-threshold)



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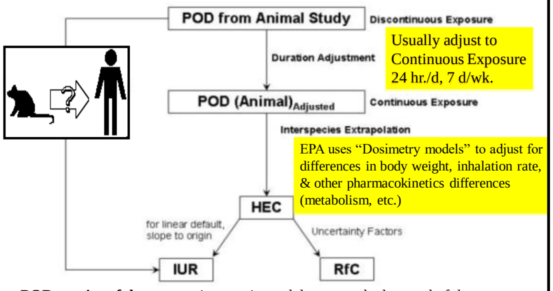
# Dose-Response Data from Animal Studies

- Animal studies data must also be <u>adjusted from animal to humans</u> in order to predict the relationship for humans. These <u>adjustments</u> are used to calculate the "**human equivalent concentration" (HEC):**
- ***Duration adjustment***: (animal inhalation exposures are about 6 hrs/day, 5 days/wk must be adjusted to <u>continuous</u> exposure)
- ***Interspecies adjustments*:** compensate for differences between humans & lab animals:
  - Differences in <u>size</u> & <u>life spans</u>
  - Differences in <u>pharmacokinetics</u> (what the body does with the chemical once its inside the body):
    - *Metabolism* (conversion to a less toxic substance)
    - *Excretion* & distribution to *storage sites* (fat, bones etc.)
    - *Absorption rate* (mainly in lungs & small intestines) i.e. for DDT, a rabbit absorbs 46.3%; a monkey 1.5%; & a man 10.4%

## Deriving a Human Equivalent Concentration (HEC) from an Animal Study



Usually adjust to Continuous Exposure 24 hr./d, 7 d/wk.

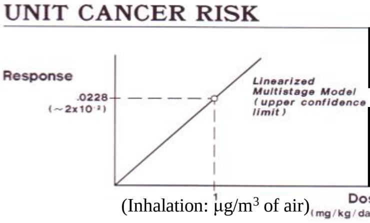
EPA uses "Dosimetry models" to adjust for differences in body weight, inhalation rate, & other pharmacokinetics differences (metabolism, etc.)

**POD – point of departure**: is an estimated dose near the low end of the observed range without extrapolation to lower doses.

---

## Dose-Response: Carcinogens

- **Unit Risk is the *slope* of the dose response line:**
  - "Lifetime cancer risk that results from continuous exposure to an agent over a lifetime (assume 70 yrs.)"
  - Also known as "**potency**"
  - Can be obtained from EPA web site: "IRIS"



(Inhalation: µg/m$^3$ of air)

**IUR (risk per µg/m3) =** Slope of the line from the point of departure to zero

**Potency for ingestion** are developed in similar fashion, but are in units of **(risk per mg/kg-day)**

---

## Limitations in Cancer Dose-Response Assessment

- Interspecies extrapolation,
- High-dose to low-dose extrapolation, and
- Limitations of dose-response studies to capture all relevant information
- Little consideration of variations in the population in susceptibility & vulnerability.

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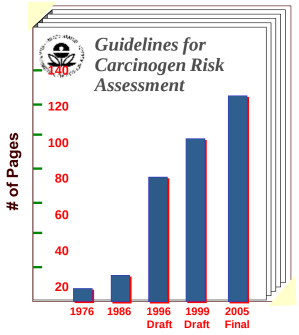


As toxicology and risk assessment advance, the guidelines have grown.

---

## Dose-Response: Non-carcinogens

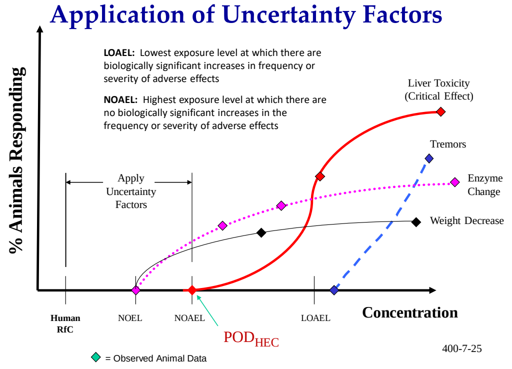
- EPA assumes that there is a *threshold* concentration - below which no observable adverse effect will occur.
- *Reference dose* (RfD)*or* ***Reference concentration*** **(RfC)** is an estimate of a daily exposure to the human population (including sensitive subgroups) that is likely to have *no risk* of the adverse effects during a lifetime.
- In IRIS, EPA includes with RfC a **statement of confidence**: High, Medium or Low
  - High: RfC are *less likely* to change w/ new info
  - Low: *most likely* to change with new info

---

## Dose-Response: Non-carcinogens

- The **first part** of this assessment parallels the same used for the carcinogenic assessment:
  - Calculate the ***"human equivalent concentration" (HEC)*** (adjusted from animal studies to humans).
  - Calculate the non-carcinogenic, ***Point of Departure*** (POD$_{HEC}$) from the NOAEL$_{HEC}$ or LOAEL$_{HEC}$ or (benchmark concentration level) BMCL
    - BMC approach involves fitting mathematical model for dose-response data to reported data (can be used for carcinogens also)
- The **second part** analyzes a series of ***uncertainty factors*** to estimate a "safe" or "reference" exposure for humans (the **Reference Concentration RfC**).

## Calculation of RfC from the NOAEL & Application of Uncertainty Factors



**LOAEL:** Lowest exposure level at which there are biologically significant increases in frequency or severity of adverse effects

**NOAEL:** Highest exposure level at which there are no biologically significant increases in the frequency or severity of adverse effects

◆ = Observed Animal Data

## Dose-Response Terminology

**Characterize Dose-Response Relationship**

Identify a **NOAEL** or **LOAEL**

Conduct dose-response modeling and **BMD (BMC) Modeling.**

**LOAEL**
Lowest-Observed-Adverse-Effect Level. Lowest dose at which significant effects are observed.

**NOAEL**
No-Observed-Adverse-Effect Level. Highest dose at which no significant adverse effects are observed.

**$LED_{10}$**
Dose that produces an adverse effect in 10% of exposed, relative to control.

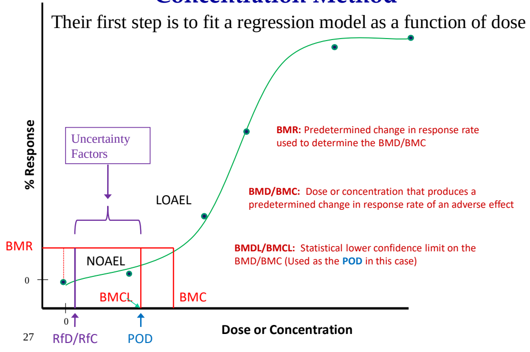
**BMD or BMC**
Benchmark Dose (or concentration). An exposure to a low dose of a substance that is linked with a low (1-10%) risk of adverse health effects, or the dose for a specific biological effect.

**BMDL or BMCL**
A lower, one-sided confidence limit on the BMD (BMC).

**THRESHOLD**
A dose below which there are no adverse effects.

## Calculation of the RfC from the Benchmark Concentration Method

Their first step is to fit a regression model as a function of dose



**BMR:** Predetermined change in response rate used to determine the BMD/BMC

**BMD/BMC:** Dose or concentration that produces a predetermined change in response rate of an adverse effect

**BMDL/BMCL:** Statistical lower confidence limit on the BMD/BMC (Used as the **POD** in this case)

## Reference Dose/Reference Concentration

$$\text{RfD or RfC} = \frac{(\text{Point of Departure})_{HEC}\ \ \textbf{NOAEL, LOAEL, or BMCL}}{\mathbf{UF_1 \times UF_2 \ldots \times UF_i \times MF}}$$

| <u>Uncertainty Factor Criteria</u> | <u>UF</u> |
|---|---|
| • **Extrapolating animal data to human** | **10, 3, or 1** |
| • **Sensitive human populations** | **10, 3, or 1** |
| • **Subchronic NOAEL instead of chronic NOAEL** | **10, 3, or 1** |
| • **LOAEL used instead of NOAEL** | **10, 3, or 1** |
| • **Uncertainties in the database for the chemical** | **10, 3, or 1** |

***The UFs are generally an order of (10), although it can be reduced to (3or 1) when considering dosimetry adjustments or other info.**

*** Older RfCs may have applied a <u>modifying factor</u> (MF) in addition to the traditional UFs (when it was felt another UF was needed).**

## Uncertainty Factors

- $UF_A$ – **Animal-to-human extrapolation**
  - When results of studies of <u>human exposure are not available</u> or are inadequate
- $UF_H$ – **Human variability**
  - Accounts for variations in susceptibility within humans (i.e. those <u>*most sensitive* to the health hazards</u> of the chemical)
- $UF_S$ – **Subchronic-to-chronic extrapolation**
  - <u>Extrapolation from less than chronic exposure</u> results on laboratory animals or humans <u>*when there are no useful long-term human data.*</u>
- $UF_L$ – **LOAEL-to-NOAEL extrapolation**
  - Derivation from a LOAEL instead of a NOAEL
- $UF_D$ – **Database deficiencies**
  - (i.e. animal study database is incomplete)

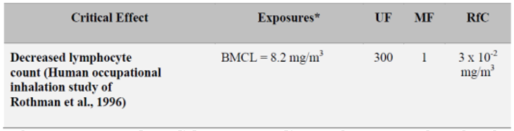
## Example RfC Calculation

| **RfC from NOAEL**<br>**Example: Diesel Engine Emissions** | **RfC from LOAEL**<br>**Example: Toluene** |
|---|---|
| *Toxicity data:*<br>144 µg chemical/$m^3$ air ($NOAEL_{HEC}$ from chronic rodent study) | *Toxicity data:*<br>119 mg chemical/$m^3$ air ($LOAEL_{HEC}$ from chronic occupational study) |
| *Uncertainty factors*: 3 x 10 = 30 | *Uncertainty factors*: 10 x 10 x 3 = 300 |
| 3 = animal-to-human extrapolation<br>10 = human to sensitive human subpopulations | 10 = human to sensitive human subpopulations<br>10 = LOAEL-to-NOAEL extrapolation<br>3 = database deficiencies |
| RfC = 144/30 = 4.8 µg/$m^3$ = 0.005 mg/$m^3$ | RfC = 119/300 mg/$m^3$ = 0.4 mg/$m^3$ |

$NOAEL_{HEC}$ = No-Observed-Adverse-Effect Level (Human Equivalent Concentration)
$LOAEL_{HEC}$ = Lowest-Observed-Adverse-Effect Level (Human Equivalent Concentration)

*Source*: EPA's IRIS database http://www.epa.gov/IRIS/. https://www.epa.gov/iris

## Benzene: Inhalation RfC (IRIS)



| Critical Effect | Exposures* | UF | MF | RfC |
|---|---|---|---|---|
| **Decreased lymphocyte count (Human occupational inhalation study of Rothman et al., 1996)** | BMCL = 8.2 mg/m$^3$ | 300 | 1 | 3 x 10$^{-2}$ mg/m$^3$ |

- The **statement of confidence** is **medium.** The principal study of Rothman (1996) used human data & not experimental animal data.
- **Uncertainty Factor** = 300 for the BMCL from the Rothman(1996).
  - First, an effect level extrapolation factor analogous to the LOAEL-to-NOAEL UF (3 will be used).
  - Second, a factor of 10 was used for intraspecies differences for protecting potentially sensitive humans.
  - Third, a UF of 3 for subchronic-to-chronic extrapolation was applied.
  - Finally, a UF of 3 was chosen to account for database deficiencies, because no reproductive & developmental toxicity studies for benzene are available.
  - Therefore, UF of 3 x 10 x 3 x 3 = 270 is rounded off to 300.

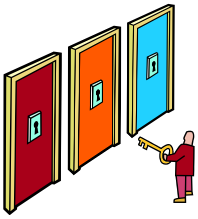
## Benzene: Cancer Risk (IRIS)

- **Inhalation Unit Risk:** 2.2 x 10$^{-6}$ per µg/m$^3$ to 7.8 x 10$^{-6}$ per µg/m$^3$
  - Different interpretations of human exposure information caused the range in IUR.
- **Weight of Evidence**: classified as a "known" human carcinogen (Category A) under the 1986 Guidelines based upon convincing human evidence as well as supporting evidence from animal studies.
  **Tumor type(s):** Leukemia (Rinsky et al., 1981, 1987 Paustenbach et al., 1993 Crump and Allen, 1984 Crump, 1992, 1994 U.S. EPA, 1998)

## Sources of Toxicity Data

**There are many choices**

- **EPA IRIS database**
- **California Hotspots program**
- **ATSDR MRLs**
- **NCEA provisional values**
- **EPA HEAST**
- **Open literature**
- **Etc.**



**Integrated Risk Information System (IRIS)**
http://www.epa.gov/iris/

**California Air- Hot Spots Guidelines**
http://www.oehha.ca.gov/air/hot_spots/index.html

**ATSDR MRL's**
http://www.atsdr.cdc.gov/mrls/index.html

## EPA's IRIS Web Page

EPA's mission is to protect human health and the environment. EPA's IRIS Program supports this mission by identifying and characterizing the health hazards of chemicals found in the environment. Each IRIS assessment can cover a chemical, a group of related chemicals, or a complex mixture.

Basic Information
- Learn About IRIS
- Guidance & Tools
- IRIS Process
- History of IRIS

IRIS Assessments
- Browse A to Z List of Chemicals
- Browse by Organ/System
- Assessments in Development

Search IRIS
By Chemical, CASRN, or Keyword
Search the IRIS database of final assessm
Search

Program Materials
- Developments in the IRIS Program
- IRIS Program Outlook
- IRIS Agenda
- IRIS Dockets
- Other Program Materials

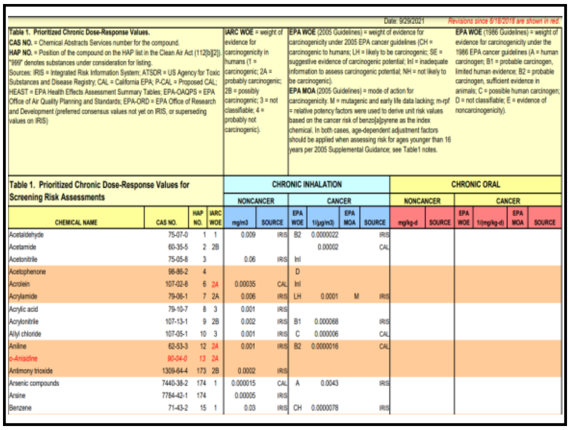
Recent Additions
- 12/19: IRIS Program Outlook Document
- 12/10-11: NAS Workshop on Strategies and Tools
- 8/30: IRIS Toxicological Review of RDX (Final Report)
- 7/05: IRIS Assessment Plan for Naphthalene

IRIS Calendar
- Public meetings & workshops - list view
- Public meetings & workshops - month view
- Stakeholder requested meetings - list view

Related Resources

## EPA's List of IURs & RfCs

- The following EPA web page has access to Table #1 (chronic) "*Dose-Response Assessment Table*" which gives a **complete list of IUR & RfC** for HAPs from IRIS or other sources &
- Table #2 *Acute Dose-Response Values for Screening Risk Assessments*
  - https://www.epa.gov/fera/dose-response-assessment-assessing-health-risks-associated-exposure-hazardous-air-pollutants



Date: 9/29/2021 *Revisions since 6/18/2018 are shown in red.*

**Table 1. Prioritized Chronic Dose-Response Values.**
**CAS NO.** = Chemical Abstracts Services number for the compound.
**HAP NO.** = Position of the compound on the HAP list in the Clean Air Act (112[b][2]). "999" denotes substances under consideration for listing.
Sources: IRIS = Integrated Risk Information System; ATSDR = US Agency for Toxic Substances and Disease Registry; CAL = California EPA; P-CAL = Proposed CAL; HEAST = EPA Health Effects Assessment Summary Tables; EPA-OAQPS = EPA Office of Air Quality Planning and Standards; EPA-ORD = EPA Office of Research and Development (preferred consensus values not yet on IRIS, or superseding values on IRIS)

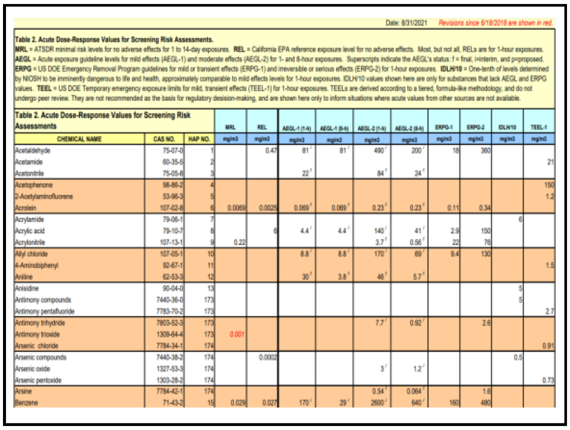
**IARC WOE** = weight of evidence for carcinogenicity in humans (1 = carcinogenic; 2A = probably carcinogenic; 2B = possibly carcinogenic; 3 = not classifiable; 4 = probably not carcinogenic).

**EPA WOE** (2005 Guidelines) = weight of evidence for carcinogenicity under 2005 EPA cancer guidelines (CH = carcinogenic to humans; LH = likely to be carcinogenic; SE = suggestive evidence of carcinogenic potential; InI = inadequate information to assess carcinogenic potential; NH = not likely to be carcinogenic).
**EPA MOA** (2005 Guidelines) = mode of action for carcinogenicity. M = mutagenic and early life data lacking; m-rpf = relative potency factors were used to derive unit risk values based on the cancer risk of benzo[a]pyrene as the index chemical. In both cases, age-dependent adjustment factors should be applied when assessing risk for ages younger than 16 years per 2005 Supplemental Guidance; see Table1 notes.

**EPA WOE** (1986 Guidelines) = weight of evidence for carcinogenicity under the 1986 EPA cancer guidelines (A = human carcinogen; B1 = probable carcinogen, limited human evidence; B2 = probable carcinogen, sufficient evidence in animals; C = possible human carcinogen; D = not classifiable; E = evidence of noncarcinogenicity).

**Table 1. Prioritized Chronic Dose-Response Values for Screening Risk Assessments**

| | | | | CHRONIC INHALATION | | | | | | CHRONIC ORAL | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | NONCANCER | | CANCER | | | | NONCANCER | | CANCER | | | |
| CHEMICAL NAME | CAS NO. | HAP NO. | IARC WOE | mg/m3 | SOURCE | EPA WOE | 1/(µg/m3) | EPA MOA | SOURCE | mg/kg-d | SOURCE | EPA WOE | 1/(mg/kg-d) | EPA MOA | SOURCE |
| Acetaldehyde | 75-07-0 | 1 | 1 | 0.009 | IRIS | B2 | 0.0000022 | | IRIS | | | | | | |
| Acetamide | 60-35-5 | 2 | 2B | | | | 0.00002 | | CAL | | | | | | |
| Acetonitrile | 75-05-8 | 3 | | 0.06 | IRIS | InI | | | | | | | | | |
| Acetophenone | 98-86-2 | 4 | | | | D | | | | | | | | | |
| Acrolein | 107-02-8 | 6 | 2A | 0.00035 | CAL | InI | | | | | | | | | |
| Acrylamide | 79-06-1 | 7 | 2A | 0.006 | IRIS | LH | 0.0001 | M | IRIS | | | | | | |
| Acrylic acid | 79-10-7 | 8 | 3 | 0.001 | IRIS | | | | | | | | | | |
| Acrylonitrile | 107-13-1 | 9 | 2B | 0.002 | IRIS | B1 | 0.000068 | | IRIS | | | | | | |
| Allyl chloride | 107-05-1 | 10 | 3 | 0.001 | IRIS | C | 0.000006 | | CAL | | | | | | |
| Aniline | 62-53-3 | 12 | 2A | 0.001 | IRIS | B2 | 0.0000016 | | CAL | | | | | | |
| o-Anisidine | 90-04-0 | 13 | 2A | | | | | | | | | | | | |
| Antimony trioxide | 1309-64-4 | 173 | 2B | 0.0002 | IRIS | | | | | | | | | | |
| Arsenic compounds | 7440-38-2 | 174 | 1 | 0.000015 | CAL | A | 0.0043 | | IRIS | | | | | | |
| Arsine | 7784-42-1 | 174 | | 0.00005 | IRIS | | | | | | | | | | |
| Benzene | 71-43-2 | 15 | 1 | 0.03 | IRIS | CH | 0.0000078 | | IRIS | | | | | | |



Date: 8/31/2021 *Revisions since 6/18/2018 are shown in red.*

**Table 2. Acute Dose-Response Values for Screening Risk Assessments.**
**MRL** = ATSDR minimal risk levels for no adverse effects for 1 to 14-day exposures. **REL** = California EPA reference exposure level for no adverse effects. Most, but not all, RELs are for 1-hour exposures.
**AEGL** = Acute exposure guideline levels for mild effects (AEGL-1) and moderate effects (AEGL-2) for 1- and 8-hour exposures. Superscripts indicate the AEGL's status: f = final, i=interim, and p=proposed.
**ERPG** = US DOE Emergency Removal Program guidelines for mild or transient effects (ERPG-1) and irreversible or serious effects (ERPG-2) for 1-hour exposures. **IDLH/10** = One-tenth of levels determined by NIOSH to be imminently dangerous to life and health, approximately comparable to mild effects levels for 1-hour exposures. IDLH/10 values shown here are only for substances that lack AEGL and ERPG values. **TEEL** = US DOE Temporary emergency exposure limits for mild, transient effects (TEEL-1) for 1-hour exposures. TEELs are derived according to a tiered, formula-like methodology, and do not undergo peer review. They are not recommended as the basis for regulatory desision-making, and are shown here only to inform situations where acute values from other sources are not available.

**Table 2. Acute Dose-Response Values for Screening Risk Assessments**

| | | | MRL | REL | AEGL-1 (1-h) | AEGL-1 (8-h) | AEGL-2 (1-h) | AEGL-2 (8-h) | ERPG-1 | ERPG-2 | IDLH/10 | TEEL-1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CHEMICAL NAME | CAS NO. | HAP NO. | mg/m3 | mg/m3 | mg/m3 | mg/m3 | mg/m3 | mg/m3 | mg/m3 | mg/m3 | mg/m3 | mg/m3 |
| Acetaldehyde | 75-07-0 | 1 | | 0.47 | 81$^f$ | 81$^f$ | 490$^f$ | 200$^f$ | 18 | 360 | | |
| Acetamide | 60-35-5 | 2 | | | | | | | | | | 21 |
| Acetonitrile | 75-05-8 | 3 | | | 22$^f$ | | 84$^f$ | 24$^f$ | | | | |
| Acetophenone | 98-86-2 | 4 | | | | | | | | | | 150 |
| 2-Acetylaminofluorene | 53-96-3 | 5 | | | | | | | | | | 1.2 |
| Acrolein | 107-02-8 | 6 | 0.0069 | 0.0025 | 0.069$^f$ | 0.069$^f$ | 0.23$^f$ | 0.23$^f$ | 0.11 | 0.34 | | |
| Acrylamide | 79-06-1 | 7 | | | | | | | | | 6 | |
| Acrylic acid | 79-10-7 | 8 | | 6 | 4.4$^f$ | 4.4$^f$ | 140$^f$ | 41$^f$ | 2.9 | 150 | | |
| Acrylonitrile | 107-13-1 | 9 | 0.22 | | | | 3.7$^f$ | 0.56$^f$ | 22 | 76 | | |
| Allyl chloride | 107-05-1 | 10 | | | 8.8$^f$ | 8.8$^f$ | 170$^f$ | 69$^f$ | 9.4 | 130 | | |
| 4-Aminobiphenyl | 92-67-1 | 11 | | | | | | | | | | 1.5 |
| Aniline | 62-53-3 | 12 | | | 30$^f$ | 3.8$^f$ | 46$^f$ | 5.7$^f$ | | | | |
| Anisidine | 90-04-0 | 13 | | | | | | | | | 5 | |
| Antimony compounds | 7440-36-0 | 173 | | | | | | | | | 5 | |
| Antimony pentafluoride | 7783-70-2 | 173 | | | | | | | | | | 2.7 |
| Antimony trihydride | 7803-52-3 | 173 | | | | | 7.7$^f$ | 0.92$^f$ | | 2.6 | | |
| Antimony trioxide | 1309-64-4 | 173 | 0.001 | | | | | | | | | |
| Arsenic chloride | 7784-34-1 | 174 | | | | | | | | | | 0.91 |
| Arsenic compounds | 7440-38-2 | 174 | | 0.0002 | | | | | | | 0.5 | |
| Arsenic oxide | 1327-53-3 | 174 | | | | | 3$^f$ | 1.2$^f$ | | | | |
| Arsenic pentoxide | 1303-28-2 | 174 | | | | | | | | | | 0.73 |
| Arsine | 7784-42-1 | 174 | | | | | 0.54$^f$ | 0.064$^f$ | | 1.6 | | |
| Benzene | 71-43-2 | 15 | 0.029 | 0.027 | 170$^f$ | 29$^f$ | 2600$^f$ | 640$^f$ | 160 | 480 | | |

## EPA: Risk Assessment Web Page

https://www.epa.gov/risk

**What is Risk?** EPA uses risk assessment to characterize the nature and magnitude of health risks to humans and ecological receptors from chemical contaminants and other stressors that may be present in the environment. Learn more about risk under the links below:

### Learn about Risk Assessment

- What is Risk?
- History of Risk Assessment at EPA
- Getting Help with Risk Assessment Issues
- Risk Management
- Risk Messaging
- Where You Live

### Human Health Risk Assessments

- Basic Information
- Conducting a Human Health Risk Assessment
- Human Health Risk Assessment Guidance
- Human Health Risk Assessment Tools and Databases
- Human Health Risk Assessment Products and Publications

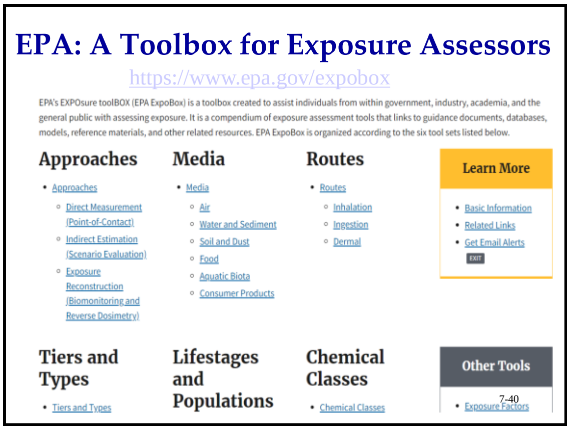
### Ecological Risk Assessments

- Basic Information
- Conducting an Ecological Risk Assessment
- Ecological Risk Assessment Guidance
- Ecological Risk Assessment Tools and Databases
- Ecological Risk Assessment Products and Publications

### Staying Connected

Explore EPA's on-going RISK activities in our recent additions section.

Subscribe to the RISK Bulletin to get the latest updates.



## EPA: A Toolbox for Exposure Assessors

https://www.epa.gov/expobox

EPA's EXPOsure toolBOX (EPA ExpoBox) is a toolbox created to assist individuals from within government, industry, academia, and the general public with assessing exposure. It is a compendium of exposure assessment tools that links to guidance documents, databases, models, reference materials, and other related resources. EPA ExpoBox is organized according to the six tool sets listed below.

### Approaches

- Approaches
  - Direct Measurement (Point-of-Contact)
  - Indirect Estimation (Scenario Evaluation)
  - Exposure Reconstruction (Biomonitoring and Reverse Dosimetry)

### Media

- Media
  - Air
  - Water and Sediment
  - Soil and Dust
  - Food
  - Aquatic Biota
  - Consumer Products

### Routes

- Routes
  - Inhalation
  - Ingestion
  - Dermal

### Learn More

- Basic Information
- Related Links
- Get Email Alerts EXIT

### Tiers and Types

- Tiers and Types

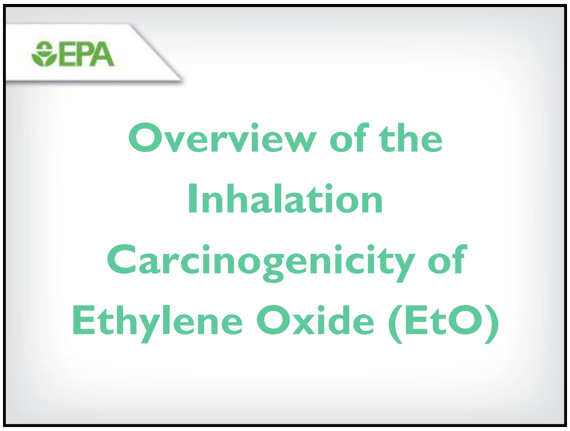
### Lifestages and Populations

### Chemical Classes

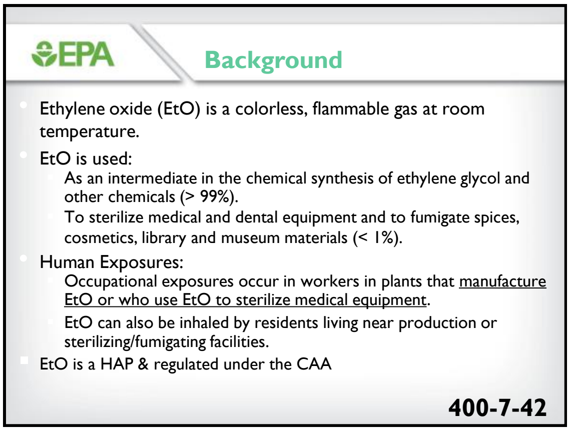
- Chemical Classes

### Other Tools

- Exposure Factors



## Overview of the Inhalation Carcinogenicity of Ethylene Oxide (EtO)



## Background

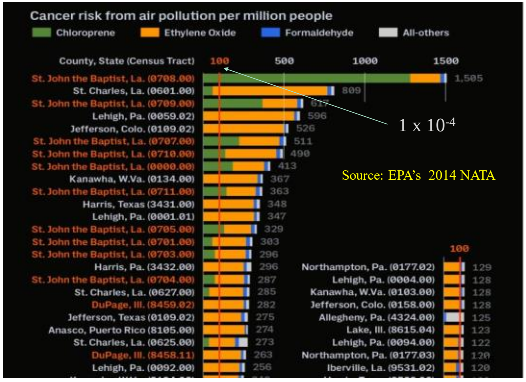
- Ethylene oxide (EtO) is a colorless, flammable gas at room temperature.
- EtO is used:
  - As an intermediate in the chemical synthesis of ethylene glycol and other chemicals (> 99%).
  - To sterilize medical and dental equipment and to fumigate spices, cosmetics, library and museum materials (< 1%).
- Human Exposures:
  - Occupational exposures occur in workers in plants that manufacture EtO or who use EtO to sterilize medical equipment.
  - EtO can also be inhaled by residents living near production or sterilizing/fumigating facilities.
- EtO is a HAP & regulated under the CAA

# Ethylene Oxide

- In 2016, EPA reassessed the **Inhalation Unit Cancer (IUR) for ethylene oxide as 5.0 x $10^{-3}$ per µg/$m^3$**, which is 50 times higher (more potent) than the IUR in EPA's 1985 assessment.
  - Also, changed the chemical's status from a "probable human carcinogen" to "**carcinogenic to humans**."
  - Based on human and animal studies, the IUR estimate for EtO combined unit risk estimates for lymphoid cancer & breast cancer to develop a total cancer unit risk estimate.
- EPA has not established a Reference Concentration (RfC) for ethylene oxide.

Protesters in front of the Oak Brook Ill. headquarters of Sterigenics on Sept. 14, 2018

## Environmental Justice



1 x $10^{-4}$

Source: EPA's 2014 NATA

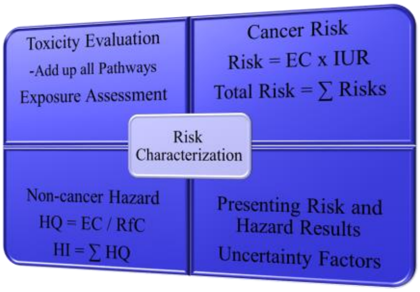
# Environmental Justice

- While the EPA was tending to the furor in Willowbrook, the agency *was not paying attention to other communities* facing dangerous threats from toxic airborne chemicals. St. John the Baptist, a small African-American community on the Mississippi River in Louisiana, may provide the best evidence that *not all air pollution crises are treated equally.*
  - Ninety percent of residents in that tract are African-American, with a per capita income of just over $17,000 a year — whereas the per capita income in Willowbrook is $71,266.
  - The St. John's cancer risk from air pollution is 1,505 per million — the very highest in the U.S. That's more than five times the highest risk faced in DuPage,Illinois.
- Although in Willowbrook the EPA has worked alongside local and state officials to address the dangerous levels of ethylene oxide, the agency has done little or nothing in St. John, where people continue to breathe in the highest levels of carcinogens in the country.

Source: *The Intercept*, Feb 2019

# Chapter Eight

## *Risk Characterization of Air Toxics*



*By: Louis DeRose*

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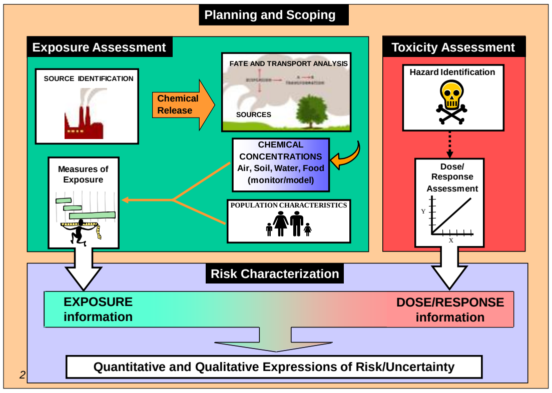
## The Detailed Air Toxics Risk Assessment Process



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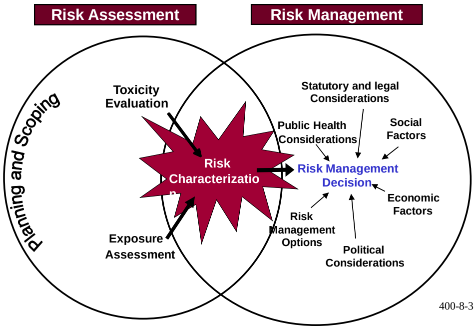
## Risk Characterization and Risk Management



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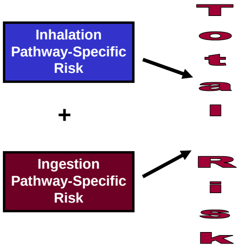
## Risk Characterization

**Combine outputs from *toxicity* & *exposure assessments***

- Quantify risks from <u>individual chemicals</u> for *each pathway separately* (e.g., inhalation, ingestion), then…
- Combine risks from <u>multiple chemicals</u> for each pathway, then…
- Combine risks from <u>all pathways</u> to give *total risk*, then…
- Repeat the process for <u>all non-cancer hazards</u>
- Assess and present <u>uncertainty</u>



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## Risk Characterization

- **Cancer risks are presented <u>separately</u> from non-cancer hazards**.
  - 1st Calculate & present <u>cancer risks</u>
  - 2nd Calculate & present <u>non-cancer hazards</u>
  - 3rd Assess & present <u>uncertainties & assumptions</u>
- **Some chemicals show up in both sets of analyses** because some chemicals can **<u>cause both cancer & non-cancer effects</u>**.
- Air toxic risk characterization <u>focuses on inhalation pathway</u> only.
  - Other pathways will be considered for persistent, bio-accumulative HAPs (i.e. mercury, dioxin).

---

## Risk Characterization: Outcome

•**Cancer Risk:** Incremental probability of developing cancer for an individual exposed to a given chemical over a lifetime.

•**Non-cancer Hazard Quotient (HQ):** *Ratio of estimated exposure to reference level* at which no adverse health effects are expected.

•**Non-cancer Hazard Index (HI):** The *sum of hazard quotients (HQs)* for substances that affect the same target organ or organ system.

## What is Exposure?

- **Exposure** is contact made between a chemical, physical, or biological agent and the outer boundary of an organism.
- **Exposure is measured** (quantified), as the amount of an agent available at the exchange boundaries of the organism (for example, the skin, lungs, or gut). Source: U.S. EPA (1992b)

## Quantify Exposure

**Scenario Evaluation**
**(Predictive Estimate)**

- Measure or estimate the amount of substance contacted at site
- Use equations and assumptions about behavior and exposure rates
- **Mathematical estimation of exposure; predictive estimate**

The final step in an exposure assessment is to estimate the amounts each person inhales. To do this, scientists combine estimates of lifespan of an average person with estimates of the amount of pollutant in that person's air.

## Exposure Assessment Equation for the Inhalation Pathway

$$\mathbf{ADD = C_{air} \times IR \times ET \times EF \times ED/BW \times AT}$$

**ADD** = Average daily dose (mass of contaminant per unit body weight over time e.g., **mg/kg-day**)
**$C_{air}$** = Concentration of contaminant in air (mg/m$^3$)
**IR** = Inhalation rate (m$^3$/hour)
**ET** = Exposure time (hours/day)
**EF** = Exposure frequency (days/year)
**ED** = Exposure duration (years)
**BW** = Body weight (kg)
**AT** = Averaging time (days) usually 70 years (lifetime) for carcinogens & 1 year for non-carcinogens.

## Exposure Assessment Concentration (EC) Equation for Use with IRIS (Inhalation)

- The EPA's **IRIS methodology accounts for inhalation rates (IR) & body weight (BW)** in the development of its Inhalation Unit Risk (IUR) dose-response slope.
  - EPA uses average adult values: IR = 20 m3/day; BW = 70 kg
  - **EC**(μg/m$^3$) = **ADD**(μg/kg-day) x **BW**(kg)/**IR**(m$^3$/day)

***Inhalation exposure concentration (EC):***

$$\text{Exposure Concentration}\left(\frac{\mu g}{m^3}\right) = \frac{\text{Concentration}\left(\frac{\mu g}{m^3}\right) \times \text{Exposure Time}\left(\frac{hours}{day}\right) \times \text{Exposure Frequency}\left(\frac{days}{year}\right) \times \text{Exposure Duration}\,(years) \times \text{Conversion Factor}\left(\frac{year}{8{,}760\ hr}\right)}{\text{Averaging Time}\,(years)}$$

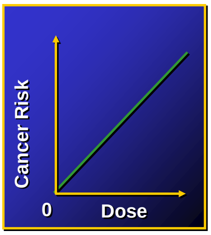
## Inhalation Unit Risk

The basic equation for calculating risk from breathing a carcinogenic air toxic is:

**Risk = EC x IUR**

EC = Long term (lifetime of 70 yrs.) inhalation *exposure concentration* for a specific HAP (ug/m$^3$)

IUR = Inhalation Unit Risk (risk/ug/m$^3$)



## Example: Inhalation Cancer Risk

**Chemical A:** Exposure Concentration = 1 μg/m$^3$
IUR = 2 x $10^{-3}$ per μg/m$^3$
Class C Possible carcinogen

RISK = (1 ug/m$^3$) x (2x$10^{-3}$/ug/m$^3$) = 0.002

**Chemical B:** Exposure Concentration = 5 μg/m$^3$
IUR = 2 x $10^{-5}$ per μg/m$^3$
Class A Known Human Carcinogen

RISK = (5 ug/m$^3$) x (2x$10^{-5}$/ug/m$^3$) = 0.0001

## Cancer Risk for Multiple Pollutants

- For multiple carcinogens: sum all the individual cancer risks for each carcinogens present in the air:

$$\mathbf{Risk_{total} = Risk_1 + Risk_2 + Risk_i}$$

- Unless there is contrary evidence, assume an additive effect from simultaneous exposures.
  - No synergistic (greater than additive) or antagonistic (lesser than additive) effects

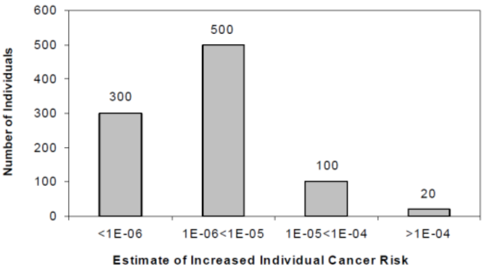
## Example Calculation to Estimate Cancer Risk

| HAP | EC<br>ug/m3 | IUR<br>1/(ug/m3) | Cancer Risk | % of $Risk_T$ |
|---|---|---|---|---|
| Benzene | 0.3 | $7.8 \times 10^{-6}$ | $.02 \times 10^{-4}$ | < 1% |
| Dichloroethyl ether | 2.5 | $3.3 \times 10^{-4}$ | $8 \times 10^{-4}$ | 88% |
| Formaldehyde | 0.2 | $1.3 \times 10^{-4}$ | $.02 \times 10^{-4}$ | < 1% |
| Cadmium compounds | 0.1 | $1.8 \times 10^{-3}$ | $1.8 \times 10^{-4}$ | 11% |
| **Total Risk ($R_T$)** | | | $9.84 \times 10^{-4}$ | |

## Estimates of Cancer Risk

- Individual lifetime risk is the cancer risk estimated to be experienced by an individual from a lifetime of exposure at a specified level.
  - Individual lifetime risk = EC x IUR
- Incidence is the # of expected cases of the disease expected over a lifetime (70 yrs.).
  - Population x total risk ($R_T$) = # of new cancer cases
- Population risk is the # of people at different risk and hazard levels.
  - Express population separately for each risk level

## Example: Population Risk

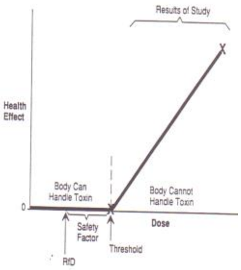


## Inhalation Non-Cancer Hazard

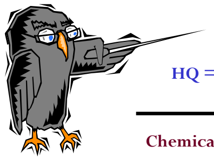
- For inhalation exposures, non-cancer hazards are estimated by:
- **HQ = (EC / RfC)**
  - HQ = "**hazard quotient**" for an individual air toxic
  - EC = exposed concentration of the air toxic
    - For chronic exposure use annual concentration
    - For acute exposure use hourly concentrations
  - RfC = reference concentration (EPA will designate a specific RfC for chronic & acute)
- **HQ ≤1** HAP no toxic effects are expected (safe);
- **HQ > 1** toxic effects may occur - must look at uncertainty factors & how high the HQ # is.

## Non-Cancer Hazard

- **The HQ is a simple comparison (not a risk) of a chemical's concentration in air to a level below which no adverse effect is likely to occur.**
- **Because RfC do not have equal accuracy (large differences in uncertainty factors):**
  - **A HQ of 100 does not mean that the hazard is 10 times > HQ of 10**
  - **Also, an HQ of 10 for one substance is not the same hazard as another substance w/ HQ of 10**



## Example: Inhalation Non-Cancer Hazard



**Chemical A:** Reduced kidney function
EC = 2 mg/m³
RfC = 1 mg/m³
UF = 30

HQ = (2 mg/m³) ÷ (1 mg/m³) = 2

---

**Chemical B:** Reduced liver function
EC = 8 mg/m³
RfC = 2 mg/m³
UF = 1000

HQ = (8 mg/m³) ÷ (2 mg/m³) = 4

## Non-Cancer Risk for Multiple Pollutants

- For multiple non-carcinogens: sum all the individual hazardous quotients for each non-carcinogen present in the air to obtain the “**hazardous index**” (HI)
- **HI = HQ$_1$ + HQ$_2$ + HQ$_i$**
  - Unless there is contrary evidence, assumes an additive effect from simultaneous exposures (no synergistic or antagonistic effects).
  - The HI for a mixture is mainly a **screening level study** because different toxins target different organs. (EPA 1989).

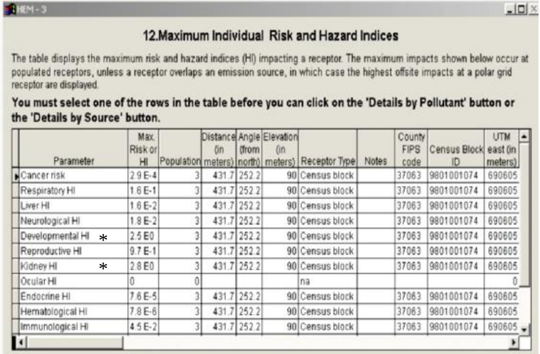
## TOSHI

- When the HI for the mixture exceeds 1.0, then the mixture should be subjected to a more technical estimation of HI, based on the Target Organ Toxicity Dose.
- In the Target Organ Toxicity Dose, identify all major effects & target organs & classify each chemical according to target organ: this produces a **“target-organ-specific-hazard-index” (TOSHI)** for each subgroup (EPA 1986).

## Example Calculation to Estimate Chronic Non-Cancer Hazard

| HAP | EC mg/m3 | RfC mg/m3 | HQ | Percent of HI |
|---|---|---|---|---|
| Benzene | 0.0006 | 0.06 | 0.01 | 1 |
| Dichloroethyl ether | 0.005 | --------- | --------- | |
| Formaldehyde | 0.0004 | 0.01 | 0.04 | 4 |
| Cadmium compounds | 0.00002 | 0.00002 | 1 | 95 |
| **Hazard Index** | | | 1.05 | |

## Presenting Results: HEM3 Video Example



12.Maximum Individual Risk and Hazard Indices

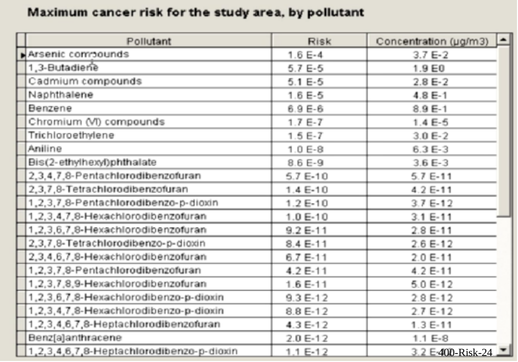
The table displays the maximum risk and hazard indices (HI) impacting a receptor. The maximum impacts shown below occur at populated receptors, unless a receptor overlaps an emission source, in which case the highest offsite impacts at a polar grid receptor are displayed.

**You must select one of the rows in the table before you can click on the 'Details by Pollutant' button or the 'Details by Source' button.**

| Parameter | Max. Risk or HI | Population | Distance (in meters) | Angle (from north) | Elevation (in meters) | Receptor Type | Notes | County FIPS code | Census Block ID | UTM east (in meters) |
|---|---|---|---|---|---|---|---|---|---|---|
| Cancer risk | 2.9 E-4 | 3 | 431.7 | 252.2 | 90 | Census block | | 37063 | 9801001074 | 690605 |
| Respiratory HI | 1.6 E-1 | 3 | 431.7 | 252.2 | 90 | Census block | | 37063 | 9801001074 | 690605 |
| Liver HI | 1.6 E-2 | 3 | 431.7 | 252.2 | 90 | Census block | | 37063 | 9801001074 | 690605 |
| Neurological HI | 1.8 E-2 | 3 | 431.7 | 252.2 | 90 | Census block | | 37063 | 9801001074 | 690605 |
| Developmental HI * | 2.5 E0 | 3 | 431.7 | 252.2 | 90 | Census block | | 37063 | 9801001074 | 690605 |
| Reproductive HI | 9.7 E-1 | 3 | 431.7 | 252.2 | 90 | Census block | | 37063 | 9801001074 | 690605 |
| Kidney HI * | 2.8 E0 | 3 | 431.7 | 252.2 | 90 | Census block | | 37063 | 9801001074 | 690605 |
| Ocular HI | 0 | 0 | | | | na | | | | 0 |
| Endocrine HI | 7.6 E-5 | 3 | 431.7 | 252.2 | 90 | Census block | | 37063 | 9801001074 | 690605 |
| Hematological HI | 7.8 E-6 | 3 | 431.7 | 252.2 | 90 | Census block | | 37063 | 9801001074 | 690605 |
| Immunological HI | 4.5 E-2 | 3 | 431.7 | 252.2 | 90 | Census block | | 37063 | 9801001074 | 690605 |

* Two maximum chronic noncancer TOSHIs that are ≥ 1.0

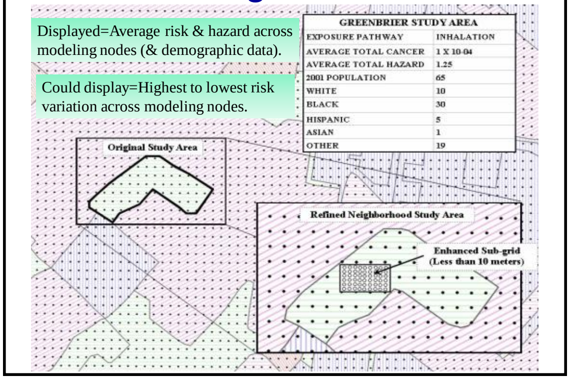
## Presenting Risk Results: HEM3 Video Example



Maximum cancer risk for the study area, by pollutant

| Pollutant | Risk | Concentration (µg/m3) |
|---|---|---|
| Arsenic compounds | 1.6 E-4 | 3.7 E-2 |
| 1,3-Butadiene | 5.7 E-5 | 1.9 E0 |
| Cadmium compounds | 5.1 E-5 | 2.8 E-2 |
| Naphthalene | 1.6 E-5 | 4.8 E-1 |
| Benzene | 6.9 E-6 | 8.9 E-1 |
| Chromium (VI) compounds | 1.7 E-7 | 1.4 E-5 |
| Trichloroethylene | 1.5 E-7 | 3.0 E-2 |
| Aniline | 1.0 E-8 | 6.3 E-3 |
| Bis(2-ethylhexyl)phthalate | 8.6 E-9 | 3.6 E-3 |
| 2,3,4,7,8-Pentachlorodibenzofuran | 5.7 E-10 | 5.7 E-11 |
| 2,3,7,8-Tetrachlorodibenzofuran | 1.4 E-10 | 4.2 E-11 |
| 1,2,3,7,8-Pentachlorodibenzo-p-dioxin | 1.2 E-10 | 3.7 E-12 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran | 1.0 E-10 | 3.1 E-11 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran | 9.2 E-11 | 2.8 E-11 |
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin | 8.4 E-11 | 2.6 E-12 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran | 6.7 E-11 | 2.0 E-11 |
| 1,2,3,7,8-Pentachlorodibenzofuran | 4.2 E-11 | 4.2 E-11 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran | 1.6 E-11 | 5.0 E-12 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin | 9.3 E-12 | 2.8 E-12 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin | 8.8 E-12 | 2.7 E-12 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran | 4.3 E-12 | 1.3 E-11 |
| Benz[a]anthracene | 2.0 E-12 | 1.1 E-8 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin | 1.1 E-12 | 3.2 E |

## Presenting Risk Results

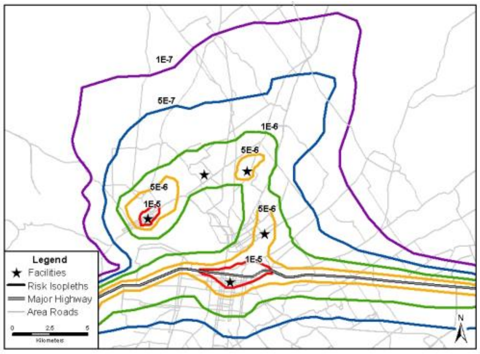


Displayed=Average risk & hazard across modeling nodes (& demographic data).

Could display=Highest to lowest risk variation across modeling nodes.

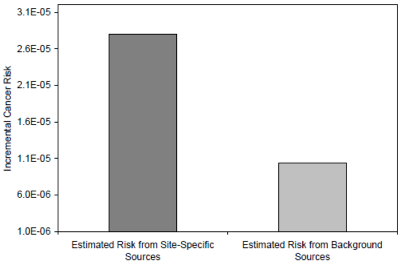
| GREENBRIER STUDY AREA | |
|---|---|
| EXPOSURE PATHWAY | INHALATION |
| AVERAGE TOTAL CANCER | 1 X 10-04 |
| AVERAGE TOTAL HAZARD | 1.25 |
| 2001 POPULATION | 65 |
| WHITE | 10 |
| BLACK | 30 |
| HISPANIC | 5 |
| ASIAN | 1 |
| OTHER | 19 |

## Presenting Risk Results



## Comparison of Risk Estimates from Site-Specific Sources to Background Sources

In this example, the estimated risk from the specific sources being evaluated in a modeling study and the estimated risk from *background sources* using *upwind* monitoring are compared side-by-side.



## Presenting Risk Results

*Source: California Air Resource Bd. "Health Risk Assessment for the BNSF Richmond Railyard" 2007*

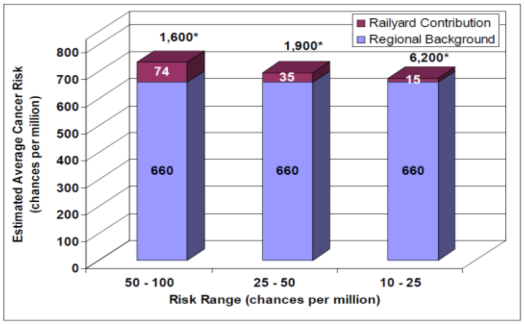
Estimated potential cancer risk (in a million) associated with on-site diesel PM emissions at the BNSF Richmond Railyard facility.

## Estimated Impacted Areas and Exposed Population for the Different Cancer Risk Levels at the BNSF Richmond Railyard.

| Estimated Risk (chances per million) | Estimated Impacted Area (acres)* | Estimated Exposed Population |
|---|---|---|
| 50 - 100 | 280 | 1,600 |
| 25 - 50 | 580 | 1,900 |
| 10 - 25 | 1,600 | 6,200 |

* inland area only.

**Background Concentration**: Comparison of estimated potential cancer risks associated with diesel PM emissions at the BNSF Richmond Railyard to the regional background cancer risk level. *(* Estimated exposed population within each cancer risk range)*



## Estimated Non-cancer Chronic Risks (indicated as Hazard Indices) Associated with Diesel PM Emissions from the BNSF Richmond Railyard.

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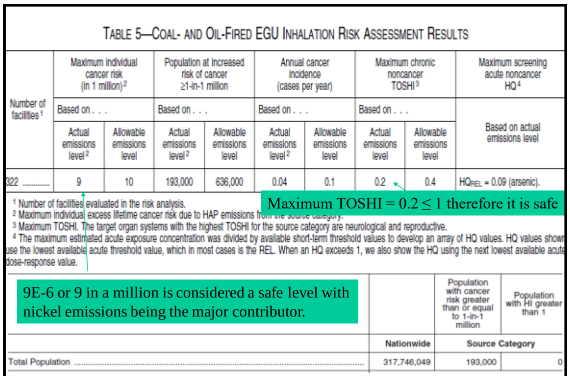


TABLE 5—COAL- AND OIL-FIRED EGU INHALATION RISK ASSESSMENT RESULTS

| Number of facilities[1] | Maximum individual cancer risk (in 1 million)[2] | | Population at increased risk of cancer ≥1-in-1 million | | Annual cancer incidence (cases per year) | | Maximum chronic noncancer TOSHI[3] | | Maximum screening acute noncancer HQ[4] |
|---|---|---|---|---|---|---|---|---|---|
| | Based on . . . | | Based on . . . | | Based on . . . | | Based on . . . | | Based on actual emissions level |
| | Actual emissions level[2] | Allowable emissions level | Actual emissions level[2] | Allowable emissions level | Actual emissions level[2] | Allowable emissions level | Actual emissions level | Allowable emissions level | |
| 322 | 9 | 10 | 193,000 | 636,000 | 0.04 | 0.1 | 0.2 | 0.4 | $HQ_{REL}$ = 0.09 (arsenic). |

[1] Number of facilities evaluated in the risk analysis.
[2] Maximum individual excess lifetime cancer risk due to HAP emissions from the source category.
[3] Maximum TOSHI. The target organ systems with the highest TOSHI for the source category are neurological and reproductive.
[4] The maximum estimated acute exposure concentration was divided by available short-term threshold values to develop an array of HQ values. HQ values shown use the lowest available acute threshold value, which in most cases is the REL. When an HQ exceeds 1, we also show the HQ using the next lowest available acute dose-response value.

| | | Population with cancer risk greater than or equal to 1-in-1 million | Population with HI greater than 1 |
|---|---|---|---|
| | Nationwide | Source Category | |
| Total Population | 317,746,049 | 193,000 | 0 |

Maximum TOSHI = 0.2 ≤ 1 therefore it is safe

9E-6 or 9 in a million is considered a safe level with nickel emissions being the major contributor.

On May 22, 2020 F.R., EPA finalizes the residual risk analysis indicating that risks are acceptable & that the current standards will be unchanged.

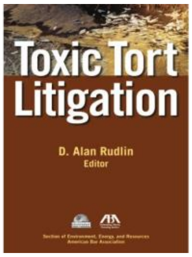
---

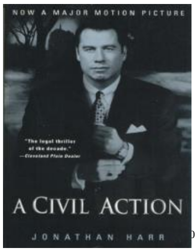
## Uncertainty Analysis

- In the final part of the risk characterization, the estimate of health risks & hazards are presented with their uncertainties & limitations in the data & methodology. Look at:
  - Exposure estimates & assumptions
  - Toxicity estimates & assumptions &
  - Any estimate of uncertainty
- Use EPA *Policy for Risk Characterization* (1995) & EPA *Guidance for Risk Characterization* (1995)

## Chapter Nine Toxic Torts: Risk Assessment in the Courtroom

*By: Lou DeRose*





## Toxic Torts

- <u>Toxic torts</u> involve some claim of harm, physical or psychological, *caused by exposure to a substance*.
- Common toxic tort <u>characteristics</u>:
  - *Large # of plaintiffs & defendants*
    - But serious injuries to a single plaintiff are not uncommon
  - *Difficult to identify the source* causing plaintiff's harm
    - Airborne toxins from one or many plants
    - Drinking water polluted from numerous contaminants (plaintiff cannot qualify the portion of harm produced by each source)
  - Use of *complex litigation procedures* (may bifurcate trial)
    - P may have to demonstrate evidence of exposure & causation first
  - Reliance on *scientific concepts* to resolve causation issues
    - Need for "experts" are common: epidemiology, hydrology & toxicology

## Plaintiff's Burden

- <u>Harm</u> suffered
  - Serious injury with unverifiable level of exposure
  - Known exposure, but injury hasn't manifested (long latency period)
    - The "<u>discovery rule</u>": tolls the statute of limitations until P discovers the injury & that the injury was caused by D.
- <u>Causal link</u> between exposure and harm
  - Did this exposure cause the harm?
  - Causation is the battle ground in toxic torts cases.
- <u>Liability</u> of defendant: did D create the exposure?
  - Are there more than one defendant? Who are they? What theory of liability: how are they liable?

## Causation Components:

- <u>Exposure & dose</u>:
  - Defendant is the source of the exposure.
  - Magnitude & duration of exposure
  - The actual *dose* received by plaintiff (liver and kidneys break down chemicals to less toxic form)
- <u>General causation</u>:
  - Is exposure to substance X capable of causing condition Y in a human?
- <u>Specific causation</u>:
  - Plaintiff must prove *how much* of the toxic chemical was plaintiff exposed to and for *how long*.

## Special Causation Challenges

- <u>Long latency period</u> from exposure to the manifestation of injury (disease or death years later).
- <u>Exposure is often problematic</u>
  - P's injury can be caused by *exposures to other chemicals* in which D is not liable.
- Little <u>hard data</u> linking toxic exposure to injury
  - *Animal studies* have only limited use for causation
    - Saccharine on rats: may keep it off market, but this "speculative" evidence will not win "preponderance of evidence"
  - *Epidemiological evidence (*human scientific studies) not simply dose-response animal studies or in vitro studies are needed to establish "general" causation

## Admissibility of Expert's Opinion

- <u>Old Rule</u>: Scientific evidence must be "generally accepted" in the scientific community (*Frye*,1923).
  - Expert opinions allowed with no scientific consensus by professional publications or expert's peers.
  - Juries making conclusions on unresolved scientific issues based on pioneered opinions.
- <u>New Rule</u> (*Daubert*,1993): Trial judge as "gatekeeper" must assess reliability of the expert's testimony to determine admissibility. Factors considered:
  - "Testability" (capable of repetition & verification)
  - Error rate of technique
  - Published after peer review
  - "Generally accepted" in scientific community

## Common Theories of Liability

- Negligence (D has a “duty” to conform to certain standard of conduct & D violates duty)
  - i.e. D had a duty to operate its facility free of releases
- Nuisance (“unreasonable interference” with the use & enjoyment of P’s land)
  - i.e. taste & odor of MTBE in water is actionable
- Trespass (“invasion” to P’s land)
  - D released fluoride particles in the air causing neighboring P’s cattle to die. Held: even though particles invisible, D liable (*Martin*, 1959)

---

## Common Theories of Liability

- Strict liability (D’s use of an “abnormally dangerous activity” caused P’s harm)
  - No “proof of fault” required
  - Louisiana Supreme Ct. (1957) imposed strict liability for property damage caused by aerial spraying of herbicides & the resulting drifting of these chemicals
  - California Supreme Ct. (1963) extended strict liability to a seller of a “defective product “for a product-related injury (now used in asbestos cases).

---

## Special Cases: Asbestos

- Asbestos exposure causes asbestosis, mesothelioma, lung cancer (w/ preexisting asbestosis)
  - Latency period: between exposure & asbestos-type disease can be 10 to 40 years - depending on exposure & sensitivity
  - In many “smoking lung cancer” cases where P did not have asbestosis, jury found cigarettes was cause - not asbestos
- Strict liability for a seller of a defective product
  - Until 1960s, workers compensation the principle remedy
    - Inadequate compensation & statute of limitations prohibitions
- Between 1940 & 1979, up to 27.5 million Americans worked in occupations where substantial asbestos exposures common (shipyards/construction/industry)

---

## Asbestos Litigation Crisis & Congress’s Failure to Act

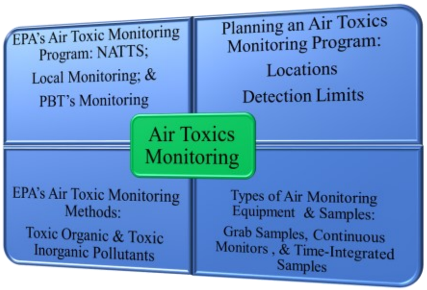
- > 600,000 people have filed asbestos lawsuits (2001)
- > 6,000 companies have been named Defendants (2001)
  - 60 have filed bankruptcy (Johns-Manville in 1982)
- Defendants & their insurers have paid approximately $54 billion to resolve claims (through 2000)
  - Claimants got $21 billion (most to non-functionally impaired)
  - 138,000 jobs not created as a result of defendant’s loss
- To date, Congress has failed to act
  - In 2005, Senator Spector sponsored a bill that would take claims out of court & create a $140 billion trust fund (lack of consensus over fundamental aspects of bill)

---

## Special Cases: Mold

- Two main types of cases:
  - Property damage & personal injury: nausea, fatigue, sore throat, asthma, & other respiratory difficulties
- Numerous liability theories
  - Breach of contract or breach of warranty (construction)
  - Negligence (duty to maintain a safe premise)
- Majority of molds are harmless (over 100,000 types)
  - P must show that the amount & location of mold resulted in exposure to cause P’s negative health effects
- Compared to Asbestos cases
  - Mold not scientifically linked to a clearly mold-caused disease & rarely causes death
  - Ds do not have deep pockets (usually owner or builders)
  - Today many insurance policies exclude mold claims

# Chapter Ten
## *Air Toxics Monitoring*



EPA's Air Toxic Monitoring Program: NATTS; Local Monitoring; & PBT's Monitoring

Planning an Air Toxics Monitoring Program: Locations Detection Limits

Air Toxics Monitoring

EPA's Air Toxic Monitoring Methods: Toxic Organic & Toxic Inorganic Pollutants

Types of Air Monitoring Equipment & Samples: Grab Samples, Continuous Monitors , & Time-Integrated Samples

## History of Ambient Air Toxics 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)

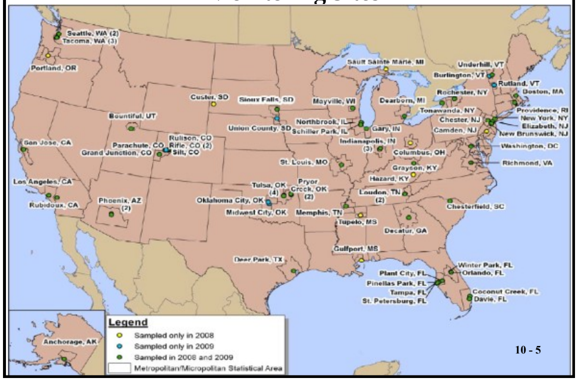
## History of Ambient Air Toxics Sampling (cont.)

- 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.

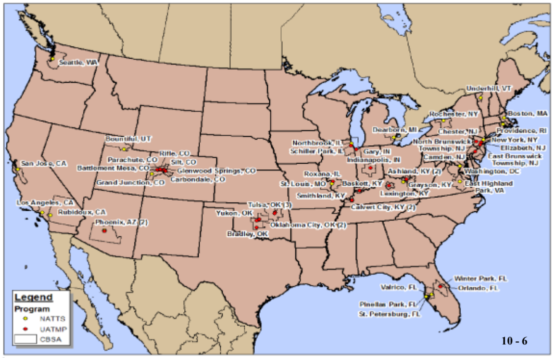
## EPA's Air Toxic Monitoring Program

- The CAA does not require a national air toxics monitoring network.
- The Urban Air Toxic Monitoring Program (UATMP) was initiated by EPA in 1987 to meet the increasing need for information on air toxics.
- Since 2000, EPA has increased its ambient air toxics monitoring efforts and funding to establish a national network and support state and local agencies' monitoring activities.
- In 2004 EPA began awarding grants to state and local agencies to conduct short-term, local-scale monitoring projects.

## Locations of the 2008-2009 National UATMP Monitoring Sites



## Locations of the 2015-2016 National Monitoring Programs Monitoring Sites[1]



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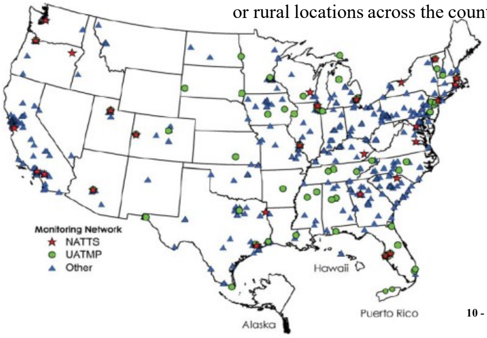
[1] Includes monitoring sites participating under the NMP with the national contract laboratory.

## EPA's 2004 "*National Air Toxic Monitoring Strategy*": 4 Groups

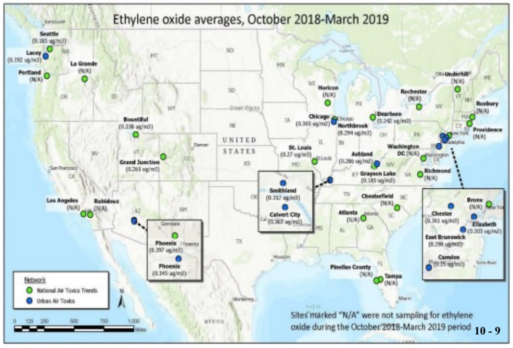
- National level
  - *National Air Toxics Trends System* (NATTS) was created to generate long-term ambient air toxics concentration data at specific fixed sites across the country.
- Local level: complement the NATTS by allowing for *flexible approaches* to address a wide range of air toxics issues. They are intended *to probe potential problem areas* that may require subsequent attention with respect to more dedicated monitoring.
- Persistent bio-accumulative toxics (PBTs): primarily consists of *deposition monitoring*, not ambient air monitoring.
- "Other" EPA-specific monitoring programs existing prior to this program.

## NATTS HAP's Monitoring Sites: 2014

The (NATTS) program is a network of monitoring stations at 30 urban or rural locations across the country.



## National Air Toxics and Urban Air Toxic Monitoring Sites


Ethylene oxide averages, October 2018-March 2019

Sites marked "N/A" were not sampling for ethylene oxide during the October 2018-March 2019 period

## Outdoor Air Quality Data Website

### Interactive Map of Air Quality Monitors

The AirData Air Quality Monitors app is a mapping application available on the web and on mobile devices that displays monitor locations and monitor-specific information. It also allows the querying and downloading of data daily and annual summary data.

Map layers include:

- Monitors for all criteria pollutants (CO, Pb, NO2, Ozone, PM10, PM2.5, and SO2)
- PM2.5 Chemical Speciation Network monitors
- IMPROVE (Interagency Monitoring of PROtected Visual Environments) monitors
- NATTS (National Air Toxics Trends Stations)
- NCORE (Multipollutant Monitoring Network)
- Nonattainment areas for all criteria pollutants
- Tribal areas
- Federal Class I areas (national parks and wilderness areas)

https://www.epa.gov/outdoor-air-quality-data/interactive-map-air-quality-monitors

## National Air Toxics Assessment

### 2014 NATA Map

The 2014 NATA Map application lets you display risks, emissions, and other NATA data on a map. You can quickly display these data by clicking on the map. The map app's search tool lets you "zoom" to places of interest anywhere in the country. You can also download all NATA data and results, and run queries to find just the information you want.

Map layers include:

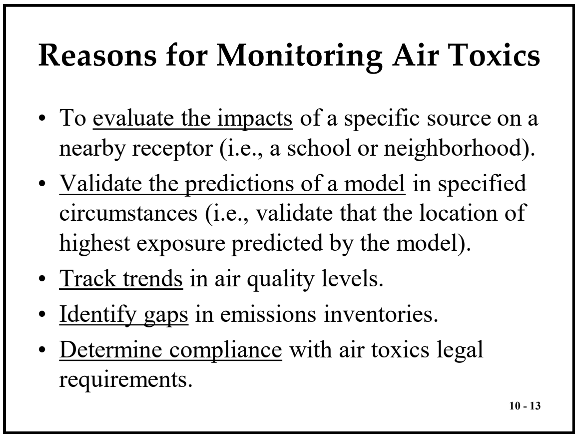
- cancer risks and respiratory hazard indexes;
- annual ambient concentrations;
- all emissions sources modeled in NATA; and
- air toxics monitoring sites with recent-year air toxics monitoring data.

https://www.epa.gov/national-air-toxics-assessment/2014-nata-map

## NATTS Monitored HAPs

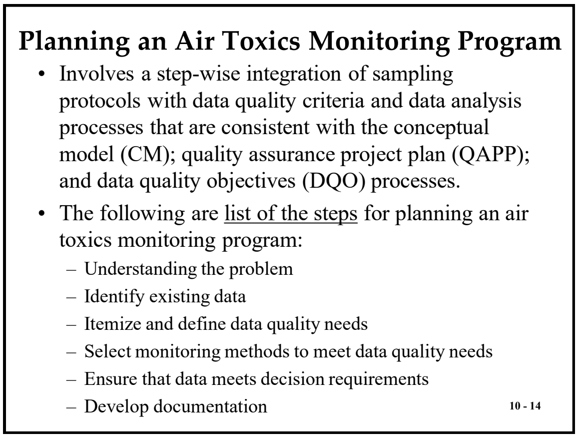
| VOCs | Metals | Aldehydes |
|---|---|---|
| 1,3-butadiene * | Arsenic * | Acrolein * |
| carbon tetrachloride | beryllium | Formaldehyde * |
| chloroform | cadmium | Acetaldehyde |
| 1,2-dichloropropene | hexavalent chromium * | |
| methylene chloride | chromium (and compounds) | |
| tetrachloroethylene | lead | |
| trichloroethylene | manganese | |
| vinyl chloride | nickel | |
| benzene * | | |

* Major risk driven HAPs



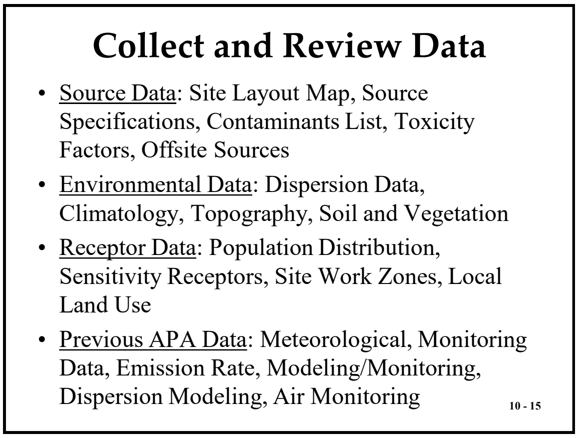
## Reasons for Monitoring Air Toxics

- To evaluate the impacts of a specific source on a nearby receptor (i.e., a school or neighborhood).
- Validate the predictions of a model in specified circumstances (i.e., validate that the location of highest exposure predicted by the model).
- Track trends in air quality levels.
- Identify gaps in emissions inventories.
- Determine compliance with air toxics legal requirements.



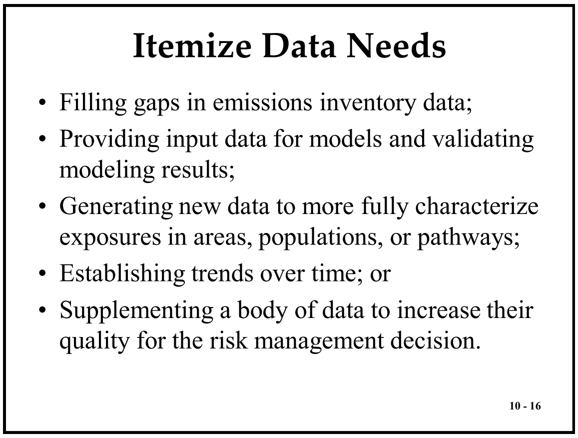
## Planning an Air Toxics Monitoring Program

- Involves a step-wise integration of sampling protocols with data quality criteria and data analysis processes that are consistent with the conceptual model (CM); quality assurance project plan (QAPP); and data quality objectives (DQO) processes.
- The following are list of the steps for planning an air toxics monitoring program:
  - Understanding the problem
  - Identify existing data
  - Itemize and define data quality needs
  - Select monitoring methods to meet data quality needs
  - Ensure that data meets decision requirements
  - Develop documentation



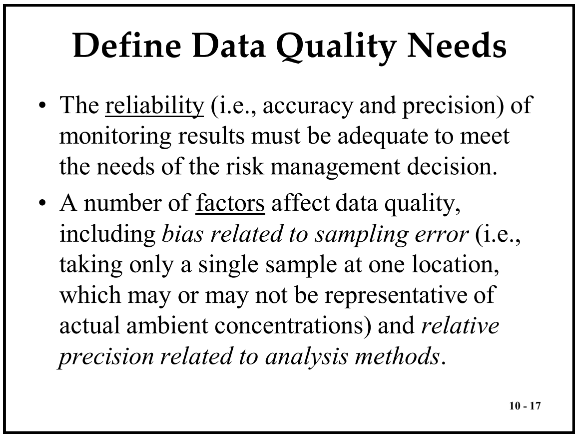
## Collect and Review Data

- Source Data: Site Layout Map, Source Specifications, Contaminants List, Toxicity Factors, Offsite Sources
- Environmental Data: Dispersion Data, Climatology, Topography, Soil and Vegetation
- Receptor Data: Population Distribution, Sensitivity Receptors, Site Work Zones, Local Land Use
- Previous APA Data: Meteorological, Monitoring Data, Emission Rate, Modeling/Monitoring, Dispersion Modeling, Air Monitoring



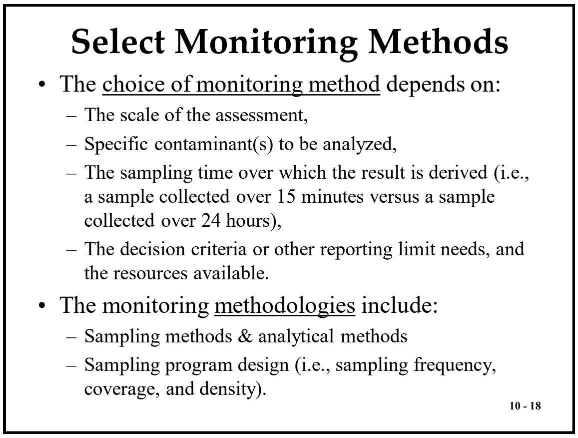
## Itemize Data Needs

- Filling gaps in emissions inventory data;
- Providing input data for models and validating modeling results;
- Generating new data to more fully characterize exposures in areas, populations, or pathways;
- Establishing trends over time; or
- Supplementing a body of data to increase their quality for the risk management decision.



## Define Data Quality Needs

- The reliability (i.e., accuracy and precision) of monitoring results must be adequate to meet the needs of the risk management decision.
- A number of factors affect data quality, including *bias related to sampling error* (i.e., taking only a single sample at one location, which may or may not be representative of actual ambient concentrations) and *relative precision related to analysis methods*.



## Select Monitoring Methods

- The choice of monitoring method depends on:
  - The scale of the assessment,
  - Specific contaminant(s) to be analyzed,
  - The sampling time over which the result is derived (i.e., a sample collected over 15 minutes versus a sample collected over 24 hours),
  - The decision criteria or other reporting limit needs, and the resources available.
- The monitoring methodologies include:
  - Sampling methods & analytical methods
  - Sampling program design (i.e., sampling frequency, coverage, and density).

## Selecting Locations for Air Monitors

- Depend on whether the goal is to quantify exposures in general, or exposures to the *maximally exposed individual*. In the latter case:
  - Locations too close to a source may underestimate exposure if the plume has not yet reached ground level where people can come into contact with the contaminant.
  - Locations too far from the source may also underestimate exposure to large groups of people due to the dispersion that takes place between the point of touch-down of the plume and the point of monitoring.

## Selecting Locations for Air Monitors

- Buildings, hills, and trees can have shielding and concentrating effects.
  - These effects may cause assessors to underestimate exposure if either measurement sites are shielded from normal air flow or if these same structures produce high concentrations downwind due to metrological effects.
- Make measurements at locations away from roads.
  - Monitoring should occur at distances ranging from 3 to 61 meters from a major traffic artery.
- Heights of monitoring and sampling devices should be consistent with the breathing zones of people.
  - This is generally between 1 and 2 meters (the lower end being for children and the upper end for adults).

## Selecting Locations for Air Monitors

- It is important to estimate background concentrations as accurately as possible at the location of measurement.
  - *Background monitors* should be placed in the predominant upwind direction (in relation to sources) in the assessment area to measure the concentrations of the chemicals of potential concern in air that is moving into the assessment area.
  - Background monitoring results should not be subtracted from assessment area monitoring results. Instead create bar-charts of background data for comparison purposes.

## Sampling Locations

- Purposive sampling refers to locating the monitor at a particular location because that location is of special interest.
  - While such sampling can be useful to address specialized questions (such as the impacts of a specific source, or the reliability of model results), they generally are less useful for risk assessment purposes.
- Random sampling involves selecting monitoring locations in a random and unbiased manner, (in a defined region).
  - Establish locations by creating a grid [x and y coordinates].
  - Advantage: easy to apply statistical methods for evaluating results, but runs the risk of missing some "hot spots."
- Systematic sampling involves establishing a grid and placing monitors systematically on the grid nodes.
  - This ensures that sampling is uniform across an area.

## Detection Limits & Limit of Quantification

- The ***detection limit*** *is the minimum concentration that an analyst can reliably expected to find (i.e., detect) in a sample*, if it is present.
  - For any given method this limit is established in the lab for each instrument and is called the **method detection limit** or **MDL**. An MDL of 1µg/m$^3$, indicates that a field sample that contains 1 µg/m$^3$ or below of contaminant will probably not be detected by the instrument in question.
- The ***limit of quantitation (LOQ)*** *is the minimum concentration for which the analyst can reliably say that the substance is present in the sample* and at a specific concentration within some pre-established limits of precision and accuracy.
  - If the limit of quantitation is 2 µg/m$^3$, then measurement results above 2 µg/m$^3$ may be reported as not only indicating the presence of the substance in the sample, but as indicating the specific concentration measured.

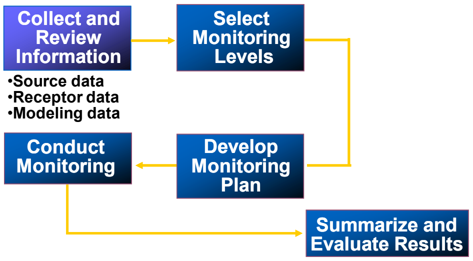
## Detection Limits & Limit of Quantification

- Measurements between the MDL and the LOQ, indicate the presence of the substance in the sample.
- Examples of LOQ:
  - when one says "benzene was not detected at a detection limit of 5 µg/m$^3$," this means "benzene was not detected; the limit of quantitation was 5 µg/m$^3$."
  - Likewise, when a lab reports a measurement as "<5 µg/m$^3$," this means "not detected; the limit of quantitation was 5 µg/m$^3$."
- When selecting the appropriate monitoring or sampling methods for the air toxic(s) to be measured, it is important that the methods selected have the sensitivity needed to monitor at concentrations likely to be of health and/or regulatory concern.
  - At a minimum, the LOQ should be below any relevant health benchmarks.

## EPA's Procedures for Air Pathway Analyses (APA) EPA-450/1-89-002

- Volume I--*Application of Air Pathway Analyses for Superfund Sites*
- Volume II--*Estimation of Baseline Emission at Superfund Sites*
- Volume III--*Estimation of Air Emission from Cleanup Activities at Superfund Sites*
- Volume IV--*Procedures for Dispersion Modeling and Air Monitoring for Superfund Air Pathway Analyses*

## Monitoring Air Pathway Analysis



**Collect and Review Information**

•Source data
•Receptor data
•Modeling data

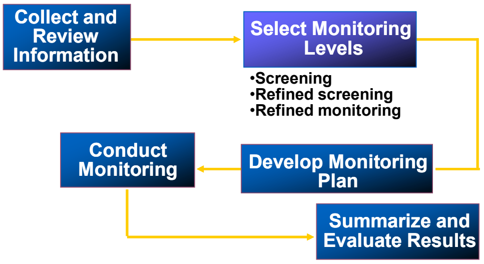
**Select Monitoring Levels**

**Develop Monitoring Plan**

**Conduct Monitoring**

**Summarize and Evaluate Results**

## Monitoring Air Pathway Analysis



**Collect and Review Information**

**Select Monitoring Levels**

•Screening
•Refined screening
•Refined monitoring

**Develop Monitoring Plan**

**Conduct Monitoring**

**Summarize and Evaluate Results**

## Screening Techniques

- High detection levels
- Limited QA/QC
- Provide real-time monitoring
- Limited to number of constituents that can be detected
- Ease of Use
- Limited accuracy

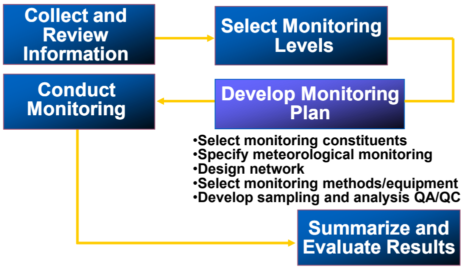
## Refined Screening Techniques

- Lower detection limits
- Greater accuracy
- Limited target analytes
- Simple matrices
- Unsophisticated QA/QC
- Use field GC laboratories and remote monitoring

## Refined Air Monitoring

- Highest degree of accuracy
- Lowest level of detection
- Refined target analyte list
- Sophisticated QA/QC
- Limitations:
  - Large number of compounds involved
  - Interference between compounds during analysis
  - Need for low detection limits

## Monitoring Air Pathway Analysis



**Collect and Review Information**

**Select Monitoring Levels**

**Develop Monitoring Plan**

- Select monitoring constituents
- Specify meteorological monitoring
- Design network
- Select monitoring methods/equipment
- Develop sampling and analysis QA/QC

**Conduct Monitoring**

**Summarize and Evaluate Results**

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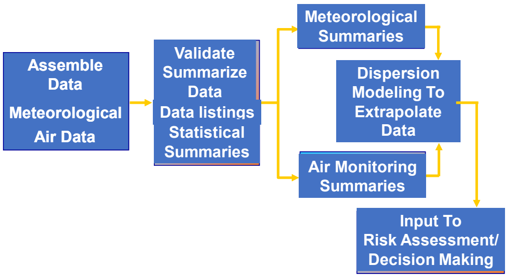
## Summarize and Evaluate Results



**Assemble Data**

**Meteorological**

**Air Data**

**Validate Summarize Data**

**Data listings**

**Statistical Summaries**

**Meteorological Summaries**

**Air Monitoring Summaries**

**Dispersion Modeling To Extrapolate Data**

**Input To Risk Assessment/ Decision Making**

---

## Air Toxics Monitoring Methods

- CAA Amendments lists 187 HAPs
- HAPs can be classified to different categories:
  - Vapor Pressure (in mm Hg at 25$^0$ C)
  - Boiling Point Temperature ($^0$ C)
- HAPs can be divided into 2 groups:
  - Organic
  - Inorganic

https://www3.epa.gov/ttnamti1/airtox.html

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## Organic Compound Classes

- Very Volatile Organic Compounds (VVOC)
- Volatile Organic Compounds (VOC)
- Semi-volatile Organic Compounds (SVOC)
- Nonvolatile Organic Compounds (NVOC)

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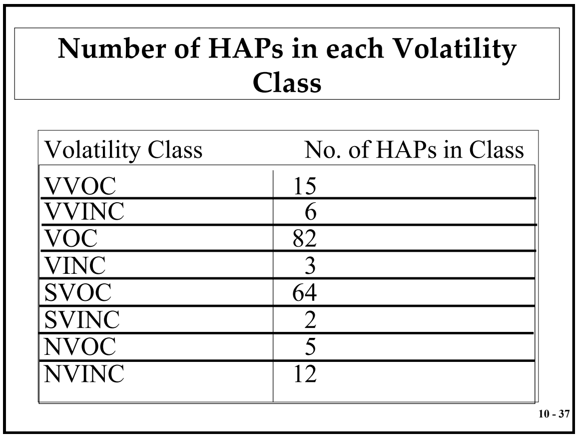
## Inorganic Compound Classes

- Very Volatile Inorganic Compounds (VVINC)
- Volatile Inorganic Compounds (VINC)
- Semi-volatile Inorganic Compounds (SVINC)
- Nonvolatile Inorganic Compounds (NVINC)

---

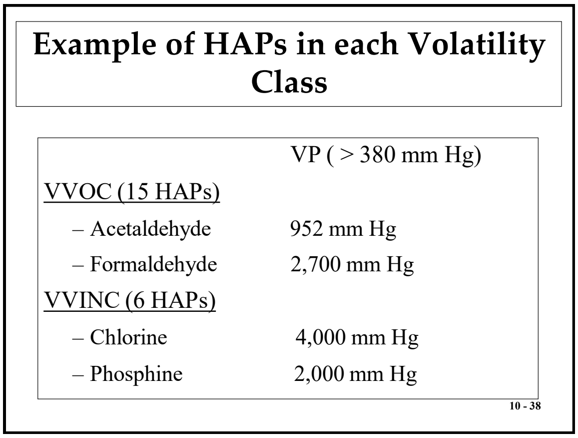
## Range of Vapor Pressure for each Volatility Class

| Volatility Class | Range of Vapor Pressure (in mm Hg at 25$^0$ C) |
|---|---|
| VVOC | > 380 |
| VVINC | > 380 |
| VOC | 0.1 to 380 |
| VINC | 0.1 to 380 |
| SVOC | $10^{-1}$ to $10^{-7}$ |
| SVINC | $10^{-1}$ to $10^{-7}$ |
| NVOC | < $10^{-7}$ |
| NVINC | < $10^{-7}$ |



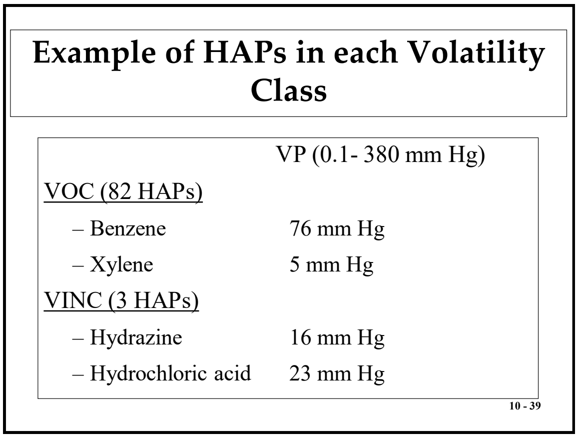
## Number of HAPs in each Volatility Class

| Volatility Class | No. of HAPs in Class |
|---|---|
| VVOC | 15 |
| VVINC | 6 |
| VOC | 82 |
| VINC | 3 |
| SVOC | 64 |
| SVINC | 2 |
| NVOC | 5 |
| NVINC | 12 |



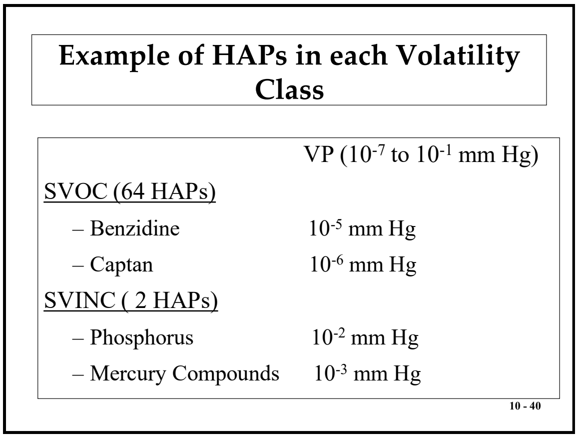
## Example of HAPs in each Volatility Class

| | VP ( > 380 mm Hg) |
|---|---|
| VVOC (15 HAPs) | |
| – Acetaldehyde | 952 mm Hg |
| – Formaldehyde | 2,700 mm Hg |
| VVINC (6 HAPs) | |
| – Chlorine | 4,000 mm Hg |
| – Phosphine | 2,000 mm Hg |



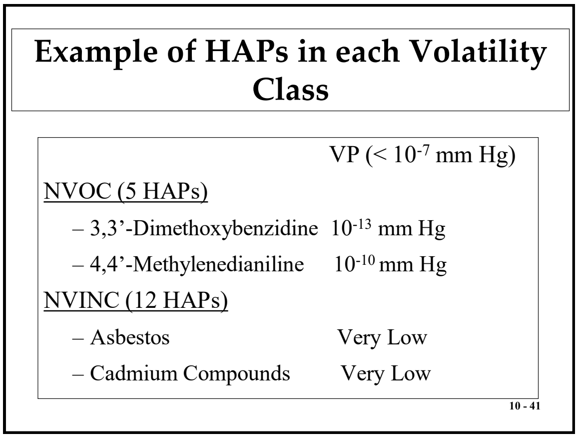
## Example of HAPs in each Volatility Class

| | VP (0.1- 380 mm Hg) |
|---|---|
| VOC (82 HAPs) | |
| – Benzene | 76 mm Hg |
| – Xylene | 5 mm Hg |
| VINC (3 HAPs) | |
| – Hydrazine | 16 mm Hg |
| – Hydrochloric acid | 23 mm Hg |



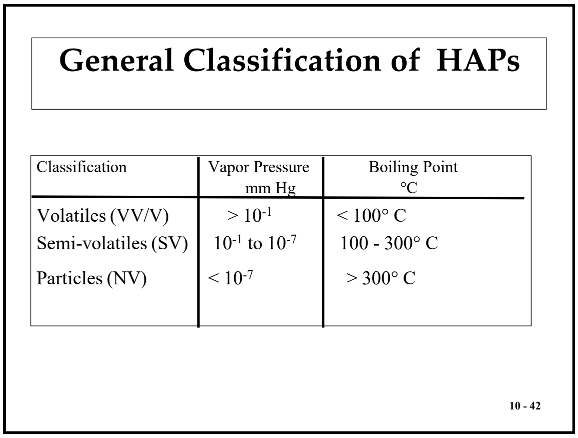
## Example of HAPs in each Volatility Class

| | VP ($10^{-7}$ to $10^{-1}$ mm Hg) |
|---|---|
| SVOC (64 HAPs) | |
| – Benzidine | $10^{-5}$ mm Hg |
| – Captan | $10^{-6}$ mm Hg |
| SVINC ( 2 HAPs) | |
| – Phosphorus | $10^{-2}$ mm Hg |
| – Mercury Compounds | $10^{-3}$ mm Hg |



## Example of HAPs in each Volatility Class

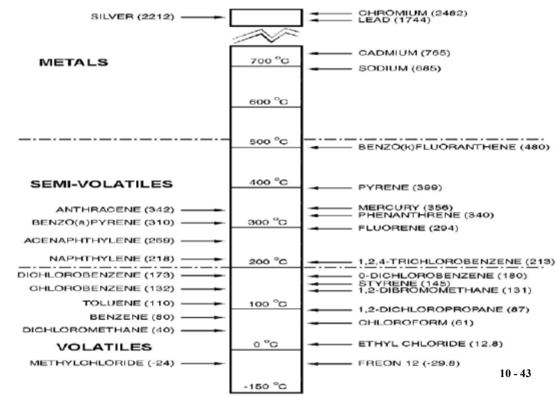
| | VP (< $10^{-7}$ mm Hg) |
|---|---|
| NVOC (5 HAPs) | |
| – 3,3'-Dimethoxybenzidine | $10^{-13}$ mm Hg |
| – 4,4'-Methylenedianiline | $10^{-10}$ mm Hg |
| NVINC (12 HAPs) | |
| – Asbestos | Very Low |
| – Cadmium Compounds | Very Low |



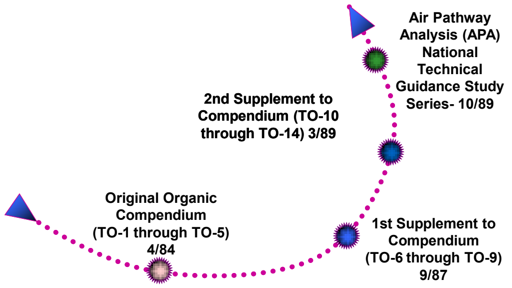
## General Classification of HAPs

| Classification | Vapor Pressure mm Hg | Boiling Point °C |
|---|---|---|
| Volatiles (VV/V) | > $10^{-1}$ | < 100° C |
| Semi-volatiles (SV) | $10^{-1}$ to $10^{-7}$ | 100 - 300° C |
| Particles (NV) | < $10^{-7}$ | > 300° C |

## Example of defining HAP's by boiling point



# HAP/Air Toxics Sampling Progression



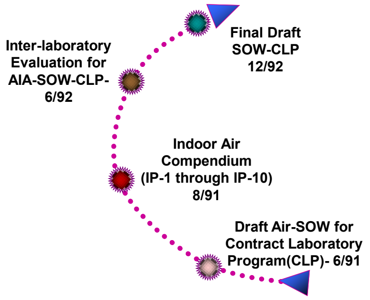
Air Pathway Analysis (APA) National Technical Guidance Study Series- 10/89

2nd Supplement to Compendium (TO-10 through TO-14) 3/89

Original Organic Compendium (TO-1 through TO-5) 4/84

1st Supplement to Compendium (TO-6 through TO-9) 9/87

# Indoor HAP/Air Toxics Sampling Progression



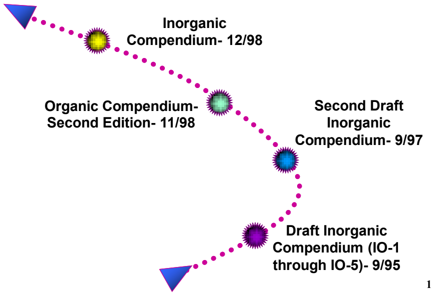
Final Draft SOW-CLP 12/92

Inter-laboratory Evaluation for AIA-SOW-CLP- 6/92

Indoor Air Compendium (IP-1 through IP-10) 8/91

Draft Air-SOW for Contract Laboratory Program(CLP)- 6/91

# Inorganic HAP/Air Toxics Sampling Progression



Inorganic Compendium- 12/98

Organic Compendium- Second Edition- 11/98

Second Draft Inorganic Compendium- 9/97

Draft Inorganic Compendium (IO-1 through IO-5)- 9/95

# *Compendia of Methods*

***Presently there are three Compendia:***

- *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air,* EPA/625/R-96-010a, June 1999 (Winberry et al., 1999a)
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition,* EPA/625/R-96-010b, January 1999 (Winberry et al., 1999b)
- *Compendium of Methods for the Determination of Air Pollutants in Indoor Air,* EPA/600/4-90-010, April 1990 (Winberry et al., 1990)

# Compendium of Methods-Inorganic

- Chapter 1: Continuous Measurement of Suspended Particulate Matter (SPM) in Ambient Air
- Chapter 2: Integrated Sampling for SPM
- Chapter 3: Chemical Species Analysis of Filter Collected by Integrated Sampling of SPM
- Chapter 4: Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles
- Chapter 5: Sampling and Analysis for Atmospheric Mercury

## Chapter IO-1: Continuous Measurement of Suspended Particulate Matter (SPM)

| | |
|---|---|
| • Method IO-1.1: | Continuous Andersen PM-10 Beta Attenuation |
| • Method IO-1.2: | Continuous TECO PM-10 Beta Attenuation |
| • Method IO-1.3: | Continuous R&P PM-10 TEOM Sampler |

## Chapter IO-2: Integrated Sampling for Suspended Particulate Matter (SPM)

| | |
|---|---|
| • Method IO-2.1: | High-Volume Particulate Sampler |
| • Method IO-2.2: | Dichotomous Particulate Sampler |
| • Method IO-2.3: | R&P Low Volume Partisol Monitor |
| • Method IO-2.4: | Calculating Standard Volume |

## Chapter IO-3: Chemical Species Analysis of Filter Collected SPM

- Method IO-3.1: Selection, Preparation and Extraction of Filter Material
- Method IO-3.2: Atomic Absorption (AA)
- Method IO-3.3: X-Ray Fluorescence (XRF)
- Method IO-3.4 & 3.5: Plasma/Mass Spectrometry (ICP/MS)
- Method IO-3.6: Proton Induced X-ray Emission (PIXE) Spectroscopy
- Method IO-3.7: Neutron Activation Analysis

## Chapter IO-4

| | |
|---|---|
| • Method IO-4.1: | Determination of Strong Acidity of Atmospheric Fine Particles (< 2.5 microns) |
| • Method IO-4.2: | Determination of Reactive Acidic and Basic Gases and Strong Acidity |

## Chapter IO-5: Sampling and Analysis for Atmospheric Mercury

- Method IO-5: Sampling and Analysis for Vapor and Particle Phase Mercury in Ambient Air Utilizing Cold Vapor Atomic Fluorescence Spectrometry

## EPA's AMTIC Web Site

- For the CAA's 187 HAPs, EPA has developed 34 monitoring methods that can be used for most of these air toxics.
  - 17 are "toxic organic" (TO), and
  - 17 are "toxic inorganic" (IO)
- These monitoring methods include everything from the sample collection devices to analytical laboratory methods.
- EPA's 34 air toxic monitoring methods can be found on EPA's Ambient Monitoring Technology Information Center (AMTIC) website: http://www.epa.gov/ttn/amtic/airtox.html.

| Method | Description |
|---|---|
| TO-1 | Method for the Determination of Volatile Organic Compounds (VOCs) in Ambient Air using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS) |
| TO-2 | Method for the Determination of VOCs in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS) |
| TO-3 | Method for the Determination of VOCs in Ambient Air using Cryogenic Preconcentration Techniques and Gas Chromatography with Flame Ionization and Electron Capture Detection |
| TO-4A | Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD) |
| TO-5 | Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography (HPLC) |
| TO-6 | Determination of Phosgene in Ambient Air Using High Performance Liquid Chromatography (HPLC) |
| TO-7 | Method for the Determination of nitrosodimethylamine (NDMA) in Ambient Air Using Gas Chromatography |
| TO-8 | Method for the Determination of Phenol and Methylphenols (Cresols) in Ambient Air Using High Performance Liquid Chromatography |
| TO-9A | Determination of Polychlorinated, Polybrominated, and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air |
| TO-10A | Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MD) |
| TO-11A | Determination of Formaldehyde in Ambient Air using Adsorbant Cartridge Followed by High Performance Liquid Chromatography (HPLC) |
| TO-12 | Method for the Determination of Non-methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID) |
| TO-13A | Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS) |
| TO-14A | Determination of VOCs in Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography |
| TO-15 | Determination of VOCs in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) |
| TO-16 | Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases |
| TO-17 | Determination of VOCs in Air Using Active Sampling Onto Sorbent Tubes |

## Compendium of Methods - Toxic Organic Compounds - Second Edition

- TO-1 through TO-5: EPA 600/4-89-017
- TO-6 through TO-9: EPA 600/3-87-006
- TO-10 through TO-14: EPA 600/4-89-018
- TO-1 through TO-17: EPA 625/R-96/010b

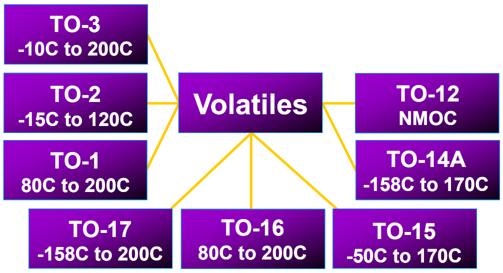
## Summary of Toxic Organic Compendium

| Compendium Method | Type of Compound | Sample Collection/ Analysis |
|---|---|---|
| TO-1 | VOCs | Tenax/GC-MS |
| TO-2 | VOCs | CMS/GC-MS |
| TO-3 | VOCs | Cryotrap/FID |
| TO-4A | Pest./PCBs | PUF/GC-MD |
| TO-5 | Ald./Ket. | Impinger/HPLC |
| TO-6 | Phosgene | Impinger/HPLC |
| TO-7 | Amines | Ads./GC-MS |
| TO-8 | Phenols | Impinger/HPLC |
| TO-9A | Dioxin/Furans | F/PUF/HRGC-MS |

## Summary of Toxic Organic Compendium

| Compendium Method | Type of Compound | Sample Collection/ Analysis |
|---|---|---|
| TO-10A | Pest./PCBs | PUF/GC-MS |
| TO-11A | Ald/Ket. | Ads./HPLC |
| TO-12 | NMOC | Can./On-line/FID |
| TO-13A | PAHs | F/PUF/GC-MS |
| TO-14A | VOCs(NP) | STC/GC-MS-MD |
| TO-15 | VOCs(P/NP) | STC/GC-MS-IT |
| TO-16 | VOCs(P/NP) | Open Path/FTIR |
| TO-17 | VOCs(P/NP) | MBA/GC-MS-FID |

## Compendium of Classification of Analytes



Volatiles

TO-3
-10C to 200C

TO-2
-15C to 120C

TO-1
80C to 200C

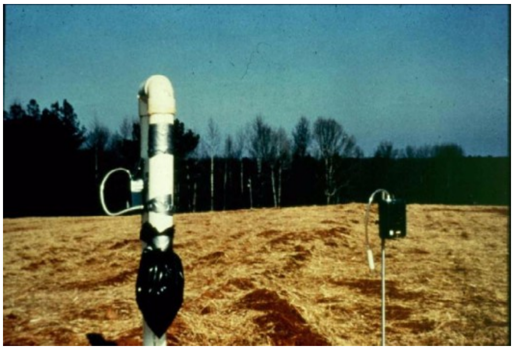
TO-12
NMOC

TO-14A
-158C to 170C

TO-17
-158C to 200C

TO-16
80C to 200C

TO-15
-50C to 170C



Encapsulated Vent Tube Sampling for PCBs Utilizing EPA Compendium Method TO-10A. (Note Portable Monitor to the Right of the Vent Tube for Ambient Monitoring of Emissions During Normal Vent Tube Emissions.)

Compendium Method TO-15 Application for Monitoring VOCs at the perimeter of a MSW Landfill

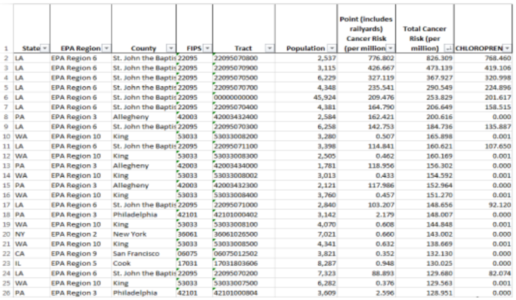
Example of Compendium Method TO-15 at Typical Ambient Monitoring Site.

## Canisters with tripod stand setup at Willowbrook Village Hall site

## Air Monitoring Around Denka Plant in Laplace, LA

https://www.epa.gov/la/laplace-st-john-baptist-parish-louisiana

## Data from 2011 NATA results showing elevated risks in LaPlace, LA – Highest risk in nation: 826 in 1M – 8 of top 10; 12 of top 25



| 1 | State | EPA Region | County | FIPS | Tract | Population | Point (includes railyards) Cancer Risk (per million | Total Cancer Risk (per million) | CHLOROPREN |
|---|---|---|---|---|---|---|---|---|---|
| 2 | LA | EPA Region 6 | St. John the Baptis | 22095 | 22095070800 | 2,537 | 776.802 | 826.309 | 768.460 |
| 3 | LA | EPA Region 6 | St. John the Baptis | 22095 | 22095070900 | 3,115 | 426.667 | 473.139 | 419.106 |
| 4 | LA | EPA Region 6 | St. John the Baptis | 22095 | 22095070500 | 6,229 | 327.119 | 367.927 | 320.998 |
| 5 | LA | EPA Region 6 | St. John the Baptis | 22095 | 22095070700 | 4,348 | 235.541 | 290.549 | 224.896 |
| 6 | LA | EPA Region 6 | St. John the Baptis | 22095 | 00000000000 | 45,924 | 209.476 | 253.829 | 201.617 |
| 7 | LA | EPA Region 6 | St. John the Baptis | 22095 | 22095070400 | 4,381 | 164.790 | 206.649 | 158.515 |
| 8 | PA | EPA Region 3 | Allegheny | 42003 | 42003432400 | 2,584 | 162.421 | 200.616 | 0.000 |
| 9 | LA | EPA Region 6 | St. John the Baptis | 22095 | 22095070300 | 6,258 | 142.753 | 184.736 | 135.887 |
| 10 | WA | EPA Region 10 | King | 53033 | 53033008200 | 3,280 | 0.507 | 165.898 | 0.001 |
| 11 | LA | EPA Region 6 | St. John the Baptis | 22095 | 22095071100 | 3,398 | 114.841 | 160.621 | 107.650 |
| 12 | WA | EPA Region 10 | King | 53033 | 53033008300 | 2,505 | 0.462 | 160.169 | 0.001 |
| 13 | PA | EPA Region 3 | Allegheny | 42003 | 42003434000 | 1,781 | 118.956 | 156.302 | 0.000 |
| 14 | WA | EPA Region 10 | King | 53033 | 53033008002 | 3,013 | 0.433 | 154.592 | 0.001 |
| 15 | PA | EPA Region 3 | Allegheny | 42003 | 42003432300 | 2,121 | 117.986 | 152.964 | 0.000 |
| 16 | WA | EPA Region 10 | King | 53033 | 53033008400 | 3,760 | 0.457 | 151.270 | 0.001 |
| 17 | LA | EPA Region 6 | St. John the Baptis | 22095 | 22095071000 | 2,840 | 103.207 | 148.656 | 92.120 |
| 18 | PA | EPA Region 3 | Philadelphia | 42101 | 42101000402 | 3,142 | 2.179 | 148.007 | 0.000 |
| 19 | WA | EPA Region 10 | King | 53033 | 53033008100 | 4,070 | 0.608 | 144.848 | 0.001 |
| 20 | NY | EPA Region 2 | New York | 36061 | 36061026500 | 7,021 | 0.660 | 143.002 | 0.000 |
| 21 | WA | EPA Region 10 | King | 53033 | 53033008500 | 4,341 | 0.632 | 138.669 | 0.001 |
| 22 | CA | EPA Region 9 | San Francisco | 06075 | 06075012502 | 3,821 | 0.352 | 132.130 | 0.000 |
| 23 | IL | EPA Region 5 | Cook | 17031 | 17031803606 | 8,287 | 0.948 | 130.025 | 0.000 |
| 24 | LA | EPA Region 6 | St. John the Baptis | 22095 | 22095070200 | 7,323 | 88.893 | 129.680 | 82.074 |
| 25 | WA | EPA Region 10 | King | 53033 | 53033007500 | 6,282 | 0.376 | 129.563 | 0.001 |
| 26 | PA | EPA Region 3 | Philadelphia | 42101 | 42101000804 | 3,609 | 2.596 | 128.951 | 0.000 |

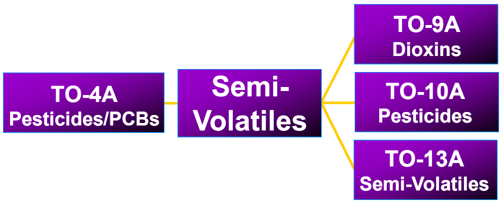
## Air canister collects ambient air samples near the Mid-America Steel Drum Co. St. Francis facility

https://www.epa.gov/wi/epa-investigating-milwaukee-company-potential-environmental-violations

Ambient Air Monitoring Locations - Ethylene Oxide
May 16-18, 2018
Willowbrook, Illinois

Service Layer Credits: Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

## Compendium of Classification of Analytes

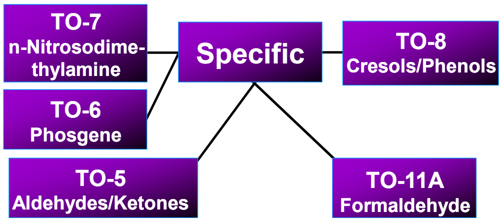


**TO-4A** Pesticides/PCBs

**Semi-Volatiles**

- **TO-9A** Dioxins
- **TO-10A** Pesticides
- **TO-13A** Semi-Volatiles

## Compendium of Classification of Analytes



**Specific**

- **TO-7** n-Nitrosodimethylamine
- **TO-6** Phosgene
- **TO-5** Aldehydes/Ketones
- **TO-8** Cresols/Phenols
- **TO-11A** Formaldehyde

Ambient Monitoring Technology Information Center (AMTIC)

Ambient monitoring is used to determine whether areas are meeting the National Ambient Air Quality Standards

What's New

Updated List of NATTS Sites

POSTPONED: 2020 National Ambient Air Monitoring Conference - August 9-13, 2020.

2020 Community-Scale Grants Competition

Air Toxics Ambient Monitoring Archive Updated

Join the ambient air monitoring listserv: join-airmonitoring@lists.epa.gov

The Ambient Monitoring Technology Information Center (AMTIC) provides information on monitoring programs and methods, quality assurance and control procedures, and federal regulations. This website is primarily intended for staff responsible for collecting ambient air monitoring data. Learn more.

**Air Monitoring Networks**
EPA, states and tribes work together to monitor air quality.

**Training and Conferences**
Stay current with emerging topics related to air monitoring.

**Air Monitoring Methods**
Access approved methodologies for air pollution monitoring.

**Quality Assurance**
Understand quality assurance procedures.

**Regulations, Guidance and Monitoring Plans**
Track current requirements and recommendations for air pollution monitoring.

**Program Review and Oversight**
Independent oversight of air monitoring programs.

**Networks, Partners, and Programs**
Access data and track other monitoring programs.

**Additional Monitoring Information**
Learn more from EPA, states, and other organizations.

https://www.epa.gov/amtic

## Monitoring Equipment: Time Scale Basis

- **Grab samples** provide a quasi-instantaneous measurement of a concentration.
  - Obtained in the field usually over a *period of 24 hours or less and then returned to the laboratory for analysis*. (The sampling may be automated, but samples still returned to lab.
- **Continuous monitors** provide a time series of measurements in the field, with a stream of data at selected intervals (i.e., once each 24 hours).
  - These monitors may be fully automated versions of grab sampling, taking samples at a set interval but then *analyzing the samples internally rather than returning to the lab*.
- **Time-integrated samples:** collected over *extended period of time*.
  - These measurements are obtained in the field and returned to a laboratory for analysis.

# Methods of Collection

- **Integrated air sampling devices** use a pump to *draw air continuously into the sample chamber, over a reactive medium, or through a filter during a prescribed period of time*; the sample is returned to the laboratory for analysis.
  - Are the predominant type of monitoring used for HAPs.
  - For metals and carbonyls air toxics this collection device consists of some type of filter or reactive material that collects the air toxics.
  - For VOC air toxics the sample is collected in a canister. The pump can be programmed to collect air for a pre-set period of time (i.e., 1 hour to 24 hours). The collected samples are then sent to a laboratory for analysis.

# Methods of Collection

- **Direct-read monitors** draw air through a measurement system and provide a direct reading of the concentration without returning samples to the lab.
- **Automated monitoring systems** collect samples, perform the analysis, and report results at regular intervals in the field.
- **Air deposition monitors** rely on deposition properties of compounds (i.e., particulates), and may consist of active and/or passive, wet and/or dry sampling methods.
- **Passive monitors** allow the compound to diffuse into contact with an active material; these generally are analyzed in the lab, although some indicate the presence of a compound by a color change.
- **Grab sampling devices** use an essentially instantaneous sampling method, such as an evacuated chamber into which ambient air is allowed to enter at a fixed rate; the sample collected is returned to the laboratory for analysis.

# PAMS target species list for use as "tracers of sources."

| Species | Major Sources | Comments |
|---|---|---|
| ethene | Mobile sources, petrochemical industry | Tracer for vehicle exhaust |
| acetylene | Mobile sources, combustion processes | Tracer for vehicle exhaust. More abundant in gasoline than diesel exhaust |
| ethane | Natural gas use | Non-reactive |
| propene | Refinery, chemical manufacturing, motor vehicle exhaust | More abundant in diesel than gasoline exhaust |
| propane | LPG and natural gas use, oil and gas production | Relatively non-reactive, often underestimated in emission inventory. Also more abundant in diesel than gasoline exhaust |
| i-butane | Consumer products, gasoline evaporative emissions, refining | Used as replacement of CFCs in consumer products |
| butene | Motor vehicle exhaust | More abundant in gasoline than diesel exhaust. A thermal decomposition product of MTBE |
| n-butane | Gasoline evaporative emission | Tracer of gasoline use |
| t-2-butene | Motor vehicle exhaust | Enriched in evaporated gasoline relative to exhaust |

# PAMS target species list for use as "tracers of sources."

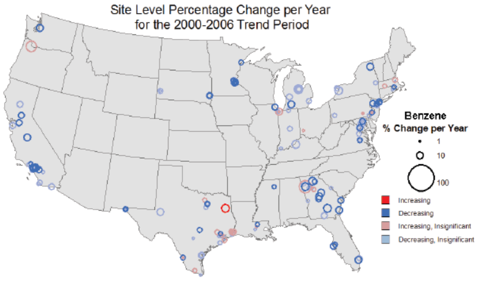
| Species | Major Sources | Comments |
|---|---|---|
| i-pentane | Solvent use, refining, mobile sources | Among most abundant species in urban air. More abundant in gasoline than diesel exhaust |
| n-pentane | Motor vehicle exhaust, gasoline evaporative emissions | Enriched in evaporative emissions relative to exhaust |
| isoprene | Biogenics | Tracer of biogenic emission; reactive |
| internal olefins (e.g., t-2-pentene) | Gasoline evaporative emissions, plastics production | Reactive |
| 2,2-dimethylbutane | Motor vehicle exhaust | More abundant in diesel than gasoline exhaust |
| benzene | Motor vehicle exhaust, combustion processes, refining | Tracer for vehicle exhaust; significantly reduced since 1995 with the introduction of reformulated gasoline |
| 2-methylhexane | Motor vehicle exhaust | More abundant in gasoline than diesel exhaust |
| 2,2,4-trimethylpentane | Gasoline evaporative emissions | Also in motor vehicle exhaust |
| n-heptane | Surface coatings, degreasing | Also in motor vehicle exhaust |

# PAMS target species list for use as "tracers of sources."

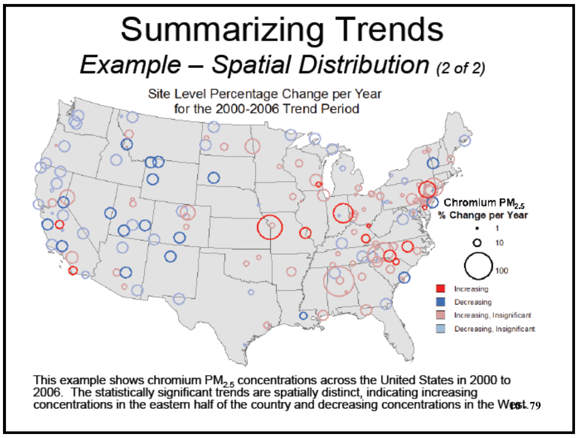
| Species | Major Sources | Comments |
|---|---|---|
| toluene | Solvent use, refining, mobile sources | Among most abundant species in urban air |
| styrene | Solvent use, chemical manufacturing | Also in motor vehicle exhaust |
| heptane and octane isomers | Oil and gas production, asphalt, gasoline | Also in motor vehicle exhaust |
| n-nonane | Dry cleaning, degreasing, motor vehicles | Also in motor vehicle exhaust |
| xylenes | Solvent use, refining, mobile sources | Reactive |
| n-decane, undecane | Fuel storage, surface coatings | More abundant in diesel than gasoline exhaust |
| formaldehyde | Fuel combustion | Also a key photochemical reaction product (secondary source) |
| acetone | Surface coating | Also most abundant VOC in landfill emissions and a product of photochemistry |
| acetaldehyde | Fuel combustion | Also a product of photochemistry |

# Summarizing Trends

## *Example – Spatial Distribution (1 of 2)*



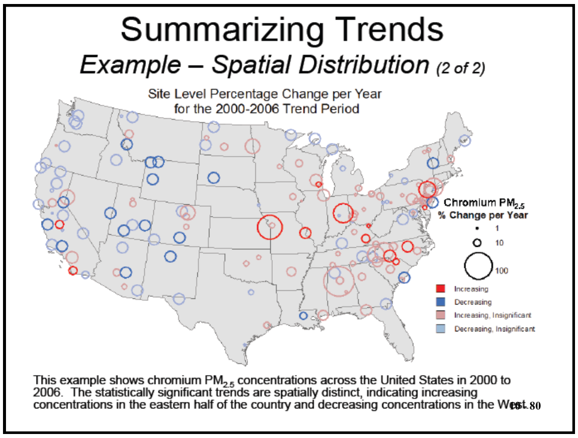
This map shows the benzene site-level percentage change per year for 2000-2006. Many sites in the United States show a statistically significant decline in benzene concentrations over the period. The sites exhibiting increases over that time are typically not statistically significant trends. These data, suggest relatively high confidence that national benzene concentrations are declining nationally compared to the 2000 level. Statistical significance was quantified using the F-test at the 95% confidence level.



# Summarizing Trends

## *Example – Spatial Distribution* (2 of 2)

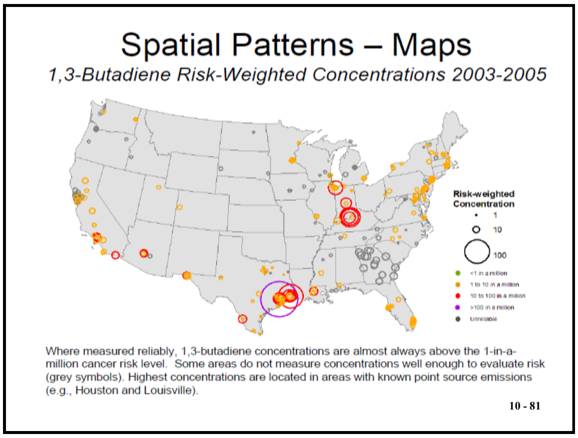
This example shows chromium $PM_{2.5}$ concentrations across the United States in 2000 to 2006. The statistically significant trends are spatially distinct, indicating increasing concentrations in the eastern half of the country and decreasing concentrations in the West.



Summarizing Trends

Example – Spatial Distribution (2 of 2)

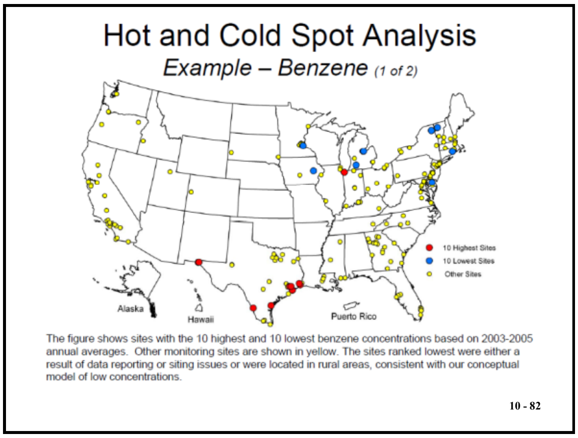
This example shows chromium $PM_{2.5}$ concentrations across the United States in 2000 to 2006. The statistically significant trends are spatially distinct, indicating increasing concentrations in the eastern half of the country and decreasing concentrations in the West.



# Spatial Patterns – Maps

## *1,3-Butadiene Risk-Weighted Concentrations 2003-2005*

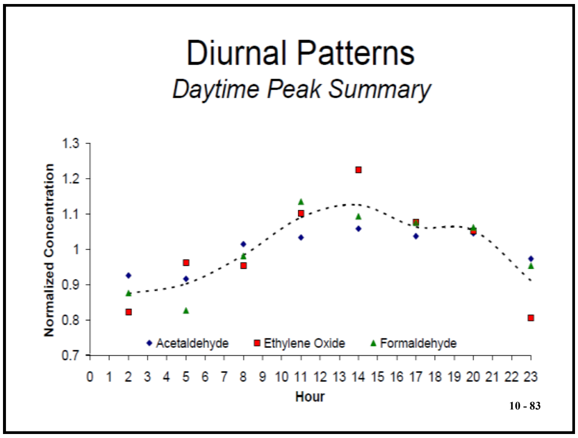
Where measured reliably, 1,3-butadiene concentrations are almost always above the 1-in-a-million cancer risk level. Some areas do not measure concentrations well enough to evaluate risk (grey symbols). Highest concentrations are located in areas with known point source emissions (e.g., Houston and Louisville).



# Hot and Cold Spot Analysis

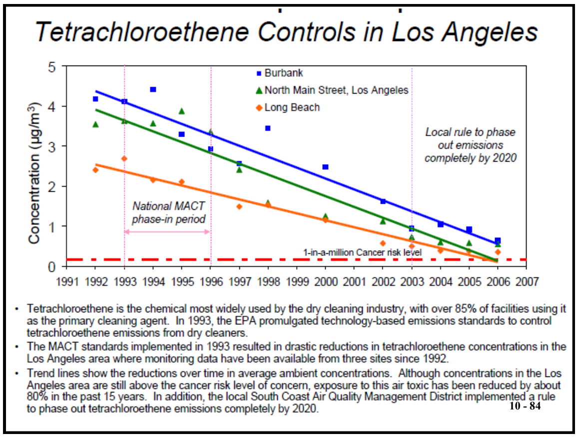
## *Example – Benzene* (1 of 2)

The figure shows sites with the 10 highest and 10 lowest benzene concentrations based on 2003-2005 annual averages. Other monitoring sites are shown in yellow. The sites ranked lowest were either a result of data reporting or siting issues or were located in rural areas, consistent with our conceptual model of low concentrations.



# Diurnal Patterns

## *Daytime Peak Summary*



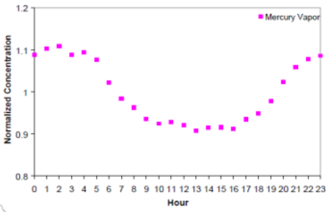
# *Tetrachloroethene Controls in Los Angeles*

- Tetrachloroethene is the chemical most widely used by the dry cleaning industry, with over 85% of facilities using it as the primary cleaning agent. In 1993, the EPA promulgated technology-based emissions standards to control tetrachloroethene emissions from dry cleaners.
- The MACT standards implemented in 1993 resulted in drastic reductions in tetrachloroethene concentrations in the Los Angeles area where monitoring data have been available from three sites since 1992.
- Trend lines show the reductions over time in average ambient concentrations. Although concentrations in the Los Angeles area are still above the cancer risk level of concern, exposure to this air toxic has been reduced by about 80% in the past 15 years. In addition, the local South Coast Air Quality Management District implemented a rule to phase out tetrachloroethene emissions completely by 2020.

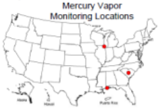
## Diurnal Patterns

### *Evening Peak*

- Mercury vapor is the only air toxic to exhibit a clear evening peak pattern in the air toxics investigated at the national level. However, data from only a few sites were available so this analysis may not be representative of a national pattern.
- Dilution appears to be the key factor affecting evening peak pollutants; emissions and sinks are likely invariant at the subdaily level.



Mercury Vapor
Monitoring Locations

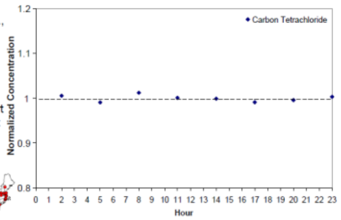


1990-2005 national hourly mercury vapor data normalized by site, pollutant, and day. The figure was created with Microsoft Excel.

## Diurnal Patterns

### *Invariant*

- Invariant patterns are observed for global background pollutants (i.e., pollutant is no longer emitted).
- These pollutants show no sources or sinks and are evenly distributed worldwide so that transport and dilution have no effect on concentration.



Carbon Tetrachloride
Monitoring Locations

The figure shows 1990-2005 national 3-hr carbon tetrachloride data normalized by site, pollutant, and day. Carbon tetrachloride is the only pollutant to exhibit an invariant diurnal pattern on the national scale. The figure was created with Microsoft Excel.

## National Concentration Plots Summary

- The national concentration plots provide perspective for local, state, regional, and tribal analysts to see how their data compare.
- Air toxics concentrations typically vary spatially by a factor of 3 to 10, depending on the pollutant.
- Almost all air toxics are below non-cancer reference concentrations (except acrolein).
- At a national level, some air toxics are above their respective chronic exposure concentration associated with a 1-in-a-million cancer risk (https://www.epa.gov/fera/dose-response-assessment-assessing-health-risks-associated-exposure-hazardous-air-pollutants ).
- Most air toxics are well above their remote background concentrations.

## How to Create a Successful Air Toxics Monitoring Program Webinars

**How to Create a Successful Air Toxics Monitoring Program Webinar Part 3, September 7, 2011**

| Title | Format | Length (hr:min:sec)<br>Size (MB) | |
|---|---|---|---|
| How to Create a Successful Air Toxics Monitoring Program Webinar – Part 3<br>September 7, 2011 | Flash | 00:95:29 | PLAY VIDEO |
| Materials 1 | PDF | 12 Pages, 182 KB | Materials |
| Materials 2 | PDF | 18 Pages, 641 KB | Materials |

⇧Top of page

**How to Create a Successful Air Toxics Monitoring Program Webinar Part 2, August 31, 2011**

| Title | Format | Length (hr:min:sec)<br>Size (MB) | |
|---|---|---|---|
| How to Create a Successful Air Toxics Monitoring Program Webinar – Part 2<br>August 31, 2011 | Flash | 01:33:00 | PLAY VIDEO |
| Materials | PDF | 28 Pages, 767 KB | Materials |

⇧Top of page

**How to Create a Successful Air Toxics Monitoring Program Webinar Part 1, August 24, 2011**

| Title | Format | Length (hr:min:sec)<br>Size (MB) | |
|---|---|---|---|
| How to Create a Successful Air Toxics Monitoring Program Webinar – Part 1<br>August 24, 2011 | Flash | 01:35:40 | PLAY VIDEO |
| Materials 1 | PDF | 16 Pages, 620 KB | Materials |
| Materials 2 | PDF | 10 Pages, 401 KB | Materials |

https://archive.epa.gov/apti/video/web/html/index-9.html

**2015-2016 National Monitoring Programs**
**Annual Report**
**(UATMP, NATTS, and CSATAM)**

**Final Report**
**EPA Contract No. EP-D-14-030**

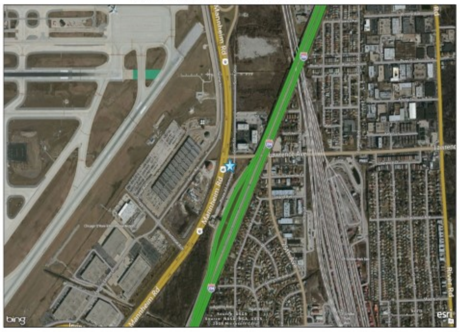
Prepared for:

Jeff Yane and David Shelow
Office of Air Quality Planning and Standards
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

July 2018

Air Toxics Monitoring National Program Reports | US EPA

Figure 10-2. Schiller Park, Illinois (SPIL) Monitoring Site



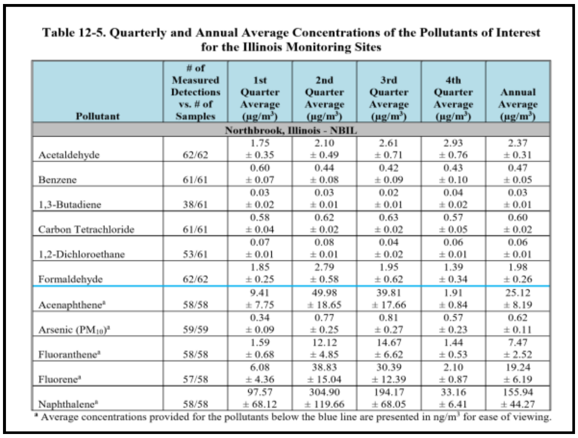


Table 12-5. Quarterly and Annual Average Concentrations of the Pollutants of Interest for the Illinois Monitoring Sites

| Pollutant | # of Measured Detections vs. # of Samples | 1st Quarter Average ($\mu g/m^3$) | 2nd Quarter Average ($\mu g/m^3$) | 3rd Quarter Average ($\mu g/m^3$) | 4th Quarter Average ($\mu g/m^3$) | Annual Average ($\mu g/m^3$) |
|---|---|---|---|---|---|---|
| **Northbrook, Illinois - NBIL** | | | | | | |
| Acetaldehyde | 62/62 | 1.75 ± 0.35 | 2.10 ± 0.49 | 2.61 ± 0.71 | 2.93 ± 0.76 | 2.37 ± 0.31 |
| Benzene | 61/61 | 0.60 ± 0.07 | 0.44 ± 0.08 | 0.42 ± 0.09 | 0.43 ± 0.10 | 0.47 ± 0.05 |
| 1,3-Butadiene | 38/61 | 0.03 ± 0.02 | 0.03 ± 0.01 | 0.02 ± 0.01 | 0.04 ± 0.02 | 0.03 ± 0.01 |
| Carbon Tetrachloride | 61/61 | 0.58 ± 0.04 | 0.62 ± 0.02 | 0.63 ± 0.02 | 0.57 ± 0.05 | 0.60 ± 0.02 |
| 1,2-Dichloroethane | 53/61 | 0.07 ± 0.01 | 0.08 ± 0.01 | 0.04 ± 0.02 | 0.06 ± 0.01 | 0.06 ± 0.01 |
| Formaldehyde | 62/62 | 1.85 ± 0.25 | 2.79 ± 0.58 | 1.95 ± 0.62 | 1.39 ± 0.34 | 1.98 ± 0.26 |
| Acenaphthene[a] | 58/58 | 9.41 ± 7.75 | 49.98 ± 18.65 | 39.81 ± 17.66 | 1.91 ± 0.84 | 25.12 ± 8.19 |
| Arsenic ($PM_{10}$)[a] | 59/59 | 0.34 ± 0.09 | 0.77 ± 0.25 | 0.81 ± 0.27 | 0.57 ± 0.23 | 0.62 ± 0.11 |
| Fluoranthene[a] | 58/58 | 1.59 ± 0.68 | 12.12 ± 4.85 | 14.67 ± 6.62 | 1.44 ± 0.53 | 7.47 ± 2.52 |
| Fluorene[a] | 57/58 | 6.08 ± 4.36 | 38.83 ± 15.04 | 30.39 ± 12.39 | 2.10 ± 0.87 | 19.24 ± 6.19 |
| Naphthalene[a] | 58/58 | 97.57 ± 68.12 | 304.90 ± 119.66 | 194.17 ± 68.05 | 33.16 ± 6.41 | 155.94 ± 44.27 |

[a] Average concentrations provided for the pollutants below the blue line are presented in ng/m$^3$ for ease of viewing.

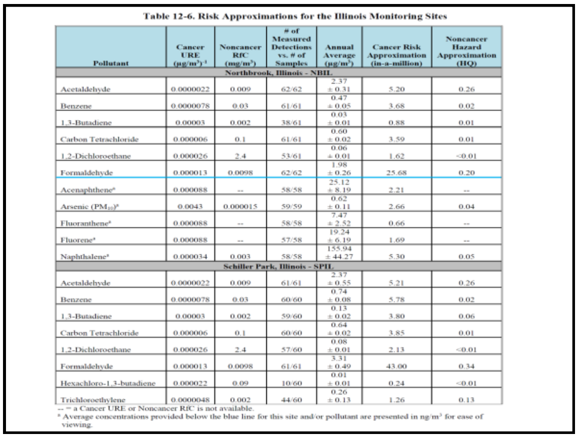


Table 12-6. Risk Approximations for the Illinois Monitoring Sites

| Pollutant | Cancer URE $(\mu g/m^3)^{-1}$ | Noncancer RfC ($mg/m^3$) | # of Measured Detections vs. # of Samples | Annual Average ($\mu g/m^3$) | Cancer Risk Approximation (in-a-million) | Noncancer Hazard Approximation (HQ) |
|---|---|---|---|---|---|---|
| **Northbrook, Illinois - NBIL** | | | | | | |
| Acetaldehyde | 0.0000022 | 0.009 | 62/62 | 2.37 ± 0.31 | 5.20 | 0.26 |
| Benzene | 0.0000078 | 0.03 | 61/61 | 0.47 ± 0.05 | 3.68 | 0.02 |
| 1,3-Butadiene | 0.00003 | 0.002 | 38/61 | 0.03 ± 0.01 | 0.88 | 0.01 |
| Carbon Tetrachloride | 0.000006 | 0.1 | 61/61 | 0.60 ± 0.02 | 3.59 | 0.01 |
| 1,2-Dichloroethane | 0.000026 | 2.4 | 53/61 | 0.06 ± 0.01 | 1.62 | <0.01 |
| Formaldehyde | 0.000013 | 0.0098 | 62/62 | 1.98 ± 0.26 | 25.68 | 0.20 |
| Acenaphthene[a] | 0.000088 | -- | 58/58 | 25.12 ± 8.19 | 2.21 | -- |
| Arsenic ($PM_{10}$)[a] | 0.0043 | 0.000015 | 59/59 | 0.62 ± 0.11 | 2.66 | 0.04 |
| Fluoranthene[a] | 0.000088 | -- | 58/58 | 7.47 ± 2.52 | 0.66 | -- |
| Fluorene[a] | 0.000088 | -- | 57/58 | 19.24 ± 6.19 | 1.69 | -- |
| Naphthalene[a] | 0.000034 | 0.003 | 58/58 | 155.94 ± 44.27 | 5.30 | 0.05 |
| **Schiller Park, Illinois - SPIL** | | | | | | |
| Acetaldehyde | 0.0000022 | 0.009 | 61/61 | 2.37 ± 0.55 | 5.21 | 0.26 |
| Benzene | 0.0000078 | 0.03 | 60/60 | 0.74 ± 0.08 | 5.78 | 0.02 |
| 1,3-Butadiene | 0.00003 | 0.002 | 59/60 | 0.13 ± 0.02 | 3.80 | 0.06 |
| Carbon Tetrachloride | 0.000006 | 0.1 | 60/60 | 0.64 ± 0.02 | 3.85 | 0.01 |
| 1,2-Dichloroethane | 0.000026 | 2.4 | 57/60 | 0.08 ± 0.01 | 2.13 | <0.01 |
| Formaldehyde | 0.000013 | 0.0098 | 61/61 | 3.31 ± 0.49 | 43.00 | 0.34 |
| Hexachloro-1,3-butadiene | 0.000022 | 0.09 | 10/60 | 0.01 ± 0.01 | 0.24 | <0.01 |
| Trichloroethylene | 0.0000048 | 0.002 | 44/60 | 0.26 ± 0.13 | 1.26 | 0.13 |

-- = a Cancer URE or Noncancer RfC is not available.

[a] Average concentrations provided below the blue line for this site and/or pollutant are presented in ng/m$^3$ for ease of viewing.

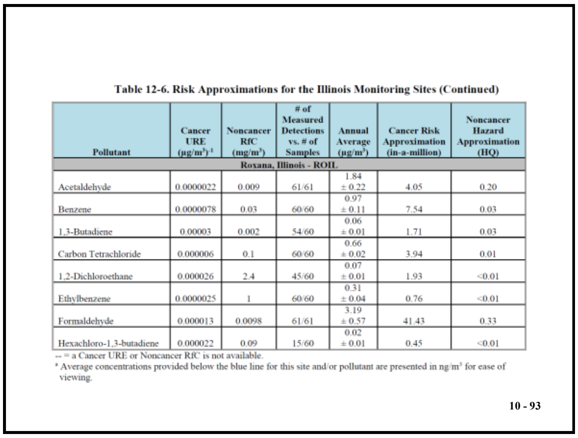


Table 12-6. Risk Approximations for the Illinois Monitoring Sites (Continued)

| Pollutant | Cancer URE $(\mu g/m^3)^{-1}$ | Noncancer RfC ($mg/m^3$) | # of Measured Detections vs. # of Samples | Annual Average ($\mu g/m^3$) | Cancer Risk Approximation (in-a-million) | Noncancer Hazard Approximation (HQ) |
|---|---|---|---|---|---|---|
| **Roxana, Illinois - ROIL** | | | | | | |
| Acetaldehyde | 0.0000022 | 0.009 | 61/61 | 1.84 ± 0.22 | 4.05 | 0.20 |
| Benzene | 0.0000078 | 0.03 | 60/60 | 0.97 ± 0.11 | 7.54 | 0.03 |
| 1,3-Butadiene | 0.00003 | 0.002 | 54/60 | 0.06 ± 0.01 | 1.71 | 0.03 |
| Carbon Tetrachloride | 0.000006 | 0.1 | 60/60 | 0.66 ± 0.02 | 3.94 | 0.01 |
| 1,2-Dichloroethane | 0.000026 | 2.4 | 45/60 | 0.07 ± 0.01 | 1.93 | <0.01 |
| Ethylbenzene | 0.0000025 | 1 | 60/60 | 0.31 ± 0.04 | 0.76 | <0.01 |
| Formaldehyde | 0.000013 | 0.0098 | 61/61 | 3.19 ± 0.57 | 41.43 | 0.33 |
| Hexachloro-1,3-butadiene | 0.000022 | 0.09 | 15/60 | 0.02 ± 0.01 | 0.45 | <0.01 |

-- = a Cancer URE or Noncancer RfC is not available.

[a] Average concentrations provided below the blue line for this site and/or pollutant are presented in ng/m$^3$ for ease of viewing.

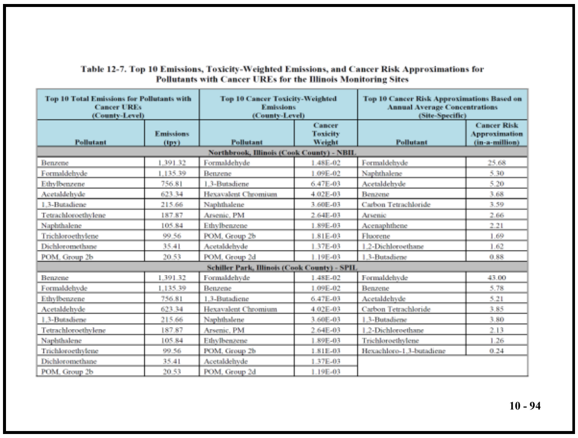


Table 12-7. Top 10 Emissions, Toxicity-Weighted Emissions, and Cancer Risk Approximations for Pollutants with Cancer UREs for the Illinois Monitoring Sites

| Top 10 Total Emissions for Pollutants with Cancer UREs (County-Level) | | Top 10 Cancer Toxicity-Weighted Emissions (County-Level) | | Top 10 Cancer Risk Approximations Based on Annual Average Concentrations (Site-Specific) | |
|---|---|---|---|---|---|
| Pollutant | Emissions (tpy) | Pollutant | Cancer Toxicity Weight | Pollutant | Cancer Risk Approximation (in-a-million) |
| **Northbrook, Illinois (Cook County) - NBIL** | | | | | |
| Benzene | 1,391.32 | Formaldehyde | 1.48E-02 | Formaldehyde | 25.68 |
| Formaldehyde | 1,135.39 | Benzene | 1.09E-02 | Naphthalene | 5.30 |
| Ethylbenzene | 756.81 | 1,3-Butadiene | 6.47E-03 | Acetaldehyde | 5.20 |
| Acetaldehyde | 623.34 | Hexavalent Chromium | 4.02E-03 | Benzene | 3.68 |
| 1,3-Butadiene | 215.66 | Naphthalene | 3.60E-03 | Carbon Tetrachloride | 3.59 |
| Tetrachloroethylene | 187.87 | Arsenic, PM | 2.64E-03 | Arsenic | 2.66 |
| Naphthalene | 105.84 | Ethylbenzene | 1.89E-03 | Acenaphthene | 2.21 |
| Trichloroethylene | 99.56 | POM, Group 2b | 1.81E-03 | Fluorene | 1.69 |
| Dichloromethane | 35.41 | Acetaldehyde | 1.37E-03 | 1,2-Dichloroethane | 1.62 |
| POM, Group 2b | 20.53 | POM, Group 2d | 1.19E-03 | 1,3-Butadiene | 0.88 |
| **Schiller Park, Illinois (Cook County) - SPIL** | | | | | |
| Benzene | 1,391.32 | Formaldehyde | 1.48E-02 | Formaldehyde | 43.00 |
| Formaldehyde | 1,135.39 | Benzene | 1.09E-02 | Benzene | 5.78 |
| Ethylbenzene | 756.81 | 1,3-Butadiene | 6.47E-03 | Acetaldehyde | 5.21 |
| Acetaldehyde | 623.34 | Hexavalent Chromium | 4.02E-03 | Carbon Tetrachloride | 3.85 |
| 1,3-Butadiene | 215.66 | Naphthalene | 3.60E-03 | 1,3-Butadiene | 3.80 |
| Tetrachloroethylene | 187.87 | Arsenic, PM | 2.64E-03 | 1,2-Dichloroethane | 2.13 |
| Naphthalene | 105.84 | Ethylbenzene | 1.89E-03 | Trichloroethylene | 1.26 |
| Trichloroethylene | 99.56 | POM, Group 2b | 1.81E-03 | Hexachloro-1,3-butadiene | 0.24 |
| Dichloromethane | 35.41 | Acetaldehyde | 1.37E-03 | | |
| POM, Group 2b | 20.53 | POM, Group 2d | 1.19E-03 | | |

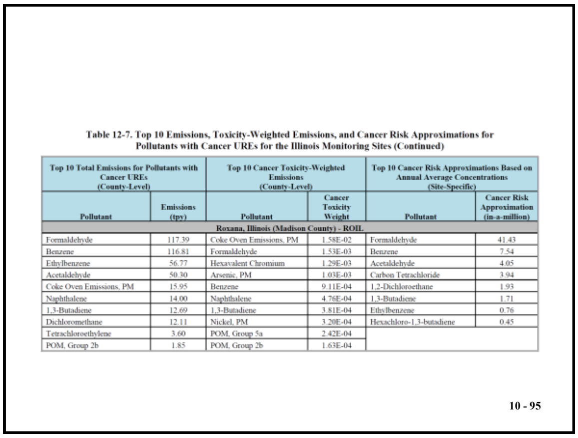
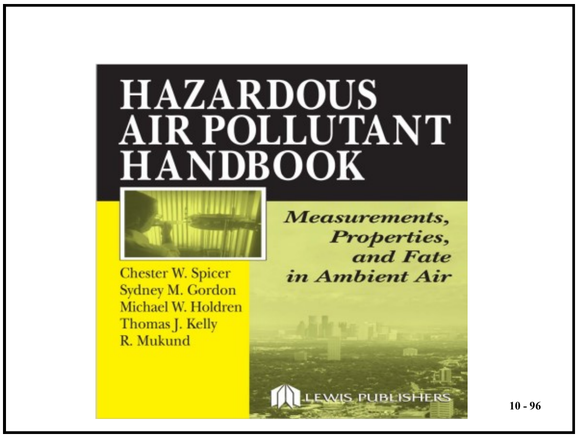


Table 12-7. Top 10 Emissions, Toxicity-Weighted Emissions, and Cancer Risk Approximations for Pollutants with Cancer UREs for the Illinois Monitoring Sites (Continued)

| Top 10 Total Emissions for Pollutants with Cancer UREs (County-Level) | | Top 10 Cancer Toxicity-Weighted Emissions (County-Level) | | Top 10 Cancer Risk Approximations Based on Annual Average Concentrations (Site-Specific) | |
|---|---|---|---|---|---|
| Pollutant | Emissions (tpy) | Pollutant | Cancer Toxicity Weight | Pollutant | Cancer Risk Approximation (in-a-million) |
| **Roxana, Illinois (Madison County) - ROIL** | | | | | |
| Formaldehyde | 117.39 | Coke Oven Emissions, PM | 1.58E-02 | Formaldehyde | 41.43 |
| Benzene | 116.81 | Formaldehyde | 1.53E-03 | Benzene | 7.54 |
| Ethylbenzene | 56.77 | Hexavalent Chromium | 1.29E-03 | Acetaldehyde | 4.05 |
| Acetaldehyde | 50.30 | Arsenic, PM | 1.03E-03 | Carbon Tetrachloride | 3.94 |
| Coke Oven Emissions, PM | 15.95 | Benzene | 9.11E-04 | 1,2-Dichloroethane | 1.93 |
| Naphthalene | 14.00 | Naphthalene | 4.76E-04 | 1,3-Butadiene | 1.71 |
| 1,3-Butadiene | 12.69 | 1,3-Butadiene | 3.81E-04 | Ethylbenzene | 0.76 |
| Dichloromethane | 12.11 | Nickel, PM | 3.20E-04 | Hexachloro-1,3-butadiene | 0.45 |
| Tetrachloroethylene | 3.60 | POM, Group 5a | 2.42E-04 | | |
| POM, Group 2b | 1.85 | POM, Group 2b | 1.63E-04 | | |



HAZARDOUS
AIR POLLUTANT
HANDBOOK

*Measurements, Properties, and Fate in Ambient Air*

Chester W. Spicer
Sydney M. Gordon
Michael W. Holdren
Thomas J. Kelly
R. Mukund

LEWIS PUBLISHERS

# Chapter 10 Questions

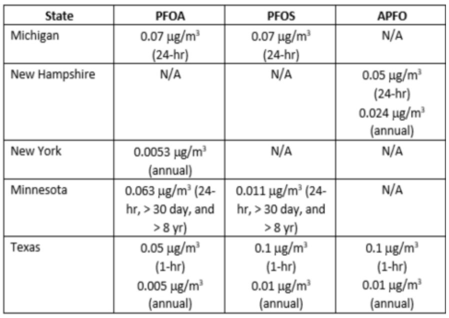
# Chapter 10 Questions/Answers

1. True or False: Air toxics programs have long used monitoring to evaluate the concentration of chemicals in air.

- Answer: True:
- In general, monitoring (sampling and analysis) results may help:
- Identify and estimate current exposures to ambient concentrations of air toxics (outdoor and/or indoor) at a specific location of concern (e.g., a school or neighborhood). As an example, EPA tracks ozone concentrations at numerous locations around the country, with results available over the Internet (http://www.epa.gov/airnow/) for many locations, virtually in real-time. As another example, air toxics monitoring can be used to evaluate the impacts of a specific source on a nearby receptor ("source-oriented" monitoring).
- Develop or refine values for specific parameters needed by air dispersion models (for example, study-specific release data, meteorological conditions).

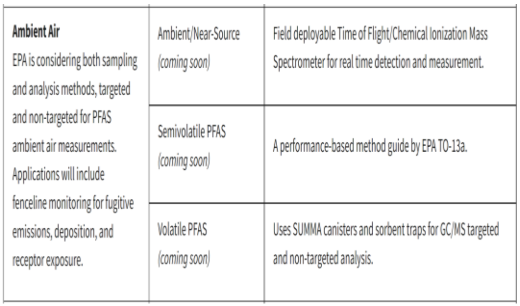
- Validate the predictions of a model in specified circumstances (e.g. validate that the location of highest exposure predicted by the model is correct, which increases confidence that a maximally exposed subpopulation has been identified – may be difficult to do without a very dense monitoring network).
- Track trends in air quality levels (e.g. to determine whether air pollution programs have generally been effective at reducing exposures).
- Identify gaps in emissions inventories (e.g., monitoring identifies an airborne chemical that is not reported in existing emissions inventories) or close gaps that might be present in existing data (e.g., concentrations of specific air toxics in specific releases).
- Determine compliance with air toxics legal requirements (e.g., permit limits at a factory, emissions limitations on motor vehicles).
- Gather data in support of enforcement actions.

- 2. How many States have begun to set their own an ambient air concentration for PFAS? Choose from the following:
- a) 5
- b) 10
- c) 15
- d) none
- Answer a) 5
- Michigan
- New Hampshire
- New York
- Minnesota
- Texas

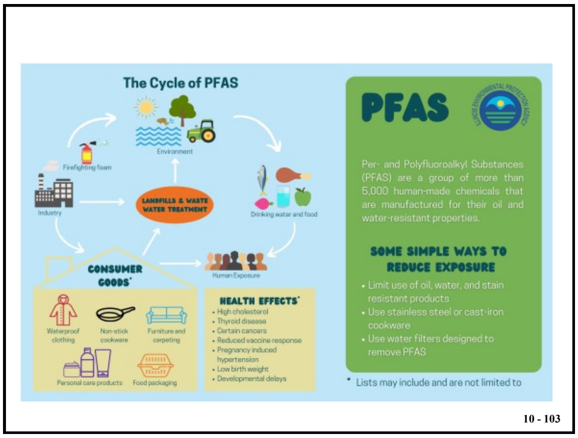


| State | PFOA | PFOS | APFO |
|---|---|---|---|
| Michigan | 0.07 µg/m³ (24-hr) | 0.07 µg/m³ (24-hr) | N/A |
| New Hampshire | N/A | N/A | 0.05 µg/m³ (24-hr)<br>0.024 µg/m³ (annual) |
| New York | 0.0053 µg/m³ (annual) | N/A | N/A |
| Minnesota | 0.063 µg/m³ (24-hr, > 30 day, and > 8 yr) | 0.011 µg/m³ (24-hr, > 30 day, and > 8 yr) | N/A |
| Texas | 0.05 µg/m³ (1-hr)<br>0.005 µg/m³ (annual) | 0.1 µg/m³ (1-hr)<br>0.01 µg/m³ (annual) | 0.1 µg/m³ (1-hr)<br>0.01 µg/m³ (annual) |

# PFOA's & PFOS's Ambient Sampling Methods



| | | |
|---|---|---|
| **Ambient Air**<br>EPA is considering both sampling and analysis methods, targeted and non-targeted for PFAS ambient air measurements. Applications will include fenceline monitoring for fugitive emissions, deposition, and receptor exposure. | Ambient/Near-Source<br>*(coming soon)* | Field deployable Time of Flight/Chemical Ionization Mass Spectrometer for real time detection and measurement. |
| | Semivolatile PFAS<br>*(coming soon)* | A performance-based method guide by EPA TO-13a. |
| | Volatile PFAS<br>*(coming soon)* | Uses SUMMA canisters and sorbent traps for GC/MS targeted and non-targeted analysis. |



## The Cycle of PFAS

**HEALTH EFFECTS***

- High cholesterol
- Thyroid disease
- Certain cancers
- Reduced vaccine response
- Pregnancy induced hypertension
- Low birth weight
- Developmental delays

## PFAS

Per- and Polyfluoroalkyl Substances (PFAS) are a group of more than 5,000 human-made chemicals that are manufactured for their oil and water-resistant properties.

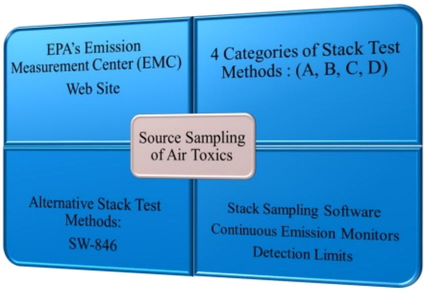
**SOME SIMPLE WAYS TO REDUCE EXPOSURE**

- Limit use of oil, water, and stain resistant products
- Use stainless steel or cast-iron cookware
- Use water filters designed to remove PFAS

* Lists may include and are not limited to

# Chapter Eleven

## *Source Sampling of Air Toxics*



EPA's Emission Measurement Center (EMC) Web Site

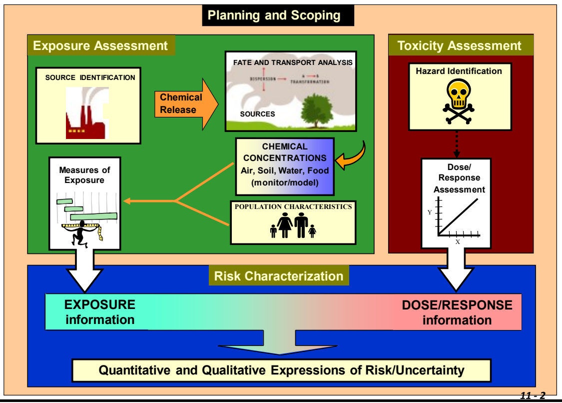
4 Categories of Stack Test Methods : (A, B, C, D)

Source Sampling of Air Toxics

Alternative Stack Test Methods: SW-846

Stack Sampling Software
Continuous Emission Monitors
Detection Limits

## The Detailed Air Toxics Risk Assessment Process



Planning and Scoping

Exposure Assessment

SOURCE IDENTIFICATION

Chemical Release

FATE AND TRANSPORT ANALYSIS

CHEMICAL CONCENTRATIONS Air, Soil, Water, Food (monitor/model)

POPULATION CHARACTERISTICS

Measures of Exposure

Toxicity Assessment

Hazard Identification

Dose/ Response Assessment

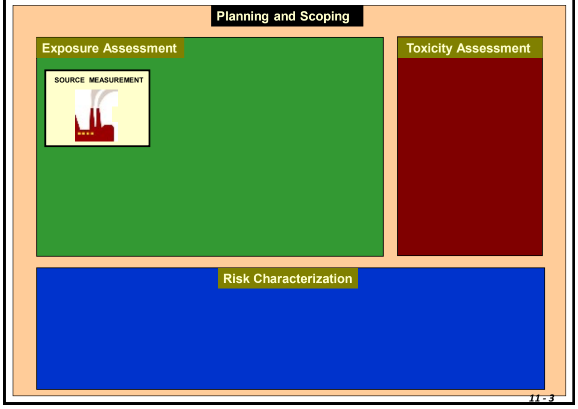
Risk Characterization

EXPOSURE information

DOSE/RESPONSE information

Quantitative and Qualitative Expressions of Risk/Uncertainty

## The Detailed Air Toxics Risk Assessment Process



Planning and Scoping

Exposure Assessment

SOURCE MEASUREMENT

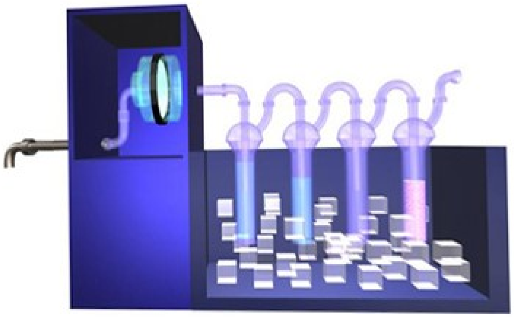
Toxicity Assessment

Risk Characterization

## Source Testing Circa 1970's

## Source Testing Circa 1970's

## EPA's Test Methods Numbering System



## EPA's Test Methods Numbering System

- **Between 1 and 100**: New Source Performance Standards (NSPSs).
  - These methods are found in 40 CFR Part 60, Appendix A.
- The **100 series**: National Emission Standards for Hazardous Air Pollutants (NESHAPs).
  - These methods are found in 40 CFR Part 61, Appendix B.
- The **200 series**: State Implementation Plans (SIPs).
  - These methods are found in 40 CFR Part 51, Appendix M.
- The **300 series**: Maximum Acievable Control Technology (MACT) standards.
  - These methods are found in 40 CFR Part 63, Appendix A

## Objectives of Stack Testing for HAP's or Any Pollutant

- The objectives of performing a stack test is to determine the pollutant mass rate (pmr) or emission rate (E) of pollutant going up the stack to:
  - determine whether compliance limits are being met,
  - Assist in establishing emission standards &
  - For screening tests that will provide a preliminary indication of levels of pollution.

https://www.epa.gov/compliance/national-emission-standards-hazardous-air-pollutants-compliance-monitoring

## What is the Driving Force

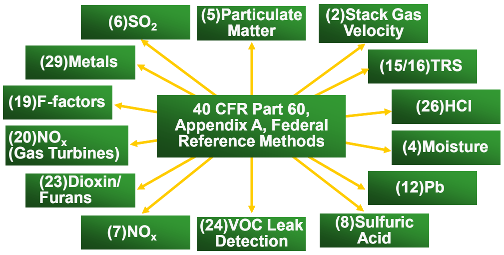
- New Source Performance Standards (NSPS-1970)
- National Emission Standards for Hazardous Air Pollutants
  - NESHAPS pre 1990 CAAA
  - NESHAPS post 1990 CAAA

## Where Do We Find the Test Methods?

- Federal Test Methods- Methods are those (Federal Reference Methods and others) specified in the applicable standards as the test methods used to demonstrate compliance with emission limits or to quantify emissions in meeting regulatory initiatives.
- EPA's Emission Measurement Center Website:
- www.epa.gov/ttn/emc/tmethods.html

## 40 CFR Part 60
## New Source Performance Standards Methods
## (00 Series, Appendix A)

## New Source Performance Standard (NSPS) Reference Methods-00 Series



40 CFR Part 60, Appendix A, Federal Reference Methods

(6)$SO_2$

(5)Particulate Matter

(2)Stack Gas Velocity

(29)Metals

(15/16)TRS

(19)F-factors

(26)HCl

(20)$NO_x$ (Gas Turbines)

(4)Moisture

(23)Dioxin/ Furans

(12)Pb

(7)$NO_x$

(24)VOC Leak Detection

(8)Sulfuric Acid

- 40 CFR Part 60 Performance Specification Test (PST) Methods (00 Series)
- 40 CFR Part 61 State Implementation Plan (SIP) Methods (200 Series, Appendix M)

## Performance Specification Test (PSTs)-00 Series

**40 CFR Part 60, Appendix B, Federal Reference Methods**

- (6)Vs/PMR
- (5)TRS
- (2)$SO_2$/$NO_2$
- (13)HCl
- (15)FTiR
- (11)PM
- (1)Opacity
- (10)Metals
- (4)CO
- (9)GC
- (12)Hg
- (7)$H_2S$
- (3)$CO_2$/$O_2$
- (8)VOCs

## State Implementation Plan (SIP)- 200 Series

**CFR Part 51, Appendix M**

- (201/201A) PM-10
- (205)Gas Dilution System Verification
- (203A,B,C) VE Observation
- (206)Ammonia
- (204 A-F) VOC Capture Efficiency
- (202) Condensibles
- (203) Transmissiometer for Opacity
- (207)Isocynates

## National Emission Standards for Hazardous Air Pollutants (NESHAPs)

- NESHAPS pre 1990 CAA Amendments
  - 40 CFR Part 61
  - 100 Series
  - Appendix B
- NESHAPS post 1990 CAA Amendments
  - 40 CFR Part 63 (MACTs)
  - 300 Series
  - Appendix A

## National Emission Standards For Hazardous Air Pollutants (NESHAPs)- 100 Series

**40 CFR Part 61, Appendix B, NESHAP**

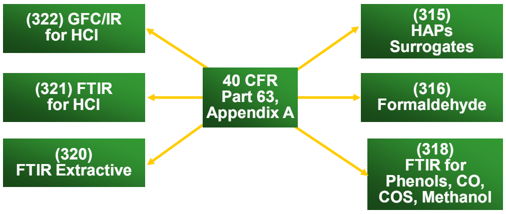
- (101/101A) Hg in air Streams
- (102) Hg in Hydrogen Streams
- (104) Revised Be Screening
- (108A,B,C) As in Ore Samples
- (106) Vinyl Chloride
- (110) Benzene
- (115) Radon-222
- (114) Radionuclides

## Maximum Achievable Control Technology (MACT)- 300 Series

**40 CFR Part 63, Appendix A**

- (305) Compound Specific Liquid Waste
- (301) Data Validation
- (302) GC/MS
- (303) Coke Oven Doors
- (304A, B) Biodegradation Rate
- (310) Hexane in EPDM Rubber
- (307)VOCs for Solvent Degreasers
- (309) Reserved
- (306) Hexavalent Chromium
- (308) Methanol

## Maximum Achievable Control Technology (MACT)-300 Series



40 CFR Part 63, Appendix A

(322) GFC/IR for HCl

(321) FTIR for HCl

(320) FTIR Extractive

(315) HAPs Surrogates

(316) Formaldehyde

(318) FTIR for Phenols, CO, COS, Methanol

## EPA's Categories of Stack Test Methods

- **Category A**: Methods proposed or promulgated in Federal Register
  - – Compliance Methods for 40 CFR Parts 60, 61, & 63
  - – Use the # Series: 00 – 100 – 200 - 300
- **Category B**: Source category approved alternative methods
  - – Are approved alternatives to the methods required by 40 CFR Parts 60, 61 and 63
  - – Methods may be used by sources for determining compliance with the requirements of these Parts without further EPA approval.

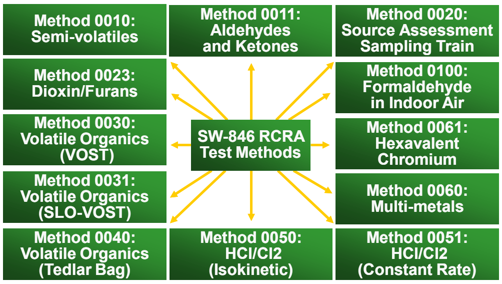
## EPA's Categories of Stack Test Methods

- **Category C**: Other test methods which have not yet been subject to Federal rulemaking process.
  - – Considered as alternative methods to meet Federal requirements under 40 CFR Parts 60, 61, and 63. However, they must be approved as alternatives before a source may use them for this purpose.
- **Category D**: Historic Methods - methods that were categorized as conditional test methods before EMC's method categories were revised.
  - – Category is closed & no new methods will be added.
  - – Must be approved as alternatives before a source may use them to meet 40 CFR Part 60, 61, and 63.

## Resource Conservation And Recovery Act (RCRA)

- Many of the stack test methods for criteria pollutants were combined with analytical methods for hazardous materials to establish sampling methods for HAPs.
- SW-846 is the compendium of analytical and test methods used in determining regulatory compliance under RCRA.
- Can be found at EPA's EMC web page

## SW-846 Stack Test Methods



SW-846 RCRA Test Methods

Method 0010: Semi-volatiles

Method 0011: Aldehydes and Ketones

Method 0020: Source Assessment Sampling Train

Method 0023: Dioxin/Furans

Method 0100: Formaldehyde in Indoor Air

Method 0030: Volatile Organics (VOST)

Method 0061: Hexavalent Chromium

Method 0031: Volatile Organics (SLO-VOST)

Method 0060: Multi-metals

Method 0040: Volatile Organics (Tedlar Bag)

Method 0050: HCl/Cl2 (Isokinetic)

Method 0051: HCl/Cl2 (Constant Rate)

## Stack Testing of VOCs

- The majority of CAA Section 112 HAPs are volatile organic compounds (VOC)
- Testing for volatile organic compounds is often confusing for a variety of reasons:
  - – There is no straightforward way to measure the VOC emissions since there is no way to separate VOCs by vapor pressure.
  - – All of the reference methods for organic compounds have inherent limitations that restrict their applicability, and
  - – No one method can satisfy characterization of organic emissions from an industrial source.

## Definitions

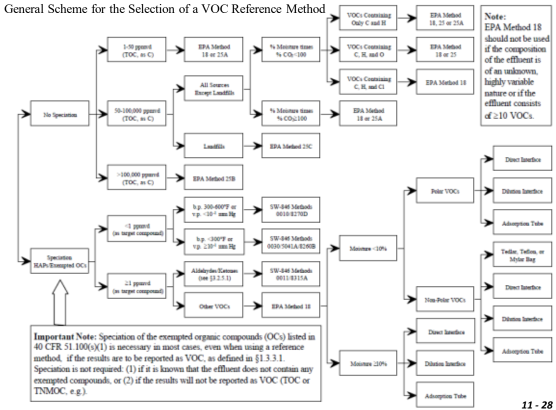
- Volatile Organic Compounds (VOCs): An organic compound that participates in atmospheric photochemical reactions; (excluding exempted compounds listed in 40 CFR §51.100(s)(1)).
  - VOCs usually have high vapor pressures (greater than 0.1 mm Hg).
- Semi-volatile Organic Compounds (SVOC): This definition can vary depending on the test method. Usually SVOCs are organic compounds with vapor pressure between 0.1 and $10^{-7}$ mm Hg.

## Definitions

- Total Organic Compounds (TOCs): The sum of all volatile organic compounds and all exempted compounds.
- Total Hydrocarbons (THCs): The subset of total organic compounds containing only carbon and hydrogen.
- Total Non-Methane Organic Compounds (TNMOCs): The sum of all volatile organic compounds and all exempted compounds listed in 40 CFR§51.100(s)(1), except methane.

## Selection of VOC Test Methods

- Pennsylvania Department of Environmental Protection, "*Source Testing Manual*" (Revision 3.3), provides a general scheme for the selection of a VOC test method.
- The selection scheme does not address all of the possibilities.
- Scheme follows 2 different paths:
  - Speciated VOCs
  - Non-speciated VOCs


General Scheme for the Selection of a VOC Reference Method

**Note:** EPA Method 18 should not be used if the composition of the effluent is of an unknown, highly variable nature or if the effluent consists of ≥10 VOCs.

**Important Note:** Speciation of the exempted organic compounds (OCs) listed in 40 CFR 51.100(s)(1) is necessary in most cases, even when using a reference method, if the results are to be reported as VOC, as defined in §1.3.3.1. Speciation is not required: (1) if it is known that the effluent does not contain any exempted compounds, or (2) if the results will not be reported as VOC (TOC or TNMOC, e.g.).

http://www.depgreenport.state.pa.us/elibrary/GetDocument?docId=7737&DocName=SOURCE%20TESTING%20MANUAL%20%28REVISION%203.3%29.PDF

## No Speciation VOC Methods

- Method 18 (VOC by gas chromatograph (GC)): Based on separating components of a gas mixture in a GC column and measuring separated components with suitable detector (i.e., Flame Ionization Detector (FID).
  - Applicable to VOC concentrations greater than 1ppm in the sampled gas.
- Method 25 (non-methane organic compounds) applies to the measurement of VOCs as total gaseous non-methane organics, condensable and non-condensable, as carbon in source emissions. (All compounds are converted to methane before measuring with a FID.)

## No Speciation VOC Methods

- Method 25A (organic concentration using a FID): This method is applicable to total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or aromatic hydrocarbons.
  - Results are expressed in terms of volume concentration of propane (or other appropriate organic calibration gas) or in terms of carbon.
- Method 25B (organic concentration using an infrared analyzer)
- Method 25C (non-methane organic compounds from landfills).

# Federal Reference Method 18

## General GC Methodology

## Canister Stack Sampling

## Method 18

Gas Chromatography (GC)

- Generic GC method
- Determines the concentration of discrete organic compounds in the sample
- Applies to the analysis of approximately 90% of total gaseous organics emitted from an industrial source

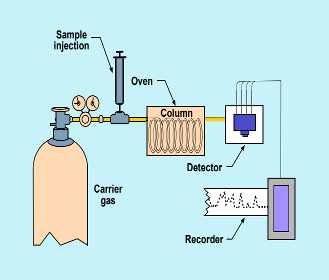
## Applicability & Principle

- Applicability: FRM 18 will not determine compounds that are
  - Polymeric (high molecular weight)
  - Analytes that can polymerize before analysis
  - Analytes that have very low vapor pressure at stack or instrument conditions
- Principle: Based on separating components of a gas mixture in a gas chromatographic column and measuring separated components with suitable detector

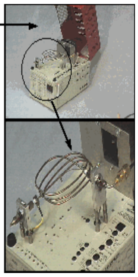
## FRM 18 Sampling Methods

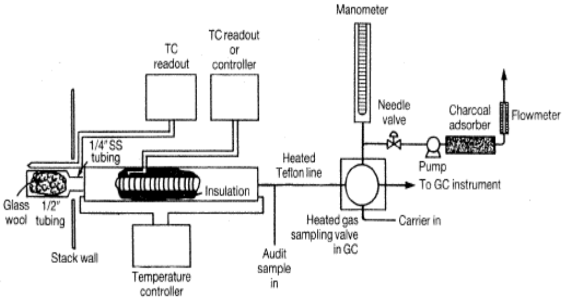
- Direct Interface
- Integrated bag
- Glass sampling flask
- Adsorbent tubes
  - Charcoal
  - Silica Gel
  - Florisil®
  - CarboTrap® 300
  - Tenax® TA

## Method 18

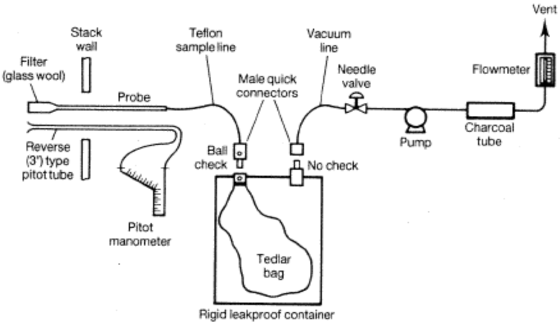


"Virtual Oven" shown mounted on 110 chassis. Column is connected to heated injector and detector blocks for higher temperature samples.





Method 18 Direct Interface Sampling



Method 18 Integrated Bag Sampling System

## Applicability of Organic Sampling Methods

| FRM | Conc. Range |
|---|---|
| FRM 25 B | 0.5-10 % |
| FRM 25 | 50 ppm-10 % |
| FRM 18 | 1 ppm – 1 % |
| FRM 25 A | 50 ppm – 1 % |
| Method 25C | < 1 ppm |
| (CTM 035) SCAQMD | < 50 ppm(C) or 25 ppm(C) in trap |

## Applicability of Methods

| | FRM 18 | FRM 25 | FRM 25A |
|---|---|---|---|
| Measures… | VOCs | TGNMO | THC |
| Principle… | GC/MD | GC/FID | FID |
| Carbon Resp… | 1:1 | 1:1 | Var. |
| Results Exp As.. | VOC | As C | Cal Gas |

## Speciation VOC Methods

- All of the following methods are from SW-846:
  - Method 0010 for semi-volatile organics
  - Method 0011 is used for aldehydes and ketones.
  - Method 0030 is used for volatile organic compounds (compounds with boiling points less than 100$^{O}$C but normally above 30$^{O}$C).

## General Classification of HAPs

| Classification | Vapor Pressure mm Hg | Boiling Point °C |
|---|---|---|
| Volatiles (VV/V) | > $10^{-1}$ | < 100° C |
| Semi-volatiles (SV) | $10^{-1}$ to $10^{-7}$ | 100 - 300° C |
| Particles (NV) | < $10^{-7}$ | > 300° C |

## Number of HAPs in each Volatility Class

| Volatility Class | No. of HAPs in Class |
|---|---|
| VVOC | 15 |
| VVINC | 6 |
| VOC | 82 |
| VINC | 3 |
| SVOC | 64 |
| SVINC | 2 |
| NVOC | 5 |
| NVINC | 12 |

## Definition of Semi-Volatiles

- Semi-volatile compounds are those with boiling points greater than 100°C
- Three major groups
  - Polycyclic aromatic hydrocarbons (PAHs)
  - Dioxin and furans (D/Fs)
  - Biphenyls (PCBs)

## Semi-Volatile Compound Boiling Points(°C)

- Bis(chloromethyl)ether - 104°C
- Chlorobenzene - 132°C
- Benzyl Chloride - 176°C
- Hexachlorobutadiene - 215°C
- 2,4,6-Trichlorophenol - 245°C
- 3,3’-Dichlorobenzidine - 402°C

## SW-846, Method 0010 Sampling and Analysis for Semi-volatile Organic Compounds

## Title III
## Method 0010 Analytes

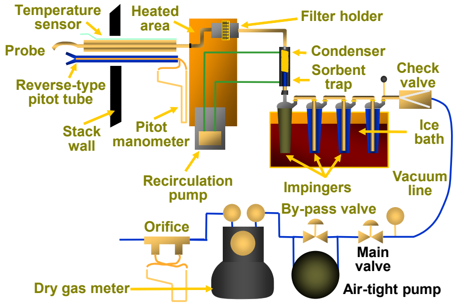
Acetaldehyde
Acetonitrile
Biphenyl
1,3 - Butadiene
Carbonyl Sulfide
Chlorobenzene
Cresols
Cumene
1,4 - Dichlorobenzene
Ethylbenzene
Ethylene Glycol
Ethylene Oxide
Methanol
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Naphthalene
Phenol
Propionaldehyde
Styrene
Toulene
Xylenes (o -, m-, p -)

## Method 0010 Sampling Train and Method 23

- Sample is collected in a sampling train that is similar to FRM 5 for particulates.

1. A high efficiency glass filter is used to collect organic-laden particulates
2. A packed bed of porous polymeric resin (XAD-2™) serves to adsorb semi-volatile organic species, and
3. A series of water filled impingers may collect some semi-volatile organics that pass through the filter and sorbent.

## Method 23 & SW-846 Method 0010 RCRA Sampling Train

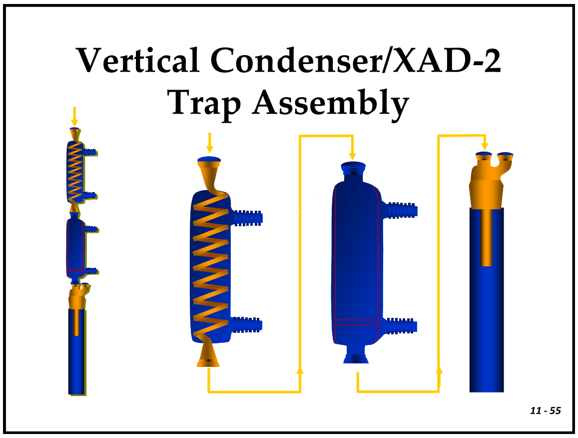


## Method 23 Configuration

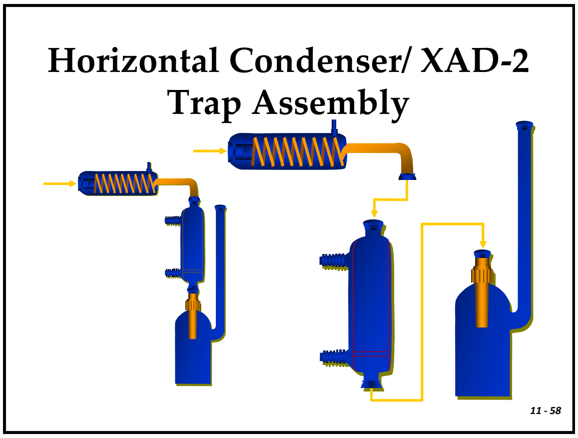
- Same configuration used for PCBs and dioxin/furans
- Collect all in one train for better detection limits
  - 10 µg for PAHs
  - 1 µg for D/F's

## XAD-2 Resin Trap

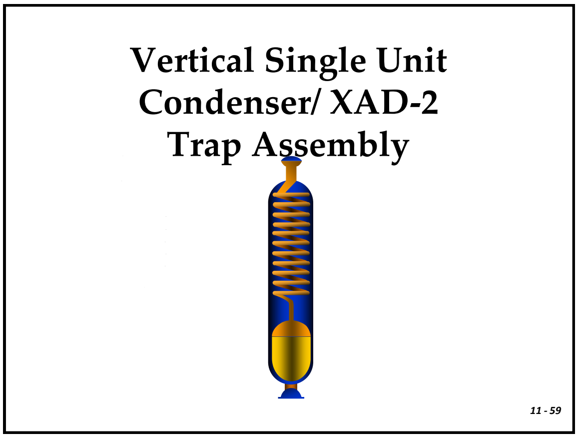
- XAD-2 is a cross-linked styrene-divinylbenzene
  - Organic Polymeric Adsorbent
- Amberlite@ XAD-2 physical characteristics
  - Mesh Size: 20-60
  - Bulk Density: 1.08 g/mL
  - Surface Area: 300 $m^2/g$
    - large surface area
  - Temp. Max: 190°C
    - Therefore, it can't be thermal debsorbed due to breakdown of XAD-2



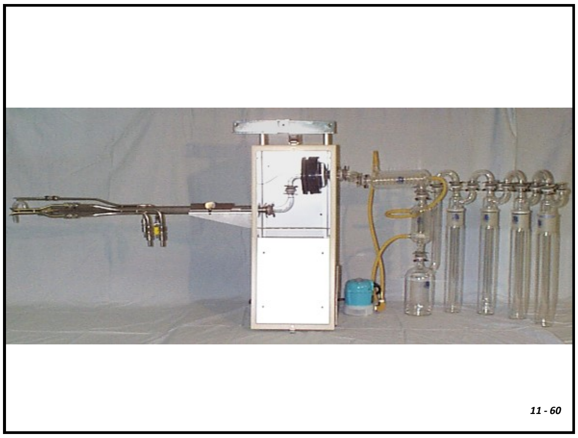
## Vertical Condenser/XAD-2 Trap Assembly



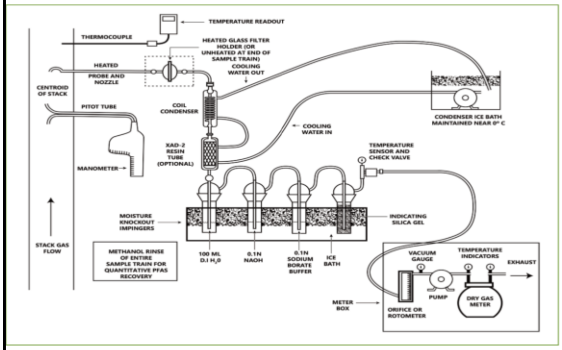
## Horizontal Condenser/ XAD-2 Trap Assembly



## Vertical Single Unit Condenser/ XAD-2 Trap Assembly

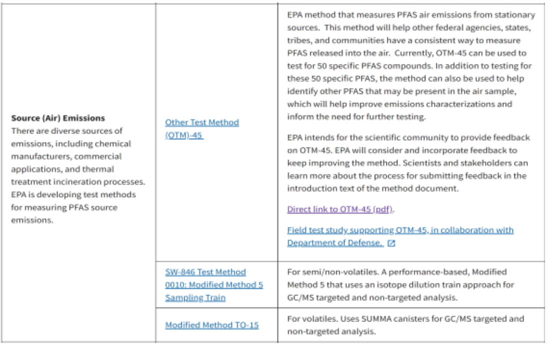


## Schematic of modified EPA Method 5 sampling train for the collection of PFAS compounds



EM Magazine May 2020

## PFOA's & PFOS's Stack Sampling Methods



| | | |
|---|---|---|
| **Source (Air) Emissions**<br>There are diverse sources of emissions, including chemical manufacturers, commercial applications, and thermal treatment incineration processes. EPA is developing test methods for measuring PFAS source emissions. | Other Test Method (OTM)-45 | EPA method that measures PFAS air emissions from stationary sources. This method will help other federal agencies, states, tribes, and communities have a consistent way to measure PFAS released into the air. Currently, OTM-45 can be used to test for 50 specific PFAS compounds. In addition to testing for these 50 specific PFAS, the method can also be used to help identify other PFAS that may be present in the air sample, which will help improve emissions characterizations and inform the need for further testing.<br>EPA intends for the scientific community to provide feedback on OTM-45. EPA will consider and incorporate feedback to keep improving the method. Scientists and stakeholders can learn more about the process for submitting feedback in the introduction text of the method document.<br>Direct link to OTM-45 (pdf).<br>Field test study supporting OTM-45, in collaboration with Department of Defense. |
| | SW-846 Test Method 0010: Modified Method 5 Sampling Train | For semi/non-volatiles. A performance-based, Modified Method 5 that uses an isotope dilution train approach for GC/MS targeted and non-targeted analysis. |
| | Modified Method TO-15 | For volatiles. Uses SUMMA canisters for GC/MS targeted and non-targeted analysis. |

PFAS Analytical Methods Development and Sampling Research | US EPA

## Definition of Volatile Organic Compounds (VOCs)

- Volatile organic compounds (VOCs) are those compounds with boiling points < 100°C, but normally above 30°C
- VOCs with boiling points < 30°C may break through adsorbent

## Volatile Organic Compounds Boiling Points

| | |
|---|---|
| Acrylonitrile(same problem) | 77.0°C |
| Benzene | 80.0°C |
| Carbon Tetrachloride | 77.0°C |
| Chloroform | 60.5°C |

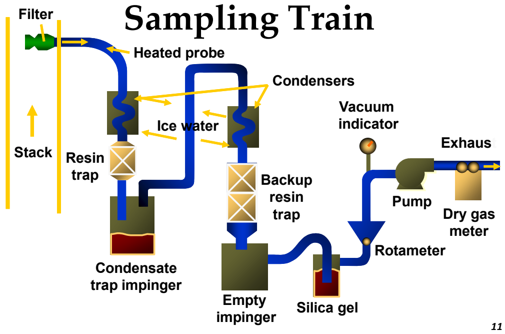
## Method 0030 in SW-846: Applicability

- This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of semi-volatile Principal Organic Hazardous Compounds (POHCs) from incinerator systems

## Title III
## Method 0030 Analytes

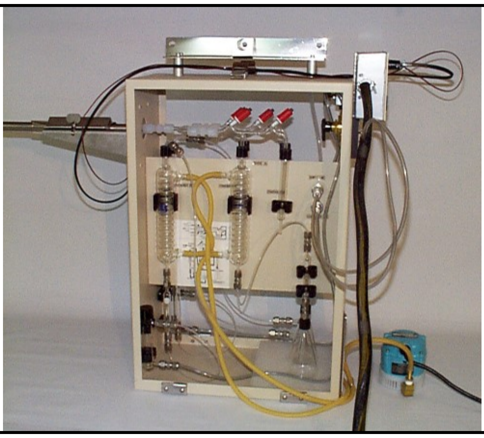
Acrylonitrile
Benzene
Carbon Disulfide
Carbon Tetrachloride
Chloroform
Chloroprene
Ethyl Chloride
Ethylene Dichloride
Methyl Chloride
Methyl Chloroform
Methylene Chloride
Propylene Dichloride
Propylene Oxide
Tetrachloroethylene
Trichloroethylene
Vinyl Acetate
Vinyl Chloride

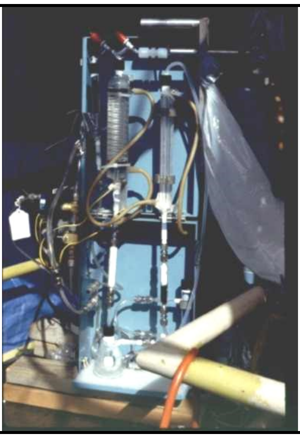
## Method 0030 Sampling Train



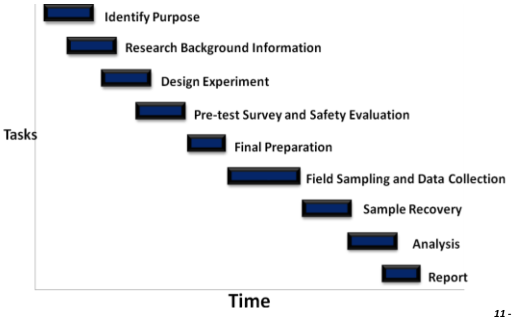
## Tenax® Resin Trap

- Tenax® is 2,6-diphenyl-p-phenylene oxide polymer
- Simultaneous sampling and analysis for polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), and semi-volatile organic compounds (SVOCs) can also be performed along with PCDDs and PCDFs





## Tasks in Planning & Conducting a Source Test



## Detection Limits

- The “limit of detection” is the smallest amount of a substance that an analytical method can reliably distinguish from zero.
  - It is the minimum concentration or amount of a target analyte that produces a signal the tester can distinguish, at a specified confidence level, from the signal produced by a blank.
- The “limit of quantification” is the minimum concentration or amount of an analyte that a method can measure with a specified degree of precision.

## EPA’s EMC Web Site: Software

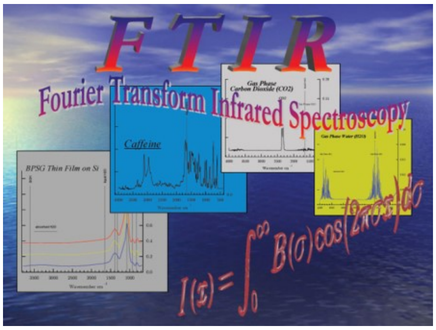
- Test Method Storage and Retrieval software, PC Nomograph program, Manual Emission Testing Cost Model PC program, and CEM cost estimation & methods spreadsheet programs.
- In 2007, EMC added: the Electronic Reporting Tool (ERT).
  - ERT replaces the time-intensive manual preparation emissions test plans and reports prepared by contractors, and the time-intensive manual quality assurance evaluations and documentation performed by State agencies.

## Continuous Emission Monitors: 2 Types

- Extractive CEMs draw a sample from a stack, condition the sample gas (i.e., remove particulate matter and moisture), and analyze for the specific compounds of interest.
- In-situ CEMs provide a measure a measure of target compounds in the stack without sample extraction or conditioning.
  - The components of in-situ CEMs commonly include a light or radiation source, a detector, and a data reduction device mounted on the stack.

## Continuous Emission Monitors

- VOC concentrations are detected using analyzer methods such as flame ionization detection (FID), photo-ionization detection (PID), or non-dispersive infrared (NDIR) absorption.
- These VOC analyzers do not specifically identify VOCs nor do they respond equally to all VOCs. They only provide a measure of the relative VOC concentration of the mixture of compounds.



## FTIR Background

- Wavelength of light absorbed is characteristic of the chemical bond
- FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint"
- The infrared spectrum of a mixture contains the superimposed spectra of each mixture component
- An FTIR CEM provides the capability to continuously measure multiple components in a sample using a single analyzer

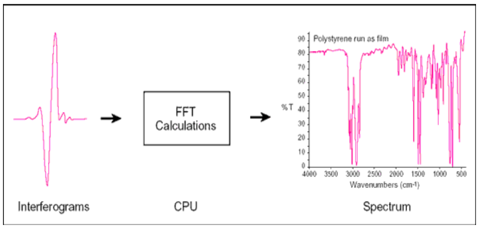
## FTIR System

- Instrument to measure spectra in the mid-infrared spectral region (500 to 4000 cm-1)
  - Infrared source
  - Interferometer
  - Sample gas cell
  - Infrared detector
  - Computer

## FTIR Interferences

- Compound Interferences In The Infrared
  - Water
  - Carbon Monoxide
  - Carbon Dioxide
  - Particulate Matter

## FTIR



*An illustration of how an interferogram is Fourier transformed to generate a single beam infrared spectrum.*

https://www3.epa.gov/ttn/emc/ftir/index.html

## Chapter 11 Question

1. The resin that is used to trap dioxin and furans in Method 0023 is:

a. Tenax®-GC
b. XAD-7®
c. Tenax®-TA
d. XAD-2®

## Chapter 11 Question/Answer

- 1. The resin that is used to trap dioxin and furans in Method 0023 is:

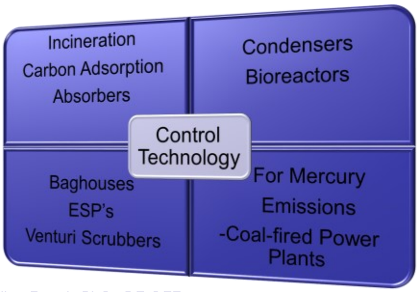
a. Tenax®-GC
b. XAD-7®
c. Tenax®-TA
d. XAD-2®

- Answer d).

- Amberlite® XAD-2 is a polyaromatic (styrene-divinylbenzene) adsorbent resin commonly used for adsorbing hydrophobic compounds up to MW 20,000: phenols, organic removal, surfactants, aroma compounds, antibiotic recovery. It is one of the most used adsorbents for dioxin/furan sampling. The nonionic macroreticular resin that adsorbs and releases analytes through hydrophobic and polar interactions is usually used under isocratic conditions.

# Chapter Twelve

*Air Toxics Controls for Stationary Sources*



Incineration
Carbon Adsorption
Absorbers

Condensers
Bioreactors

Control Technology

Baghouses
ESP's
Venturi Scrubbers

For Mercury Emissions
-Coal-fired Power Plants

*By: William Franek, Ph.D., P.E.,DEE*

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## Control Techniques For HAP's

| | **Organic Vapors** | **Inorganic Vapors** | **Particulate Matter** | **SOx and NOx** |
|---|---|---|---|---|
| Incineration | X | | | |
| Adsorption | X | | | |
| Condensation | X | | | |
| Absorption | X | X | | X |
| Filtration | | | X | |
| Electrostatic Precipitation | | | X | |
| Wet Scrubbing | X | X | X | X |
| Combustion Modification | | | | X |
| Chemical Reductions | | | | X |
| Bio-filtration | X | X | | |

---

## Types of Control Technologies for Gaseous Hazardous Air Pollutants

- **Thermal Incineration (Oxidation)**
- **Catalytic Incineration**
- **Flares**
- **Boilers/Process Heaters**
- **Adsorption**
- **Absorption**
- **Condensers**
- **Biofilters**

---

## Thermal Incineration (Oxidation)

- VOC-laden air stream is heated to temperatures several hundred degrees Fahrenheit above the auto-ignition temperatures of the HAP/VOC compounds that need to be oxidized.
- Due to these very high temperatures, thermal oxidizers are refractory-lined combustion chambers (also called fume incinerators)

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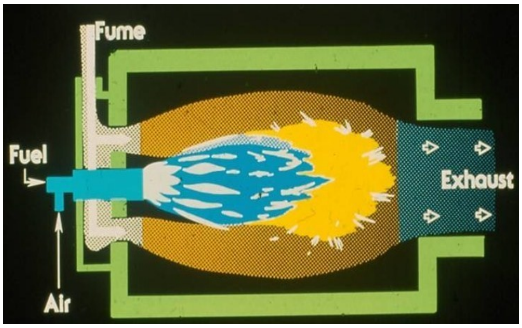
## Thermal Incineration (Oxidation)



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## Thermal Incineration (Oxidation)

- The HAP/VOC-laden gas stream is held at this temperature for residence times ranging from a fraction of a second to more than two seconds.
- Temperatures of the exhaust gas from the refractory-lined combustion chambers are often 1,000 to 2,000°F.
- Thermal oxidizers usually provide VOC destruction efficiencies that exceed 95% and often exceed 99%.

## Thermal Incineration (Oxidation)

- One limitations of thermal oxidizers is the large amount of fuel required to heat the gas stream to the temperature necessary for high-efficiency HAP/VOC destruction.
- Heat exchangers are used to recover some of this heat. A recuperative heat exchanger. has a heat recovery efficiency ranging from 30 to 60% depending on the size of the unit.

## Thermal Incineration (Oxidation)

- Some types of thermal oxidizers use large regenerative beds for heat exchange. These beds have heat recovery efficiencies up to 95%.
- Regenerative thermal oxidizers (RTOs) require less fuel to maintain the combustion chamber at the necessary temperature.

## Thermal Incineration (Oxidation)

- Thermal oxidizers can be used for almost any HAP/VOC compound in a gas streams.
- It can handle VOC concentrations in a range of less than 10 ppm up to the very high concentrations approaching 10,000 ppm.

## LEL and Thermal Incinerators

- Thermal oxidizers are rarely used on gas streams having VOC concentrations exceeding approximately 25% of the lower explosive limit (LEL).
- This limit is imposed due to the possibility that a short-term concentration spike would exceed the LEL, and the gas stream would explode.
- The 25% LEL limit depends on the actual gas constituents and usually is in the 10,000 to 25,000 ppm range (1% to 2.5%).

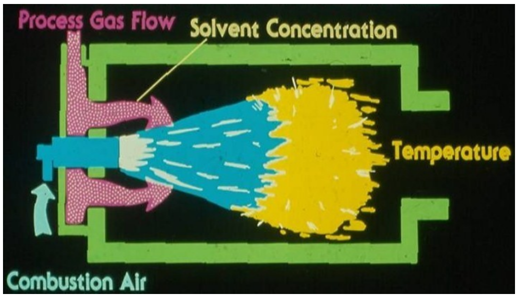
## Limits of Flammability of Combustible Organic Compounds in Air at Atmospheric Pressure, Room Temperature

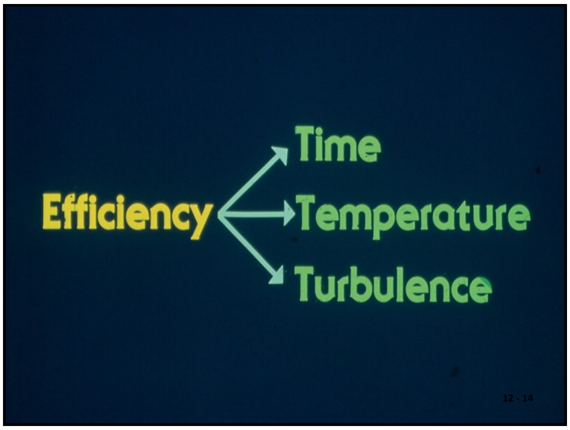
| Compound | Molecular Weight | LEL (volume %) | UEL (volume %) |
|---|---|---|---|
| Methane | 16.04 | 5.00 | 15.00 |
| Ethane | 30.07 | 3.00 | 12.50 |
| Propane | 44.09 | 2.12 | 9.35 |
| Butane | 58.12 | 1.86 | 8.41 |
| Pentane | 72.15 | 1.40 | 7.80 |
| Hexane | 86.17 | 1.18 | 7.40 |
| Octane | 114.23 | 0.95 | |
| Nonane | 128.25 | 0.83 | |
| Decane | 142.28 | 0.77 | |
| Ethylene | 28.05 | 2.75 | 28.60 |
| Propylene | 42.08 | 2.00 | 11.10 |
| Acetylene | 26.04 | 2.50 | 80.00 |
| Cyclohexane | 84.16 | 1.26 | 7.75 |
| Benzene | 78.11 | 1.40 | 7.10 |
| Toluene | 92.13 | 1.27 | 6.75 |

## Additional LEL Information

- Additional flammability characteristics of combustible organic compounds can be found on Table 4.2.1 in “Control Technologies for Hazardous Air Pollutants” by USEPA at the following web site:
- https://nepis.epa.gov
- The manual is a revision of the first (1986) edition of the Evaluation of *Control Technologies for Hazardous Air Pollutants*, which incorporated information from numerous sources into a single, self-contained reference source.

## Thermal Incineration Design Parameters

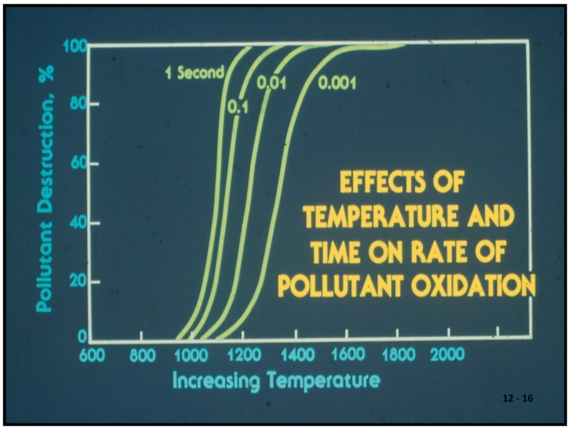




Efficiency → Time
Efficiency → Temperature
Efficiency → Turbulence

## Turbulence

- Complete mixing of oxygen and VOC/HAP is required for chemical oxidation reactions to occur.
- Turbulence is generally defined by the Reynolds number and is calculated as follows: $R_e = DV\varrho/\mu$
- The Reynolds Number should be greater than 10,000 to ensure complete turbulence.



EFFECTS OF TEMPERATURE AND TIME ON RATE OF POLLUTANT OXIDATION

## General Incineration Design Ranges

| | |
|---|---|
| **Temperature** | **1300° - 1500°F** |
| **Retention Time** | **0.3 – 0.5 seconds** |

## Destruction Efficiencies

- VOC/HAP destruction efficiency depends on design criteria (i.e. chamber temperature, residence time, inlet VOC concentration, compound type, and degree of mixing).
- Typical thermal incinerator design efficiencies range from 98 to 99.99%, depending on system requirements and characteristics of the contaminated stream.
- The typical design conditions to meet 98% or greater control or a 20 ppm by volume compound exit concentration are 1600 ° F combustion temperature and 0.75 second residence time.

## Efficient Operating Conditions for Incinerations

- **Sufficient Residence Time**
- **No Dependency**
- **Low fuel/Oxygen Rate**
- **Unaltered Flame and Radiation Pattern**
- **Non-fouling or Acid Fumes**

## Thermal Design Factors

**Efficiency Increases with:**

- Operating temperature
- Retention time
- Higher inlet VOC concentration
- Increasing flame/VOC contact
- Good gas mixing
- Increasing CO removal (at temperatures > 1300 °F)

## Residence Time

- Although the residence time a pollutant in gas stream has in a TO, does not have the same impact as temperature on VOC/HAP destruction, Sufficient time is required for the kinetic reactions to occur.

## Theoretical Combustion Temperatures Requirements for 99.99% Destruction Efficiencies of HAP/VOC Compounds

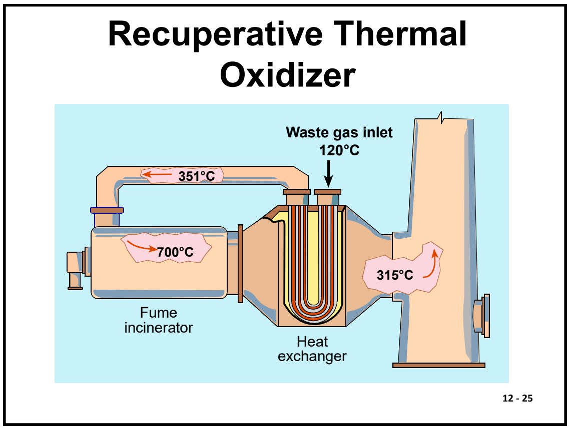
| Compound | Combustion Temperature (° F) for 1 second residence time | Combustion Temperature (° F) for 2 second residence time |
|---|---|---|
| Acrylonitrile | 1,344 | 975 |
| Allyl chloride | 1,276 | 1200 |
| Benzene | 1,350 | 1322 |
| Chlorobenzene | 1,407 | 1372 |
| 1,2- dichloroethane | 1,368 | 1328 |
| Methyl chloride | 1,596 | 1295 |
| Toluene | 1,341 | 1332 |
| Vinyl chloride | 1,369 | 1332 |

## Specific Thermal Incinerator Design Variables

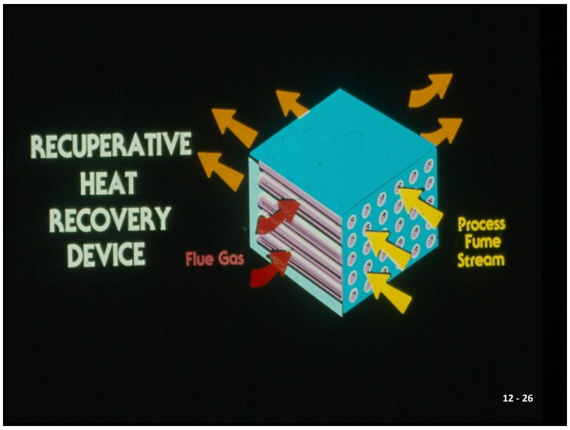
| | Non-Halogenated Stream | | Halogenated Stream | |
|---|---|---|---|---|
| Required Destruction Efficiency ( DE) (%) | Combustion Temperature T (ºF) | Residence Time $t_r$ (sec) | Combustion Temperature T (ºF) | Residence Time $t_r$ (sec) |
| **98** | **1600** | **0.75** | **2000** | **1.0** |
| **99** | **1800** | **0.75** | **2200** | **1.0** |

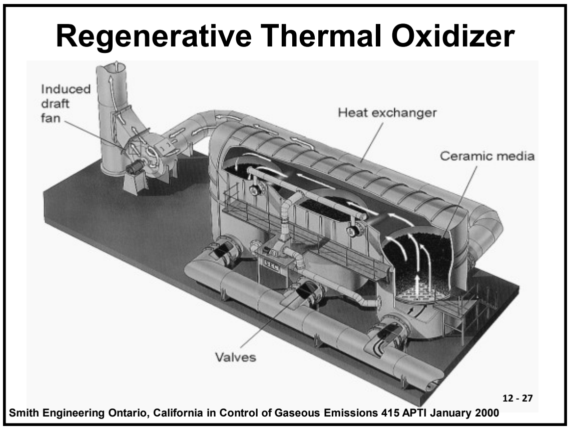
## Generation of Problematic Compounds

- Thermal oxidizers handling HAP/VOC materials that contain chlorine, fluorine, or bromine atoms generate HCl, $Cl_2$, HF, and HBr as additional reaction products during oxidation.
- A gaseous absorber (scrubber) can be used as part of the air pollution control system to collect these contaminants prior to gas stream release to the atmosphere.



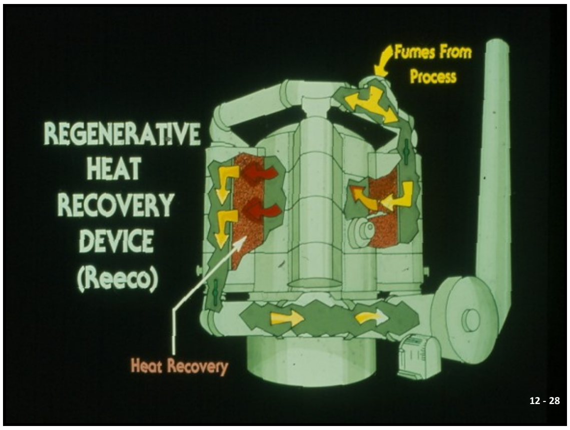
## Recuperative Thermal Oxidizer

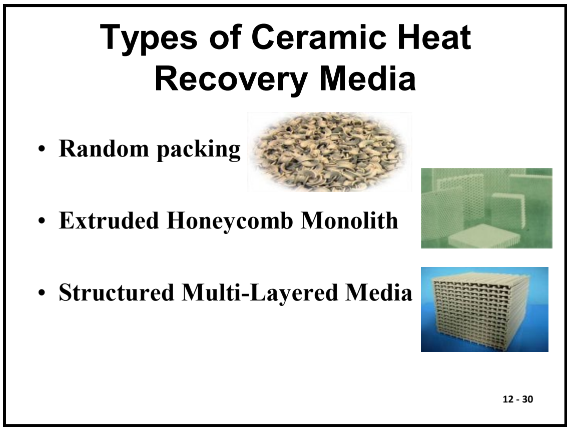




## Regenerative Thermal Oxidizer

Smith Engineering Ontario, California in Control of Gaseous Emissions 415 APTI January 2000

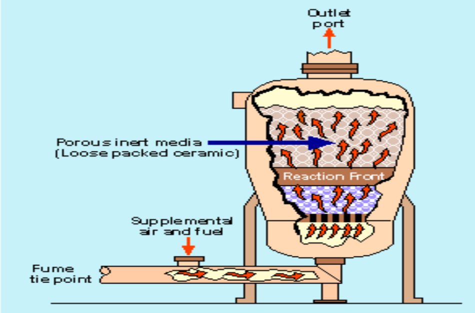




## Types of Ceramic Heat Recovery Media

- Random packing
- Extruded Honeycomb Monolith
- Structured Multi-Layered Media

## Flameless Thermal Oxidizer



Flameless Thermal Oxdizers (FTOs) | Linde US Engineering (leamericas.com)

Flameless Thermal Oxidizers - Process Combustion Corporation (pcc-group.com)

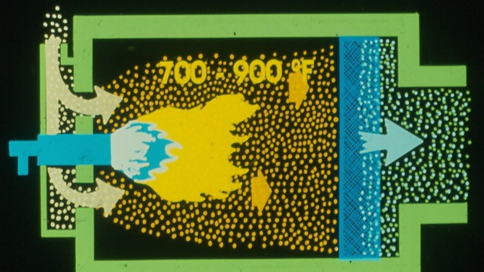
## Flameless Thermal Oxidizer

- Combustion in FTO systems occurs within a chemically inert, porous ceramic bed heated to oxidation temperatures.
- The mixing zone for the FTTO is where the fuel is pre-mixed with off-gas at the inlet of the reactor before it passes through a pre-heated ceramic matrix, which heats the organic vapors.
- Once the vapors reach oxidation temperature, they auto-ignite in the system's reaction zone.

## Flameless Thermal Oxidizer

- The FTO is a destructive technology that has been used for process and waste stream off-gas treatment of VOC's and in the treatment of VOC and chlorinated volatile organic compounds (CVOCs) off gases generated during site remediation.
- The FTO process converts the VOCs and CVOCs to $CO_2$, $H_2O$ and HCl.
- The FTO provides destruction and removal efficiencies (DREs) in excess of 99.99 for VOCs and CVOCs.

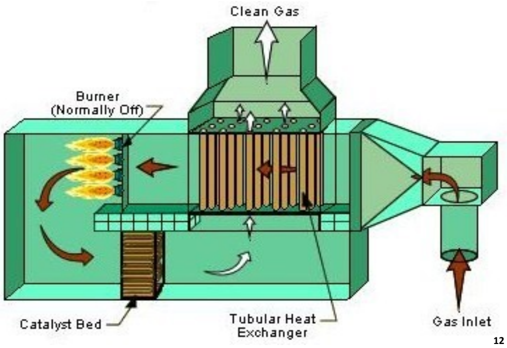
## CATALYTIC INCINERATION



## Catalytic Oxidation

- Catalytic oxidizers operate at substantially lower temperatures than thermal oxidizers. The catalytic oxidation reactions can be performed at temperatures in the range of 500 to 1000°F.
- Common types of catalysts include noble metals (i.e. platinum and palladium) and ceramic materials. HAP/VOC destruction by catalytic oxidizers usually exceeds 95% and could exceeds 99%.

## Catalytic Oxidizer



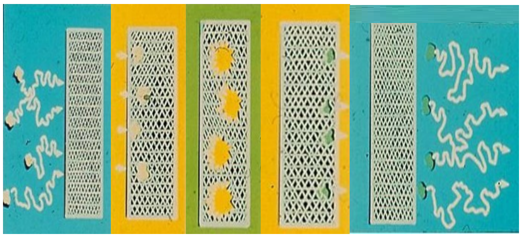
## Catalytic Oxidation

- The relatively low gas temperatures in the combustion chamber, can eliminate the need for a refractory lining.
- The overall weight is minimized for and provides an option for mounting the units on roofs close to the point of VOC generation.
- This can also reduce the overall cost of the system by limiting the distance the VOC-laden stream must be transported in ductwork.

## Catalytic Incineration Principles of Operation

- **Diffusion**
- **Adsorption**
- **Reaction**
- **Desorption**
- **Diffusion and Mixing**

## Catalytic Incineration Principles of Operation



## Common Types of Catalysts

**Noble Metals**

- **Platinum**
- **Palladium**
- **Rhodium**

**Metal Oxides**

- **Chromium oxide**
- **Magnesium oxide**
- **Cobalt oxide**
- **Alumina**

## Platinum Catalytic Suppressants

- **Sulfur**
- **Halogens**

**Suppressant Action is reversible**

## Platinum Catalyst Poisons

| Fast Acting | Slow Acting | High Temperature |
|---|---|---|
| P | Zn | (2500°F) |
| Bi | Pb | Fe |
| As | Sn | Cu |
| Sb | | |
| Hg | | |

## Fixed-Bed Catalytic Incinerators

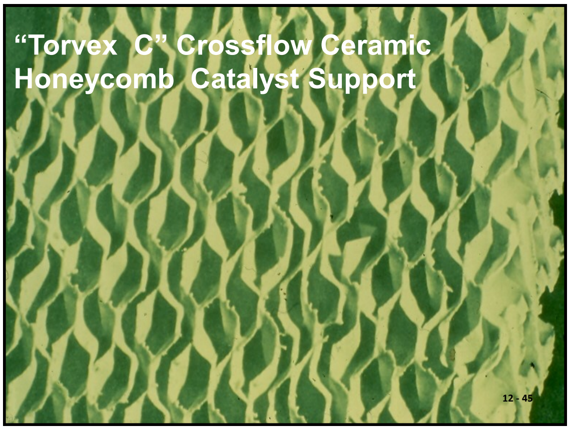
Fixed-bed catalytic incinerators may use a monolith catalyst or a packed-bed catalyst.

- The most widespread method of contacting the VOC containing stream with the catalyst is the catalyst monolith. The catalyst is impregnated on a porous solid block containing parallel, non-intersecting channels aligned in the direction of the gas flow.
- Monoliths offer the advantages of minimal attrition due to thermal expansion/ contraction during startup/shutdown and low overall pressure drop.

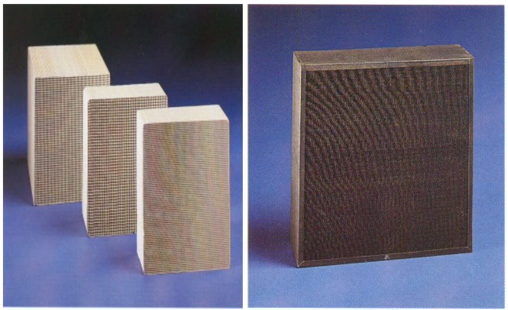
## Packed-Bed Catalytic Incinerators

- In packed-bed catalytic incinerators, the catalyst particles are supported, either in a tube or in shallow trays through in which the gases pass through. However, it has higher pressure drop, compared to a monolith.
- In a tray type arrangement the catalyst is pelletized and is used within several industries (e.g., heat-set web-offset printing).
- Use of pelletized catalyst is advantageous where large amounts of such contaminants as phosphorous or silicon compounds are present.

## "Torvex C" Crossflow Ceramic Honeycomb Catalyst Support



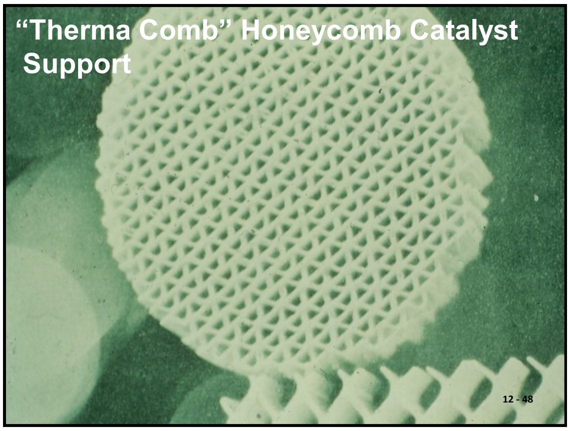
## Ceramic and Metallic Monolith Catalysts (Prototech Company)



http://www.sud-chemie.com/scmcms/web/page_en_6283.htm

## "Torvex B" Honeycomb Alumina Catalyst Support

## "Therma Comb" Honeycomb Catalyst Support



## Thermal Oxidizer Operation

- Inlet VOC concentration maintained at <25% LEL
- Combustion chamber kept at 200 °F to 300°F above the autoignition temperature
- Combustion chambers sized for residence times of 0.5 to 2.0 seconds

## Catalytic Incinerator System Design Variables

| | | | Space Velocity- SV ($hr^{-1}$) SV = Flow rate/Bed Volume | |
|---|---|---|---|---|
| **Required Destruction Efficiency (%)** | **Temperature at the Catalyst Bed Inlet °F** | **Temperature at the Catalyst Bed Outlet °F** | **Base Metal** | **Precious Metal** |
| **95** | **600** | **1000 - 1200** | **10,000 – 15,000** | **30,000 – 40,000** |
| **98 - 99** | **600** | **1000 - 1200** | **Based on Specific Process Conditions** | **Based on Specific Process Conditions** |

## HAP/VOC Destruction Efficiency for Catalytic Incinerators

- In a US EPA pilot scale study ("Parametric Evaluation of VOC/HAP" Destruction Via Catalytic Incineration) testing verified that destruction efficiencies in the 98 to 99 percent range are achievable for the following compounds:
- Alcohols, acetates, ketones, cellosolve compounds/dioxane, aldehydes, aromatics and ethylene/ethylene oxide.
- Destruction efficiencies of at least 97% are achievable for acrylonitrile and cresol.

## HAP/VOC Destruction Efficiency for Catalytic Incinerators

- Catalytic incinerators can achieve efficiencies on the order of 98 to 99% for HAP/VOCs in selected industries.
- The destruction efficiency for a given compound may vary depending on whether the compound is the only VOC in the gas stream or part of a mixture.

## Advantages of Catalytic Incineration

- **Lower operating Temperatures**
- **Lower supplemental fuel use**
- **Lower construction materials cost**

## Disadvantages of Catalytic Incineration

- **Particulate fouling**
- **Thermal aging**
- **Catalytic poisoning**
- **Suppressants**

## Oxidizer Manufacturers’ web sites

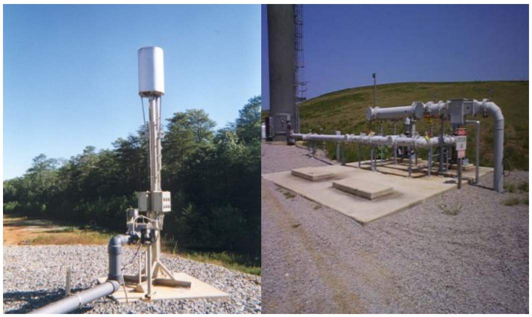
http://www.anguil.com/prregthe.php

http://www.smithenvironmental.com/splash.asp

http://www.megtec.com/index.php

http://www.met-prosystems.com/

## FLARES

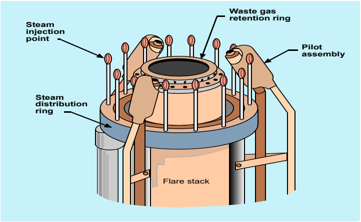


## Type of Flares

- **Steam-Assisted Flares**
- **Air-Assisted Flares**
- **Non-Assisted Flares**
- **Pressure-Assisted Flares**
- **Enclosed Ground Flares**

## Flare Performance Requirements

- **The EPA requirements for steam-assisted, air-assisted, and non-assisted open flares are specified in 40 CFR Section 60.18.**



## Flare Design Criteria

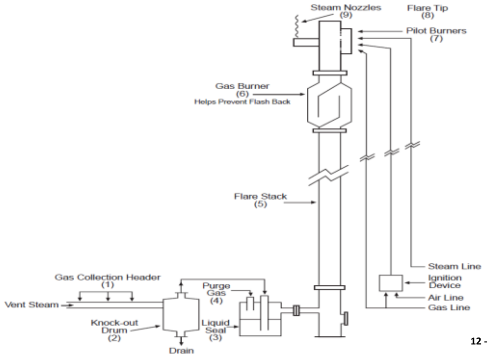
The design and operating requirements for steam-assisted, elevated flares state are:

- An exit velocity at the flare tip of less than 60 ft/sec for 300 Btu/scf gas streams less than 400 ft/sec for >1,000 Btu/scf gas streams.
- For gas streams between 300-1,000 Btu/scf the maximum permitted velocity $V_{max}$, in ft/sec is determined by the following equation: $\log_{10}(V_{max}) = \frac{B_V + 1{,}214}{852}$

## Steam-Assisted Flares

- Steam-assisted flares are single burner tips, elevated above ground level for safety reasons.
- They burn the vented gas in essentially a diffusion flame.
- To ensure an adequate air supply and good mixing, this type of flare system injects steam into the combustion zone to promote turbulence for mixing and to induce air into the flame.

## Typical Steam Assisted Flare System



## Air-Assisted Flares

- These flares use forced air to provide the combustion air and the mixing required for smokeless operation.
- They are built with a spider-shaped burner (with many small gas orifices) located inside but near the top of a steel cylinder two feet or more in diameter.
- Combustion air is provided by a fan in the bottom of the cylinder. The amount of combustion air can be varied by varying the fan speed.

## Non-Assisted Flares

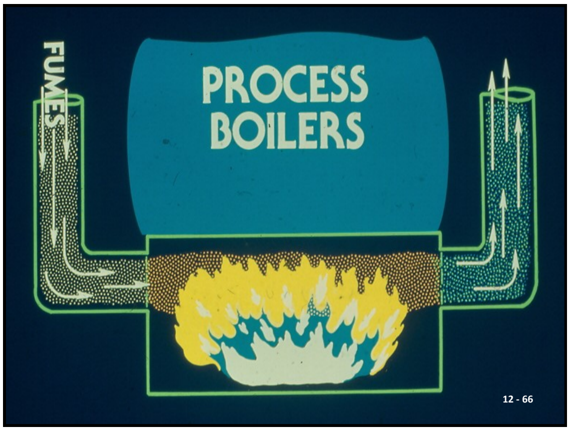
- The non-assisted flare is just a flare tip without any auxiliary provision for enhancing the mixing of air into its flame.
- Its use is limited essentially to gas streams that have a low heat content and a low carbon/hydrogen ratio that burn readily without producing smoke.
- These streams require less air for complete combustion, have lower combustion temperatures that minimize cracking reactions.

## Pressure-Assisted Flares

- Pressure-assisted flares use the vent stream pressure to promote mixing at the burner tip.
- These flares can be applied to streams previously requiring steam or air assist for smokeless operation.
- Pressure-assisted flares generally (but not necessarily) have the burner arrangement at ground level, They have multiple burner heads that are staged to operate based on the quantity of gas being released.

## Enclosed Ground Flares

- An enclosed flare's burner heads are inside a shell that is internally insulated shell which reduces noise, luminosity, and heat radiation and provides wind protection.
- The height must be adequate for creating enough draft for sufficient and for dispersion of the thermal plume.
- Enclosed flares are used to combust continuous and constant flow vent streams.
- Enclosed flares are typically found at landfills.



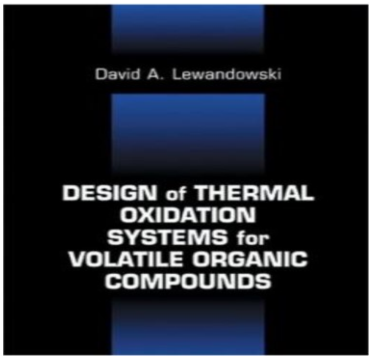
## Process Equipment for Emission Control

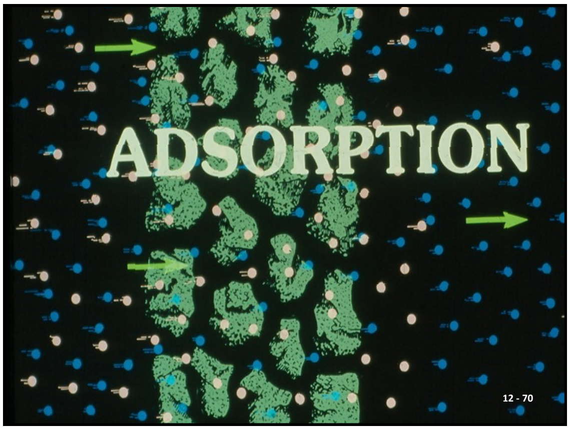
- Fired-process equipment or furnaces include boilers, heaters and incinerators. Indirect- fired furnaces (boilers and process heaters) are those in which heating media are separated from the process streams.
- The parameters that affect the destruction efficiency for boilers and process heaters are the same traditional thermal oxidizing devices. They are temperature, residence time, inlet concentration, compound type and flow regime.

## Process Control Effectiveness

- A series of EPA-sponsored studies of organic vapor destruction efficiencies for industrial boilers and process heaters were conducted in 1998.
- The results of these tests showed 98 to 99 percent overall destruction efficiencies for $C_1$ to $C_6$ hydrocarbons.
- The Boiler/Heater must operate continuously and concurrently with the pollution generating source.

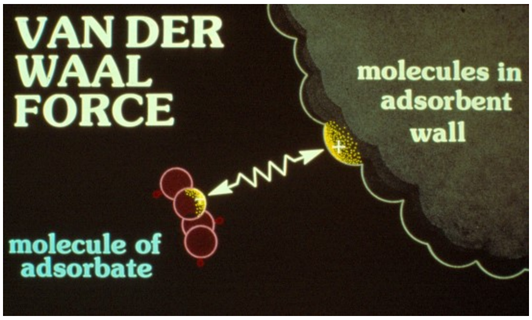
## Additional Reference Materials

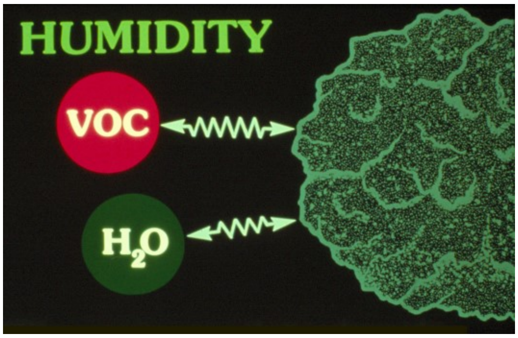




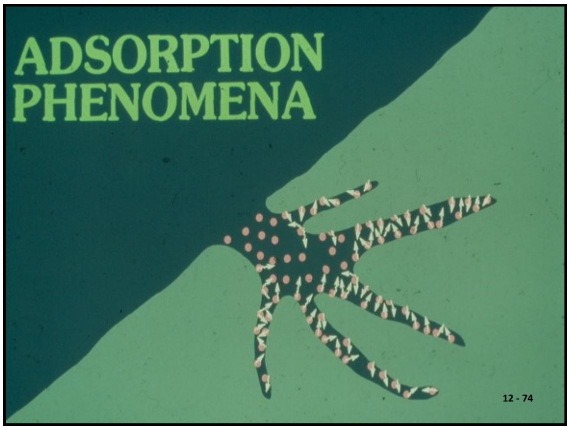
## WHAT ARE ADSORBERS?

- Adsorption is where the pollutant is adsorbed on the surface (mostly on the internal surface) of a granule, bead, or crystal of adsorbent material.
- The adsorbed material is held physically (not chemically) and can be released (desorbed) rather easily by either heat or vacuum.

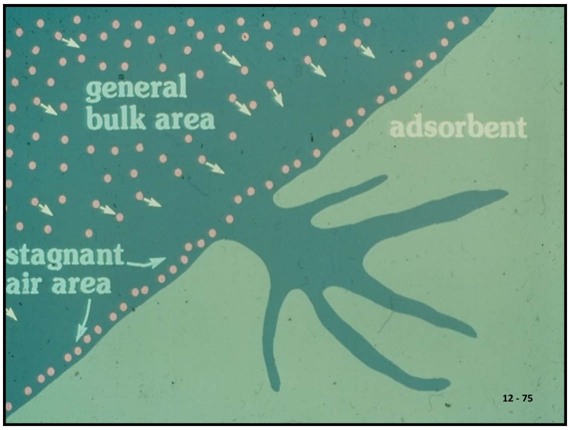


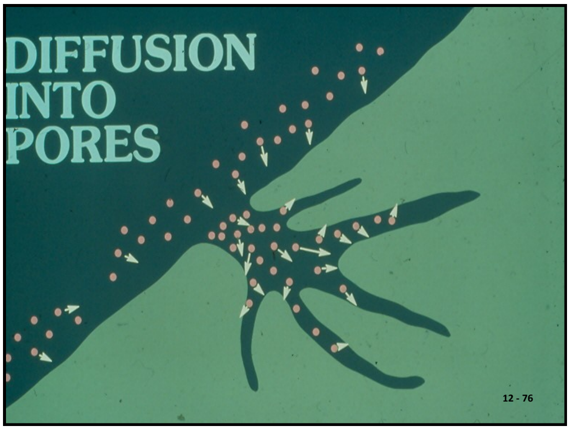


## HUMIDITY

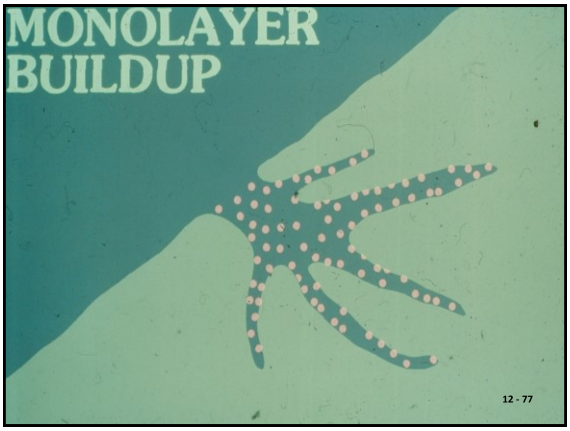


## ADSORPTION PHENOMENA

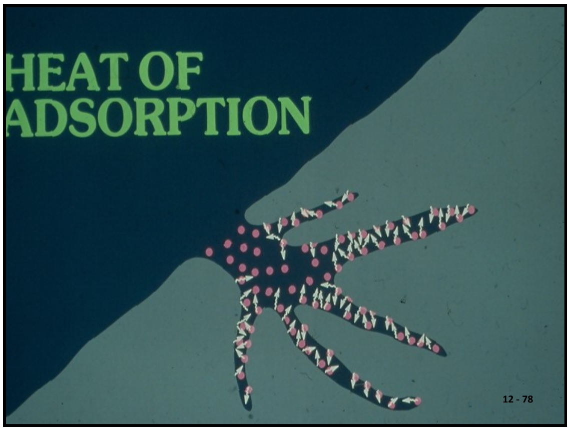




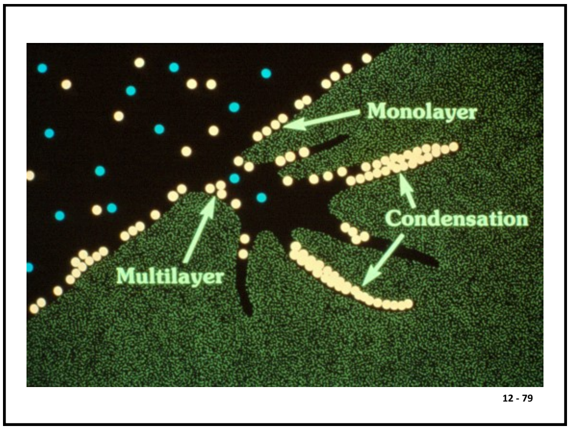
## DIFFUSION INTO PORES

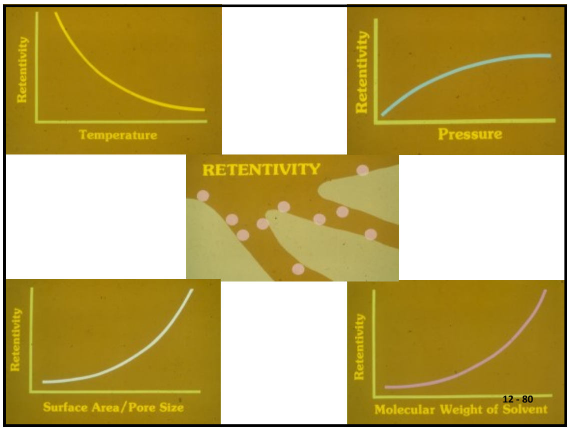


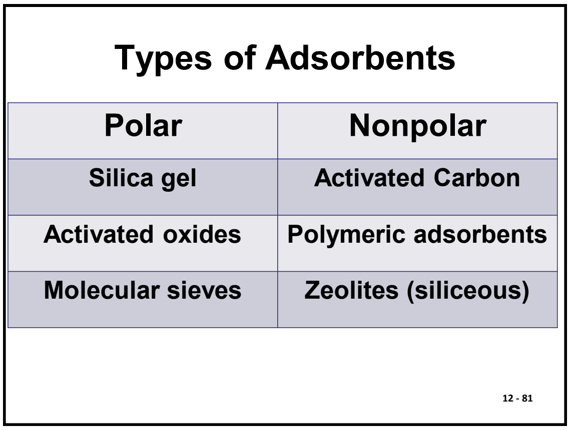
## MONOLAYER BUILDUP



## HEAT OF ADSORPTION

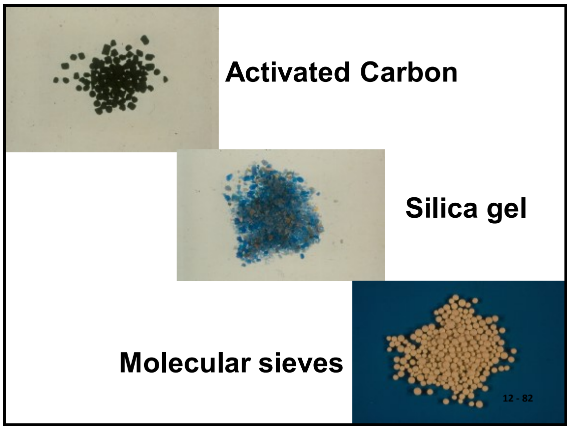


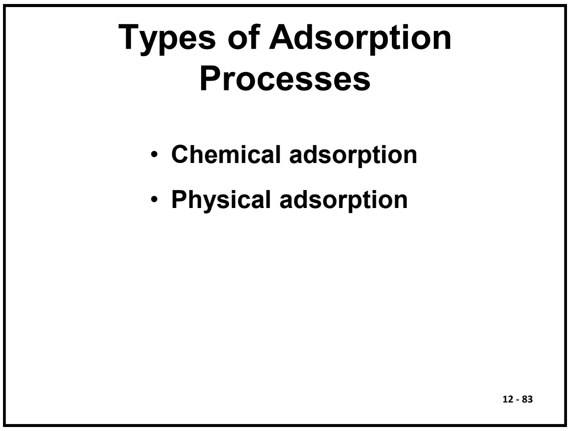




## Types of Adsorbents

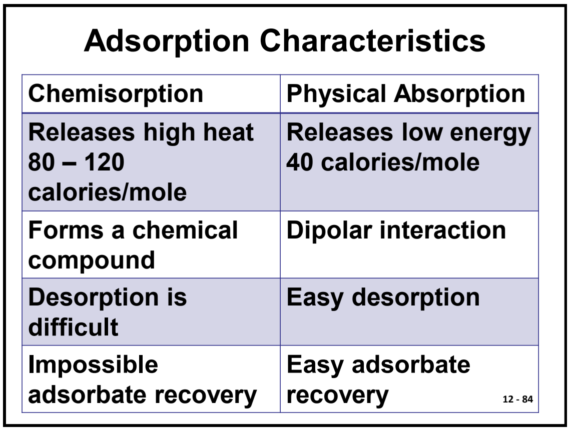
| Polar | Nonpolar |
|---|---|
| Silica gel | Activated Carbon |
| Activated oxides | Polymeric adsorbents |
| Molecular sieves | Zeolites (siliceous) |





## Types of Adsorption Processes

- Chemical adsorption
- Physical adsorption



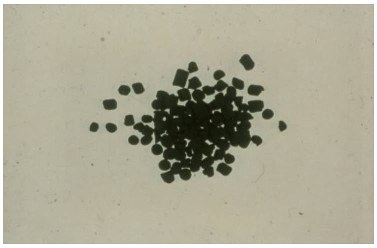
## Adsorption Characteristics

| Chemisorption | Physical Absorption |
|---|---|
| Releases high heat 80 – 120 calories/mole | Releases low energy 40 calories/mole |
| Forms a chemical compound | Dipolar interaction |
| Desorption is difficult | Easy desorption |
| Impossible adsorbate recovery | Easy adsorbate recovery |

## Adsorption Systems

- **Non-regenerative**
- **Regenerative**

## Carbon Adsorption



## Activated Carbon

- One of the adsorbents is called “absorbent carbon.” This persisting misnomer came from the time before adsorption became understood in the 1920's. A better term is “activated carbon.”
- Carbon is activated by the pyrolysis of carbon/organic feed stocks which remove all the volatile material as a gas or vapor, and leave only the carbon. This carbon may then also be partially oxidized to enlarge its pores.

## Activated Carbon

- Classes of feed stock materials
- Produced from coal, wood, nut shells and petroleum-based products
- Activation process
  - Heat material to ~1,100°F without oxygen
  - Use stream, air or $CO_2$ to increase pore structure

### Stereo Scan Electron Micrograph Photos of Activated Carbons from Cameron Carbon web site

Coal Coconut Wood

http://www.cameroncarbon.com/activated_carbons.html

## Zeolite Adsorbers

- Another adsorbent is the alumino-silicate crystal structure known as “zeolite,” which has uniformly sized pores (also called windows) throughout its crystal structure.
- The crystal structure for the 118 established types of zeolite is determined by the ratio of silicon to aluminum in the crystal when the crystal is formed.

## Zeolite Adsorbers

- All naturally occurring zeolite is hydrophilic (having an affinity for polar molecules, such as water) and contains aluminum.
- Dealuminizing natural zeolite makes it hydrophobic (having affinity for non-polar substances, such as many VOC).
- Zeolite is dealuminized by chemical replacement of the aluminum with silicon without changing the crystal structure.

## Adsorber Control Description

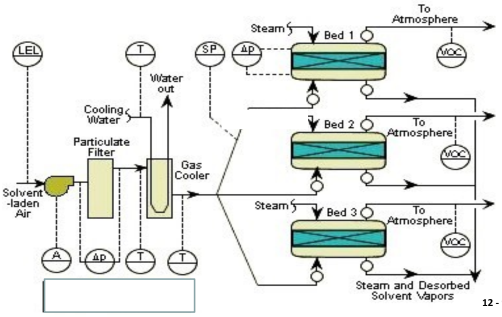
- Adsorption technology can control the HAP/VOCs in concentrations from 20 ppm to one-fourth of the Lower Explosive Limit (LEL).
- In the lower end of this range the small concentrations may be difficult or uneconomical to control by another technology.
- Incinerators, membrane separators, and condensers may be economically feasible when used in place of adsorbers at the upper end of the range.

## Adsorber Control Description

**Adsorption systems beds are generally used in the following different situations:**

- When the VOC-laden gas stream only contains one to three organic solvent compounds, and it is economical to recover and reuse these compounds
- When the VOC-laden gas stream contains a large number of organic compounds at low concentration, and it is necessary to pre-concentrate these organics prior to thermal or catalytic oxidation.

## Multi-Bed Adsorber System for Solvent Recovery



## Adsorber Operation

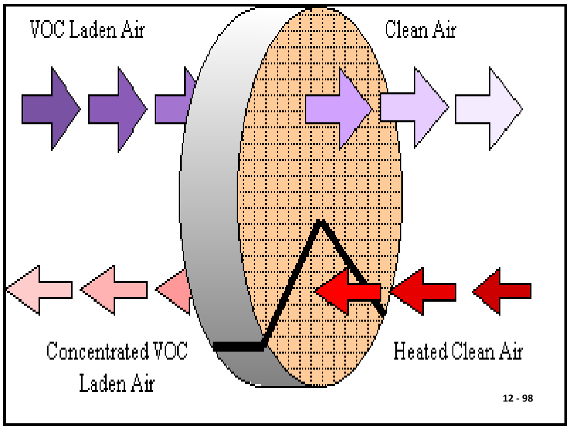
- The VOC-laden gas is often cooled prior to entry into the adsorption system because the effectiveness of adsorption improves at cold temperatures.
- When the adsorbent is approaching saturation with organic vapor, a bed is isolated from the gas stream and desorbed.
- Low-pressure steam or hot nitrogen gas is often used to remove the weakly adsorbed organics.

## Adsorber Operation

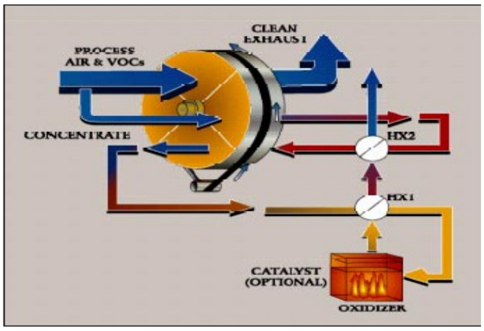
- The concentrated stream from the desorption cycle is treated to recover the organic compounds.
- After desorption, the adsorption bed is returned to service, and another bed in the system is isolated and desorbed.

## Pre-concentrator Adsorber systems

- In pre-concentrator systems, the VOC-laden stream passes through a rotary wheel containing zeolite or carbon-based adsorbents.
- Approximately 75-90% of the wheel is in adsorption service while the remaining portion of the adsorbent passes through an area where the organics are desorbed into a very small, moderately hot gas stream.
- The concentrated organic vapors are then transported to a thermal or catalytic oxidizer for destruction and reduces the fuel usage.

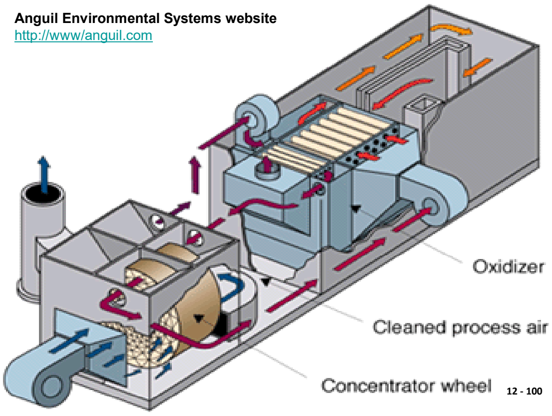


## Munters ZEOL: Innovative Solutions for VOC Abatement Brochure



http://www.munters.us/upload/Case%20studies/Munters%20Zeol%20Brochure-Zeolite%20Rotor%20Concentrators.pdf

**Anguil Environmental Systems website**
http://www/anguil.com

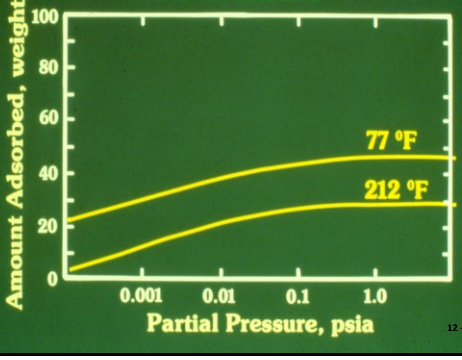


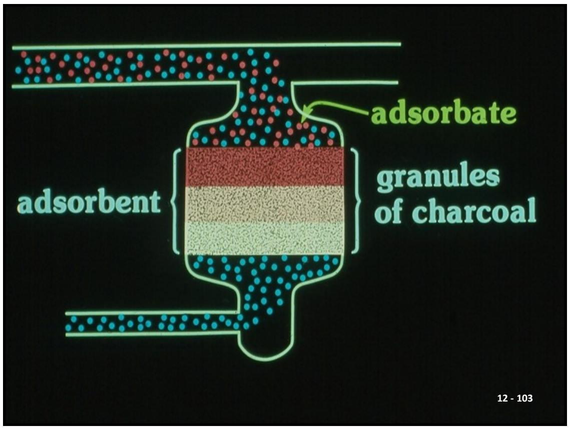
## Adsorption Capacity

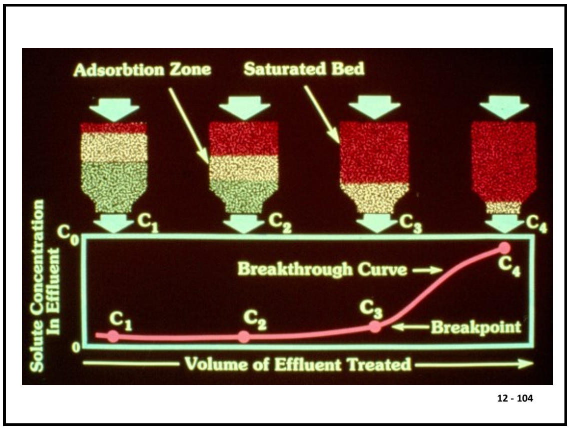
### Retention

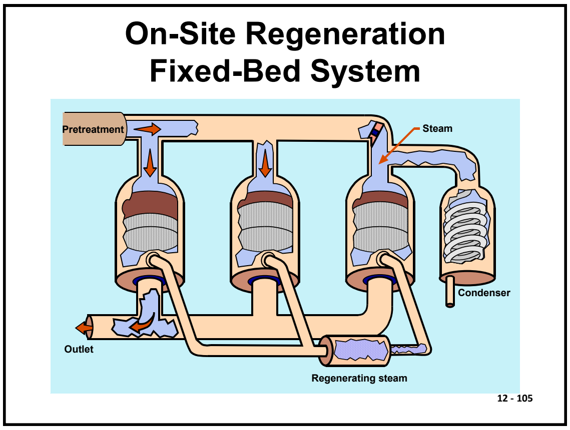
- **Lbs of VOC adsorbed per 100 lbs of carbon**
- **Weight percent**

## TYPICAL ADSORPTION ISOTHERM

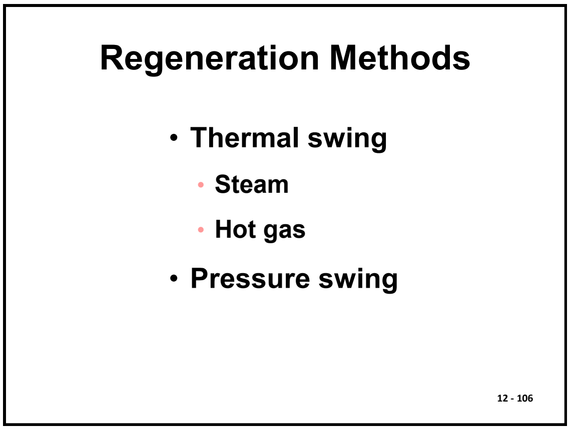






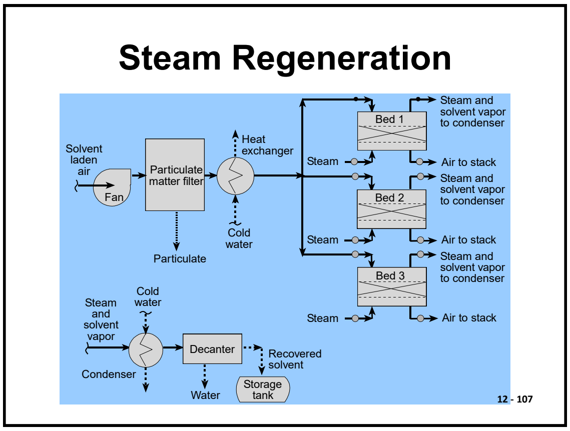


## On-Site Regeneration Fixed-Bed System

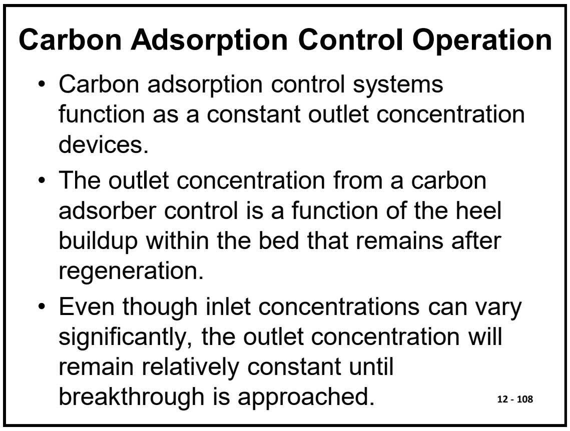


## Regeneration Methods

- Thermal swing
  - Steam
  - Hot gas
- Pressure swing



## Steam Regeneration



## Carbon Adsorption Control Operation

- Carbon adsorption control systems function as a constant outlet concentration devices.
- The outlet concentration from a carbon adsorber control is a function of the heel buildup within the bed that remains after regeneration.
- Even though inlet concentrations can vary significantly, the outlet concentration will remain relatively constant until breakthrough is approached.

## Carbon Adsorption Control Operation

- The removal efficiency of a properly sized and operated carbon adsorber is largely dependant on the inlet concentration and the regeneration of the bed.
- The more rigorous the generation, the lower the outlet concentration.

## Carbon Adsorption Control Operation

- Carbon adsorption systems must be designed based on 1) specific compound or compounds being recovered, 2) mass loading of pollutant, 3) gas stream flowrate and 4) gas stream temperature.
- When specific adsorbed compounds (i.e. cyclohexanone) react on the carbons surface to form higher molecular weight products, the subsequent build up can result in a steady decrease in adsorptive capacity.

## Carbon Adsorption Control Operation

- As a carbon bed ages, it’s total adsorptive capacity gradually decreases due to fouling.
- The working capacity can be maintained in some cases by increasing steam flow during desorption which would also increase operating costs.
- Maintaining design values and high removal efficiency can be accomplished by frequent carbon changes, but will also increase operating.

## Carbon Adsorber HAP Control Parameters

| Outlet HAP Concentration (ppmv) | Adsorption Cycle Time (hr) | Regeneration Cycle (hr) | Steam Requirement for Regeneration (lb steam/lb carbon) |
|---|---|---|---|
| 70 | 2 | 2 | 0.3 |
| 10 - 12 | 2 | 2 | 1.0 |

## HAP/VOC Adsorption Control Efficiency & Bed Life

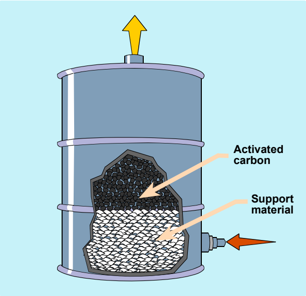
| Facility | Solvent Blend | Reported Bed Life | Removal Efficiency(%) |
|---|---|---|---|
| A | 44% Cyclohexanone<br>14% MEK<br>23% Tetrahydrofuram<br>19% Toluene | | 99.4 |
| B | 50% Toluene<br>50% Isopropyl Acetate | > 6 Years | 98.0 |
| C | 95% Toluene<br>5% Hexane | 10 Years | 99.5 |
| D | MEK | 5 Years | 99.5 |

## Adsorption Control Efficiency for Various Inorganic Vapors [1]

| Inorganic Vapor | Adsorbent | Removal Efficiency(%) |
|---|---|---|
| Mercury (Hg) | Sulfur – impregnated activated carbon | 90 |
| Hydrogen Sulfide ($H_2S$) | Ammonia – impregnated activated carbon | 100 |
| Hydrogen Fluoride (HF) | Calcined Alumina | 99 |

[1] Control Technologies for Toxic and Hazardous Air Pollutants Illinois Institute for Environmental Quality Chicago, Illinois 1975

## Non-Regenerable Canister Adsorber



## Uses of Non-regenerable Adsorbers

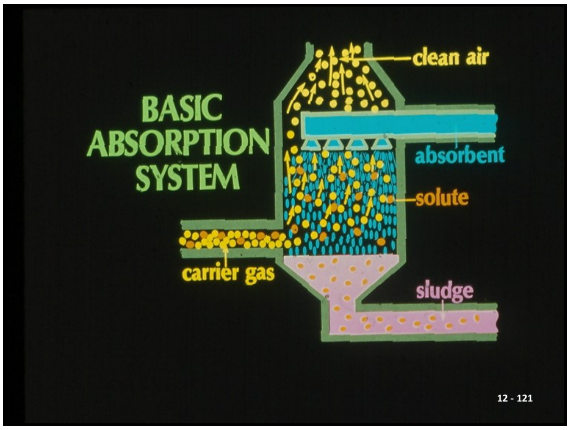
- Control of odors
- Control of trace contaminants

Non-Regenerative Carbon Adsorption Drums controlling mercaptan odors from re-refined crankcase oil product

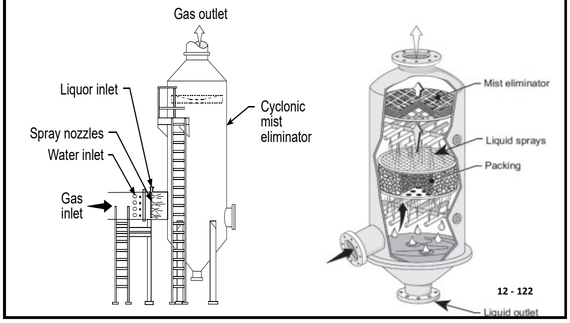
## Additional Information

- Additional information on adsorption systems can be found in
  CATC TECHNICAL BULLETIN
- CHOOSING AN ADSORPTION SYSTEM FOR VOC: CARBON, ZEOLITE, OR POLYMERS?
- EPA-456/F-99-004 May 1999
- http://www.epa.gov/ttn/catc/dir1/fadsorb.pdf

# Absorption



## Types and Components of Absorbers (Scrubbers)



## Absorber Operation

- Absorbers are used for a wide variety of organic and acid gas compounds. Absorber systems can be divided into two fundamentally different groups:
  - (1) those limited by solubility equilibrium limits
  - (2) those using reactions in solution to minimize equilibrium limits
- In both systems, there must be sufficient scrubbing liquid to provide good gas-liquid contact. In absorbers subject to solubility equilibrium limits, there must also be sufficient liquid to effectively capture the gaseous contaminant.

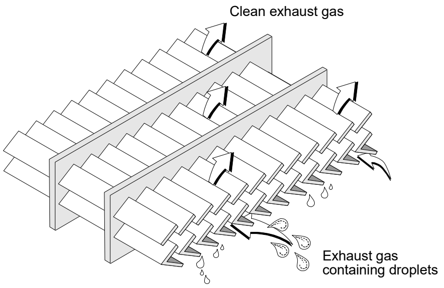
## Absorption Principles

- **Daltons Law** $Y = p_A/P_{total}$
- **Henry's Law** $Y = H x_A$
- **where** $H = \frac{\text{mole fraction in gas}}{\text{mole fraction in liquid}}$

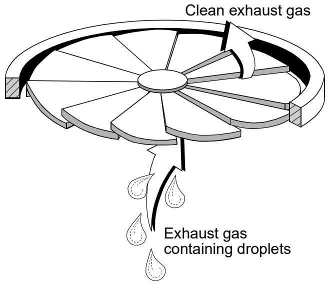
**Venturi Scrubbers are used to remove very fine dust, mist and can also remove gases.**

**Packed Towers are primarily used for gas absorption.**

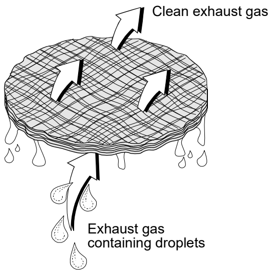
## Chevron Mist Eliminators on Absorbers



## Radial vane mist eliminator on Absorbers



## Mesh Pad Mist Eliminators for Absorbers



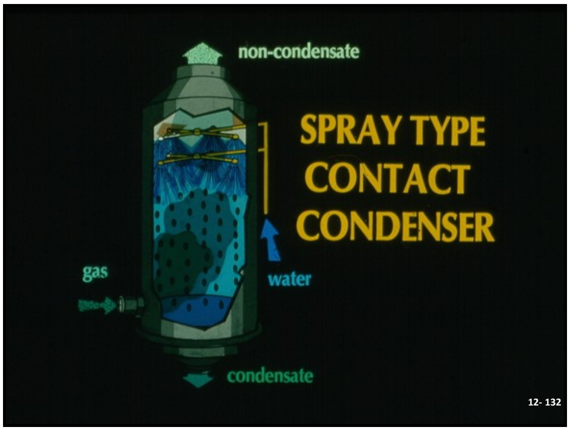
## Control Methods for Various Inorganic HAP Vapors

| | Absorption | | Adsorption | |
|---|---|---|---|---|
| Inorganic Vapor | Reported Removal Efficiency(%) | Solvent | Reported Removal Efficiency(%) | Adsorbant |
| Mercury (Hg) | 95 | Brine/ hypochlorite | 90 | Sulfur impregnated activated carbon |
| Hydrogen Chloride (HCl) | 98 | Water | | |
| Hydrogen Sulfide (H2S) | 98 | Sodium carbonate/Water | 100 | Ammonia impregnated activated carbon |
| Calcium Fluoride (CaF2) | 95 | Water | | |
| Silicon Tetrafluoride (SiF4) | 95 | Water | | |
| Hydrogen Fluoride (HF) | 85 – 95 | Water | 99 | Calcined alumina |
| Hydrogen Bromide (HBr) | 99.95 | Water | | |
| Titanium tetrachloride | 99 | Water | | |
| Chlorine (Cl2) | 90 | Alkali Solution | | |
| Hydrogen Cyanide (HCN) | | | | Ammonia impregnated activated carbon |

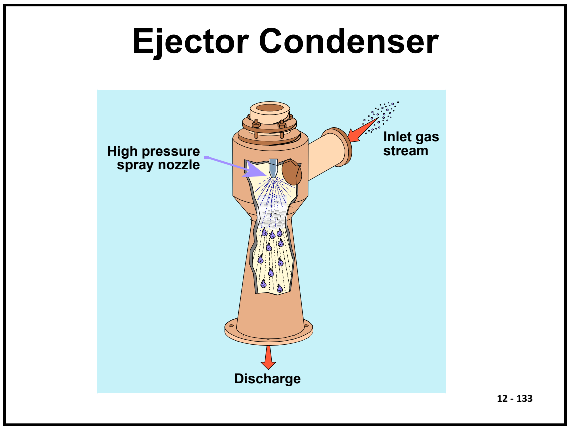
## Condensers

## Types of Condensers

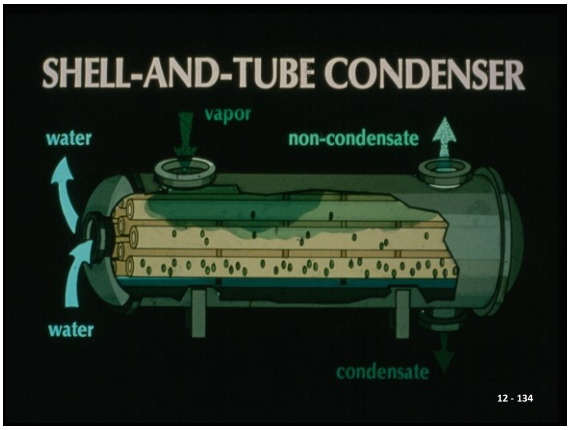
- Contact
- Surface
- Refrigeration



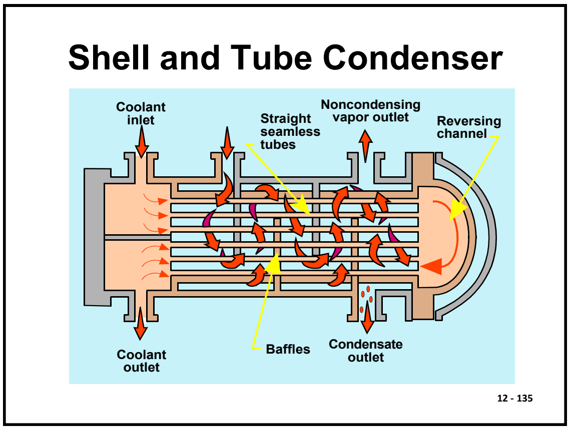
## Ejector Condenser



## SHELL-AND-TUBE CONDENSER

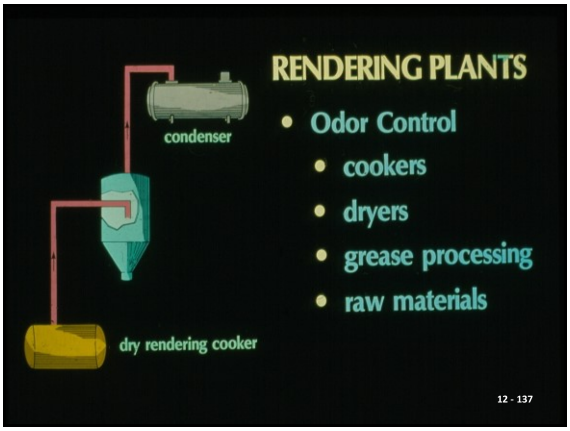


## Shell and Tube Condenser



## Surface and Contact Condenser Comparison

| **Surface Condensers** | **Contact Condensers** |
|---|---|
| • less coolant required | • simpler |
| • less condensate produced | • less expensive |
| • Product easily recovered | • less maintenance required |
| • No separation problem | • separation problems |
| | • (coolant and pollutant) |



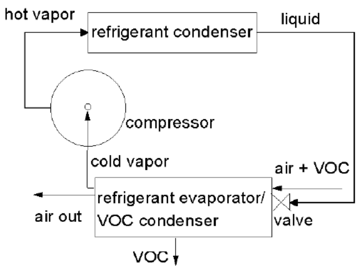
## RENDERING PLANTS

- Odor Control
  - cookers
  - dryers
  - grease processing
  - raw materials

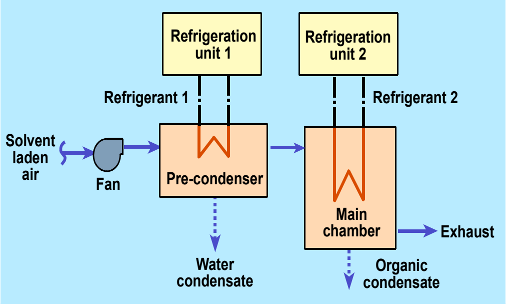
## Refrigeration Condenser

- Refrigeration units are basically “heat pumps,” absorbing heat on the “cold side” of the system and releasing heat on the “hot side” of the system.
- All refrigeration systems have a hot side and a cold side. Some have a compressor.
- The difference between refrigeration systems is whether the refrigerant is actually liquified within the apparatus and how low a temperature the “cold side” can reach.

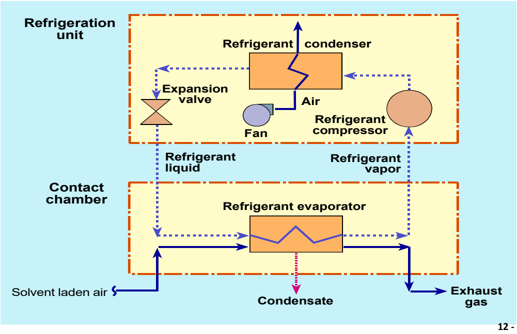
## Mechanical Compression Refrigeration System

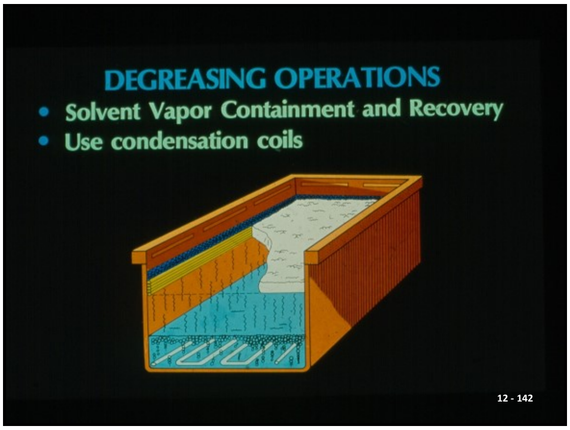


## Refrigeration System

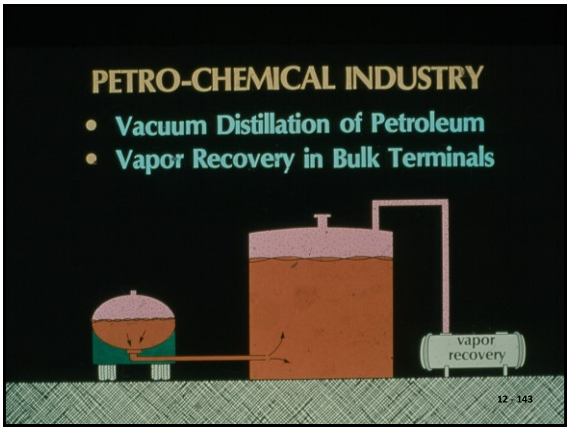


## Refrigeration Cycle




DEGREASING OPERATIONS

- Solvent Vapor Containment and Recovery
- Use condensation coils


PETRO-CHEMICAL INDUSTRY

- Vacuum Distillation of Petroleum
- Vapor Recovery in Bulk Terminals

## Bioreactors and Biofiltration

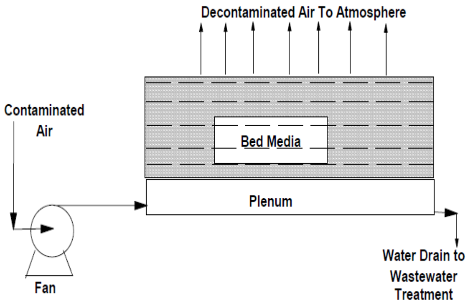
## Biofiltration or Bioreactors

- In air pollution, biofiltration or bioreaction is the use of microbes to consume pollutants from a contaminated air stream.
- Most substances, with the help of microbes, will decompose (decay) given the proper environment and is especially true for organic compounds.
- Certain microbes can also consume inorganic compounds such as hydrogen sulfide and nitrogen oxides.

## How Biofiltration or Bioreactors Work

- Bioreactors use microbes to remove pollutants from emissions by consuming the pollutants.
- About sixty years ago, Europeans began using bioreactors to treat contaminated air (odors), particularly emissions from sewage treatment plants and rendering plants.
- The initial process used a device called a "biofilter“ is a filter (usually a rectangular box) that contains an enclosed plenum on the bottom, a support rack above the plenum, and several feet of media (bed) on top of the support rack.

## Basic Biofilter



## Biofilter Basics

- Various materials are used for bed media such as peat, composted yard waste, bark, coarse soil, gravel or plastic shapes .
- Oyster shells (for neutralizing acid build-up) and fertilizer (for macronutrients) can be mixed with bed media.
- The support rack is perforated to allow air from the plenum to move into the bed media to contact microbes that live in the bed. The perforations also permit excess, condensed moisture to drain out of the bed to the plenum.
- A fan is used to collect contaminated air from a building or process.

## Biofilter Basics

- If the air is too hot, too cold, too dry, or too dirty (with suspended solids), it may be necessary to pre-treat the contaminated air stream to obtain optimum conditions before introducing it into a bioreactor.
- Contaminated air is ducted to a plenum and emissions flow through the bed media, the pollutants are absorbed by moisture on the bed media and come into contact with microbes.
- Microbes reduce pollutant concentrations by consuming and metabolizing pollutants. During the digestion process, enzymes in the microbes convert compounds into energy, CO2 and water.
- Material that is indigestible is left over and becomes residue.

## Bioreactors and Biofiltration

- Three primary mechanisms that are responsible for this transfer and the subsequent biodegradation in organic media biofilters are:
- 1. Gas stream → adsorption on organic media → desorption/ dissolution in aqueous phase → biodegradation.
- 2. Gas stream → direct adsorption in biofilm → biodegradation.
- 3. Gas stream → dissolution in aqueous phase → biodegradation.

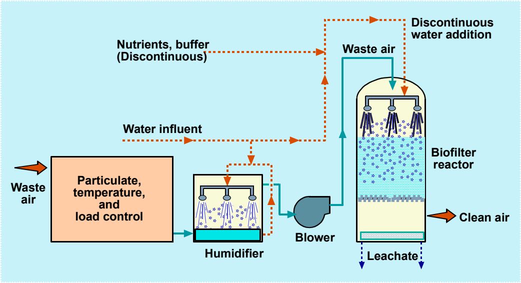
# Microbial Population Requirements

- Sufficient moisture
- Sufficient nutrients
- Temperature of 60°F to 85°F
- pH of 6 to 8

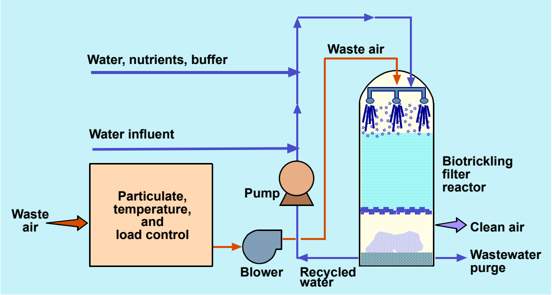
# Bioreaction

- Biofilters
- Biotrickling filters
- Bioscrubbers

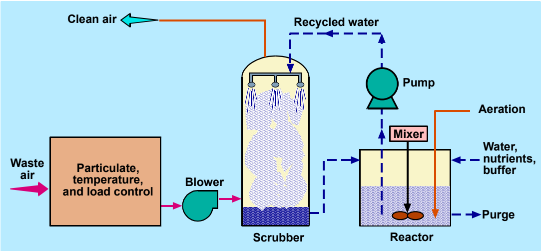
# Biofilter System



# Biotrickling Filter System



# Bioscrubber System



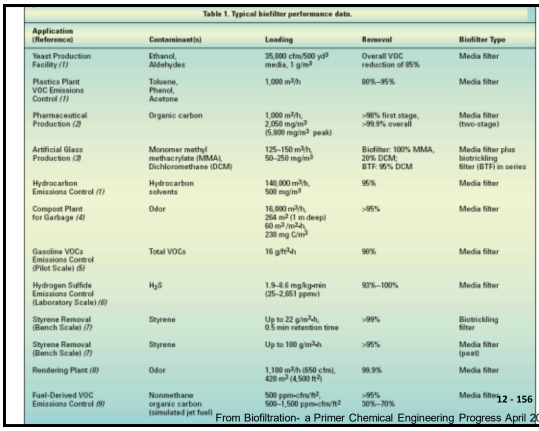


Table 1. Typical biofilter performance data.

| Application (Reference) | Contaminant(s) | Loading | Removal | Biofilter Type |
|---|---|---|---|---|
| Yeast Production Facility *(1)* | Ethanol,<br>Aldehydes | 35,000 cfm/500 yd$^3$ media, 1 g/m$^3$ | Overall VOC reduction of 85% | Media filter |
| Plastics Plant VOC Emissions Control *(1)* | Toluene,<br>Phenol,<br>Acetone | 1,000 m$^3$/h | 80%–95% | Media filter |
| Pharmaceutical Production *(2)* | Organic carbon | 1,000 m$^3$/h,<br>2,050 mg/m$^3$<br>(5,800 mg/m$^3$ peak) | >98% first stage,<br>>99.9% overall | Media filter (two-stage) |
| Artificial Glass Production *(3)* | Monomer methyl methacrylate (MMA),<br>Dichloromethane (DCM) | 125–150 m$^3$/h,<br>50–250 mg/m$^3$ | Biofilter: 100% MMA, 20% DCM;<br>BTF: 95% DCM | Media filter plus biotrickling filter (BTF) in series |
| Hydrocarbon Emissions Control *(1)* | Hydrocarbon solvents | 140,000 m$^3$/h,<br>500 mg/m$^3$ | 95% | Media filter |
| Compost Plant for Garbage *(4)* | Odor | 16,000 m$^3$/h,<br>264 m$^2$ (1 m deep)<br>60 m$^3$/m$^2$·h,<br>230 mg C/m$^3$ | >95% | Media filter |
| Gasoline VOCs Emissions Control (Pilot Scale) *(5)* | Total VOCs | 16 g/ft$^3$·h | 90% | Media filter |
| Hydrogen Sulfide Emissions Control (Laboratory Scale) *(6)* | $H_2S$ | 1.9–8.6 mg/kg·min<br>(25–2,651 ppmv) | 93%–100% | Media filter |
| Styrene Removal (Bench Scale) *(7)* | Styrene | Up to 22 g/m$^3$·h,<br>0.5 min retention time | >99% | Biotrickling filter |
| Styrene Removal (Bench Scale) *(7)* | Styrene | Up to 100 g/m$^3$·h | >95% | Media filter (peat) |
| Rendering Plant *(8)* | Odor | 1,100 m$^3$/h (650 cfm),<br>420 m$^2$ (4,500 ft$^2$) | 99.9% | Media filter |
| Fuel-Derived VOC Emissions Control *(9)* | Nonmethane organic carbon (simulated jet fuel) | 500 ppm·cfm/ft$^2$,<br>500–1,500 ppm·cfm/ft$^2$ | >95%<br>30%–70% | Media filter |

From Biofiltration- a Primer Chemical Engineering Progress April 2001

## US EPA Bioreactor Publication

"USING BIOREACTORS TO CONTROL AIR POLLUTION" EPA-456/R-03-003

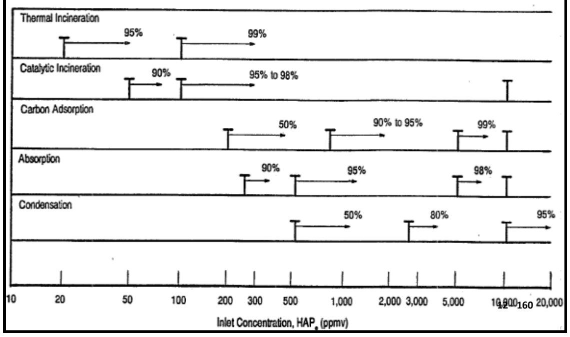
http://www.epa.gov/ttn/catc/dir1/fbiorect.pdf

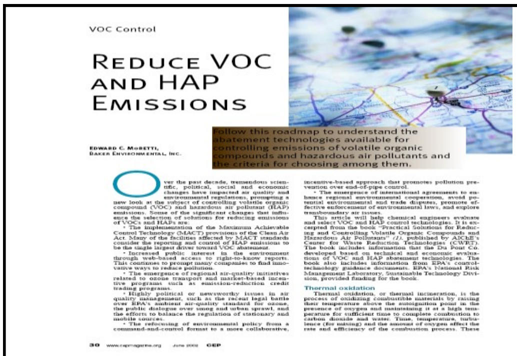
## Review of Control Technologies for Gaseous Hazardous Air Pollutants

## Emission Stream & HAP Characteristics for Selecting Control Techniques

| | Emission Stream Characteristics | | | | | HAP Characteristics | | | |
|---|---|---|---|---|---|---|---|---|---|
| Control Device | HAP/Organic Contents (ppmv) | Heat Content Btu/scf | Moisture Content % | Flow Rate (scfm) | Temp (°F) | Molecular Weight (lb/lb-mole) | Solubility | Vapor Pressure (mm Hg) | Adsorptive Properties) |
| Thermal Incinerator | ➢20; (< 25% of LEL) | | | < 50,000 | | | | | |
| Catalytic Incinerator | 50 – 10,000; (<25% of LEL) | | | < 50,000 | | | | | |
| Flare | | >300 | | < 2,000,000 | | | | | |
| Boiler/ Process Heater | | >150 | | Steady | | | | | Must be able to adsorb and desorb from adsorbent |
| Carbon Adsorber | 700 – 10,000 (<25% of LEL) | | <50% | 300-200,000 | < 130 | 45-130 | | | |
| Absorber | 250 – 10,000 | | | 1,000-100,000 | | | Must be soluble in water or other solvents | | |
| condenser | >5,000 – 10,000 | | | <2000 | | | | >10 at room temperature | |

## Approximate Percent HAP Reduction Ranges for Applicable Control Devices




VOC Control

# REDUCE VOC AND HAP EMISSIONS

Follow this roadmap to understand the abatement technologies available for controlling emissions of volatile organic compounds and hazardous air pollutants and the criteria for choosing among them.

EDWARD C. MORETTI,
BAKER ENVIRONMENTAL, INC.

Over the past decade, tremendous scientific, political, social and economic changes have impacted air quality and environmental regulations, prompting a new look at the subject of controlling volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions. Some of the significant changes that influence the selection of solutions for reducing emissions of VOCs and HAPs are:

- The implementation of the Maximum Achievable Control Technology (MACT) provisions of the Clean Air Act. Many of the facilities affected by MACT standards consider the reporting and control of HAP emissions to be the single largest driver toward VOC abatement.
- Increased public interest in the environment through web-based access to right-to-know reports. This continues to prompt many companies to find innovative ways to reduce pollution.
- The emergence of regional air-quality initiatives related to ozone transport and market-based incentive programs such as emission-reduction credit trading programs.
- Highly political or newsworthy issues in air quality management, such as the recent legal battle over EPA's ambient air-quality standard for ozone, the public dialogue over smog and urban sprawl, and the efforts to balance the regulation of stationary and mobile sources.
- The refocusing of environmental policy from a command-and-control format to a more collaborative, incentive-based approach that promotes pollution prevention over end-of-pipe control.
- The emergence of international agreements to enhance regional environmental cooperation, avoid potential environmental and trade disputes, promote effective enforcement of environmental laws, and explore transboundary air issues.

This article will help chemical engineers evaluate and select VOC and HAP control technologies. It is excerpted from the book "Practical Solutions for Reducing and Controlling Volatile Organic Compounds and Hazardous Air Pollutants" *(1)*, published by AIChE's Center for Waste Reduction Technologies (CWRT). The book includes information that the Du Pont Co. developed based on technical and economic evaluations of VOC and HAP abatement technologies. The book also includes information from EPA's control-technology guidance documents. EPA's National Risk Management Laboratory, Sustainable Technology Division, provided funding for the book.

### Thermal oxidation

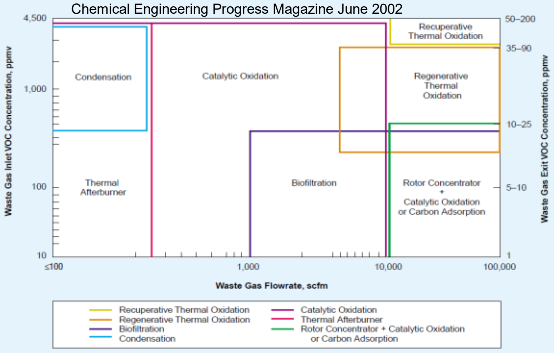
Thermal oxidation, or thermal incineration, is the process of oxidizing combustible materials by raising their temperature above the autoignition point in the presence of oxygen and maintaining it at a high temperature for sufficient time to complete combustion to carbon dioxide and water. Time, temperature, turbulence (for mixing) and the amount of oxygen affect the rate and efficiency of the combustion process. These

30 www.cepmagazine.org June 2002 CEP

Chemical Engineering Progress Magazine June 2002

https://www.aiche.org/resources/publications/cep/2002/june/reduce-voc-and-hap-emissions

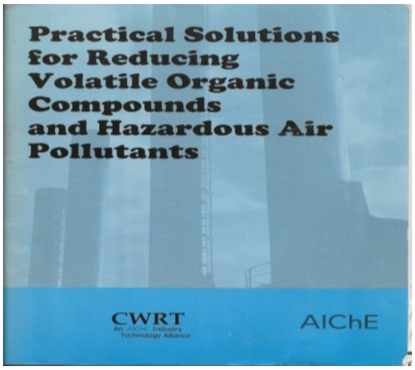
Chemical Engineering Progress Magazine June 2002



Basis: 4,500 ppmv = 25% of Lower Explosive Limit
Contains no halogenated organics
Contains no catalyst poisons
Contains no particulates

Note: Consider carbon adsorption for recovery when
- Recovered solvent value > $0.15/lb
- Concentration > 500 ppmv
- Gas flowrate > 1,000 scfm > 500 ppmv

https://www.aiche.org/resources/publications/cep/2002/june/reduce-voc-and-hap-emissions



Practical Solutions for Reducing Volatile Organic Compounds and Hazardous Air Pollutants

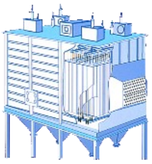
CWRT
An AIChE Industry Technology Alliance

AIChE

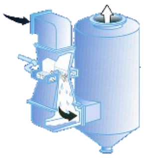
## Control Technologies for Particle Hazardous Air Pollutants Emissions

## Efficient Types of Control Technologies for Particle Hazardous Air Pollutants

**Fabric Filters**



**Electrostatic Precipitators**



**Venturi Wet Collectors**

## Control Devices for HAP's Particle Emissions

- The of control devices applicable to particulate laden emission streams from point sources are: fabric filters (baghouses), electrostatic precipitators (ESP's), and venturi scrubbers.
- The control efficiencies and applicability of these devices are dependant on the physical and/or chemical/electrical properties of the airborne particulate matter under consideration.

## Selection of Control Devices for HAP's Particle Emissions

- Selection of the these control devices is determined following studies of the specific stream characteristics (i.e., particle size, temperature, corrosiveness, resistivity, and moisture content) and the parameters (i.e., required collection efficiency) that affect the applicability of each control device.

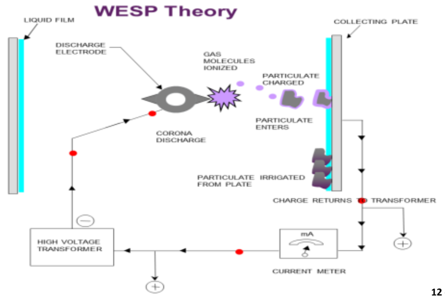
## Fabric Filters (Baghouses)

- Fabric filters collect particles (submicron to several hundred microns in diameter) at efficiencies generally in excess of 99 or 99.9 percent.
- The layer of dust, or dust cake, collected on the fabric is primarily responsible for such high efficiency.
- Gas temperatures up to about $500^{O}$F, with surges to about $550^{O}$F can be accommodated with high temperature bags.

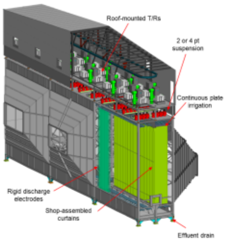
## Electrostatic Precipitators (ESP's)

- In an ESP particles are given an electrical charge by forcing them to pass through a corona glow region around charging electrodes in which gaseous ions are flowing.
- The electrical field quickly draws the charged particles to the walls (collecting plates) from charging electrodes which are maintained at high voltage in the center of the flow lanes between plates.
- An ESP can achieve a 99.9% overall mass collection efficiency and over 97-98% of all 0-5 micron particles.

## Wet Electrostatic Precipitators (WESP)



## Wheelabrator APC WESP

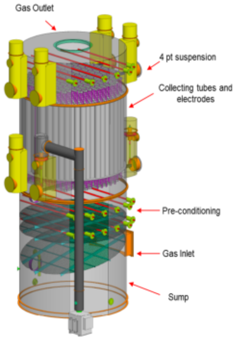


HIPWESP (Horizontal Irrigated Plate WESP)

FEATURES

- Horizontal gas flow for wide range of gas volumes
- Multiple electrical sectionalization for high removal capability
- Continuous collecting plate irrigation provides superior performance to spray cleaning designs
- Intermittent spray washing for corrosion protection of wetted equip
- Vertical, shop assembled collecting curtains. Alloy construction.
- 2 or 4 pt high voltage suspension
- Rigid discharge electrodes for increased performance and enhanced reliability
- Full penthouse/insulator encl.
- Access at top and bottom of fields

## Wheelabrator APC WESP



Condensing WESP

FEATURES

- Vertical gas flow for small footprint
- Superior performance to spray cleaning designs due to continuous plate irrigation via condensation
- Intermittent spray washing capability as secondary means of cleaning
- Modular construction for ease of installation. Rectangular or round.
- Round tubes for symmetrical electrical field
- 4 pt high voltage suspension
- Rigid discharge electrodes for increased performance and reliability
- Multiple electrical fields possible
- Pre-conditioning via water sprays or scrubbing

## DURR MEGTEC WESP

Next generation wet electrostatic precipitator - Dürr (durr.com)

## Venturi Scrubbers

- A venturi scrubber has a "converging-diverging" flow channel.
- The narrowest area is referred to as the "throat " where the decrease in area causes high gas velocities and turbulence to increase.
- Scrubbing liquid is injected into the scrubber slightly upstream of the throat or directly into the throat section.
- High collection efficiencies, ranging from 70% to 99% for smaller diameter particles.

## Web Sites For Additional EPA Control Device Information

- http://www.epa.gov/ttn/catc/products.html
- http://cfpub.epa.gov/oarweb/mkb/control.cfm

## Control Technologies for Mercury Emissions

- Mercury's high vapor pressure at typical APCD operating temperatures causes collection by PM control devices is highly variable.
- Factors that enhance mercury control are low temperature, high levels of carbon in the fly ash and the presence of hydrogen chloride (HCl).
- Conversely, sulfur dioxide ($SO_2$) in flue gas can convert oxidized mercury to elemental mercury, making it more difficult to collect.

## Common Controls to Reduce Mercury Emissions

Some of the most common add-on controls to reduce mercury emissions include:

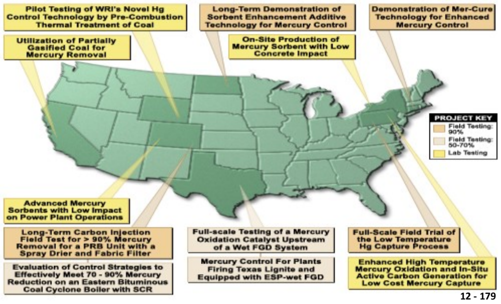
- Carbon filter beds
- Wet scrubbing
- Selenium filters
- Activated carbon injection

## Controlling Power Plant Mercury Emissions

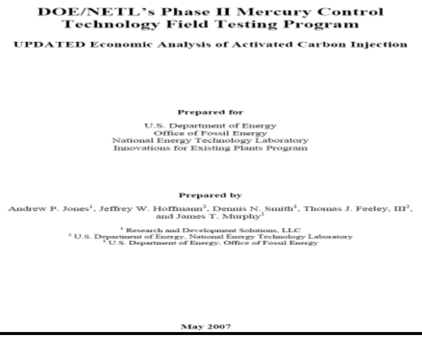
Currently, there are two main approaches being considered for controlling power plant mercury emissions:

- Reducing mercury emissions using technologies primarily designed to remove $SO_2$, $NO_X$, and particulate emissions (often called co-benefit reductions), and
- Reducing mercury emissions using technologies specifically designed to reduce mercury in coal prior to burning.

## DOE/NETL's Phase II Mercury Emission Control Program



## DOE/NETL's Phase II Mercury Control Program



**DOE/NETL's Phase II Mercury Control Technology Field Testing Program**

**UPDATED Economic Analysis of Activated Carbon Injection**

**Prepared for**

U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory
Innovations for Existing Plants Program

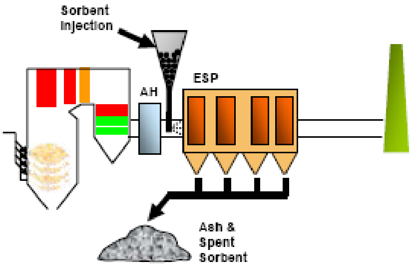
**Prepared by**

Andrew P. Jones[1], Jeffrey W. Hoffmann[2], Dennis N. Smith[3], Thomas J. Feeley, III[2], and James T. Murphy[1]

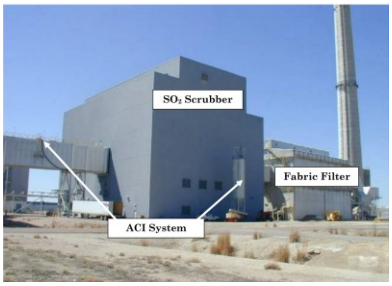
[1] Research and Development Solutions, LLC
[2] U.S. Department of Energy, National Energy Technology Laboratory
[3] U.S. Department of Energy, Office of Fossil Energy

**May 2007**

## Activated Carbon Injection Technology Schematic

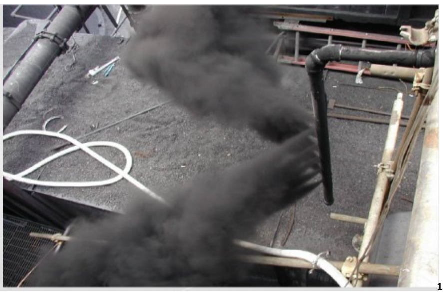


## Activated Carbon Injection System Capable of Achieving 90% Capture of Mercury Emissions at a Power Plant

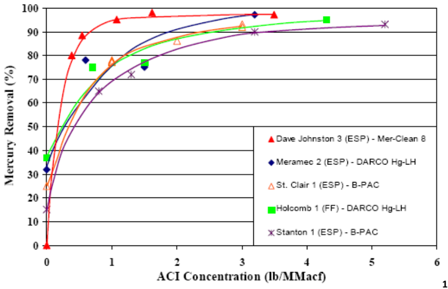


ICAC Mercury Control Technology Survey (senate.gov)

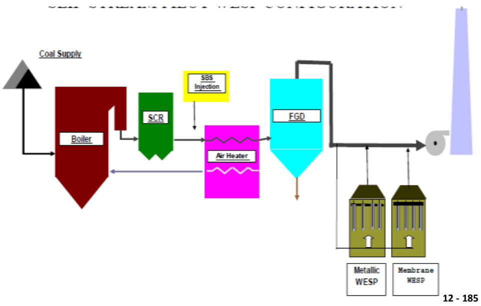
## Powdered Activated Carbon Injection



## ACI Performance Data for Phase II Units Firing PRB Coal



## Multi-pollutant Control Technology



## Multi-pollutant Control Technology

EPA United States Environmental Protection Agency

EPA-600/R-02/073
October 2002

Final Report

ENGINEERING AND ECONOMIC FACTORS AFFECTING THE INSTALLATION OF CONTROL TECHNOLOGIES FOR MULTIPOLLUTANT STRATEGIES

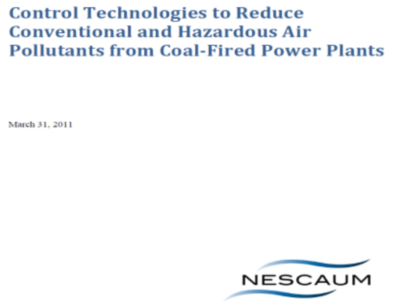
## NETL's Web Site

http://www.netl.doe.gov/technologies/coalpower/ewr/mercury/index.html

**2006 Mercury Control Technology Conference December 11-13, 2006 Table of Contents**

http://www.netl.doe.gov/publications/proceedings/06/mercury/index.html#oxidation

http://www.nescaum.org/topics/air-pollution-control-technologies



**Control Technologies to Reduce Conventional and Hazardous Air Pollutants from Coal-Fired Power Plants**

March 31, 2011

NESCAUM

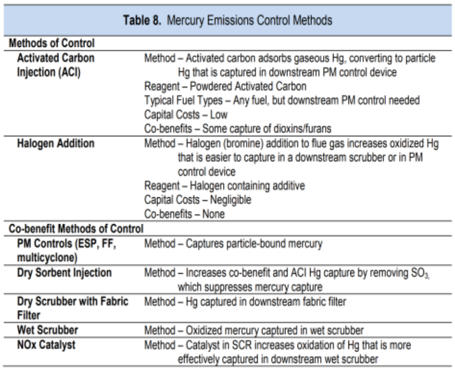


**Table 8.** Mercury Emissions Control Methods

| | |
|---|---|
| **Methods of Control** | |
| **Activated Carbon Injection (ACI)** | Method – Activated carbon adsorbs gaseous Hg, converting to particle Hg that is captured in downstream PM control device<br>Reagent – Powdered Activated Carbon<br>Typical Fuel Types – Any fuel, but downstream PM control needed<br>Capital Costs – Low<br>Co-benefits – Some capture of dioxins/furans |
| **Halogen Addition** | Method – Halogen (bromine) addition to flue gas increases oxidized Hg that is easier to capture in a downstream scrubber or in PM control device<br>Reagent – Halogen containing additive<br>Capital Costs – Negligible<br>Co-benefits – None |
| **Co-benefit Methods of Control** | |
| **PM Controls (ESP, FF, multicyclone)** | Method – Captures particle-bound mercury |
| **Dry Sorbent Injection** | Method – Increases co-benefit and ACI Hg capture by removing $SO_3$, which suppresses mercury capture |
| **Dry Scrubber with Fabric Filter** | Method – Hg captured in downstream fabric filter |
| **Wet Scrubber** | Method – Oxidized mercury captured in wet scrubber |
| **NOx Catalyst** | Method – Catalyst in SCR increases oxidation of Hg that is more effectively captured in downstream wet scrubber |

- **Chapter 12 Questions**

## Chapter 12 Control of HAP's for Stationary Sources Questions

- 1. What is the primary purpose of the packing material in a packed bed scrubber?

a. Provide liquid surface area for mass transfer.

b. Provide liquid sheet impaction targets .

c. Decrease the gas stream velocity.

d. None of the above

Answer:

## Chapter 12 Control of HAP's for Stationary Sources

- 2. What type of air pollution control system is generally used to collect acid gases formed during the oxidation of halogenated organic compounds?
- a. Absorbers
- b. Adsorbers
- c. Condensers
- d. None of the above
- Answer: