Chapter One

Air Toxics: A Legislative History

Air Toxics

Epidemiology and Toxicology: A History of Air Toxics

Risk Assessment: Process and History

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?
- 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): "all substances are poison & there is none that is not a poison"

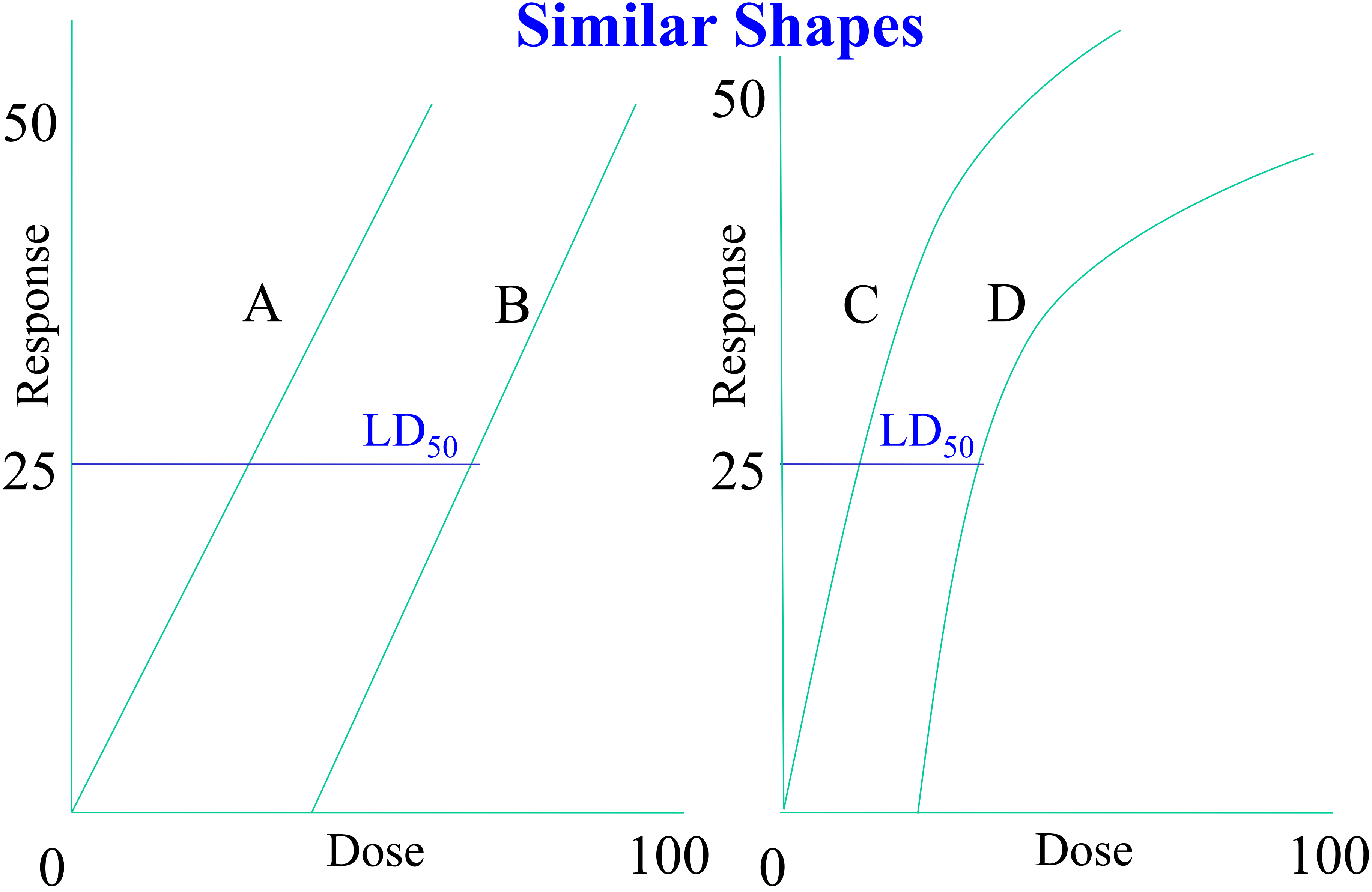
Epidemiology

- *Adverse effects are observed & their causes sought.*
- Early Romans: exposure to lead fumes caused health injuries.
- 1775: Percival Pott noted scrotal cancer in chimney sweeps.
- 1854: John Snow traced London’s cholera outbreak to the use of a contaminated well.

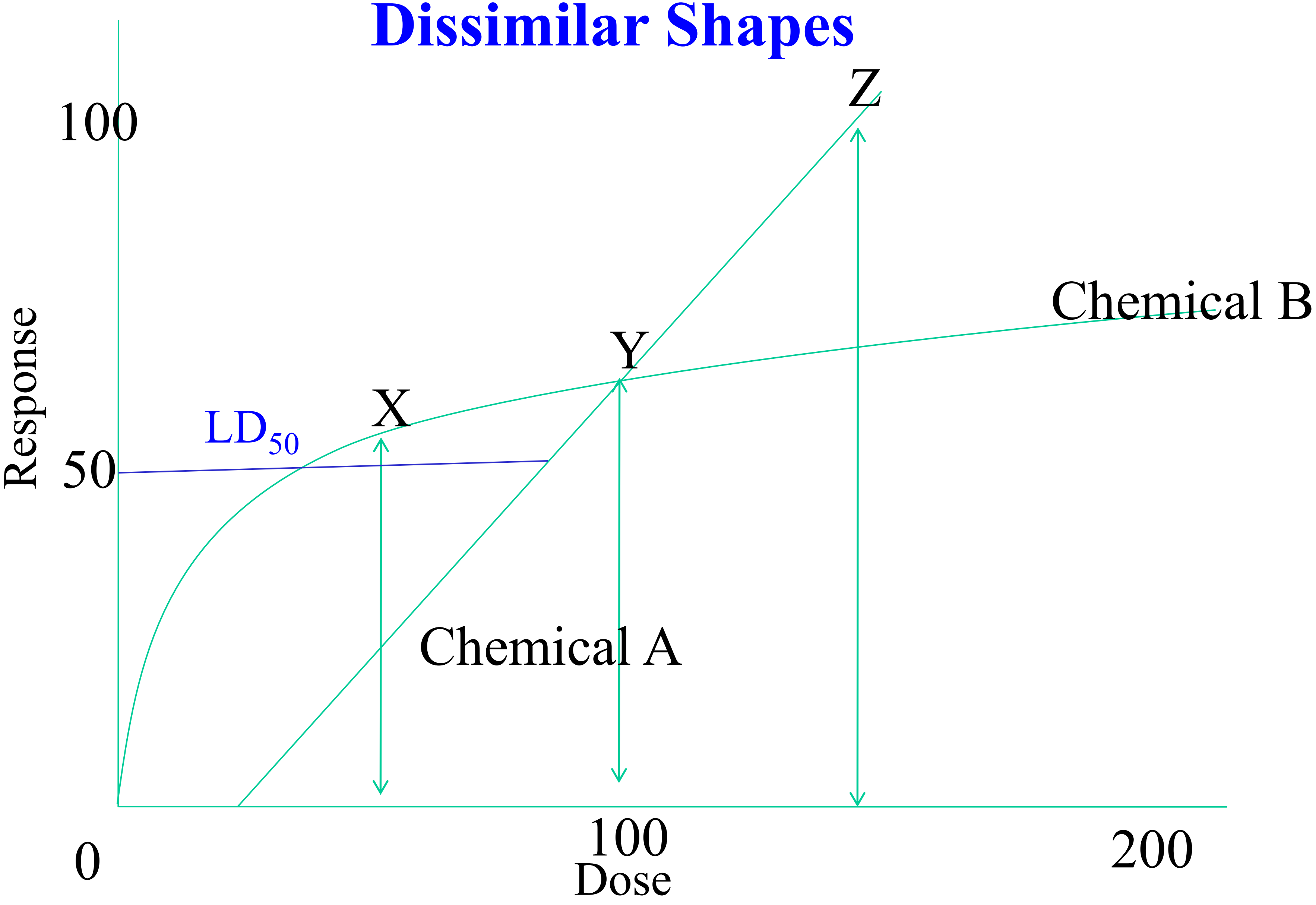
Toxicology

- 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



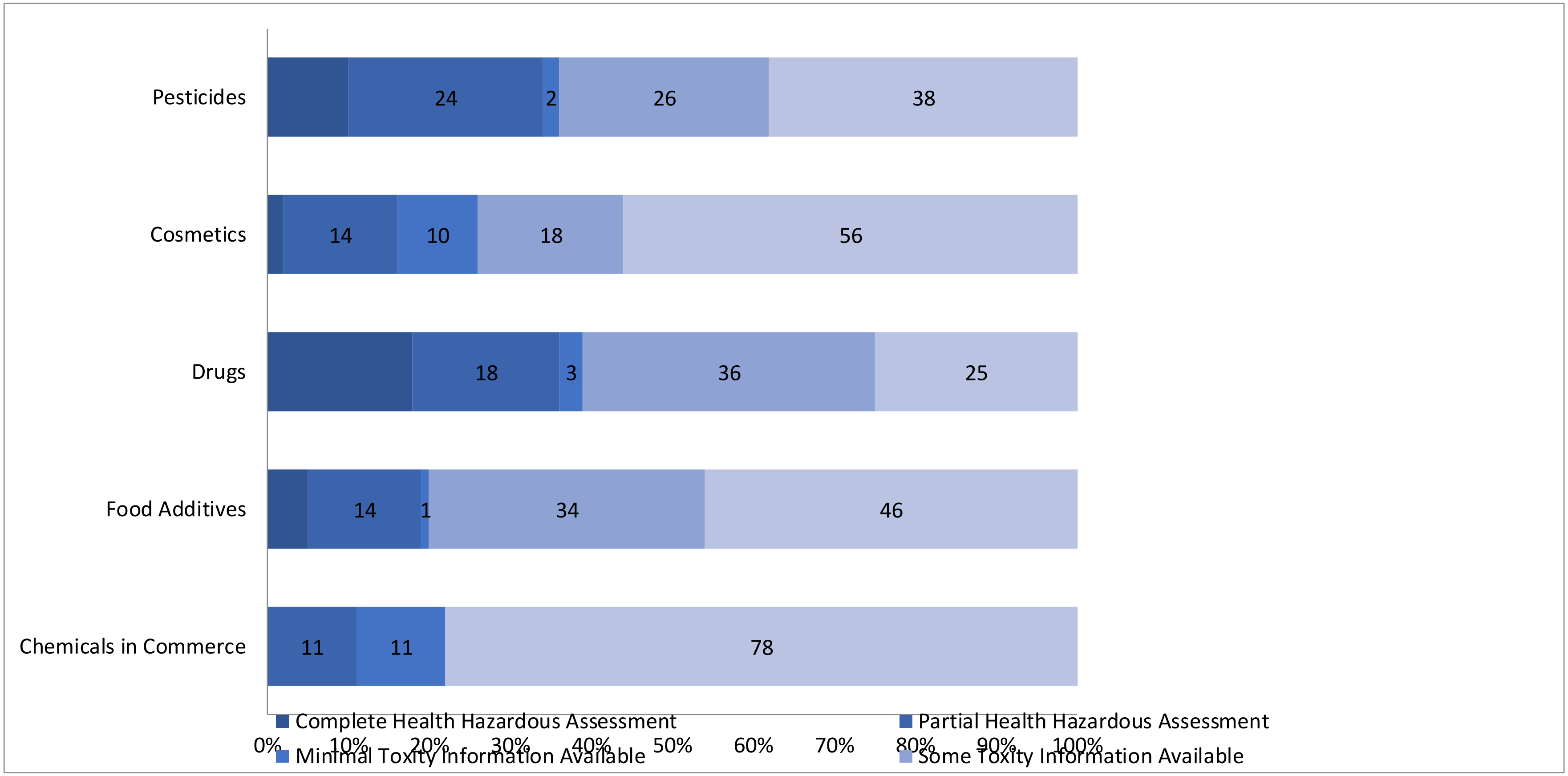
Toxicology

- 1950: Standard test for toxicity: if animal didn’t drop dead, the chemical was safe. Long term impacts of lower level of exposure were unknown.
- In 1953, Mary Amdur wanted to know the long term impacts of lower levels of exposure.
  - Her research found that the more acid in the air, the more lung damage; the smaller the particles, the deeper they penetrated the lungs.

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
- *Known Chemicals; Known Risks* (from a 1985 National Academy of Science Report)
  - 5 + million chemicals: Americans potentially exposed to about 70,000 of them
  - 2% - sufficient testing for complete hazardous health assessment
  - 14% - sufficient testing for a partial hazardous health assessment
  - 84% - minimal or no toxicity data available

Availability of Health-Hazard Data for Six Categories of Chemicals



Data from a 1984 National Resource Council Document

Changes in Society & Economy

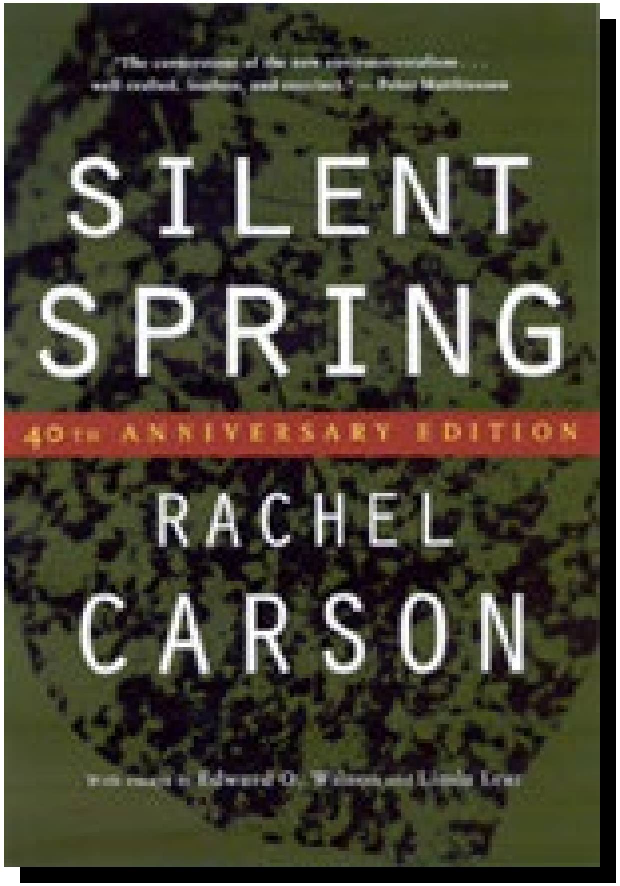
- By 1950, there were many changes in society & the economy, but we still did not know the adverse effects of air pollution.
- Longer Life Expectancy:
  - 1900: Life Expectancy of 50 years: (pneumonia, influenza & tuberculosis)
  - 1940: Life Expectancy of 63 years: (degenerative diseases: heart disease & cancer)
- Increased middle class: society can afford to be concerned about environment etc.

1955: Air Pollution Control Act

- Federal Research Funding

U.S. PUBLIC HEALTH SERVICE
• 1798 •

1962: Toxic Awareness



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 distinguished between:
  - *Air toxics* : "chemicals which may reasonably be anticipated to cause adverse effects" **with the main focus on cancer**.
  - *Criteria pollutants:* such as ozone, & PM etc. came from "criteria documents" pollutants studied during '50s & '60s.

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

Cancer

Kidney,
Liver
Damage

Skin Rashes

Developmental
Problems in
Children

Nervous
System
Damage

Cough,
Throat
Irritation

Birth Defects,
Miscarriages

Asthma,
Chronic
Bronchitis

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?
    - 2nd Take action to reduce risk (considered 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

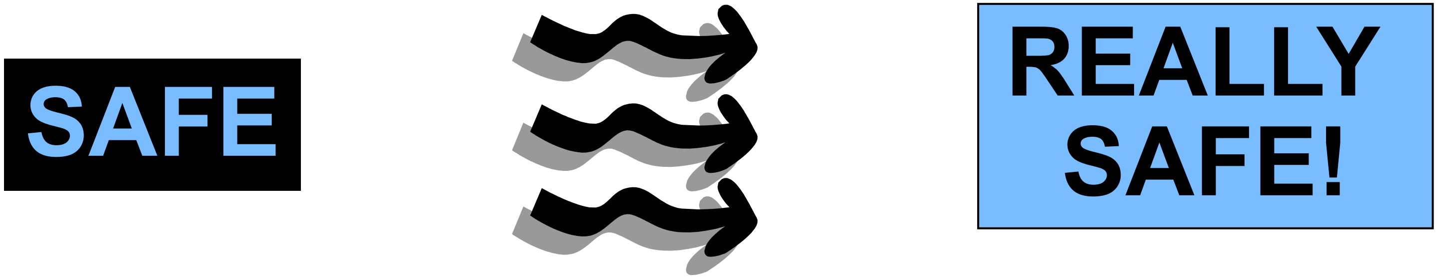
SAFE

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

No further action needed

Risk may be Acceptable

Look at Health Issues

Then consider costs/ technical feasibility before deciding if emissions reductions are needed

Risk is unacceptable

Take action to reduce risks

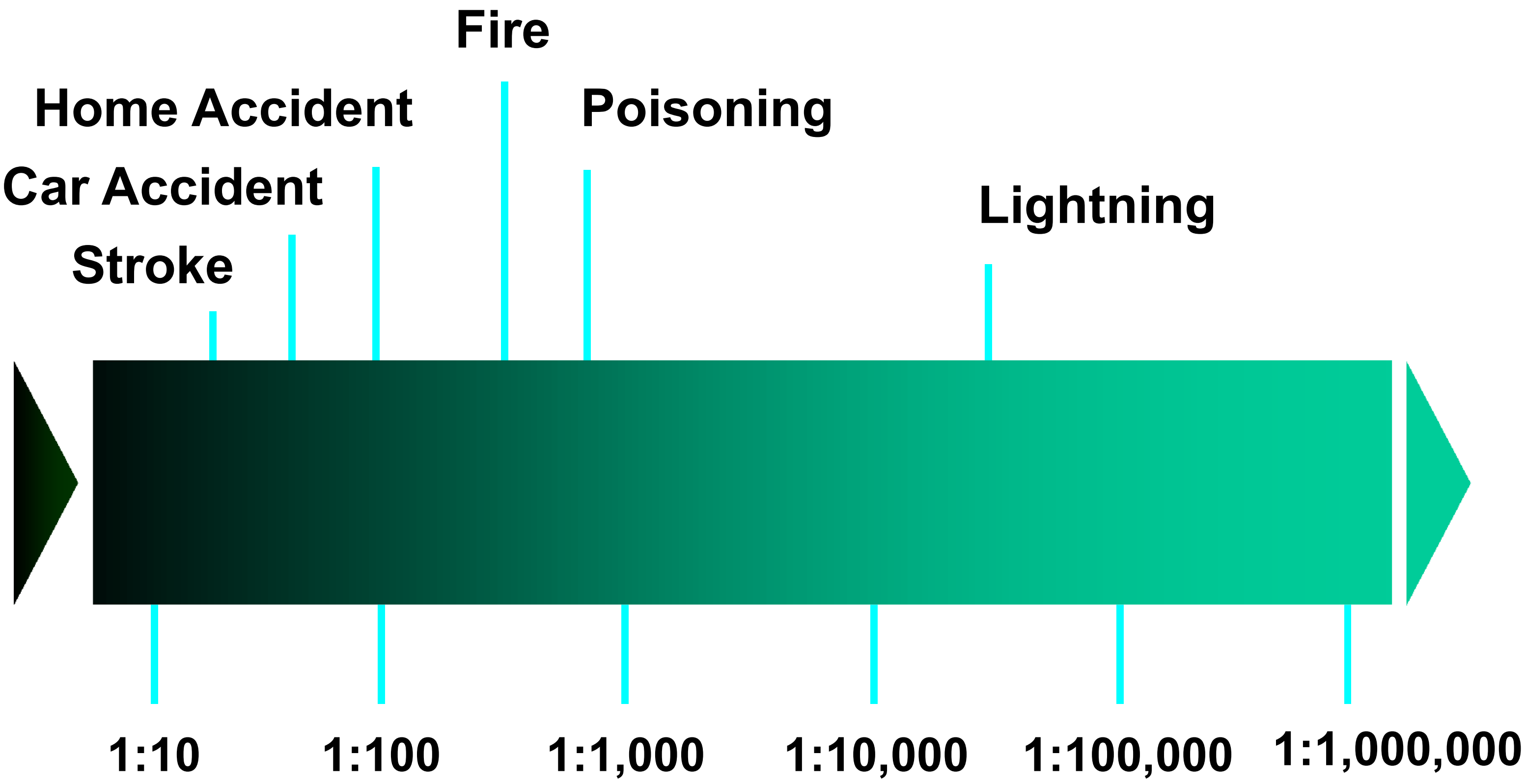
Can only consider health

1×10^{-6} 1×10^{-4}

Risk →

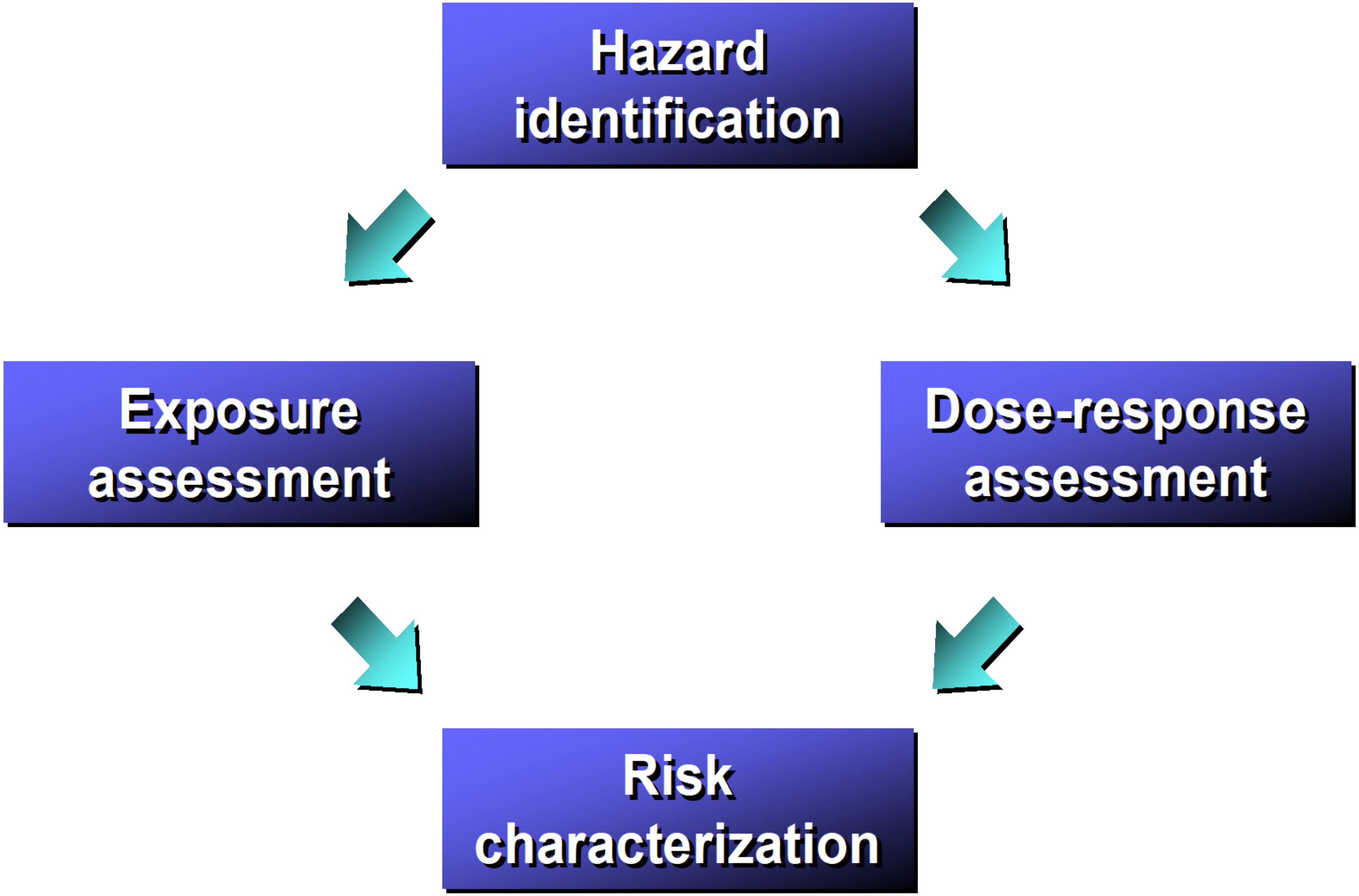
1989

Putting Risks in Perspective



Lifetime Risk of Death

Risk Assessment Process



Hazard identification

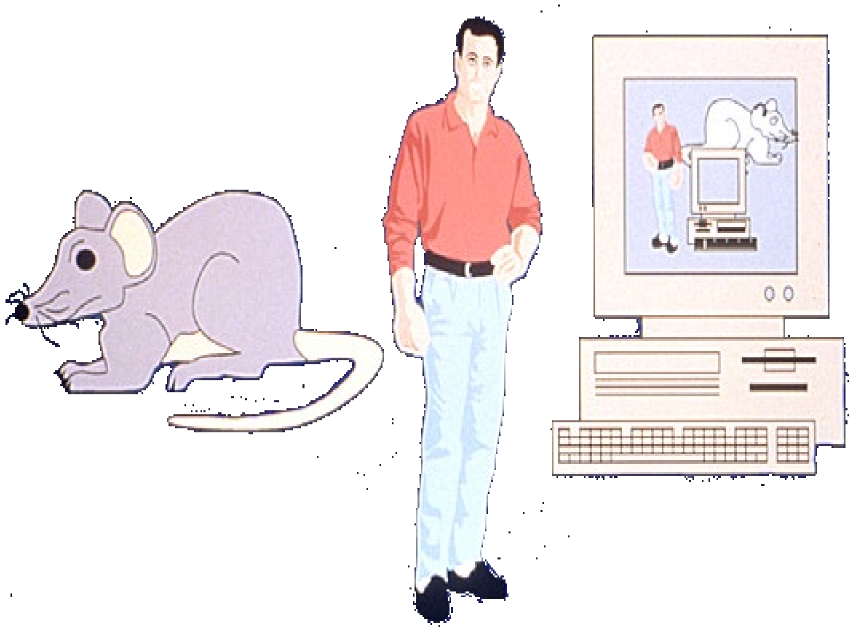
Exposure assessment

Dose-response assessment

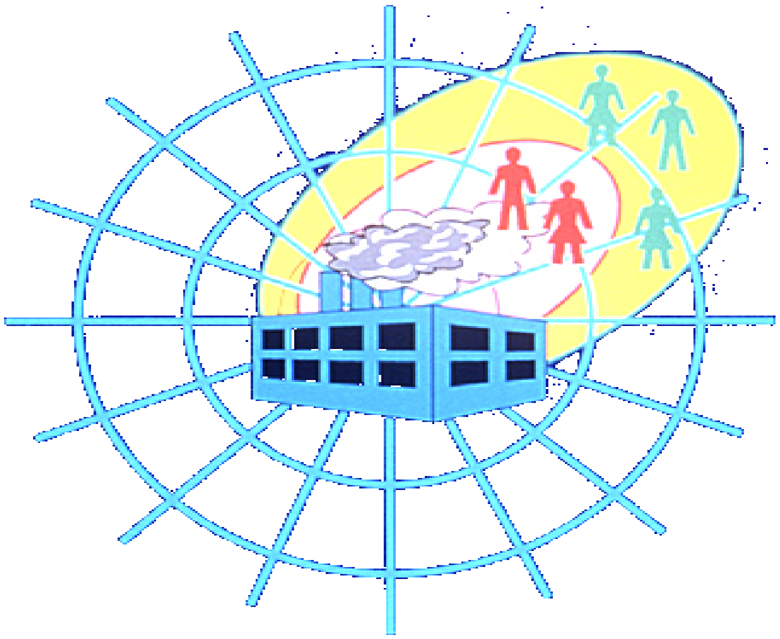
Risk characterization

Risk Assessment

- **Hazardous Identification:** Does the pollutant cause adverse health effects? Use human & animal studies.



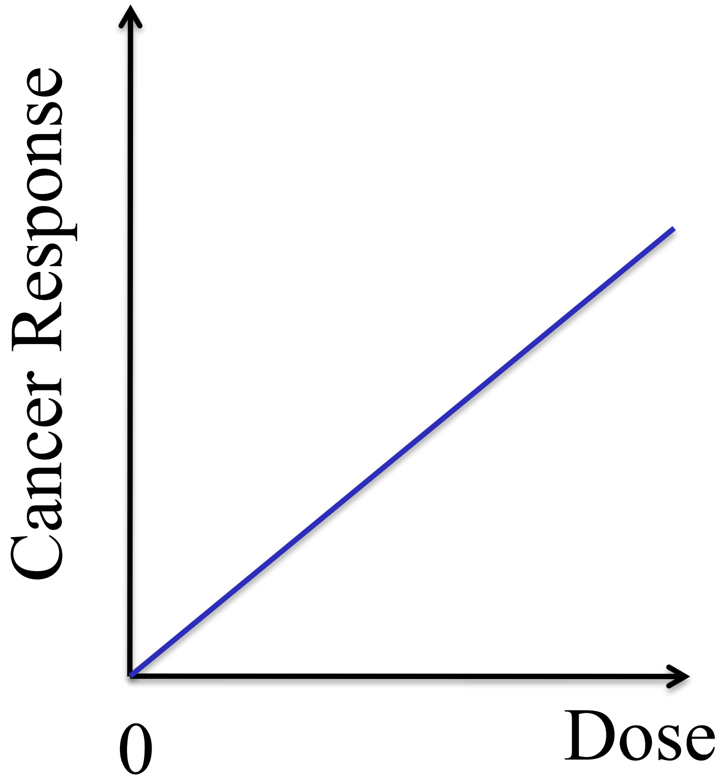
- **Exposure Assessment**: How much of the pollutant are people exposed to?



Dose-Response Relationship

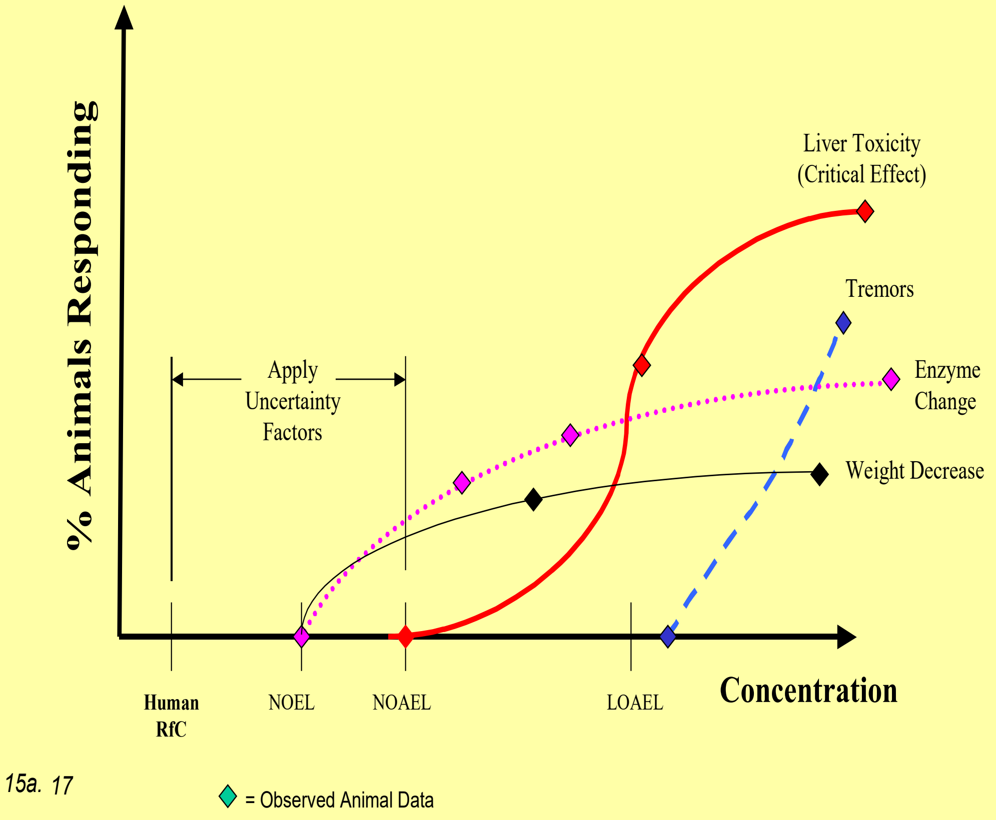
How much pollutant will cause an adverse effect?

Dose/Response - Cancer



Unit Risk = Slope of the Line

Dose/Response - Noncancer

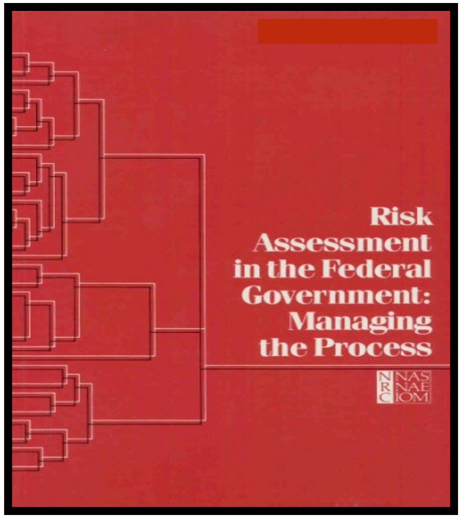


Risk Assessment

- **Risk Characterization**: What is the extra risk of health problems in the exposed population?
  - Cancer: Individual lifetime risk
  - Non-cancer: Less than the NOAEL to compensate for uncertainties

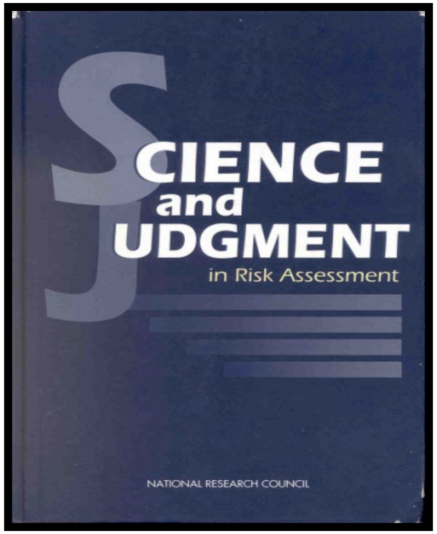
- **Uncertainties in Risk Estimates**:
- Too few human or animal studies of the health effects of chemicals
- Interspecies adjustment i.e.
  - Metabolism & absorption rates
  - Size, life span & exposure route
- Extrapolation from high to low doses

Three Fundamental Books



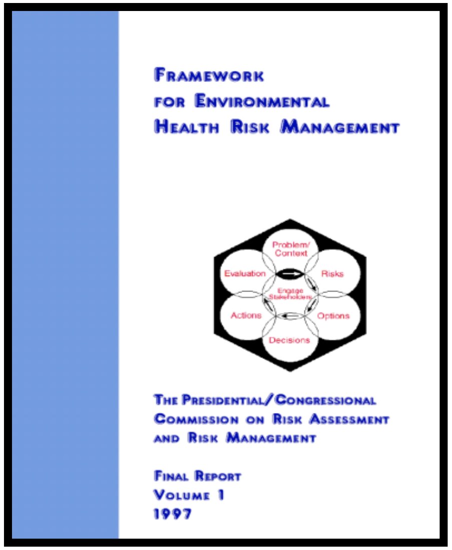
Risk Assessment in the Federal Government: Managing the Process

NRC NAS NAE IOM



SCIENCE and JUDGMENT in Risk Assessment

NATIONAL RESEARCH COUNCIL



FRAMEWORK
FOR ENVIRONMENTAL
HEALTH RISK MANAGEMENT

THE PRESIDENTIAL/CONGRESSIONAL
COMMISSION ON RISK ASSESSMENT
AND RISK MANAGEMENT

FINAL REPORT
VOLUME 1
1997

The Red Book

The Blue Book

The White Book

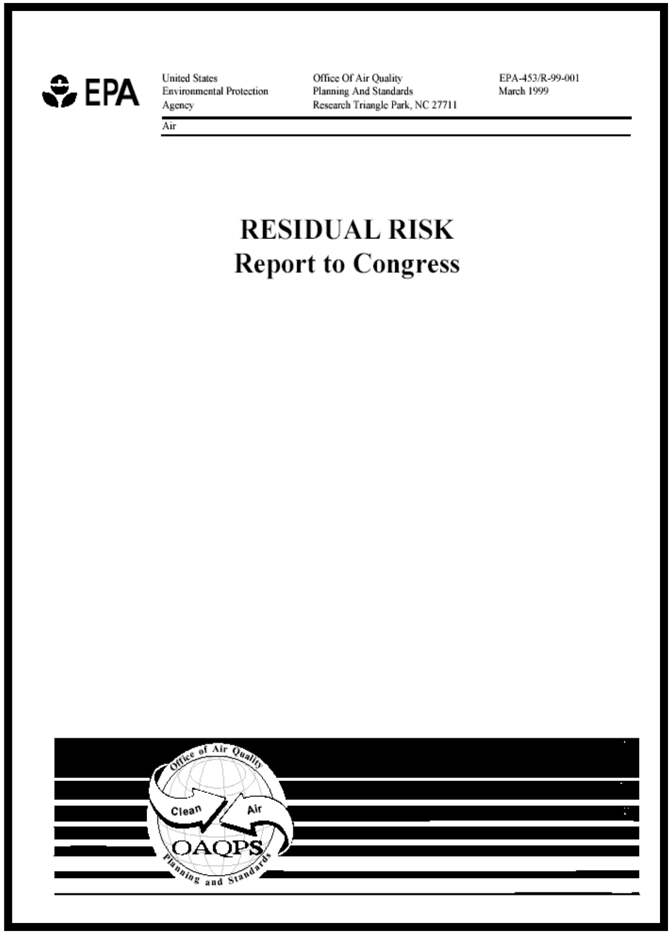
1983: First time 4 step RA process identified

1994: Reviewed EPA's RA methods

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 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

United States
Environmental Protection
Agency

Office Of Air Quality
Planning And Standards
Research Triangle Park, NC 27711

EPA-453/R-99-001
March 1999

Air

RESIDUAL RISK
Report to Congress

EPA's Risk Assessment Guideline Documents

- EPA has developed a series of *guideline documents* concerning risk assessment:
  - Cancer
  - Developmental Toxicity
  - Exposure Assessment
  - Neurotoxicity
  - Chemical Mixtures
  - Ecological Assessment
  - Mutagenicity
  - Reproductive Toxicity
- Documents at EPA's "Risk Assessment Portal": http://www.epa.gov/risk/guidance.htm

Air Toxics Risk Assessment Library

- EPA's Office of Air Quality Planning and Standards has developed methods and guidance for conducting facility-specific and community-scale air toxics assessments in a 3 volume set called the "Air Toxics Risk Assessment Library":
- Web site: http://www.epa.gov/ttn/fera/risk_atra_main.html
- Volume 1: Technical Resource Manual
- Volume 2: Facility-specific Assessment
- Volume 3: Community-Level Assessment

The National Center for Environmental Assessment (NCEA)

- NCEA is EPA’s resource center for human health & ecological risk assessment.
- Provides guidance & support to risk assessors.
- Many risk assessment documents are available on NECA; including the Integrated Risk Information System (IRIS).

NCEA

www.epa.gov/ncea

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 permanently disabled
- A subsequent release from a Western Virginia facility sent 100 people to the hospital.
- Result: states started toxic air programs.

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 amount must cooperate in emergency plan preparation.

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* 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	50,000 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 312: Annually to all of the above	Annually to EPA and the State

EPA's EPCRA Web Page

- EPCRA Overview | Emergency Management | US EPA

- http://www.epa.gov/emergencies/content/lawsregs/epcraover.htm

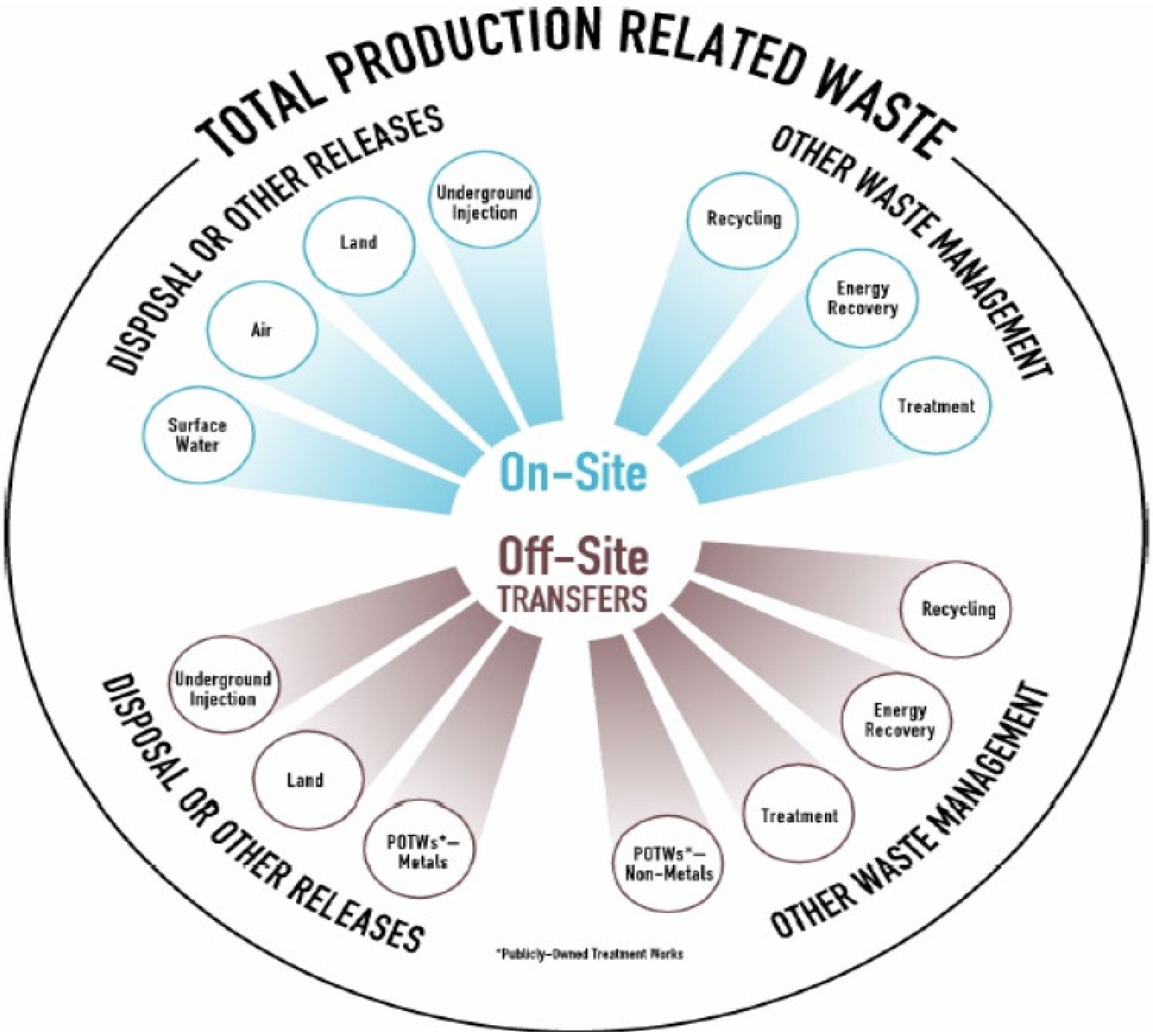
Toxic Release Inventory (Section 313)

- Facilities must *report annually* the amount of toxic chemicals *released* to the environment *each year*. Applicable facilities:
  - Are a designated facility (by industrial sectors: SIC codes);
  - Has 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 chemicals.

Toxic Release Inventory (Section 313)

- Facilities report using a *Toxic Chemical Release Inventory Form* for each of the 600 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.


TOTAL PRODUCTION RELATED WASTE
DISPOSAL OR OTHER RELEASES
Surface Water
Air
Land
Underground Injection
OTHER WASTE MANAGEMENT
Recycling
Energy Recovery
Treatment
On-Site
Off-Site
TRANSFERS
Underground Injection
Land
POTWs*—Metals
POTWs*—Non-Metals
Treatment
Energy Recovery
Recycling
DISPOSAL OR OTHER RELEASES
OTHER WASTE MANAGEMENT
*Publicly-Owned Treatment Works

EPCRA: Section 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.
- TRI reporting is not an accident prevention program.
- http://www.epa.gov/tri/

Toxics Release Inventory, 2006

22,880

TRI facilities

reported 4.25 billion

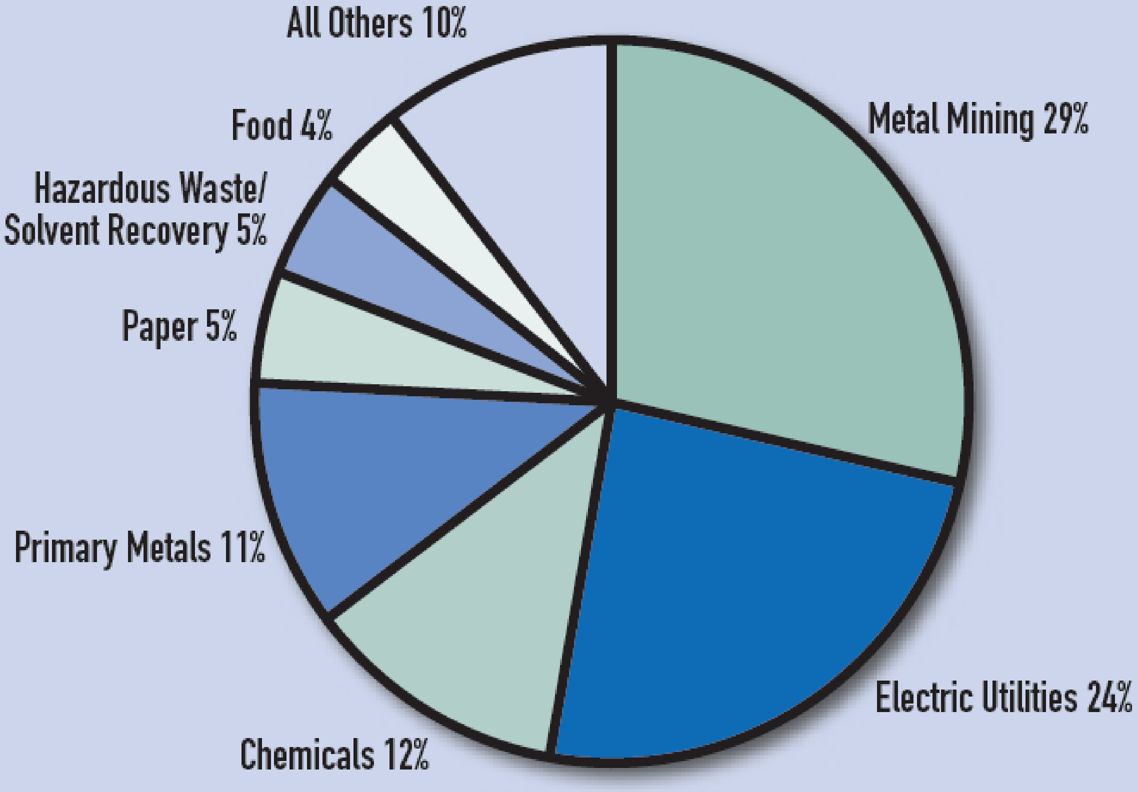
pounds of on- and

off-site disposal

or other releases

for RY 2006

Figure 2: 2006 TRI Total Disposal or Other Releases
4.25 billion pounds



Data are from TRI Form R, Section 5 (all parts) and 6.1 (metals and metal compounds only) and 6.2 (disposal codes only and metals and metal compounds reported under codes M40 and M61) as of February 2008.

TABLE 1: TRI ON-SITE AND OFF-SITE DISPOSAL OR OTHER RELEASES, 2006

ON-SITE DISPOSAL OR OTHER RELEASES	POUNDS	PERCENT
Air	1,408,281,830	33.1
Water	242,951,617	5.7
Underground Injection	219,785,762	5.2
Land	1,854,526,427	43.6
TOTAL ON-SITE DISPOSAL OR OTHER RELEASES	3,725,545,636	87.7
OFF-SITE DISPOSAL OR OTHER RELEASES		
Underground Injection	16,551,995	0.4
Land	361,308,179	8.5
POTWs and Wastewater Treatment	5,000,334	0.1
Other	140,459,086	3.3
TOTAL OFF-SITE DISPOSAL OR OTHER RELEASES	523,319,595	12.3
TOTAL ON- AND OFF-SITE DISPOSAL OR OTHER RELEASES	4,248,865,230	100.0

Note: Data are from TRI Form, Sections 5 (all parts) and 6.1 (metals and metal compounds only) and 6.2 (Disposal codes only and metals and metal compounds reported under codes M40 and M61). Does not include transfers to disposal or other releases sent to other TRI facilities that reported the amounts as on-site disposal or other releases. Data as of February 2008.

Chapter Two
Regulation of Air Toxics

1900 CAA Amendments
HAPs List
HAPs Source Categories

NESHAPs (MACTs)
Residual Risk Program

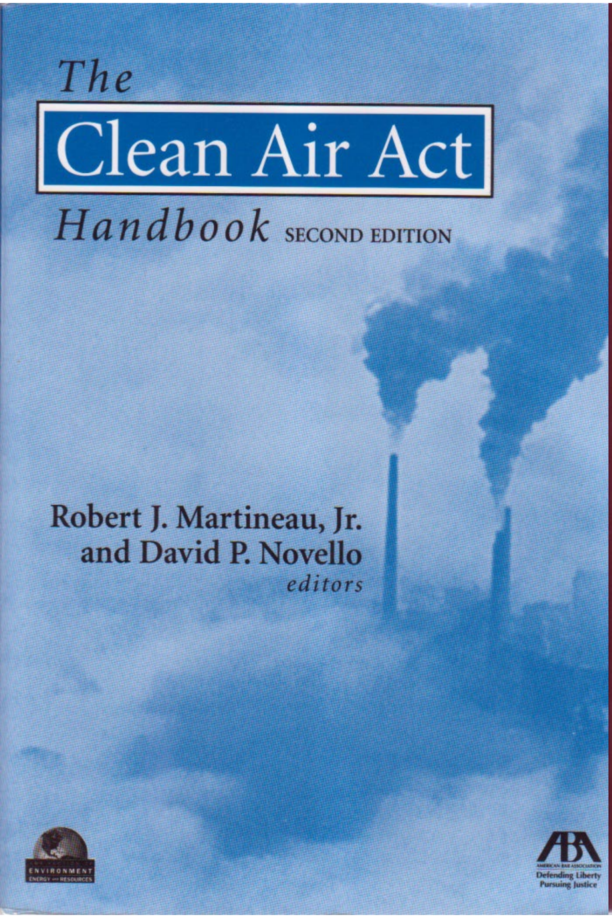
Clean Air Act
Section 112

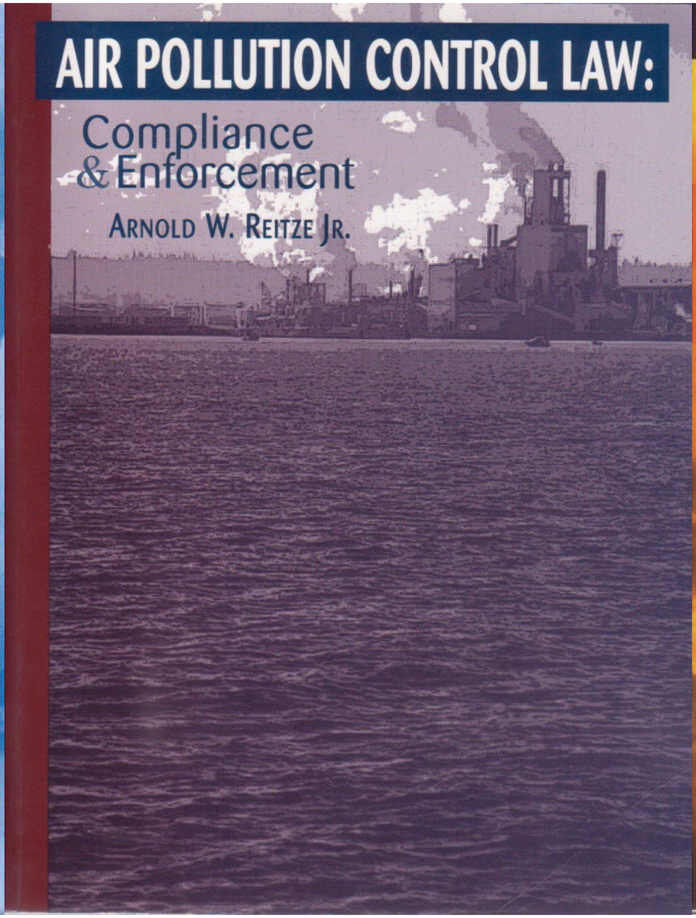
Major and Area Sources
Urban Air Toxics
Mobile Source Air Toxics

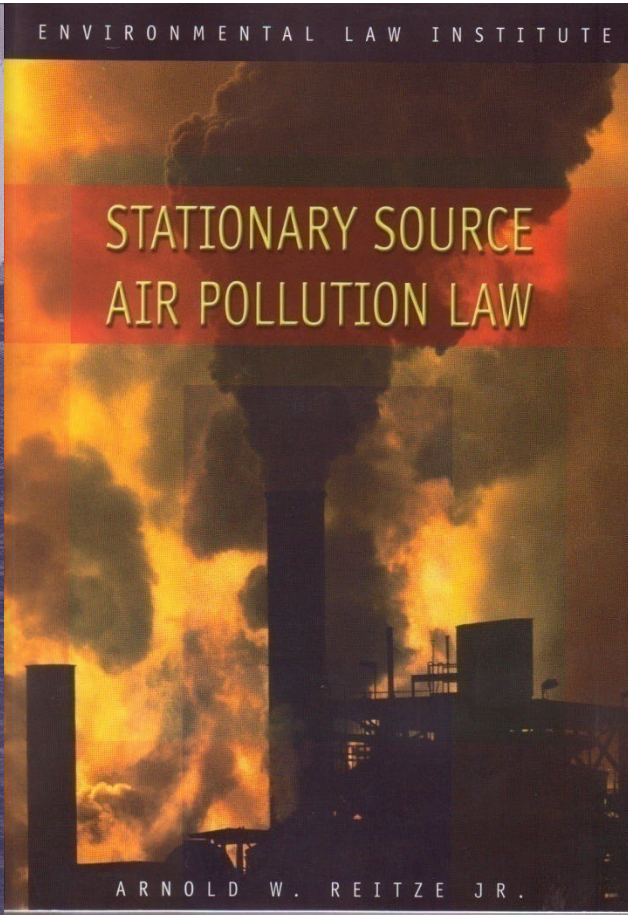
Mercury form Power Plants
State Air Toxics Program
Prevention of Accidental Releases
Air Toxic Monitoring & Trends

By: Louis DeRose

Air Toxics Regulation Reference Books

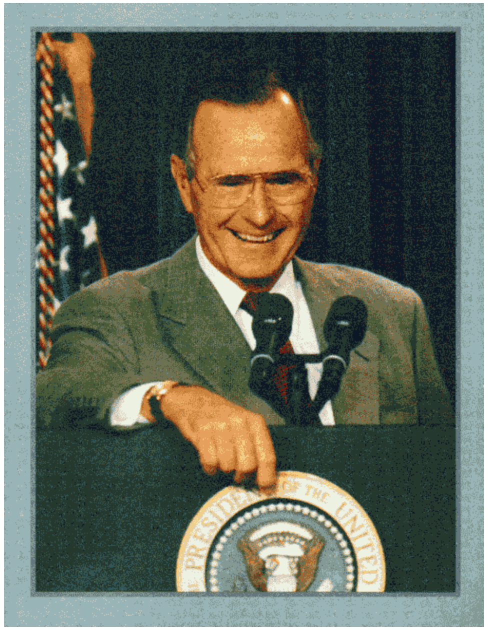






The Clean Air Act Amendments (CAAA) of 1990

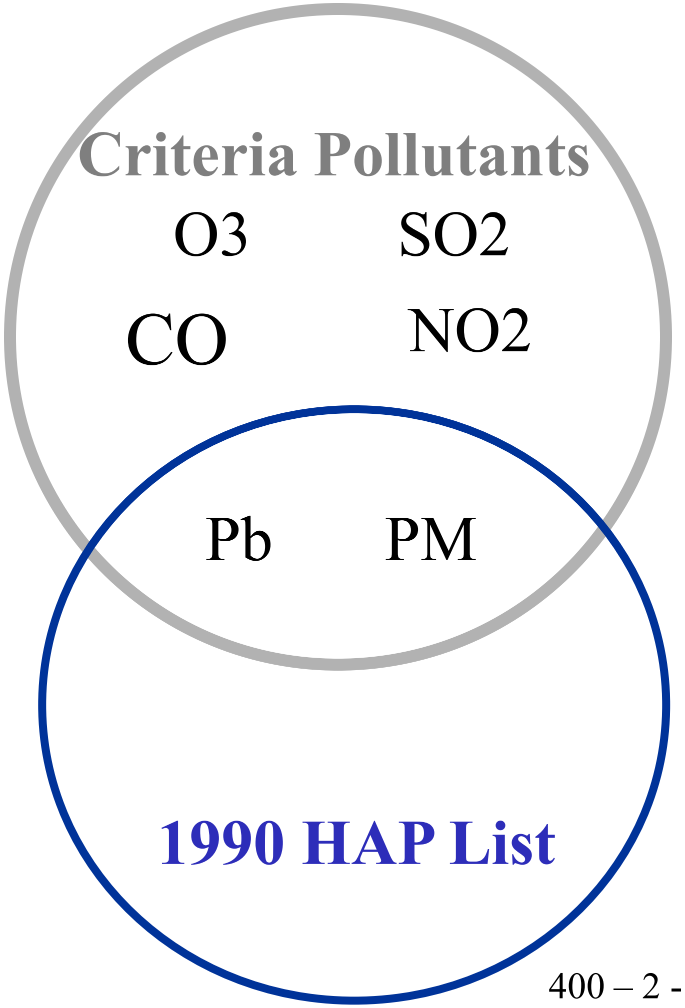
- The 1970 CAAA required EPA to list a HAP and required "ample margin of safety" protection (*health-based* standard)
- The 1990 CAAA:
  - – *Lists the HAP* and
  - – Required a *technology-based* control standard



1990

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



1990 CAAA: HAPs (Section 112)

- Congress originally listed 189 substances as HAPs
  - EPA can add or delete (delist)
  - Hydrogen Sulfide removed (clerical error)
  - Caprolactam (delisted June 1996)
  - Methyl Ethyl Ketone (MEK) (delisted Dec. 2005)
- EPA required to list source categories that emit one or more of §112 listed HAPs
  - 174 *major* and 8 *area* source categories
  - EPA can add or delete

1990 CAAA: HAPs (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)

EPA HAP Web Site: “Rules & Implementation”

- Located: Air Toxic Web site
- Link to “HAP list”
- Link to “source categories” of HAPs
- Link to all NESHAP (MACT) rules
- Link to other CAA air toxic programs
- Rules and Implementation | Technology Transfer Network Air Toxics Web site | US EPA

Rules and Implementation: NESHAP

- Rule Information (Federal Register)
  - Proposed and Final Rules
- Technical Information
  - Background Information Documents
  - Fact Sheets
  - Risk Assessment Information
- Implementation Information
  - Overview Brochure (tri-fold)
- Source Identification & Location Information
- Outreach Training Information
- Compliance & Enforcement Information

NESHAP Brochures

- Industrial Commercial and Institutional Boilers and Process Heater – 40 CFR 63 Subpart DDDDD (vacated in 2007)
  - Applies to “major sources” only
- Gasoline Distribution Bulk Terminals, Bulk Plants, and Pipeline Facilities – 40 CFR 63 Subpart BBBBBB
  - Applies to “area sources” only

Read the Boilers NESHAP carefully.

The following information helps you determine how your boiler or process heater may be affected by the Boilers NESHAP. However, the Boilers NESHAP is complex and affects units differently based on rated heat input, fuel type, and utilization. Find the Boilers NESHAP and compliance information at www.epa.gov/ttn/atw/boiler/boilerpg.html.

Which units are affected?

Affected:

Boilers or process heaters located at a major source of hazardous air pollutants (HAP).

Major source: Potential to emit 10 tons/year of one HAP or 25 tons/year of all HAP combined. Emissions from the entire facility, including non-boiler or process heater sources, count toward major source status.

Hazardous air pollutants: Boilers and process heaters emit HAP such as arsenic, cadmium, chromium, hydrogen chloride, hydrogen fluoride, lead, manganese, mercury, and nickel. Emissions from each boiler or process heater vary. HAP are listed at www.epa.gov/ttn/atw/188polls.html.

Not Affected:

- Solid waste incineration units covered under section 129 of the Clean Air Act
- Units covered by another NESHAP under 40 CFR part 63 (including hazardous waste units, chemical recovery boilers at pulp mills, secondary lead refining kettles, ethylene cracking furnaces, blast furnace gas fuel-fired units)
- Hot water heaters, blast furnace stoves, temporary boilers
- Direct-fired (contact) combustion units (e.g., direct contact dryers) where the combustion gases come into contact with the process materials
- Research and development units

Affected units with no requirements or only initial notification:

- **No requirements:** Existing small units (all fuel types) and new small units (gas fuel) have no emission limits and no requirements: No monitoring, no records, no notifications.
- **Initial notification:** Existing large units (gas and liquid fuel), new small units (distillate oil only or combined with gas fuel) have no emission limits and submit only an initial notification. No other requirements.

Emission limits apply to these boilers or process heaters:

FUEL TYPE	EXISTING UNITS	NEW UNITS
Solid	PM or TSM HCl Hg	PM or TSM HCl Hg CO
Liquid	None	PM HCl CO
Gas	None	CO

Solid: Burns any amount of solid fuel
Liquid: Burns liquid fuel alone or with gas
Gas: Burns only gaseous fuel

Regulated Pollutants

- Particulate matter (PM) or total selected metals (TSM) as surrogate for metallic HAP. TSM: Arsenic, beryllium, cadmium, chromium, lead, manganese, nickel, selenium
- Hydrogen chloride (HCl) as surrogate for inorganic HAP
- Mercury (Hg)
- Carbon monoxide (CO) as surrogate for organic HAP

NEW UNITS: Commenced construction or reconstruction on or after January 13, 2003

EXISTING UNITS: Commenced construction before January 13, 2003

SMALL UNITS: Any firetube boiler (regardless of size) and any other boiler or process heater ≤10 MMBtu/hr

LARGE UNITS: Any watertube boiler or process heater >10 MMBtu/hr

Compliance Alternatives

Units can meet emission limits through a combination of the following:

- Conduct performance testing for units that have new or existing control devices
  - ➢ Use emissions averaging (certain units)
  - ➢ For HCl (measured as HCl and chlorine) and manganese, demonstrate low public risk
- For HCl, TSM, Hg, limit HAP content of fuel, demonstrate compliance through fuel analysis

GASOLINE DISTRIBUTION BULK TERMINALS, BULK PLANTS, AND PIPELINE FACILITIES (SUBPART BBBBBB)

What Is an Area Source?

Any source that is not a major source. (A major source is a facility that emits, or has the potential to emit in the absence of controls, at least 10 tons per year (TPY) of individual hazardous air pollutants (HAP) or 25 TPY of combined HAP.)

Who Does This Rule Apply To?

This rule applies to area source bulk gasoline terminals, pipeline breakout stations, pipeline pumping stations, and bulk gasoline plants.

What Am I Required To Do?

This rule includes emission limits and management practices for storage tanks, cargo tanks (railcars and tank trucks), loading racks, and equipment leaks. (See Table 1.)

Compliance Demonstration

Control devices used on loading racks at bulk terminals must be tested to demonstrate compliance with the emission limit.

Closed vent systems and control devices used on storage tanks also must be tested to demonstrate compliance with the emission limit.

Table 1. National Air Toxic Standards for Gasoline Distribution Bulk Terminals, Bulk Plants, and Pipeline Facilities (40 CFR 63, Subpart BBBBBB)[1]

Facility Type	Storage Tanks	Cargo Tank Loading Racks	Equipment Leaks
Bulk Gasoline Plant (less than 20,000 gallons per day	For storage tanks ≥ 250 gallons capacity, load storage tank using submerged fill with discharge that is no more than the following from the bottom of tank: a) 12 inches for pipes installed on or before 11/9/2006 b) 6 inches for pipes installed after 11/9/2006	Use submerged filling	Same for all facilities: Implement monthly equipment leak inspection; standards allow a sight, sound, and smell inspection of all equipment components in gasoline liquid or vapor service
Bulk Gasoline Terminal (greater than or equal to 20,000 gallons per day)	**≥ 75 cubic meters capacity:** use specified floating roofs and seals or a closed vent system and control device to reduce emissions by 95%	**Gasoline throughput ≥ 250,000 gallons per day :** 1) reduce HAP emissions to 80 milligrams (mg) or less, per liter of gasoline loaded into cargo tanks, and 2) limit the loading of gasoline into cargo tanks demonstrated to be vapor tight[2] using Reference Method 27 or equivalent	
	<75 cubic meters capacity: cover tank with a fixed roof mounted in a stationary manner and maintain all openings in a closed position at all times when not in use	**Gasoline throughput < 250,000 gallons per day:** use submerged filling for the loading of cargo tanks	
Pipeline Breakout Station	Same as bulk gasoline terminals	Not Applicable	
Pipeline Pumping Station	Not Applicable	Not Applicable	

1. This is a summary table; compliance will only be determined by compliance with actual rule text in 40 CFR 63, subpart BBBBBB.

2. Must be tested annually and meet a maximum allowable pressure/vacuum change of 3 inches of water in 5 minutes.

HAP Program Definitions of: Major Source and Area Source

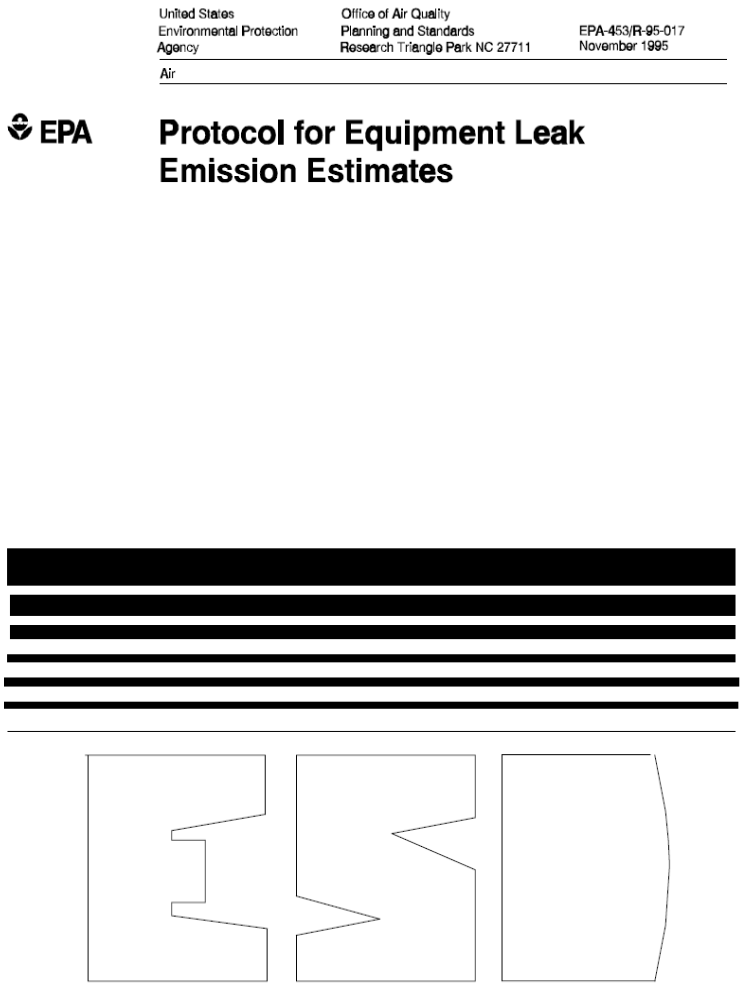
- Major source is any stationary source or group of stationary sources that are contiguous & under common control that has the potential to emit considering controls *at least*:
  - 10 tons/yr of a listed HAP, or
  - 25 tons/yr of a combination of listed HAPs
- Area source is a stationary source of HAPs that is not a major source.

HAP Major Source

- <u>Source</u>: (same as NSPS) small as an emission unit or as large as the entire facility
  - Does <u>not</u> have to have the same SIC code (industrial category) & does <u>not</u> have to be functional related
  - *Fugitive emissions* <u>must</u> be included
- <u>Contiguous</u>: same as in NSR & PSD programs
- <u>Common Control</u>: same ownership
- <u>Potential to emit</u>: maximum design capacity of the source <u>after</u> pollution controls & restrictions on hours of operation or type & amount of material combusted or processed
  - Limitations must be "federally enforceable"

HAP Fugitive Emissions

- EPA has developed emission factors associated with equipment leaks at petroleum facilities and chemical plants.
- The EPA document "*Protocol for Equipment Leak Emission Factors*" is available at http://www.epa.gov/ttn/chief/efdocs/equiplks.pdf.
- The factors in this document can be used for estimating emissions of VOC HAPs by using the percentage of the given air toxic to the total VOC emission rate.



United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-453/R-95-017
November 1995

Air

EPA

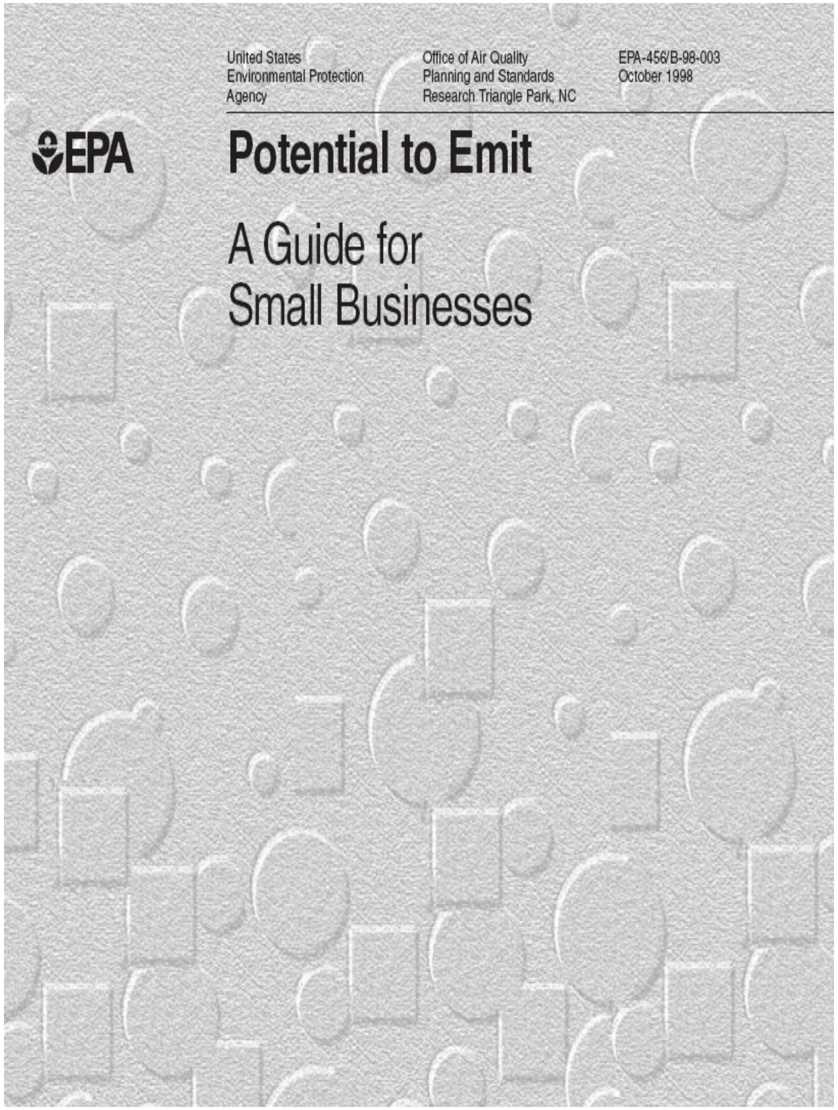
Protocol for Equipment Leak Emission Estimates

Example: Fugitive Emission Calculation

- A chemical facility has 145 valves in active liquid VOC service. The material is 3% benzene. Calculate fugitive benzene emissions from valve leaks.
- The VOC emission factor from Table 2-1 in the "*Protocol for Equipment Leak Emission Factors*" is 0.00597 kg/hr/valve (0.0132 lb/hr/valve).
- VOC emissions would be calculated as:
  - 145 valves x 0.0132 lb/hr/valve = 1.914 lb/hr
- Benzene emissions would be calculated as:
  - (hourly) 1.914 lb/hr x 3% = 0.057 lb/hr
  - (annual) 0.057 lb/hr x 8,760 hr/yr = 499 lb/yr = *0.25 tons/yr*

PTE Guidance

- Good example of calculating PTE from a printing operation for HAP
- To obtain copy:
- http://www.epa.gov/ttn/atw/publicat.html
- For PTE guidance info:
- http://www.epa.gov/ttn/atw/pte/ptepg.html



United States
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Agency

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Planning and Standards
Research Triangle Park, NC

EPA-456/B-98-003
October 1998

EPA

Potential to Emit

A Guide for
Small Businesses

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

“Once-in-always-in” policy

- A major source that reduces HAP emissions below 10 tons/yr. for a single HAP or 25 tons/yr. combined HAPs:
  - Remains a major source and *cannot become an area source* (which is not subject to MACT) if it reduces total HAP emissions below the required amount (May 16, 1995 EPA Policy Memo).
  - On Jan 3, 2007, EPA proposed rule: allows a major source to become an area source if it reduces total HAP emissions below the required amount.

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)
  - Best controlled similar sources (MACT floors)
- Existing sources
  - 3 years to comply after promulgation of rule
  - 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 Dry Cleaning Facilities with: 1. Only Dry-to-Dry Machines 2. Only Transfer Machines 3. Both Dry-to-Dry and Transfer Machines	Consuming <: 140 gallons PCE/yr. 200 gallons PCE/yr. 140 gallons PCE/yr.	Consuming equal to or between PCE/yr): 140 – 2,100 gallons 200 – 1,000 gallons 140 – 1,800 gallons	Consuming >: 2,100 gallons PCE/yr. 1,800 gallons PCE/yr. 1,800 gallons PCE/yr.
Process Vent Controls: Existing Facilities	None	Refrigerated condenser (or equivalent) 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: Existing Facilities	- Leak detection/repair - Store all PCE solvent & waste in sealed containers		Transfer machine systems are contained inside a room enclosure
New Facilities	- Leak detection/repair - Store PCE solvent & waste in sealed containers - No new transfer machine systems allowed		

Requirement	Small Area Source	Large Area Source	Major Source
Monitoring:	New: Same as large area source 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.) 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: 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.

NESHAP Guidelines

- 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*.
- 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.

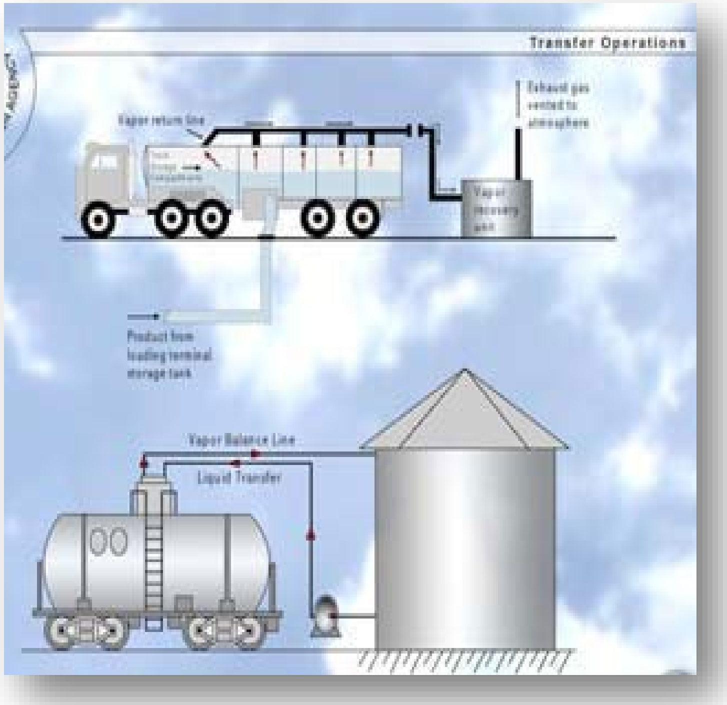
General Provisions for NESHAP

- (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**: CMS system is required for 4 specified control devices.
- §63.428 **Reporting and Recordkeeping**

NESHAP: "Affected Source"

- NESHAP applies only to the "affected source(s)" that are listed in the rule.
- The "affected source(s) " will be defined in the rule.
- General Provisions define the term "*affected source*" to designate specific source or group of emissions units that are subject to a particular §112 rule.
- Example: Gasoline Distribution MACT:
  - 2 defined "affected sources": bulk gasoline terminals (BGT) and pipeline breakout stations (PBS).
  - 3 regulated *emission units* which have control requirements: storage vessels (for both BGT and PBS), loading racks (for BGT only), & equipment leaks (for both BGT and PBS).

Rule Applicability: Post 1990, NESHAP (MACT)

1. Determine whether the facility is a HAP major source.
2. Identify the source categories for each applicable MACT at the plant site; and
3. Identify the emission units that fall under each MACT's source category.
   - Each source category is regulated by a specific NESHAP (MACT) rule.
   - Each NESHAP (MACT) rule will define what "*affected sources*" and emission points it regulates.
   - There should be *no overlap* of NESHAP (MACT) rules for an emission point.

Rule Applicability: NSPS & Pre 1990 NESHAPS

- The individual NESHAP /NSPS will define what emission units are part of its source category & subject to its regulation.
  - NSPS have more than 70 source categories.
  - NSPS uses the term "affected facility" the same way MACT uses the term "affected source."
  - The regulation will define emission unit applicability (i.e. size, material stored, vapor pressure, etc).

Example: Rule Applicability

- Delta Petroleum Corporation is a petroleum refinery & chemical company that produces petroleum distillates & petrochemicals.
- The first step is to determine whether the facility (plant site) is a *major source* of HAPs.
  - Delta Petroleum is a "major" source of HAPs because it has a potential to emit 100 tons per year of total HAPs (which is more than the 25 tons per year limit for total HAPs).

List of Source Categories & Their MACTs

- The second step is to determine which *individual source categories* at the plant site are subject to an applicable MACT rule:
- Petroleum refinery (40CFR63 Subpart CC)
- Fluid catalytic cracking (FCC) (40 CFR 63 Subpart UUU)
- Hazardous organic NESHAP (HON) (40 CFR 63 Subparts F,G,H)
- Gasoline distribution (40 CFR 63 Subpart R)
- Organic liquid distribution (OLD) (40 CFR 63 Subpart EEEE)
- Industrial boilers/process heaters (40 CFR 63 Subpart DDDDD)
  - MACT *vacated* in 2007
- Industrial cooling towers (40 CFR 63 Subpart Q)
- Benzene waste operations (40 CFR 61 Subpart FF)

Assign NESHAPs to Applicable Emission Units

- The third step is to identify the plant site's process equipment (*emission points*) to the appropriate source category.
  - It entails listing all the "affected sources" and emission units at the plant site and assign it to a particular NESHAP (MACT).
  - No overlap of NESHAPs for an emission point
- The next 2 slides are a summary of the NESHAP applicability to the "affected sources" at the plant site.

“Affected Sources” at Plant Site	Applicability of NESHAP (MACT)
Petroleum refinery: miscellaneous process vents; storage vessels; wastewater treatment facilities; cooling towers; equipment leaks; marine vessel loading; and gasoline loading racks	All petroleum refinery “affected sources” emission units are regulated by the Petroleum Refinery MACT.
HON: process vents, storage vessels, transfer racks, wastewater treatment facilities, and equipment leak components	Only 2 storage vessels are regulated by HON. These vessels store liquid organic HAPs that are listed in the HON. The remaining HON emission units are exempt from HON because they are petroleum refinery process units.
Bulk gasoline terminal emission units are: storage tanks, loading racks and equipment leaks components	Gasoline Distribution MACT does not apply because its emission units are already regulated under Petroleum Refinery MACT.
OLD: Storage vessels, transfer racks, transport vehicles, containers, and equipment leak components (applies only to storing of organic liquids listed in OLD MACT Table 1 – no gasoline)	OLD MACT is not applicable because the emission units are already regulated under Refinery MACT and remaining units do not handle material with a Table 1 HAP > 5%

"Affected Sources" at Plant Site	Applicability of NESHAP (MACT)
Boilers and process heaters	Since the Industrial Boiler & Process Heater MACT has been vacated – the state should set regulation on a case-by-case basis (hammer?)
Cooling towers	Cooling Tower NESHAP is not applicable because the towers do not use chromium-based treatment of chemicals
FCC unit: catalytic reformer units, and the sulfur recovery units	These sulfur removal emission units are regulated by NESHAP for Petroleum Refinery FCC, Catalytic Reformer Units, and the Sulfur Plant Units
Benzene waste operations (tanks, treatment, etc.)	Regulated by Benzene Waste Operation NESHAP

MACT Hammer

- Codified at CAA § 112(j).
- This provision mandates that if EPA *fails to pass* a MACT standard within 18 months of the regulatory deadline, major sources of HAP emissions are required to obtain an equivalent emission limitation by permit (Title V permit).
  - state must establish source-specific MACT standards on a case-by-case basis

MACT Hammer

- Some MACTs have been "*vacated*" (in 2007):
  - Brick & Structural Clay Products Manufacturing,
  - Clay Ceramics Manufacturing, and
  - Industrial/Commercial Boilers and Process Heaters
- At issue is whether CAA § 112(j) applies when EPA has passed the MACT, but the MACT is subsequently vacated.
  - States have received no guidance from the EPA
  - NACAA (http://www.4cleanair.org) has available a Mercury Model Rule and Boiler Model Permit Guidance information available.

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

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"
- 8 years after MACT, EPA must pass a residual risk standard (if necessary)
  - Protect with an "ample margin of safety" (health-based standard
- Begin in mid to late 1990s, giving time for EPA to improve risk assessment methods.

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 std.

Risk & Technology Review (RTR) Assessment Plan

- As of April 2007, EPA passed 8 residual risks standards that covers 14 source categories. These are now called Phase I. (There were still 160 categories which EPA must do residual risk review).
- Nov. 2006, EPA published its RTR Assessment Plan which combines risk & technology review for several industrial sectors into single regulatory actions (more efficient)(called Phase II).
  - Phase II is divided into 3 groups (Group I, II & III) & groups can be further subdivided (Group II(a), II(b), II (c).)
- http://www.epa.gov/ttn/atw/rrisk/rtrpg.html

Area Sources

- An area source is any stationary source that is not a major source
- 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 MACT: requires the source to be major for boiler emission units to be regulated by the MACT)
- An area source, under §112(d)(5), may be regulated by a less stringent requirement: (GACT) "generally available control technology"
  - No floor analysis & no residual risk standard required

Urban Area Sources

- CAA 112(c)(3) required EPA to:
  - List at least 30 HAP that pose the greatest potential health threat in urban areas. (EPA identified a list of 33 HAP in their Integrated Urban Air Toxic Strategy)
  - List area source categories (EPA identified 70)
  - Pass control standards for them by Nov, 2000 (By 6/2007: EPA issued stds. for only 28 of 70 area source categories)
- A 3/06 Ct. Order directed EPA to issue emission standards for 4 area sources by 12/15/06 & continue issuing standards every 6 months until 6/15/09 (50 area source categories in total).
  - 8/2009: all passed except 17 extended (10/2009 & 7/2010)
- http://www.epa.gov/ttn/atw/area/arearules.html

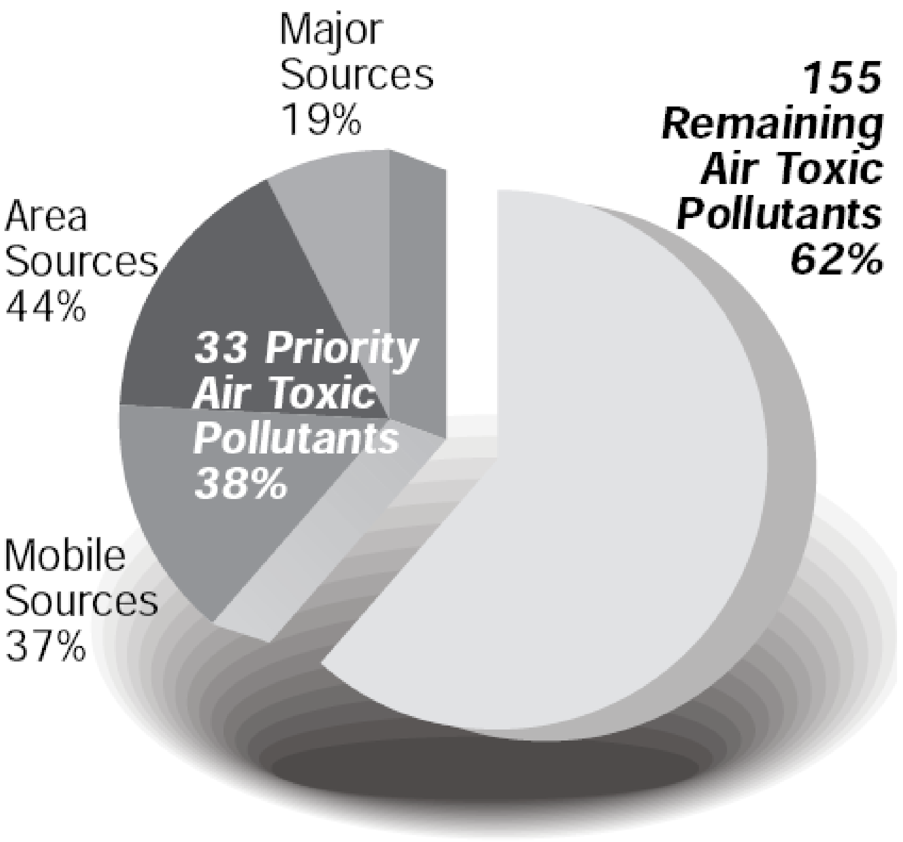
Integrated Urban Air Toxics Strategy

- CAA 112(k)(3) *overlapped* 112(c)(3): both required EPA to list least 30 HAPs that causes the greatest threat to public health from urban area sources
- 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, mobile and indoor 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
- http://www.epa.gov/ttn/atw/urban/urbanpg.html

33 Urban HAP

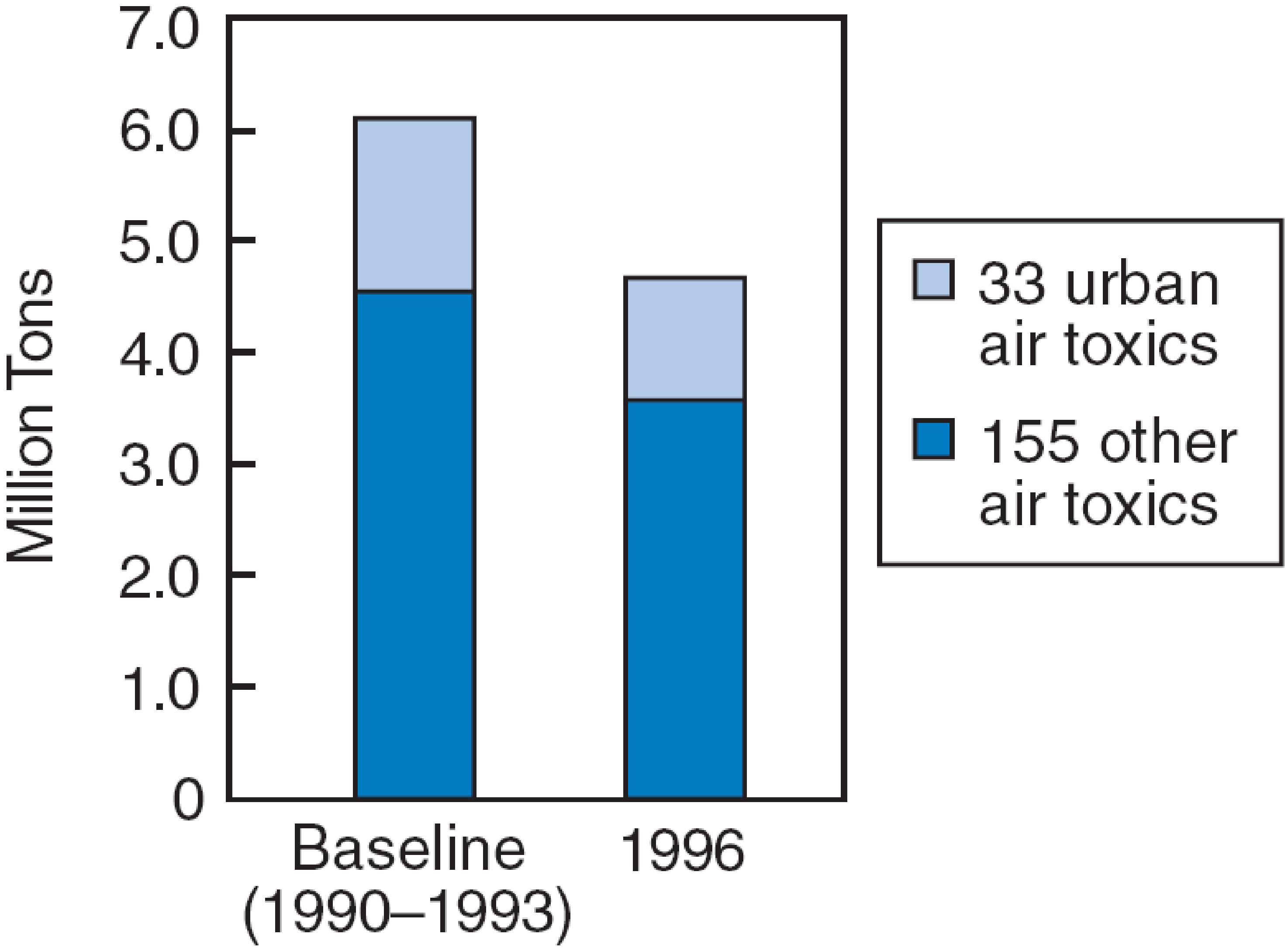
List of 33 Priority Air Toxics for the Integrated Urban Air Toxics Strategy

- 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-tetrachlorodibenzo-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

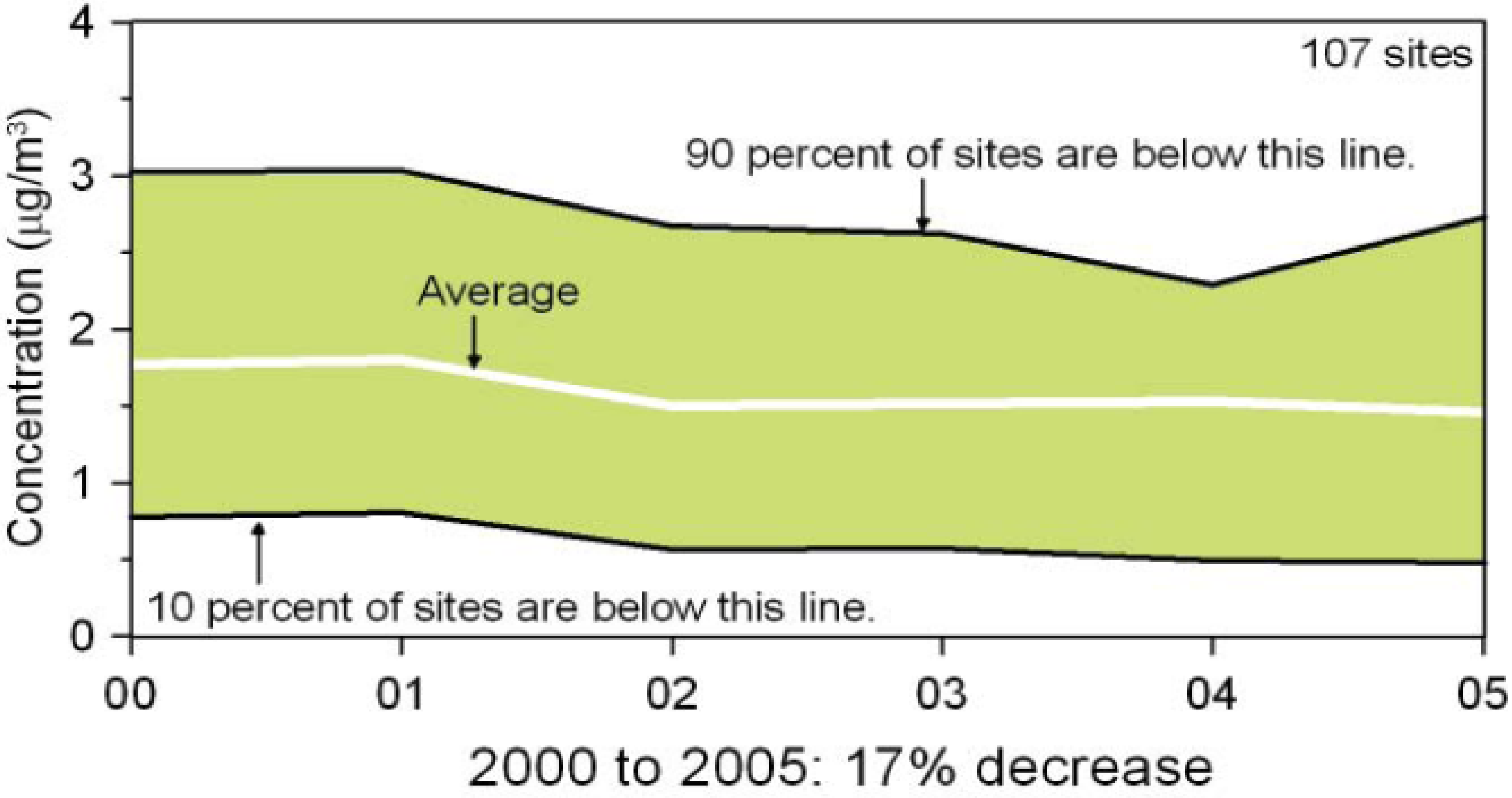


Distribution of Emissions of 188 Air Toxic Pollutants

Total for all 188 HAP



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

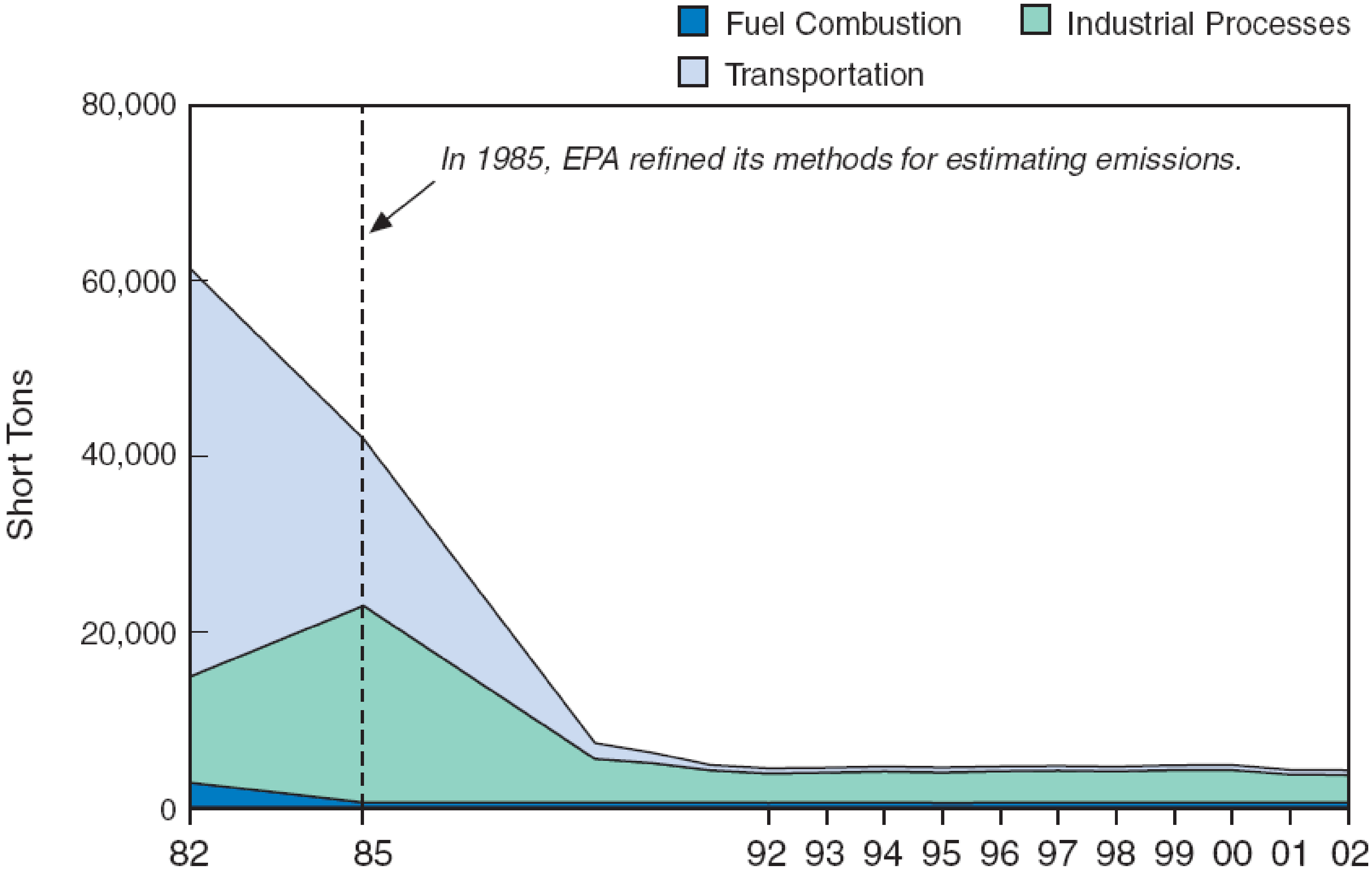


Benzene, the most widely monitored toxic air pollutant, is the most significant HAP for which cancer risks can be estimated (contributes 25% of the average individual cancer risk in 1999 assessment).

Mobile Sources: Lead Regulations

- 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.
- 1978: EPA promulgated a NAAQS for lead.
- 1990 CAAA: airborne "lead compounds" made a HAP.

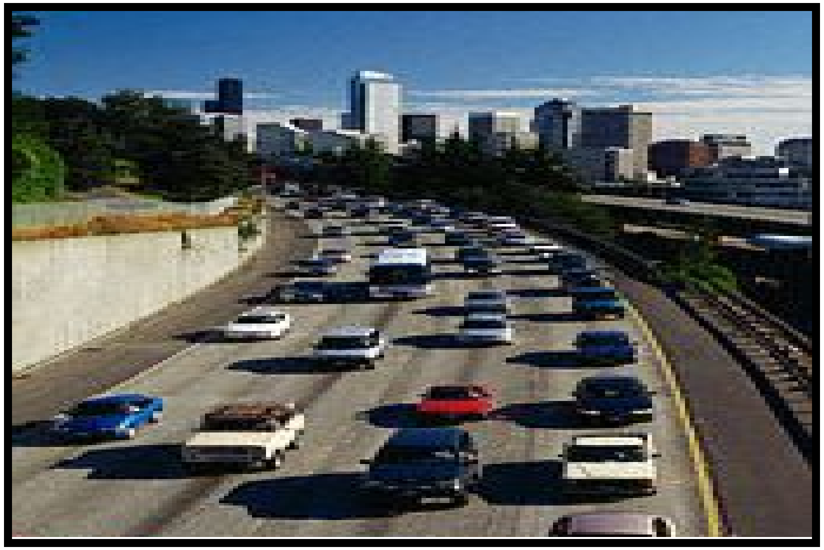
Pb Emissions, 1982 to 2002

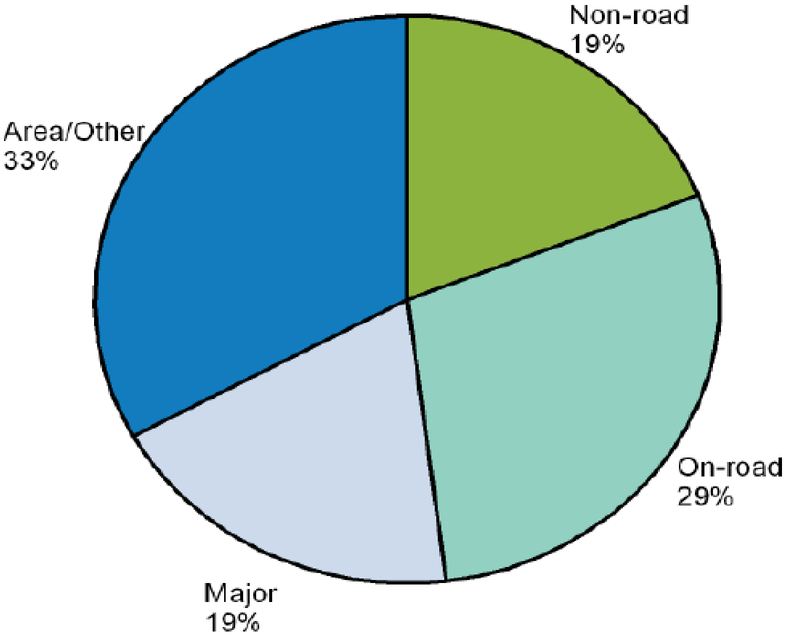


1982–02: 93% decrease[a]
1993–02: 5% decrease

Air Toxics from Mobile Sources

- Diesel exhaust: PM & VOC
  - Animal studies: diesel exhaust more carcinogenic & mutagenic than gasoline exhaust.
  - EPA (1999 Report): diesel exhaust a likely human carcinogen – risks to difficult to quantify.
  - EPA: will use Integrated Urban Air Toxics Strategy plus MSAT rule to regulate HAP from mobile sources.
  - The diesel rule (2001) regulates only sulfur content of fuel (no HAP regs).
- 1990 CAAA §202(l) addressed toxic pollutants from mobile sources for the first time.





U.S. HAP Emissions by Source: 2002

Mobile Source Air Toxic Program

- Section 202 (l) directed EPA to study need & feasibility of controlling HAP: especially benzene, 1,3-butadiene & formaldehyde. (1993 & 1999: EPA completed studies).
- Section 202(l) also directed EPA to set HAP standards from motor vehicles and their fuels:
  - 2001: Mobile Source Air Toxic **(MSAT) Rule** (FR66:17230)
    - EPA identified 21 mobile source HAP
    - Established toxic emission performance stds for gasoline refineries
  - Feb. 2007: Final rule to reduce mobile source air toxics:
    - By 2011 refineries: lower benzene in gas to 0.62% (today 1%)
    - Reducing NMHC exhaust stds from cars when operating cold
  - Mobile Source Air Toxics | Overview: Pollutants and Programs | US EPA (http://epa.gov/otaq/toxic.html)

Mobile Source Air Toxics Listed in 2001 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

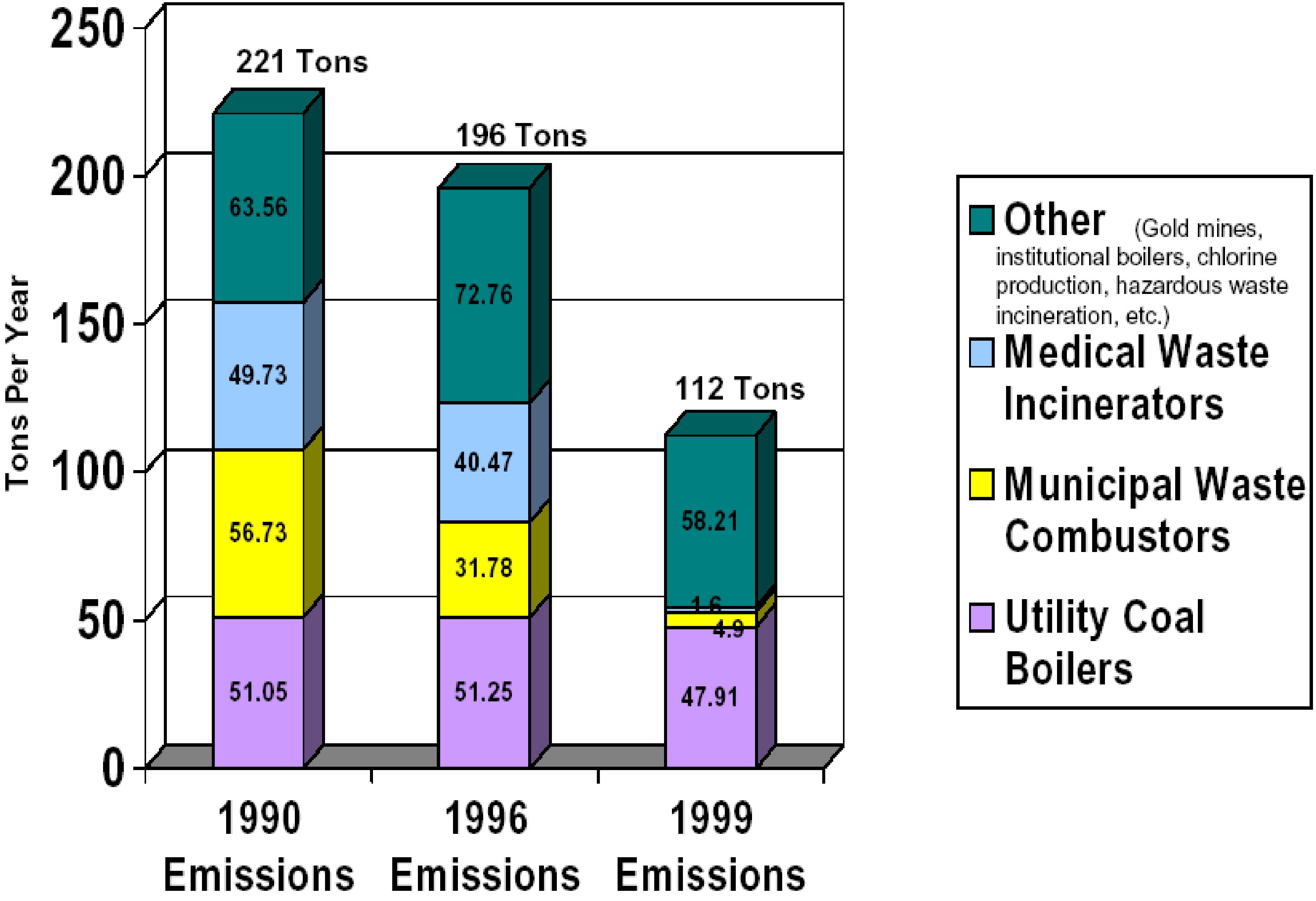
Coal Fired Electric Power Plants

- 1990 CAAA required EPA to study & report on mercury emissions & its sources, possible controls & impacts. 1997 Mercury Report:
  - Primary mercury source is coal fired utilities &
  - Control technology is in research stage.
- 1990 CAAA required EPA to study & report on HAP from power plants. 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 2002, Bush proposed "Clear Skies Initiative" that called for 70% reduction in mercury emissions from power plants by 2018

Clean Air Mercury Rule (CAMR)

- CAMR was passed in 3/2005:
  - By 2018: reduce mercury emissions from coal-fired power plants by nearly 70% from 1999 levels,
  - Established "standards of performance" limiting mercury emissions from new & existing power plants, &
  - Created "cap & trade" for mercury emissions from power plants.
- EPA also said that MACT approach is not necessary for mercury emissions from power plants.
- By 2007, 23 states were pursuing their own programs
  - set mercury emission limits for power plants & prohibited interstate emission trading by power plants.
- Feb. 2008: D.C. Circuit Ct. vacated CAMR because the rule failed to satisfy EPA's CAA §112 requirement to regulate mercury as a HAP.

Mercury Emissions Have Dropped 45% Since 1990



Source: EPA

Prevention of Accidental Releases: CAA §112(r)

- Purpose: prevent disastrous accidental releases
- Facilities 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
- Risk management plan (RMP) due 1999 (5 yr. updates):
  - – Hazardous assessment
    - Hazardous effects
    - Facility's history of releases
  - – Program to prevent accidental releases
  - – Emergency response program
- RMP Information | Emergency Management | US EPA

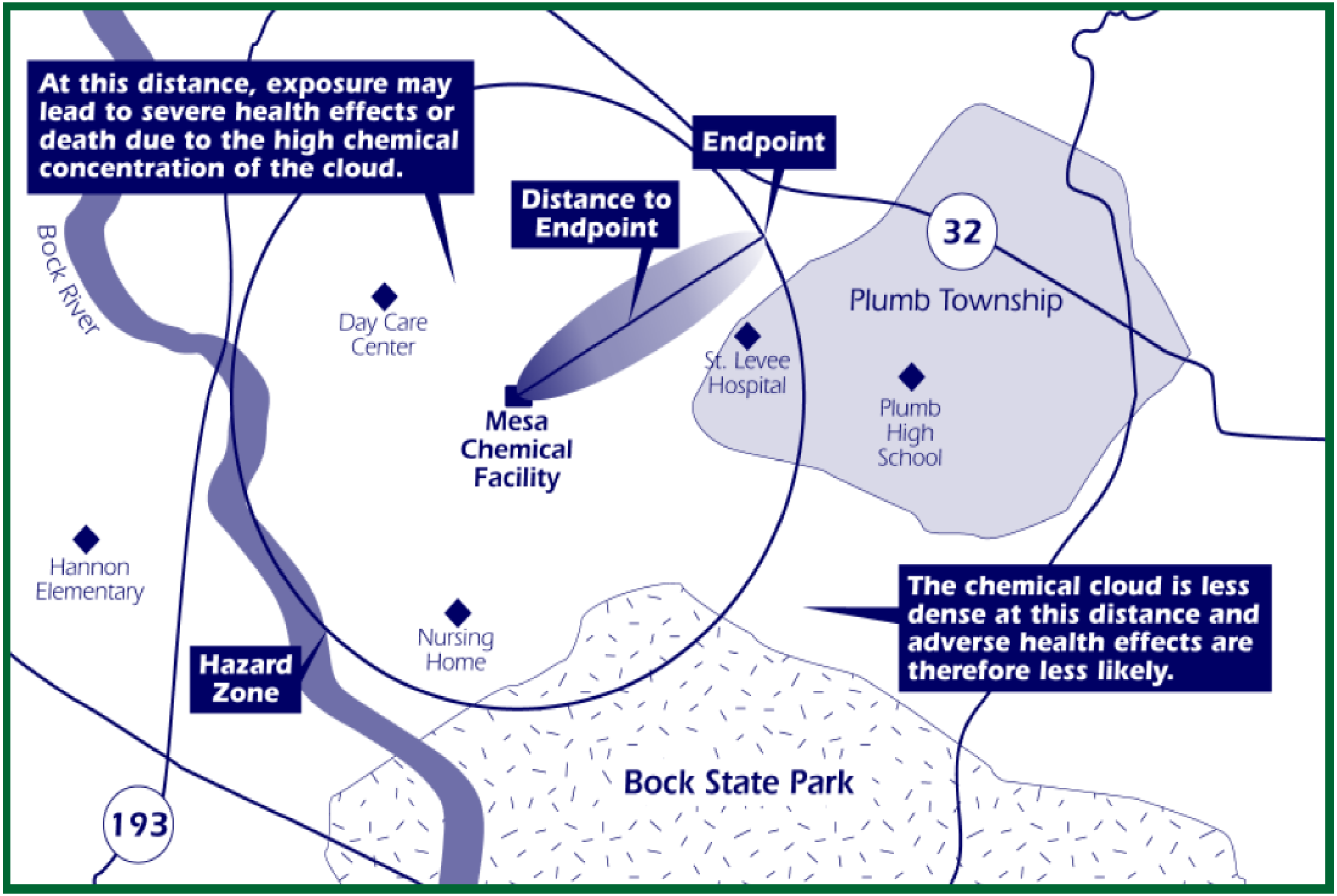
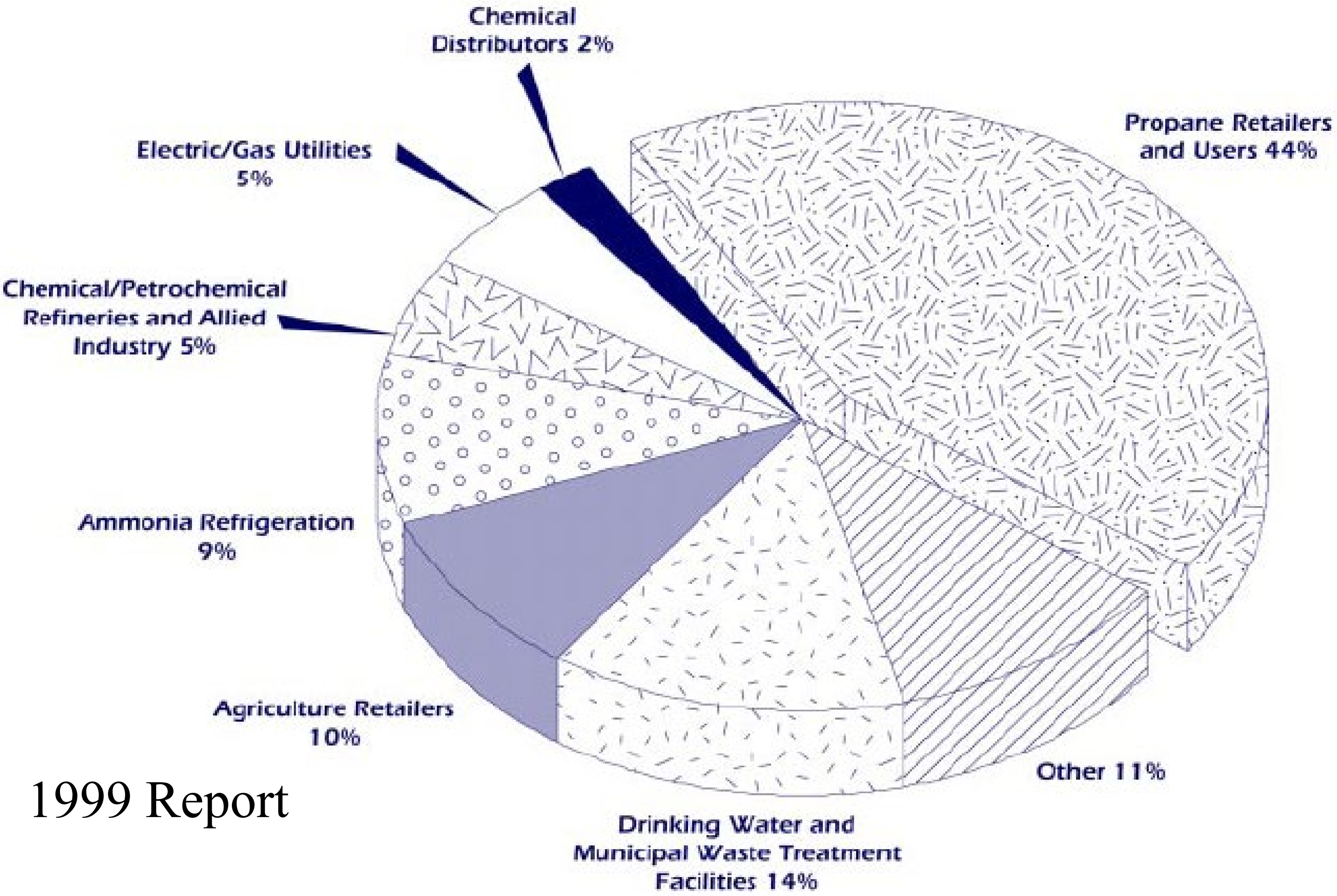


Figure 3: This is a typical map found in an RMP, showing hazardous areas, vulnerable populations, and sensitive environments. This map shows the endpoint, distance to endpoint, and the hazard zone for one possible scenario. The hazard zone is a circle because wind variability could cause the toxic cloud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

Types of Facilities Regulated by the Risk Management Program Rule



1999 Report

Great Waters Study

- CAAA required a study of atmospheric deposition of HAP in the Great Lakes, Lake Champlain, the Chesapeake Bay & many U.S. coastal waters.
- Focused on 15 HAP because of persistence & potential to bioaccumulate (i.e. mercury).
- (1994)(1997)(2000) Studies suggests
  - Deposition is constant or declining
  - Because of long range atmospheric transport, its difficult to determine emission sources
- The Great Waters Program | Air Quality Planning & Standards | Air & Radiation | US EPA
- www.epa.gov/oar/oaqps/gr8water/

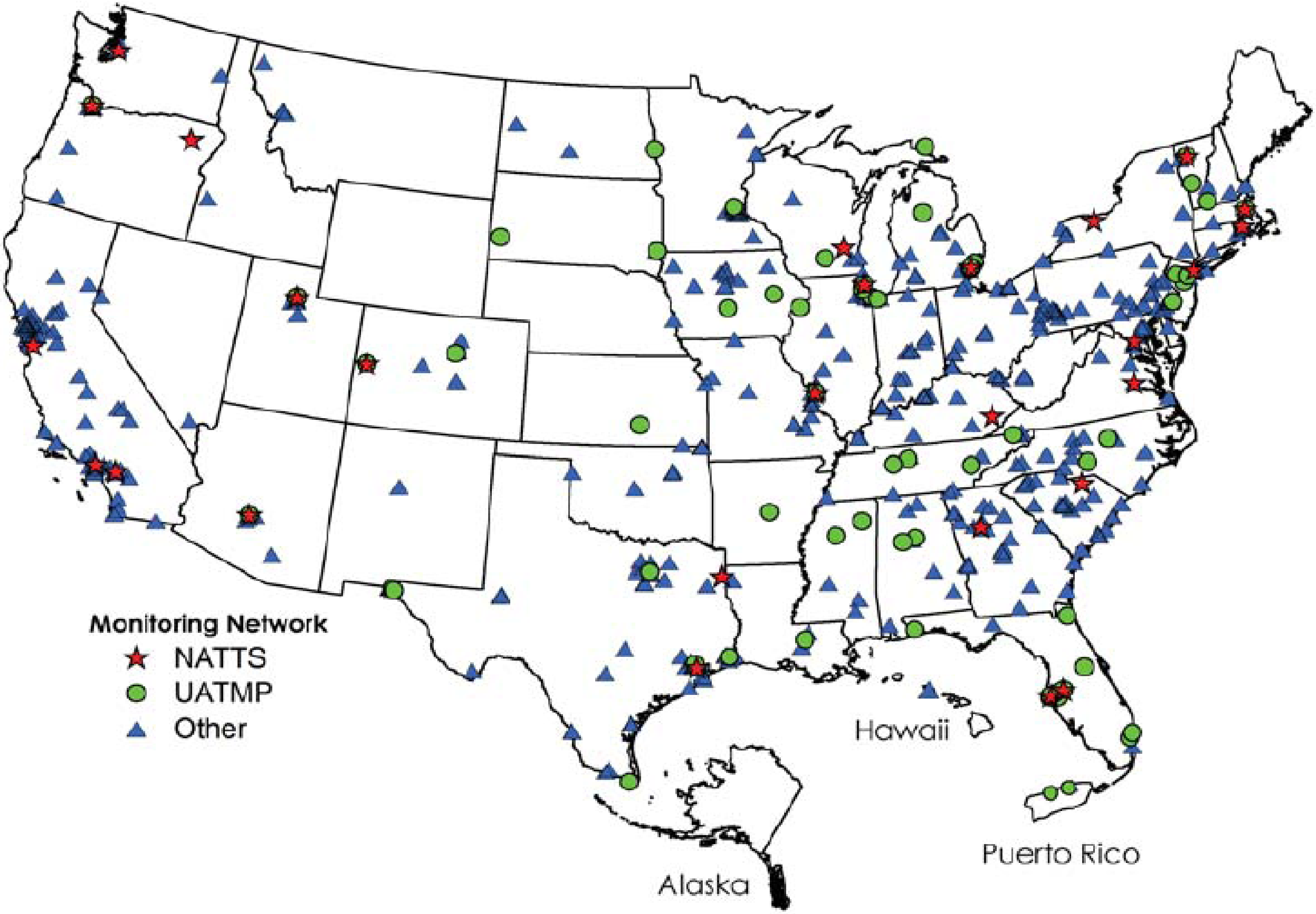
State Programs

- CAA sect. 112(l) allows state & local programs to be implemented rather than other applicable section 112 standards. Delegation in 3 ways:
  - 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.
  - EPA may delegate to state authority to implement fed HAP program.
  - State, Local, Tribal and Federal Partnerships | Technology Transfer Network Air Toxics Web site | US EPA

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).

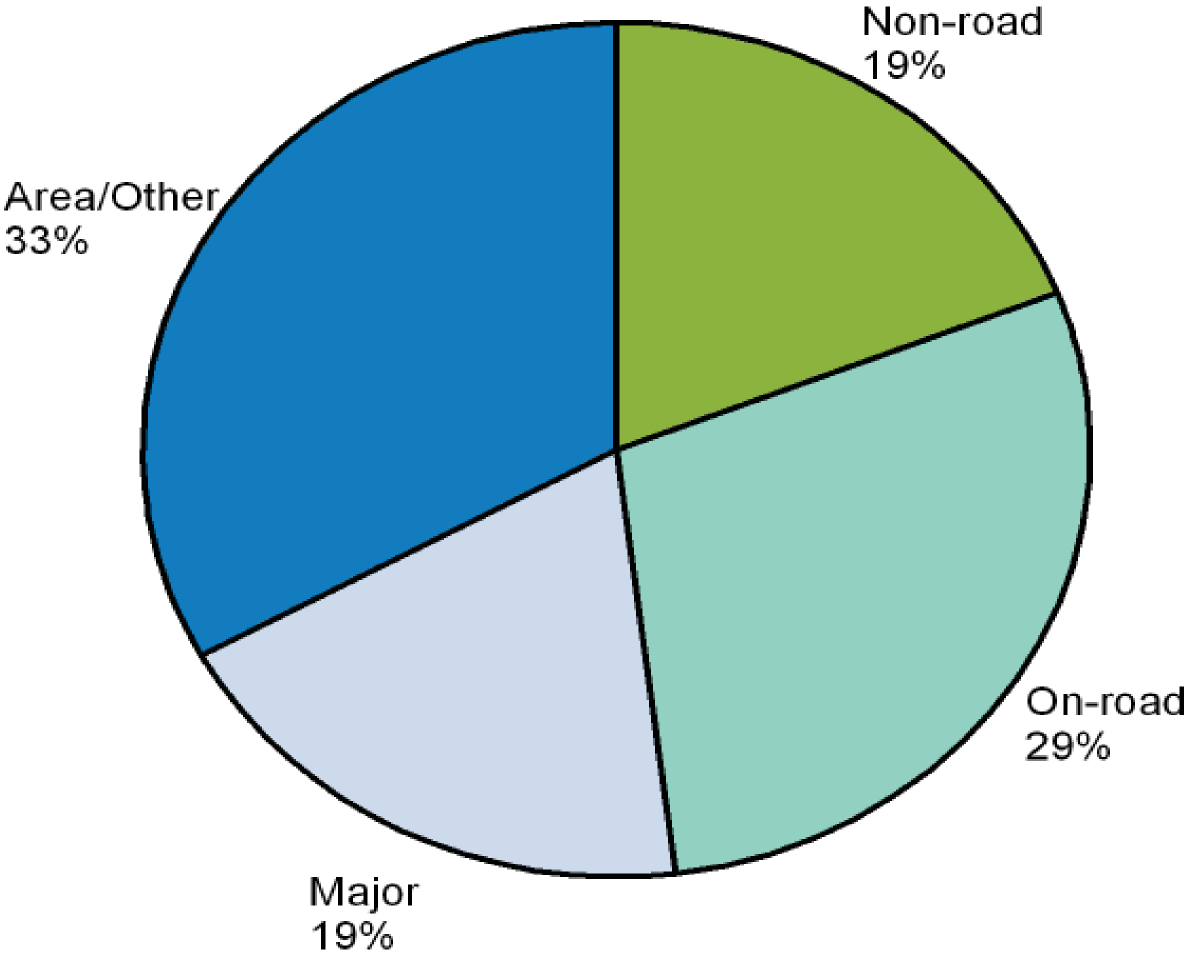
HAP Monitoring Sites: 2007



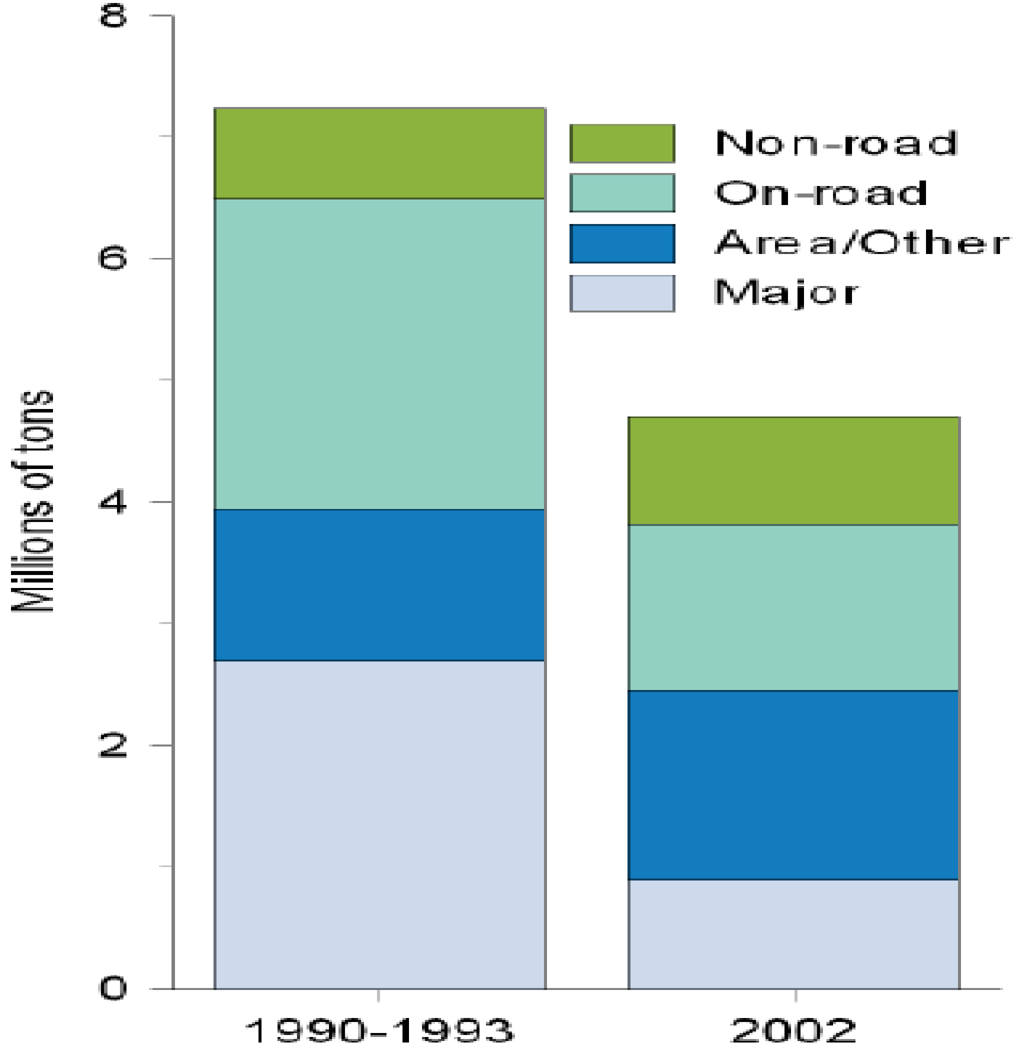
Trends in Toxic Air Pollutants

- Today, National Emission Inventory (NEI) tracks both HAP & criteria pollutants. What is the National Emissions Inventory (NEI)? | Clearinghouse for Emission Inventories and Emissions Factors | Technology Transfer Network | US EPA previously,
  - HAP data from 1993 to 1996: National Toxics Inventory (NTI) database
  - Criteria pollutants from 1985 to 1998: National Emission trends (NET) database
- EPA uses the NEI to estimate and track national emissions trends for the187 HAPs

Percent Contribution by Source Sector To National Air Toxic Emissions, 2002



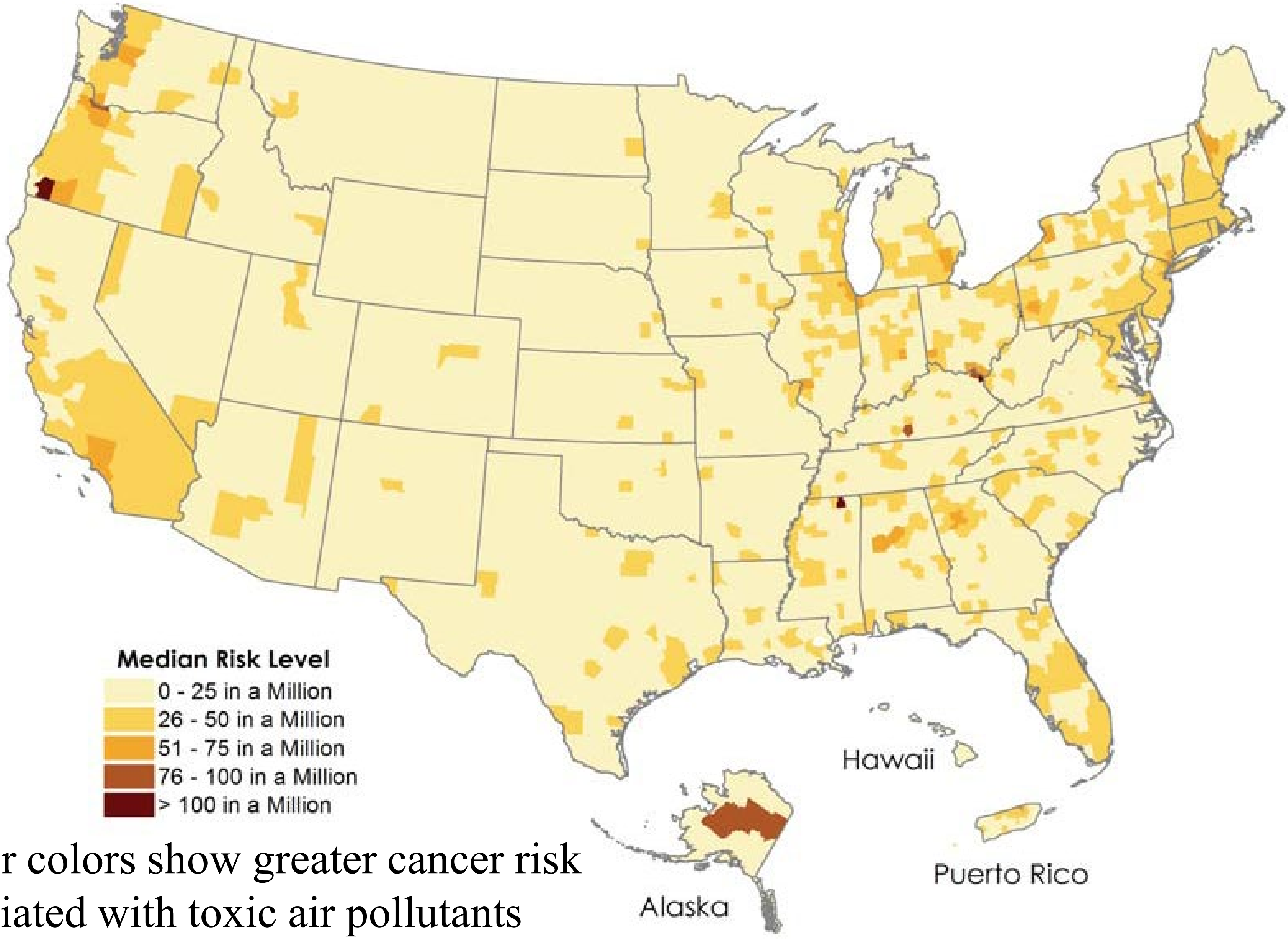
Trends in U.S. HAP Emissions



National Air Toxic Assessment (NATA)

- Because *ambient monitoring data is limited* for air toxics, EPA frequently relies on ambient modeling studies to better define trends in toxic air pollutants.
- One such *modeling study*, the **National-Scale Air Toxic Assessment** (NATA), is a nationwide study of ambient levels, inhalation exposures, and health risks associated with emissions of 177 toxic air pollutants (a subset of the CAA's list of 187 toxic air pollutants).
- NATA was formed in 2002 by the EPA
- NATA assessment is based on data from the most recent NEI.

Estimated County-Level Cancer Risk from the 2002 NATA



Darker colors show greater cancer risk associated with toxic air pollutants

United States Government Accountability Office

GAO

Report to Congressional Requesters

June 2006

CLEAN AIR ACT

EPA Should Improve the Management of Its Air Toxics Program

GAO-06-669

GAO Study: Results in Brief

- Major sources: most of the completed requirements were met late (last MACT in 2004 instead of 2000)
  - Delays residual risk evaluations (until 2012 instead of 2008)
- Area sources: completed only 16 of 70 NESHAPs
  - Area sources responsible for 1/3 of all HAPs (2002)
- Mobile sources: proposed only one rule
- EPA has failed to review & update list of HAP despite evidence that potentially harmful chemicals remain unregulated
- Reason: EPA puts a low priority on HAP program compared to other air programs (i.e. smog)

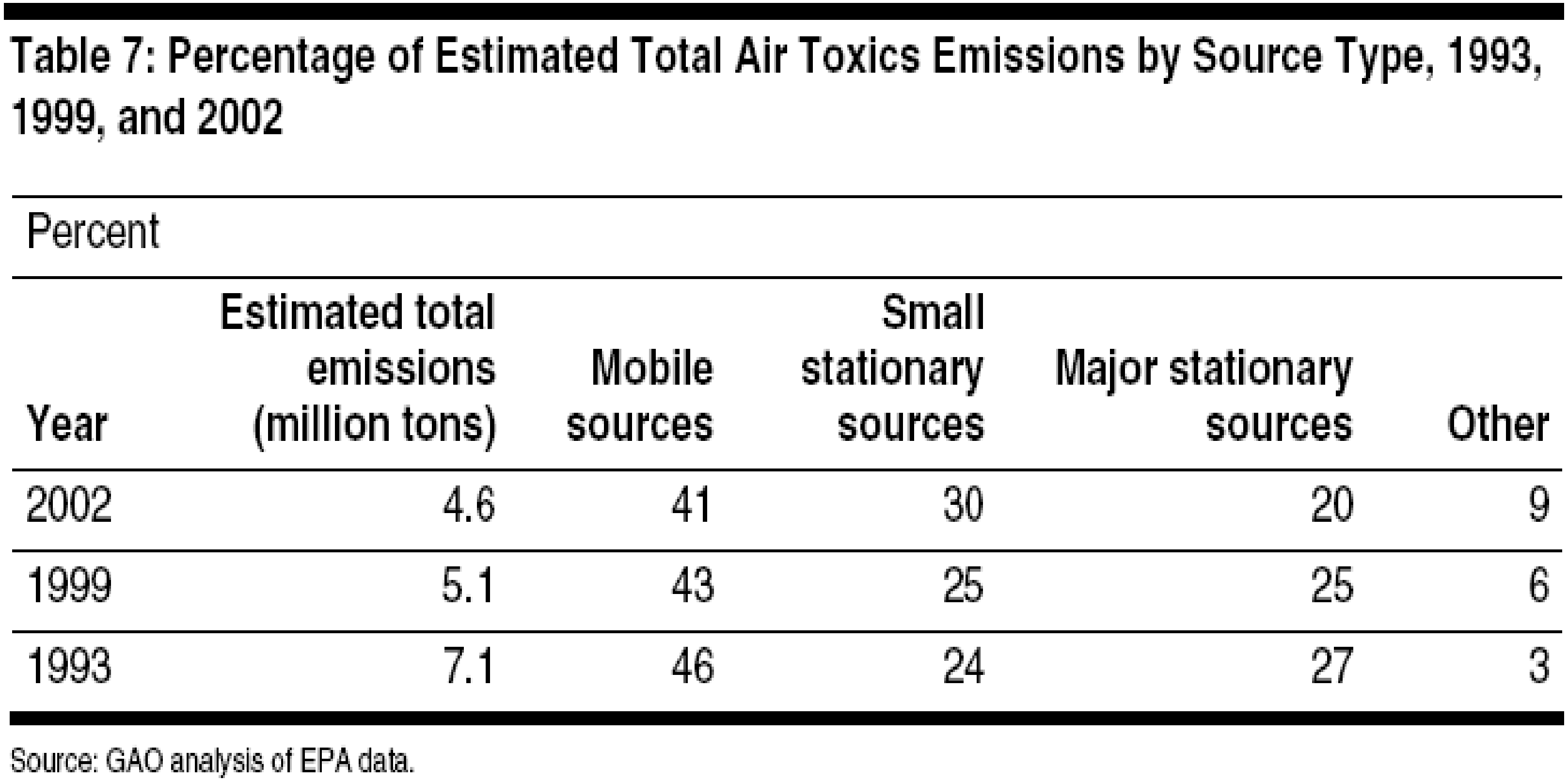


Table 7: Percentage of Estimated Total Air Toxics Emissions by Source Type, 1993, 1999, and 2002

Percent

Year	Estimated total emissions (million tons)	Mobile sources	Small stationary sources	Major stationary sources	Other
2002	4.6	41	30	20	9
1999	5.1	43	25	25	6
1993	7.1	46	24	27	3

Source: GAO analysis of EPA data.

Most of EPA’s progress relates to issuing emissions standards for large stationary sources, although EPA completed these standards about 4 years behind schedule. However, many of the unmet requirements pertain to limiting emissions from small stationary and mobile sources, which collectively account for most emissions of air toxics.

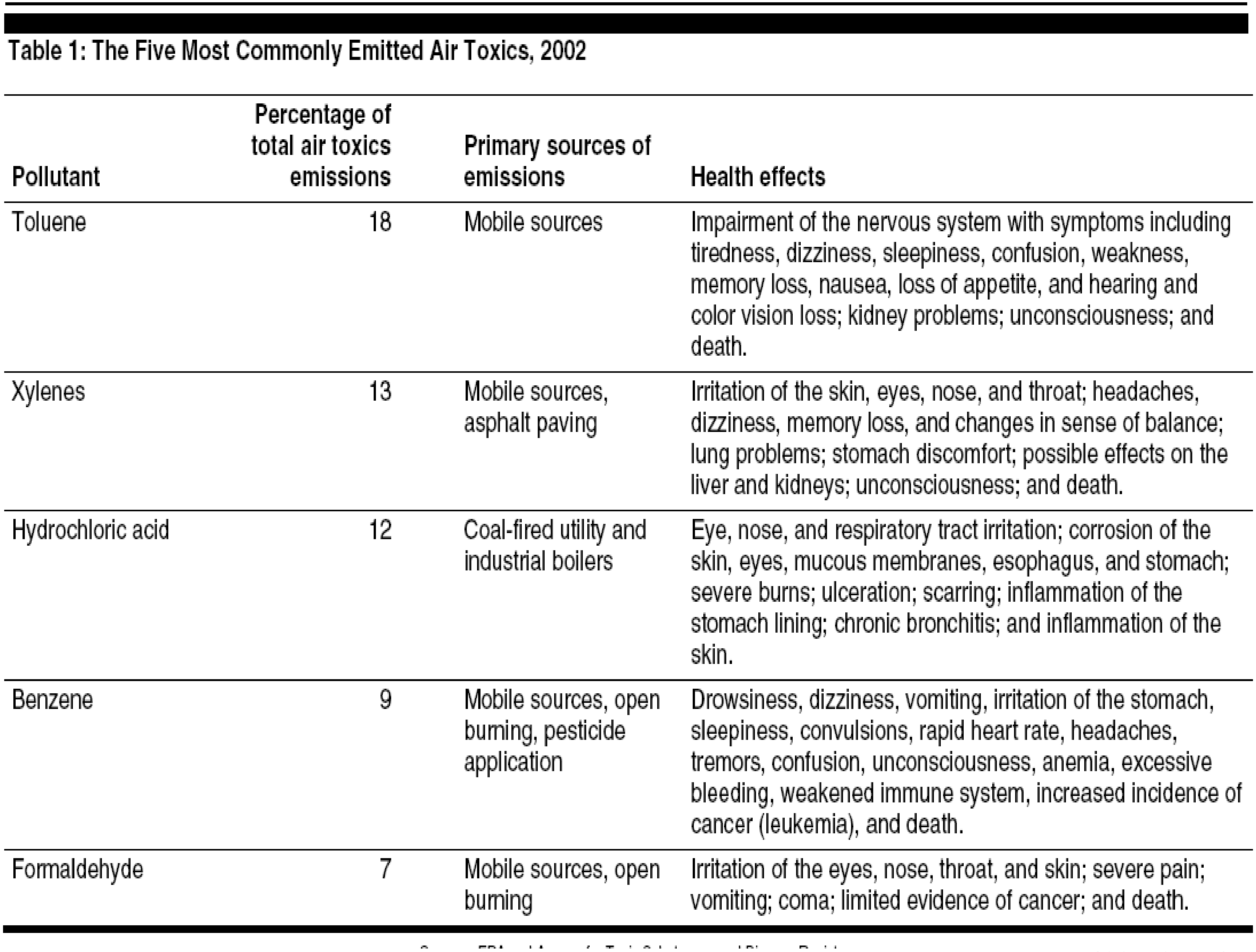


Table 1: The Five Most Commonly Emitted Air Toxics, 2002

Pollutant	Percentage of total air toxics emissions	Primary sources of emissions	Health effects
Toluene	18	Mobile sources	Impairment of the nervous system with symptoms including tiredness, dizziness, sleepiness, confusion, weakness, memory loss, nausea, loss of appetite, and hearing and color vision loss; kidney problems; unconsciousness; and death.
Xylenes	13	Mobile sources, asphalt paving	Irritation of the skin, eyes, nose, and throat; headaches, dizziness, memory loss, and changes in sense of balance; lung problems; stomach discomfort; possible effects on the liver and kidneys; unconsciousness; and death.
Hydrochloric acid	12	Coal-fired utility and industrial boilers	Eye, nose, and respiratory tract irritation; corrosion of the skin, eyes, mucous membranes, esophagus, and stomach; severe burns; ulceration; scarring; inflammation of the stomach lining; chronic bronchitis; and inflammation of the skin.
Benzene	9	Mobile sources, open burning, pesticide application	Drowsiness, dizziness, vomiting, irritation of the stomach, sleepiness, convulsions, rapid heart rate, headaches, tremors, confusion, unconsciousness, anemia, excessive bleeding, weakened immune system, increased incidence of cancer (leukemia), and death.
Formaldehyde	7	Mobile sources, open burning	Irritation of the eyes, nose, throat, and skin; severe pain; vomiting; coma; limited evidence of cancer; and death.

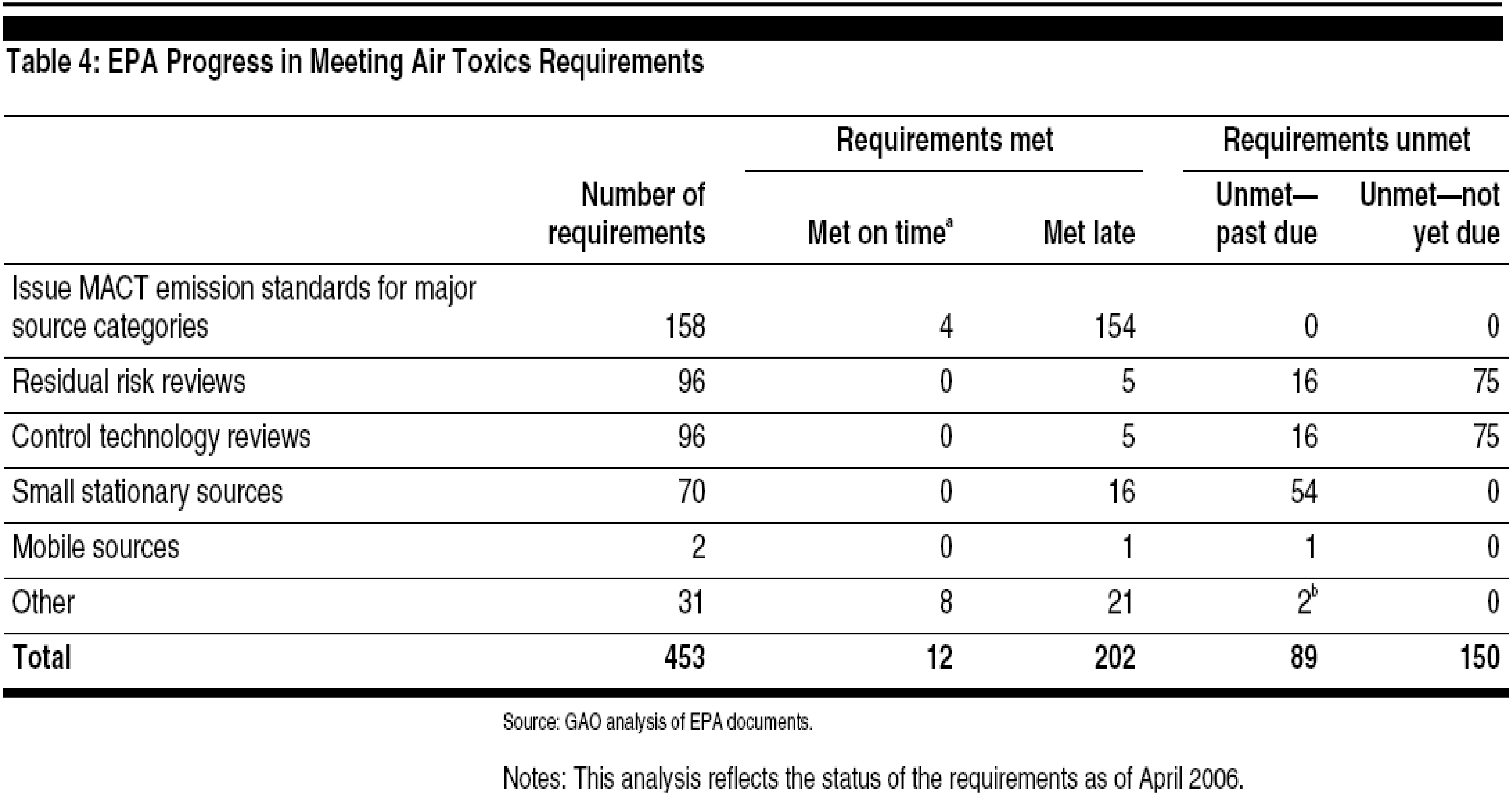


Table 4: EPA Progress in Meeting Air Toxics Requirements

	Number of requirements	Requirements met		Requirements unmet	
		Met on time[a]	Met late	Unmet—past due	Unmet—not yet due
Issue MACT emission standards for major source categories	158	4	154	0	0
Residual risk reviews	96	0	5	16	75
Control technology reviews	96	0	5	16	75
Small stationary sources	70	0	16	54	0
Mobile sources	2	0	1	1	0
Other	31	8	21	2[b]	0
Total	**453**	**12**	**202**	**89**	**150**

Source: GAO analysis of EPA documents.

Notes: This analysis reflects the status of the requirements as of April 2006.

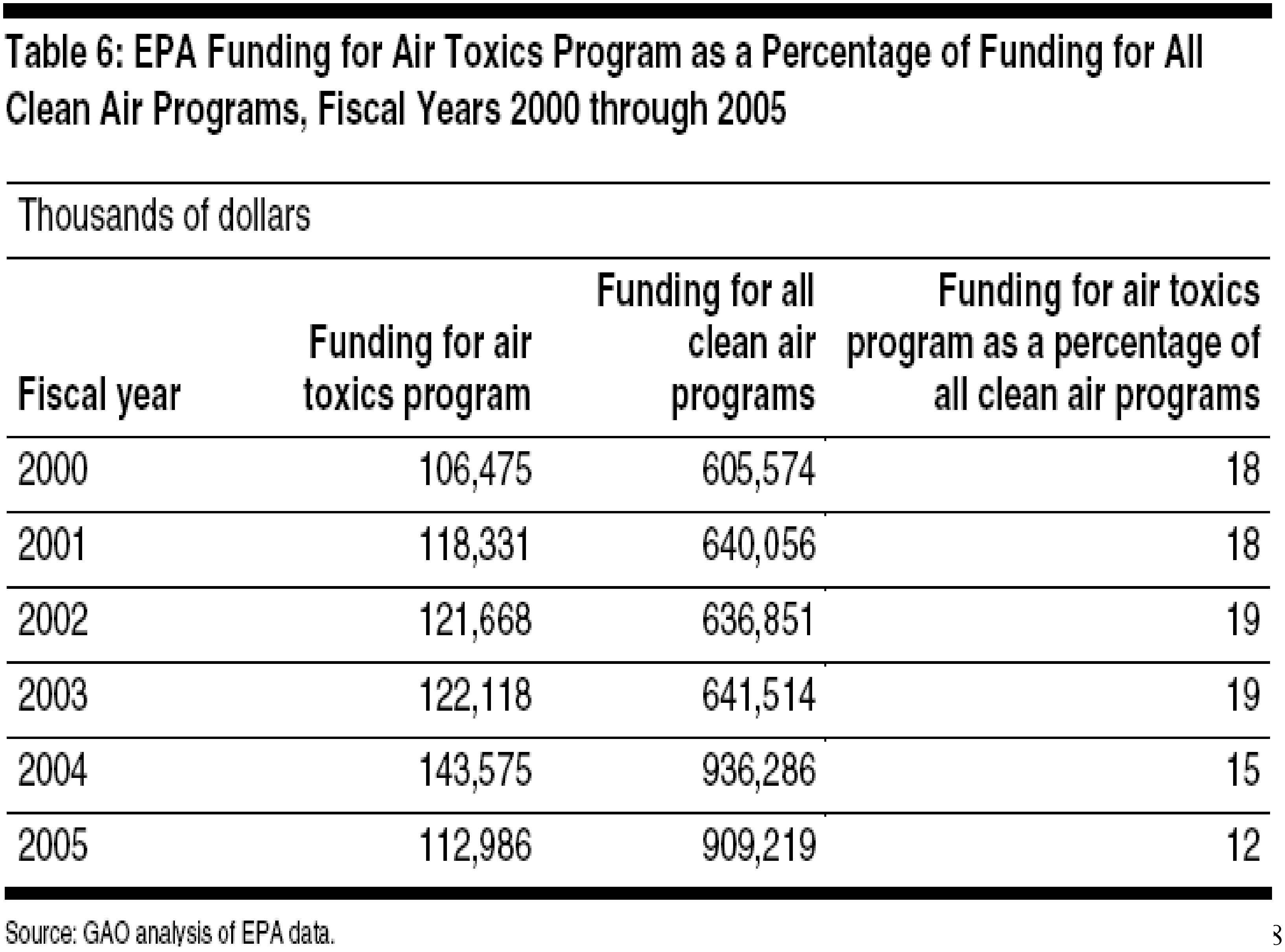


Table 6: EPA Funding for Air Toxics Program as a Percentage of Funding for All Clean Air Programs, Fiscal Years 2000 through 2005

Thousands of dollars

Fiscal year	Funding for air toxics program	Funding for all clean air programs	Funding for air toxics program as a percentage of all clean air programs
2000	106,475	605,574	18
2001	118,331	640,056	18
2002	121,668	636,851	19
2003	122,118	641,514	19
2004	143,575	936,286	15
2005	112,986	909,219	12

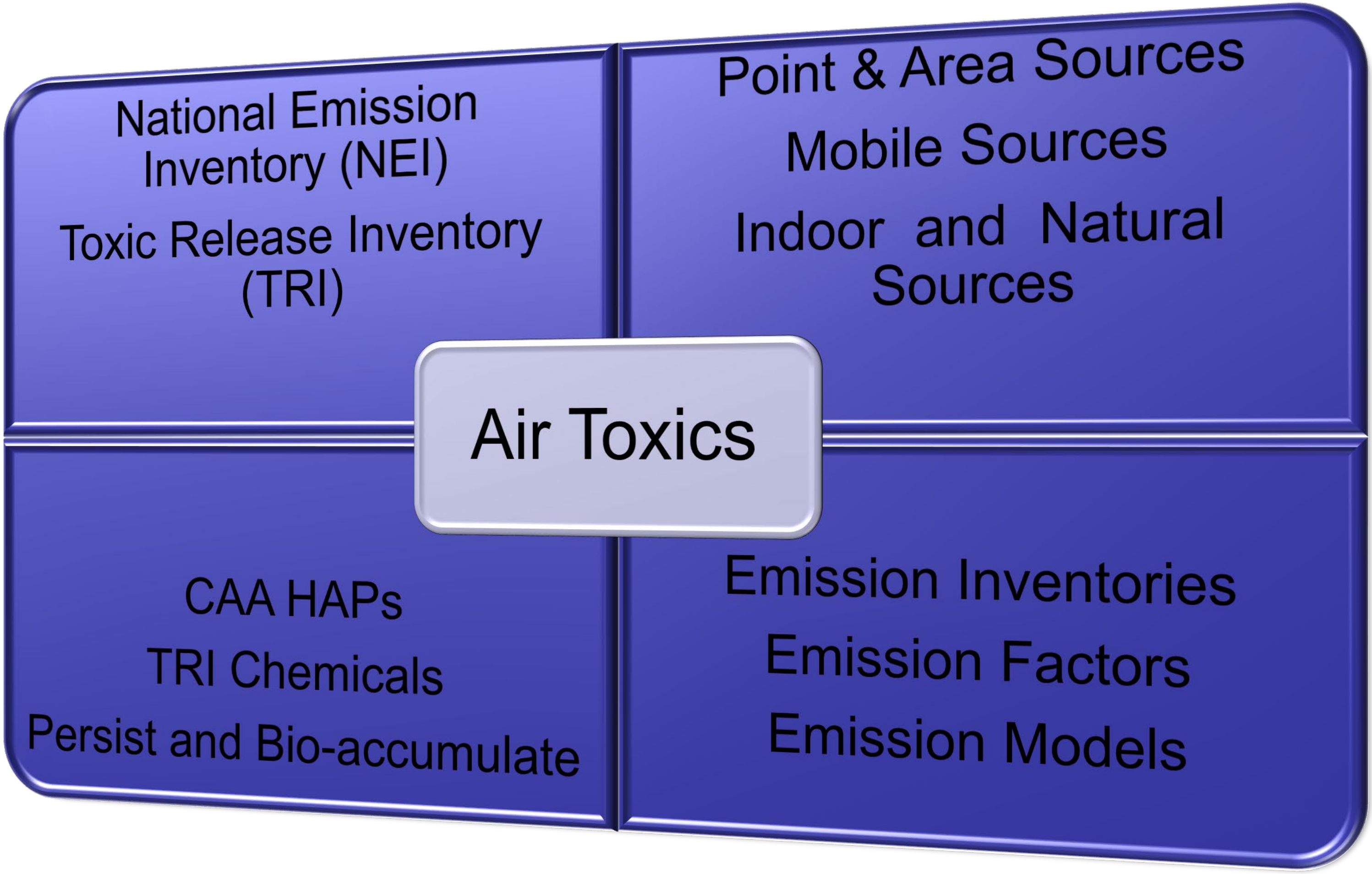
Source: GAO analysis of EPA data.

GAO Study: Results in Brief

- HAP program lacks a detailed cost-benefit analysis
  - Economic costs for all standards
  - Benefits of standards (i.e. decreased incident of cancer)
- 5 state/local programs could enhance Fed HAP program (Wisconsin, Oregon, California, New Jersey & Louisville, Ky.)
  - Wisconsin: lists 535 HAPs, facility subject to regulation if it emits over threshold amounts (i.e. emissions < 1 #/yr –depends on toxicity)
  - Similarly, New Jersey's HAP program regulates smaller facilities than those required by EPA's MACT standards
  - Several states use modeling & monitoring to identify chemicals, areas & facilities of concern for regulation (whereas, EPA concentrates on large stationary sources)

Chapter 3

Air Toxics: Chemicals, Sources and Emission Inventories



Air Toxics

National Emission Inventory (NEI)

Toxic Release Inventory (TRI)

Point & Area Sources

Mobile Sources

Indoor and Natural Sources

CAA HAPs

TRI Chemicals

Persist and Bio-accumulate

Emission Inventories

Emission Factors

Emission Models

Air Toxic 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

HAP Groups in the CAA

- Polycyclic organic matter (POM) & naphthalene
- Dioxins and furans
- Metals
- Cyanide compounds
- Glycol Ethers
- Xylenes
- Cresols

Polycyclic Organic Matter (POM)

- "Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100^0 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

- Dibenzofurans and 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) are listed on the 188 list
- EPA inventories all dioxins and furans
- Compounds can be grouped by 2,3,7,8 TCDD 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)

Air Toxic Metals

- Antimony
- Arsenic
- Beryllium
- Cadmium
- Chromium
- Hexavalent and trivalent
- Cobalt
- Lead
- Organic and inorganic
- Manganese
- Mercury
- Particulate, gaseous elemental, and gaseous divalent
- Nickel
- 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 AgCN= 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
- http://daq.state.nc.us/toxics/glycol/

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

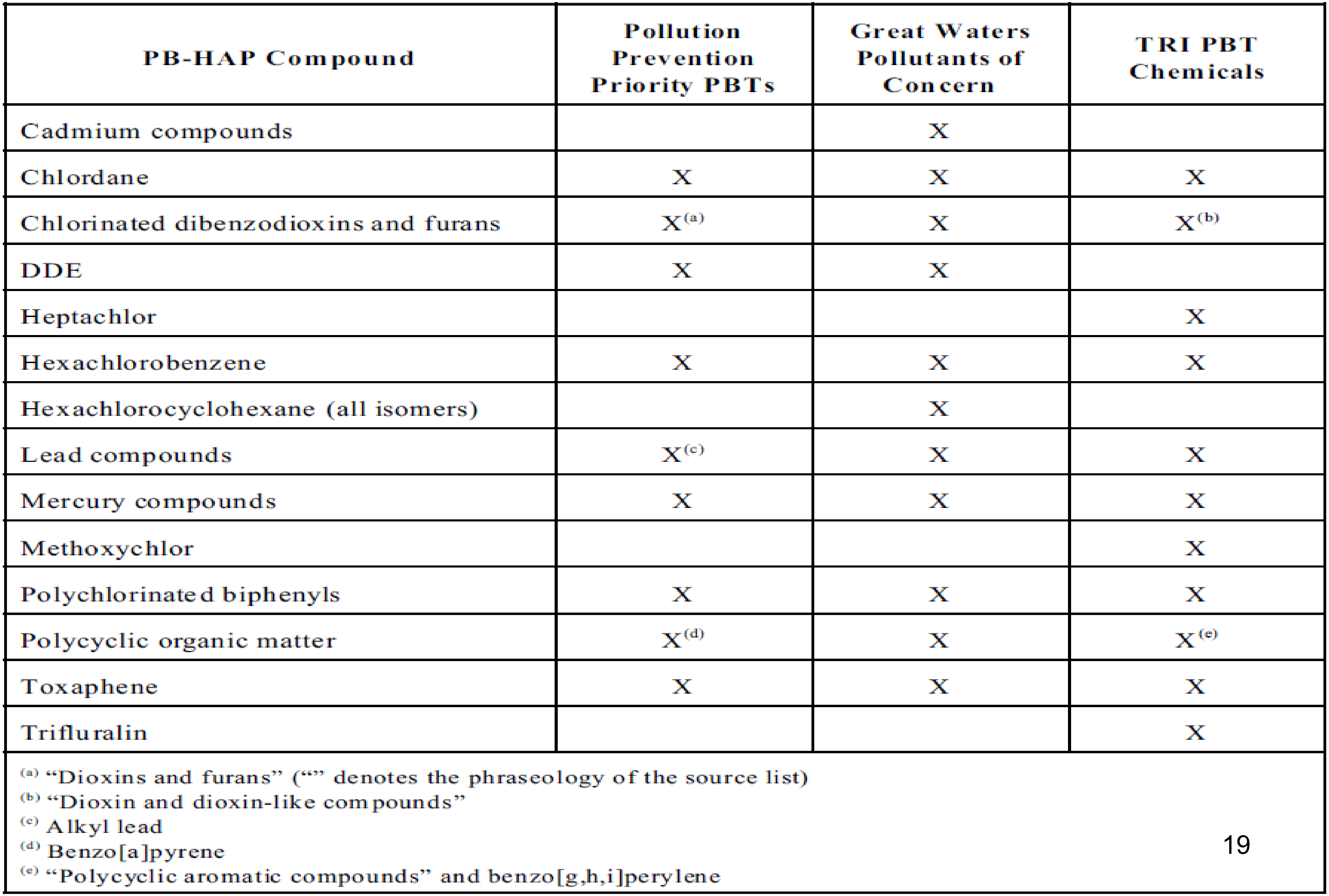
Acetaldehyde
Acrolein
Acrylonitrile
Arsenic compounds
Benzene
Beryllium compounds
1, 3-Butadiene
Cadmium compounds
Carbon tetrachloride
Chloroform
Chromium compounds
Coke oven emissions
1, 3-Dichloropropene
Diesel particulate matter
Ethylene dibromide
Ethylene dichloride
Ethylene oxide
Formaldehyde
Hexachlorobenzene
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

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/oppfead1/international/lrtap2pg.htm**

LRTAP Chemicals

- Aldrin
- polychlorinated biphenyls (PCBs)
- cadmium
- Dichlorodiphenyltrichloro-ethane (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

Reporting Year 2006

EMERGENCY PLANNING AND COMMUNITY RIGHT-TO-KNOW ACT (EPCRA) Section 313

EPA

Toxic Release Inventory 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**

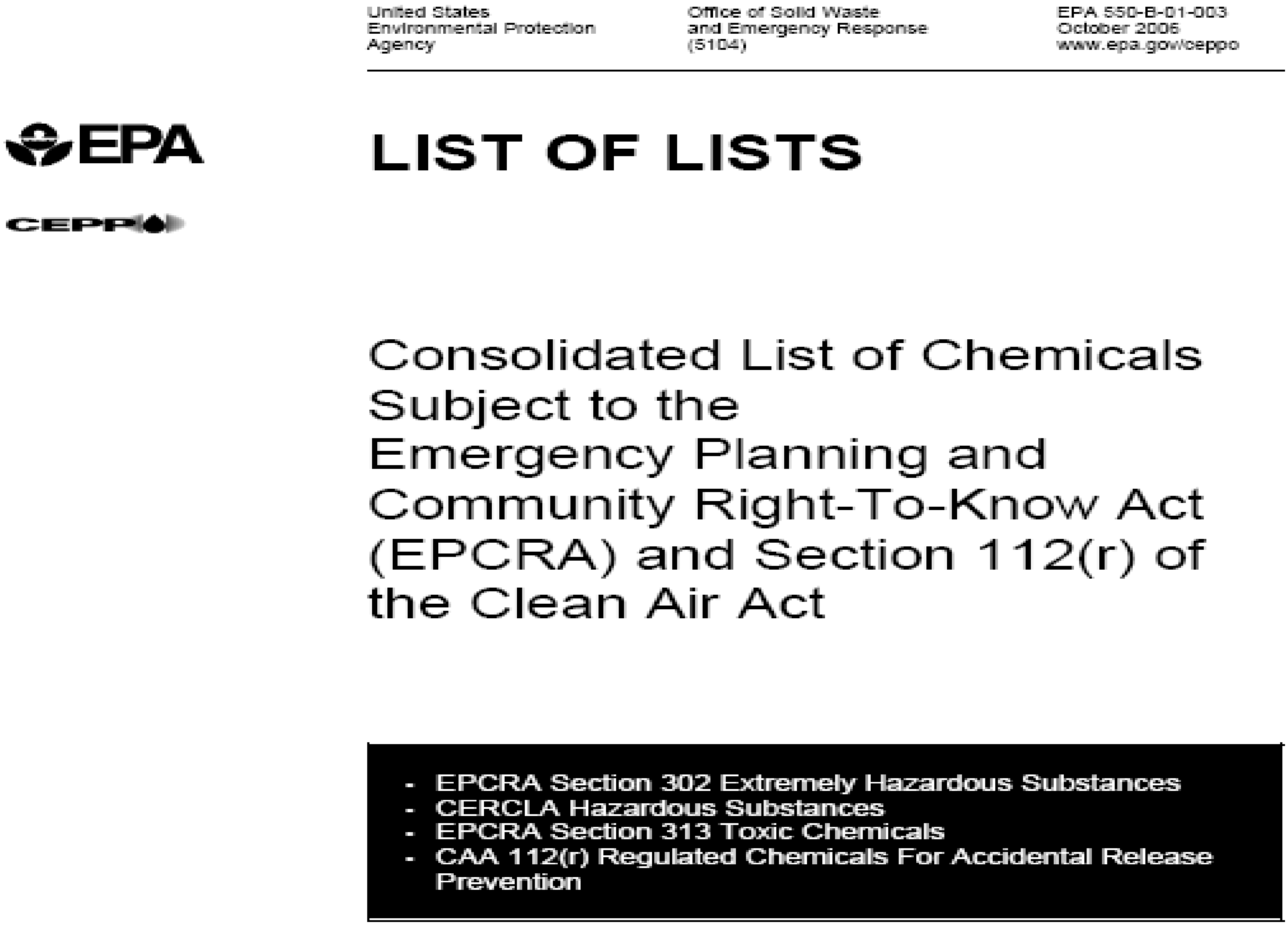
.......by July 1st for preceding calendar year's activities (aka Reporting Year (RY))

[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:

- http://www.epa.gov/ceppo/pubs/title3.pdf
- EPA hotline at 1-800-535-0202
  (hotline is operated by contractor; provides “shield” from EPA inquiries)



United States
Environmental Protection
Agency

Office of Solid Waste
and Emergency Response
(5104)

EPA 550-B-01-003
October 2006
www.epa.gov/ceppo

LIST OF LISTS

Consolidated List of Chemicals Subject to the Emergency Planning and Community Right-To-Know Act (EPCRA) and Section 112(r) of the Clean Air Act

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

State Agency's Air Toxics Definitions/LIST

Example of State Air Toxics Regulations:

New York State Department of Environmental Conservation

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/agcsgc07.pdf

Chemical Air Toxics Lists: Overlap and Differences

- 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)

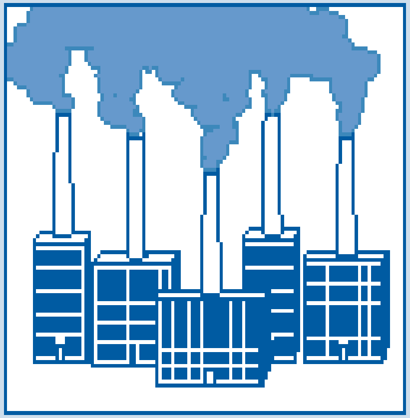
http://www.epa.gov/ttn/chief/nif/index.html#ver3

EPA Office of Environmental Information

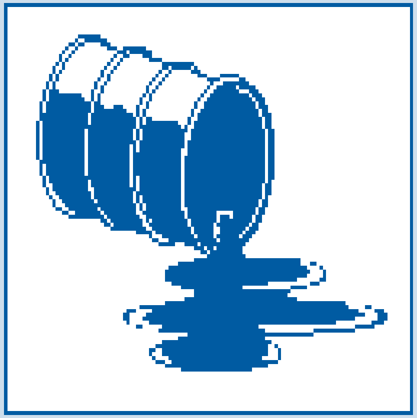
Substance Registry System www.epa.gov/srs

Sources of Air Toxics

SOURCES OF AIR TOXICS

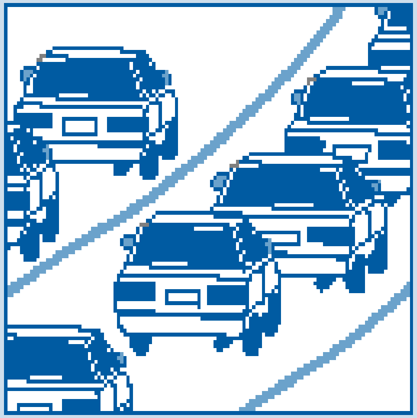


Routine Emissions From Stationary Sources

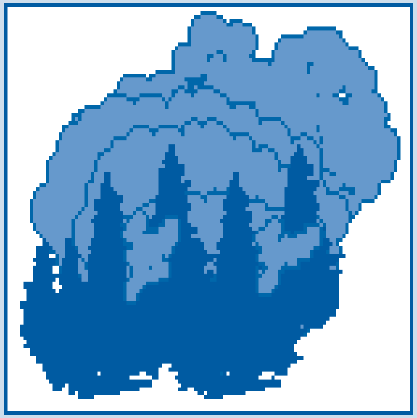


Accidental Releases

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

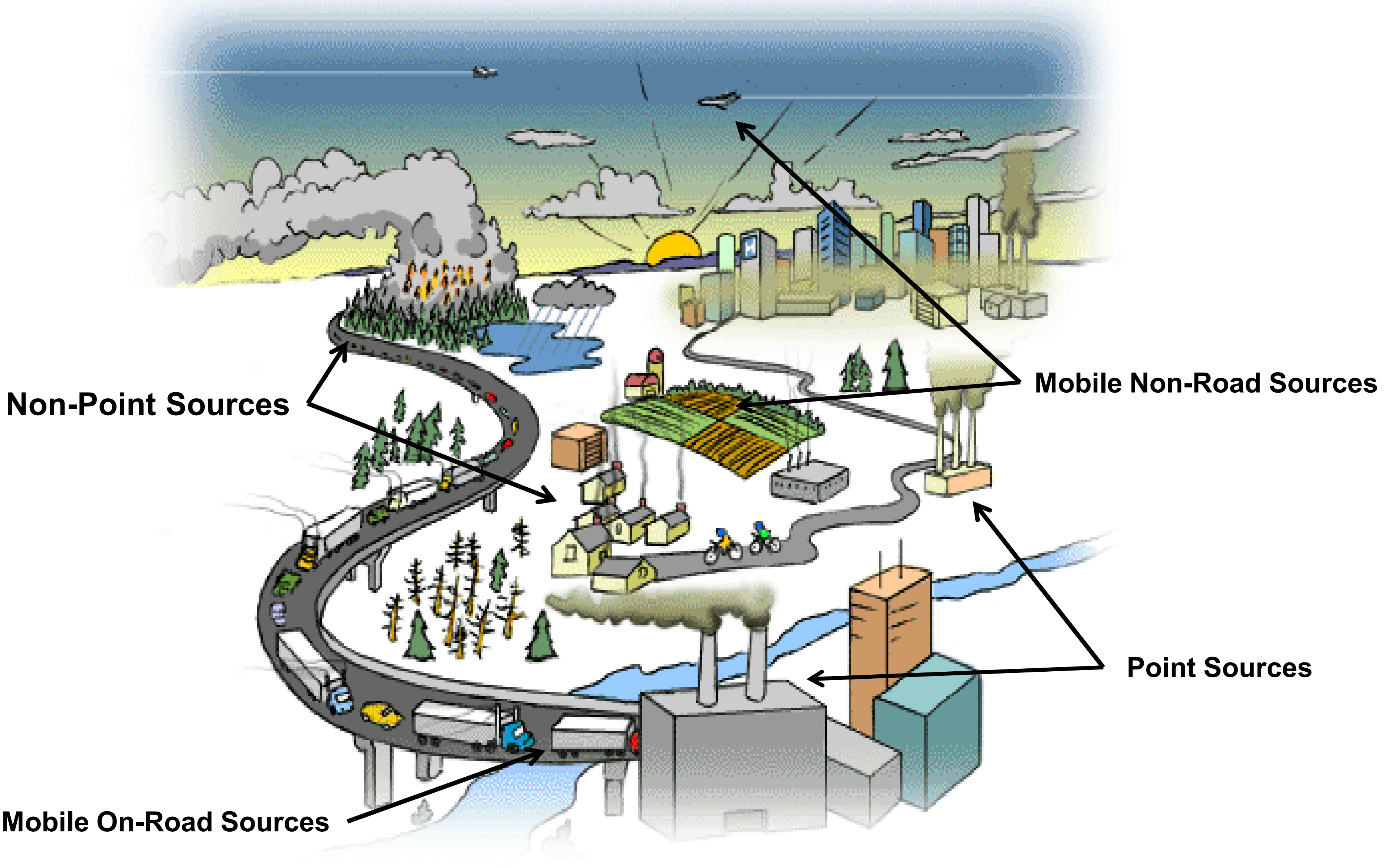


Mobile Sources



Forest Fires

Potential Sources Everywhere -- Where to Start???



Non-Point Sources

Mobile Non-Road Sources

Point Sources

Mobile On-Road Sources

Major Air Toxic Source Types

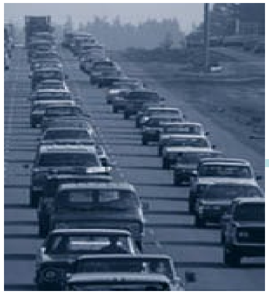
- Point sources;
- Nonpoint sources;
- On-road mobile sources;
- Non-road mobile sources;
- Indoor sources;
- Natural sources; and
- Exempt sources.

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 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

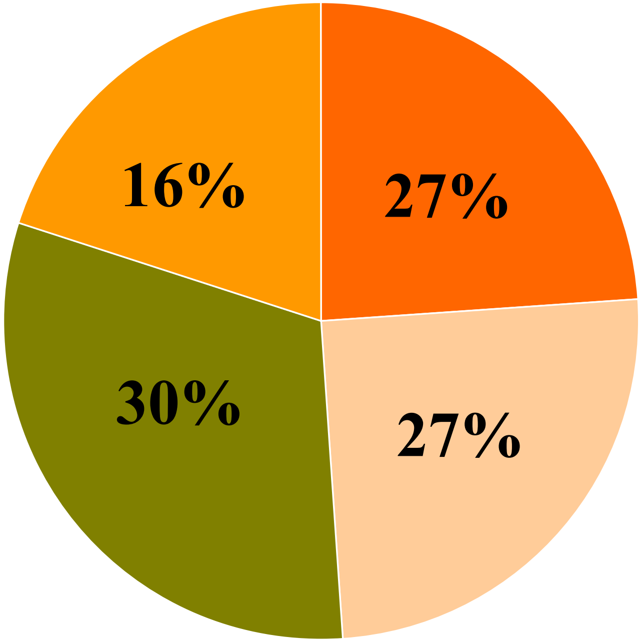
TRI/ EPCRA Chemicals

Types of HAP's Sources

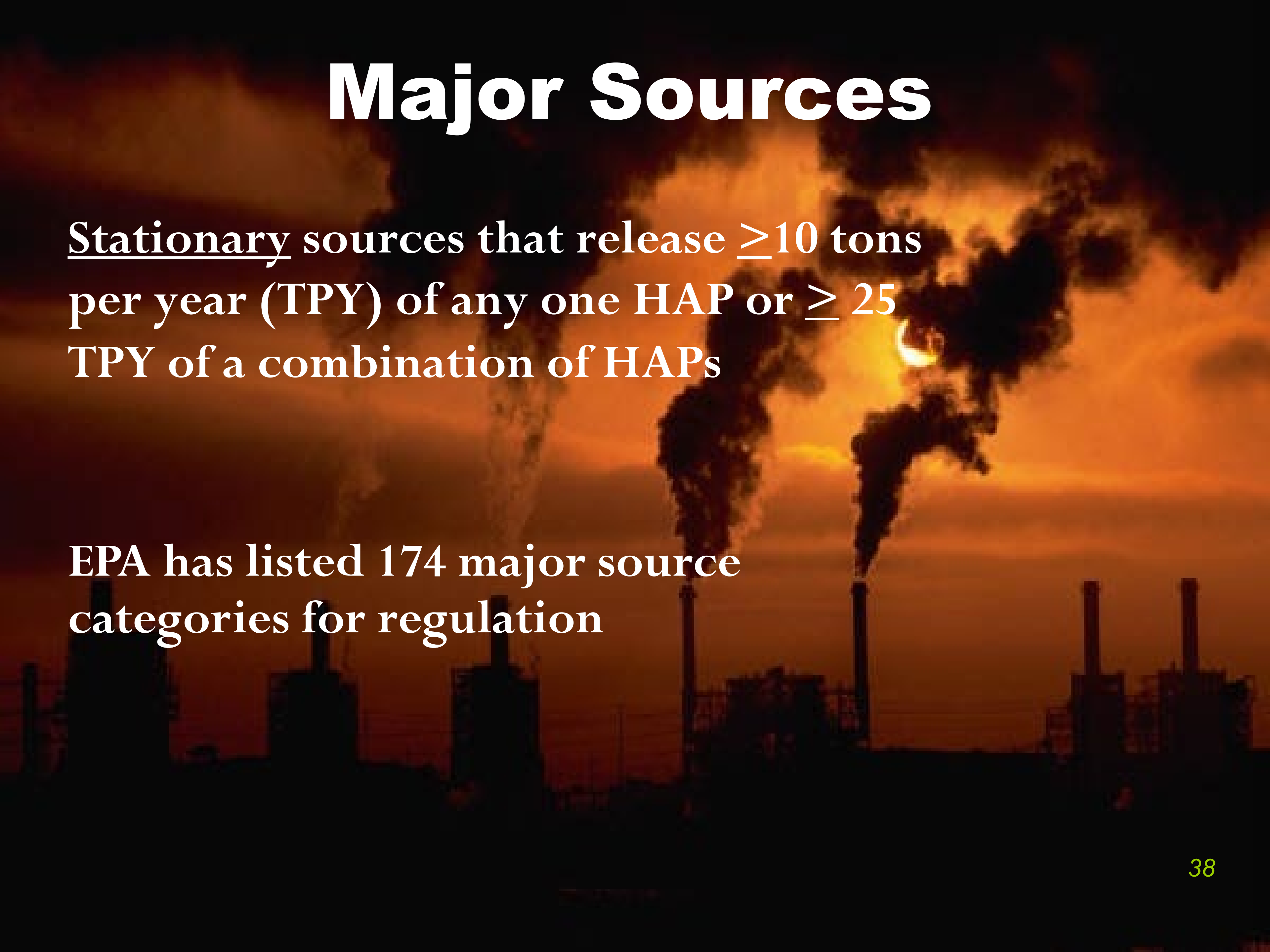
EPA divides ambient emission sources into four main groups:

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

National Air Toxics Emissions, 1999
4.75 M tons



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

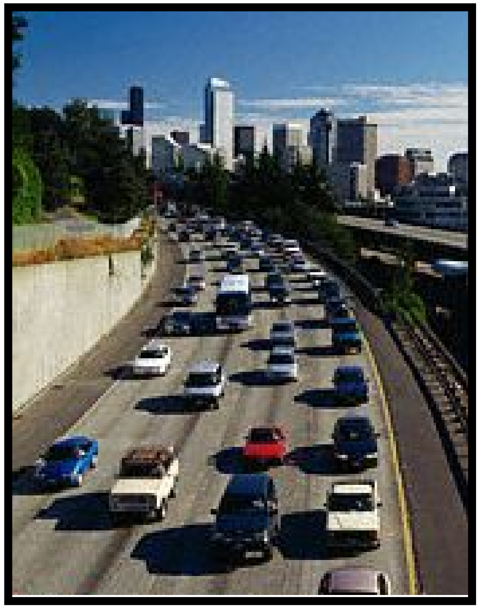
Stationary sources that emit <10 tons per year of a single air toxic, or <25 tons per year of a combination of air toxics

- 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

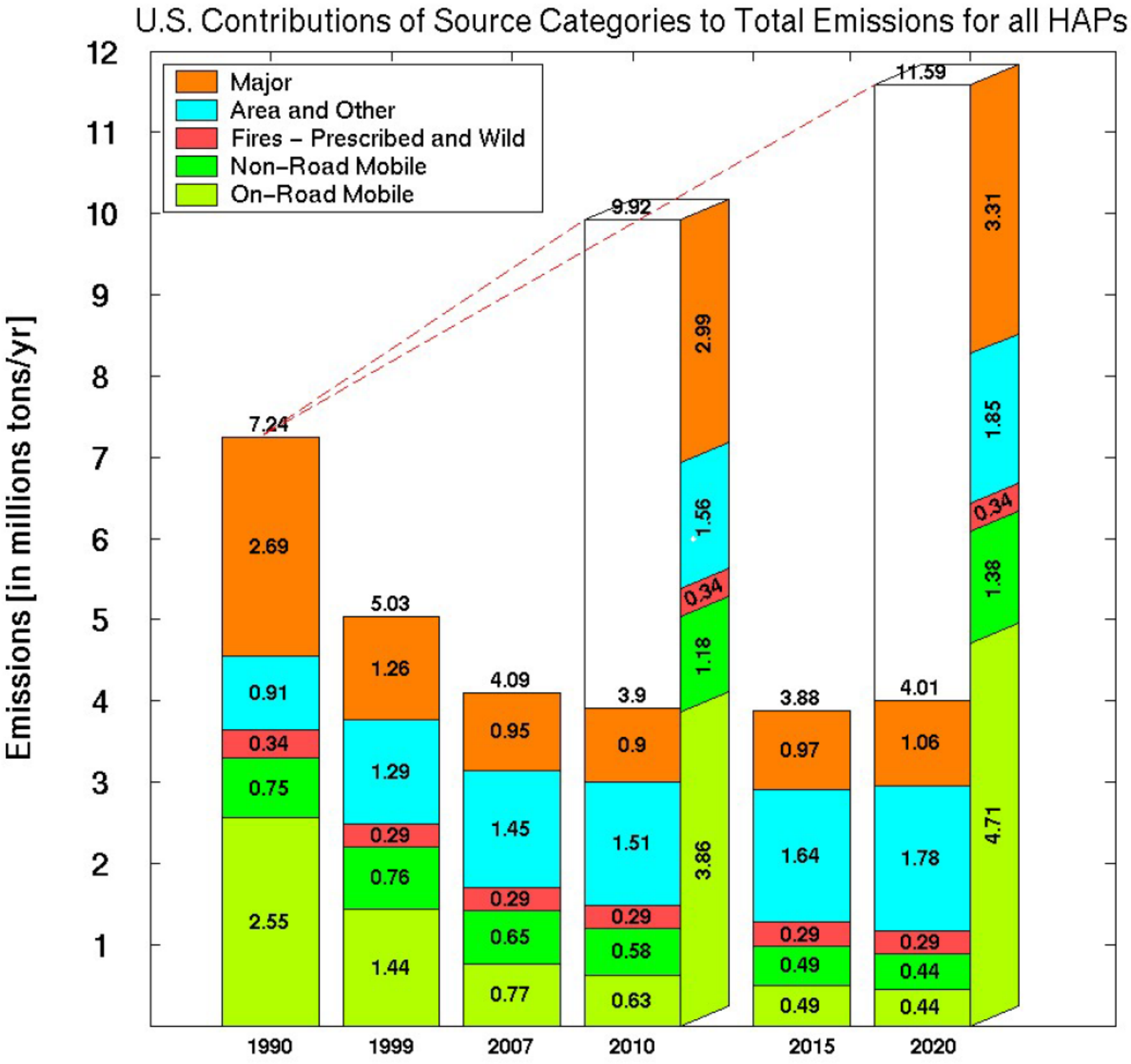
Non-road engines are also significant sources of air toxics and are coming under increasing focus

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

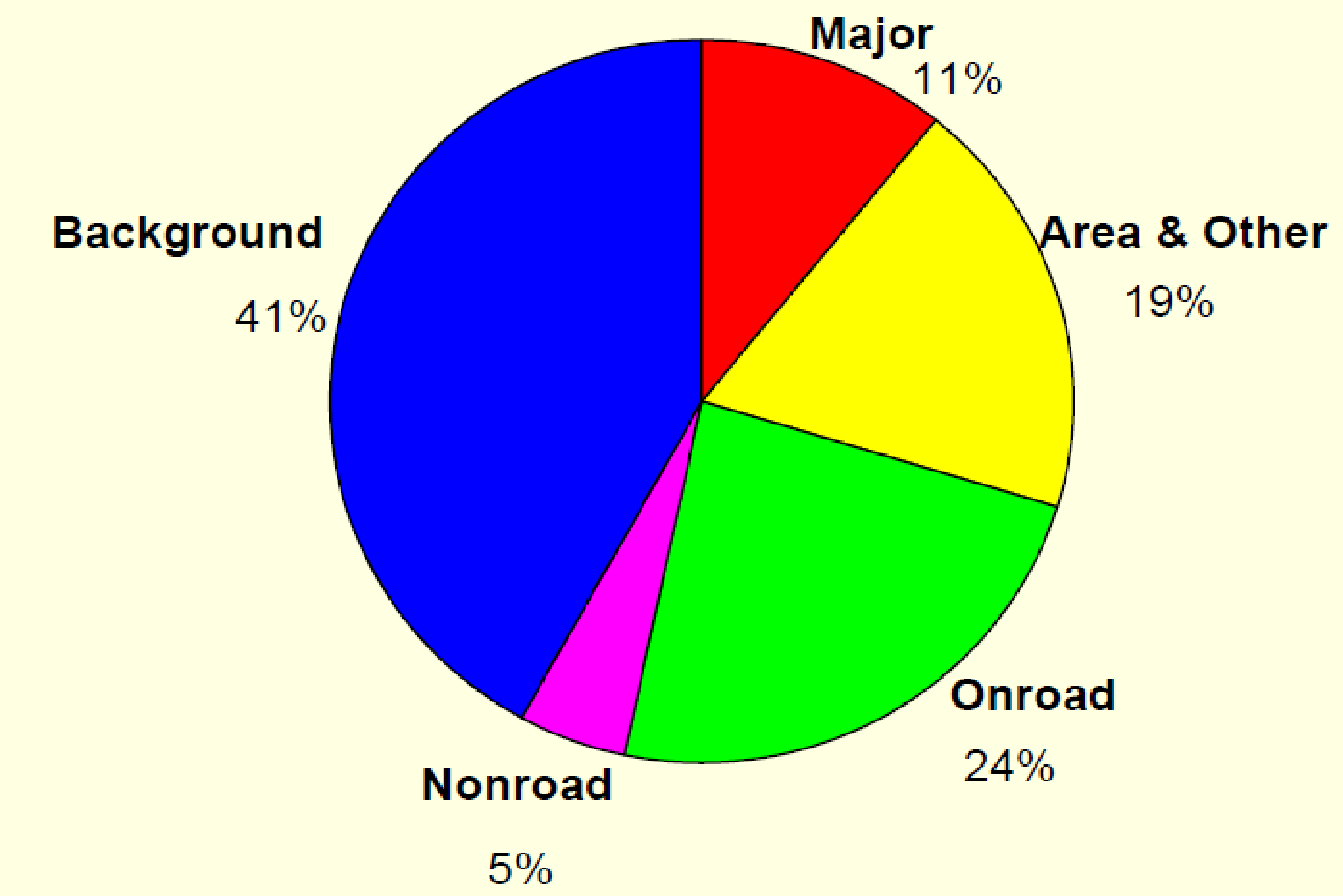


Key Findings

- 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

1999 NATA Cancer Risk Source Sector Contributions



Air Toxic Source Types

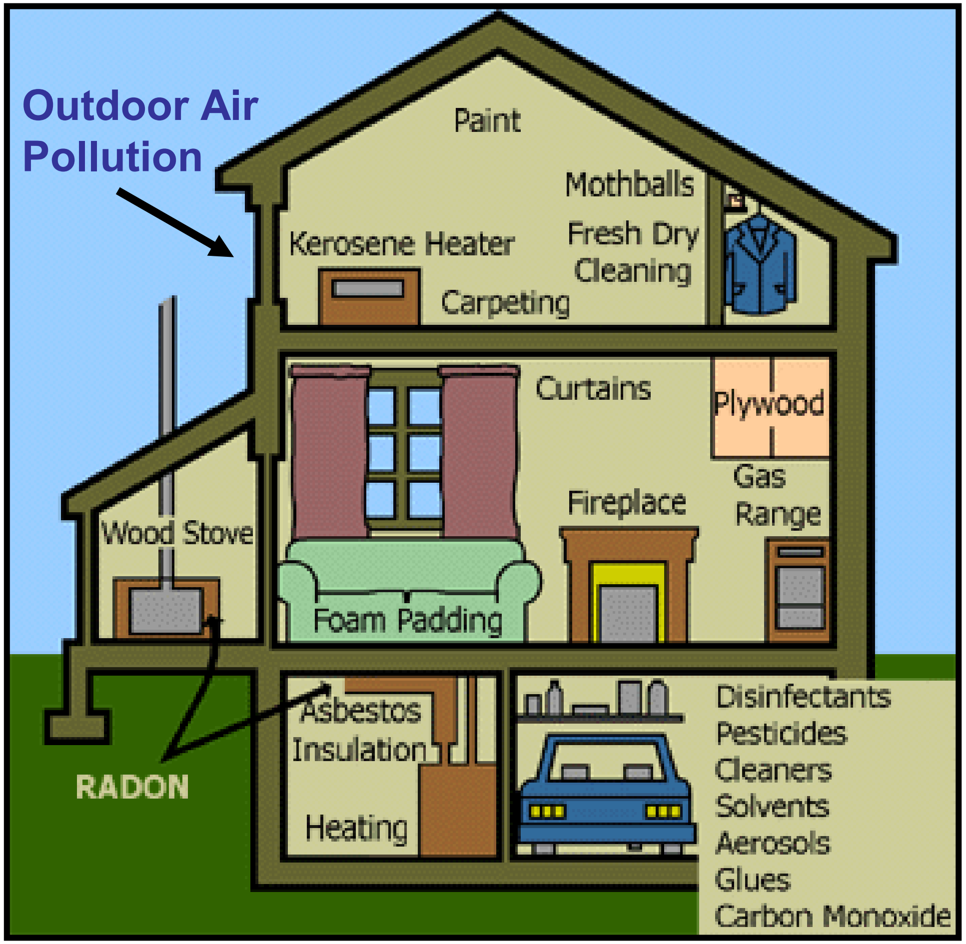
- Four primary categories used in compiling the NEI or used by the CAA or TRI:
  - Point and area sources
  - On and off-road mobile sources
- Five other sources of air toxics which are <u>not</u> captured by NEI, CAA or TRI are:
  - Indoor sources,
  - Natural sources,
  - Secondary formation of air 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	• Sulphuric, hydrofluoric and hydrochloric acids • Radon • Nitrogen oxides	• Volcanic gases • Radioactive decay of rock • Soils, lightning
Biogenic	• Ammonia • Methane • VOCs	• Animals wastes • Animal wastes, plant decay • Vegetation
Marine	• Dimethyl sulfide, ammonia, chlorides, sulfates, alkyl halides, nitrous oxides	• Sea spray released by breaking waves

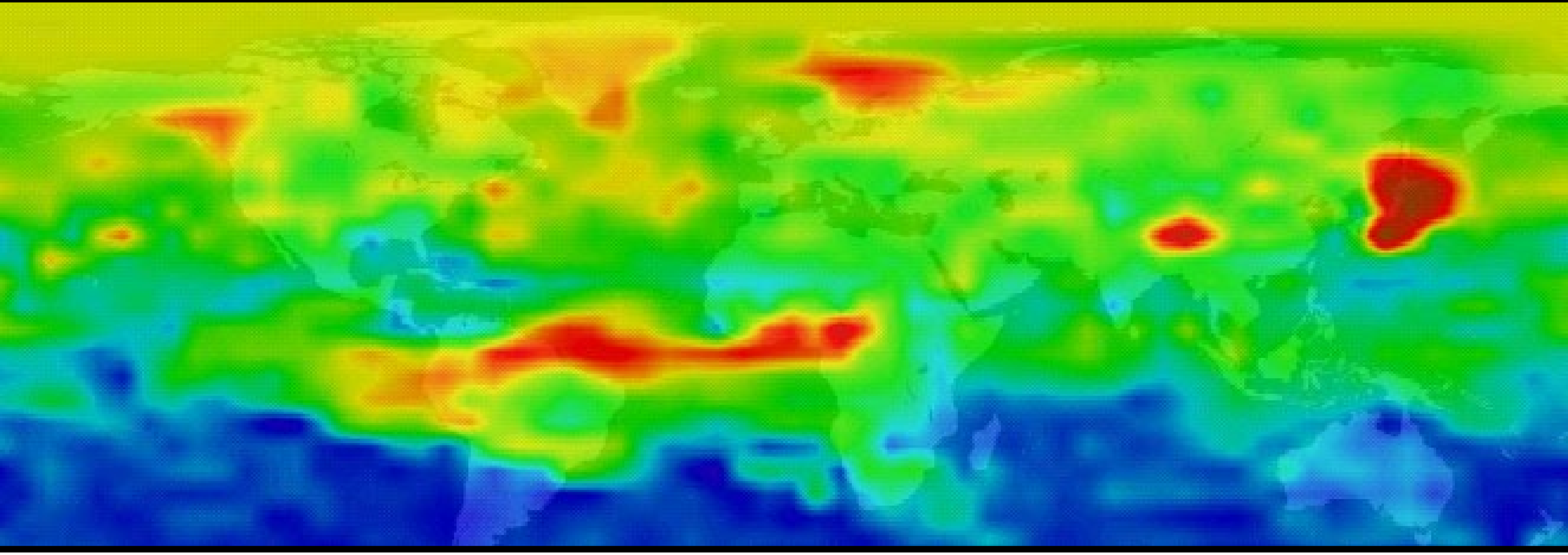
Source: *International Fertilizer Industry Association. 2001. Food and Agriculture Organization of the* United Nations. *Global estimates of gaseous emissions of NH3, NO and N2O from agricultural land. ISBN 92-5-104698-1. Available at:* www.fao.org/DOCREP/004/Y2780E/y2780e01.htm.

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



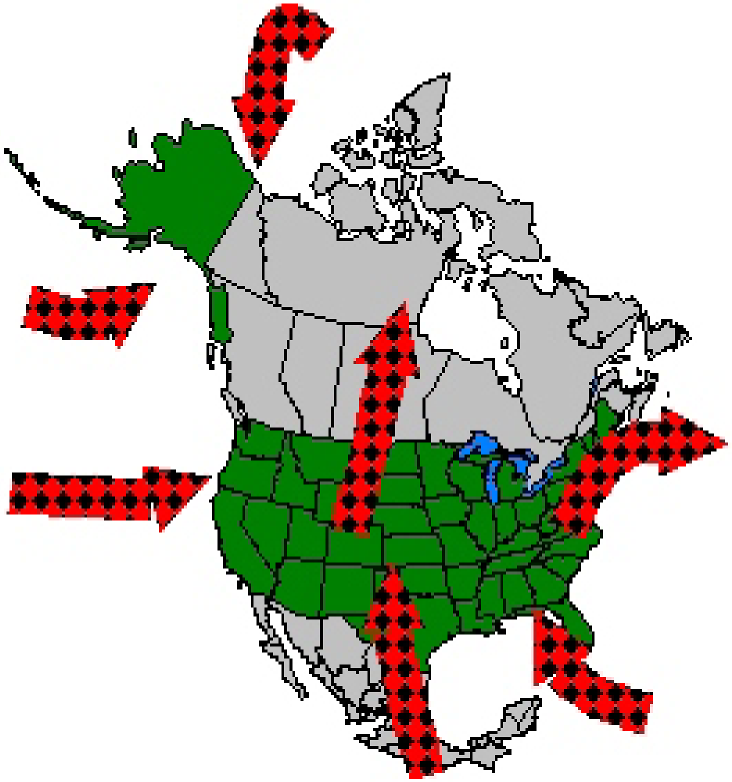
- Long-range transport of air pollutants (Hg) (PCB's) (Pesticides)

http://www.epa.gov/airnow/2007conference/monday/eagan.ppt#265,1,Saharan

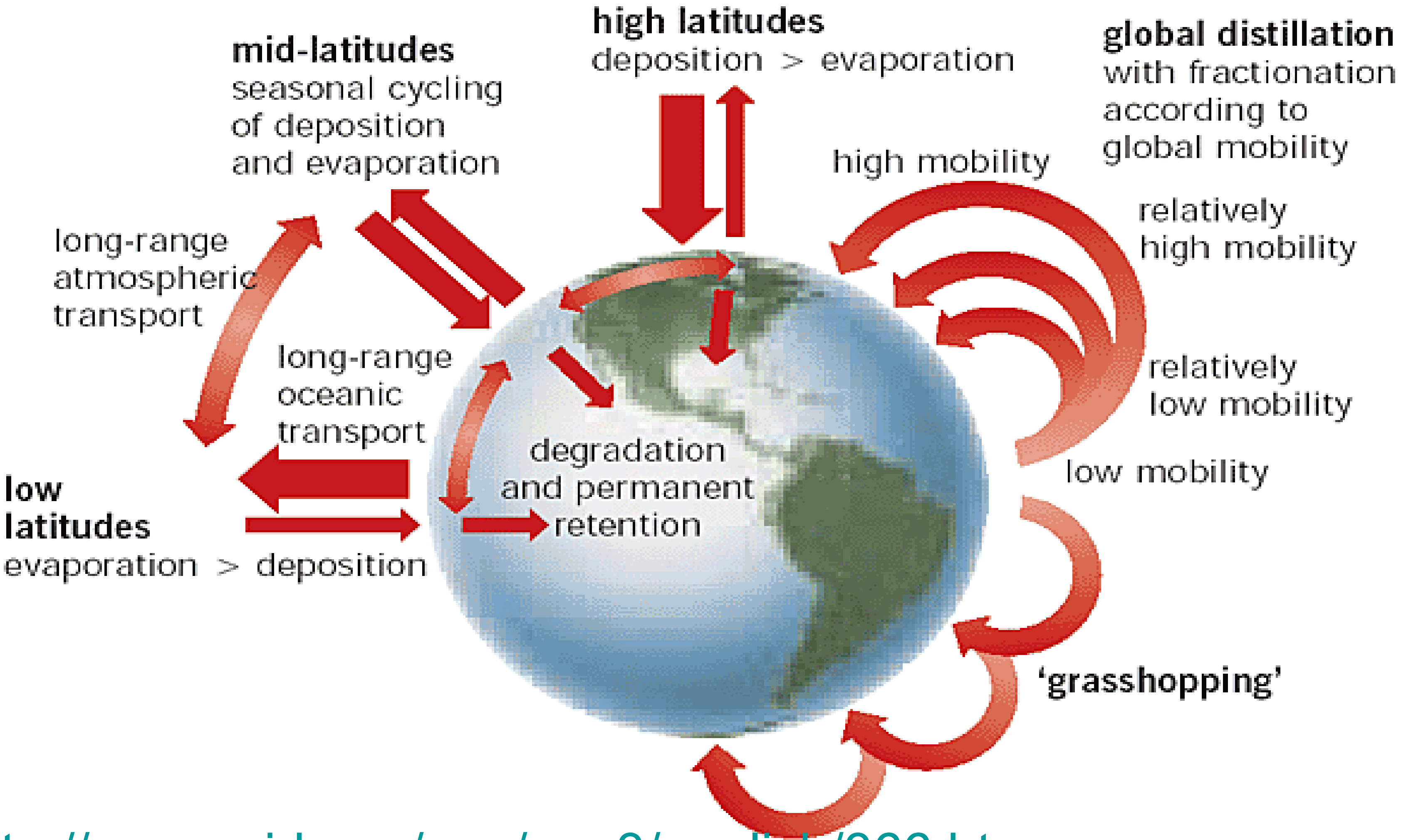
- Dust Event Impacts on Florida Particulate Concentrations

- 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

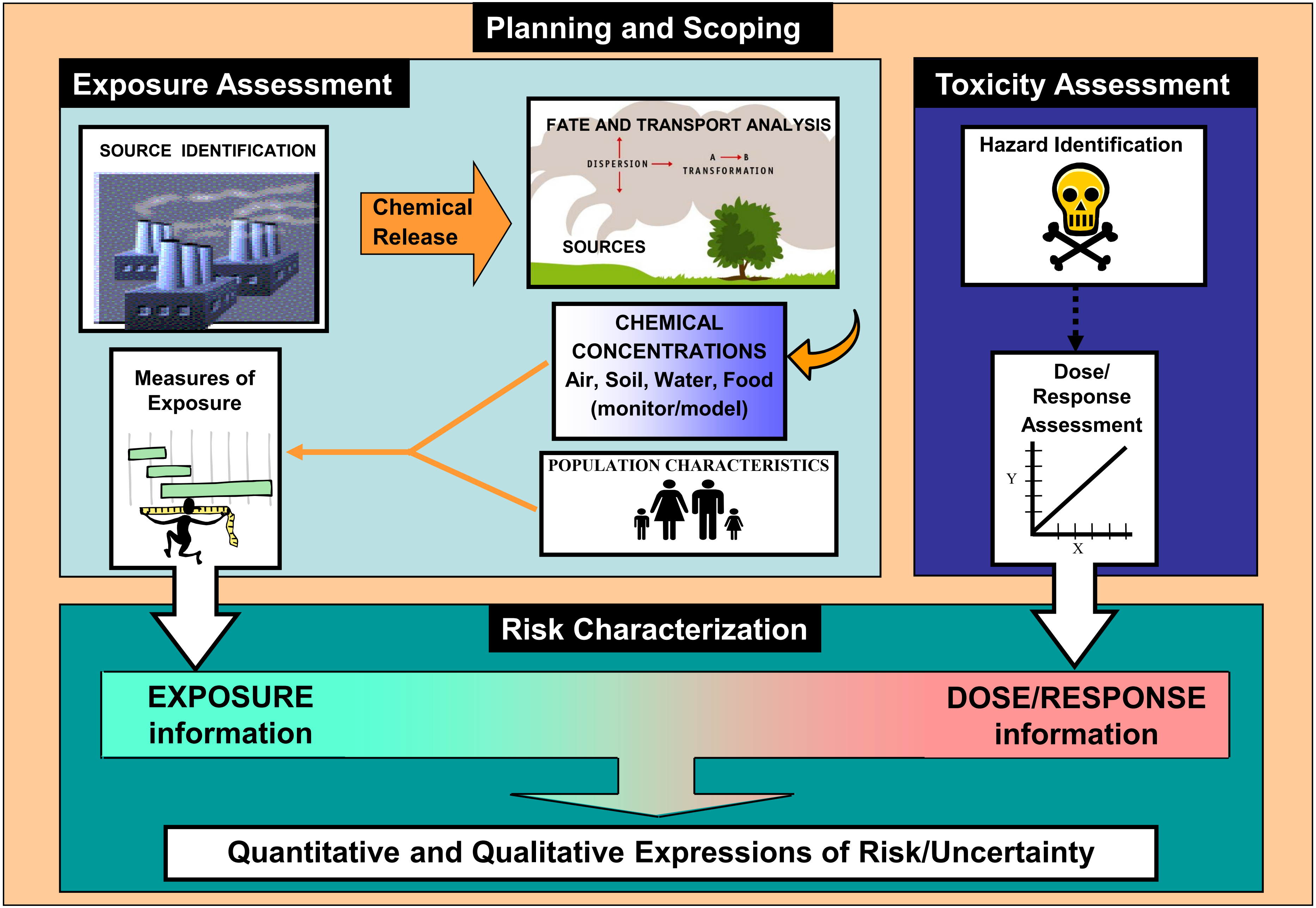


http://www.grida.no/geo/geo3/english/366.htm

http://literacynet.org/polar/pop/html/project-pops.html

Emission Inventories

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

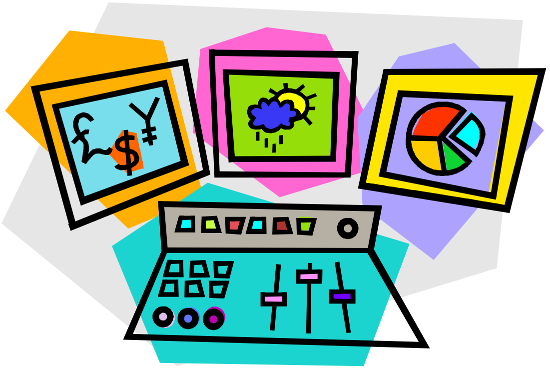
Risk Characterization

EXPOSURE information

DOSE/RESPONSE information

Quantitative and Qualitative Expressions of Risk/Uncertainty

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

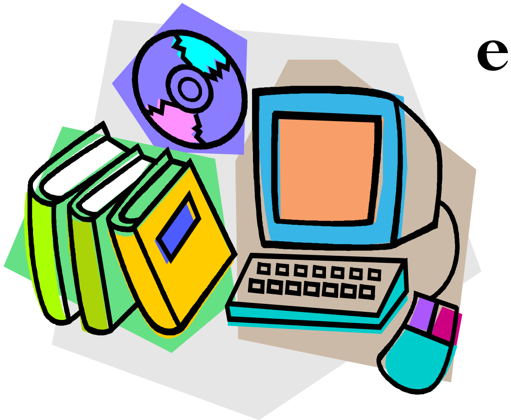
The NEI is a "modeling inventory"

- 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.

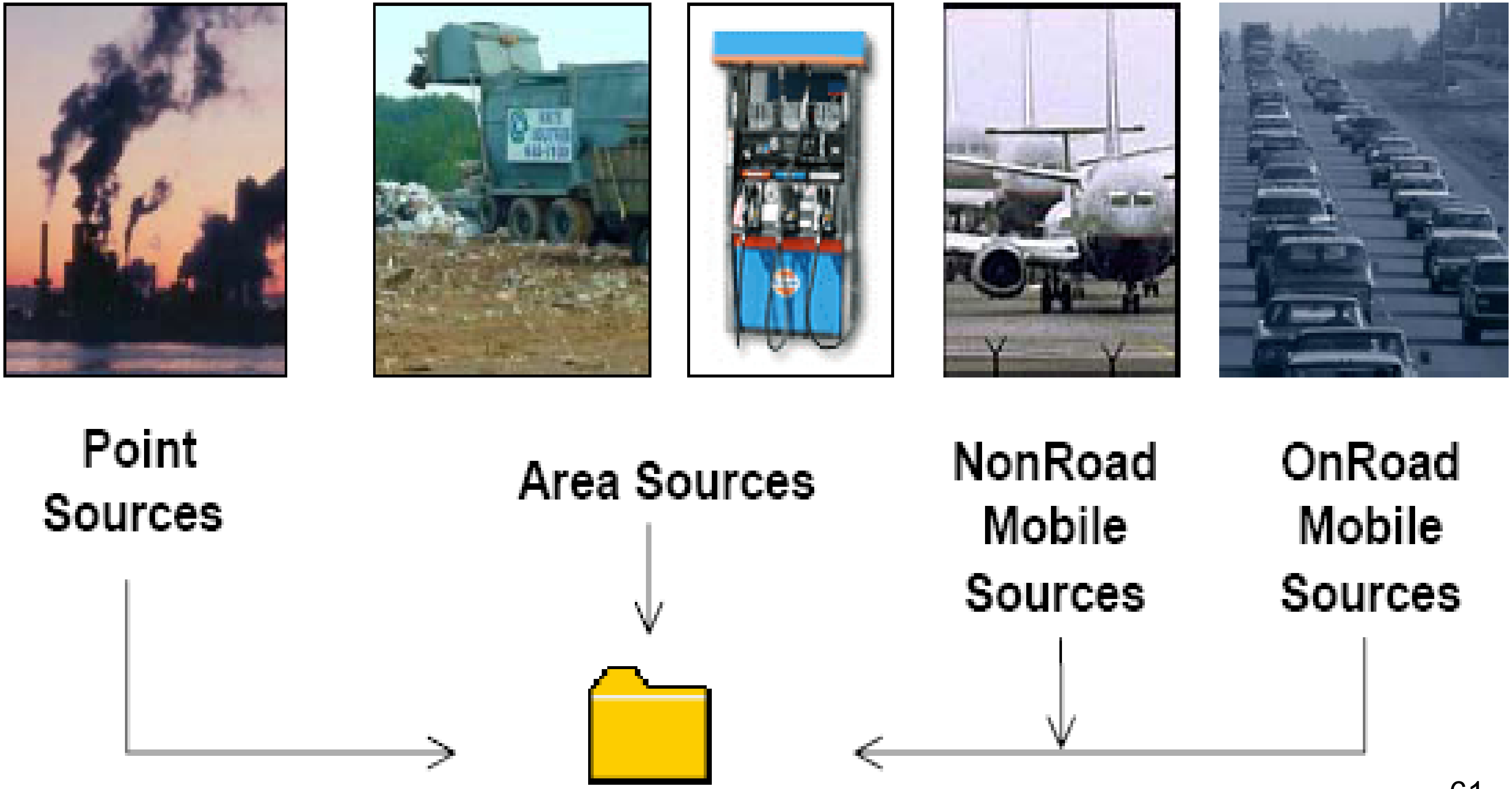
Developing An Emission Inventory

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:



Point Sources

Area Sources

NonRoad Mobile Sources

OnRoad Mobile Sources

Inventory

How do you Quantify Emissions?

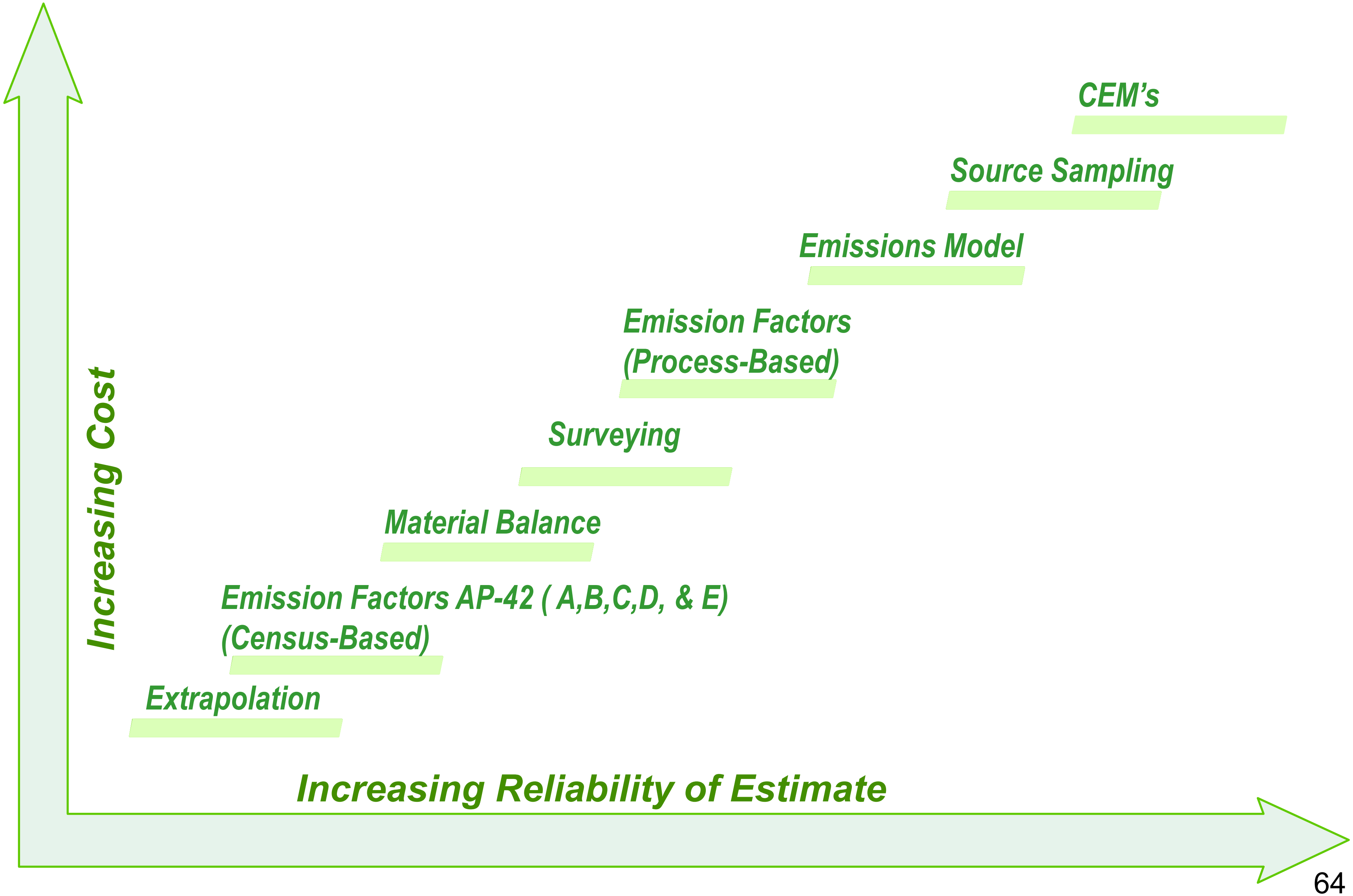
Once we have identified the sources of air toxics, we want to accurately estimate the amount of chemicals that are released from those sources

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



CEM's

Source Sampling

Emissions Model

Emission Factors
(Process-Based)

Surveying

Material Balance

Emission Factors AP-42 (A,B,C,D, & E)
(Census-Based)

Extrapolation

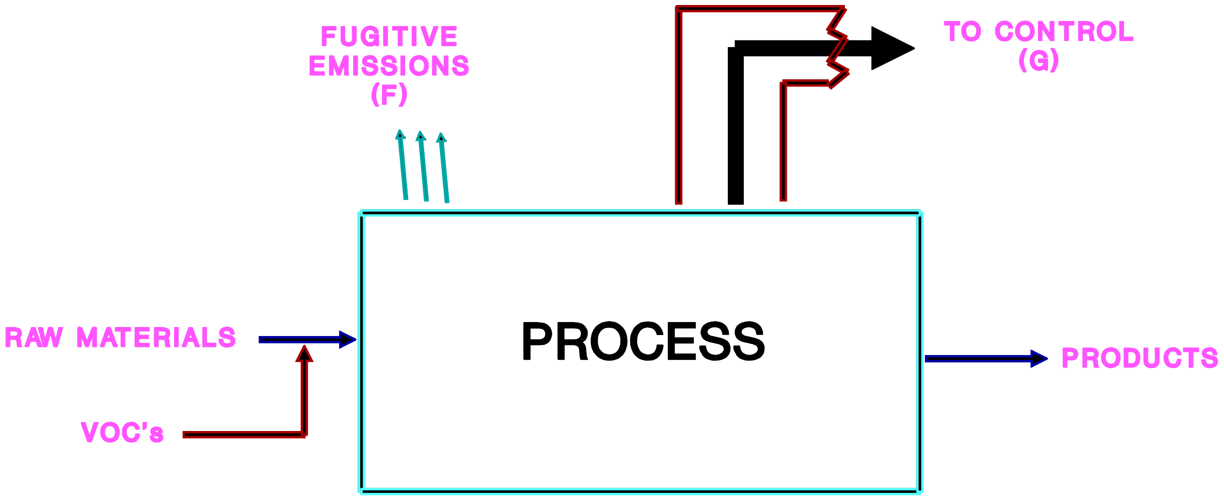
Increasing Cost

Increasing Reliability of Estimate

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.



FUGITIVE EMISSIONS (F)

TO CONTROL (G)

RAW MATERIALS

VOC's

PROCESS

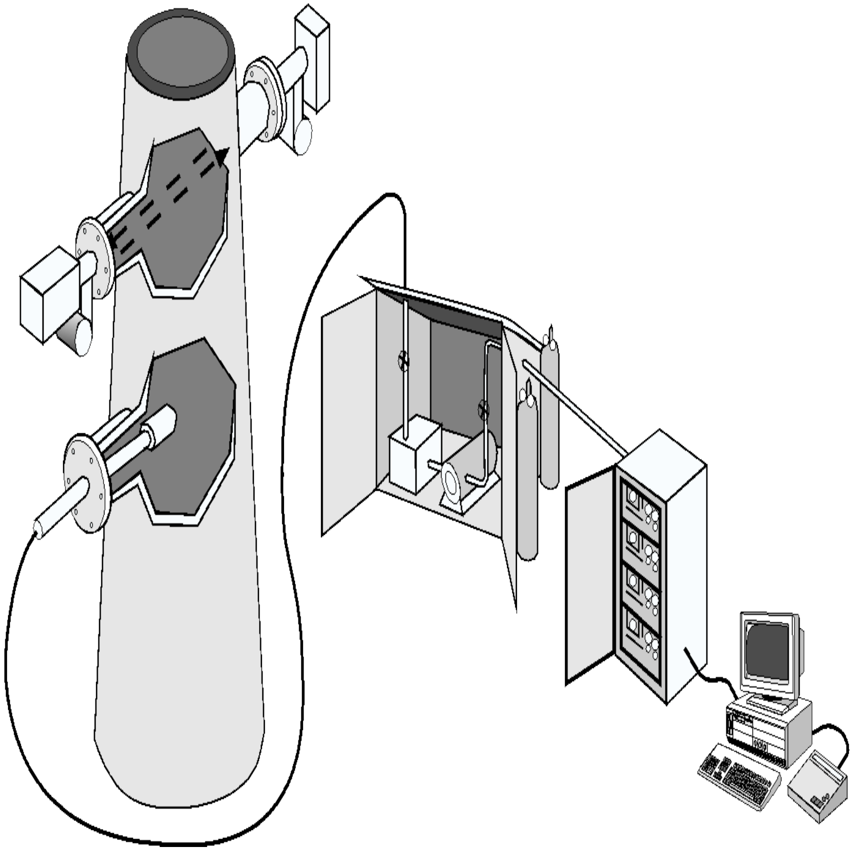
PRODUCTS

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

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.

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.

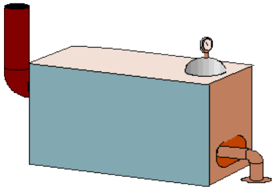
Emission Factors

- 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

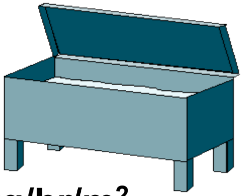
Process-Based Emission Factors

Natural Gas Boiler



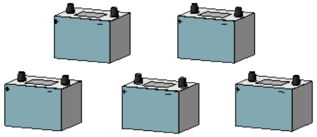
kg/10^6m^3

Vapor Degreaser



kg/hr/m^2

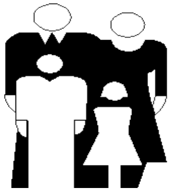
Battery Manufacturing



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

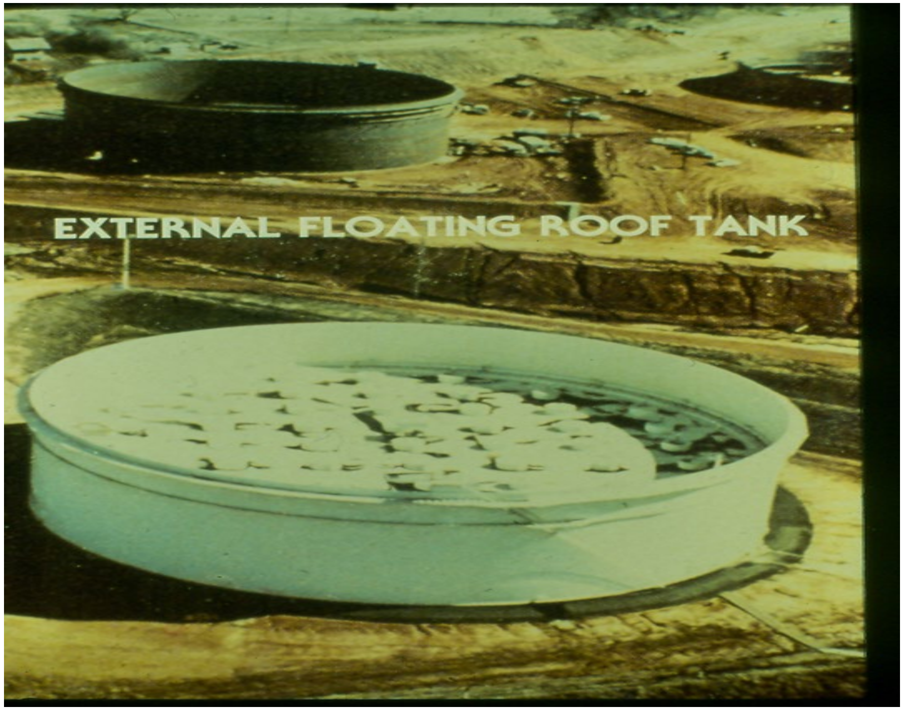
- *WebFIRE* The FIRE database includes EPA's recommended emission estimation factors for criteria and hazardous air pollutants.
- *TANKS* Estimates volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions from fixed- and floating-roof storage tanks.
- *SPECIATE* is EPA's repository 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

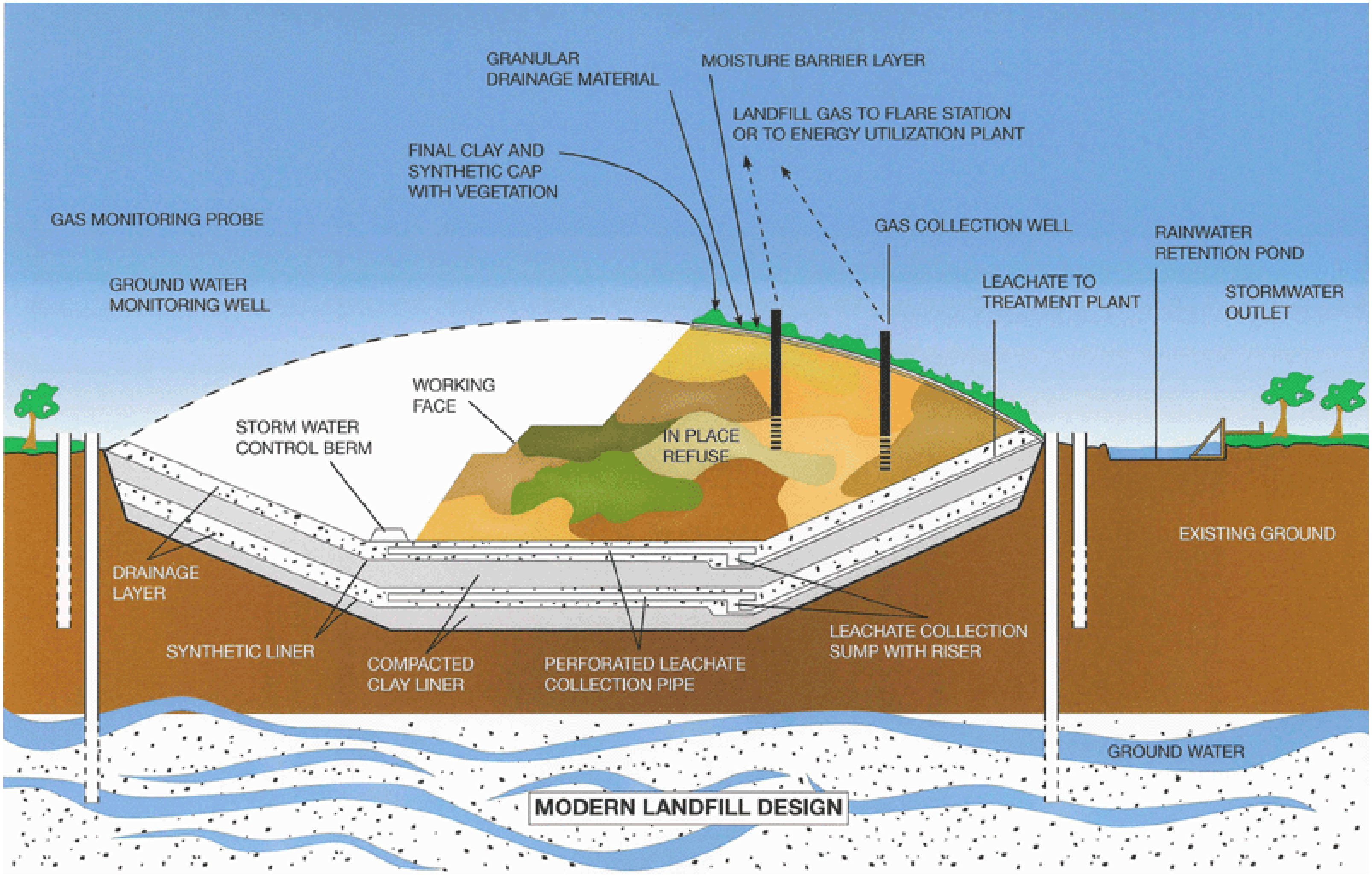
http://www.epa.gov/ttn/chief/software/tanks/index.html#new



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



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
  ====================================

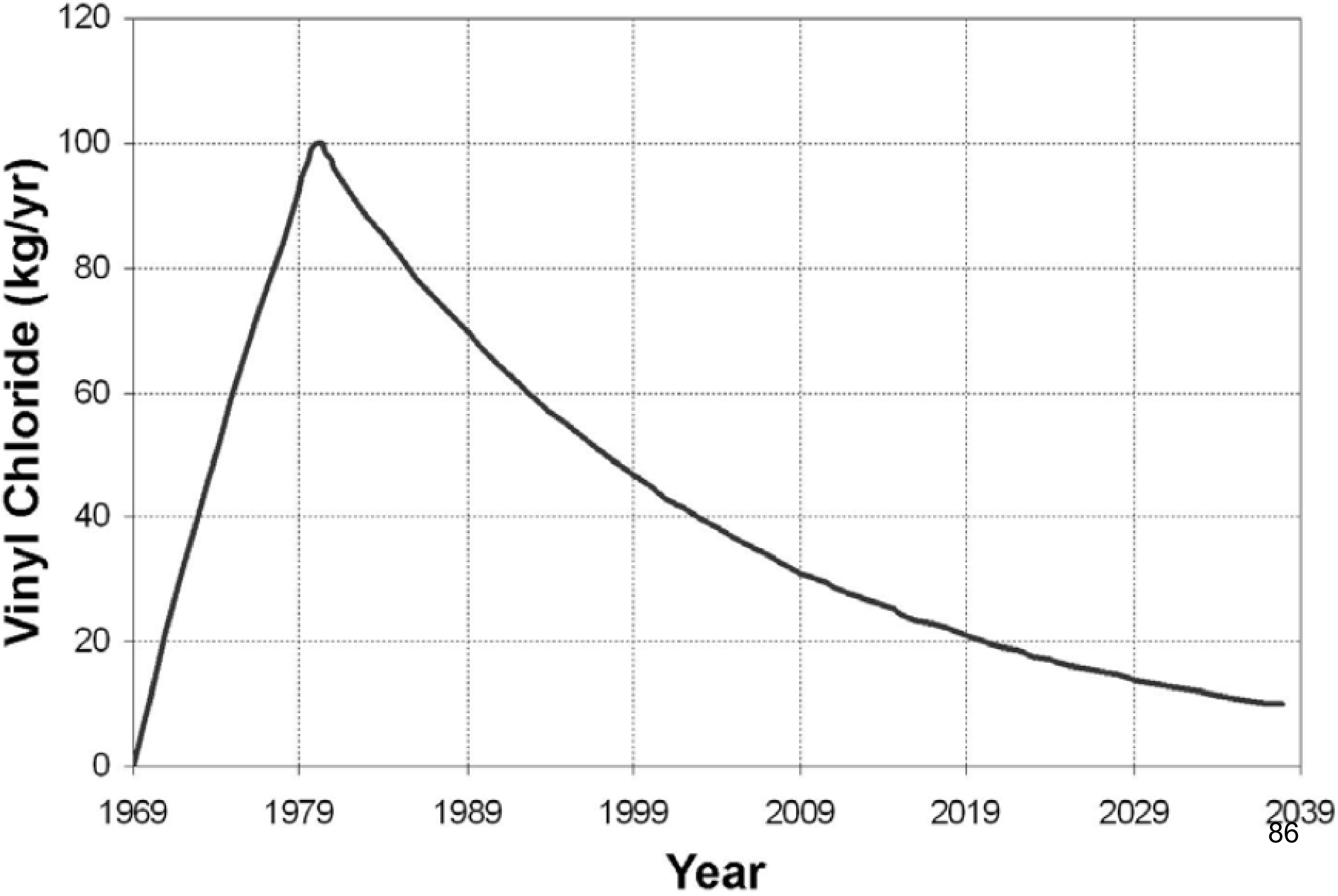
  Landfill Parameters
  Landfill type : Co-Disposal
  Year Opened : 1969 Current Year : 1999 Closure Year: 1980
  Capacity : 792000 Mg
  Average Acceptance Rate Required from
  Current Year to Closure Year : 0.00 Mg/year

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

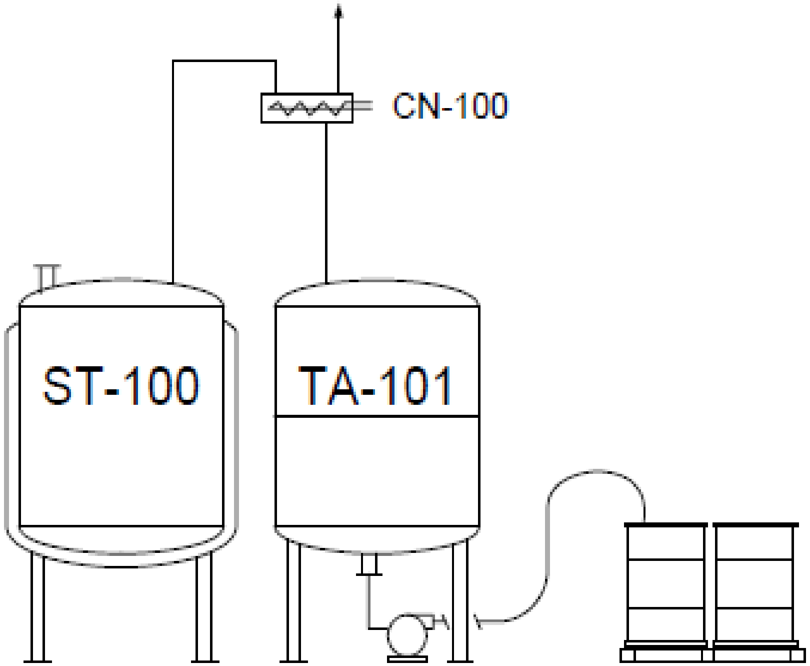
Example Compounds Of Principal Concern Emission Estimates Produced by LandGEM



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

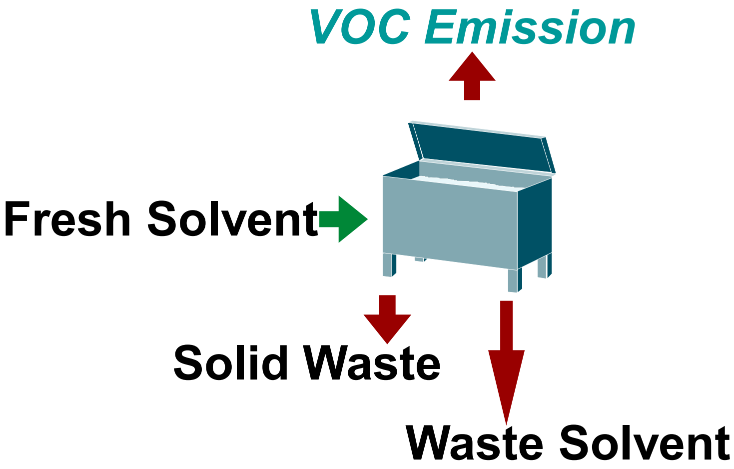
Estimation Methods: Material Balance

- 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



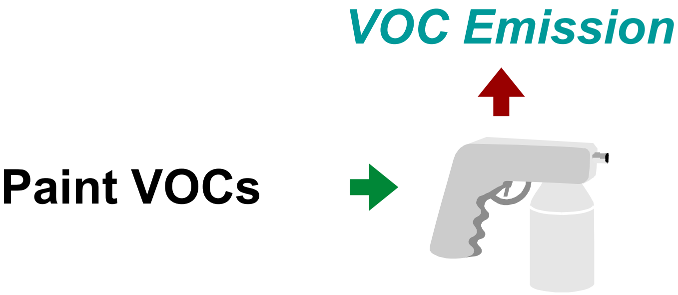
VOC Emission

Fresh Solvent

Solid Waste

Waste Solvent

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



VOC Emission

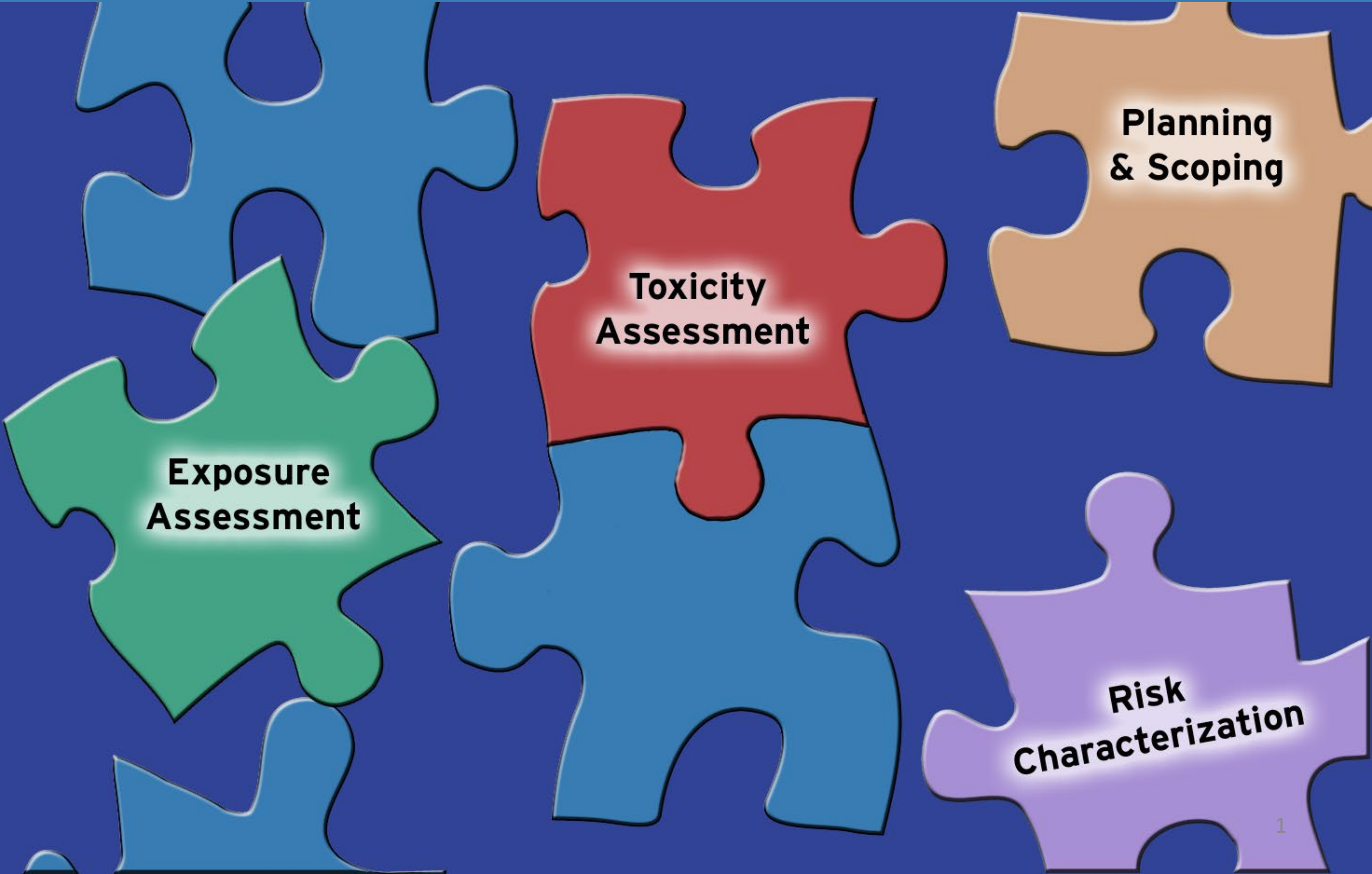
Paint VOCs

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

Introduction to Air Toxics Risk Assessment



Planning & Scoping

Toxicity Assessment

Exposure Assessment

Risk Characterization

The World of Risk

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

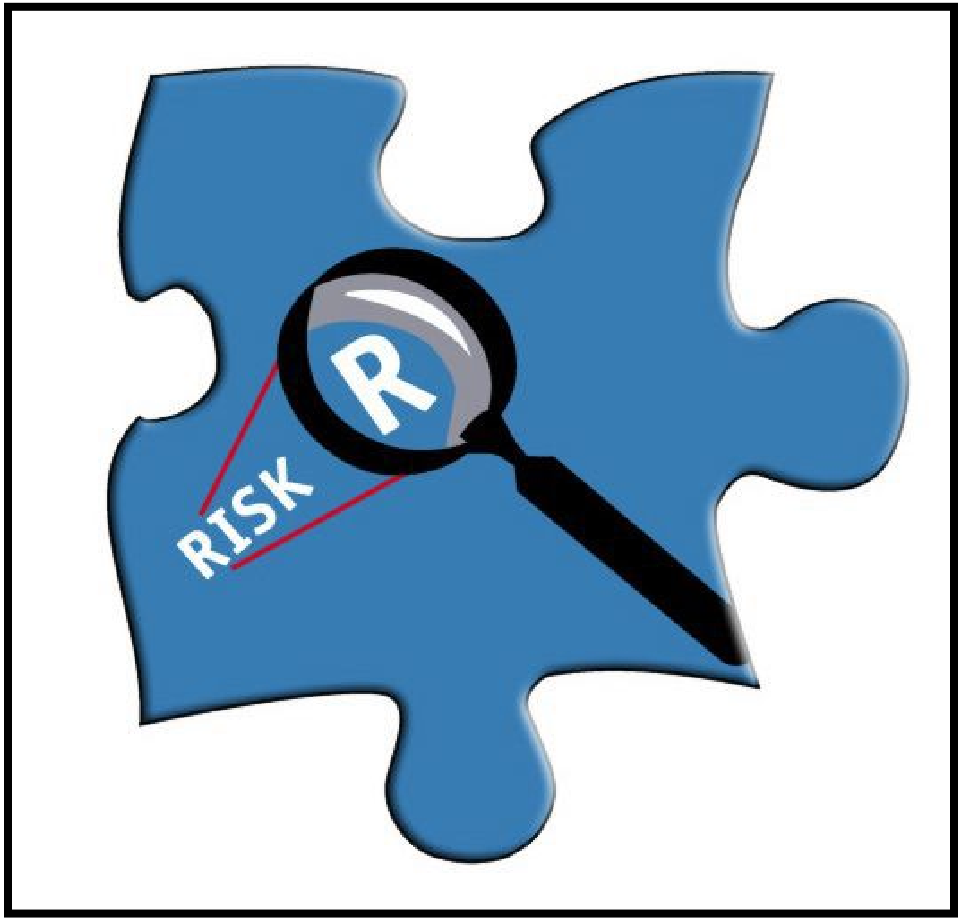
- A simple mathematical formula can show the basis for human health risk assessment.
- Potential for Injury or Disease (i.e., the "Risk") = ƒ (metric of exposure, metric of toxicity)
  - Specifically, the likelihood that injury or disease may occur from exposure to air toxics can be described as a function 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/ 2.75×10^{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 x 2×10^{6} persons x 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>…

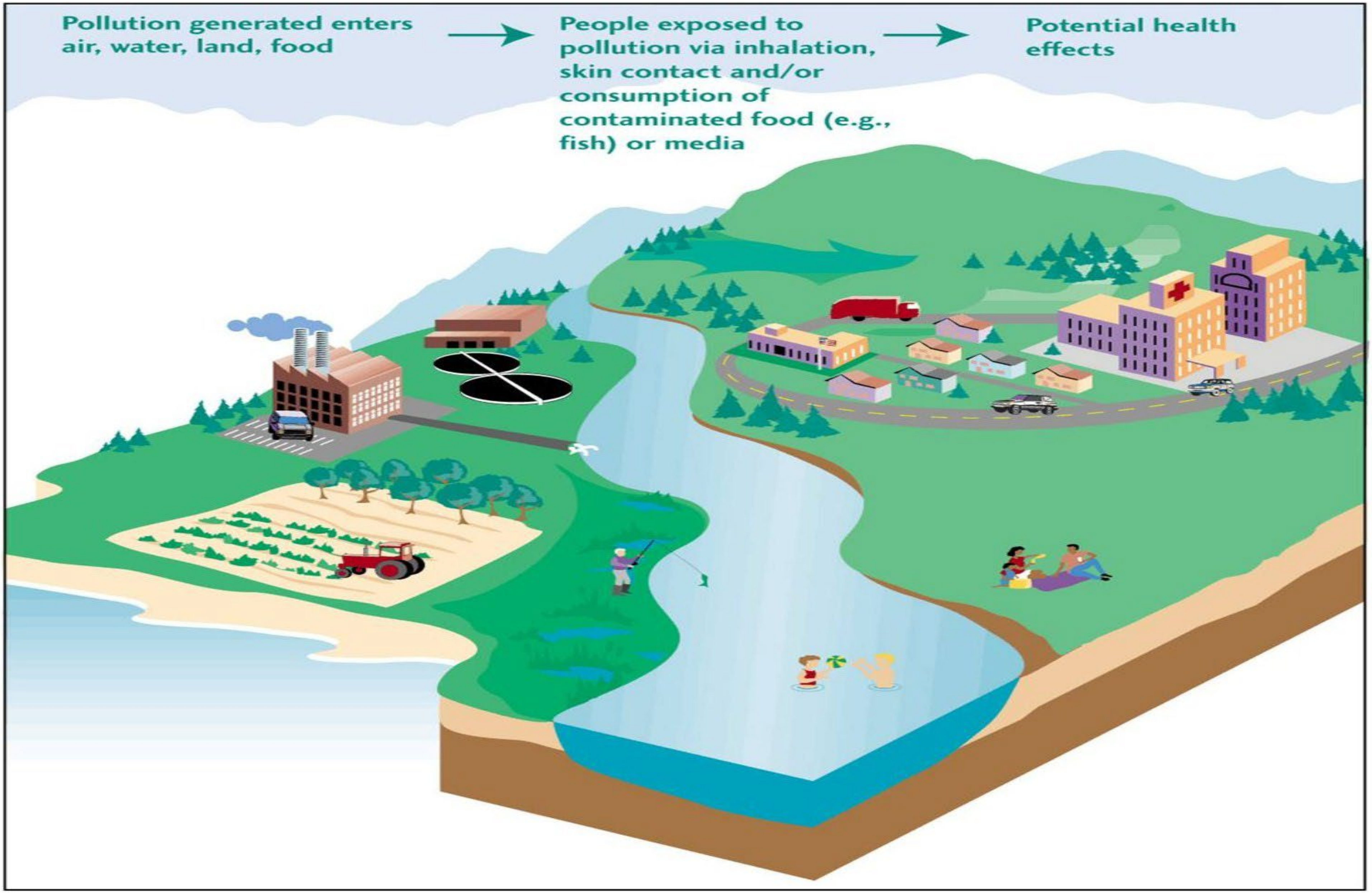
In this class, we are going to study the process EPA uses to evaluate the risks posed to human health from <u>toxic air pollutants</u> and their control or abatement.



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



Pollution generated enters air, water, land, food → People exposed to pollution via inhalation, skin contact and/or consumption of contaminated food (e.g., fish) or media → Potential health effects

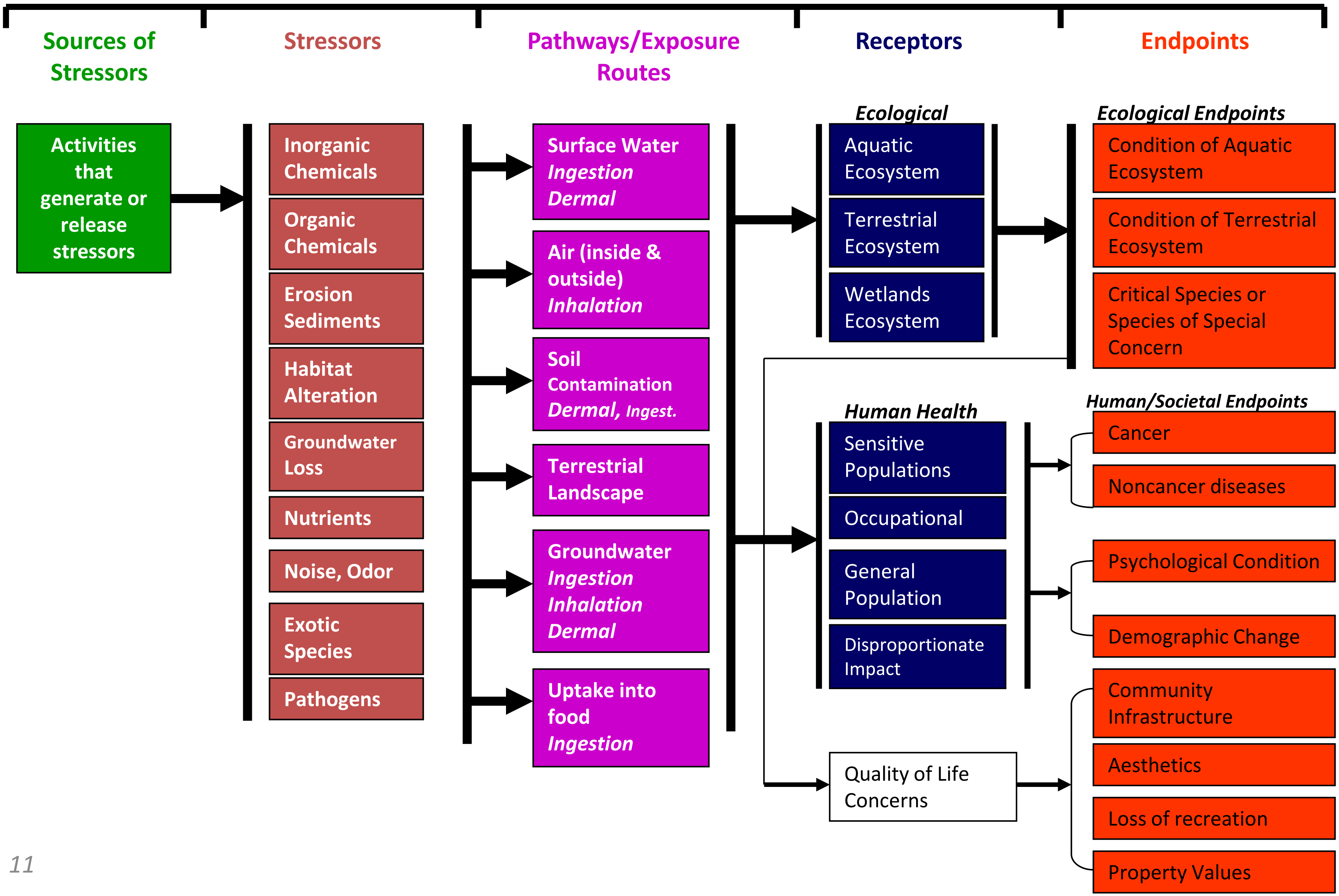
Environmental Risk

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

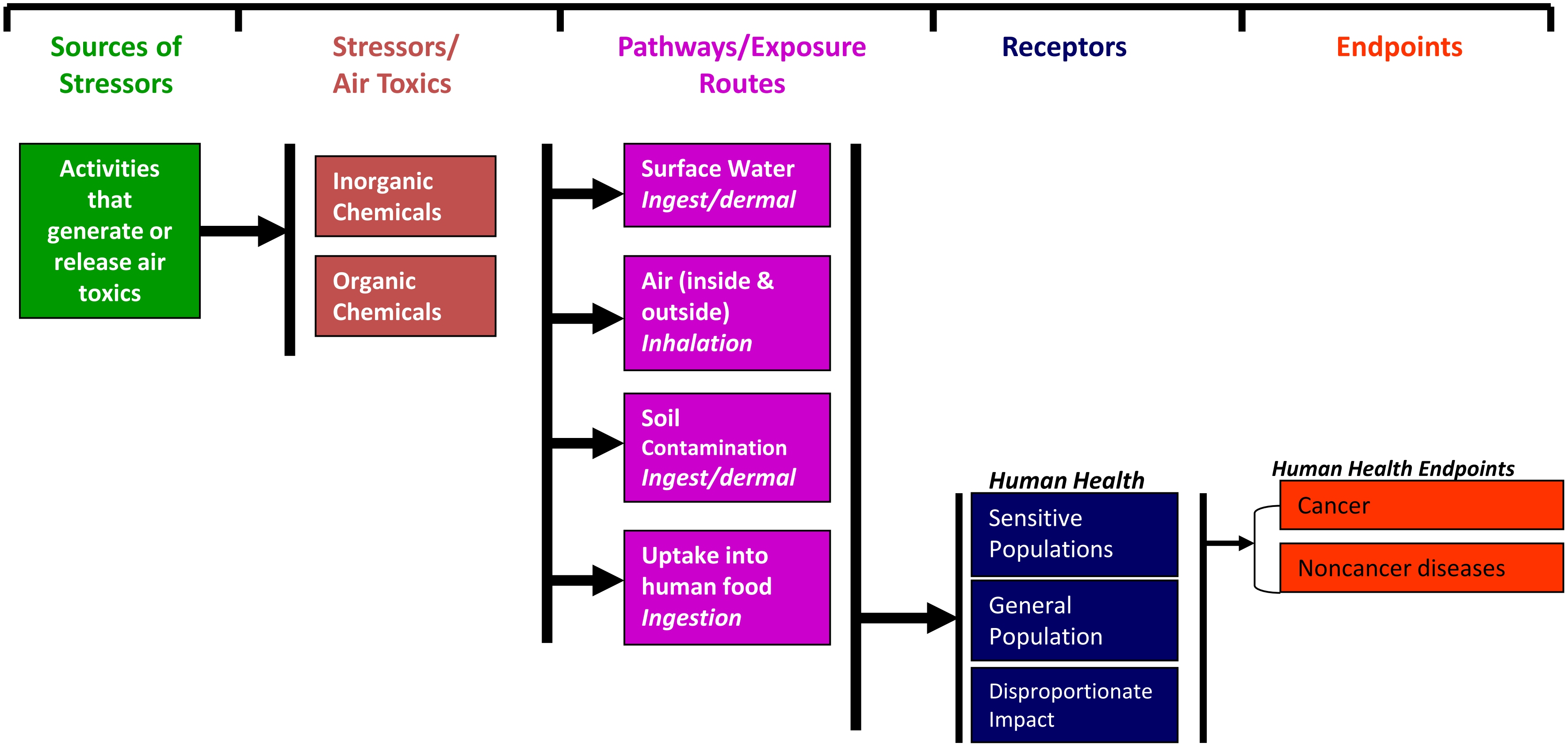
Community Infrastructure

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!

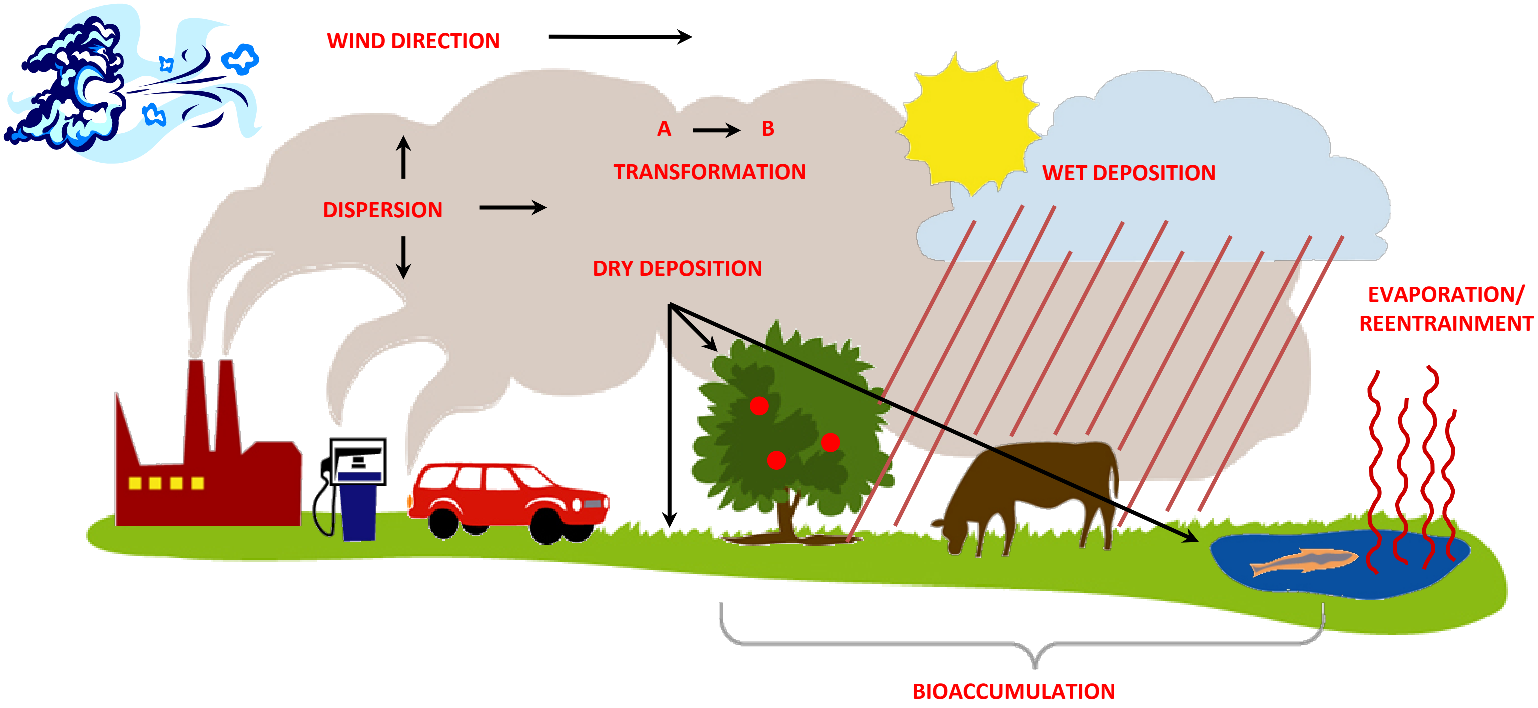
Redraw this conceptual model with *pictures* of what we think may be happening in the real world when dangerous chemicals are released to the air…

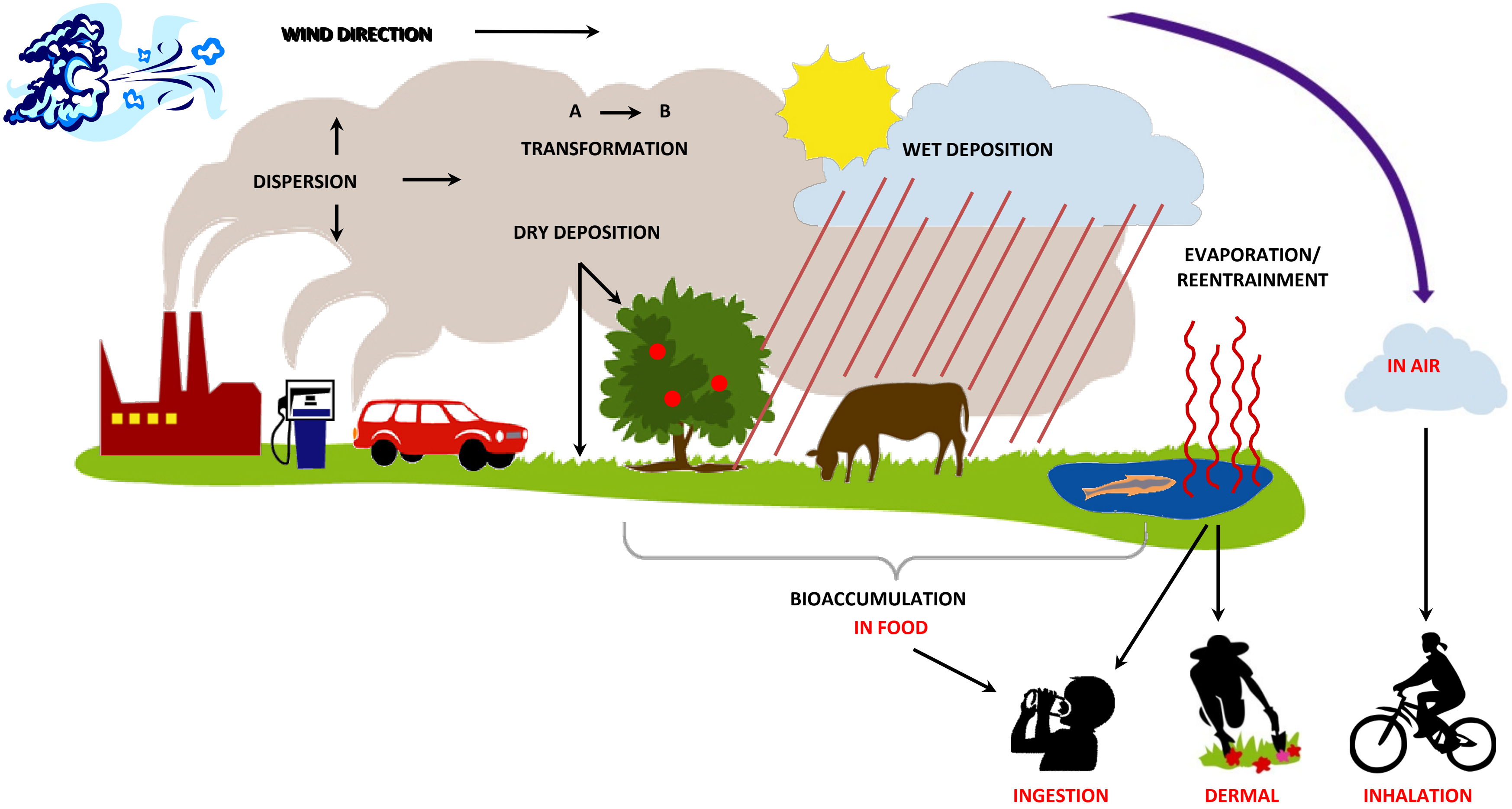
Conceptual Model

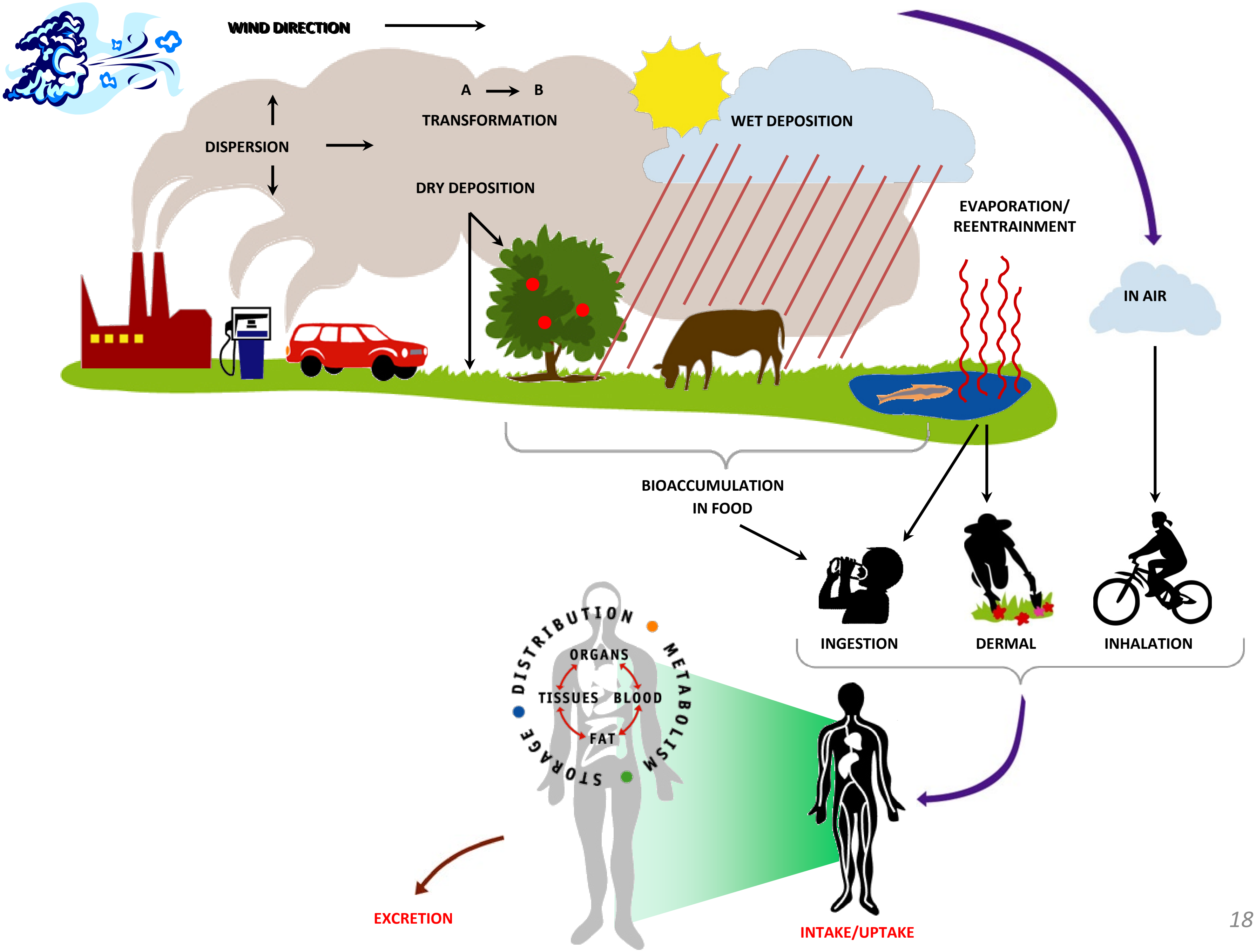
- The conceptual model that follows illustrates how air toxics risk assessments usually focuses, at a minimum, on the inhalation of contaminated air.
- However, for a small subset of air toxics, the risk assessment also may need to address ingestion of or dermal contact with soils, water, or food that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


WIND DIRECTION
A → B
TRANSFORMATION
WET DEPOSITION
DISPERSION
DRY DEPOSITION
EVAPORATION/
REENTRAINMENT
BIOACCUMULATION


WIND DIRECTION
A B
TRANSFORMATION
DISPERSION
DRY DEPOSITION
WET DEPOSITION
EVAPORATION/
REENTRAINMENT
IN AIR
BIOACCUMULATION
IN FOOD
INGESTION
DERMAL
INHALATION



WIND DIRECTION

A → B

TRANSFORMATION

DISPERSION

DRY DEPOSITION

WET DEPOSITION

EVAPORATION/
REENTRAINMENT

IN AIR

BIOACCUMULATION
IN FOOD

INGESTION

DERMAL

INHALATION

DISTRIBUTION

METABOLISM

STORAGE

ORGANS

TISSUES

BLOOD

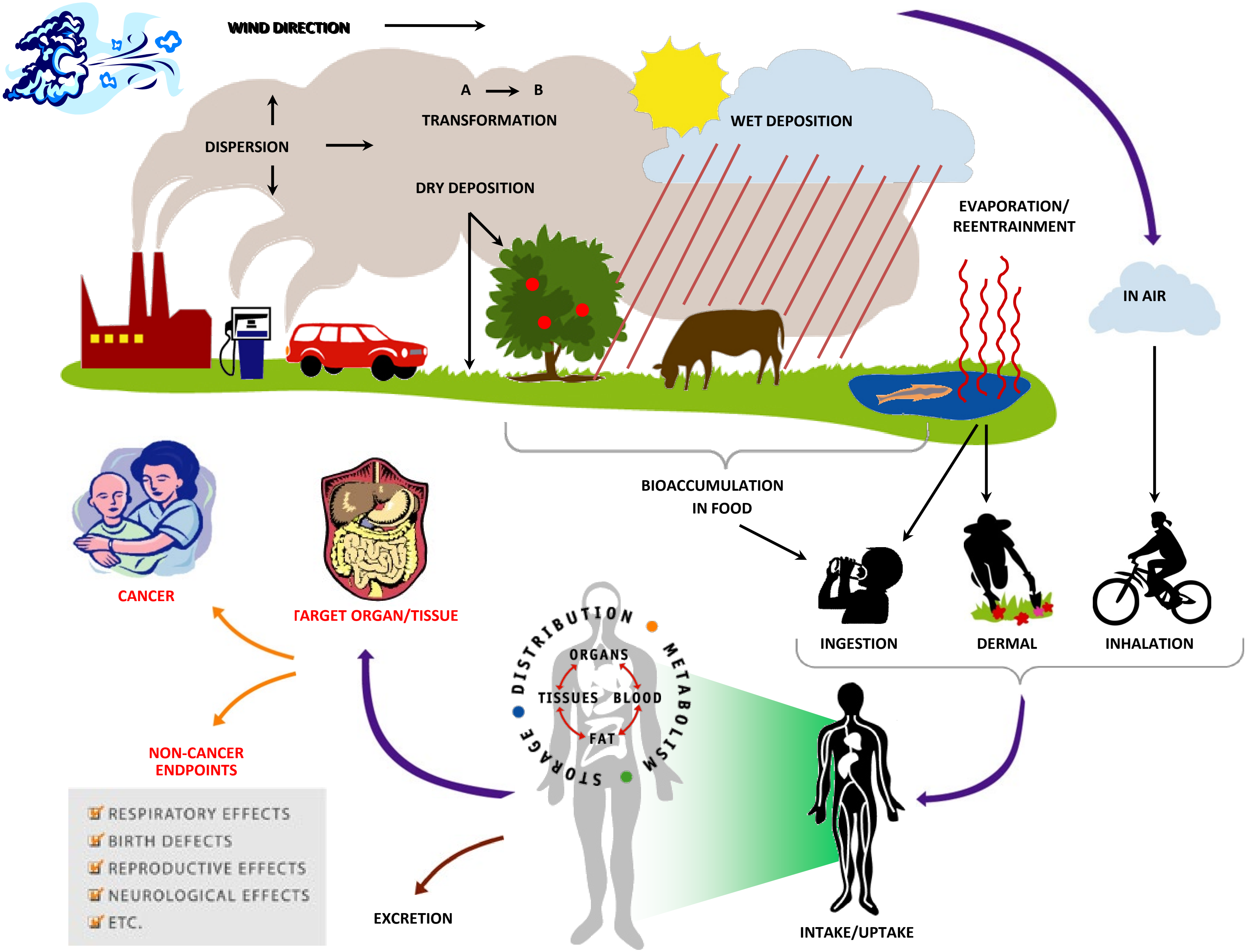
FAT

EXCRETION

INTAKE/UPTAKE

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.



WIND DIRECTION

DISPERSION

A → B

TRANSFORMATION

DRY DEPOSITION

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EVAPORATION/
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DISTRIBUTION

METABOLISM

STORAGE

ORGANS

TISSUES

BLOOD

FAT

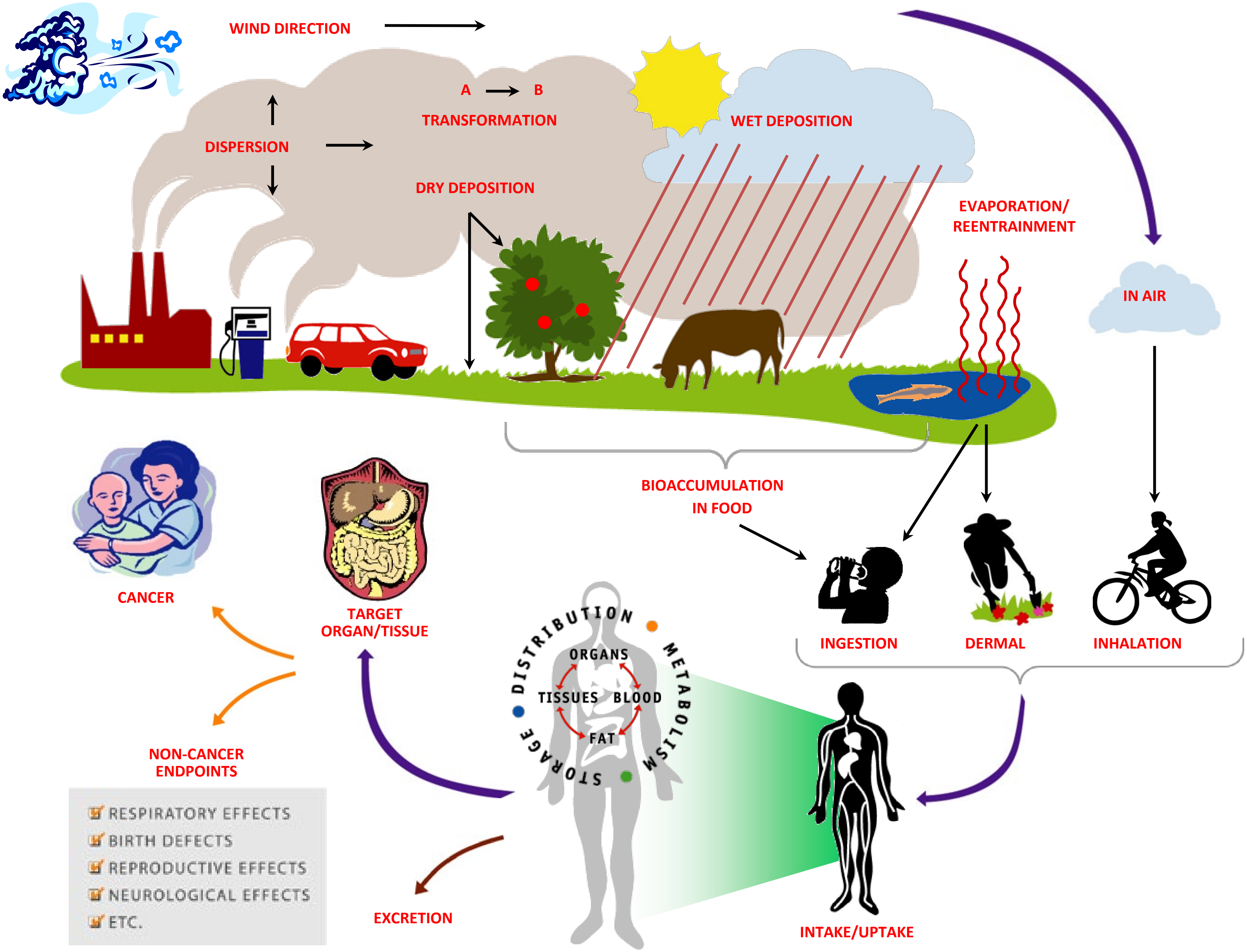
EXCRETION

TARGET ORGAN/TISSUE

CANCER

NON-CANCER
ENDPOINTS

- ☑ RESPIRATORY EFFECTS
- ☑ BIRTH DEFECTS
- ☑ REPRODUCTIVE EFFECTS
- ☑ NEUROLOGICAL EFFECTS
- ☑ ETC.



WIND DIRECTION

DISPERSION

A → B

TRANSFORMATION

DRY DEPOSITION

WET DEPOSITION

EVAPORATION/
REENTRAINMENT

IN AIR

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TARGET
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CANCER

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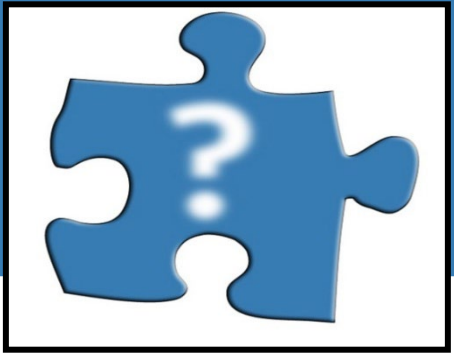
ENDPOINTS

- ☑ RESPIRATORY EFFECTS
- ☑ BIRTH DEFECTS
- ☑ REPRODUCTIVE EFFECTS
- ☑ NEUROLOGICAL EFFECTS
- ☑ ETC.

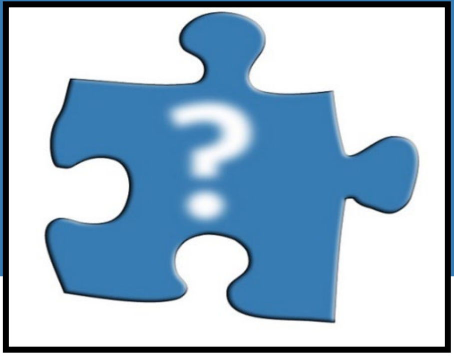
EXCRETION

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?

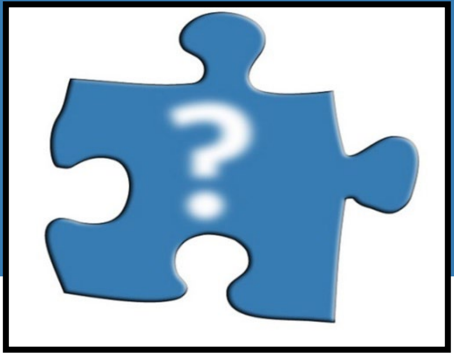


One possible definition…

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

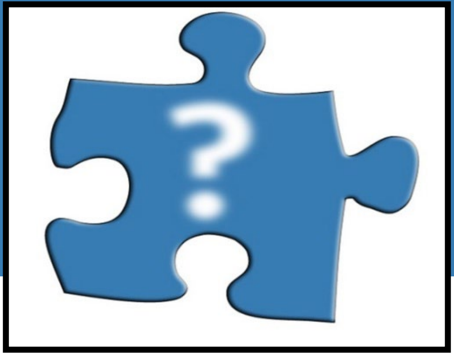
What is Risk Assessment?



Basic Questions for the Risk Assessment Process:

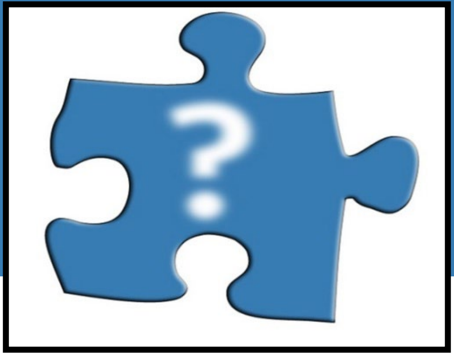
- *Who is exposed to the environmental pollutants?*
- *What pollutants are they exposed to?*
- *How are they exposed?*
- *How toxic are the agents they are exposed to?*
- *What is the likelihood that harm will occur?*

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?

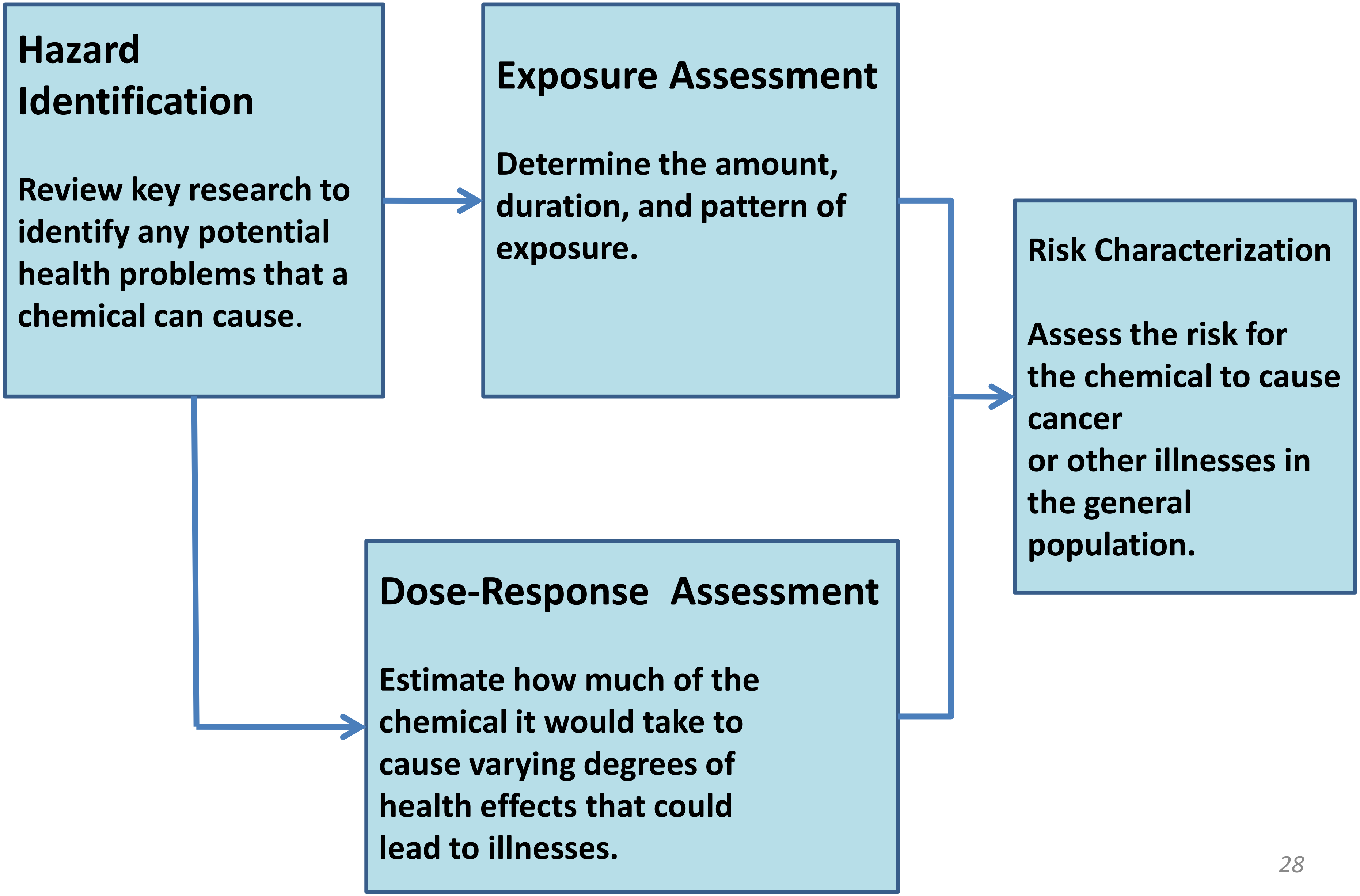


The current cancer guidelines revision effort emphasizes full characterization of all information, the expanded role of mode-of-action information (key events and processes, starting with the interaction of an agent with a cell, through functional and anatomical changes, resulting in cancer or other 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 1992, 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?

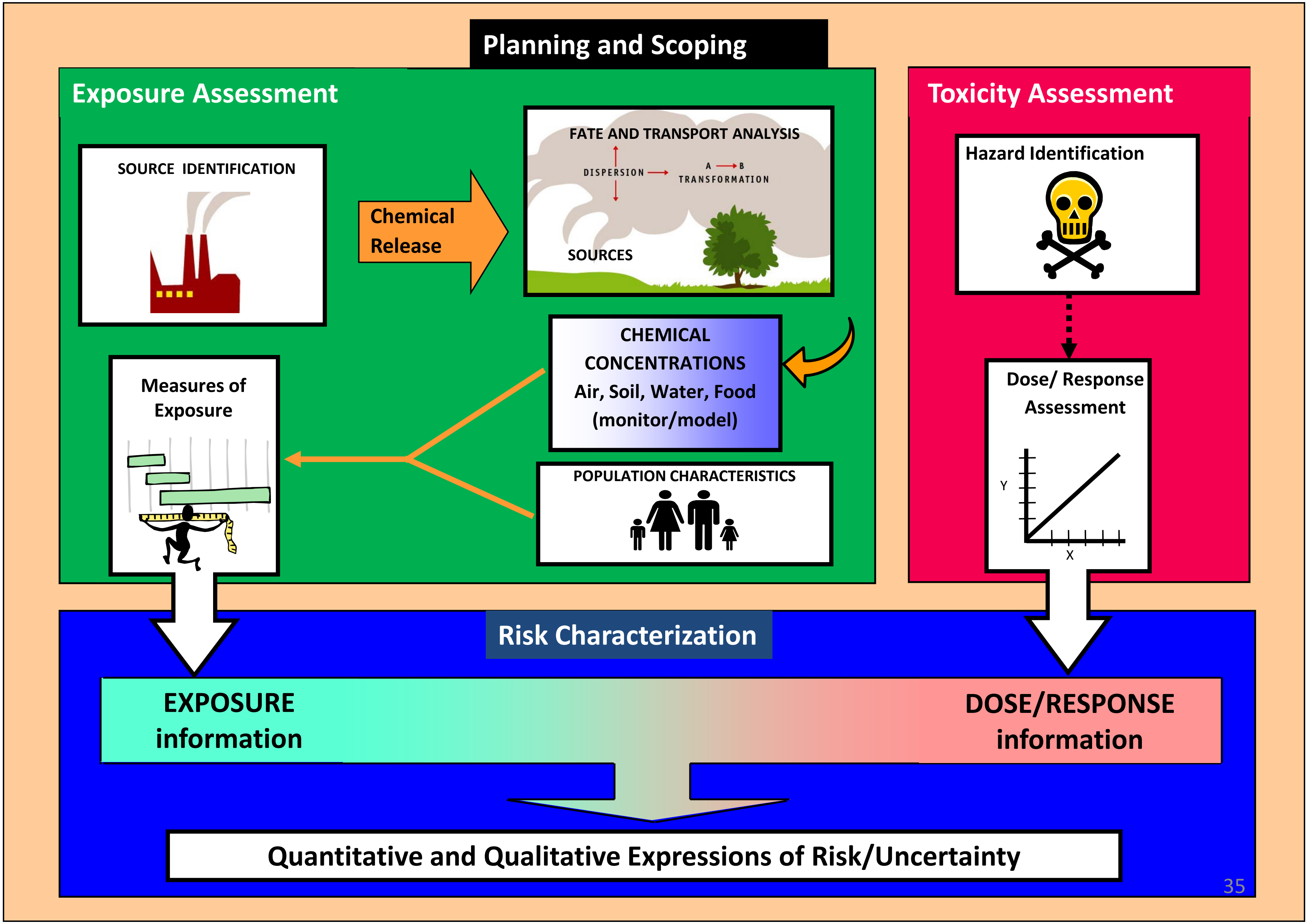
What is the relationship between the dose of a chemical and the response that results?

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

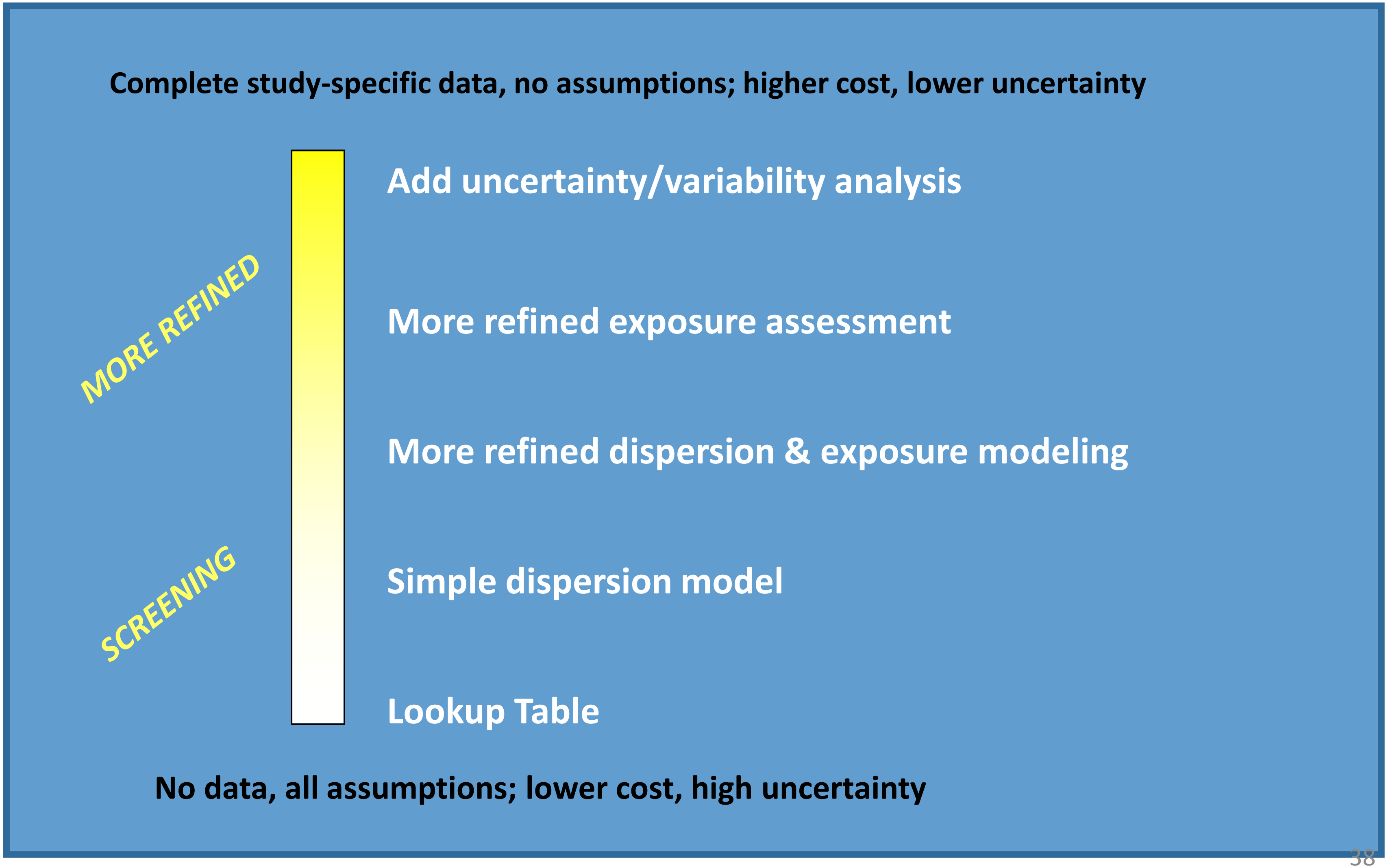
Tiered Approach for Risk Assessment

- 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

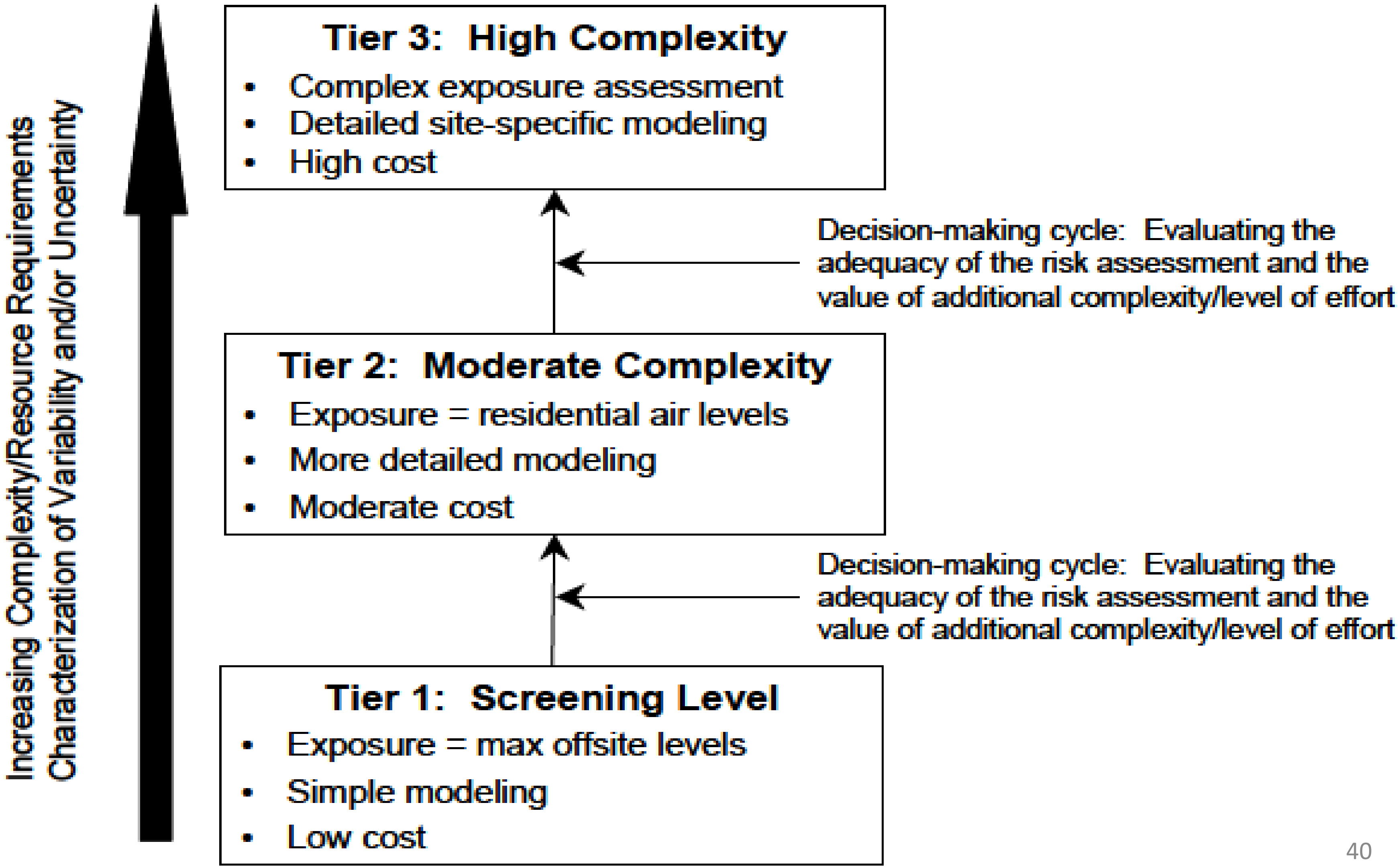
Lookup Table

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).

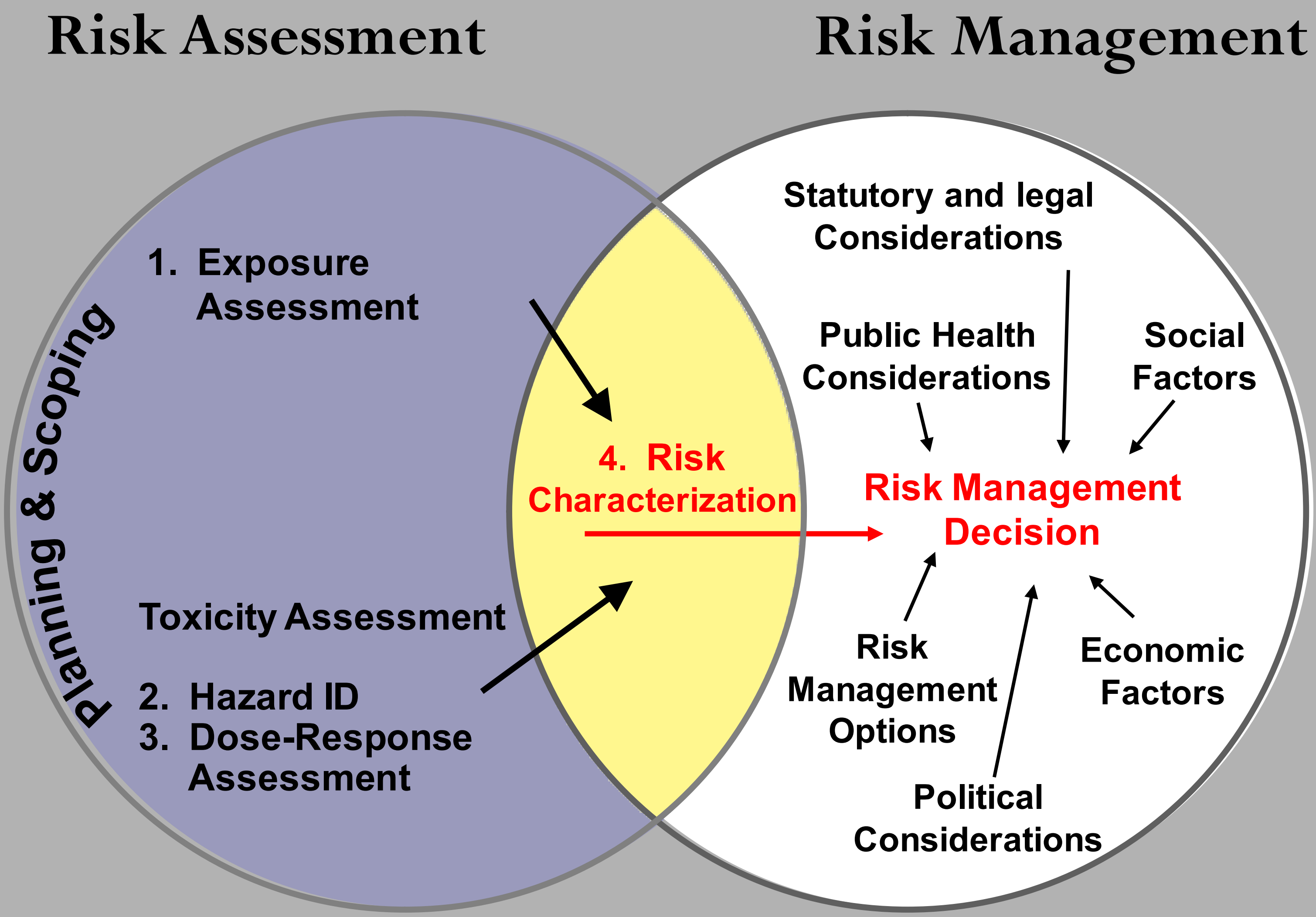
Tier 2 & Tier 3

- **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

Risk Management Decision

Statutory and legal Considerations

Public Health Considerations

Social Factors

Risk Management Options

Economic Factors

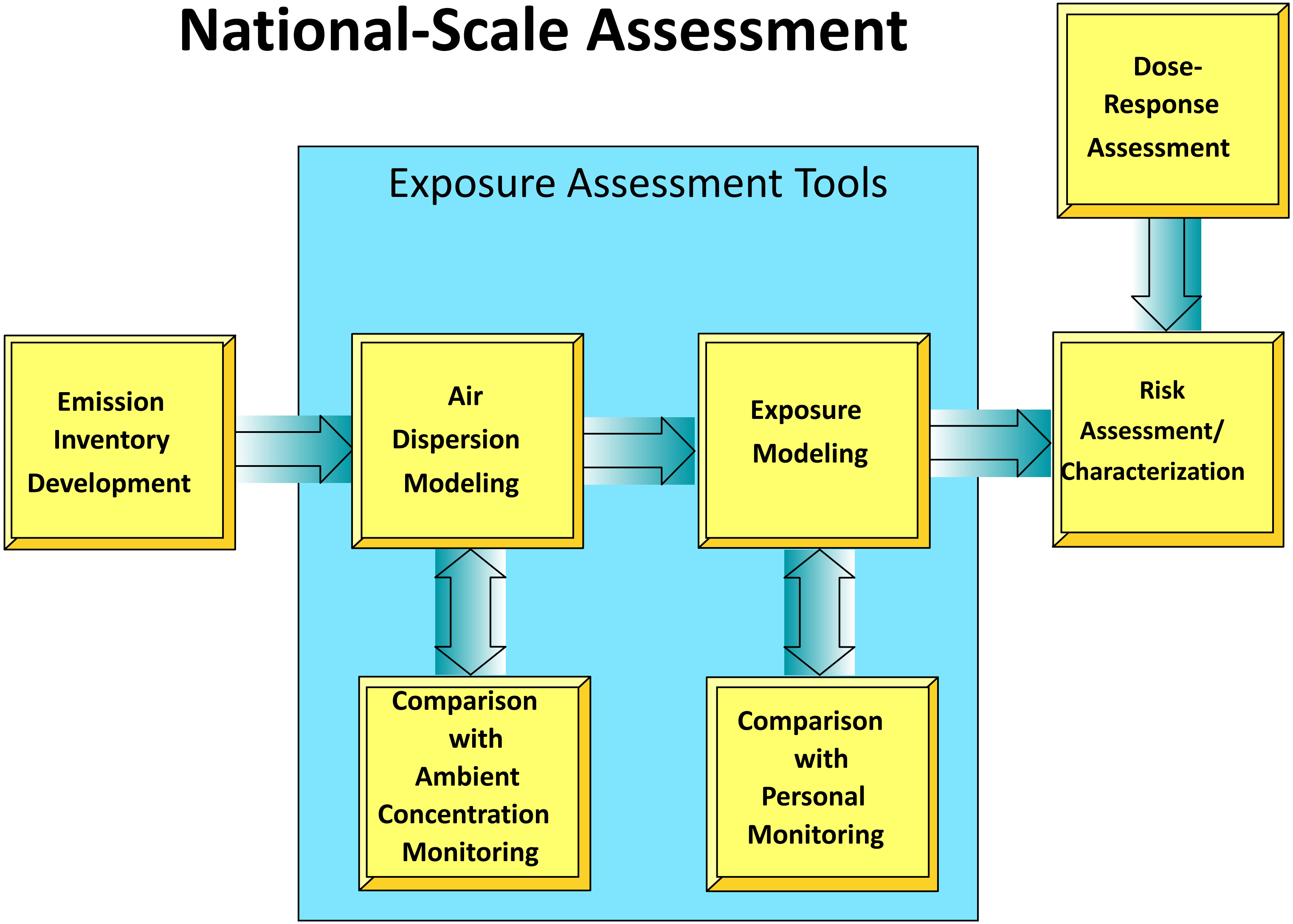
Political Considerations

Examples of Risk Assessments National and Local Community

National-Scale Air Toxics Assessment (NATA)

- Characterization of air toxics across the nation
- Nationwide assessment with *census tract resolution for 177 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*

Components of the National-Scale Assessment



Exposure Assessment Tools

Emission Inventory Development

Air Dispersion Modeling

Exposure Modeling

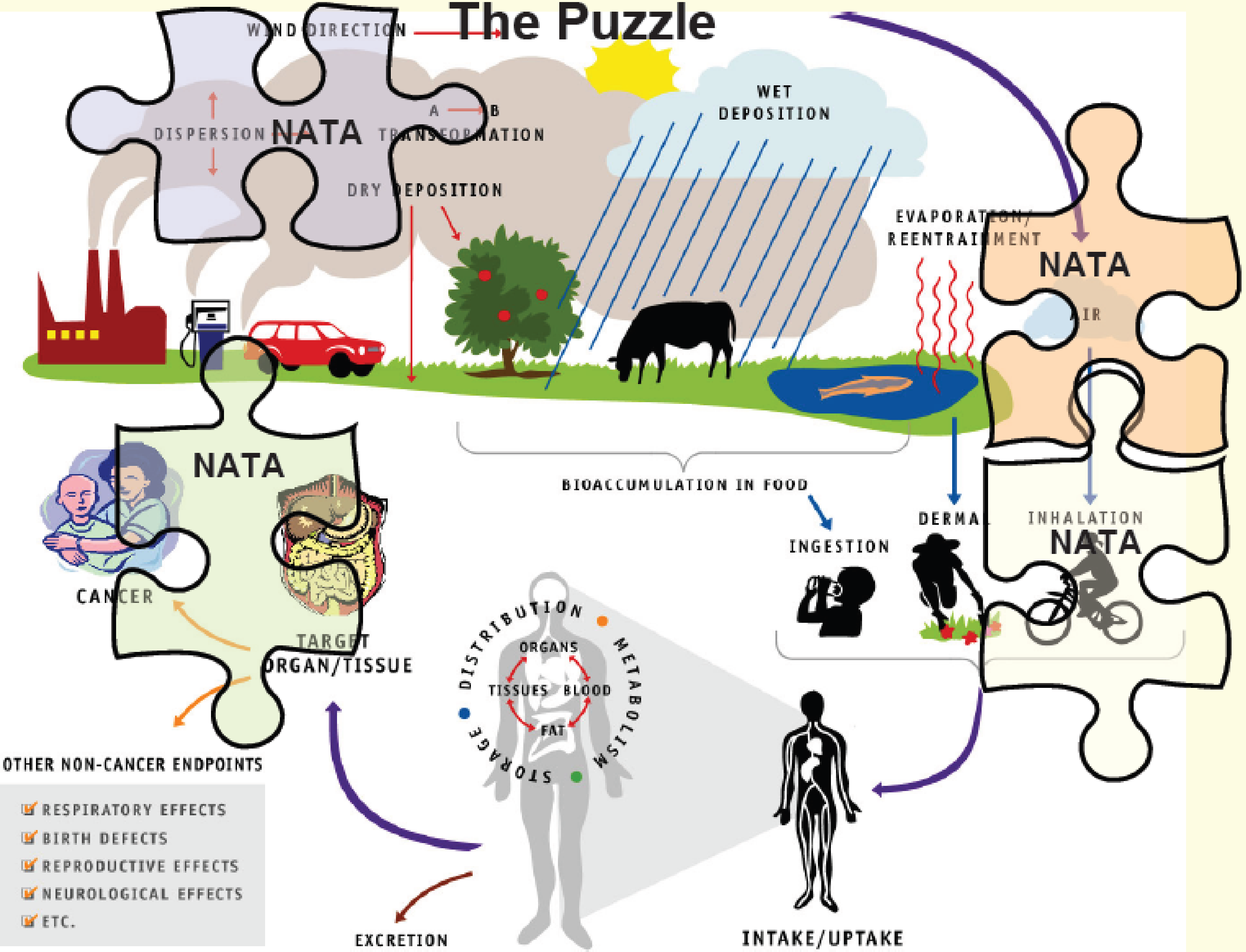
Dose-Response Assessment

Risk Assessment/ Characterization

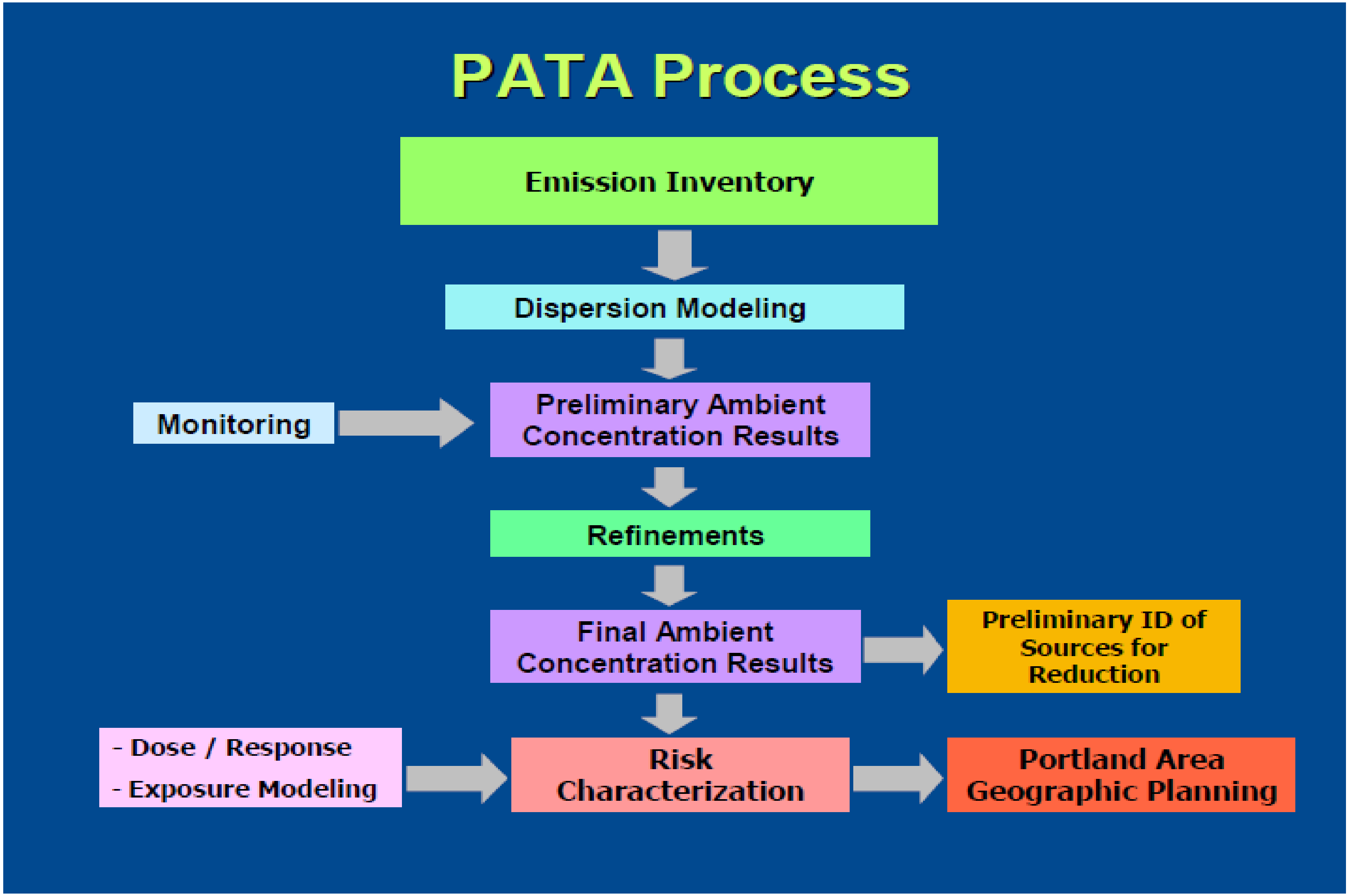
Comparison with Ambient Concentration Monitoring

Comparison with Personal Monitoring

The Puzzle


WIND DIRECTION
NATA
DISPERSION
A
B
TRANSFORMATION
DRY DEPOSITION
WET DEPOSITION
EVAPORATION/ REENTRAINMENT
NATA
AIR
NATA
BIOACCUMULATION IN FOOD
INGESTION
DERMAL
INHALATION
NATA
CANCER
TARGET ORGAN/TISSUE
DISTRIBUTION
METABOLISM
STORAGE
ORGANS
TISSUES
BLOOD
FAT
OTHER NON-CANCER ENDPOINTS
☑ RESPIRATORY EFFECTS
☑ BIRTH DEFECTS
☑ REPRODUCTIVE EFFECTS
☑ NEUROLOGICAL EFFECTS
☑ ETC.
EXCRETION
INTAKE/UPTAKE

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

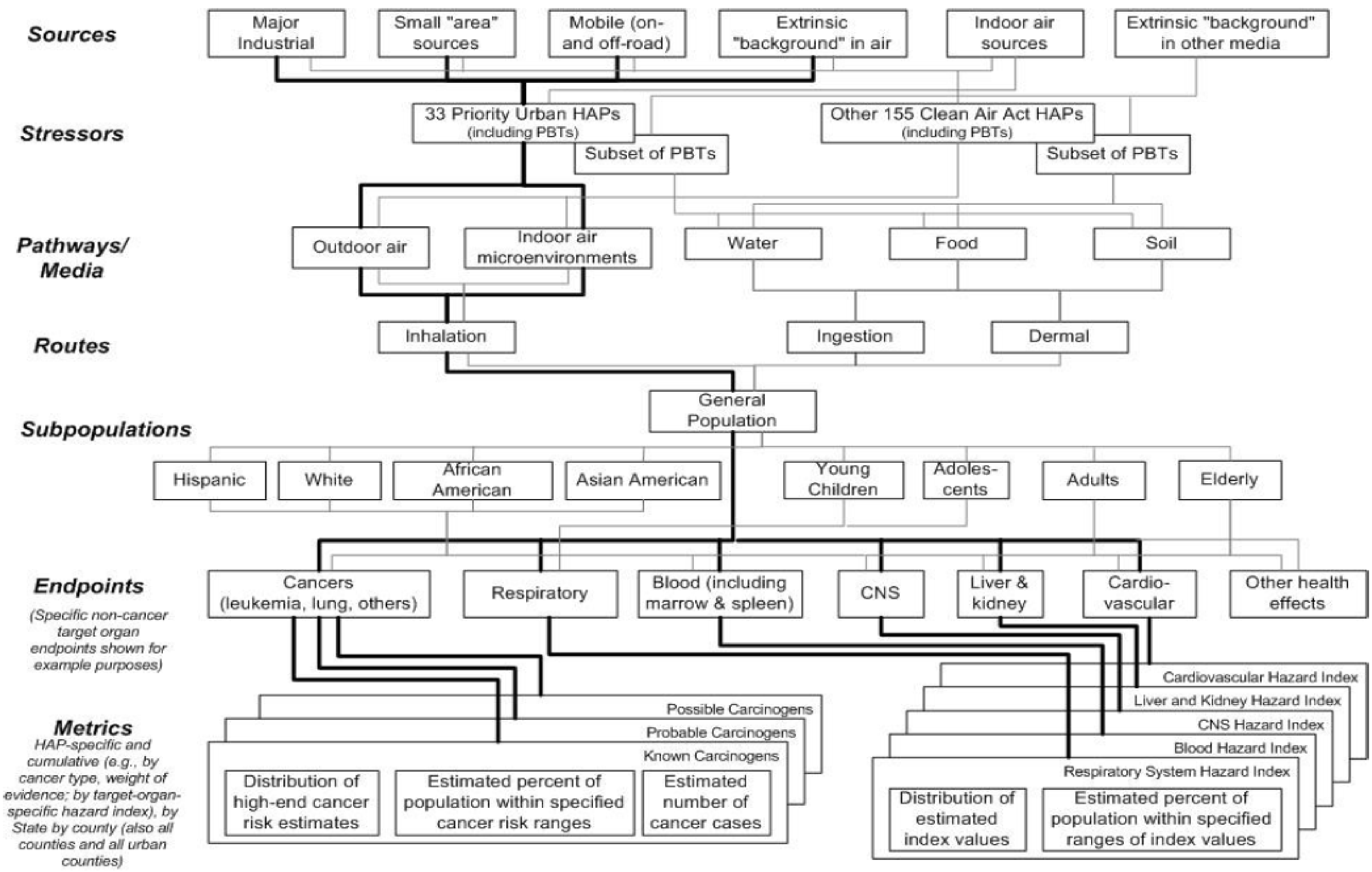
Risk Characterization

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



Sources

Major Industrial

Small "area" sources

Mobile (on- and off-road)

Extrinsic "background" in air

Indoor air sources

Extrinsic "background" in other media

Stressors

33 Priority Urban HAPs (including PBTs)

Subset of PBTs

Other 155 Clean Air Act HAPs (including PBTs)

Subset of PBTs

Pathways/ Media

Outdoor air

Indoor air microenvironments

Water

Food

Soil

Routes

Inhalation

Ingestion

Dermal

Subpopulations

General Population

Hispanic

White

African American

Asian American

Young Children

Adolescents

Adults

Elderly

Endpoints

(Specific non-cancer target organ endpoints shown for example purposes)

Cancers (leukemia, lung, others)

Respiratory

Blood (including marrow & spleen)

CNS

Liver & kidney

Cardiovascular

Other health effects

Metrics

HAP-specific and cumulative (e.g., by cancer type, weight of evidence; by target-organ-specific hazard index), by State by county (also all counties and all urban counties)

Possible Carcinogens

Probable Carcinogens

Known Carcinogens

Distribution of high-end cancer risk estimates

Estimated percent of population within specified cancer risk ranges

Estimated number of cancer cases

Cardiovascular Hazard Index

Liver and Kidney Hazard Index

CNS Hazard Index

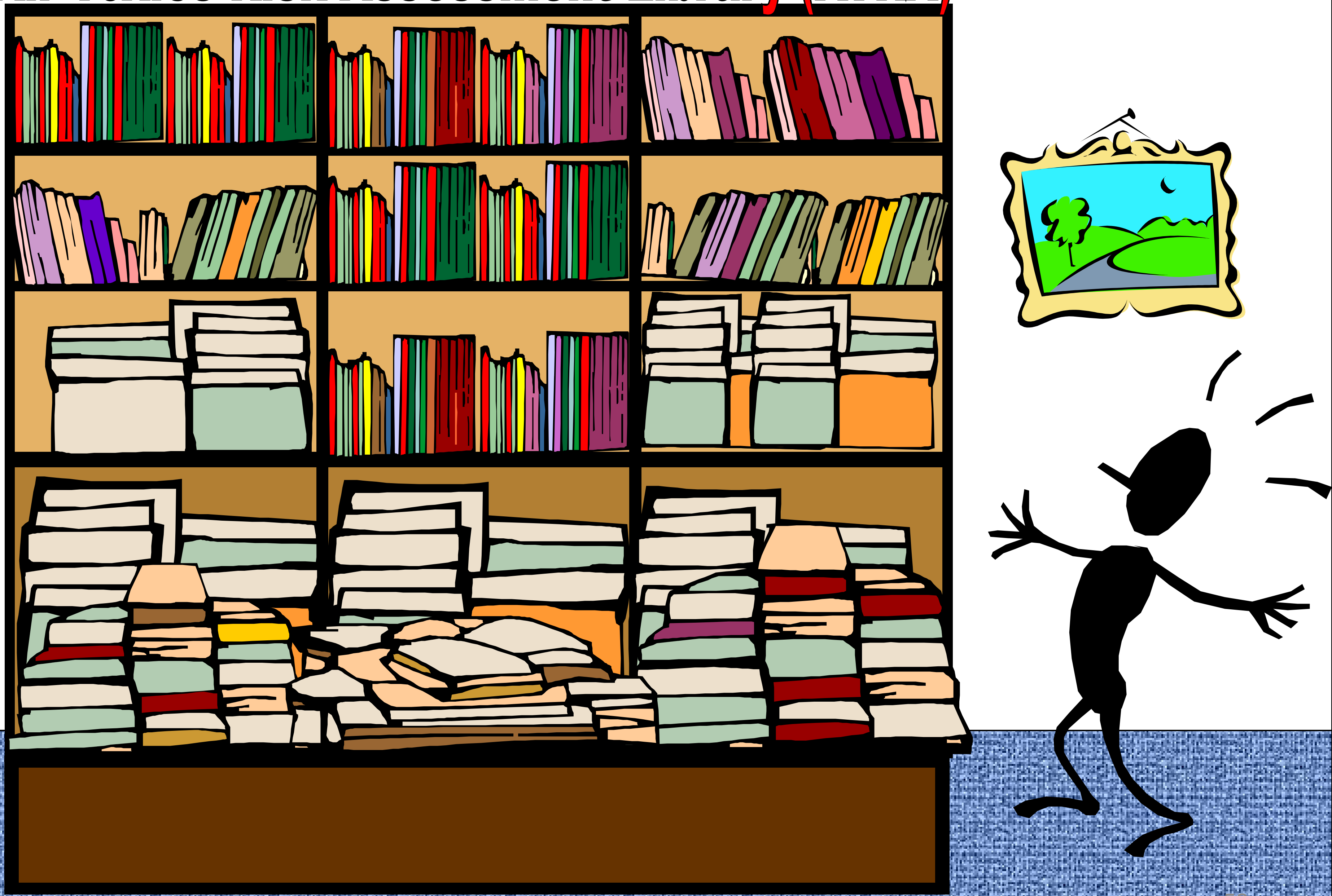
Blood Hazard Index

Respiratory System Hazard Index

Distribution of estimated index values

Estimated percent of population within specified ranges of index values

Air Toxics Risk Assessment Library (ATRA)

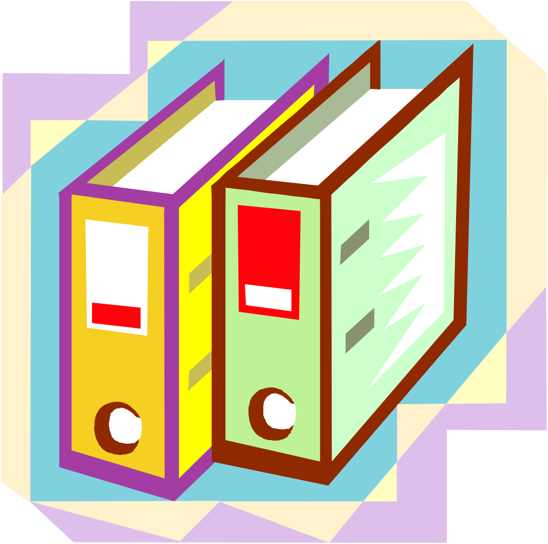


Air Toxics Risk Assessment Library (ATRA)

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

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

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

United States Environmental Protection Agency

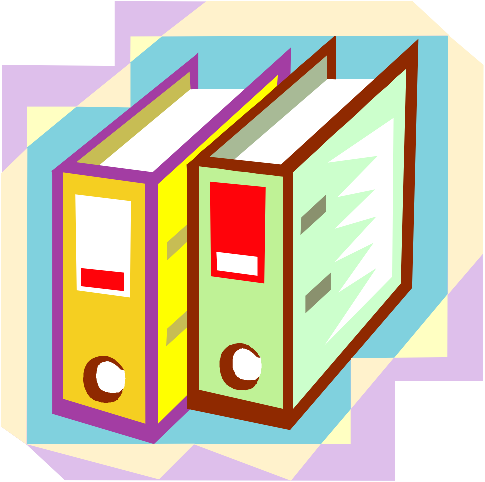
Volume 1

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

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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

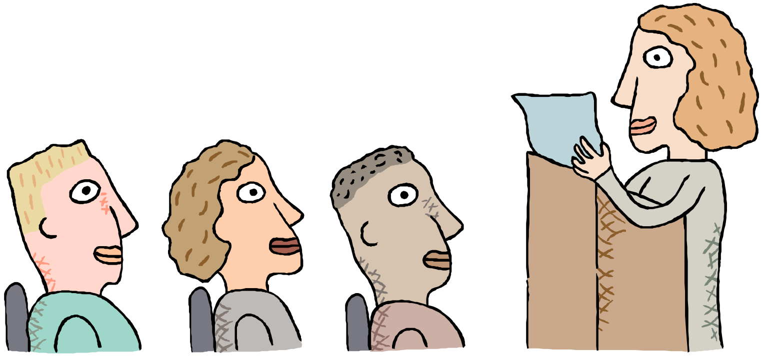
Volume 3
Community-Scale Assessment

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

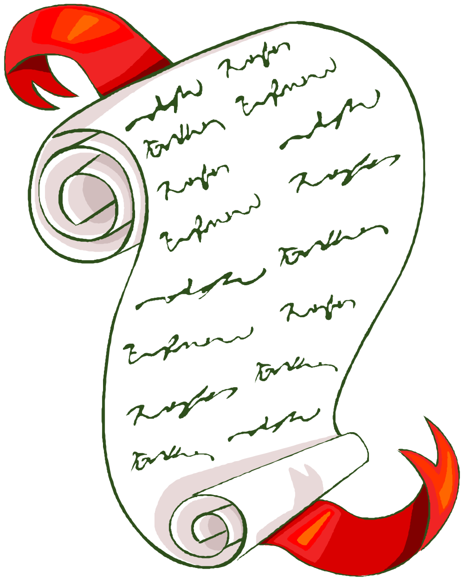
Volume 3 - Intended Audiences

- 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.



Environmental Fate & Transport

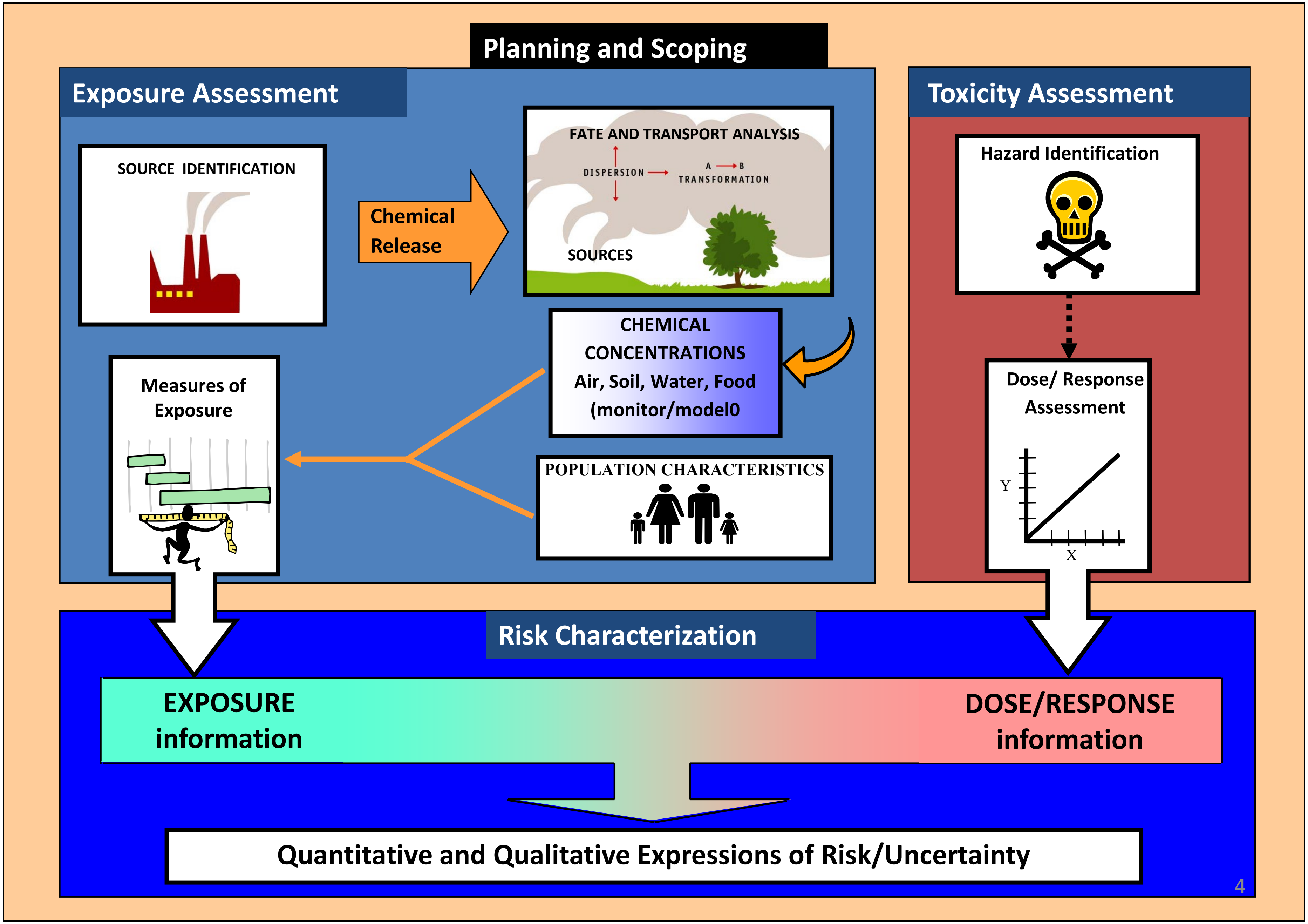
Dispersion, Transport, and Fate: What's the Difference?

- 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/model0

POPULATION CHARACTERISTICS

Measures of Exposure

Toxicity Assessment

Hazard Identification

Dose/ Response Assessment

Risk Characterization

EXPOSURE information

DOSE/RESPONSE information

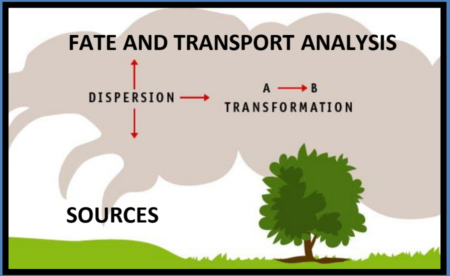
Quantitative and Qualitative Expressions of Risk/Uncertainty

The Detailed Air Toxics Risk Assessment Process

Planning and Scoping

Exposure Assessment

Chemical Release



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

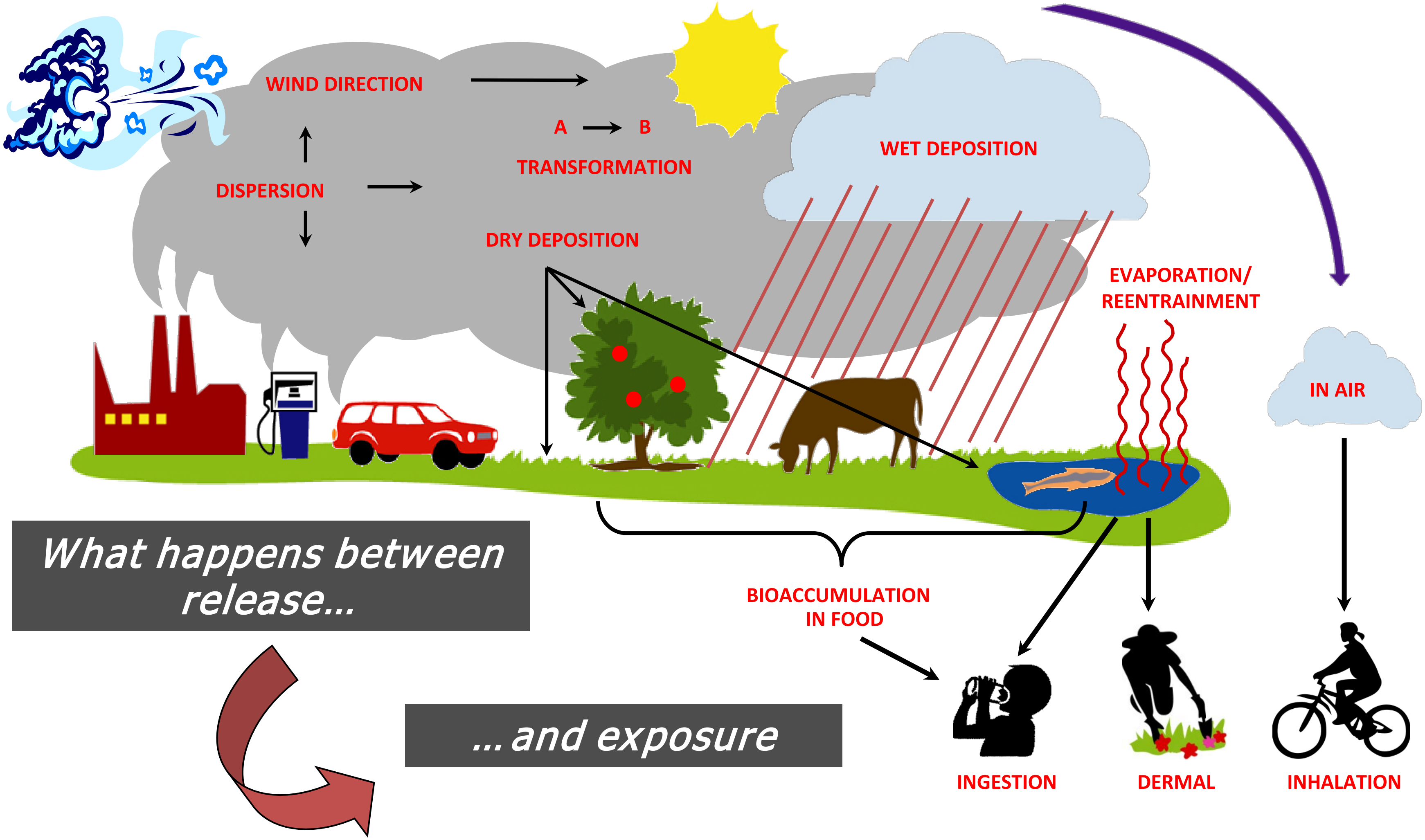
Toxicity Assessment

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

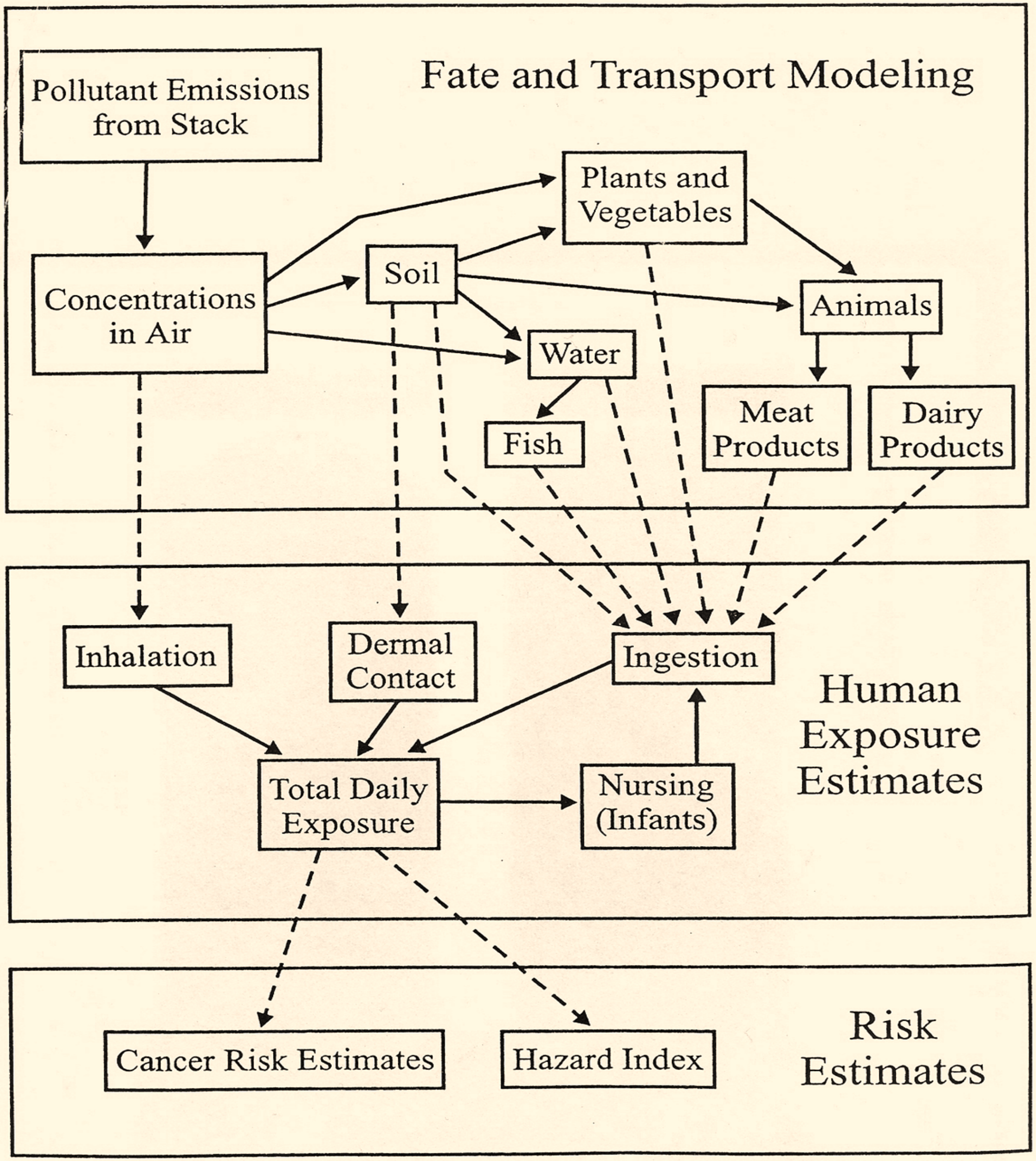


What happens between release…

… 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).

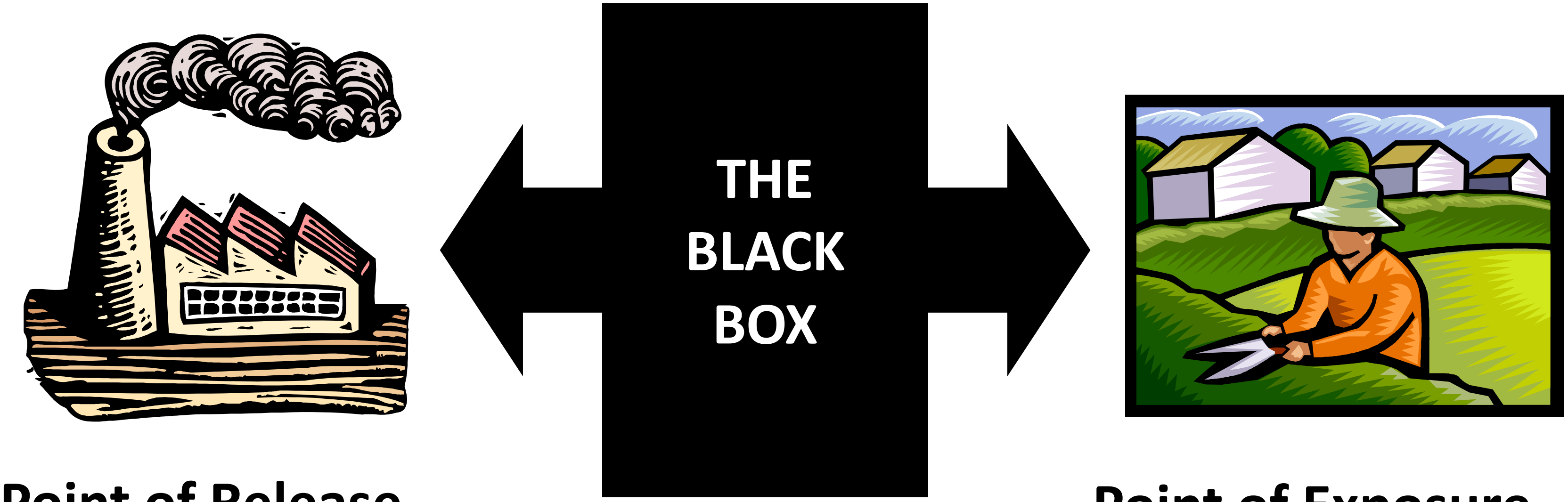
Once air toxics are transported beyond the immediate vicinity of the source, atmospheric and meteorological factors (particularly wind speed and direction) will govern the dispersion and transport of air toxics .

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



THE BLACK BOX

Point of Release

Point of Exposure

Mechanisms that affect where pollutant will end up.

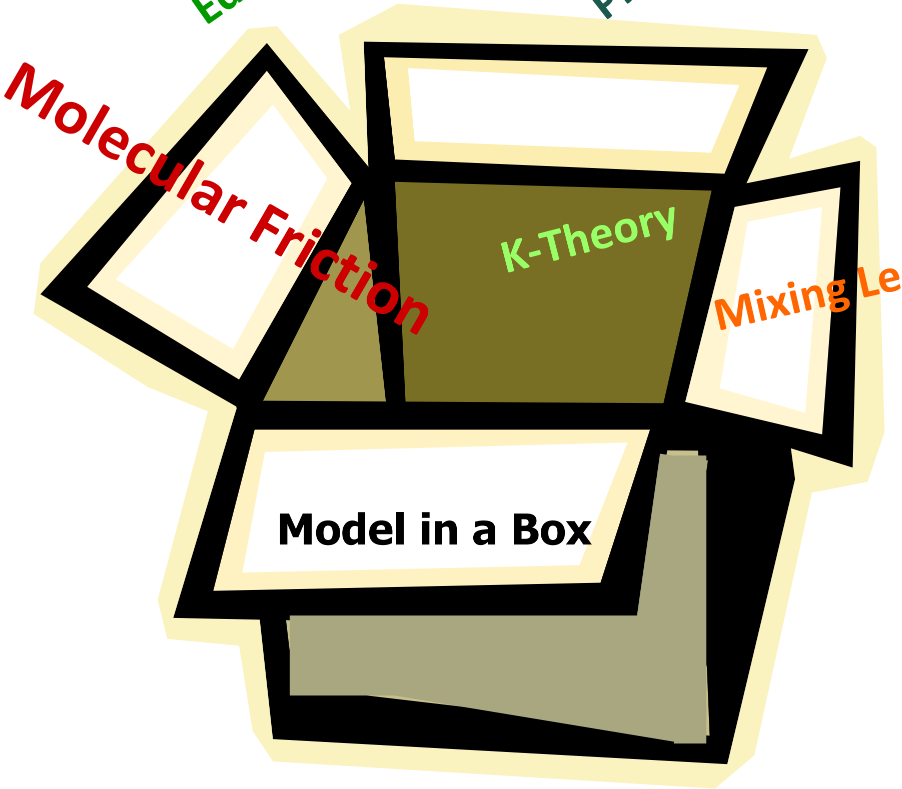
Richardson Number

Eddy Energy Equations

Planetary Boundary Layer

Gaussian Plume Equation

Turbulence/Dispersion



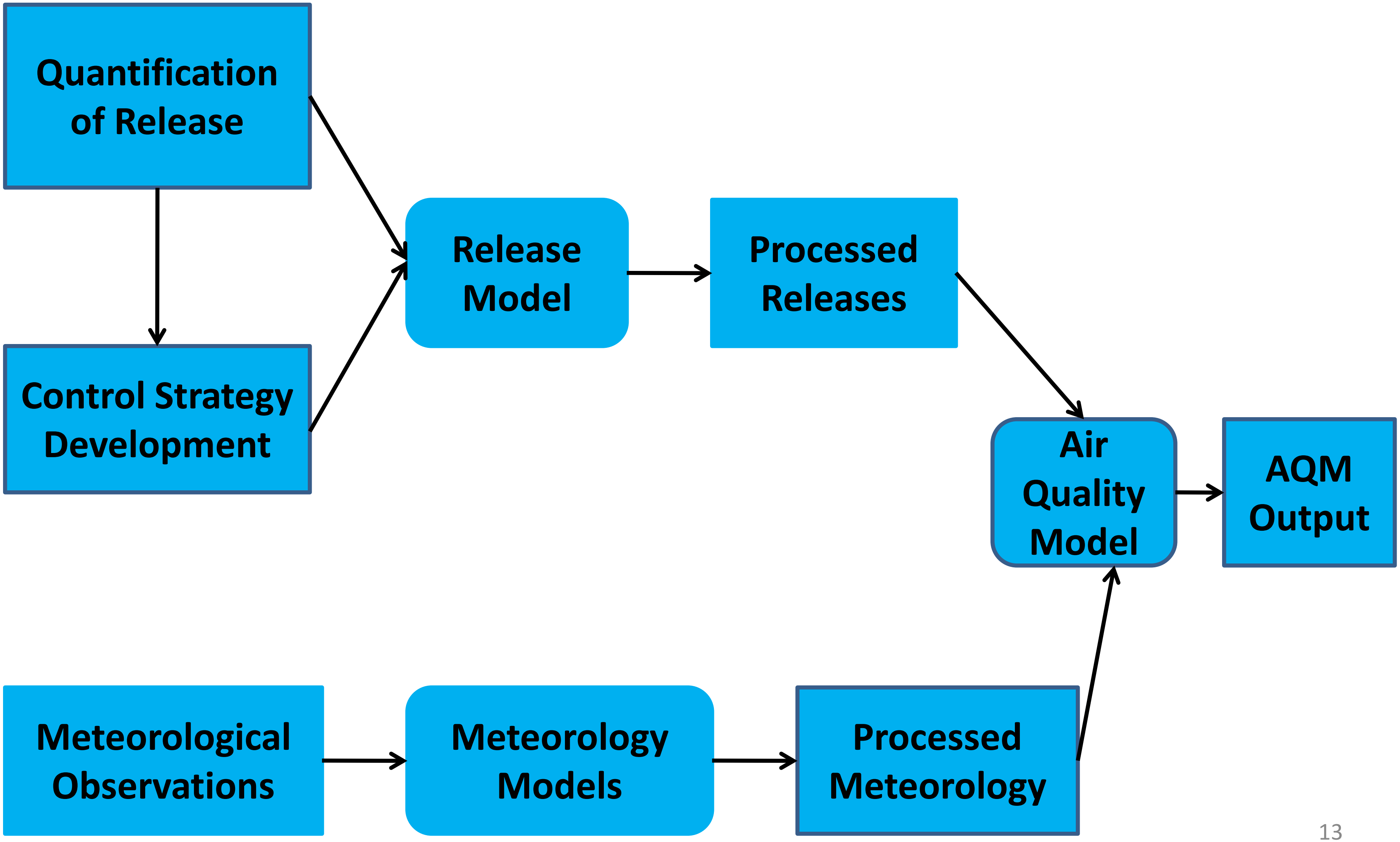
Molecular Friction

K-Theory

Mixing Length Theory

Model in a Box

Basic Components of an Air Quality Modeling System



Quantification of Release

Control Strategy Development

Release Model

Processed Releases

Air Quality Model

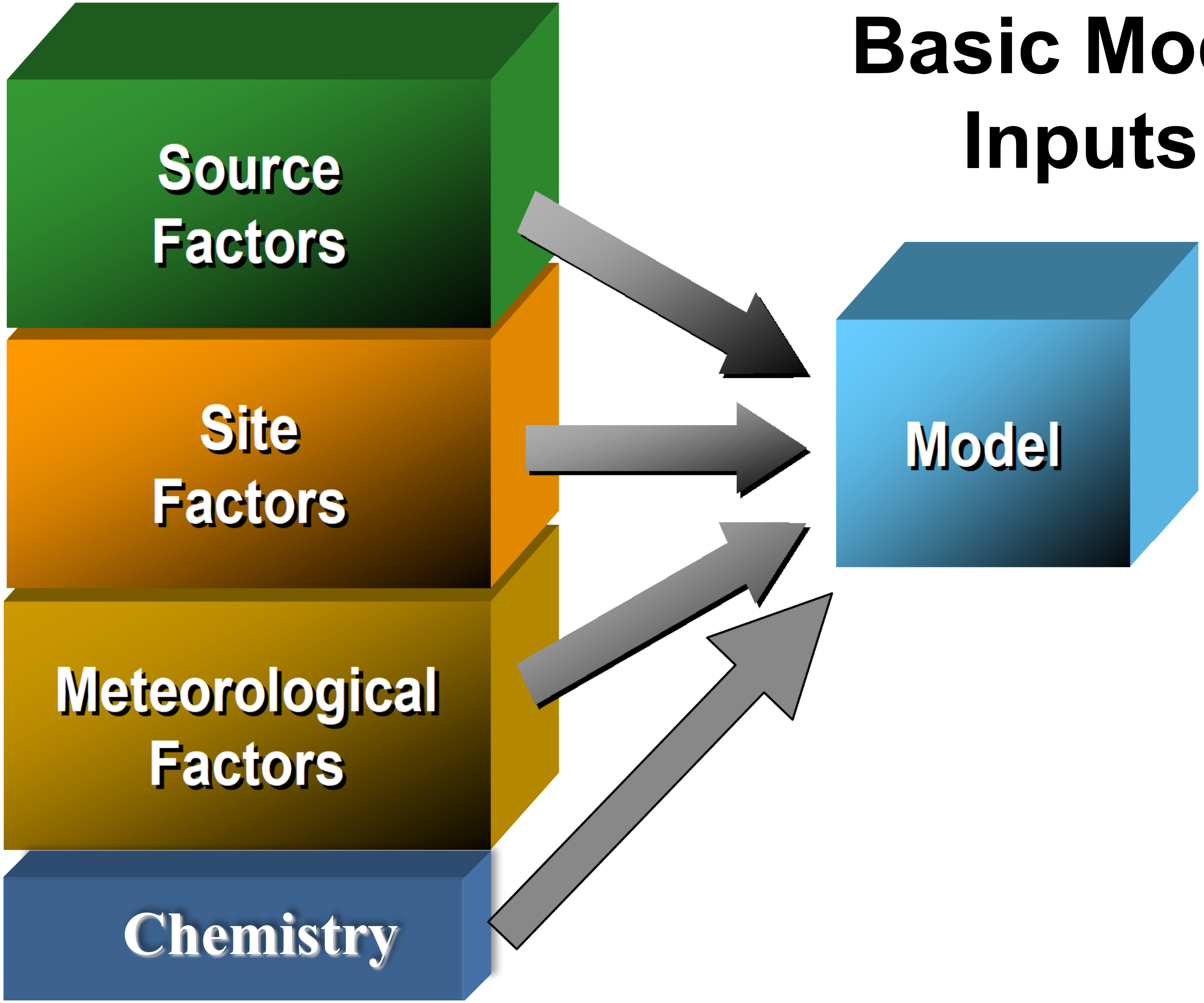
AQM Output

Meteorological Observations

Meteorology Models

Processed Meteorology

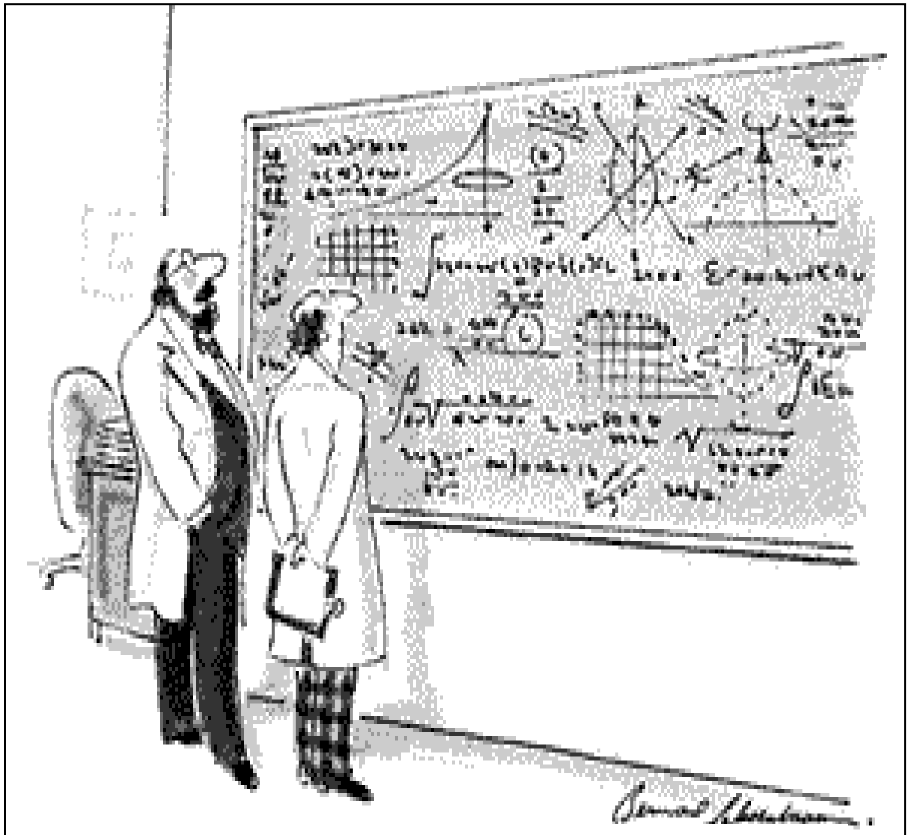
Basic Model Inputs



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

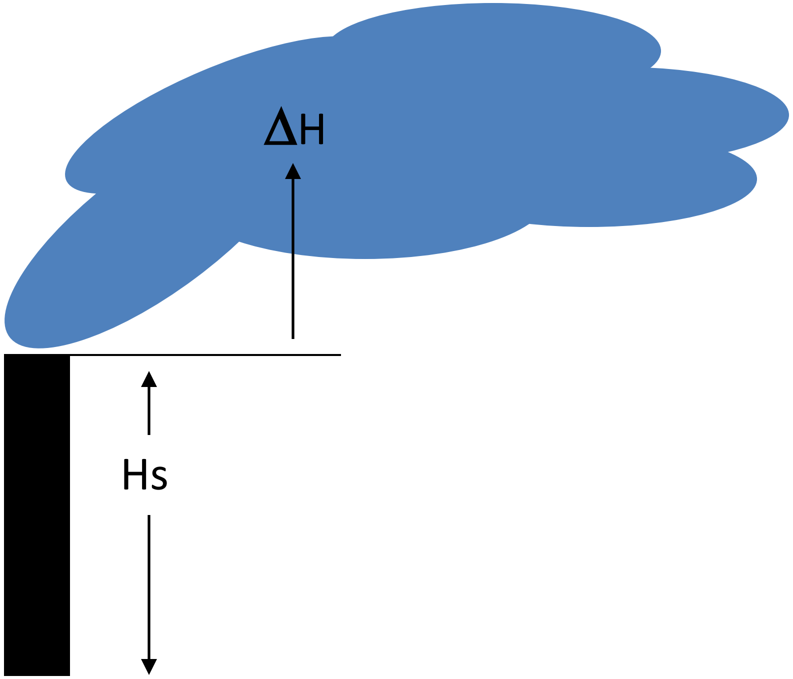
- Plume height = Hs + ΔH

  *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



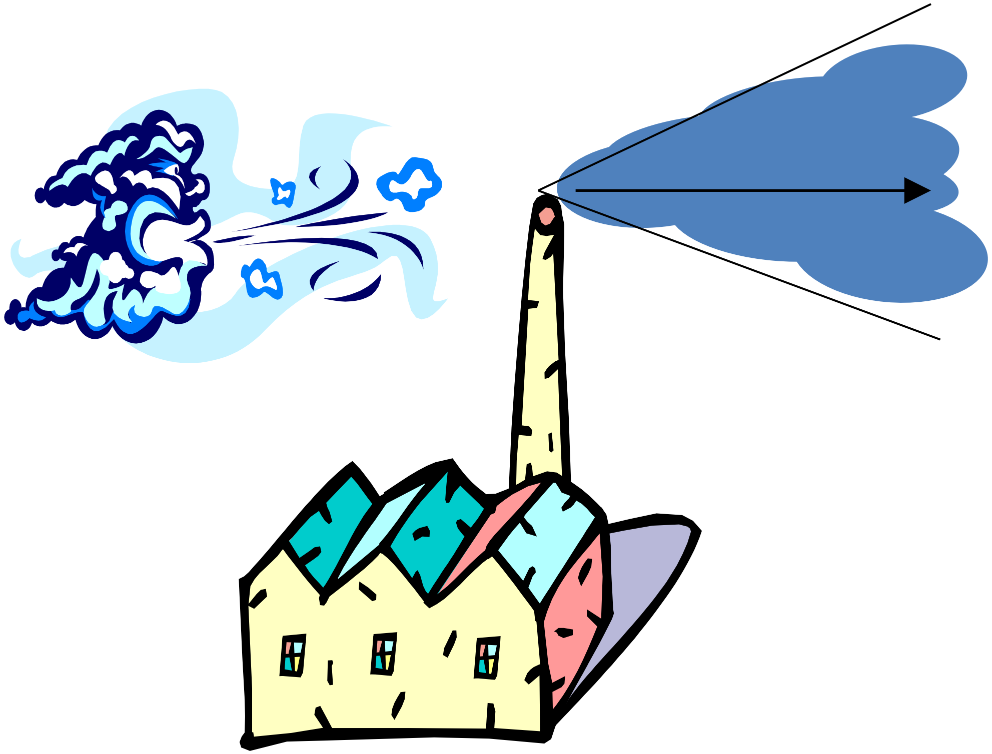
Meteorology

An number of important meteorological factors influence Fate & Transport:

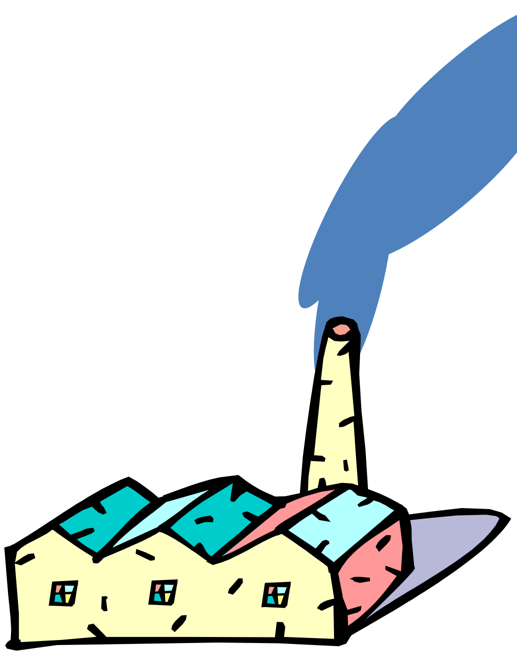
- Wind
- Atmospheric Stability
- Precipitation

Meteorology - Winds

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

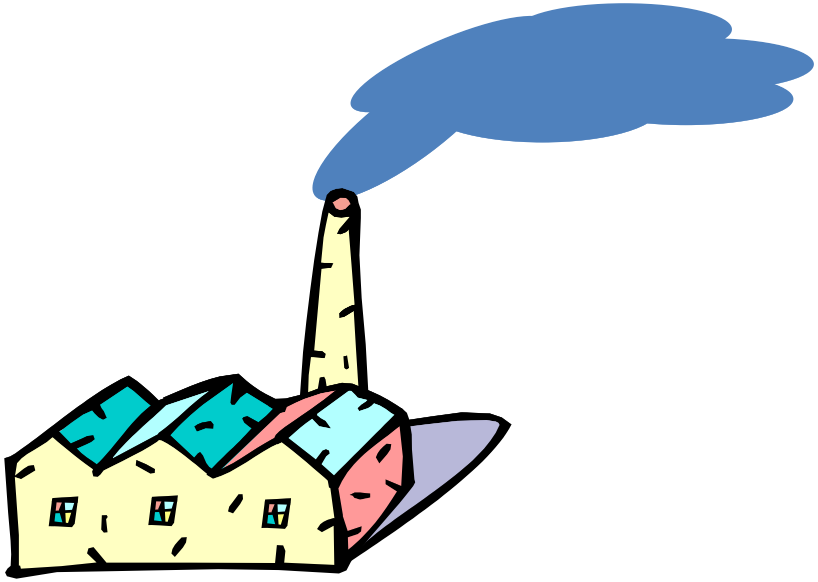


Meteorology - Winds



When the winds are light, the plume rise is high

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



Meteorology - Winds

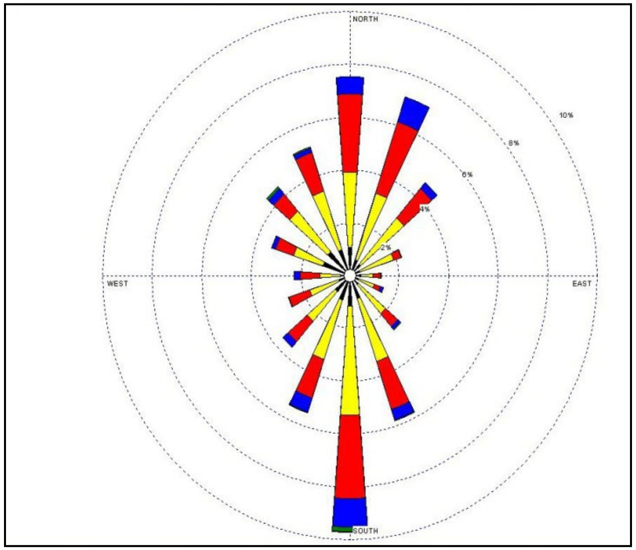
A windrose groups wind direction and speed over a period of time and presents it visually.

The bars represent the direction the wind is blowing from.

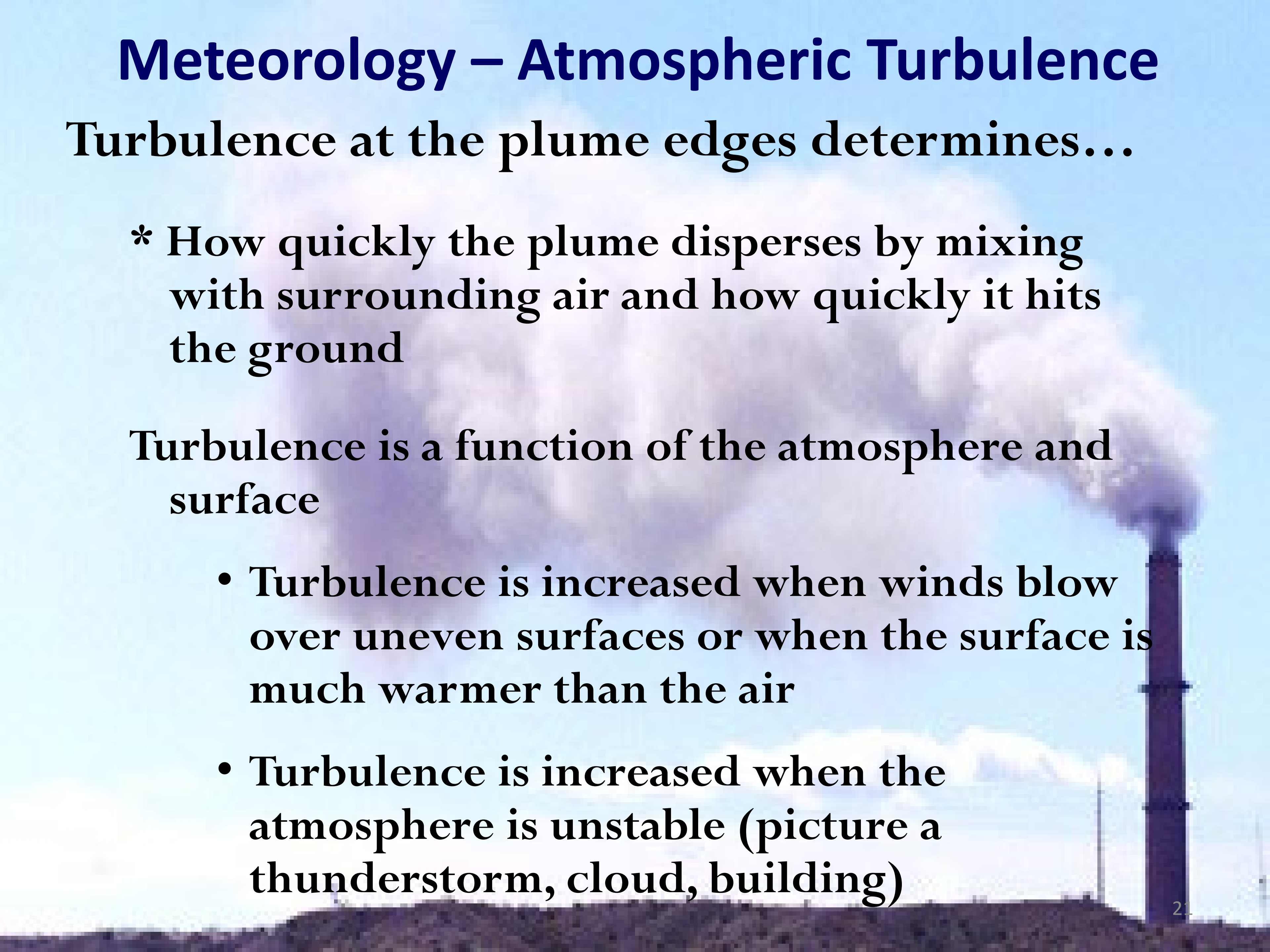
They are broken into segments, representing increasing speed groupings as you move out from the center.

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

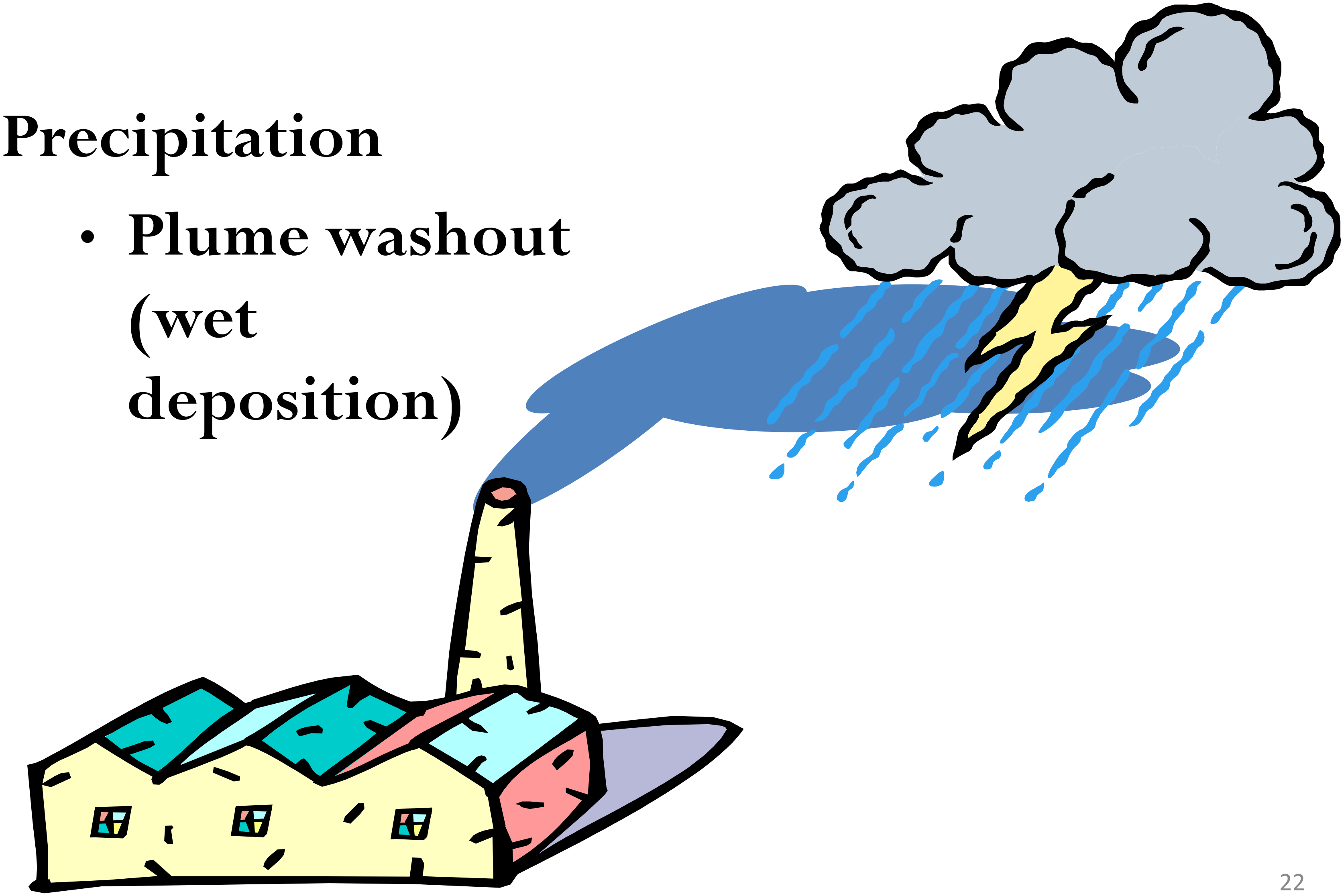
Turbulence is a function of the atmosphere and surface

- 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

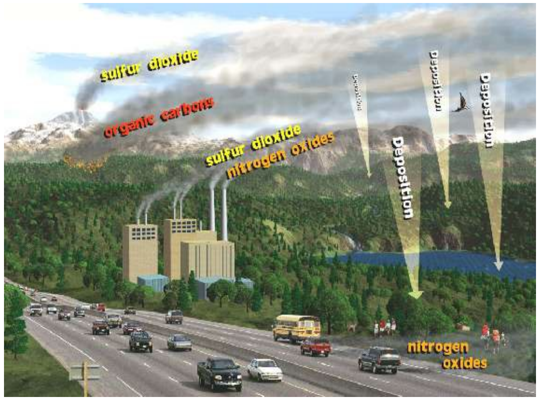
Precipitation

- Plume washout (wet deposition)



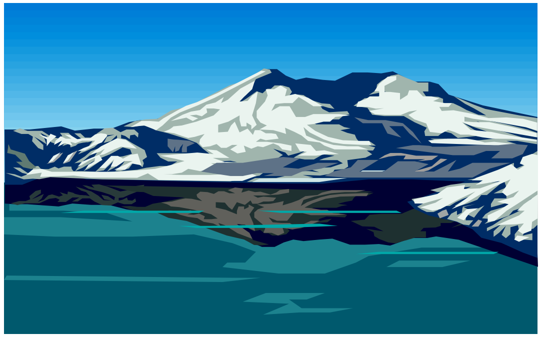
Physical Factors

- Pollutant properties (e.g., settling velocity - dry deposition)

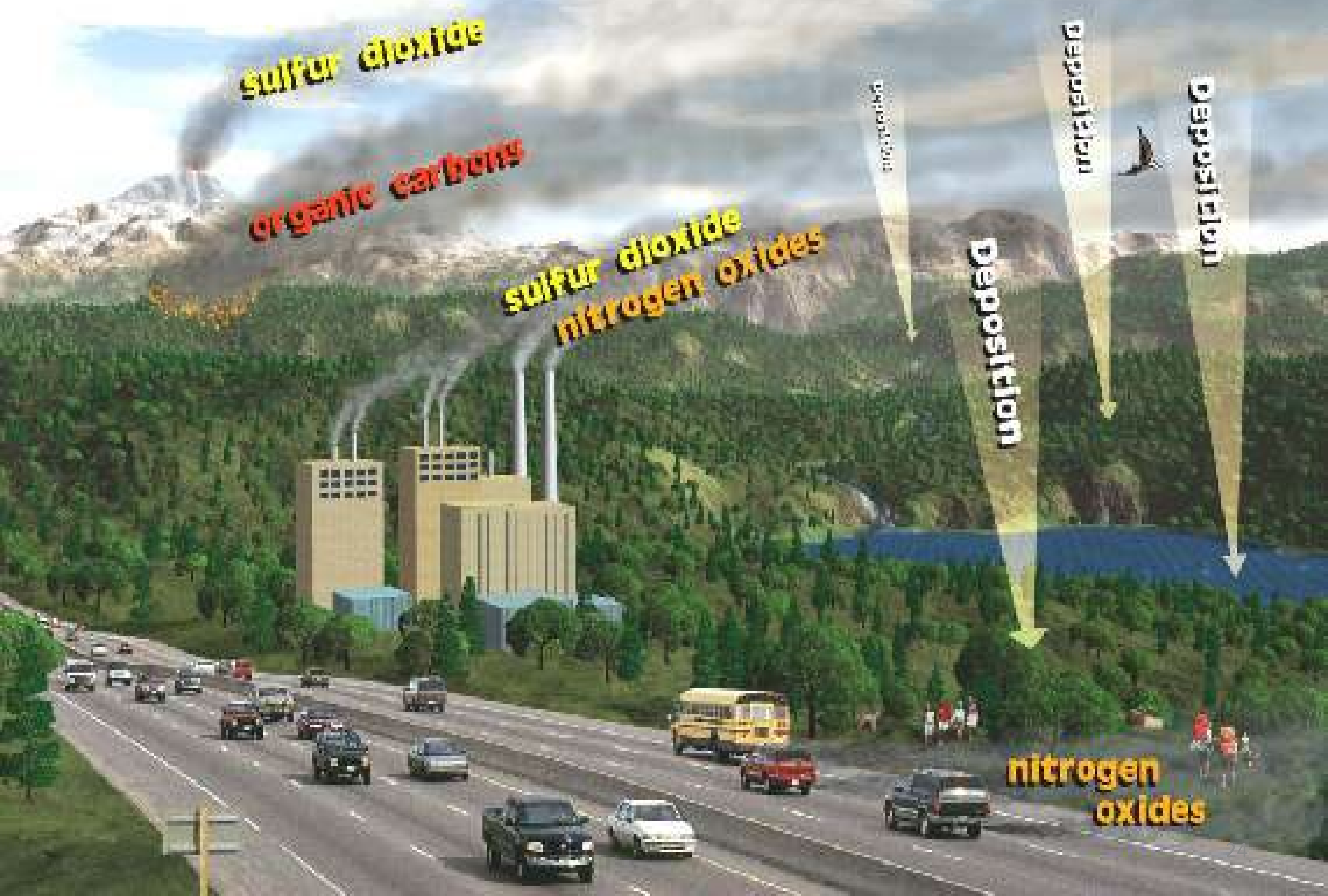


- Building downwash

- 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).

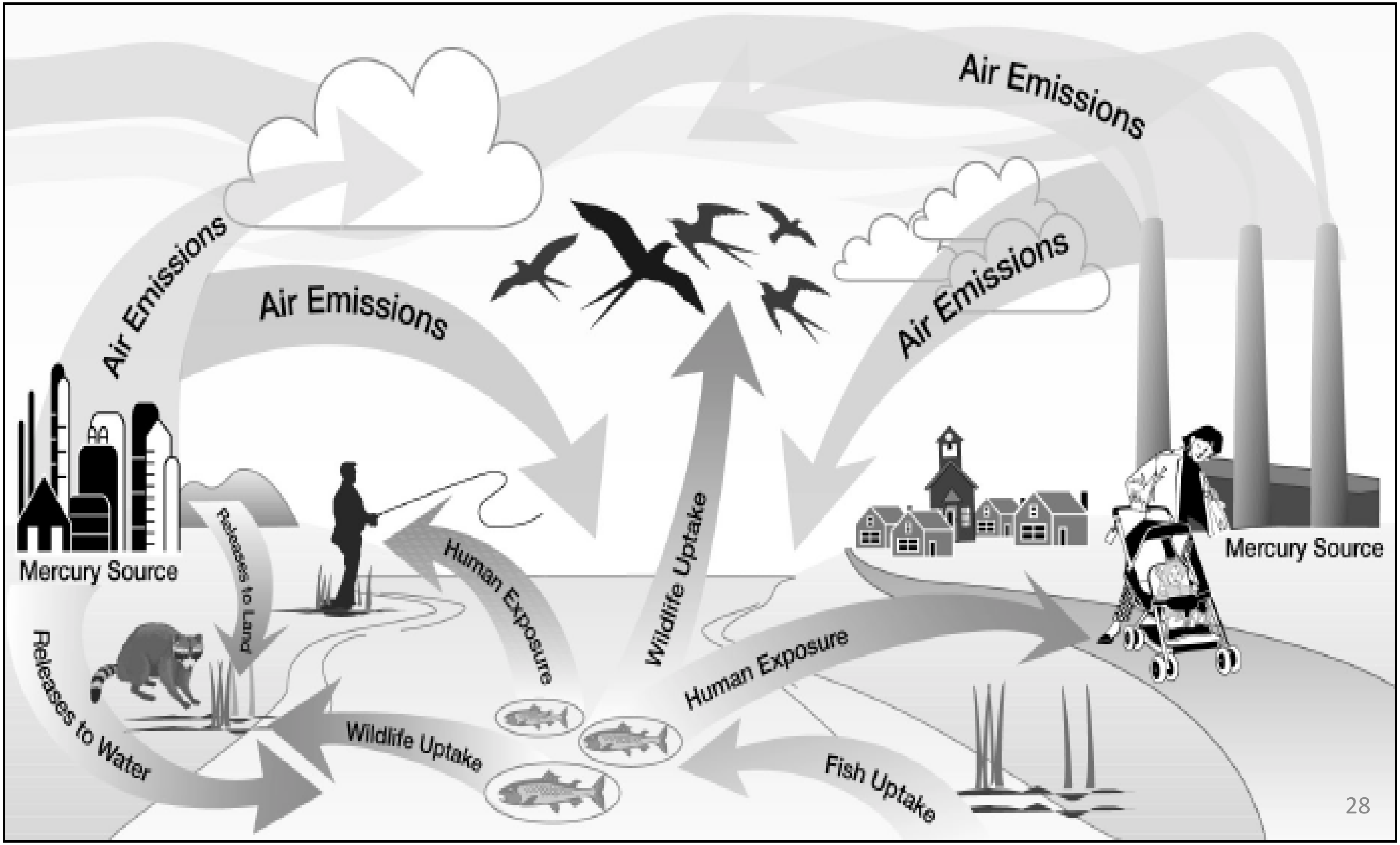
Pollutant Properties – Particle Size

- 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.

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

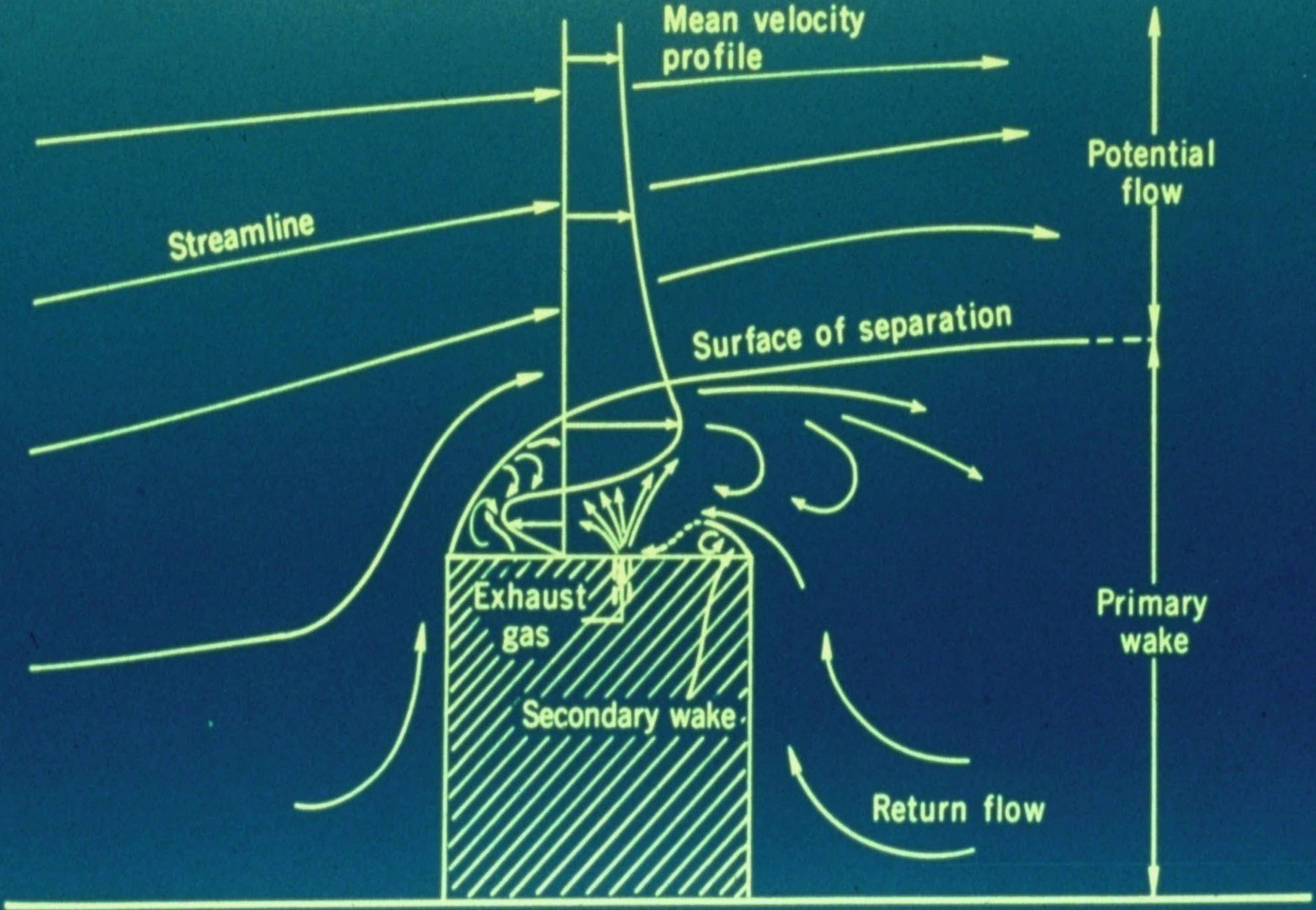
- Wet Hg Deposition Sites:
  - Steubenville, Ohio
  - Underhill, Vermont
- Dry Hg Deposition Sites:
  - “Plant A,” North Dakota
  - Springfield, Illinois
  - Mount Pleasant, Texas
- Total Hg Deposition:
  - Bow, New Hampshire

USEPA Mercury Home Page

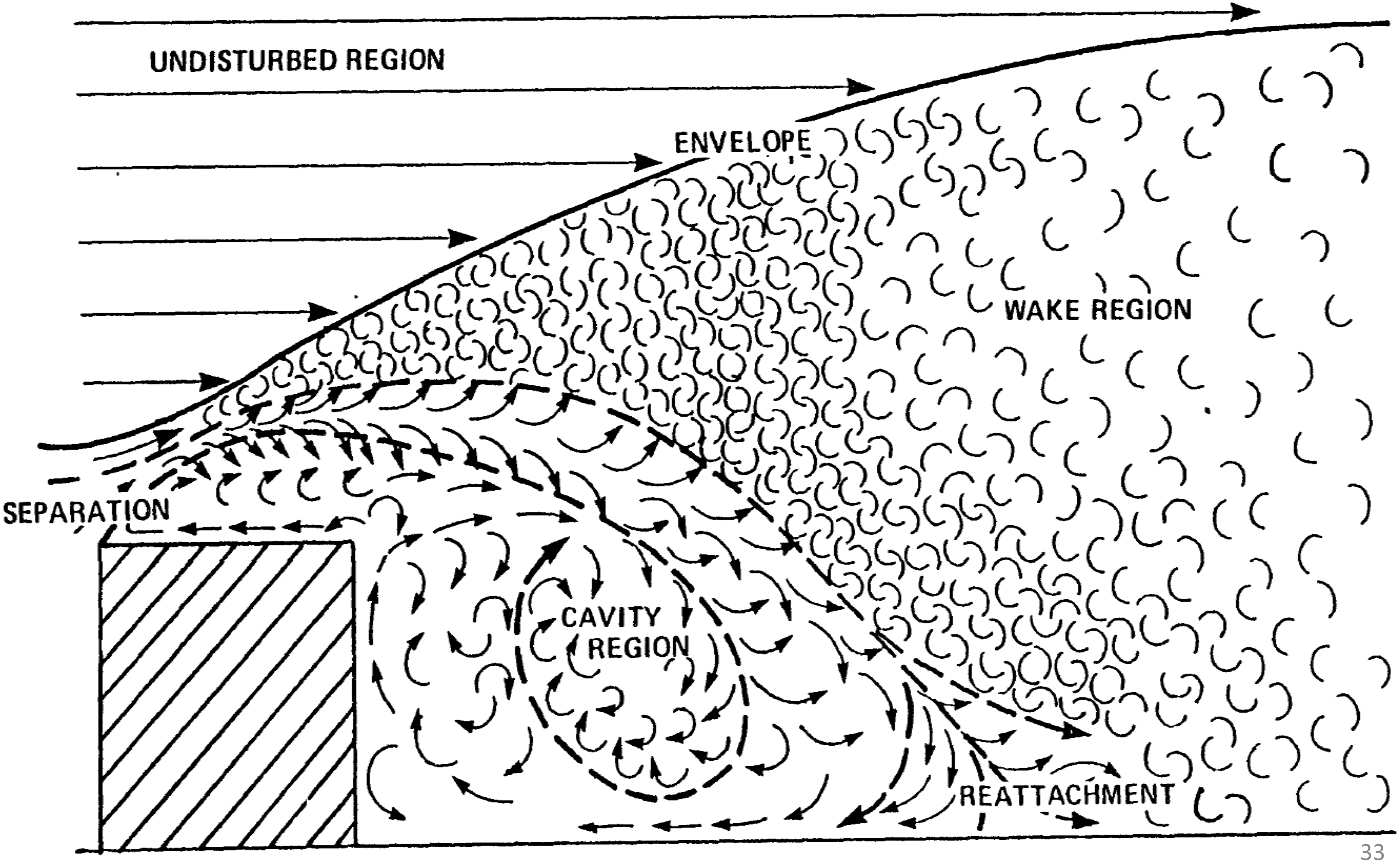
http://www.epa.gov/mercury/index.htm

Building Downwash

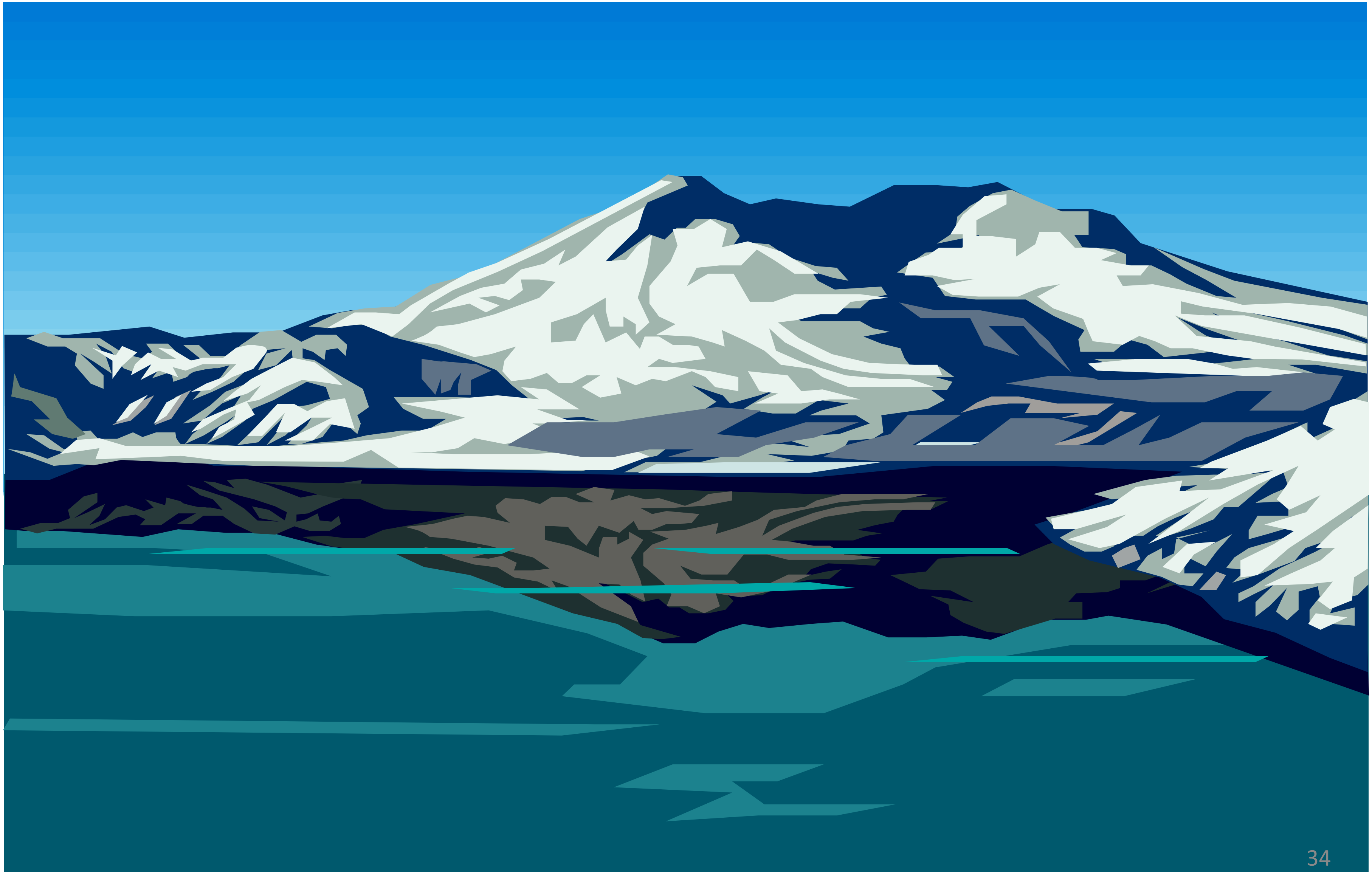
TYPICAL FLOW PATTERN AROUND A CUBE WITH ONE FACE NORMAL TO THE WIND



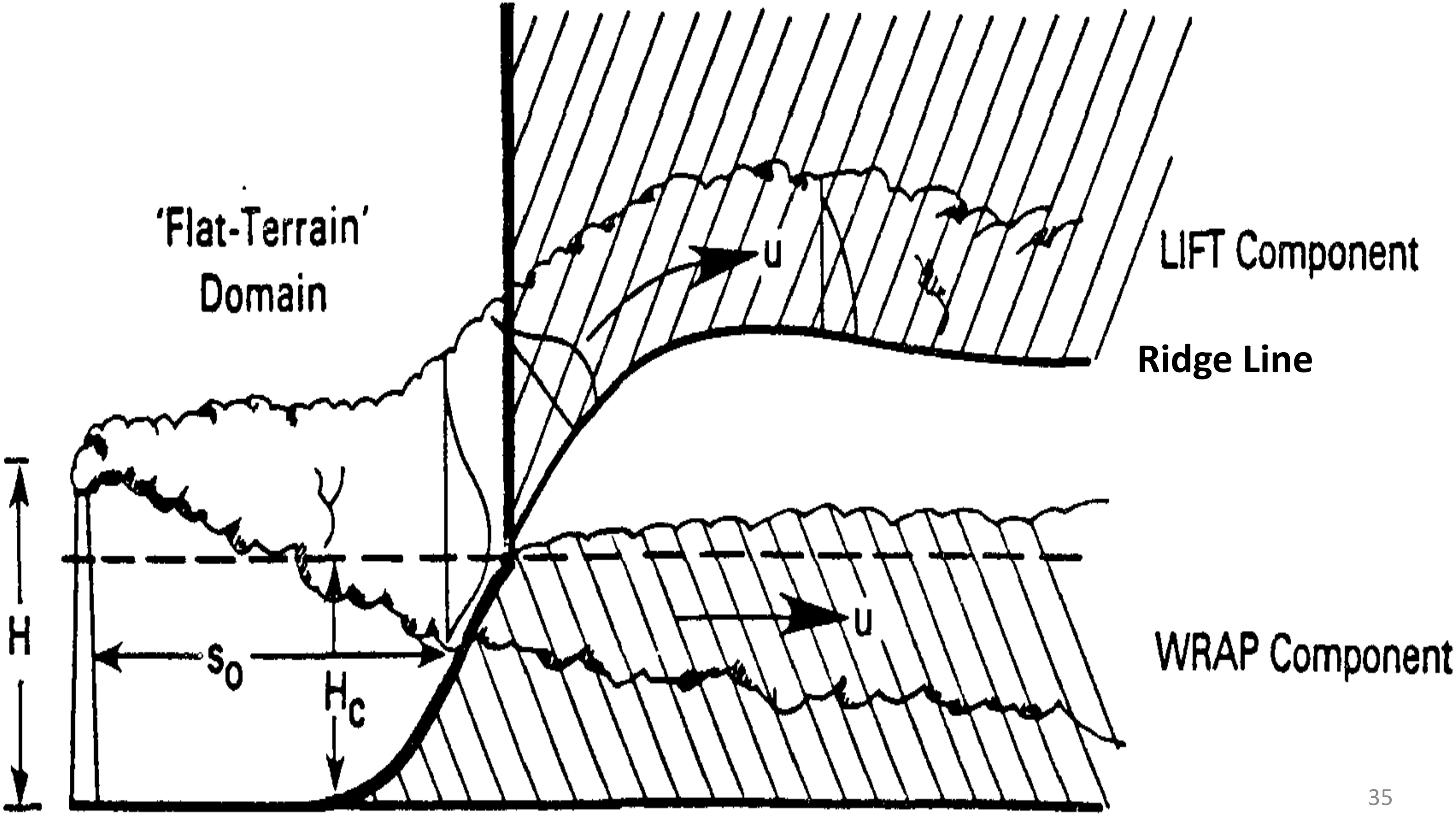
Envelope and Cavity Regions in the Wake of a Building will Concentrate Released Pollutant Levels Near the Source



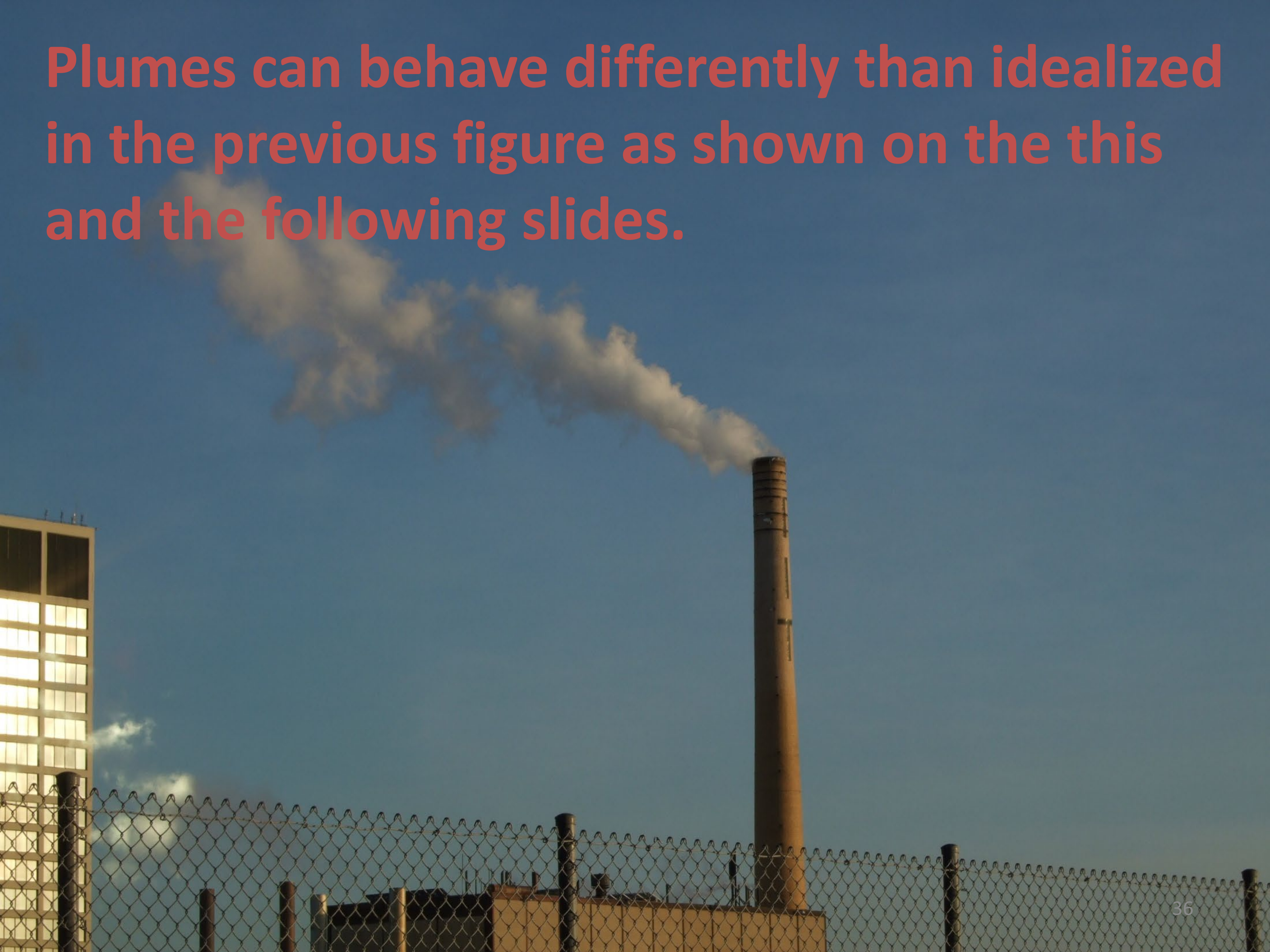
Terrain effects



Plume Behavior in Stable Flow Around a Terrain Obstacle



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

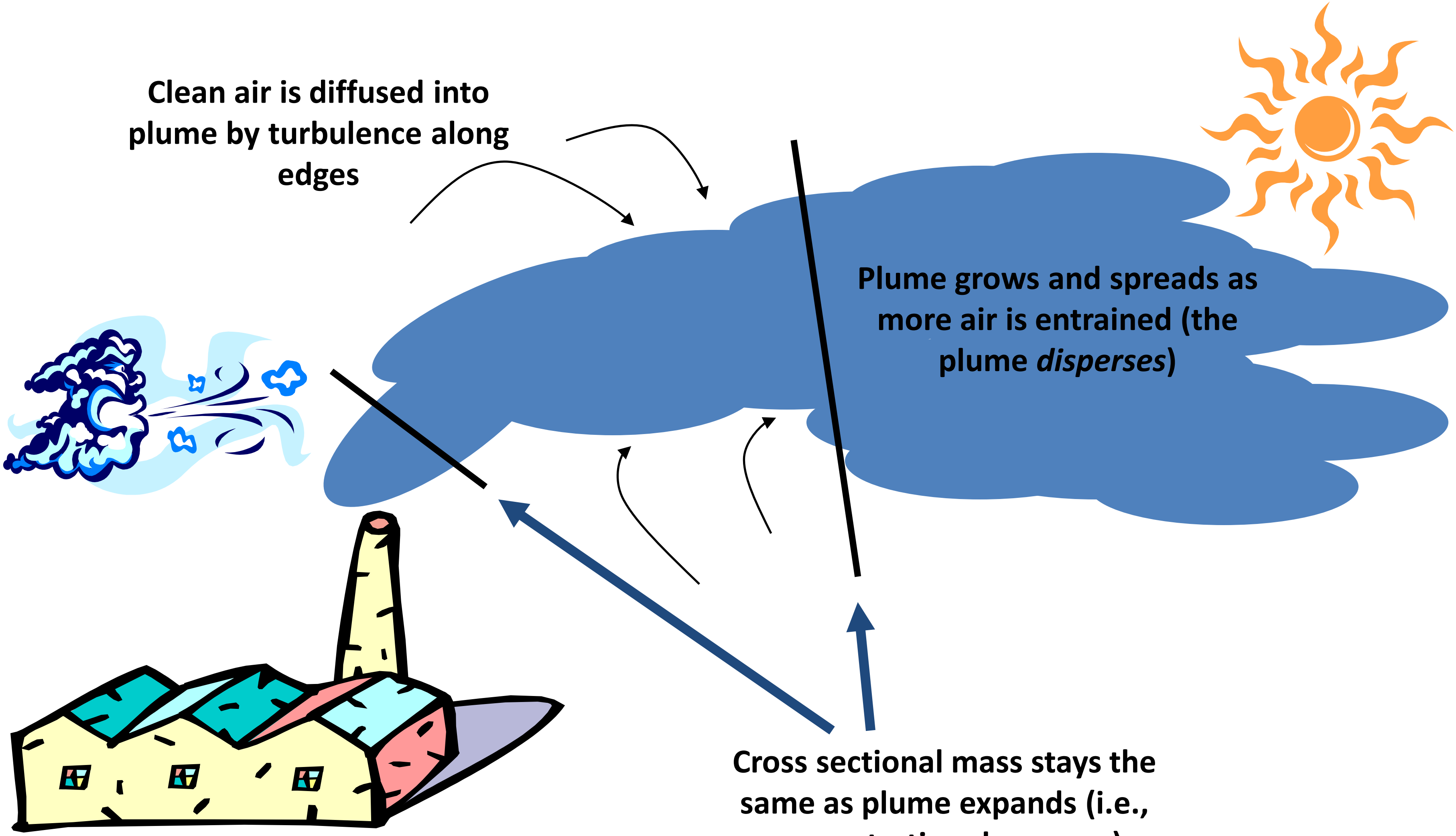


Same Day Later Time
Wind Speed Increasing

Same Day Later Time Wind Speed Increasing More

Same Day Later Time
Wind Speed Increasing Even More

What does this mean for a plume?

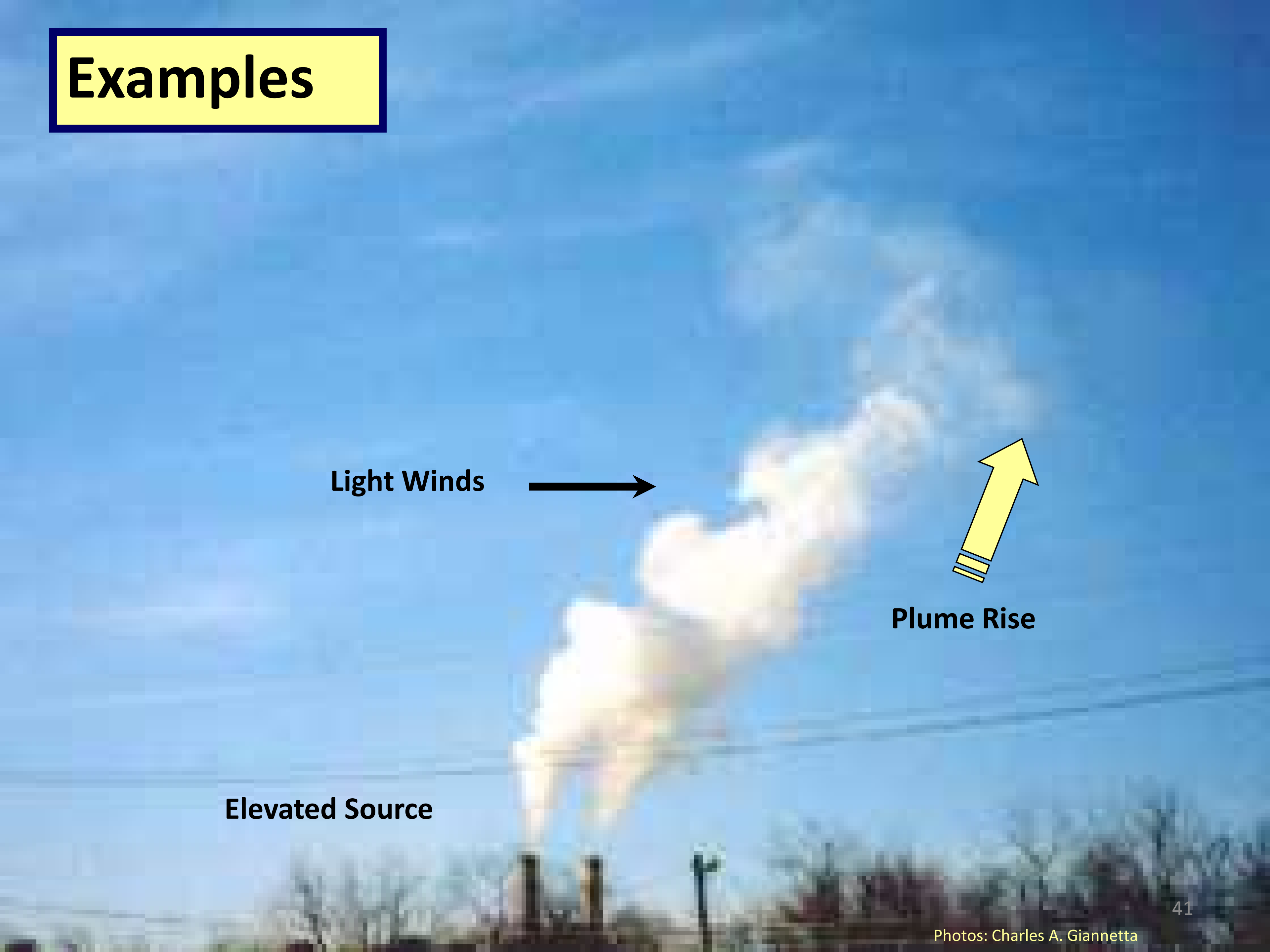


Clean air is diffused into plume by turbulence along edges

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)

Examples

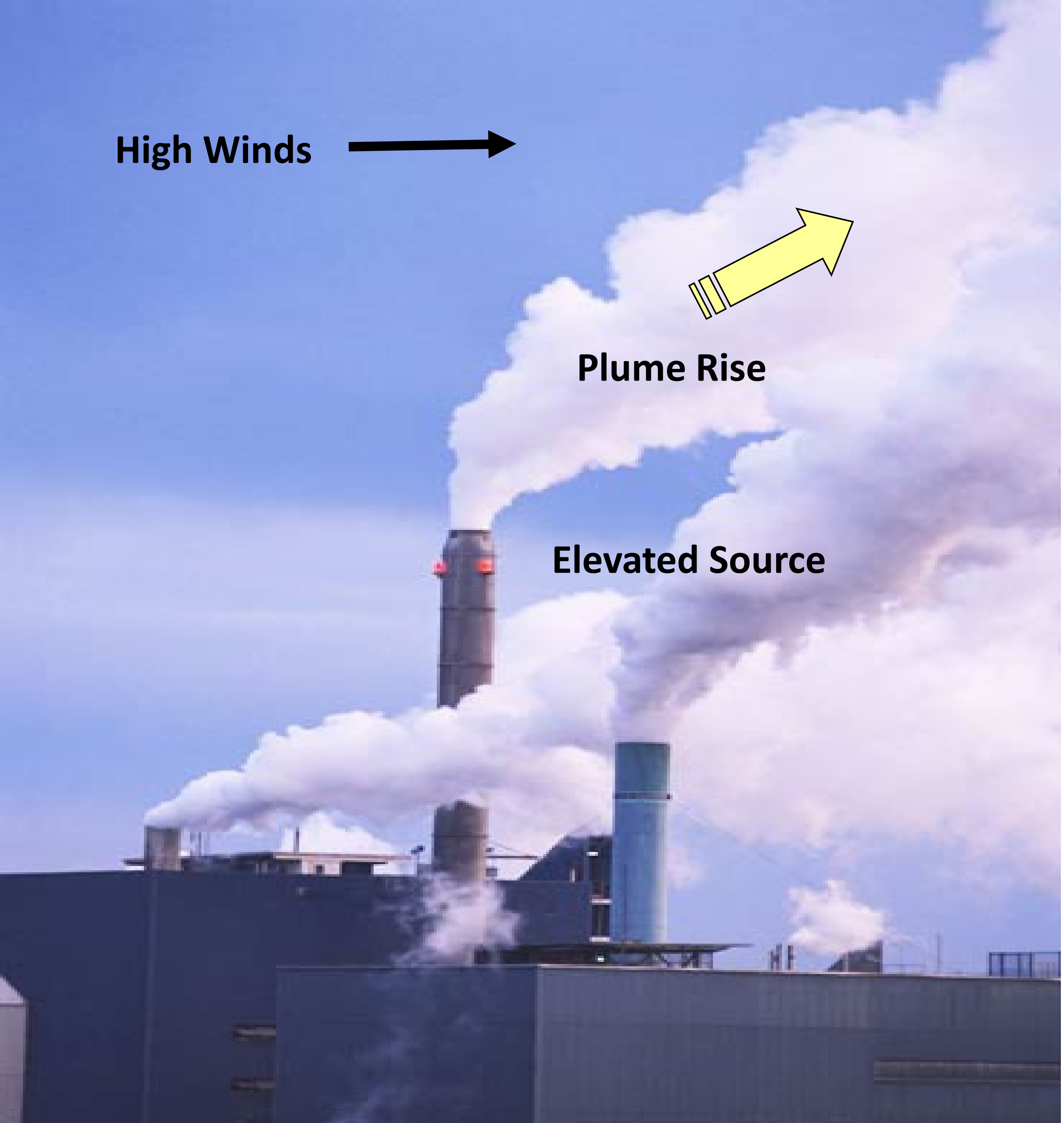


Light Winds

Plume Rise

Elevated Source

Photos: Charles A. Giannetta



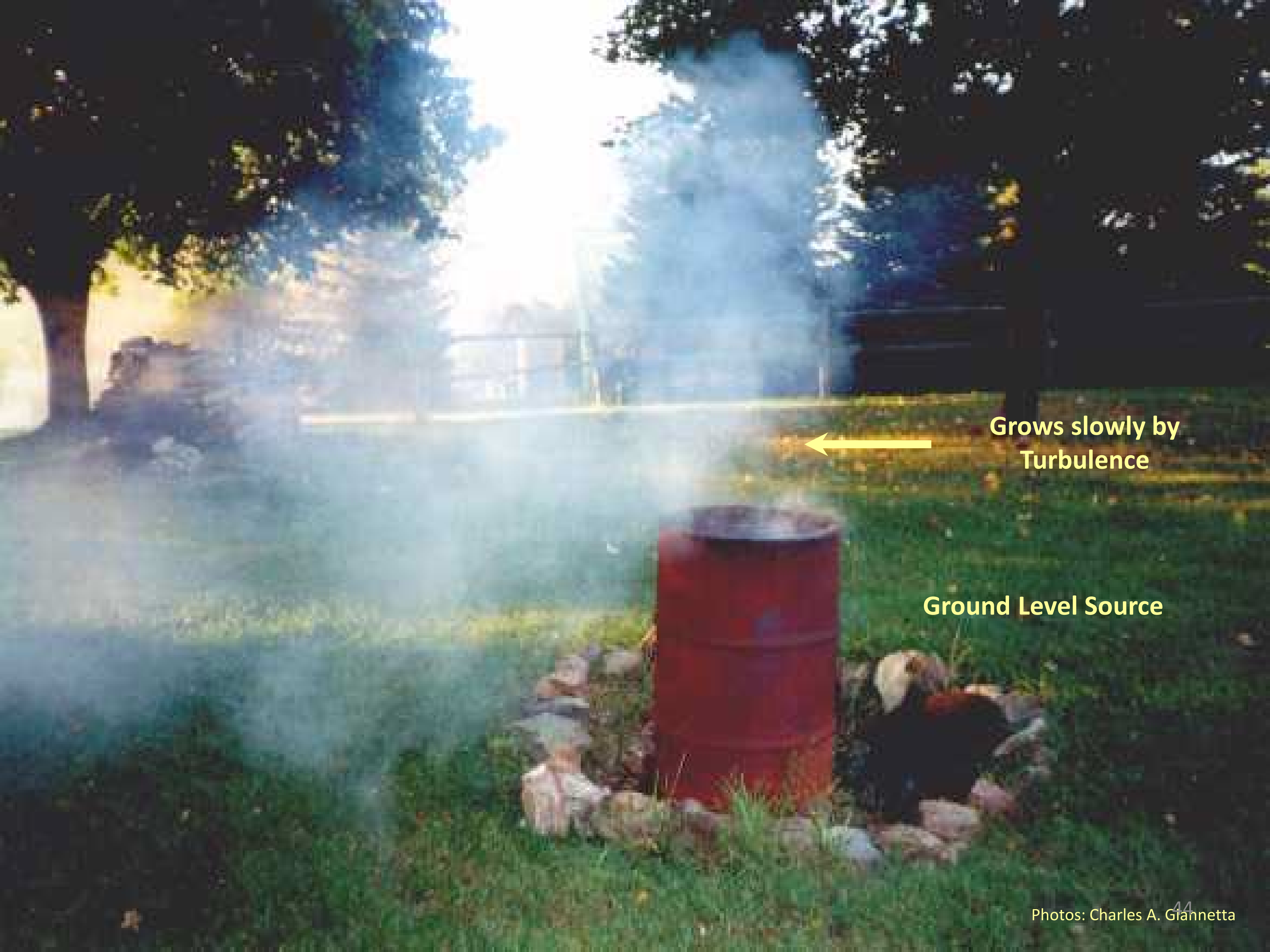
EXAMPLE

Photo: NASA

Light Winds

Ground Level Source

Photos: Charles A. Giannetta



Grows slowly by Turbulence

Ground Level Source

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

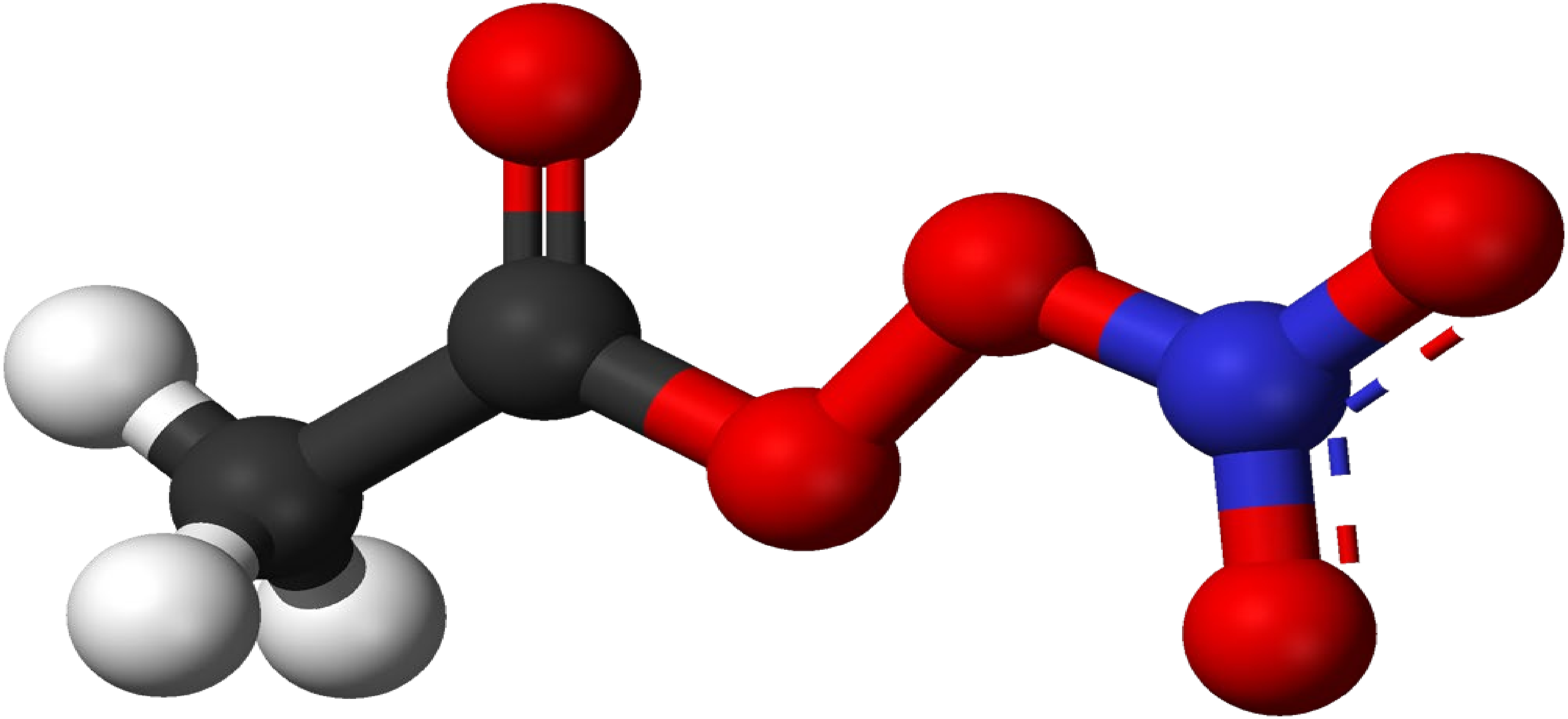
Pollutant	Pollutant Formed From
Acetaldehyde	propene, 2-butene
acrolein	1,3-butadiene
carbonyl sulfide	carbon disulfide
o-cresol	toluene
formaldehyde	ethene, propene
hydrogen chloride	nitric acid, chlorinated organics
methylethyl ketone	butane, branched alkenes
N–nitroso-N–methylurea	N–methylurea
N–nitrosodiethylamine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

Source: Rosenbaum et al., 1998

Chemistry

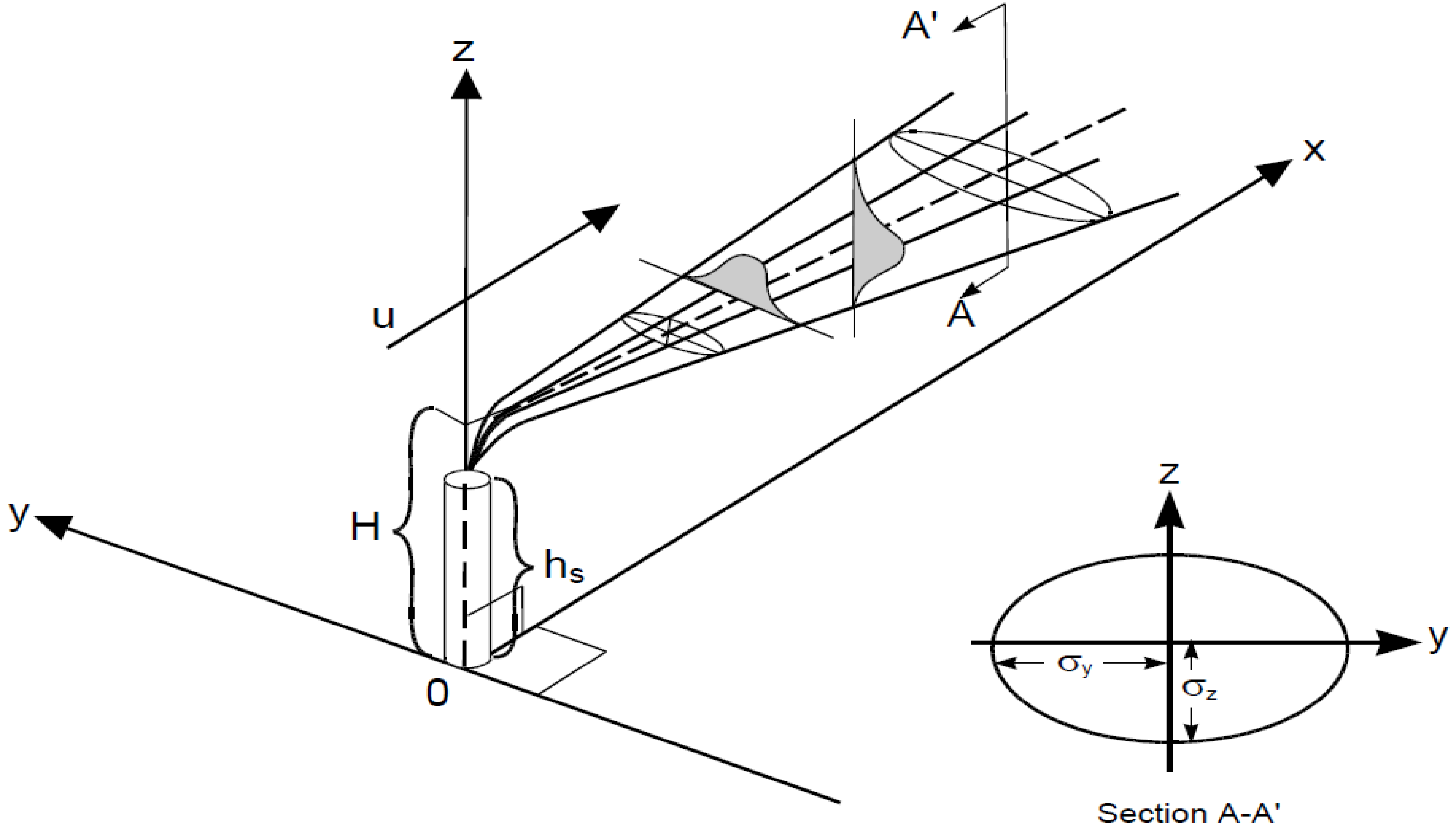
- **The formation of greatest concern would be when an unlisted compound from unregulated sources which reacts to form a HAP.**
- **Propylene is an example compound of this scenario, which is not regulated under Title III. It also has emissions of tens of millions of pounds in to the atmosphere from 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.**

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 (σy and σz respectively) are the standard deviation from normal on the Gaussian distribution curve in the y and z directions.
- The coefficients, σy and σz, 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

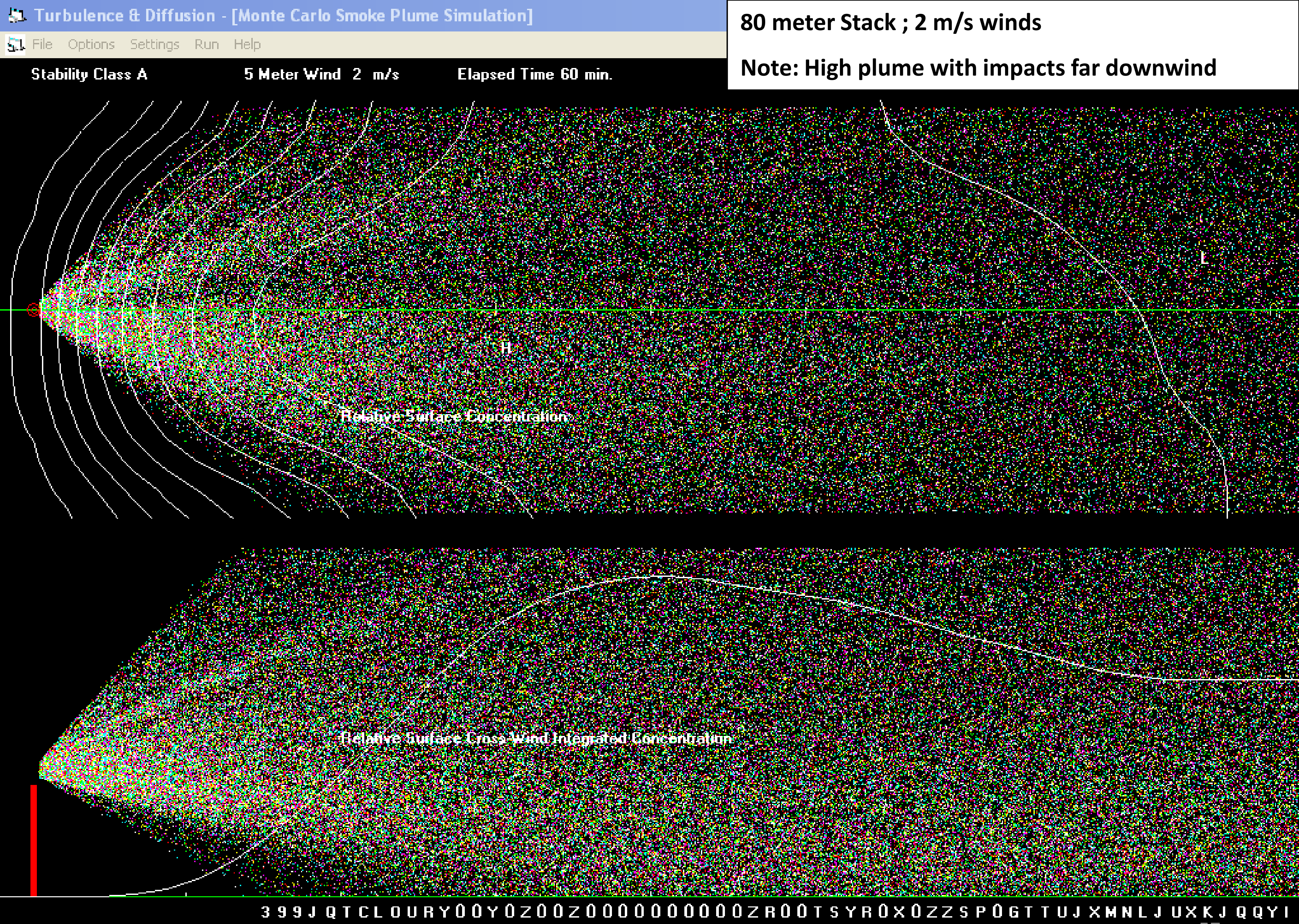
Fate and Transport

The Blackadar
Monte Carlo
Smoke Plume Simulation

(Note Stability Class, Stack Height and Wind Speed)

80 meter Stack ; 2 m/s winds

Note: High plume with impacts far downwind



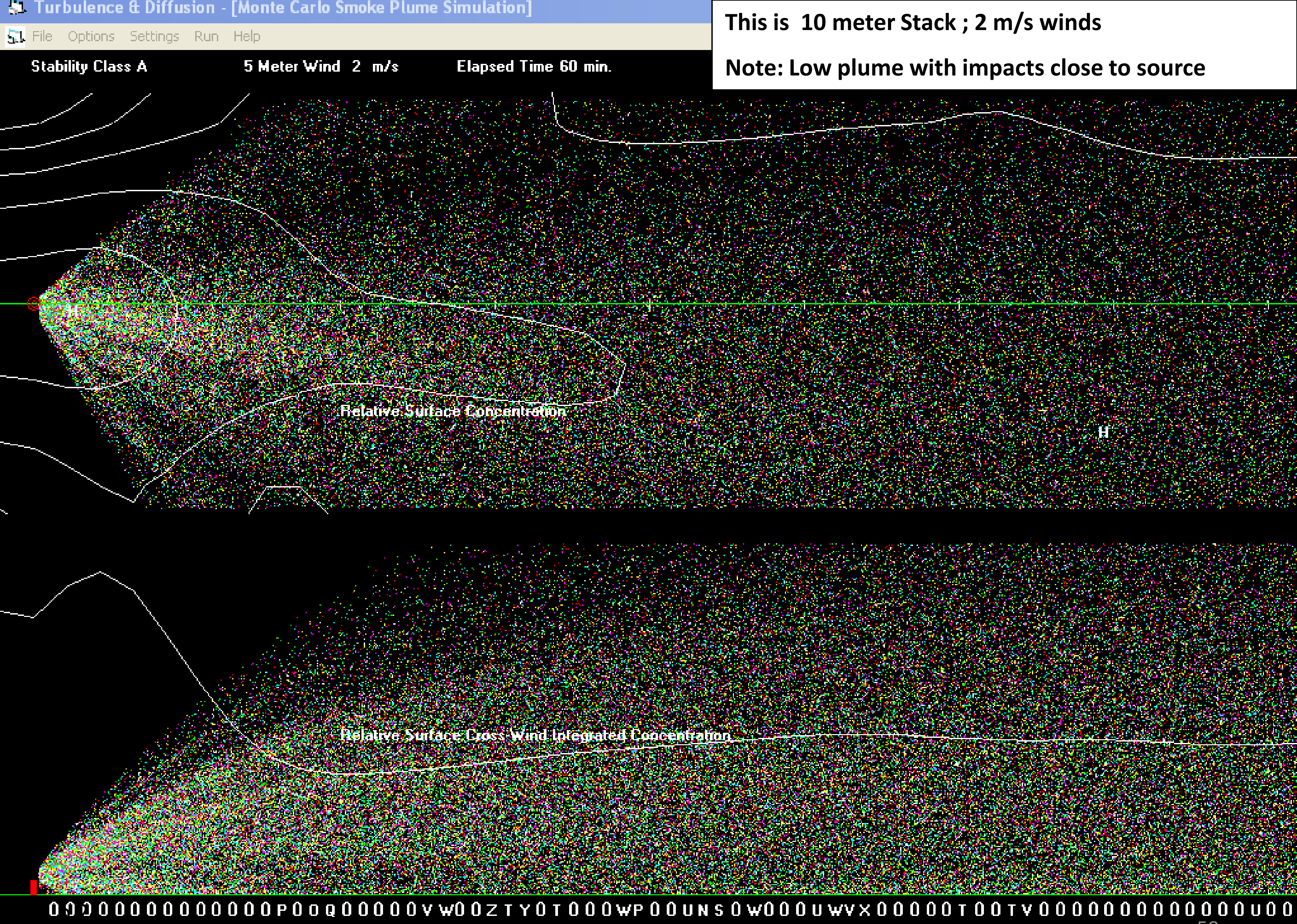
Stability Class A

5 Meter Wind 2 m/s

Elapsed Time 60 min.

This is 10 meter Stack ; 2 m/s winds

Note: Low plume with impacts close to source

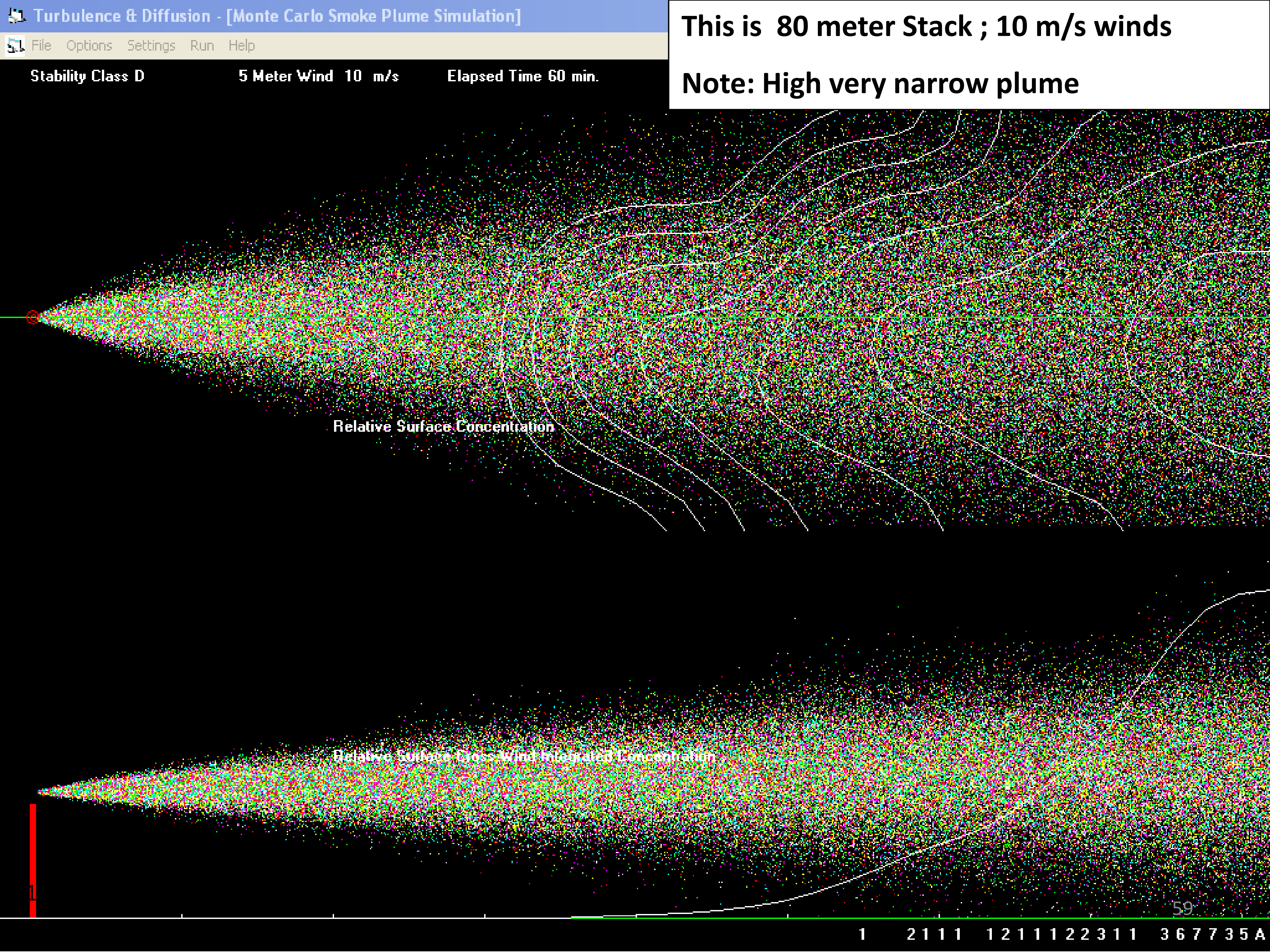


Stability Class A   5 Meter Wind 2 m/s   Elapsed Time 60 min.

```
0 0 0 0 0 0 0 0 0 0 0 0 0 0 P 0 0 Q 0 0 0 0 0 V W 0 0 Z T Y 0 T 0 0 0 W P 0 0 U N S 0 W 0 0 0 U W V X 0 0 0 0 0 T 0 0 T V 0 0 0 0 0 0 0 0 0 0 0 0 0 U 0 0
```

This is 80 meter Stack ; 10 m/s winds

Note: High very narrow plume



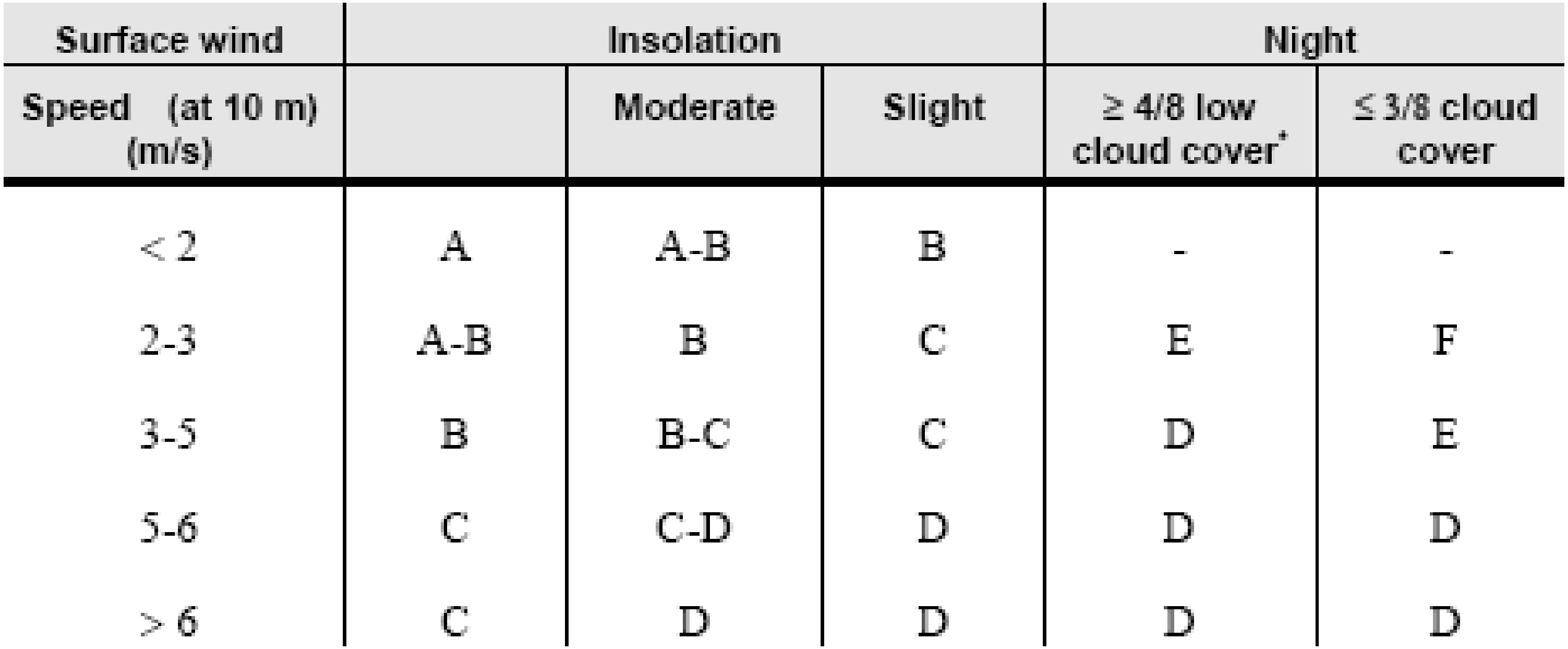
Turbulence & Diffusion - [Monte Carlo Smoke Plume Simulation]

Stability Class D

5 Meter Wind 10 m/s

Elapsed Time 60 min.

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

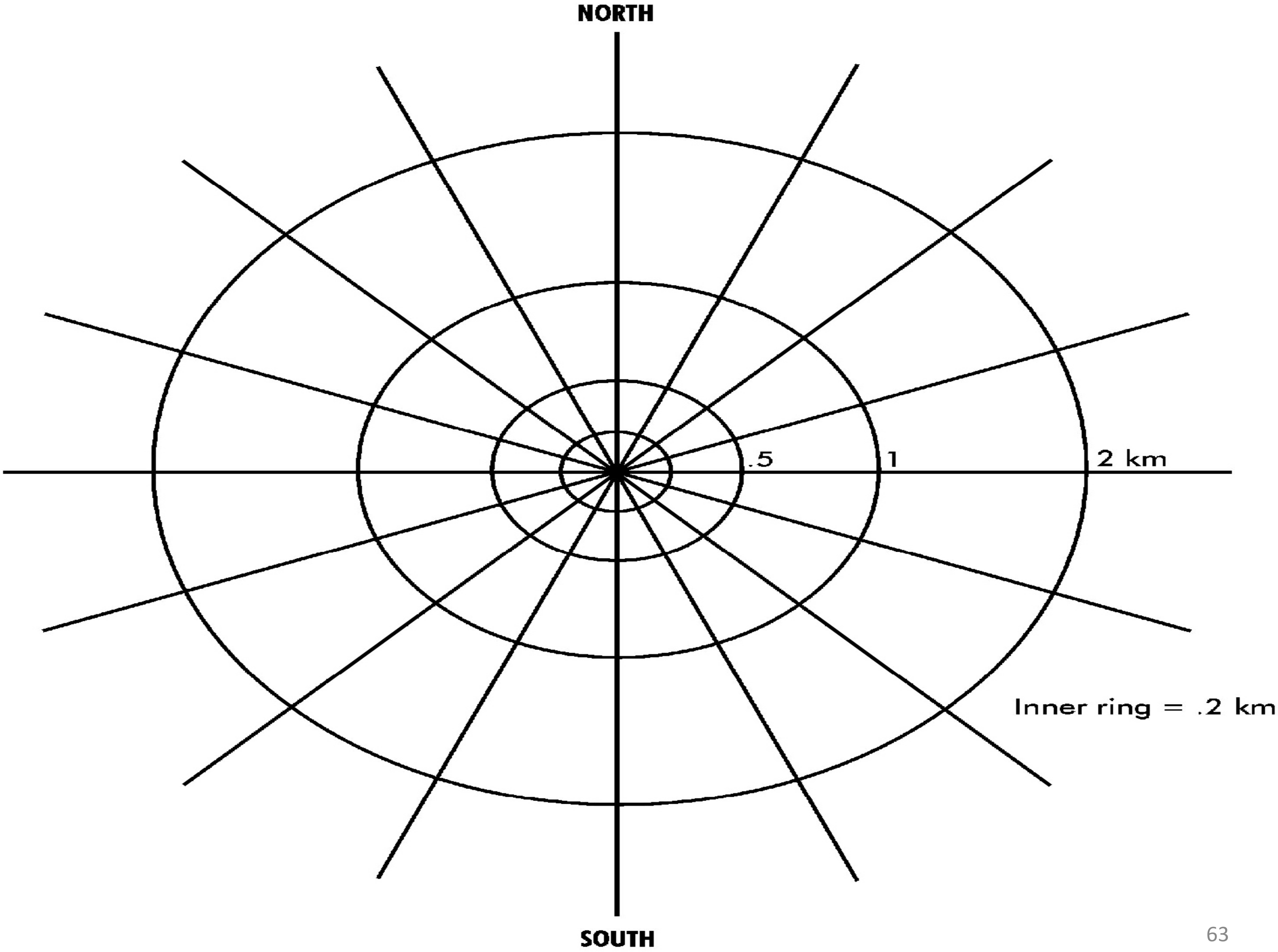
Stabilities A, B, and C refer to daytime hours with unstable conditions. Stability D is representative of overcast days or nights with neutral conditions. Stabilities E and F refer to nighttime, stable conditions and are based on the amount of cloud cover. Thus, classification A represents conditions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

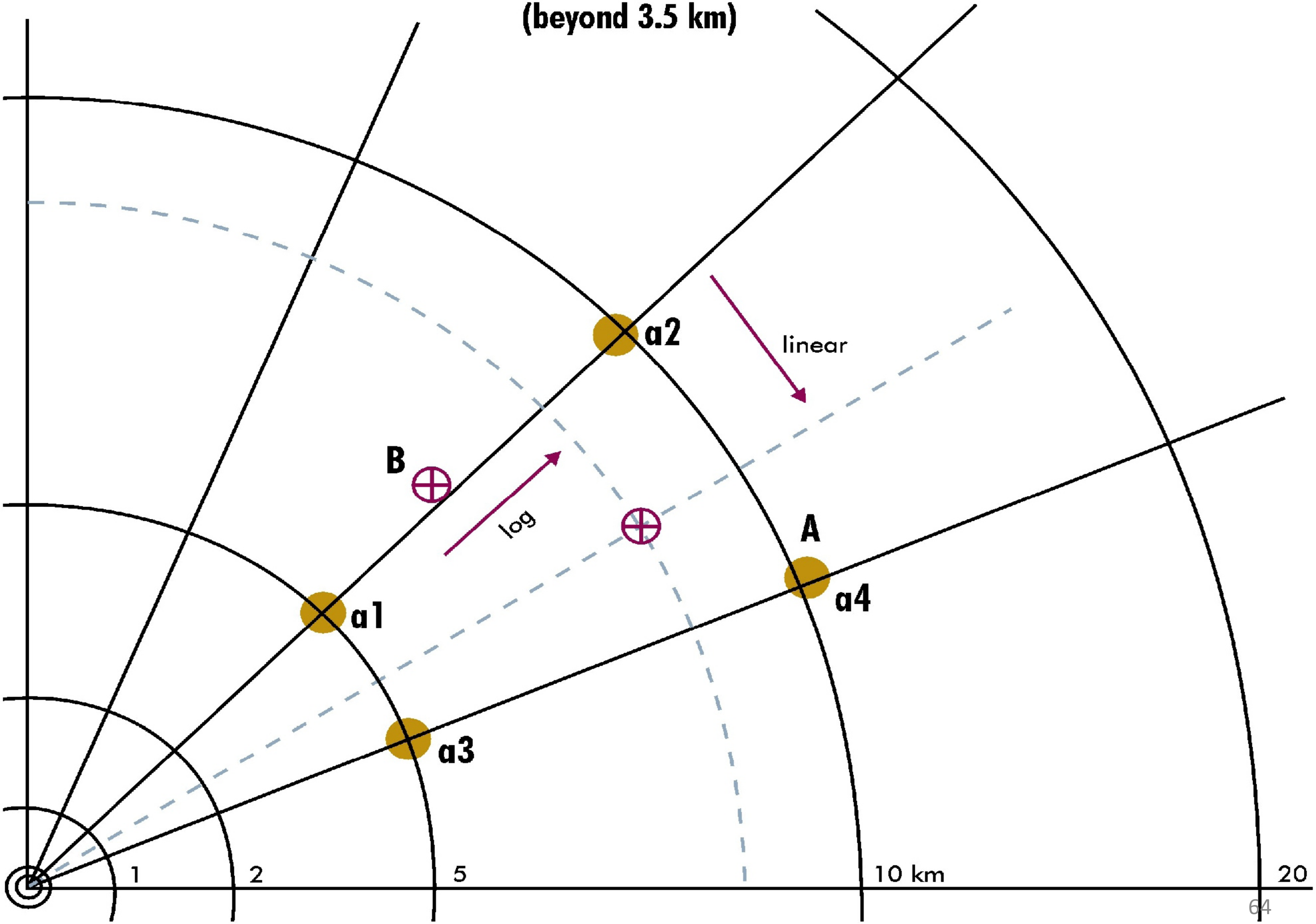
Model Calculations of Ambient Concentrations (cont.)

- 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).


NORTH
.5
1
2 km
Inner ring = .2 km
SOUTH

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/m3.
- Dose-response values often are reported as parts per million (ppm), parts per billion (ppb), or mg/m3.
- 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/m3 to ppm can be expressed as:
- Concentration [ppm] = Concentration [mg/m3] × 24.45 [L/mole] / MW

Modeling Exposure Concentrations: Units are Important

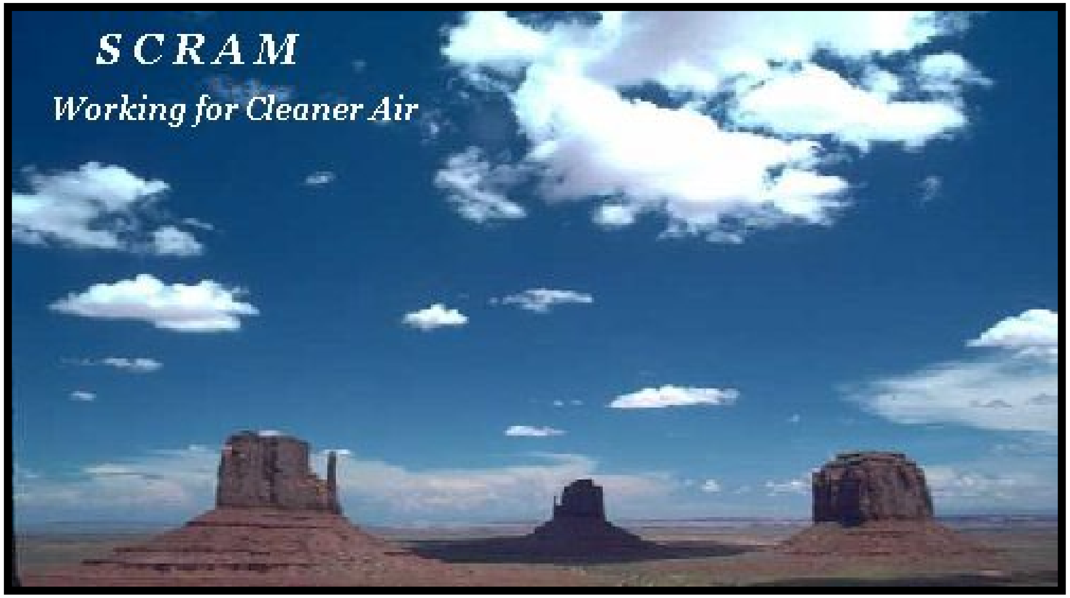
- The conversion from ppm to mg/m3 is:
- Concentration [mg/m3] = Concentration [ppm] × MW / 24.45 [L/mole],
  - where MW is the molecular weight of the air toxic in g/mole and 24.45 is the volume in liters of one mole of an ideal gas at 1 atmosphere and 25 degrees Celsius. Note also that ppb = 1,000 × ppm and that here, ppm is volume-based. Also, μg/m3 = 1,000 × mg/m3.
- Tip: In the development of the analysis plan, stipulate that all laboratory and modeling results be reported in μg/m3. 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

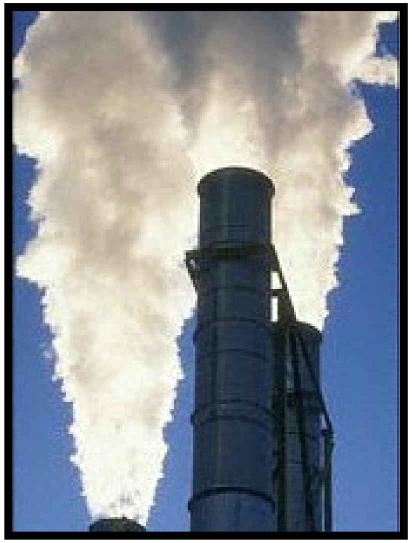
	Averaging Period	Terrain Type	Single Source		Multiple Sources	
			Rural	Urban	Rural	Urban
Screening Models	Short Term (1-24 hour average)	Simple	SCREEN3	SCREEN3	ISCST3, AERMOD	ISCST3, AERMOD
		Complex	SCREEN3, ISCST3	SCREEN3, ISCST3	ISCST3	ISCST3
	Long Term (Monthly-Annual)	Simple	ISCLT3	ISCLT3	ISCLT3,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



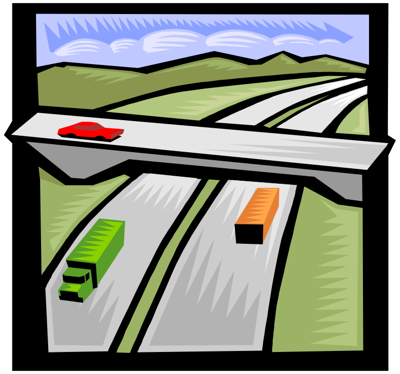
Fugitive Releases, such as leaks from joints and evaporation of chemicals from wastewater ponds, aren't so easily pinpointed or assessed

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

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 - http://www.epa.gov/air/data/

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

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

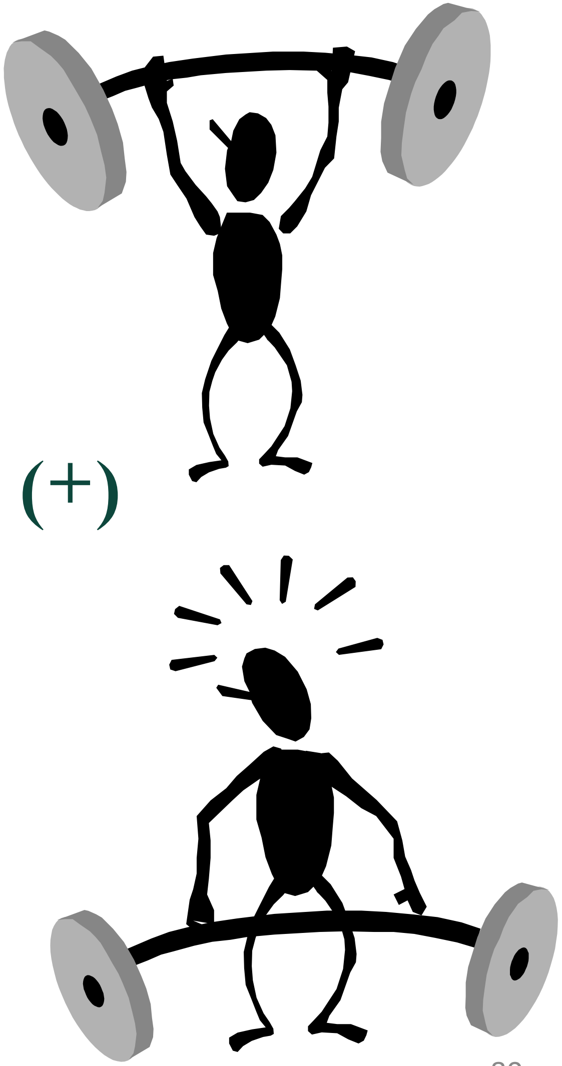
- Information and files on ambient air quality monitoring programs
- Details on monitoring methods
- Documents and articles
- Information on air quality trends and nonattainment areas
- Federal regulations related to ambient air quality monitoring

State websites

Strengths/Weaknesses

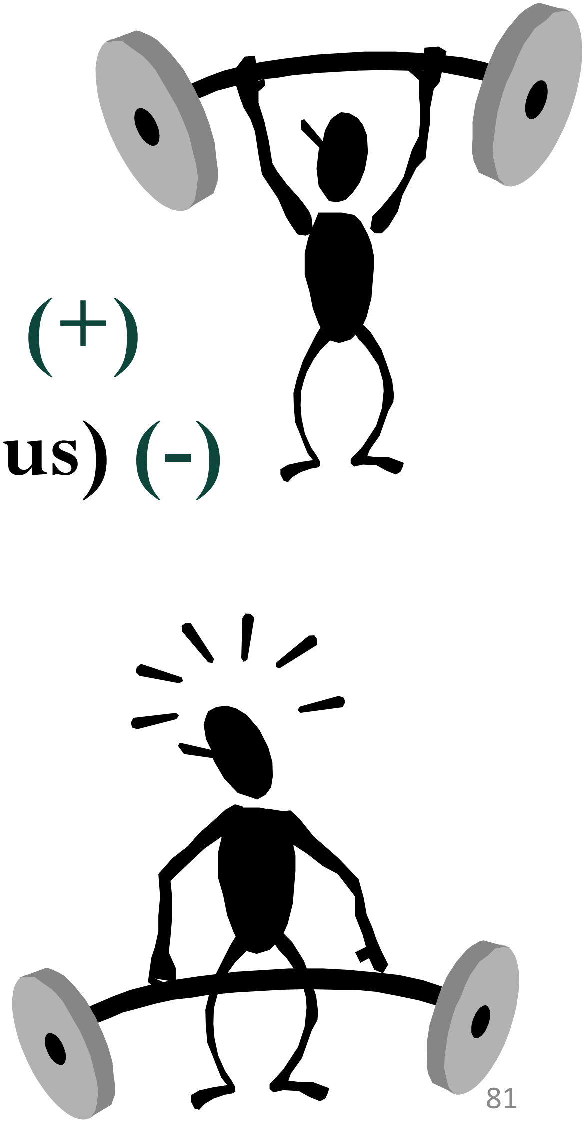
Air Quality Modeling

- 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



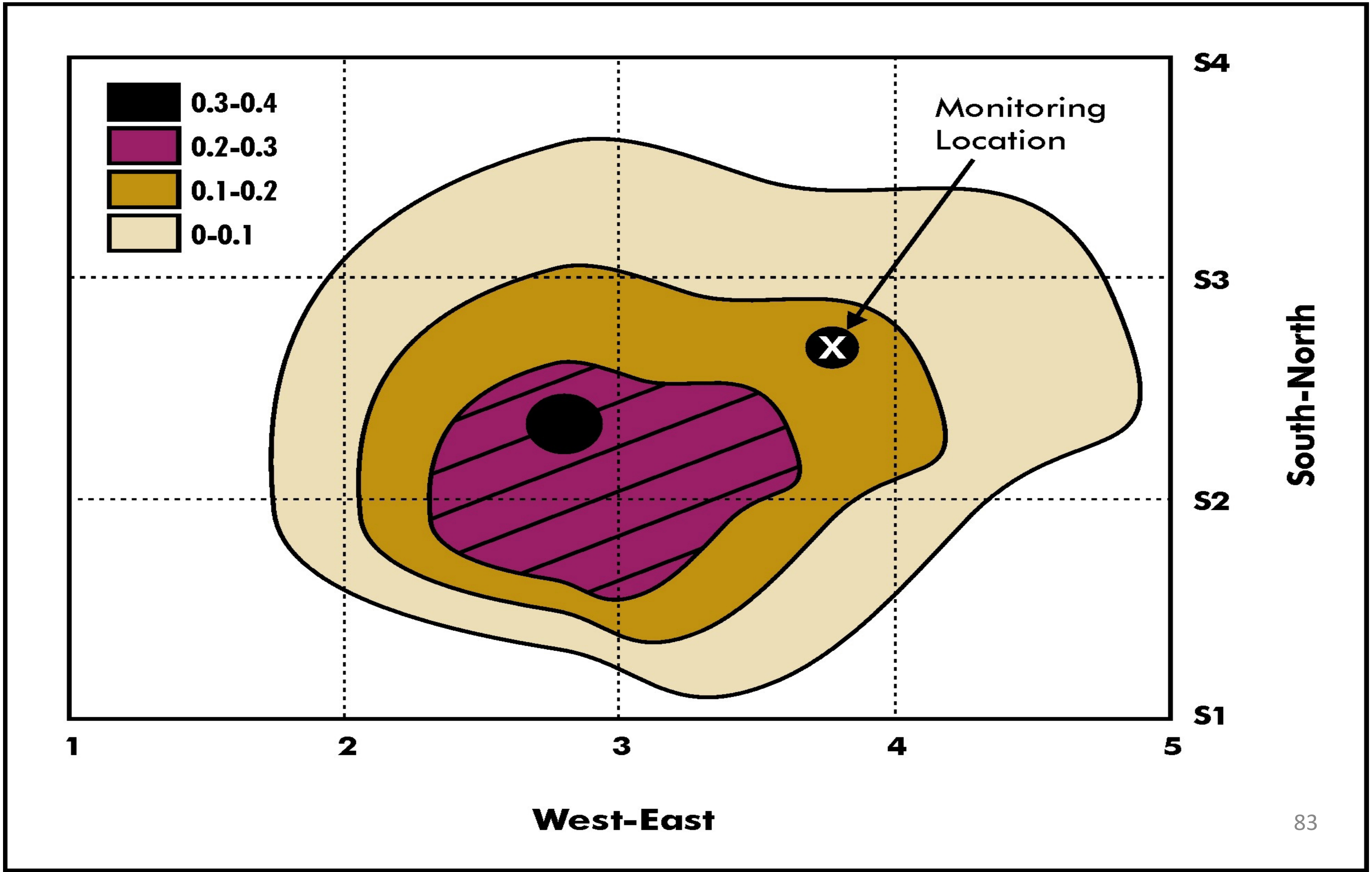
- Less uncertainty in measurements (in most cases) (+)
- Time consuming (real time plus) (-)
- Methodological limits (-)
- Logistics issues (-)
- Relatively expensive (-)
- Results over a limited spatial domain (-)

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

Hypothetical Example of a Combined Modeling and Monitoring Program



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

- <u>CAMEO</u>, contains a chemical database of over 6,000 hazardous chemicals, 80,000 synonyms, and product trade names.
- <u>CAMEO</u> 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/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

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.

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

Newsletter Contacts:
For *RMP*: Kelly Huynh at huynh.kelly@epa.gov.

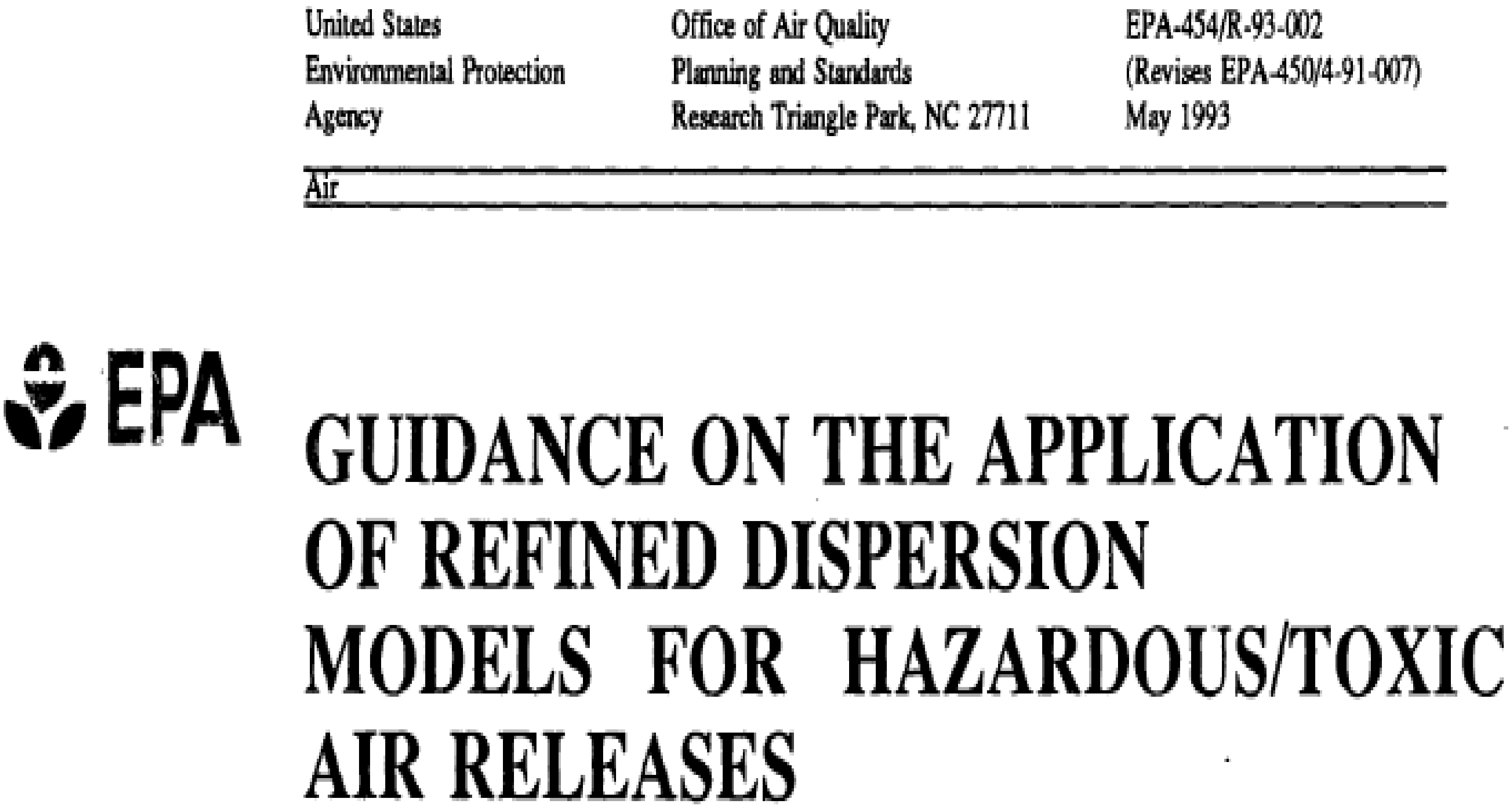
For *EPCRA*: Suzanne Powers at powers.suzanne@epa.gov

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

Appropriate models for various accidental release scenarios

Source type	Release Type			
	Continuous	Finite	Transient	Instantaneous
Ground Level	DEGADIS SLAB AFTOX	DEGADIS SLAB AFTOX	DEGADIS	AFTOX
Evaporating Liquid Spill	DEGADIS SLAB AFTOX	DEGADIS SLAB AFTOX		DEGADIS SLAB AFTOX
Vertical Jet/ Plume	DEGADIS SLAB INPUFF	DEGADIS SLAB 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

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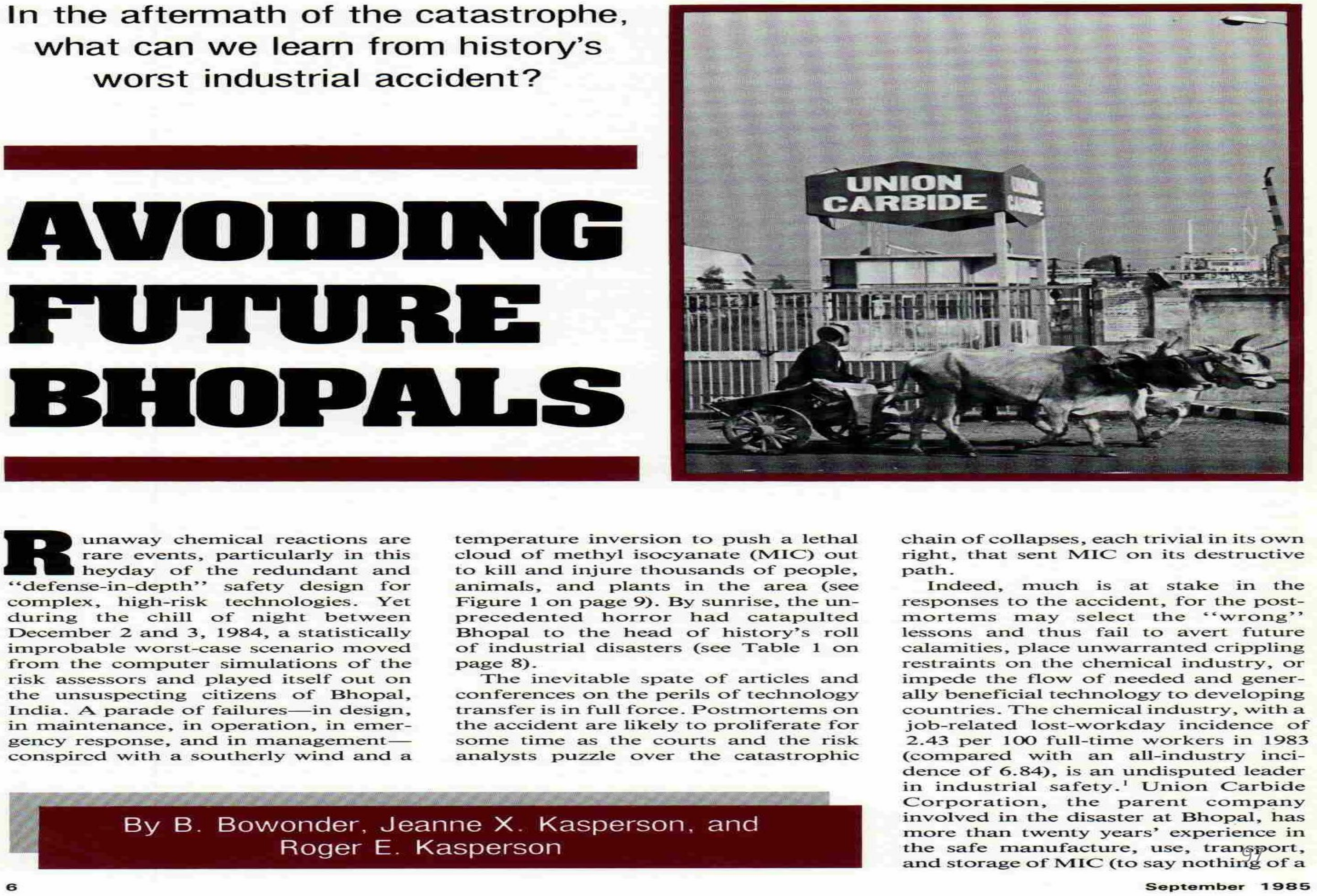
CASE STUDY – APPLYING MODELS PROPERLY

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

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

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

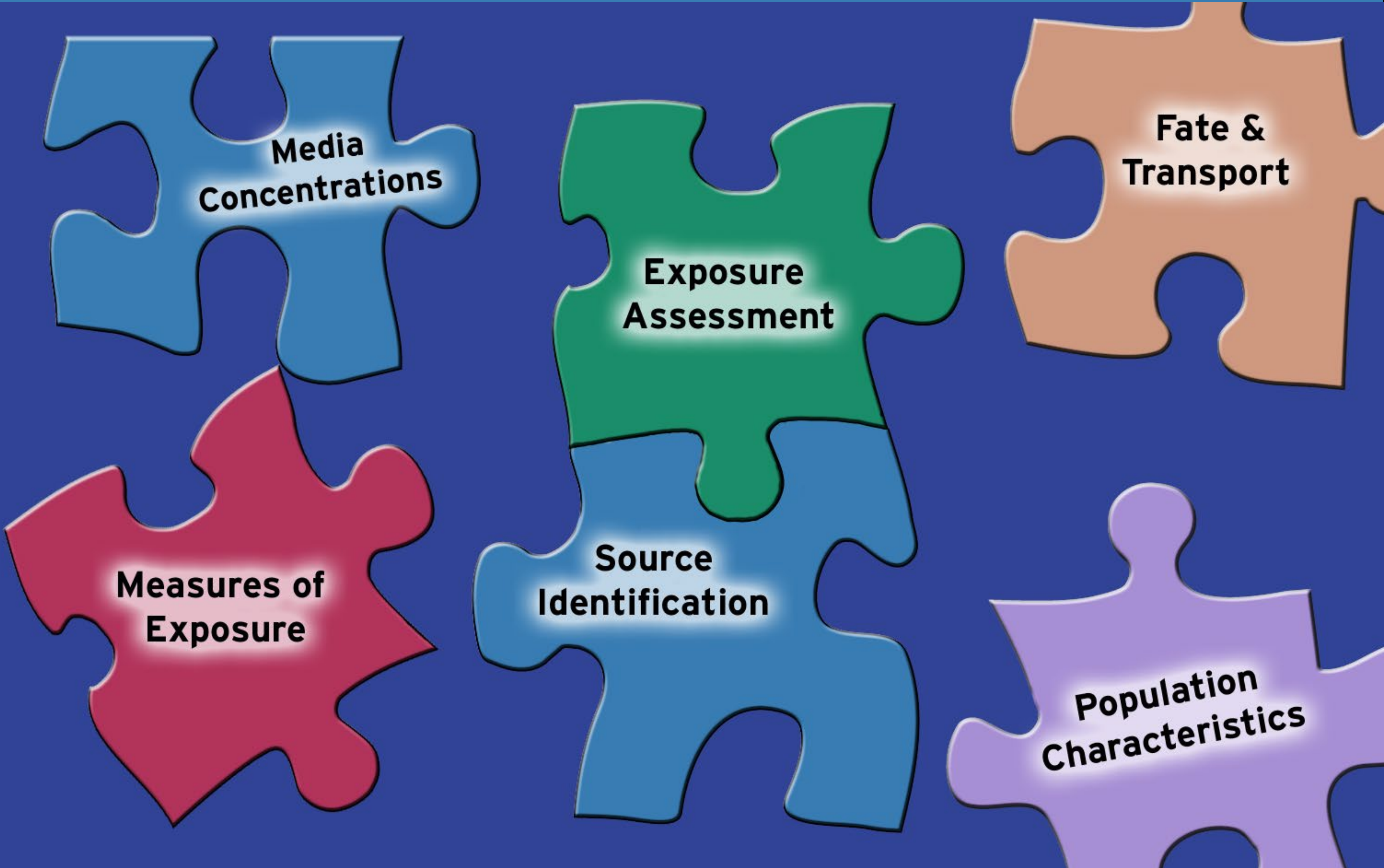
http://www.epa.gov/oms/m6.htm

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

Exposure Assessment for Air Toxics



Media Concentrations

Exposure Assessment

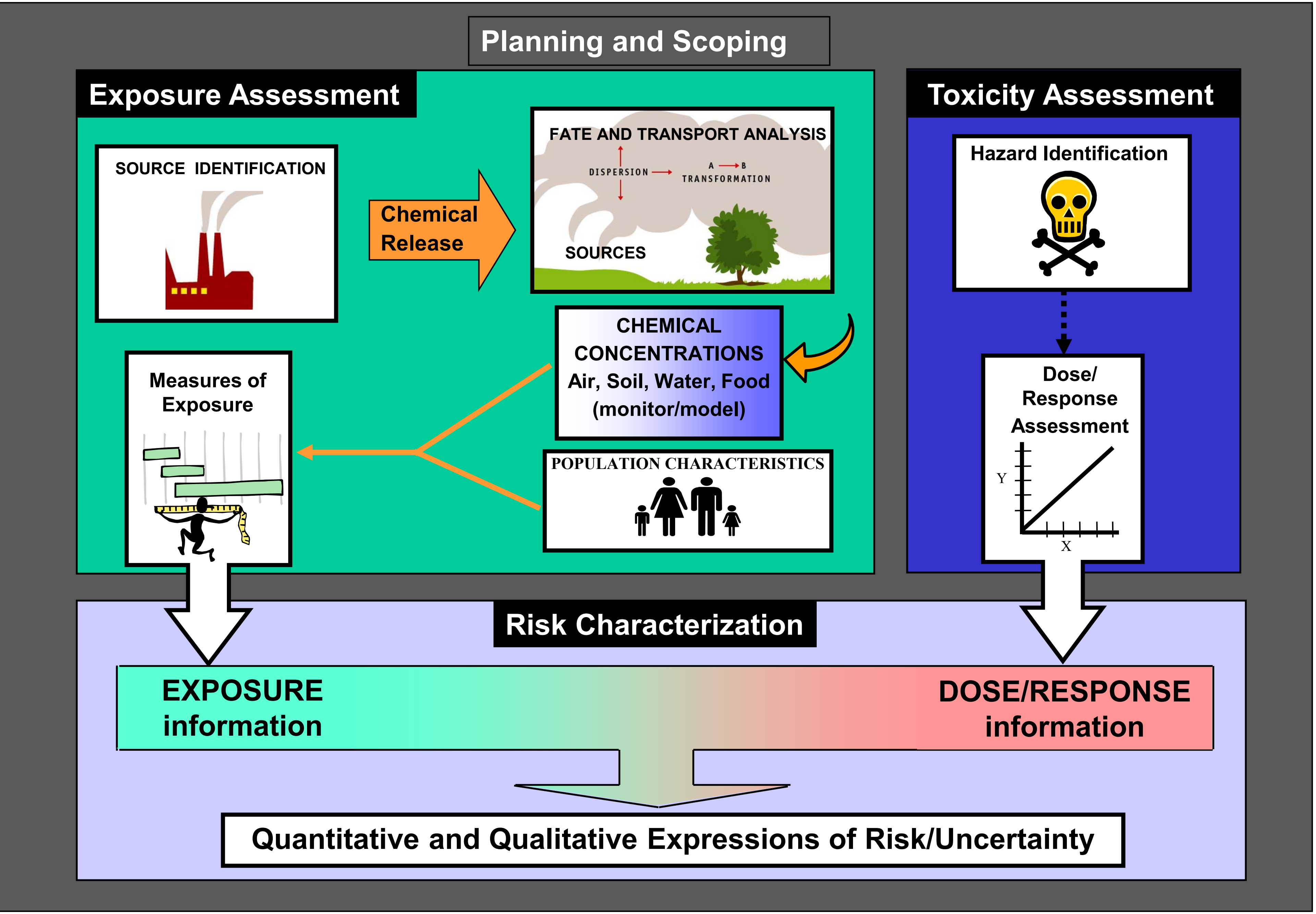
Fate & Transport

Measures of Exposure

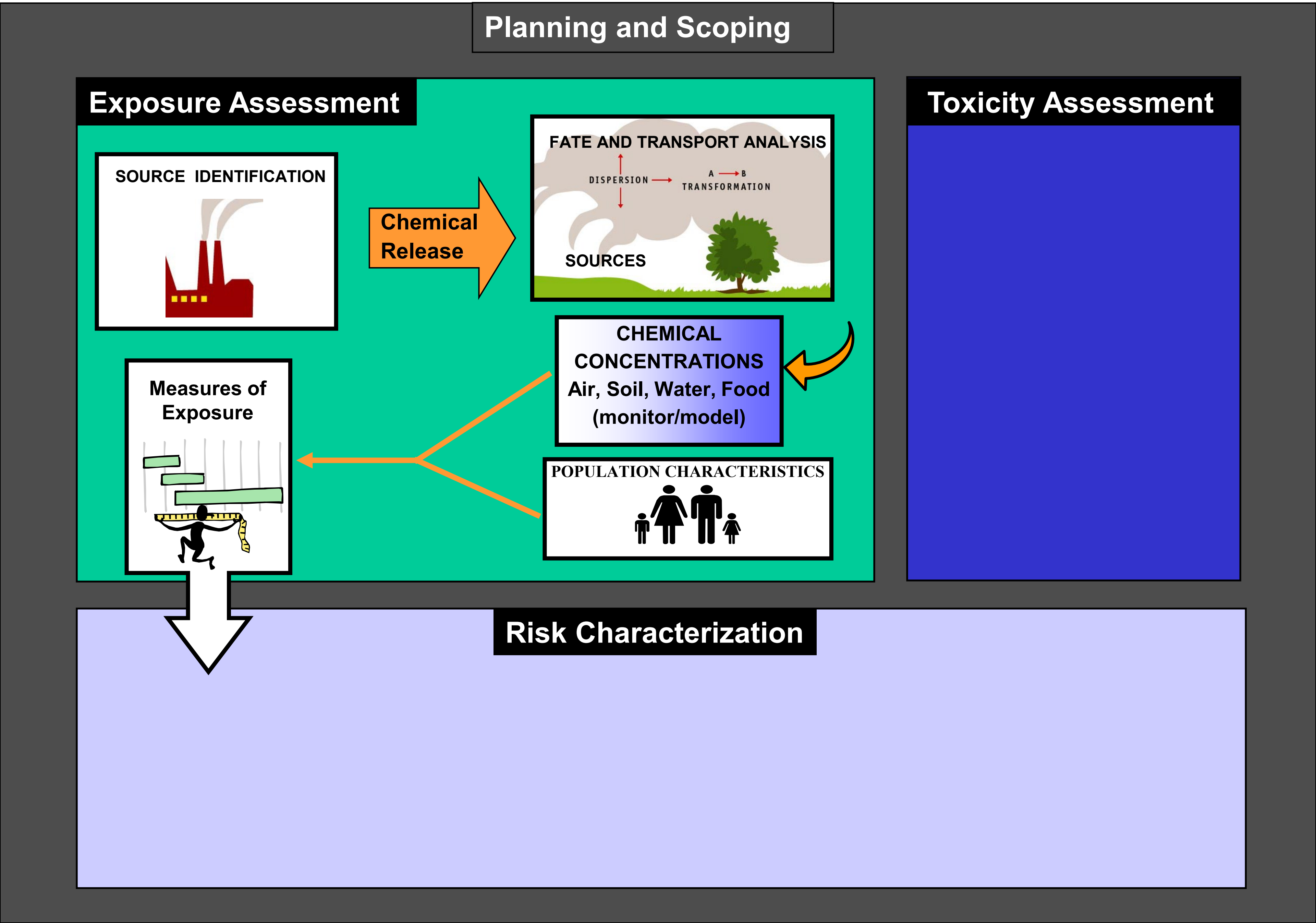
Source Identification

Population Characteristics

The Detailed Air Toxics Risk Assessment Process



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

Risk Characterization

Risk Assessment – The Actual Process

$$\text{Risk} = f\left[\underbrace{(\text{Measure of Exposure})}, (\text{Measure of Toxicity})\right]$$

Who is exposed to a chemical?

How are they exposed to the chemical?

Exposure vs. Exposure Assessment

Exposure is contact of a person with a chemical

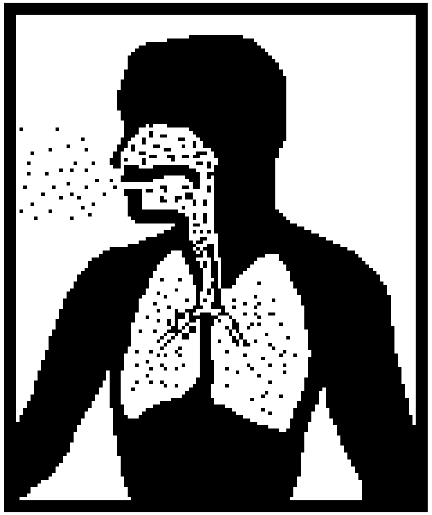
Exposure assessment is the evaluation (qualitative or quantitative) of the magnitude, frequency, duration, and route of the exposure

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



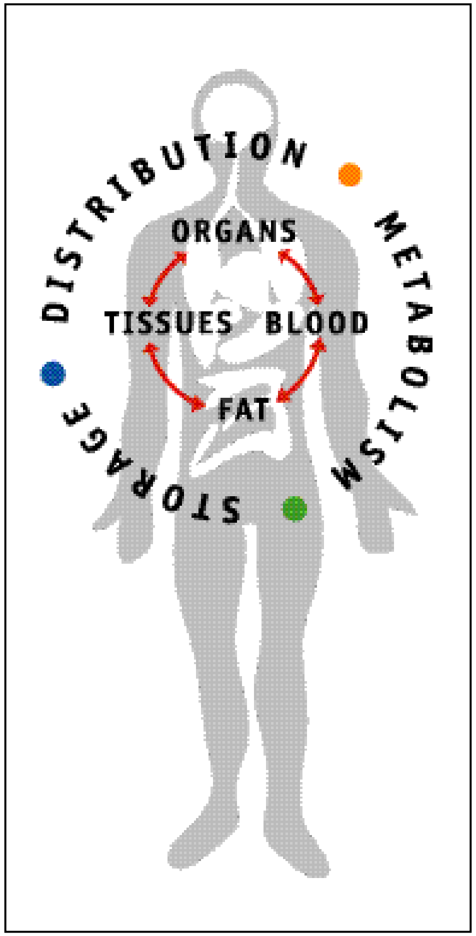
For air toxics human health risk assessments, we will usually focus on exposure to people by:

- 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)

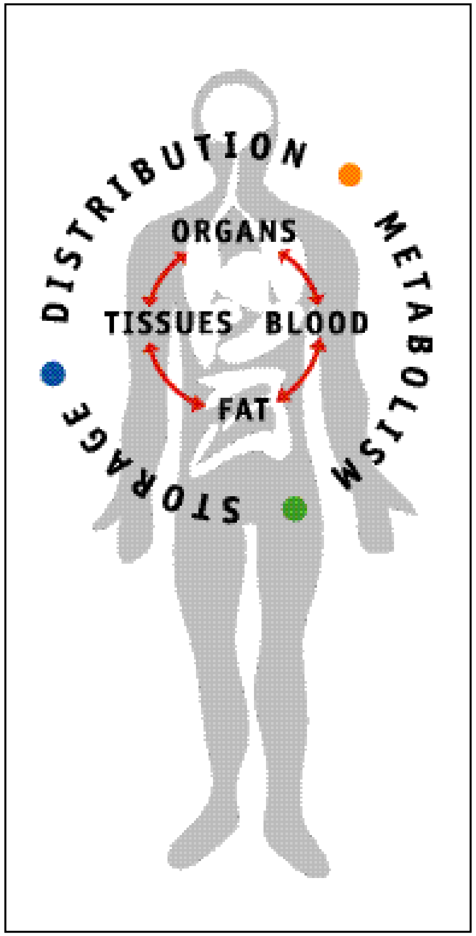
- Toxic effect can occur at the initial point of entry in the body (e.g., the respiratory or digestive tracts)
- Portal of entry effect
- Toxic effect can occur at a point(s) distant from the portal of entry



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

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

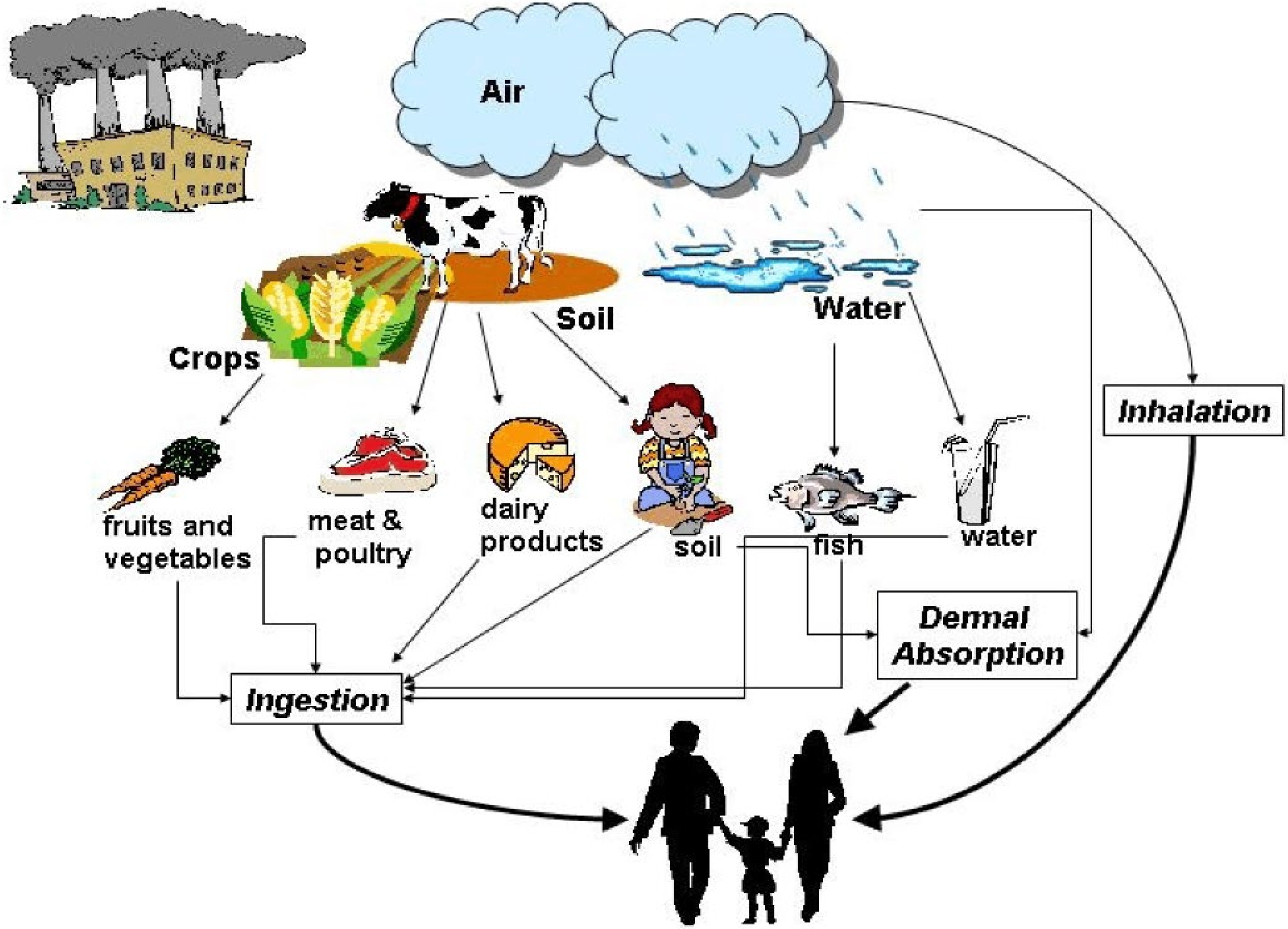
- Pathway analysis is a concept that is linked strongly to environmental fate and transport.
- The exposure pathway is the course that a toxic chemical takes from its source to the exposed receptor.
- An exposure pathway describes a unique mechanism by which an individual or population is exposed to 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 Multipathway Exposure Pathways/Routes



Focus on Ingestion

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 bioaccumulative (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

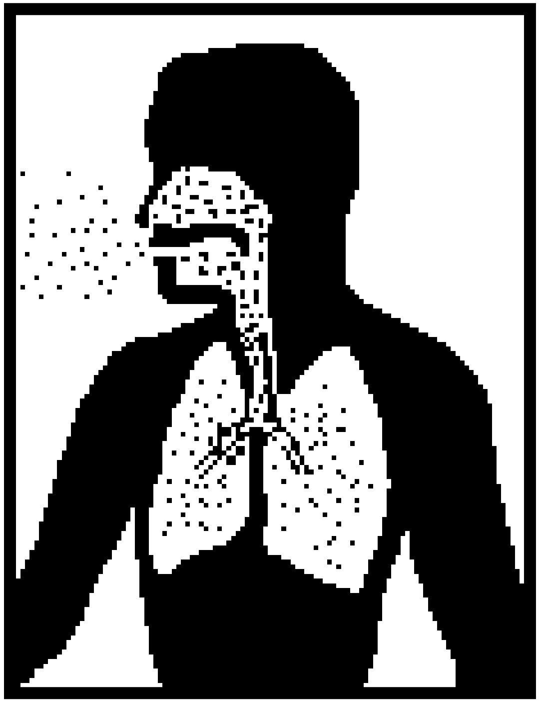
ED = Exposure duration

BW = Body weight

AT = Averaging time

Focus on Inhalation

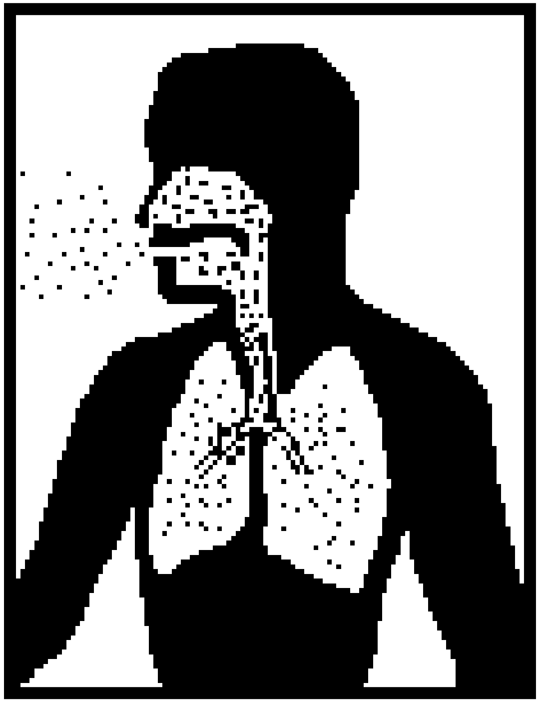
For the **inhalation pathway**, the concentration (C) of the chemical in air (in ug/m^3) at the point of exposure (called the exposure concentration or **EC**) can be used as a measure of exposure



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

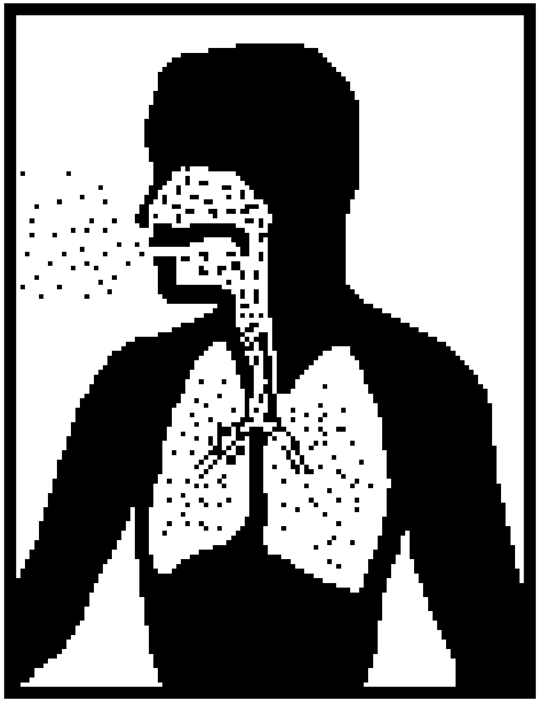
Focus on Inhalation

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 $\mu g/m^3$).
- 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:

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

- 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).**

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:

$$EC = (0.1 \times 80) + (0.5 \times 20) + (0.4 \times 10) = 22\ \mu g/m^3$$

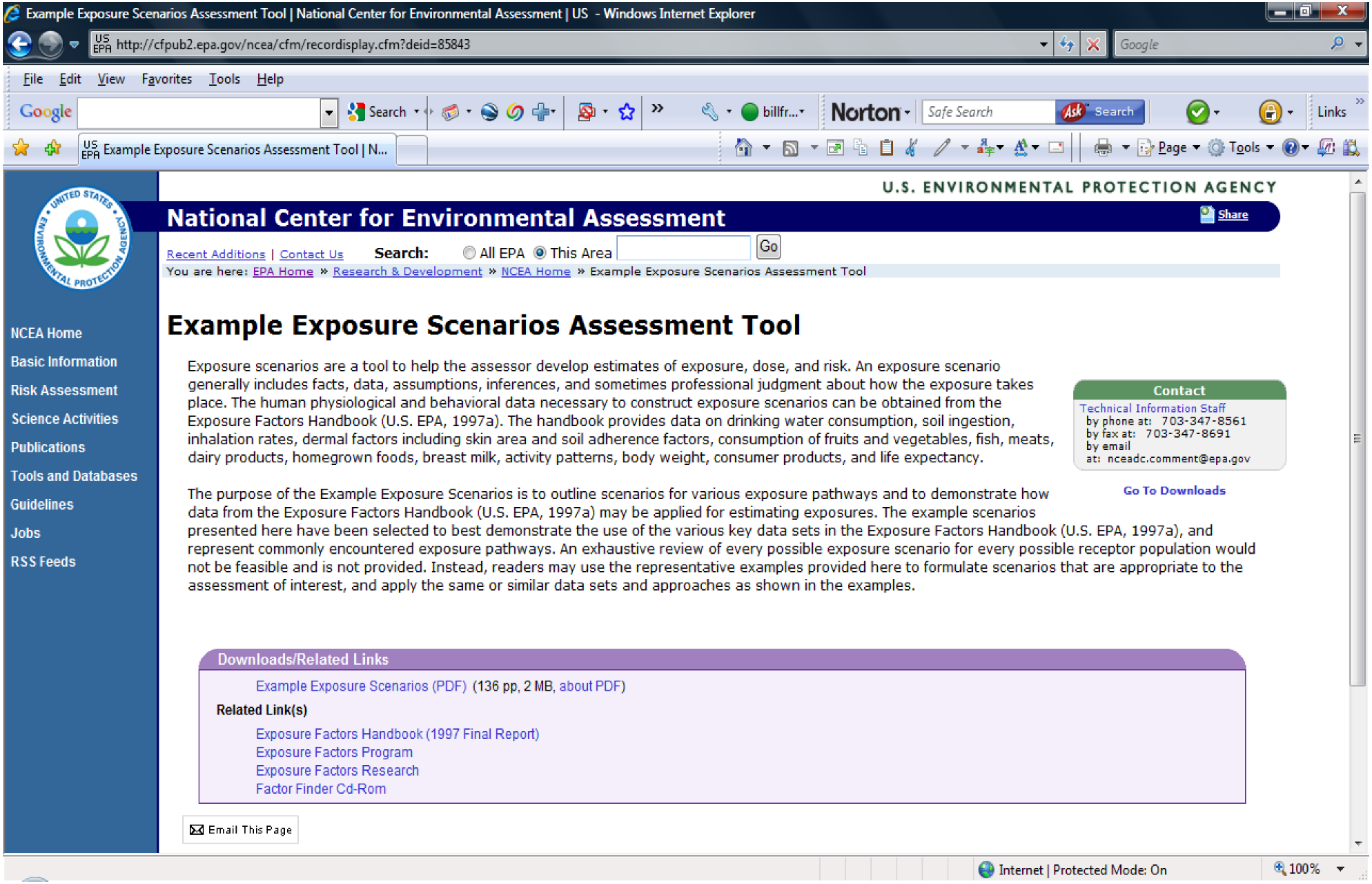
April 2004

EXAMPLE EXPOSURE SCENARIOS

http://cfpub2.epa.gov/ncea/cfm/recordisplay.cfm?deid=85843

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

Example Exposure Scenarios Assessment Tool Web site



National Center for Environmental Assessment

You are here: EPA Home » Research & Development » NCEA Home » Example Exposure Scenarios Assessment Tool

Example Exposure Scenarios Assessment Tool

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.

Contact

Technical Information Staff
by phone at: 703-347-8561
by fax at: 703-347-8691
by email
at: nceadc.comment@epa.gov

Go To Downloads

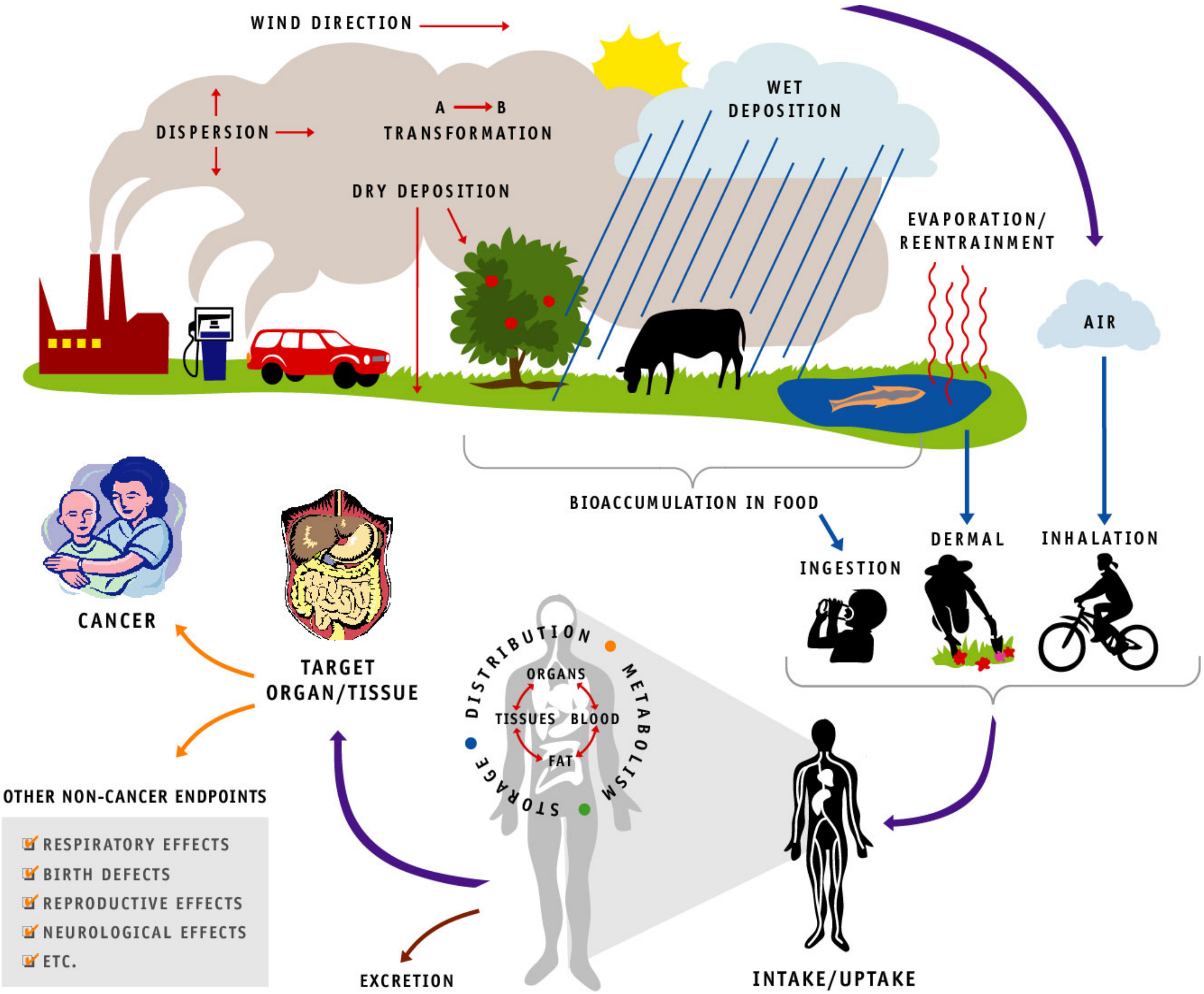
Downloads/Related Links

Example Exposure Scenarios (PDF) (136 pp, 2 MB, about PDF)

Related Link(s)

Exposure Factors Handbook (1997 Final Report)
Exposure Factors Program
Exposure Factors Research
Factor Finder Cd-Rom

Exposure and Effects from Air Toxics



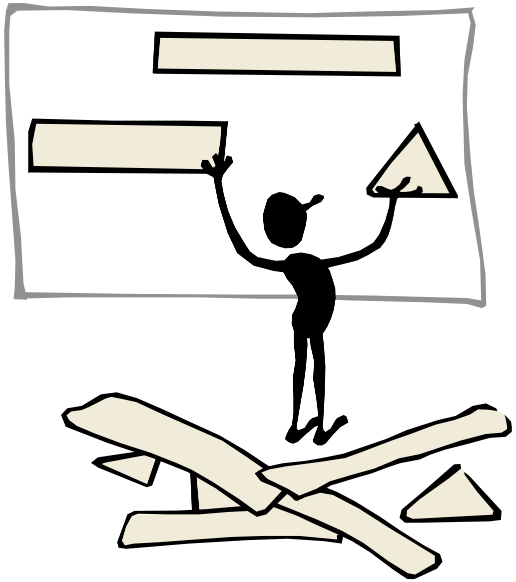
Exposure Assessment for Air Toxics

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

Air Toxics EA - The Process

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.

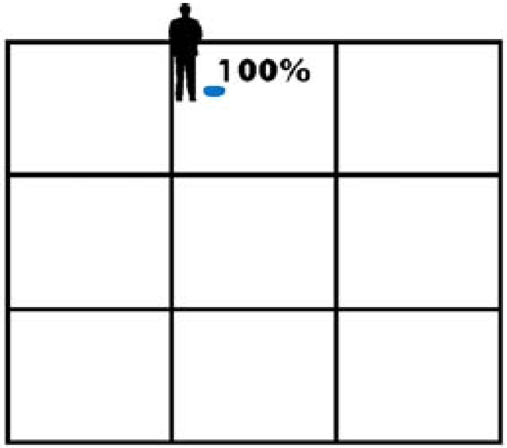
General Approaches to Derive Exposure Concentrations

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

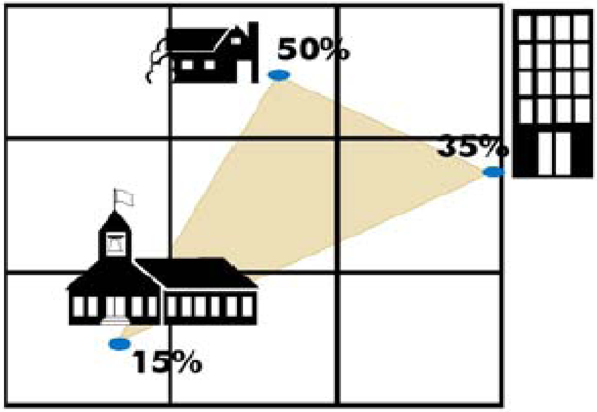
- *General Air Quality Assessment* and
- *Exposure Modeling*

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

Two General Approaches to Derive Exposure Concentrations



General Air Quality Assessment



Assessment Using Microenvironment Concept

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)*."

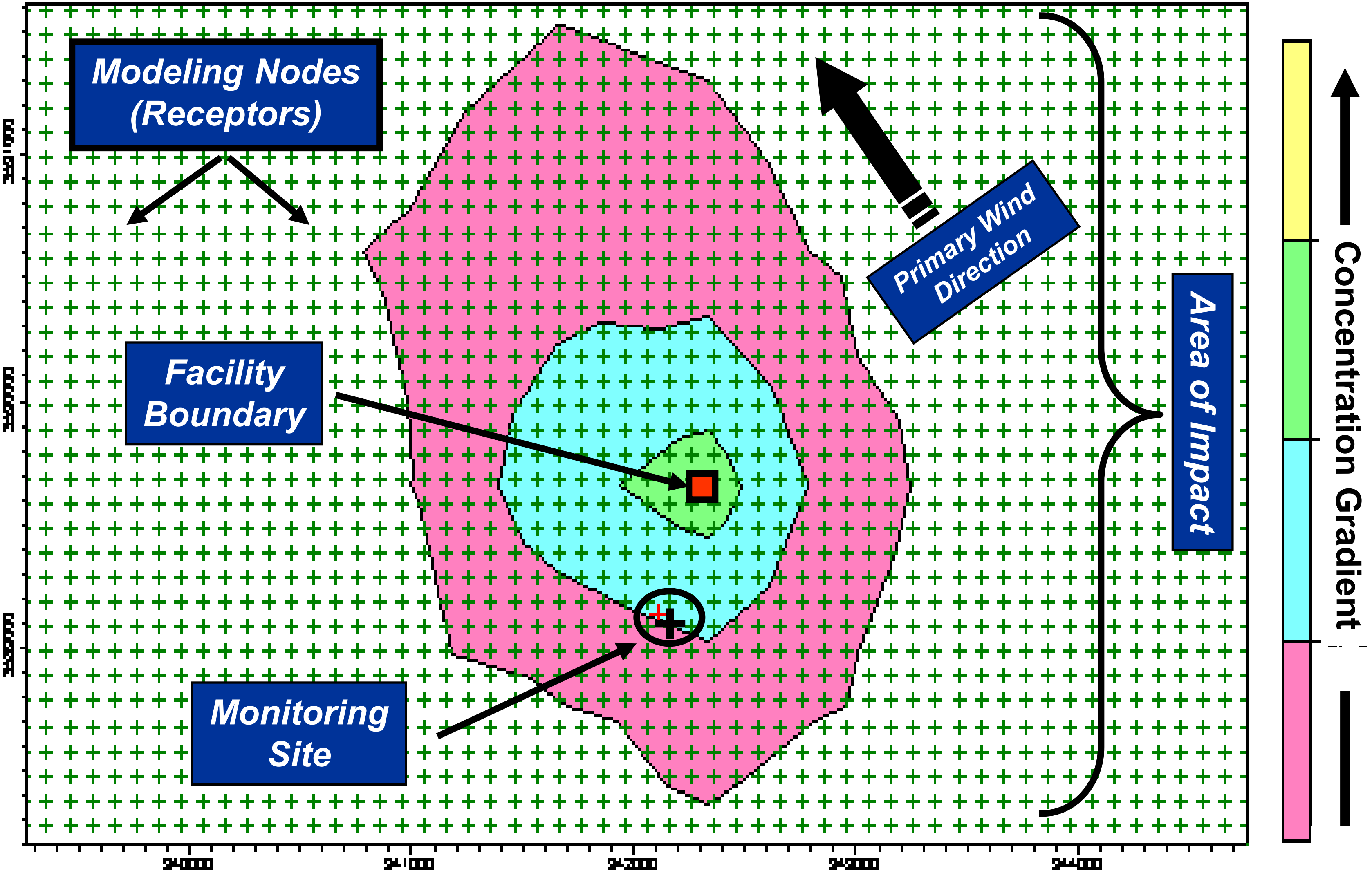
Common Ways to Estimate Exposure Concentrations(cont.)

- *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).*"

How do we determine the Exposure Concentration?

An example
for the inhalation pathway

Air Dispersion Modeling and/or Air Monitoring

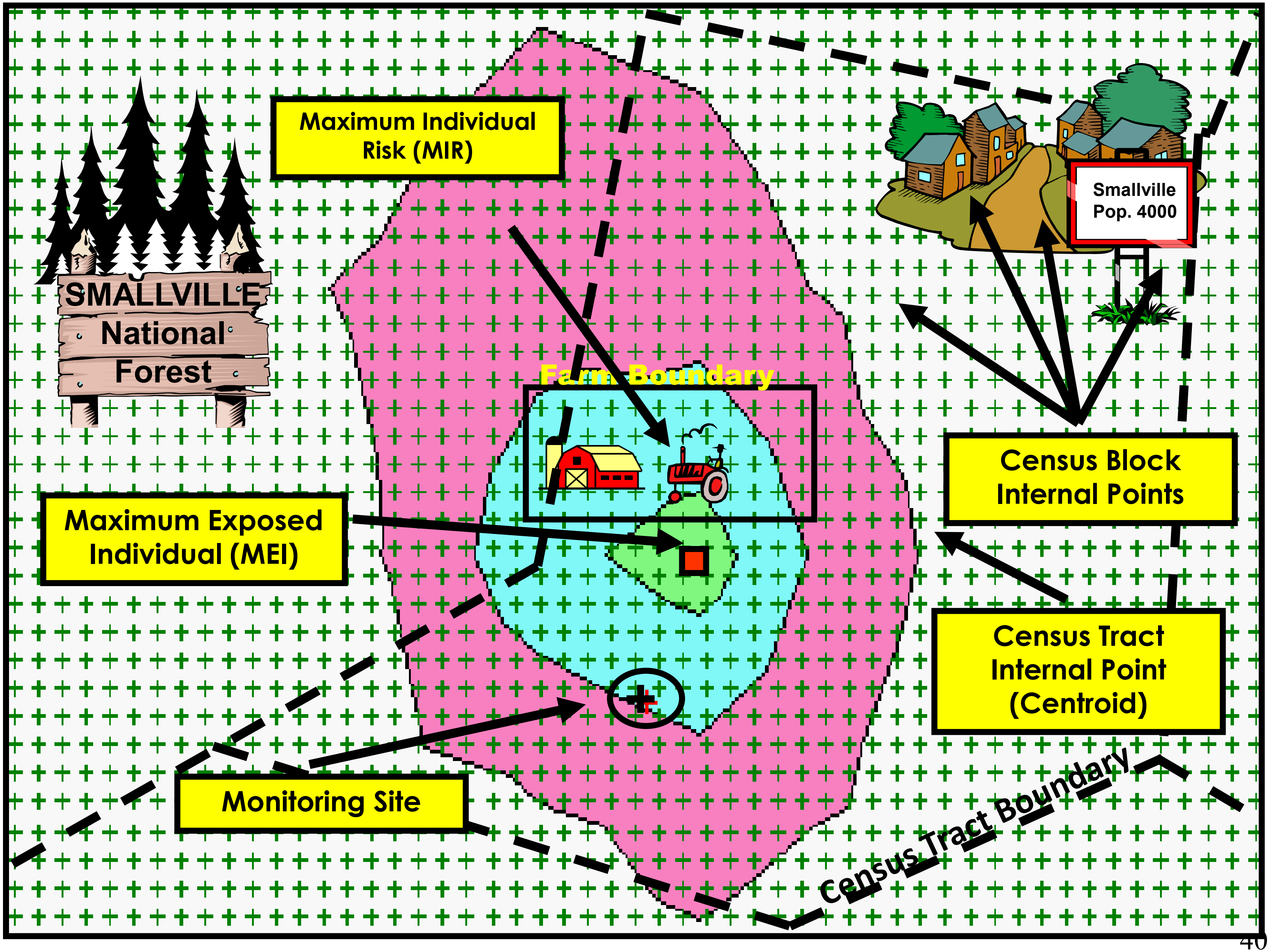


100 meter modeling grid

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).

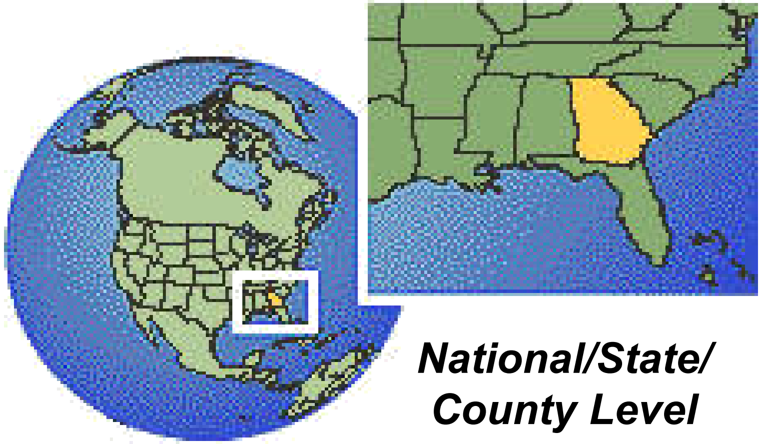
Which of the many points do we use to represent exposure concentration?



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



National/State/ County Level

Community Level

Neighborhood Level

Personal Level

Organ Level

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

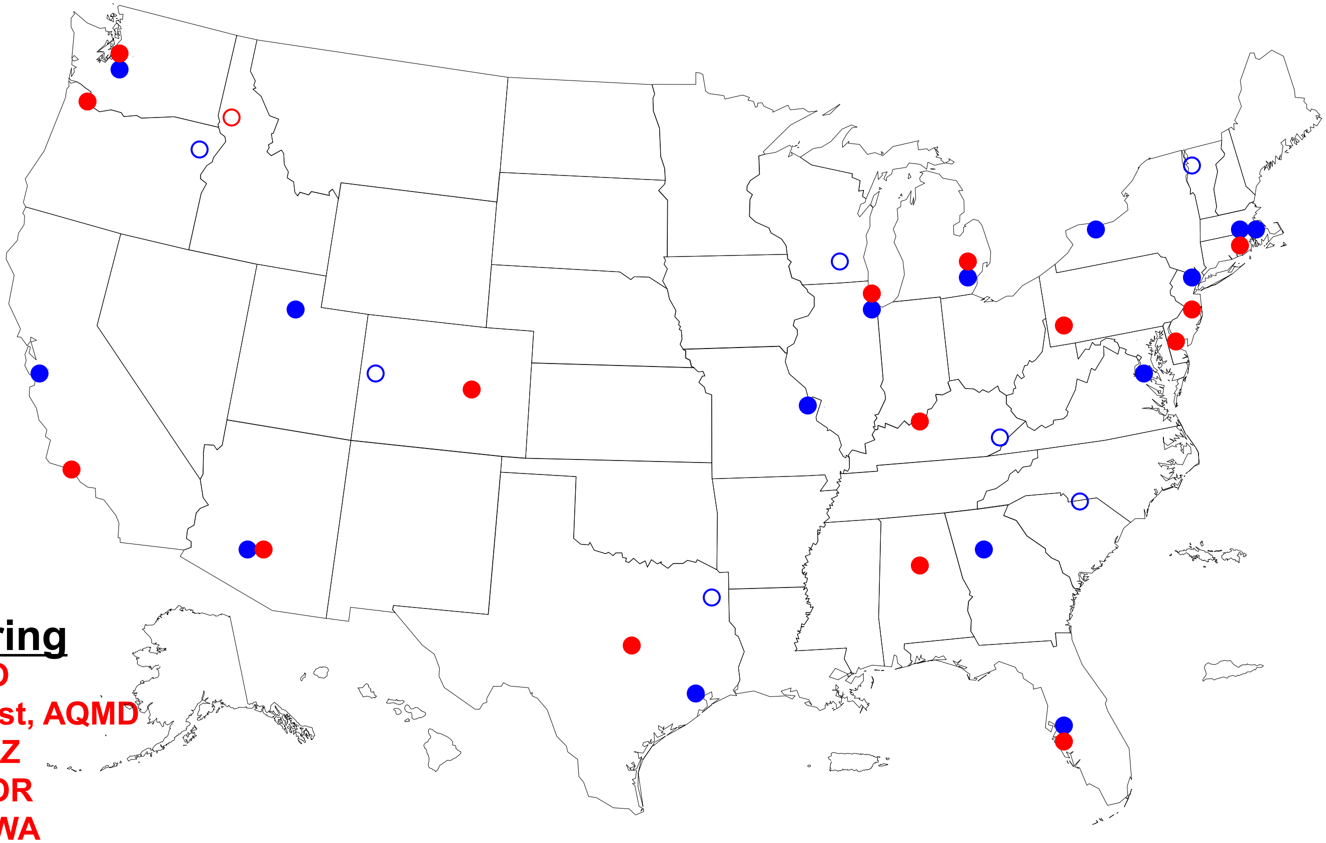
NATTS

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)

Community Monitoring

Chicago, IL
Birmingham, AL
Warwick, RI
Paterson City, NJ
Wilmington, DE
Louisville, KY
Detroit, MI
Austin, TX

Denver, CO
South Coast, AQMD
Phoenix, AZ
Portland, OR
Spokane, WA
Nez Perce, ID (Rural)
Hillsborough Count, FL
Allegheny County, PA



● Urban ○ Rural

http://www.epa.gov/ttnamti1/natts.html

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

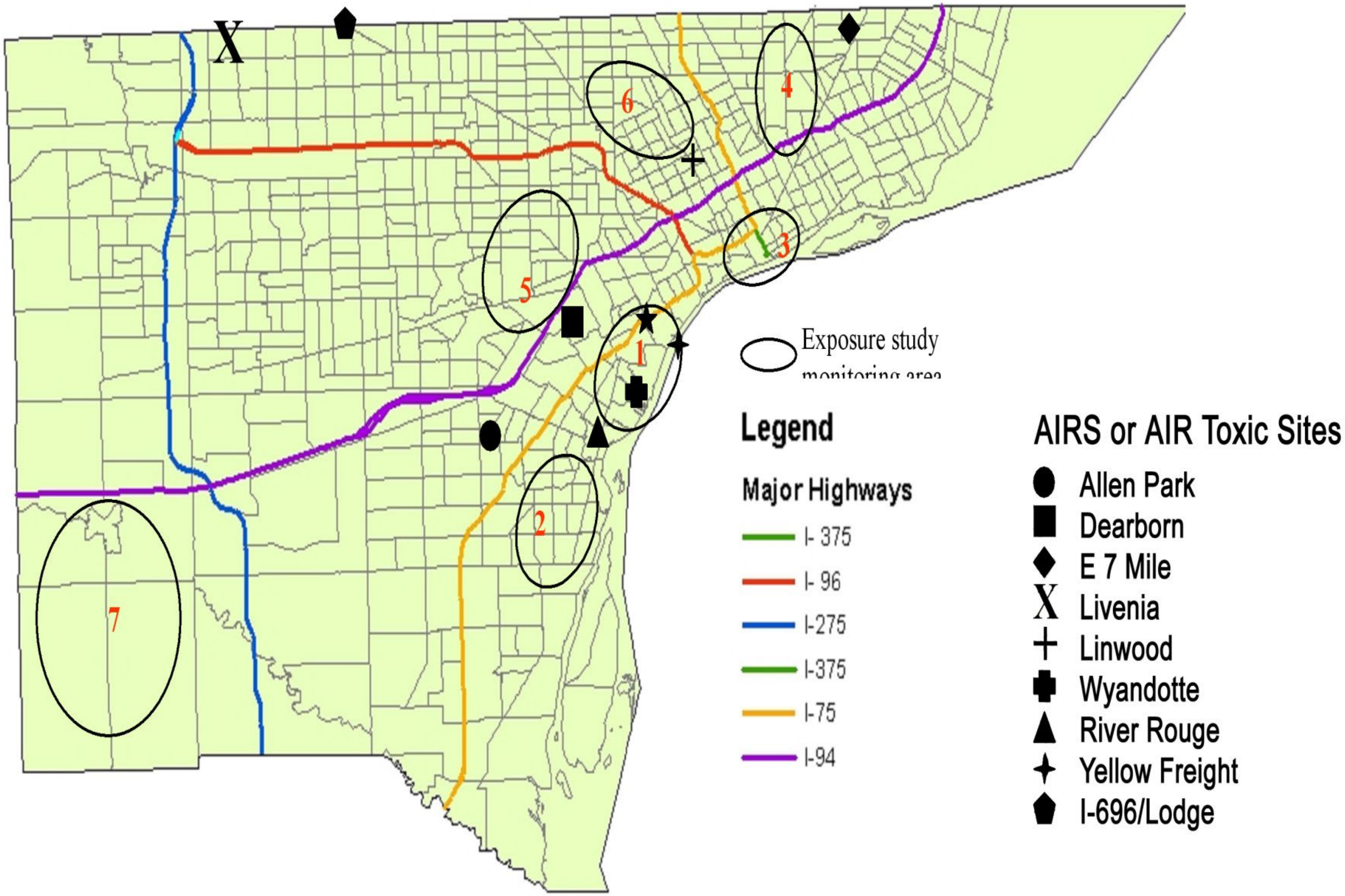
Detroit Exposure and Aerosol Research Study (DEARS)

- 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

http://www.epa.gov/ttn/atw/urban/mainwks.html

Air Quality and Exposure Modeling

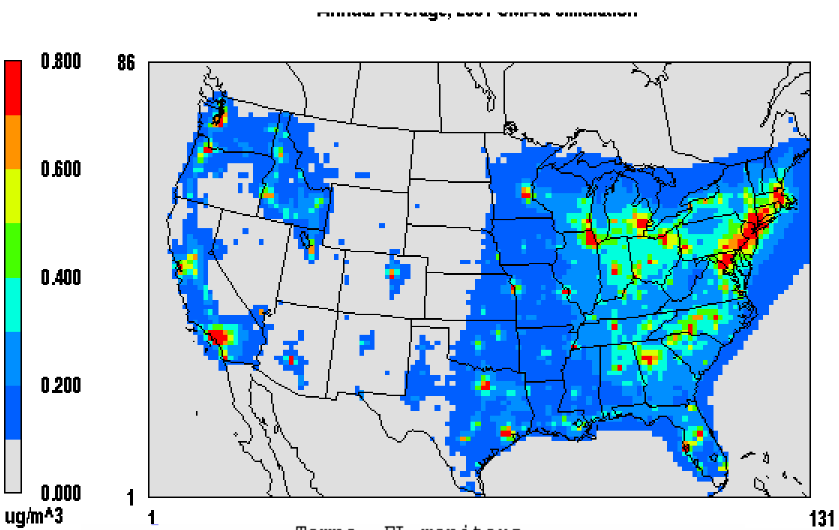
Enhanced EPA Modeling Tools

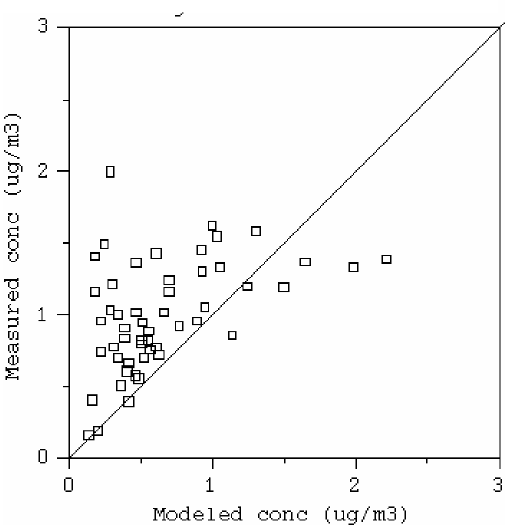
- Ambient Dispersion Models
  - Community Multiscale Air Quality (CMAQ)
- Exposure Models
  - Stochastic Human Exposure and Dose Simulation (SHEDS)
  - Total Risk Integrated Methodology (TRIM)
- Modeling Collaborations

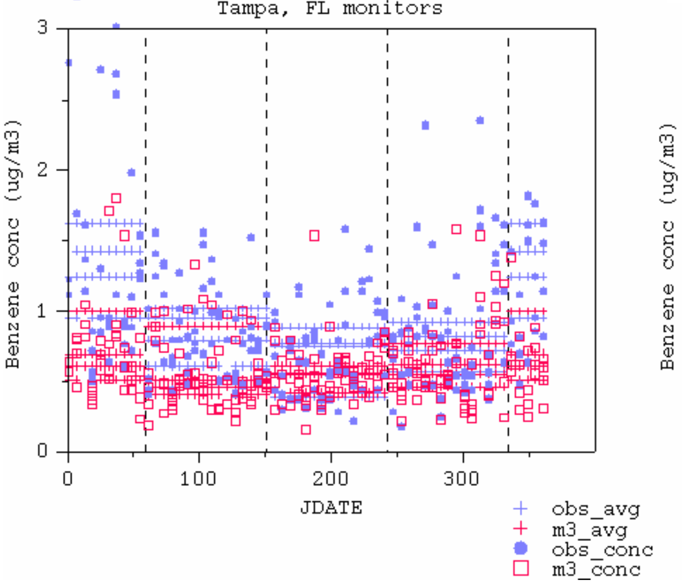
Community Multiscale Air Quality (CMAQ) Model

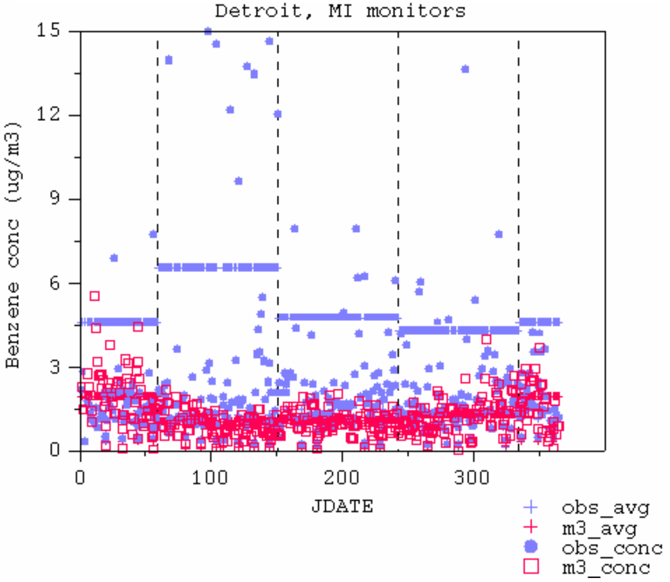
- Extended the capability of CMAQ to Air Toxics
  - Completed annual (2001 CY) simulation of 20 HAPs
  - Simulations especially relevant for air toxics with significant secondary formation, e.g., formaldehyde, acetaldehyde and acrolein.
- Community-scale modeling
  - Model HAP concentrations at high 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.

CMAQ Benzene Results







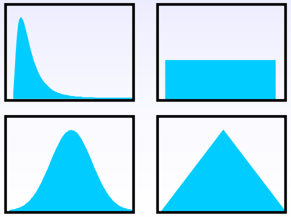


SHEDS Model Structure

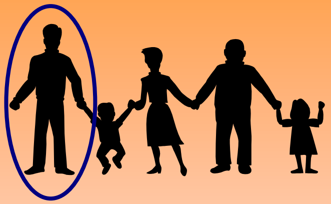
Input Databases

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

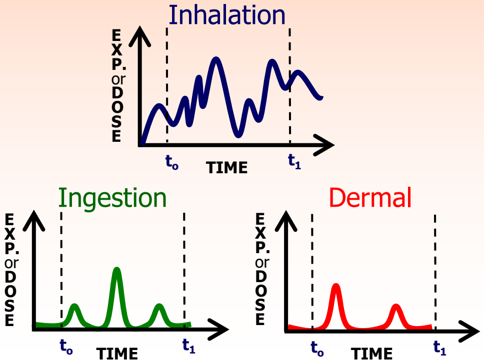
Exposure Factor Distributions



Algorithms

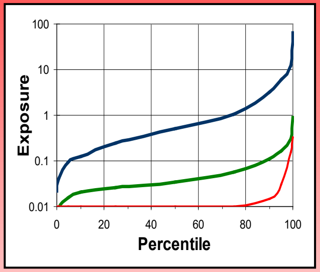


- Calculate Individual Exposure/Dose Profile

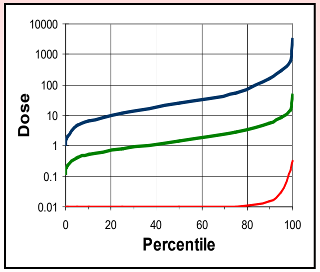


Output

- Population Exposure



- Population Dose



Stochastic Human Exposure and Dose Simulation (SHEDS) Model

- A model for improving estimates of human exposure and dose to multimedia, multipathway pollutants
- SHEDS can:
  - Predict population exposures and dose
  - Characterize variability and 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 (initial)
  - Aldehydes (planned)
  - Arsenic (planned)

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

http://www.epa.gov/ncea/efh/pdfs/efh-front-gloss.pdf

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.**
- **http://www.epa.gov/heds/index.htm**

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.htm

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	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)

- 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)

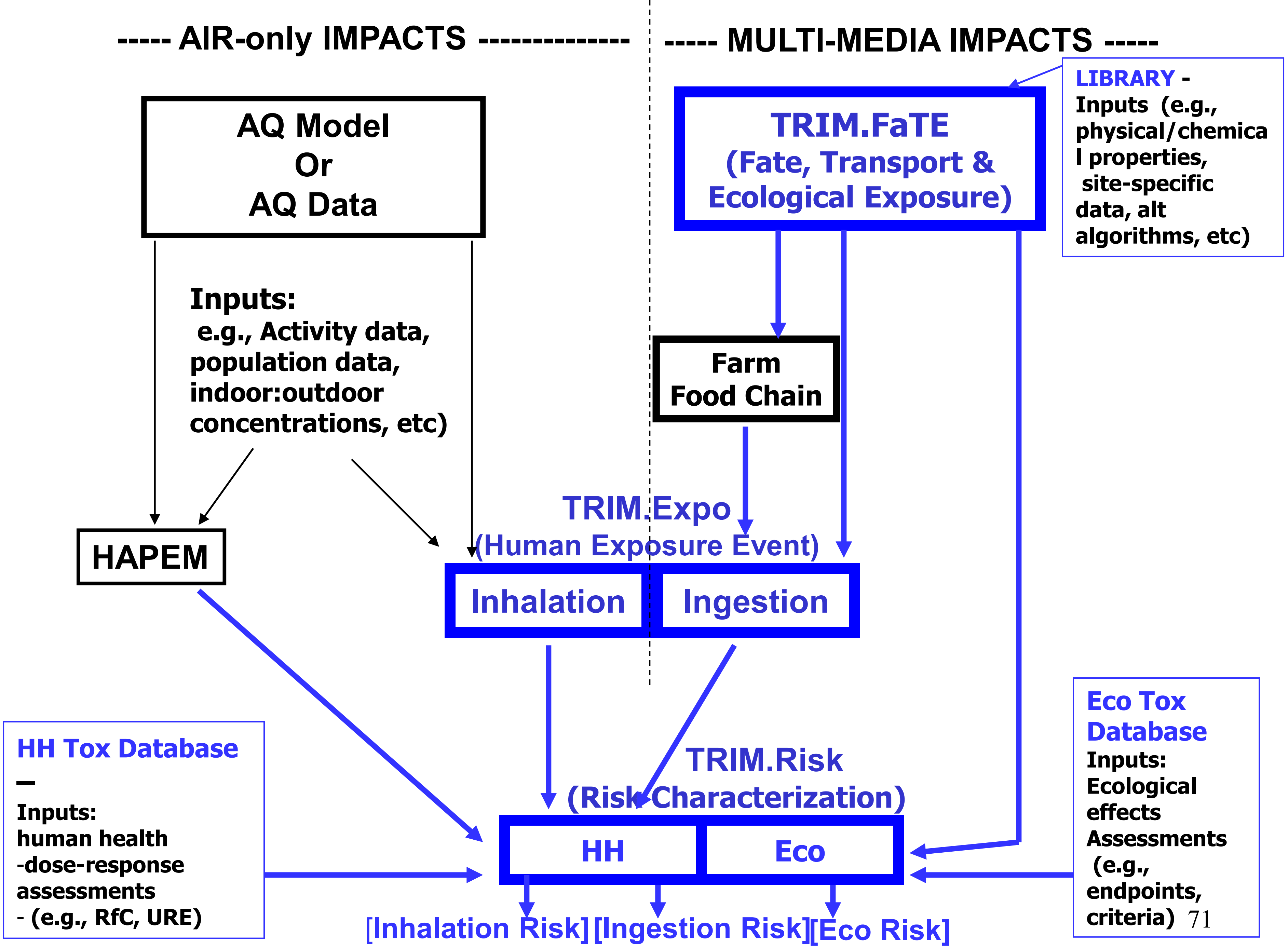
The HEM contains:

(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.

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

- The HAPEM 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.
- Two versions of this model are currently available; HAPEM5 and HAPEM6.



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

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

AQ Model
Or
AQ Data

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

TRIM.FaTE
(Fate, Transport & Ecological Exposure)

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

Farm
Food Chain

HAPEM

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, ..

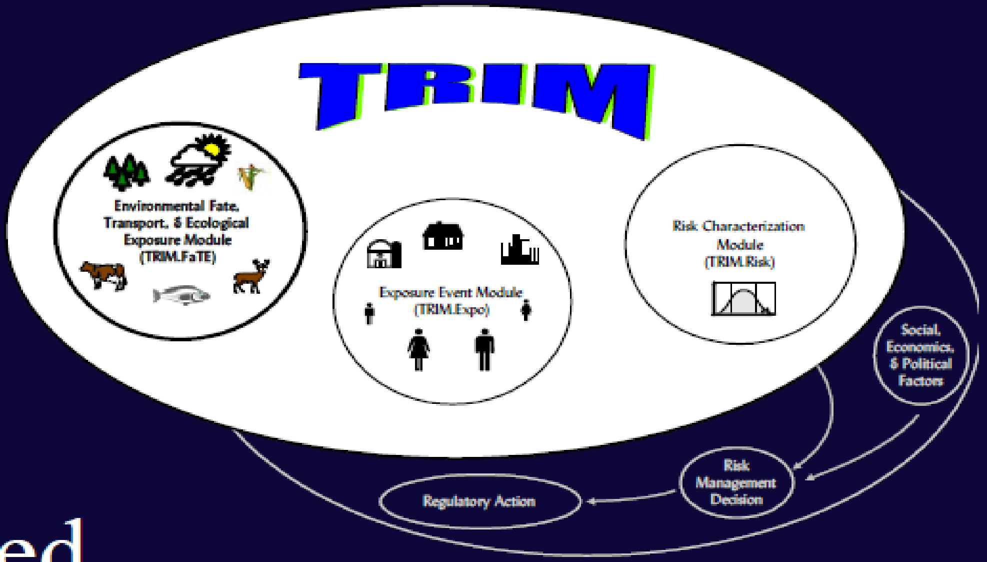
Total Risk Integrated Methodology

Total

Risk

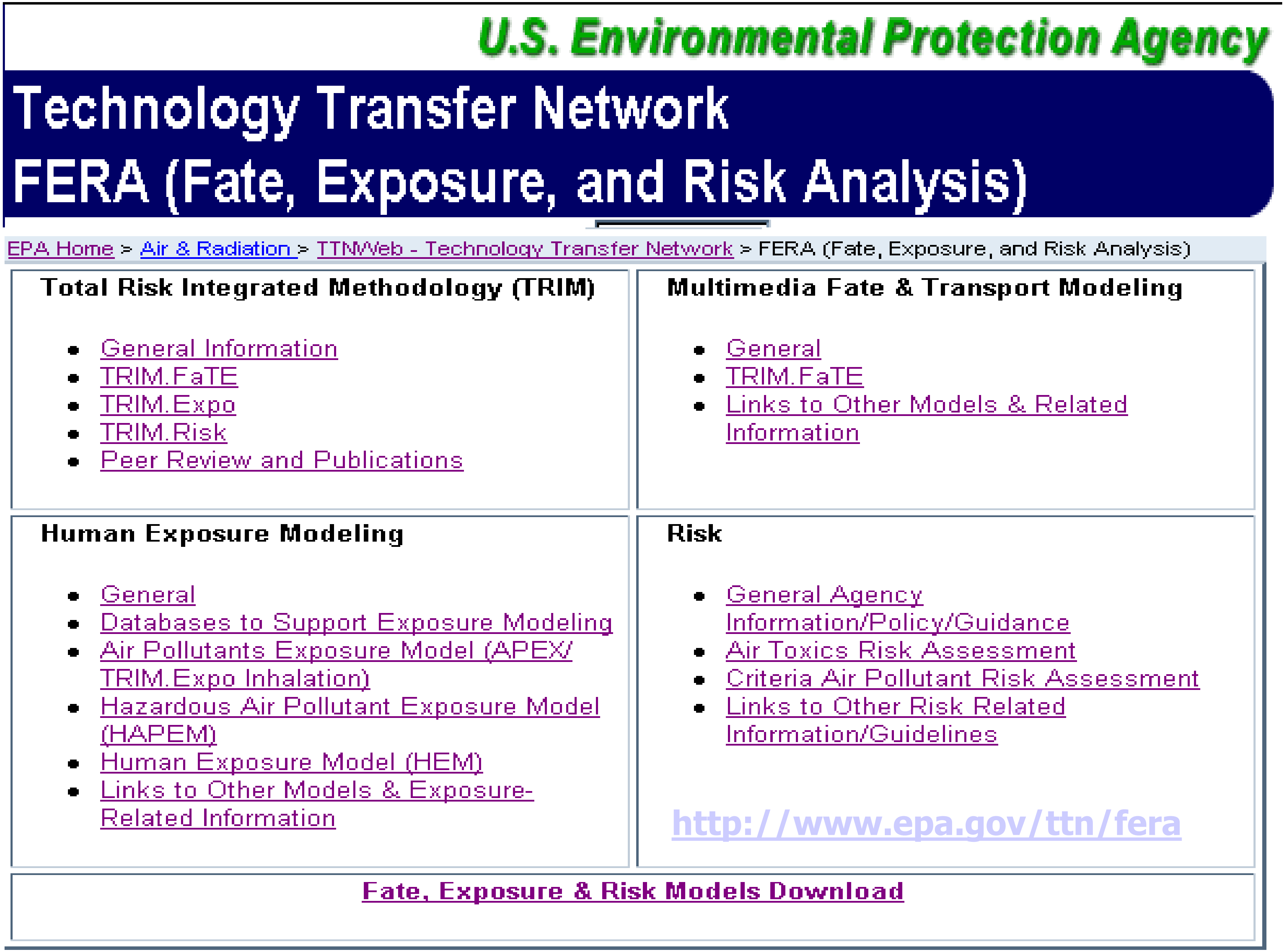
Integrated

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



U.S. Environmental Protection Agency

Technology Transfer Network
FERA (Fate, Exposure, and Risk Analysis)

EPA Home > Air & Radiation > TTNWeb - Technology Transfer Network > FERA (Fate, Exposure, and Risk Analysis)

Total Risk Integrated Methodology (TRIM)

- General Information
- TRIM.FaTE
- TRIM.Expo
- TRIM.Risk
- Peer Review and Publications

Multimedia Fate & Transport Modeling

- General
- TRIM.FaTE
- Links to Other Models & Related Information

Human Exposure Modeling

- General
- Databases to Support Exposure Modeling
- Air Pollutants Exposure Model (APEX/ TRIM.Expo Inhalation)
- Hazardous Air Pollutant Exposure Model (HAPEM)
- Human Exposure Model (HEM)
- Links to Other Models & Exposure-Related Information

Risk

- General Agency Information/Policy/Guidance
- Air Toxics Risk Assessment
- Criteria Air Pollutant Risk Assessment
- Links to Other Risk Related Information/Guidelines

http://www.epa.gov/ttn/fera

Fate, Exposure & Risk Models Download

Comparison of Exposure Assessment Tools

	PRO	CON
Ambient Monitoring	-"True" measure of ambient concentration	- Spatial and temporal gaps - Costly to monitor everywhere - Surrogate for personal exposure
Personal Monitoring	- "True" measure of personal exposure	- Spatial and temporal gaps - Can't monitor everyone all the time (costs and personal inconvenience)
Ambient Modeling	- Good spatial and temporal coverage - Relatively low cost	- Uncertainty - Surrogate for personal exposure
Human Exposure Modeling	- Estimates true human exposure - Relatively low cost	- Uncertainty
The best approach is to utilize a combination of the above.		

Chapter Seven
Toxicity Assessment of Air Toxics

Toxicity Assessment

Hazard Identification:

-Human & Animal Data

-Weight of Evidence

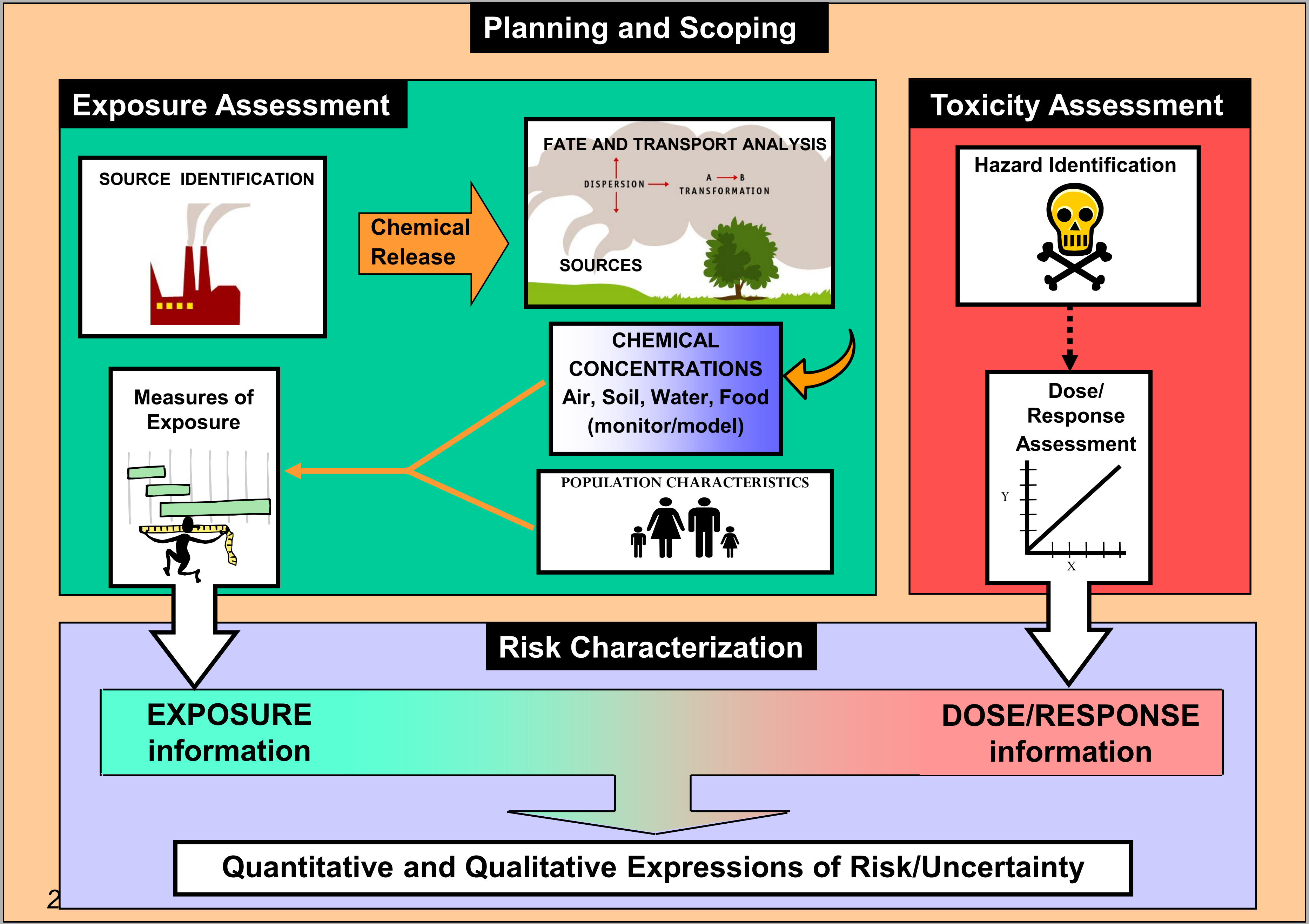
Dose Response:

-Unit Risk

-Reference Concentration

By: Louis DeRose

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

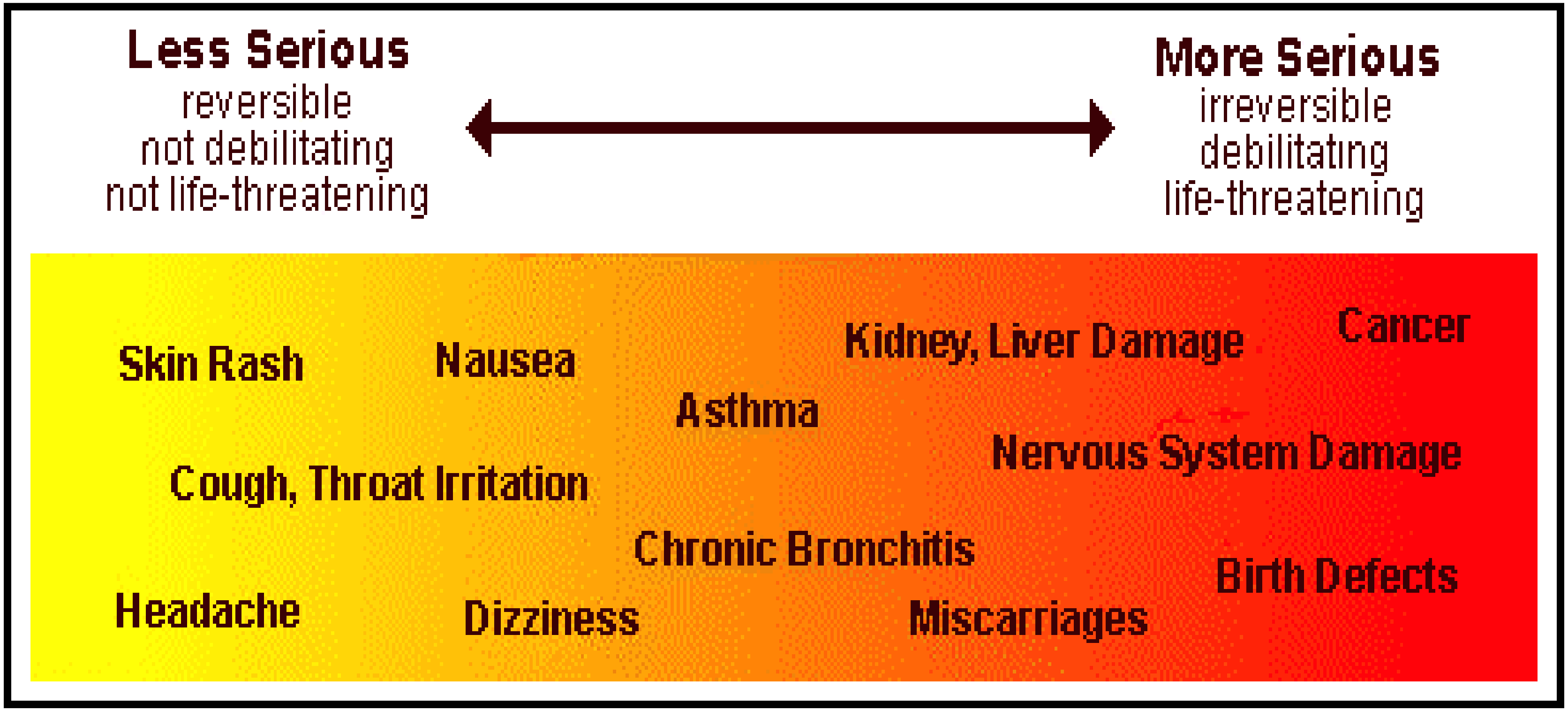
Quantitative and Qualitative Expressions of Risk/Uncertainty

Toxicity Assessment: Two Parts

- Hazard Identification determines whether exposure to a chemical *can cause adverse health effect* (e.g., cancer, birth defects, etc.) & looks at the *strength of evidence of causation & circumstances* that cause these effects (e.g., long term vs. short term exposure, animal vs. human data, inhalation/ingestion).
  - Very often little new toxicological evaluation of primary data is required.
- 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).

Hazardous Identification: 2 Steps

- <u>Review & analyze toxicity data</u>: to see if exposure to a chemical can cause particular health effects, &
- <u>Weigh the evidence</u>: the strength of the evidence that the chemical causes various toxic effects.



Less Serious
reversible
not debilitating
not life-threatening

More Serious
irreversible
debilitating
life-threatening

Skin Rash
Nausea
Kidney, Liver Damage
Cancer
Asthma
Nervous System Damage
Cough, Throat Irritation
Chronic Bronchitis
Birth Defects
Headache
Dizziness
Miscarriages

Effects Considered by Hazard Identification

Biological Effects

- Lethality (LD_{50}, LC_{50})
- Impairment of normal biological function (e.g., liver damage)
- Heritable genetic change
- Increases/decreases in species population size or range
- Health/productivity of ecosystems
- Etc.

Non-Biological Effects

- Reduced visibility from airborne particulates
- Damage to historic structures by air pollutants
- Climate change from global warming

Numerous Biological Endpoints

Non-Cancer

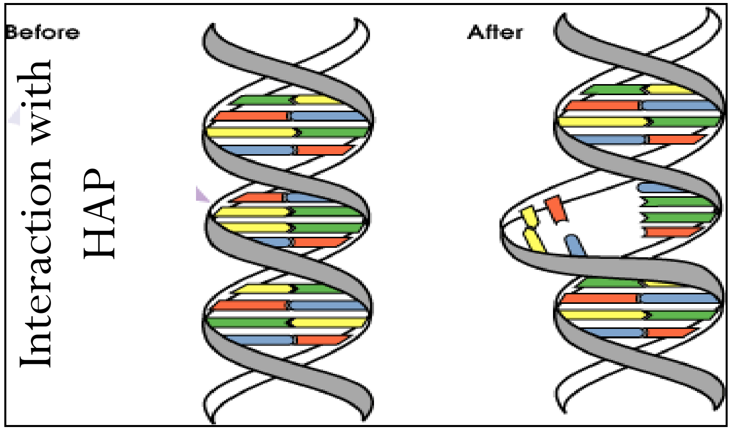
- **Reproductive,developmental, neurological disorders**
- **Immunologic effects**
- **Acute effects (edema, CNS depression)**
- **Various other systemic effects (e.g., liver, kidney, lung damage)**

→ Multiple Adverse Endpoints

Cancer

- **Mutations**
- **DNA damage**
- **Etc.**

→ Uncontrolled Growth of Cells



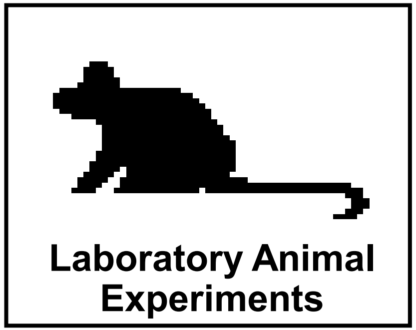
Step One: Hazard Identification

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

Epidemiological Studies

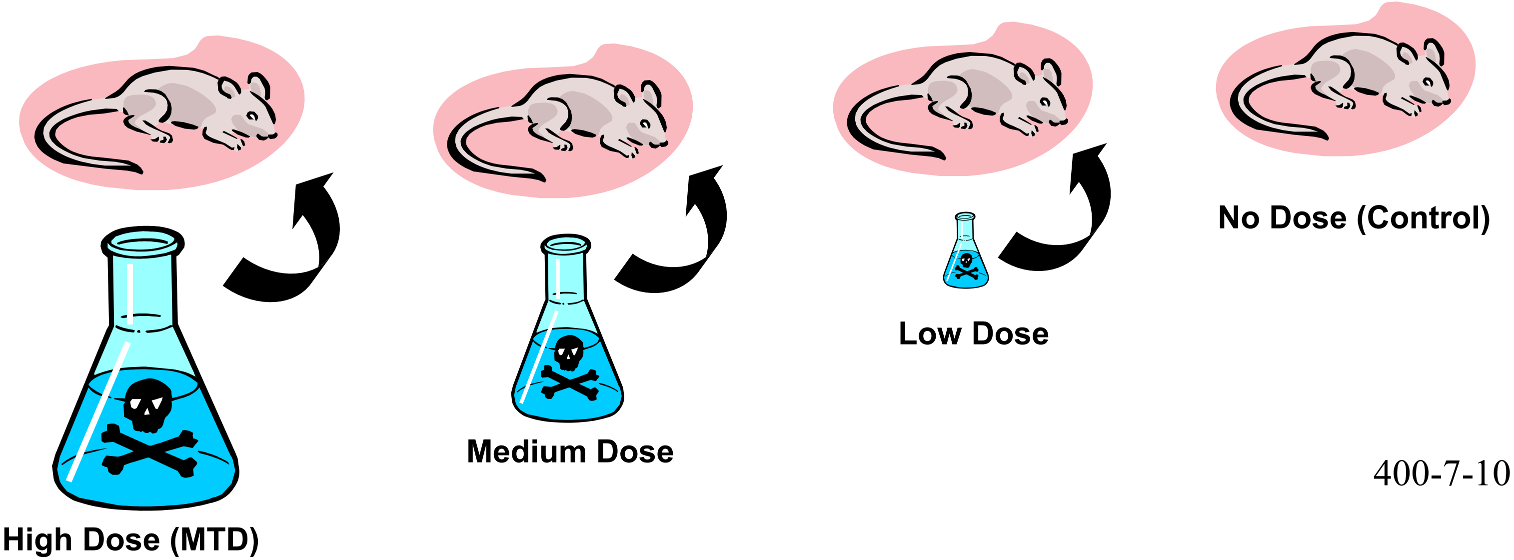
- Controlled exposure studies (usually occupational i.e. asbestos workers)
  - Exposure concentrations & durations are known
  - Usually limited to acute exposure durations
- Accidental exposure studies (i.e. Bhopal)
  - Exposure concentrations usually high
  - Effects usually acute rather than chronic
- Advantages: animal to human extrapolation not necessary & uses real exposure concentrations
- Disadvantages: no control over exposure amount or exposure to other toxins or lifestyle differences
  - 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"

Example: Cancer Rodent Studies

- Two species, both sexes (usually rats and mice)
- At least 50 animals in each group
- Expose from ~6 weeks through full lifespan (~24 mo.)
    - Dose at Maximum Tolerated Dose (MTD), fractions of MTD, and control (no dose)
    - Route of exposure similar to human exposure
- Observe outcomes (animals are sacrificed)



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

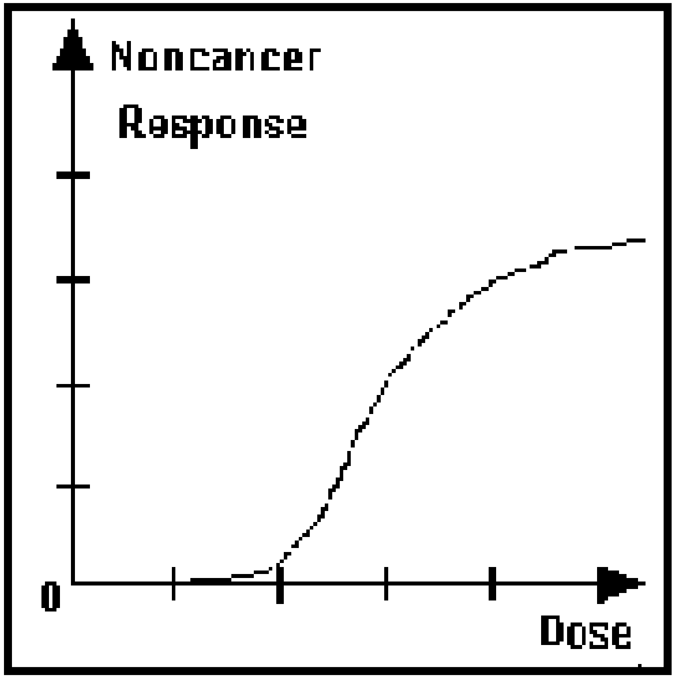
EPA's New WOE Scheme for Carcinogens

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**

Step Two: Dose-Response Assessment

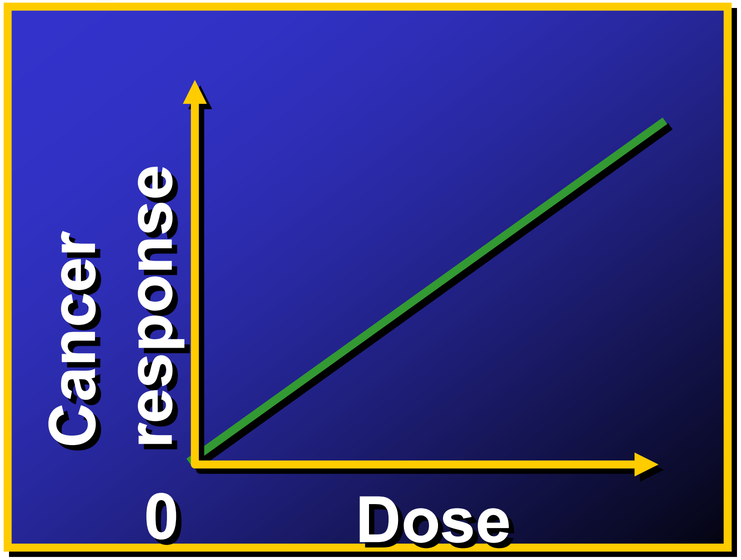
- Now that we've established that a chemical is toxic…
- We need to understand how much dose gives how much response (how potent is the chemical?)



Dose-Response Assessment

Cancer Risk

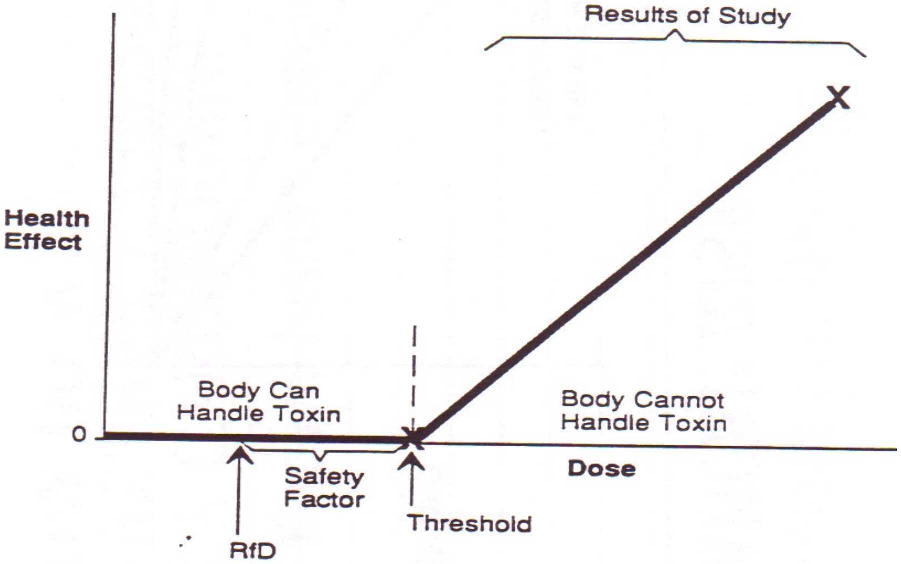
- **Non-threshold:** <u>no</u> exposure is without risk



- **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 Assessment

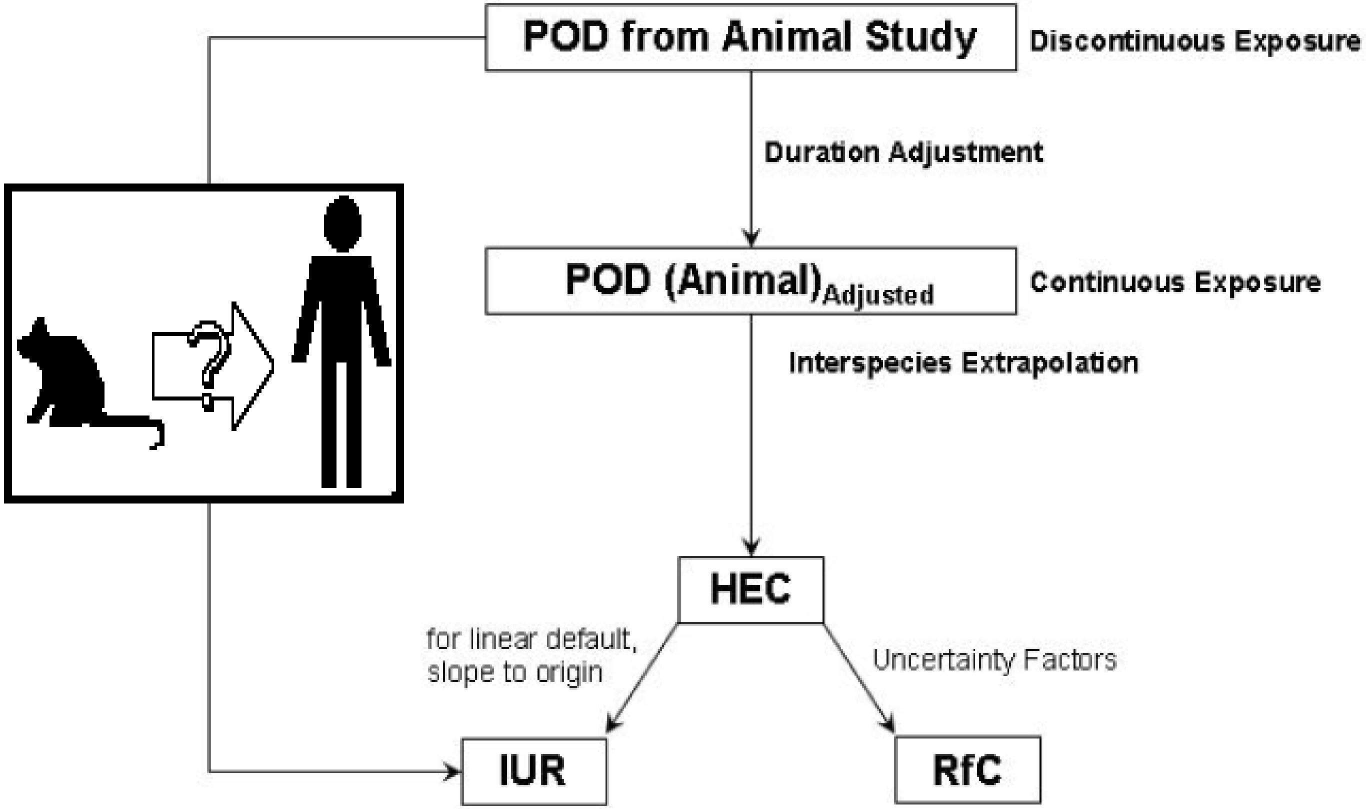
- Exposure: amount of agent *near where it enters* the body (via: inhalation, ingestion, dermal absorption)
- Dose: amount that *actually enters* the body
- For inhalation, EPA's *derivation of exposure concentration–response values* are derived from exposure concentration, dose and dosimetry (how the body handles a chemical once its inhaled).
- Adjustments made in order to calculate the "human equivalent concentration" (HEC)
  - *Duration adjustment*: (animal inhalation exposures only about 6 hrs/day, 5 days/wk must be adjusted to continuous inhalation exposure)
  - *Interspecies adjustments*: compensate for differences between humans & lab animals

Interspecies Adjustments

- Differences in exposure route (orally or inhaled)
- Differences in size & life spans
- Differences in pharmacokinetics (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)

Pesticide	**Rabbit**	**Monkey**	**Man**
DDT	46.3%	1.5%	10.4%
Lindane	51.2%	16.0%	9.3%
Parathion	97.5%	30.3%	9.7%

Deriving an Inhalation Unit Risk (IUR) & Reference Concentration (RfC) from an Animal Study



POD from Animal Study

Discontinuous Exposure

Duration Adjustment

POD $(\text{Animal})_{\text{Adjusted}}$

Continuous Exposure

Interspecies Extrapolation

HEC

for linear default,
slope to origin

Uncertainty Factors

IUR

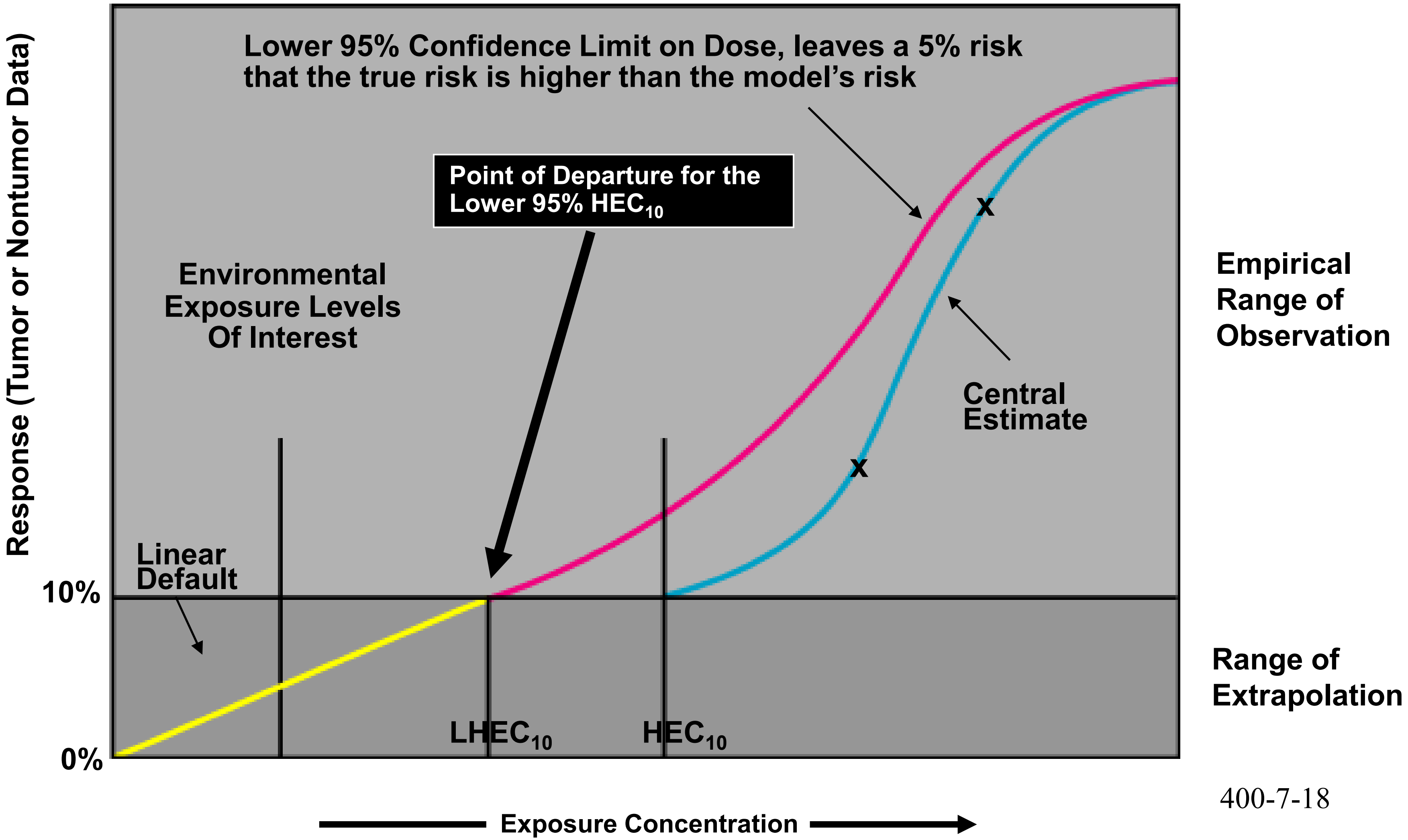
RfC

HEC – human equivalent concentration

POD – point of departure: is an estimated dose near the low end of the observed range without extrapolation to lower doses.

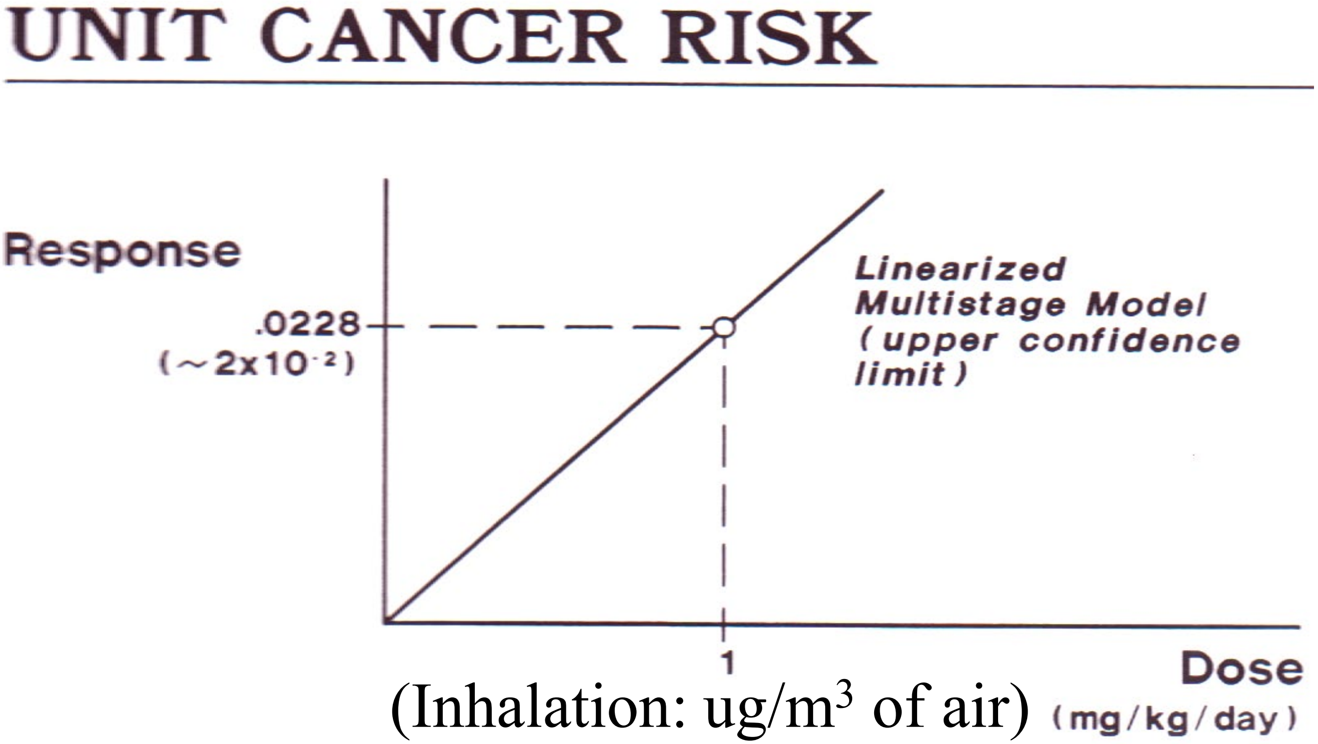
Dose-Response - Cancer

High to low dose linear extrapolation from POD to 0,0 (non-threshold)

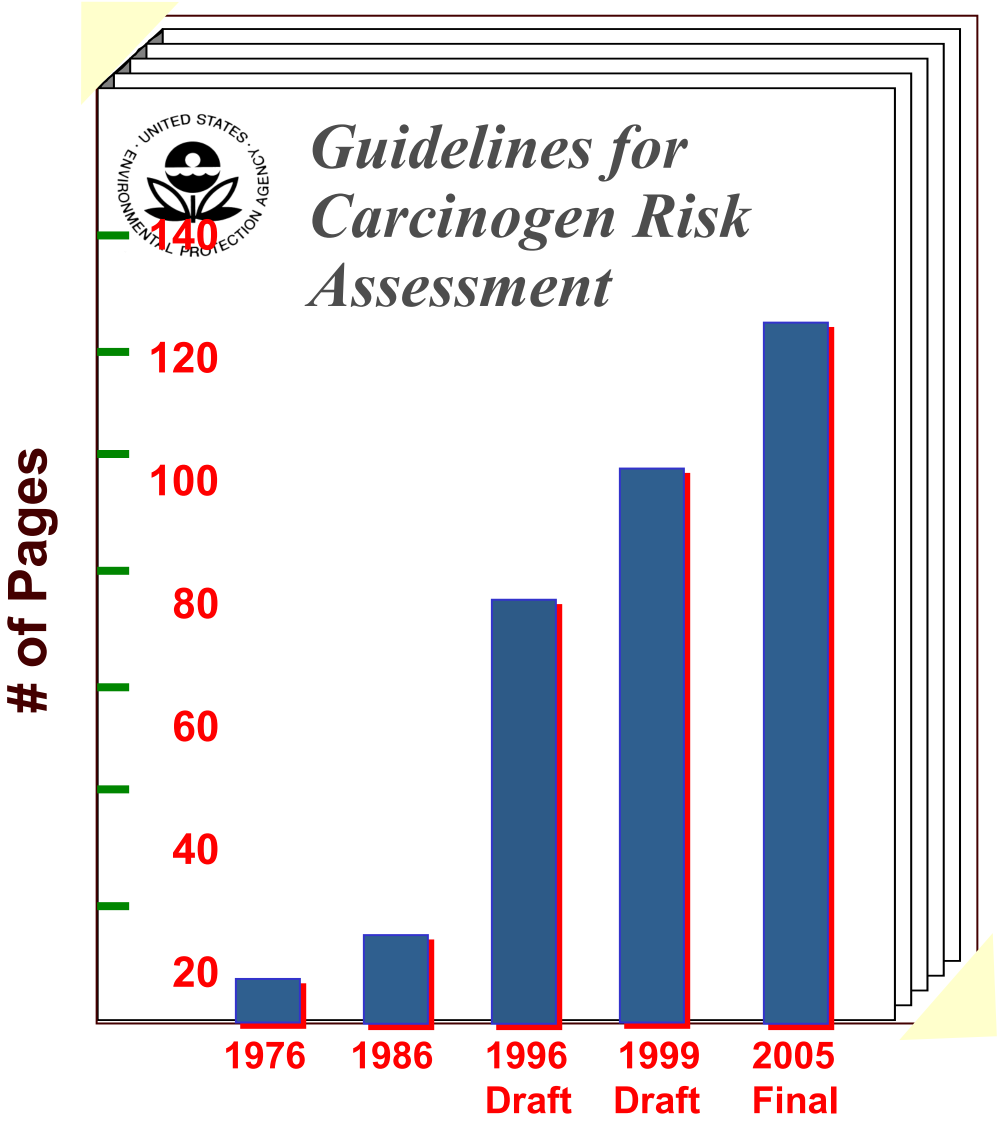


Dose-Response: Carcinogens

- 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: ug/m^3 of air)



As toxicology and risk assessment advance, the guidelines have grown.

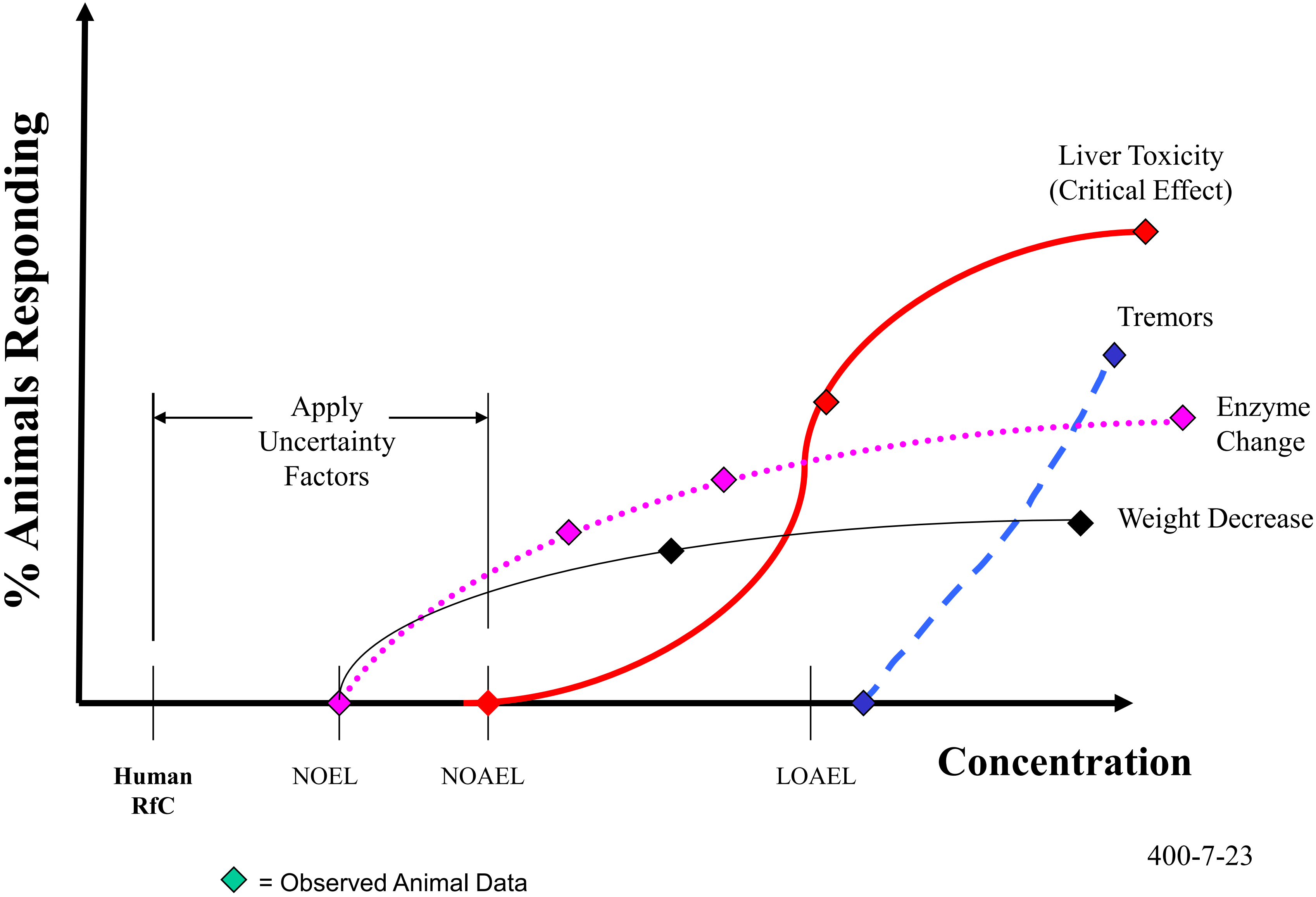
Dose-Response: Non-carcinogens

- EPA assumes that there is a *threshold* concentration - below which no observable adverse effect will occur
- *Reference dose or concentration* 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: *calculation of the HEC*
  - Carcinogen: POD_{HEC}
  - Non-carcinogenic: $NOAEL_{HEC}$ or $LOAEL_{HEC}$ or (benchmark concentration level) BMCL
    - BMC approach involves fitting various mathematical models 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
- RfC methodology from: USEPA 1994 *Methods for Derivation of Inhalation Reference Concentrations and Application of Inhalation Dosimetry*

Dose/Response - Noncancer



Inhalation RfC

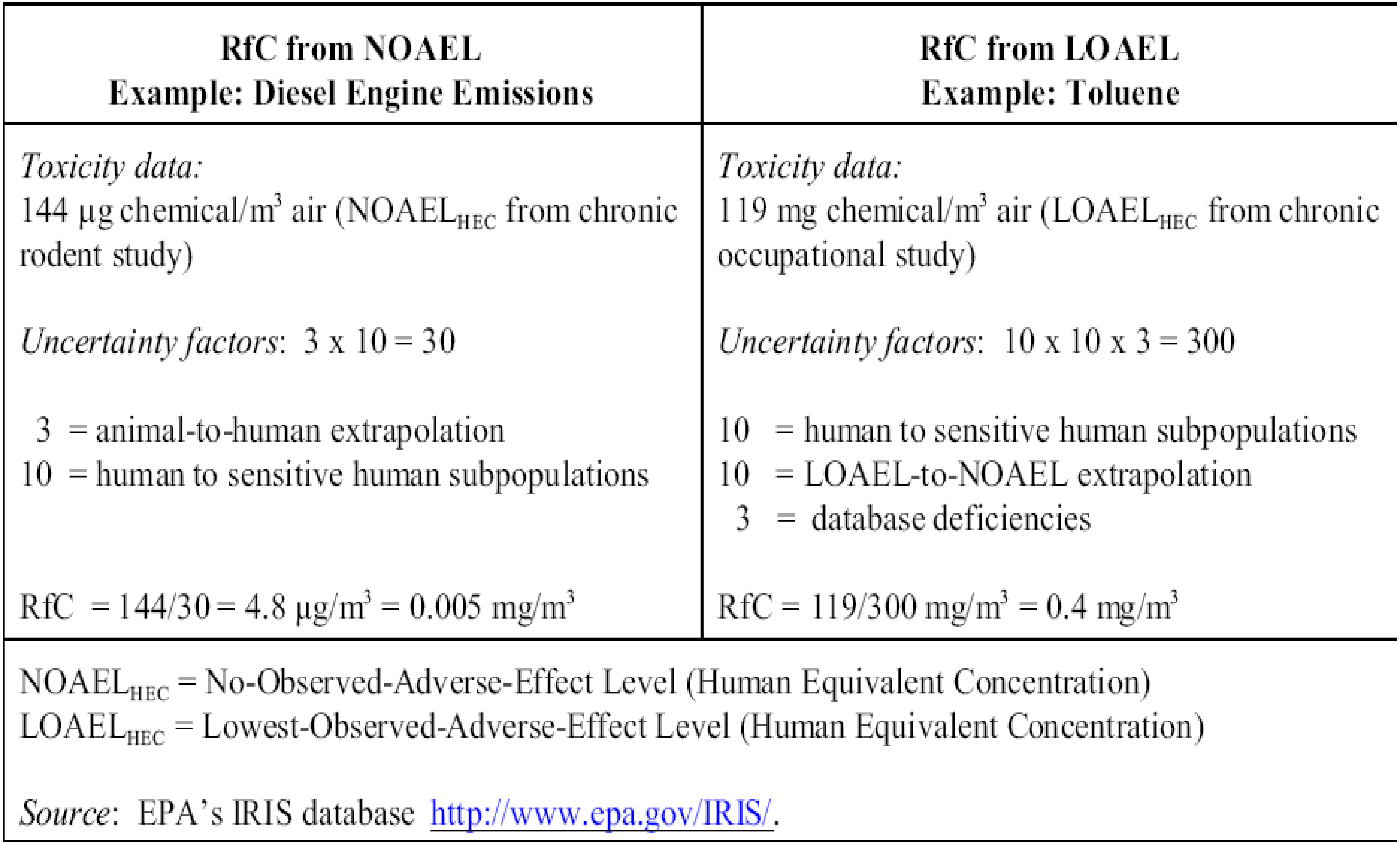
$$\boxed{RfC\,(mg/m^3) = \frac{NOAEL \text{ or } LOAEL\ (HEC)}{UF_1 \, x \, UF_2 \ \ldots \ \text{x} \ UF_i}}$$

Uncertainty Factor Criteria	**UF**
• **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 information.**

*** Some older RfCs may have applied a modifying factor (MF) in addition to the traditional UFs (when another it felt another UF was needed).**

Example RfC Calculation



RfC from NOAEL **Example: Diesel Engine Emissions**	**RfC from LOAEL** **Example: Toluene**
Toxicity data: 144 µg chemical/m^3 air (NOAEL$_{HEC}$ from chronic rodent study)	*Toxicity data:* 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 10 = human to sensitive human subpopulations	10 = human to sensitive human subpopulations 10 = LOAEL-to-NOAEL extrapolation 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

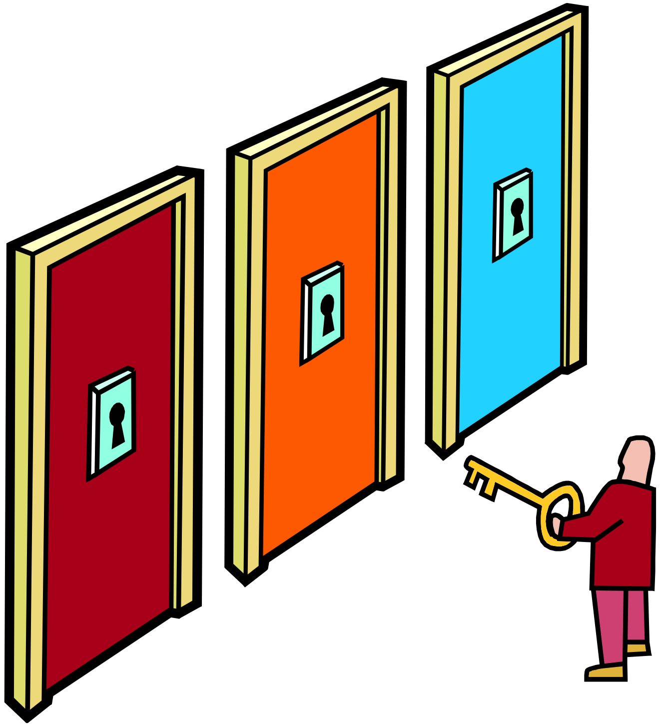
NOAEL$_{HEC}$ = No-Observed-Adverse-Effect Level (Human Equivalent Concentration)
LOAEL$_{HEC}$ = Lowest-Observed-Adverse-Effect Level (Human Equivalent Concentration)

Source: EPA's IRIS database http://www.epa.gov/IRIS/.

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

Sources of Toxicity Data

For air toxics risk assessments…

OAQPS has developed and maintains a list of recommended chronic toxicity values for each of the HAPs

- **Inhalation IURs and RfCs**
- **Oral slope factors and RfDs**

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Also in Appendix C of the 1st of the 3 volume RA set

http://www.epa.gov/ttn/atw/toxsource/summary120202.html

National Center for Environmental Assessment (NCEA)

NCEA is EPA’s resource center for health & environmental risk assessment: *providing guidance, research & conducts risk assessments*.

NCEA Risk Assessment Guidelines Series:

[NCEA Home Page | National Center for Environmental Assessment | US EPA]

- Cancer
- Chemical Mixtures
- Developmental Toxicity
- Ecological Assessment
- Exposure Assessment
- Mutagenicity
- Neurotoxicity
- Reproductive Toxicity

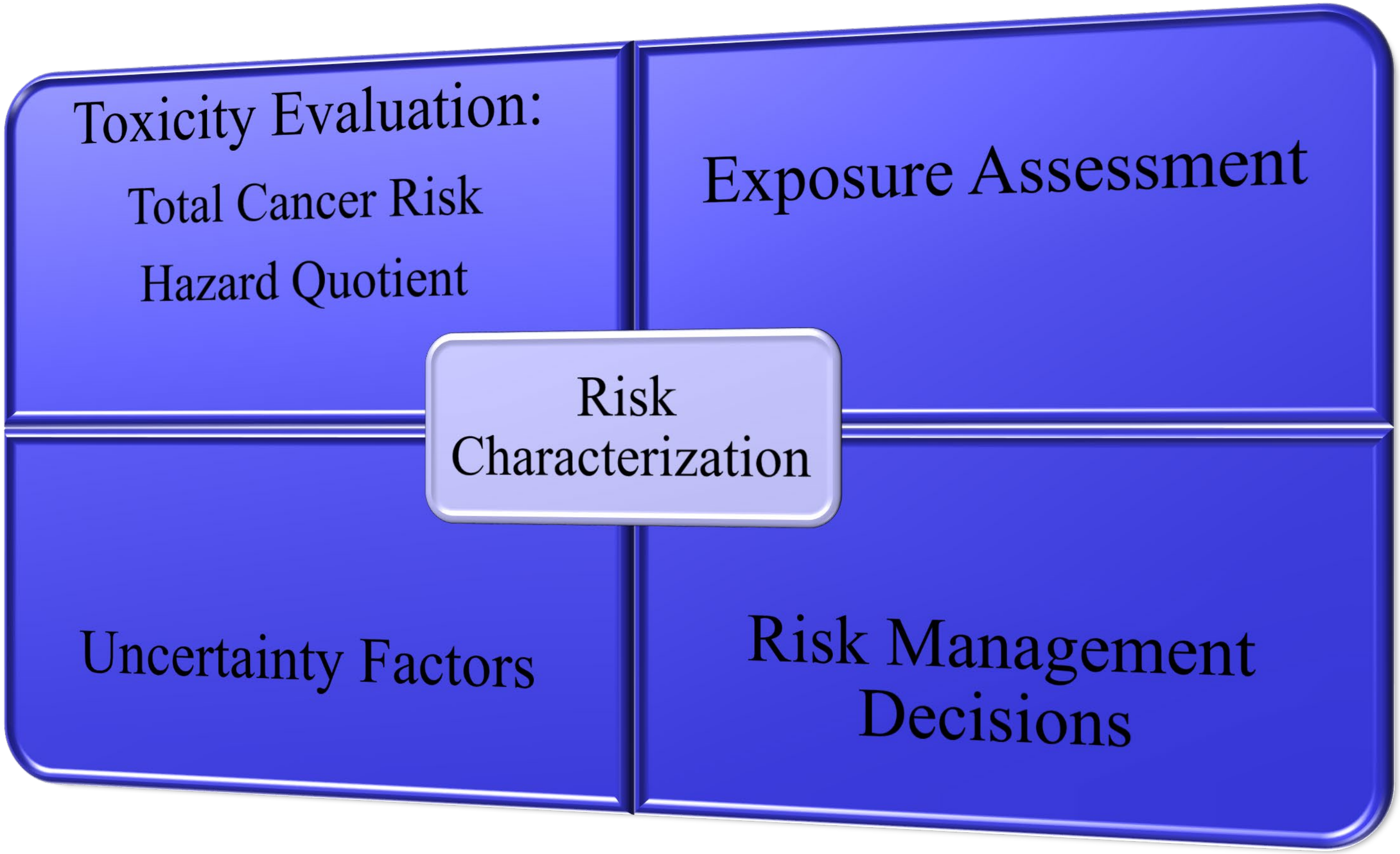
www.epa.gov/ncea

Health Effects Notebook for Hazardous Air Pollutants

http://www.epa.gov/ttn/atw/hlthef/hapindex.html

Chapter Eight

Risk Characterization of Air Toxics



Toxicity Evaluation:

Total Cancer Risk

Hazard Quotient

Exposure Assessment

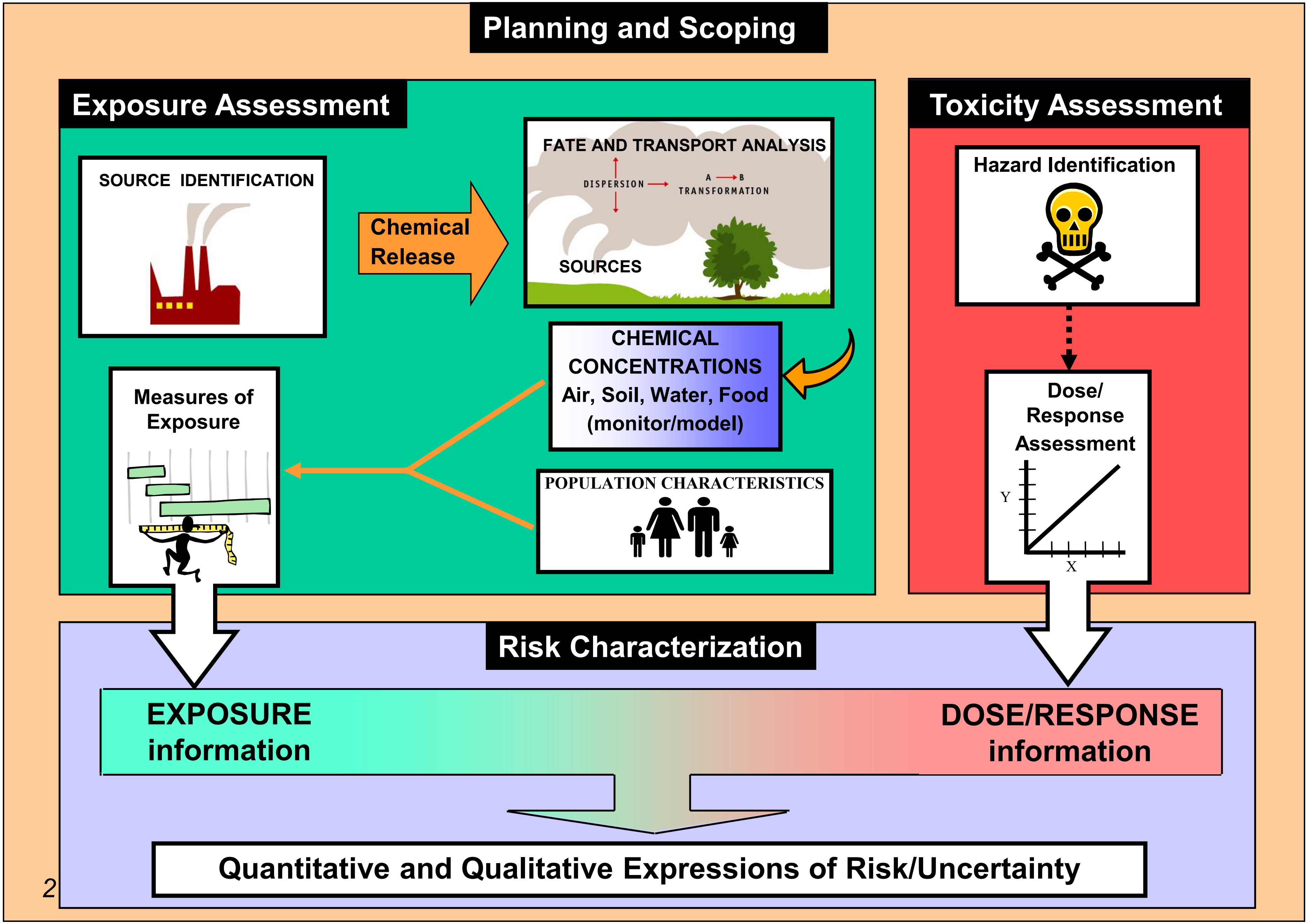
Risk Characterization

Uncertainty Factors

Risk Management Decisions

By: Louis DeRose

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

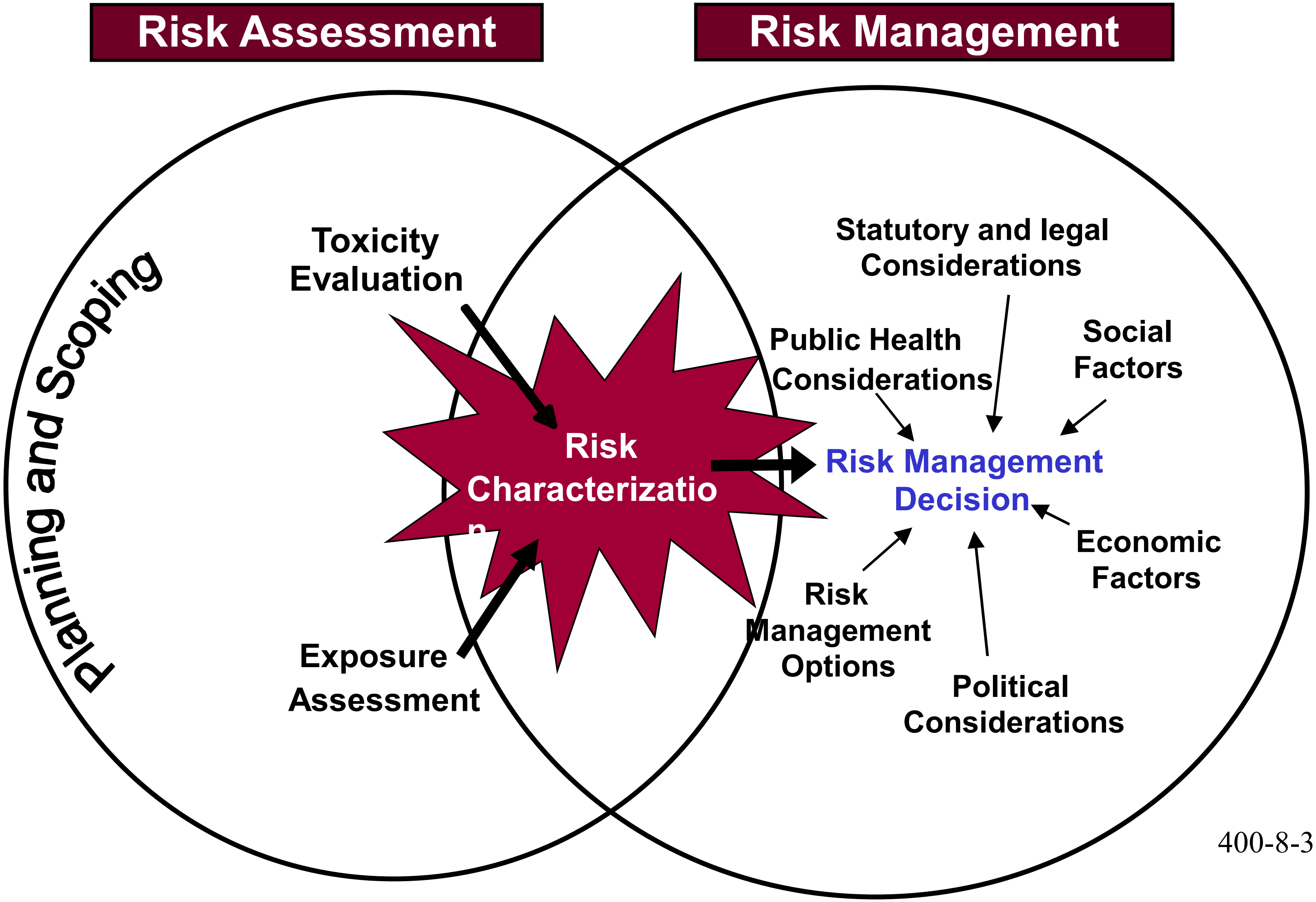
Risk Characterization

EXPOSURE information

DOSE/RESPONSE information

Quantitative and Qualitative Expressions of Risk/Uncertainty

Risk Characterization and Risk Management



Risk Assessment

Risk Management

Planning and Scoping

Toxicity Evaluation

Exposure Assessment

Risk Characterization

Risk Management Decision

Statutory and legal Considerations

Public Health Considerations

Social Factors

Economic Factors

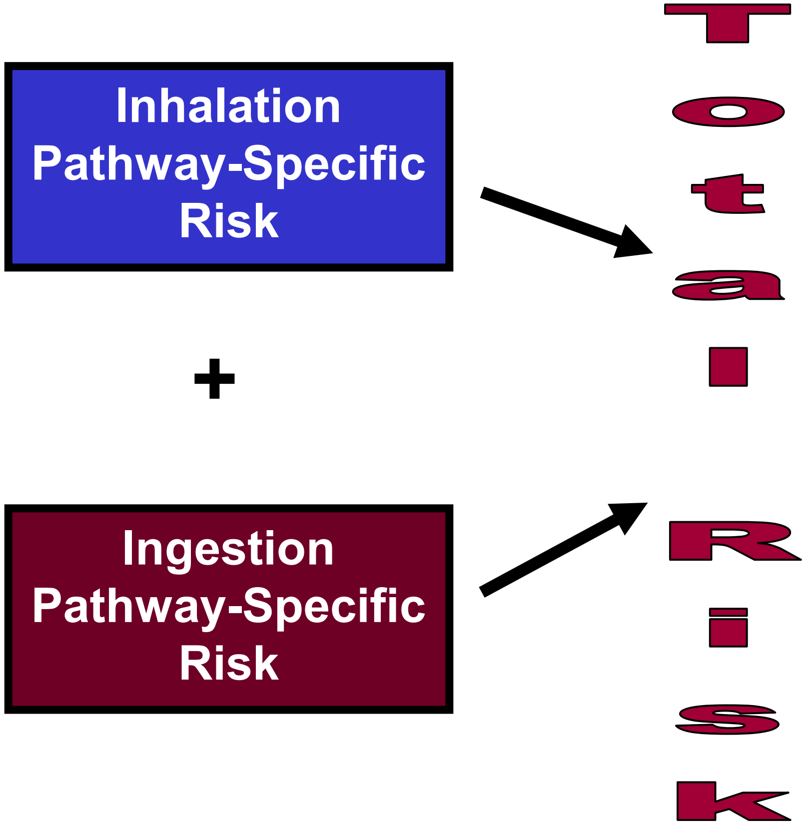
Political Considerations

Risk Management Options

Risk Characterization

Combine outputs from *toxicity* & *exposure assessments*

- Quantify risks from individual chemicals for *each pathway separately* (e.g., inhalation, ingestion), then…
- Combine risks from multiple chemicals for each pathway, then…
- Combine risks from all pathways to give *total risk*, then…
- Repeat the process for all non-cancer hazards
- Assess and present uncertainty



Inhalation Pathway-Specific Risk

+

Ingestion Pathway-Specific Risk

Total Risk

Risk Characterization

- Cancer risks are presented separately from non-cancer hazards.
  - 1st Calculate & present cancer risks
  - 2nd Calculate & present non-cancer hazards
  - 3rd Assess & present uncertainties & assumptions
- Some chemicals show up in both sets of analyses because some chemicals can cause both cancer & non-cancer effects.
- Air toxic risk characterization focuses on inhalation pathway only.
  - Other pathways will be considered for persistent, bio-accumulative HAPs (i.e. mercury, dioxin).

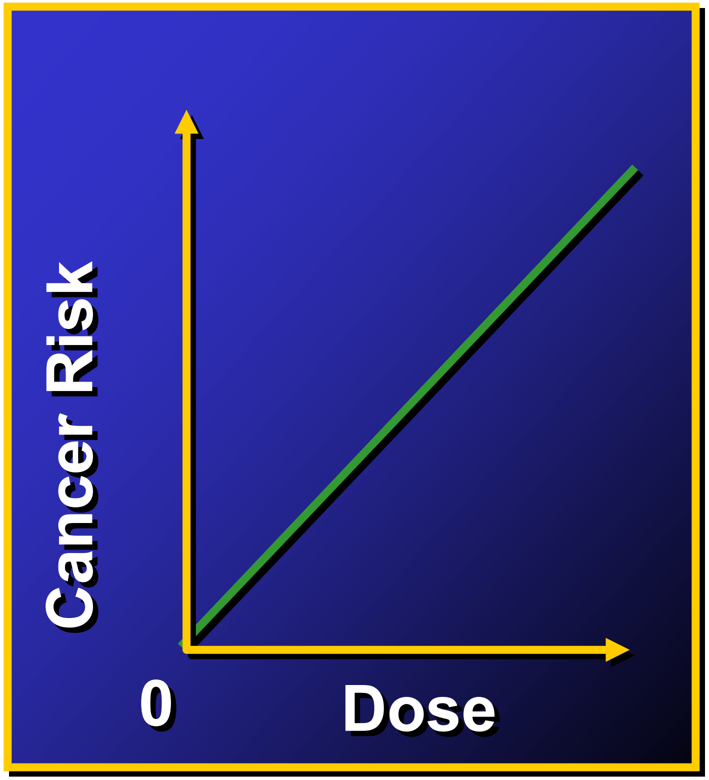
Inhalation Unit Risk

The basic equation for calculating risk from breathing a carcinogenic air toxic is:

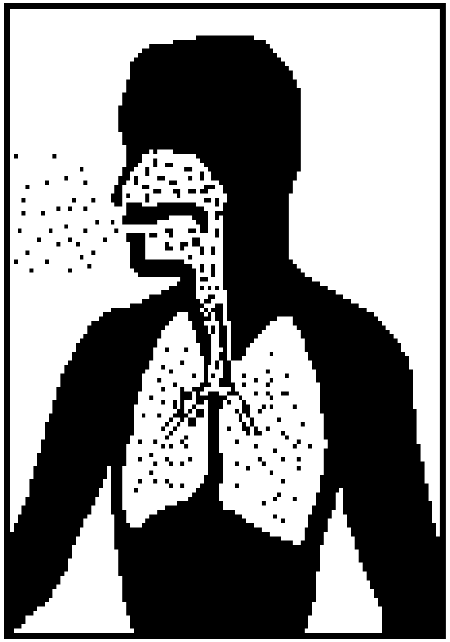
Risk = EC x IUR

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 $\mu g/m^3$
IUR = 2×10^{-3} per $\mu g/m^3$
Class C Possible carcinogen

RISK = $(1\ ug/m^3) \times (2x10^{-3}/ug/m^3) = 0.002$

Chemical B: Exposure Concentration = 5 $\mu g/m^3$
IUR = 2×10^{-5} per $\mu g/m^3$
Class A Known Human Carcinogen

RISK = $(5\ ug/m^3) \times (2x10^{-5}/ug/m^3) = 0.0001$

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

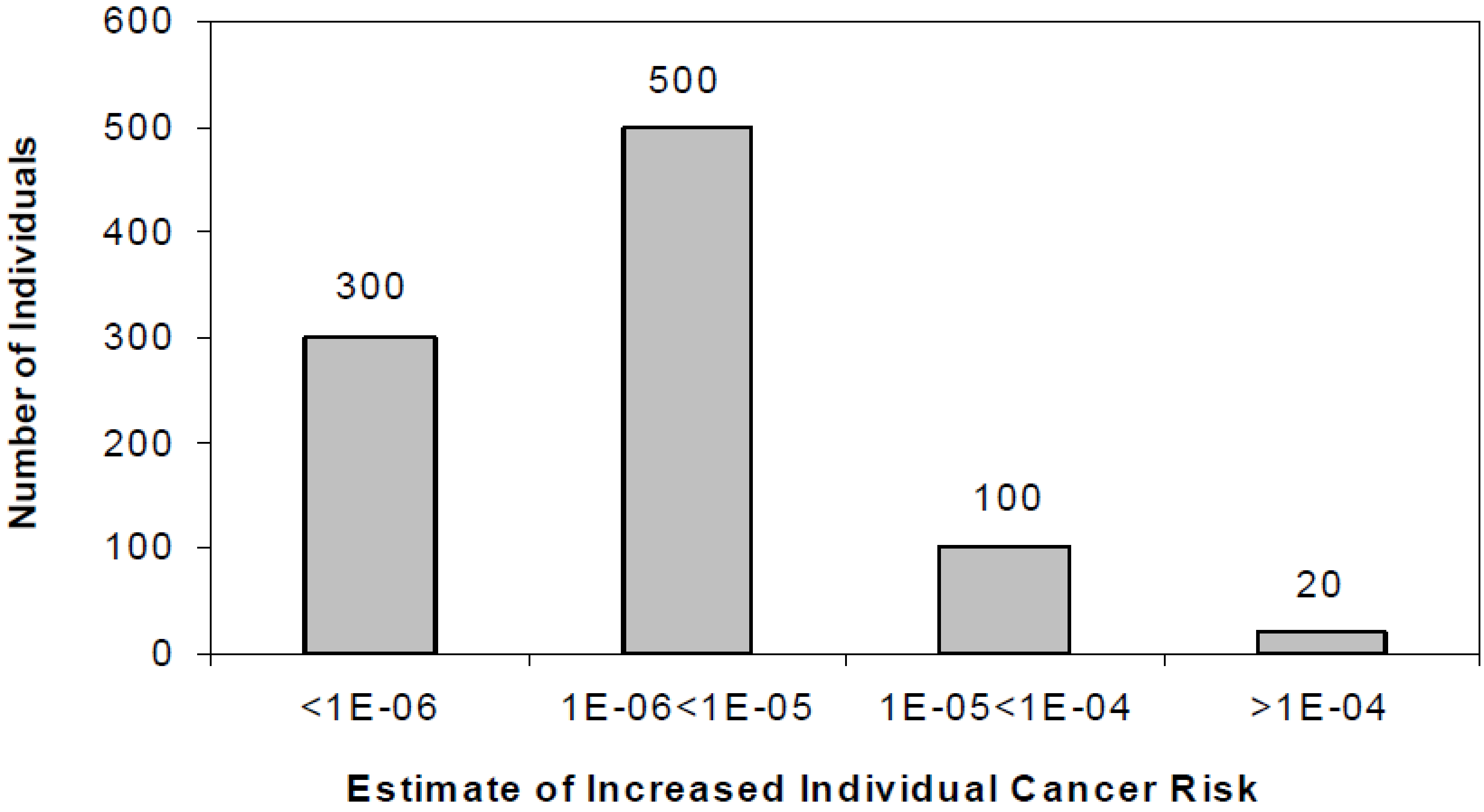
Example Calculation to Estimate Cancer Risk

HAP	**EC ug/m3**	**IUR 1/(ug/m3)**	**Cancer Risk**	**% of Risk_T**
Benzene	0.3	7.8×10^{-6}	$.02 \times 10^{-4}$	< 1%
Dichloroethyl ether	2.5	3.3×10^{-4}	8×10^{-4}	88%
Formaldehyde	0.2	1.3×10^{-4}	$.02 \times 10^{-4}$	< 1%
Cadmium compounds	0.1	1.8×10^{-3}	1.8×10^{-4}	11%
Total Risk (R_T)			9.84×10^{-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.
  - Use *average* or *maximum* risk for individuals within population of interest
- Incidence is the # of expected cases of the disease expected over a lifetime (70 yrs.)
  - Population x unit risk = # 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

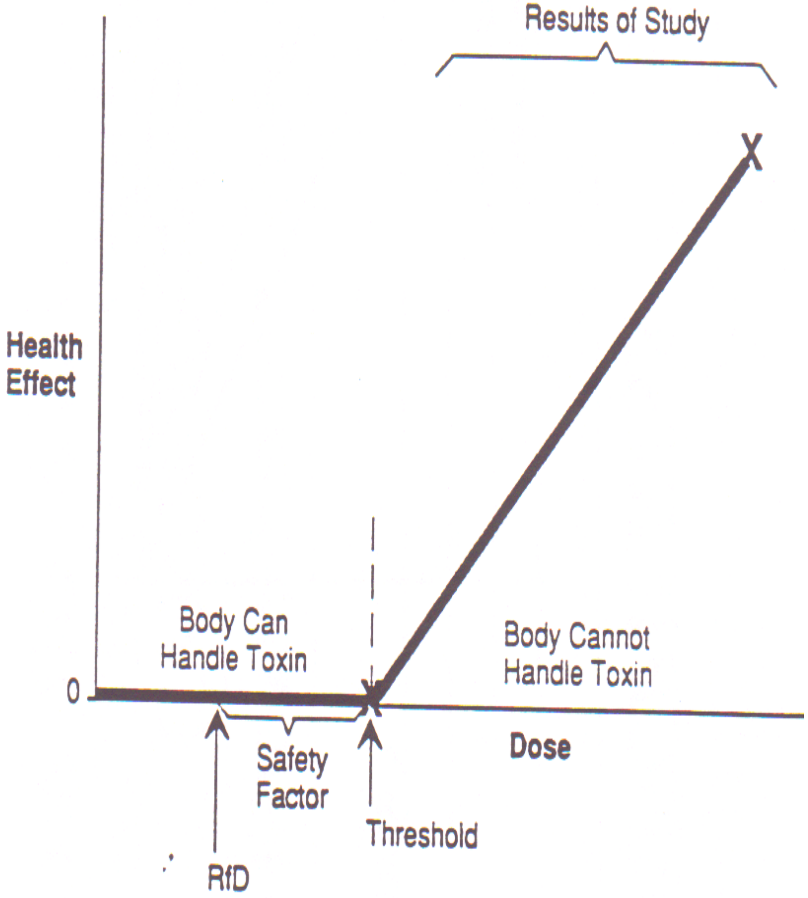


Inhalation Non-Cancer Hazard

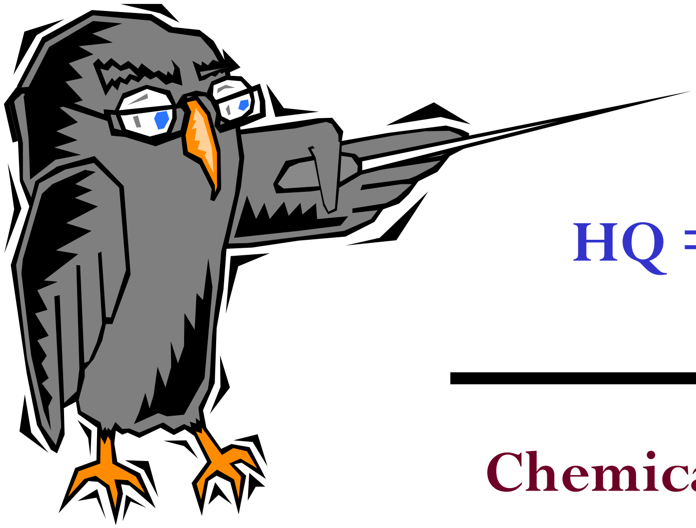
- For inhalation exposures, non-cancer hazards are estimated by:
- **HQ = (EC / RfC)**
- Where:
  - HQ = "**hazard quotient**" for an individual air toxic
  - EC = exposed concentration of the air toxic
    - For chronic exposure use annual concentration
    - For acute exposure use hourly concentrations
  - RfC = reference concentration (EPA will designate a specific RfC for chronic & acute)

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/ a HQ of 10



Example: Inhalation Non-Cancer Hazard



Chemical A: Reduced kidney function

EC = 2 mg/m^3

RfC = 1 mg/m^3

UF = 30

HQ = (2 mg/m^3) ÷ (1 mg/m^3) = 2

Chemical B: Reduced liver function

EC = 8 mg/m^3

RfC = 2 mg/m^3

UF = 1000

HQ = (8 mg/m^3) ÷ (2 mg/m^3) = 4

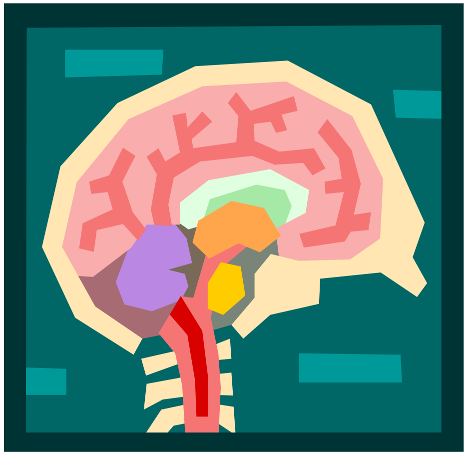
Non-Cancer Risk for Multiple Pollutants

- For multiple non-carcinogens: sum all the individual hazardous quotients for each non-carcinogen present in the air to obtain the "**hazardous index**" (HI)
- $\mathbf{HI = HQ_1 + HQ_2 + HQ_i}$
  - Unless there is contrary evidence, assumes an additive effect from simultaneous exposures (no synergistic or antagonistic effects)

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	

TOSHI



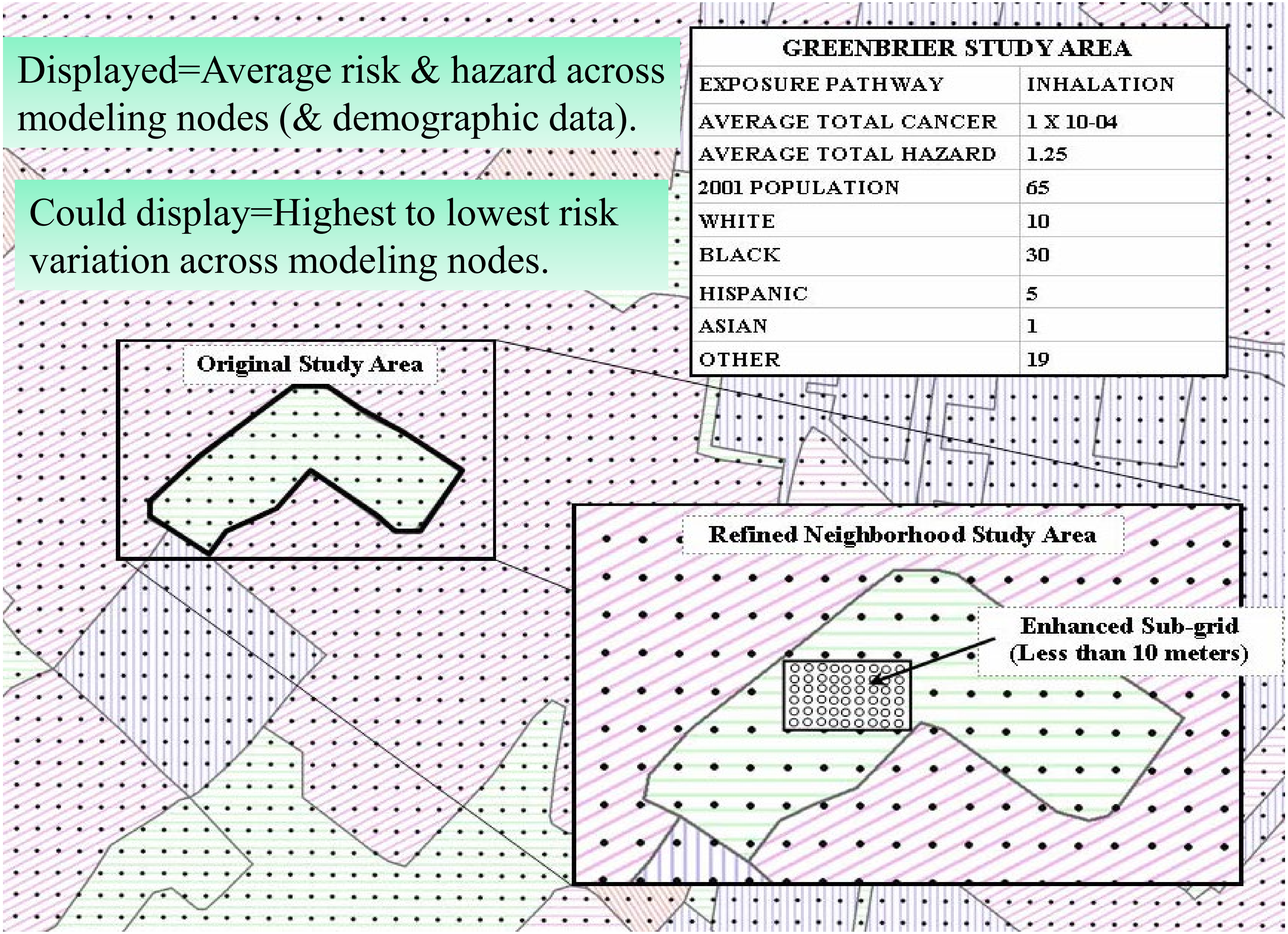
- The HI for a mixture of non-carcinogenic chemicals is mainly a <u>screening level study</u> because different toxins <u>target different organs</u>.
- Identify all major effects & target organs & classify each chemical according to target organ: this produces a **"target-organ-specific-hazard-index" (TOSHI)** for each subgroup.
- Should be performed by an experienced toxicologist

Presenting Risk Results

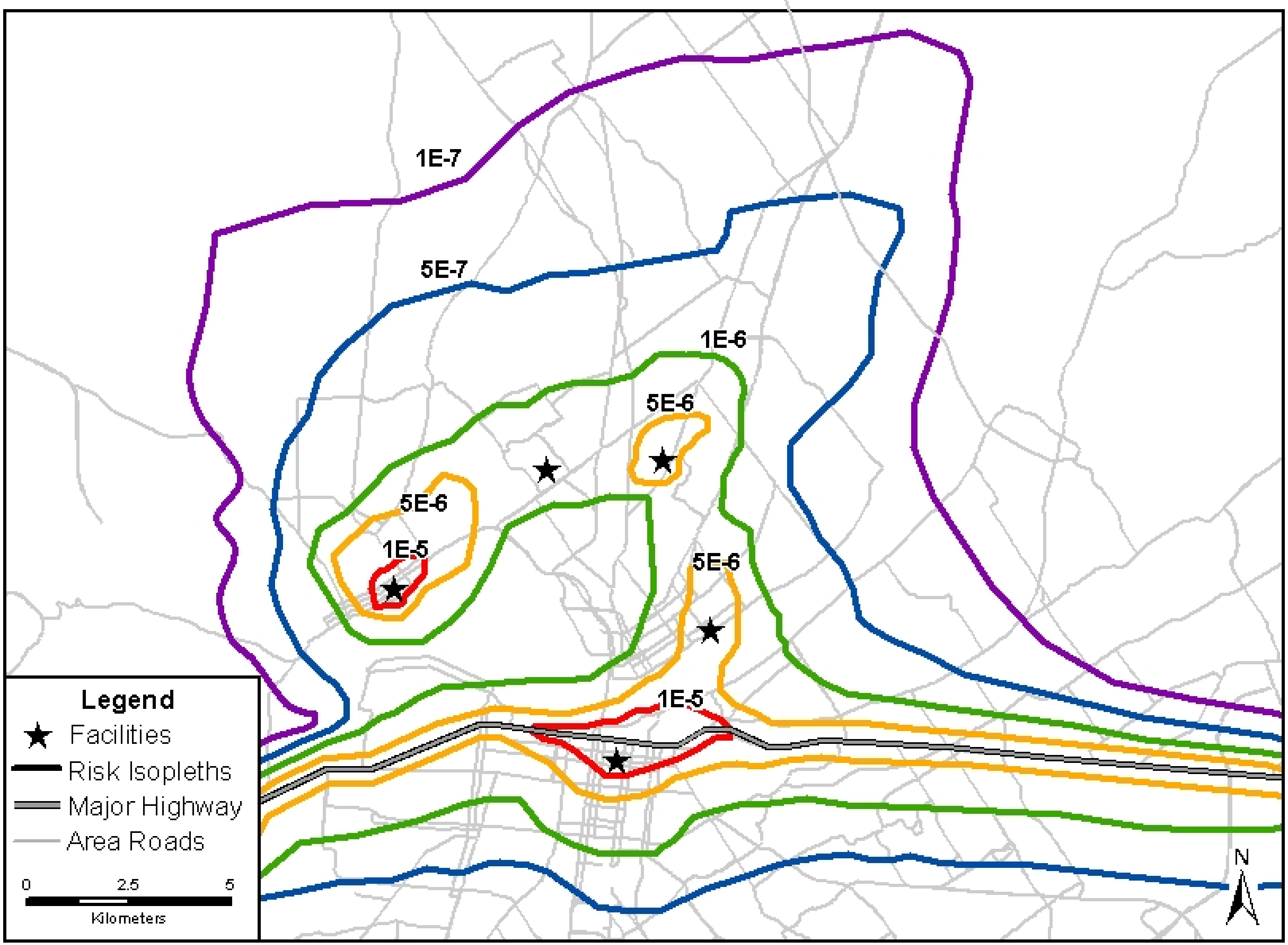
Displayed=Average risk & hazard across modeling nodes (& demographic data).

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

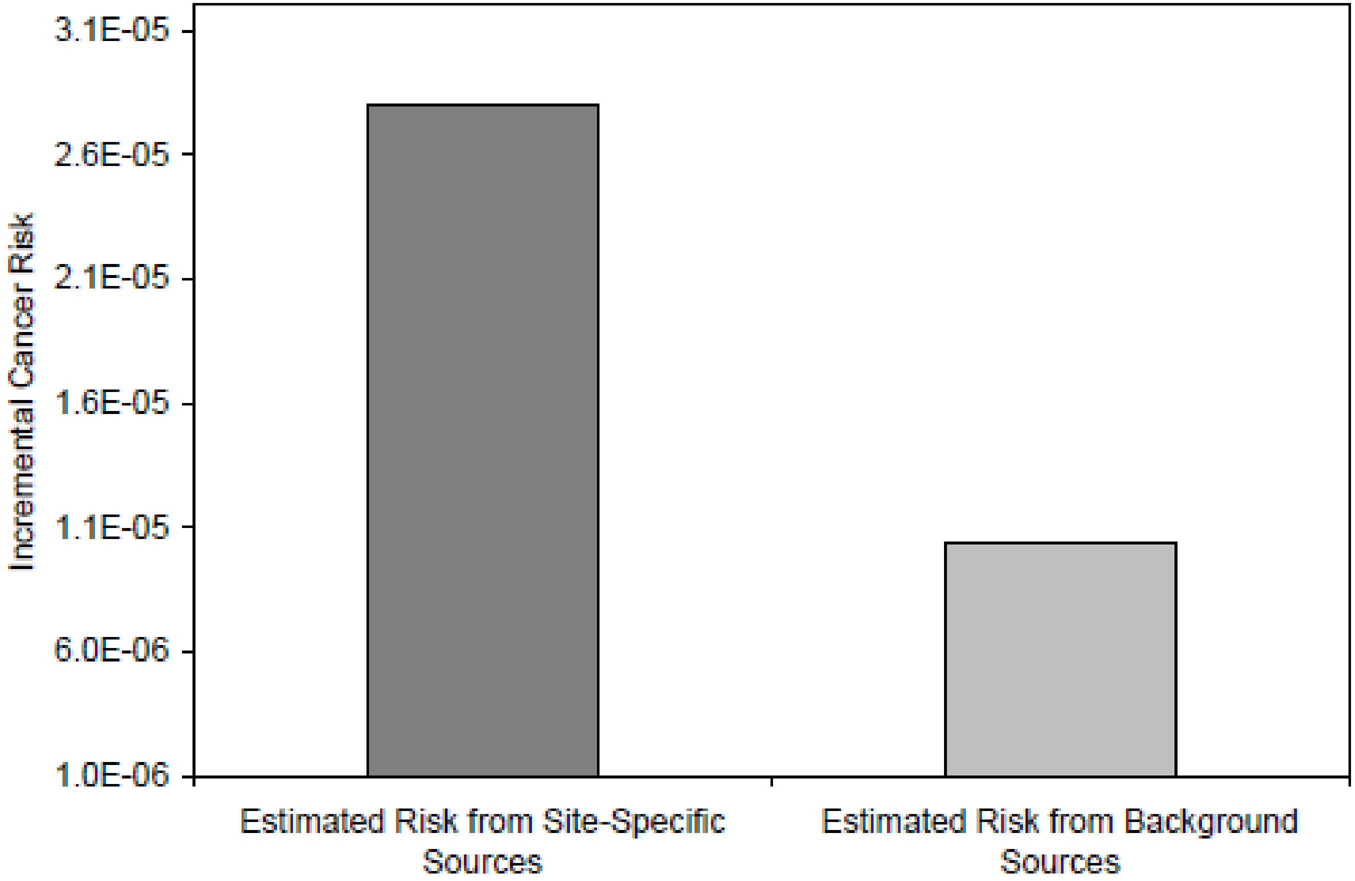


Presenting Risk Results



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.

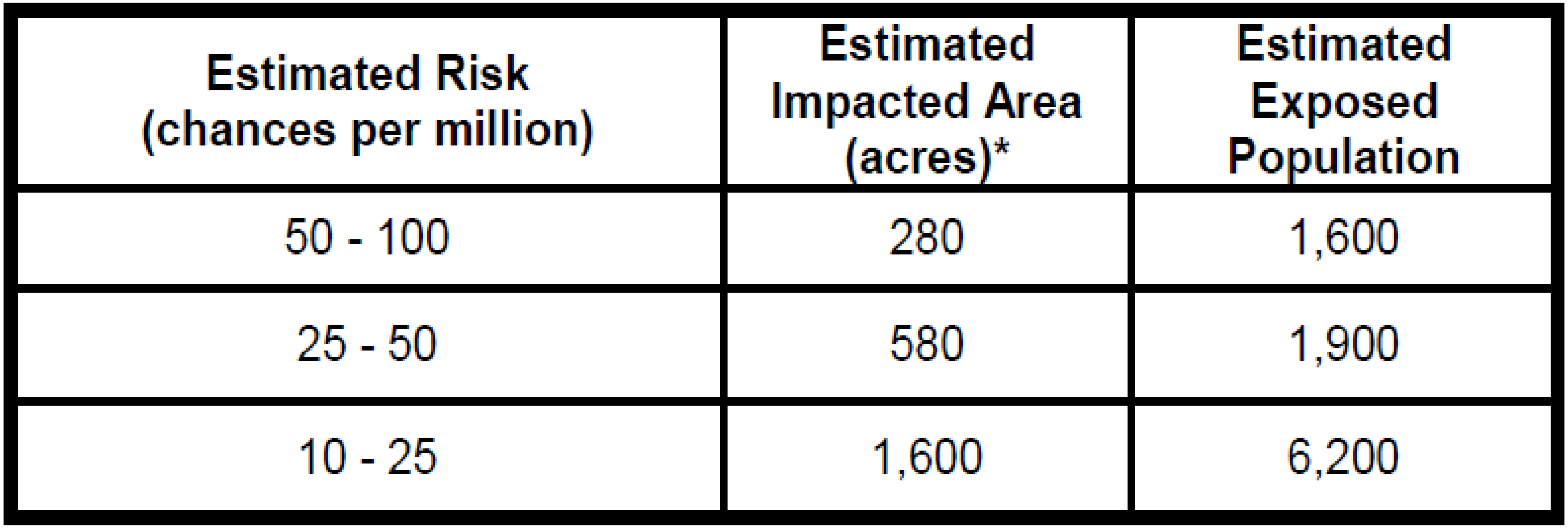


Presenting Risk Results

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.

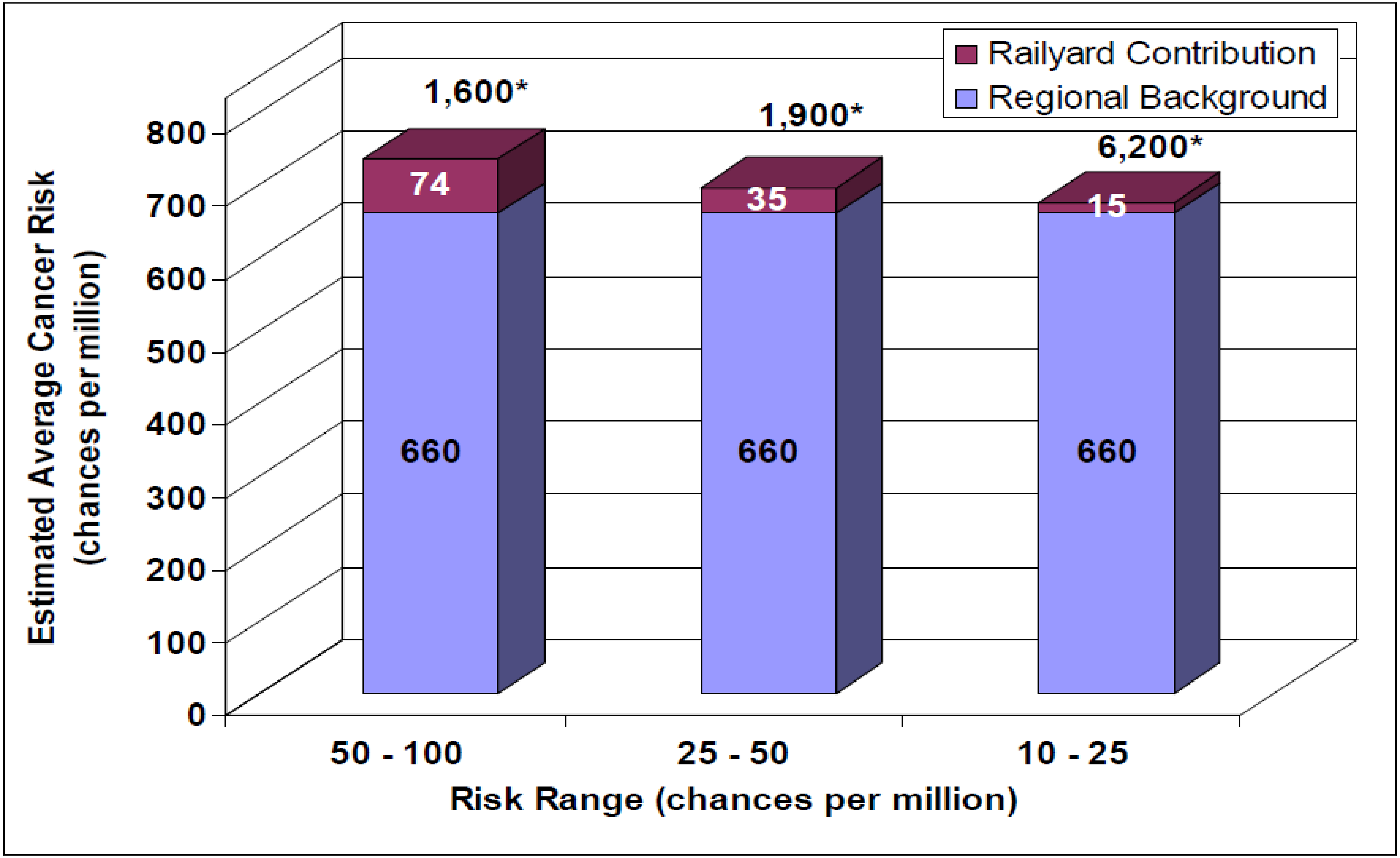
Estimated Impacted Areas and Exposed Population for the Different Cancer Risk Levels at the BNSF Richmond Railyard.



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)*



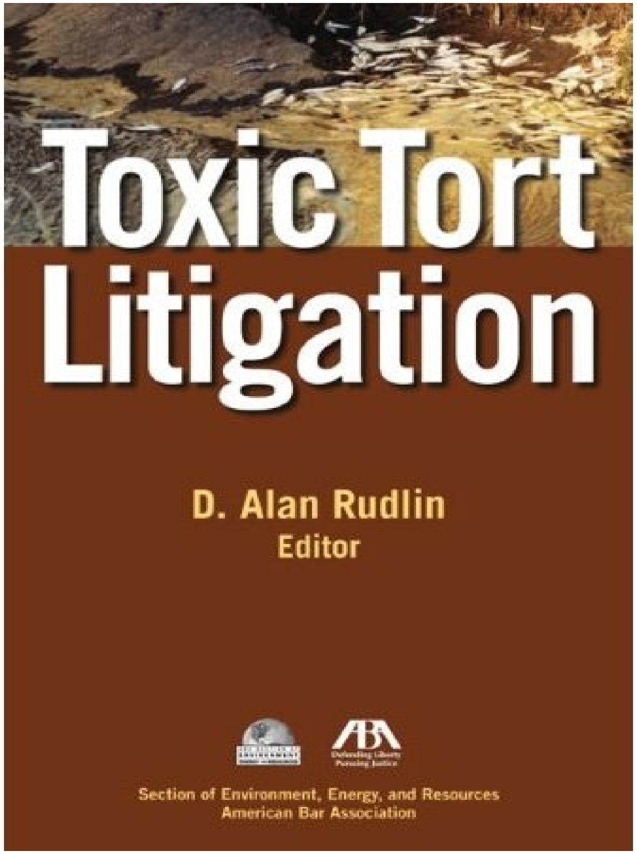
Estimated Non-cancer Chronic Risks (indicated as Hazard Indices) Associated with Diesel PM Emissions from the BNSF Richmond Railyard.

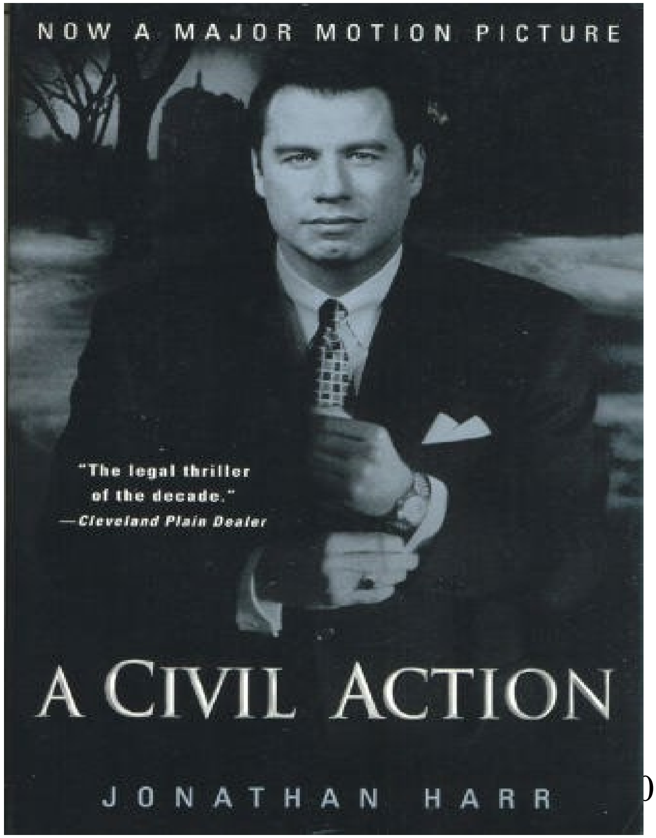
Uncertainty Analysis

- 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

- Toxic torts involve some claim of harm, physical or psychological, *caused by exposure to a substance*.
- Common toxic tort characteristics:
  - *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

- Harm suffered
  - Serious injury with unverifiable level of exposure
  - Known exposure, but injury hasn't manifested (long latency period)
    - The "discovery rule": tolls the statute of limitations until P discovers the injury & that the injury was caused by D.
- Causal link between exposure and harm
  - Did this exposure cause the this harm?
  - Causation is the battle ground in toxic torts cases.
- Liability 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:

- Exposure & dose:
  - 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)
- General causation:
  - Is exposure to substance X capable of causing condition Y in a human?
- Specific causation:
  - Plaintiff must prove *how much* of the toxic chemical was plaintiff exposed to and for *how long*.

Special Causation Challenges

- Long latency period from exposure to the manifestation of injury (disease or death years later)
- Exposure is often problematic
  - P's injury can be caused by *exposures to other chemicals* in which D is not liable
- Little hard data 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

- Old Rule: 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
- New Rule (*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

Special Cases: MTBE

- Methyl-tertiary-butyl-ether(MTBE): a fuel additive used in
  - Premium unleaded gas (to raise octane rating)
  - Oxygenated fuels: in CO non-attainment areas (1990 CAAA)
    - MTBE & ethanol are common oxygenates
  - Reformulated gas (RFG): in severe O_3 non-attainment areas
    - Oxygen content in fuel > 2% (1990 CAAA)
- Cases allege water supplies (groundwater) have been contaminated via leaking underground tanks etc.
  - EPA: MTBE is a possible human carcinogen (animal inhalation studies)
  - EPA on drinking water: there is little likelihood that MTBE concentrations between 20 & 40 micrograms/L would cause adverse effect
  - MTBE: highly soluble & has a strong taste & smell (so even in small amounts in water make it undrinkable)

MTBE Regulation

- 23 states have banned or restricted MTBE in motor vehicles
- Energy Policy Act of 2005
  - Does not ban MTBE, but will reduce its demand by mandating:
    - The elimination the requirement that RFG must contain at least 2% oxygen
    - Increases the use of renewable fuels (ethanol)

Chapter Ten
Air Toxics Monitoring

Air Toxics Monitoring

EPA's Air Toxic Monitoring Program: NATTS;

Local Monitoring; &

PBT's Monitoring

Planning an Air Toxics Monitoring Program:

Locations

Detection Limits

EPA's Air Toxic Monitoring Methods:

Toxic Organic & Toxic Inorganic Pollutants

Types of Air Monitoring Equipment & Samples:

Grab Samples, Continuous Monitors , & Time-Integrated Samples

EPA's Air Toxic Monitoring Program

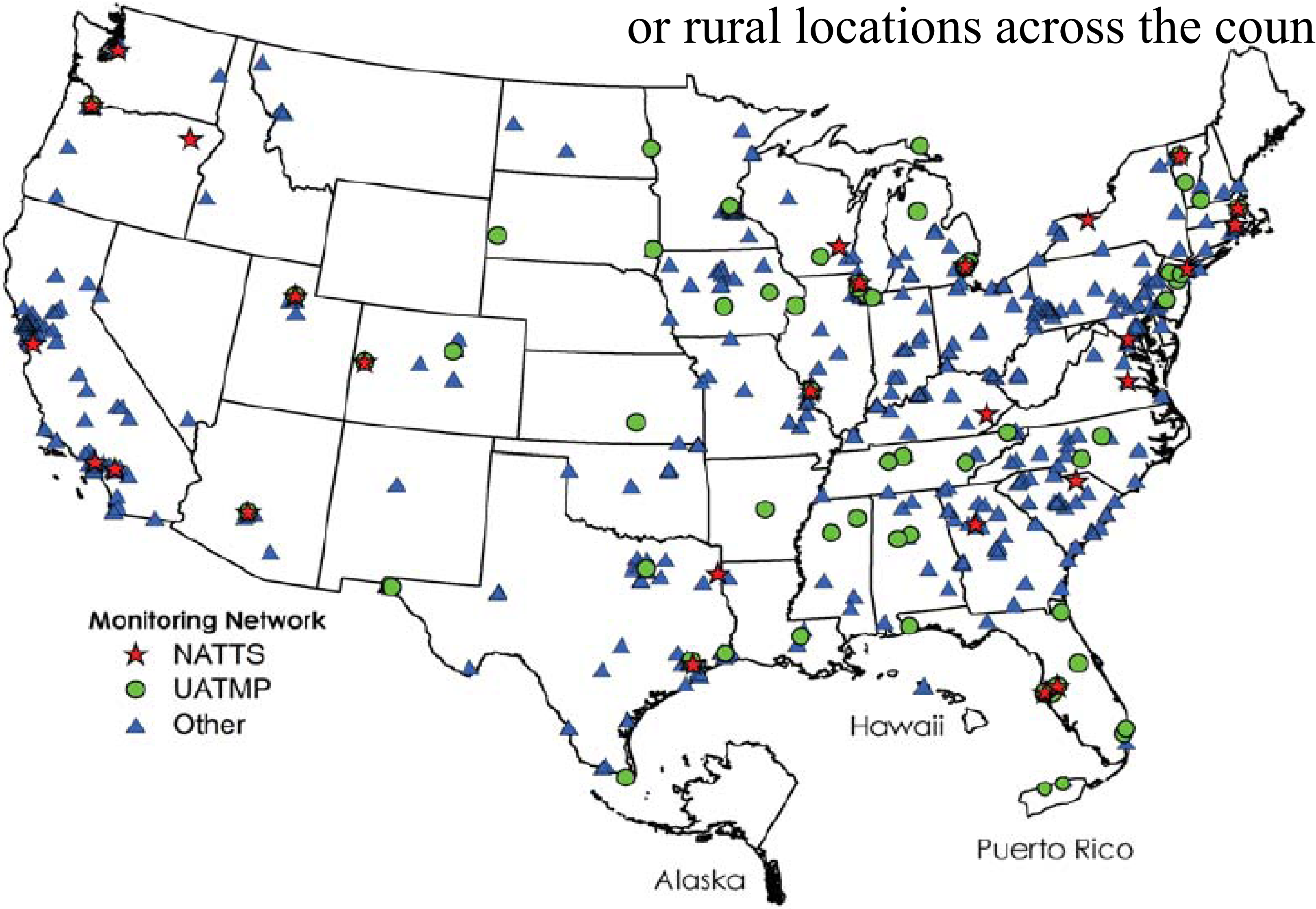
- The CAA does not require a national air toxics monitoring network.
- The Urban Air Toxic Monitoring Program (UATMP) was initiated by EPA in 1987 to meet the increasing need for information on air toxics.
- Since 2000, EPA has increased its ambient air toxics monitoring efforts and funding to establish 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.

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.

HAP Monitoring Sites: 2007

The (NATTS) program is a network of monitoring stations at 27 urban or rural locations across the country.



NATTS Monitored HAPs

VOCs	**Metals**	**Aldehydes**
1,3-butadiene * carbon tetrachloride chloroform 1,2-dichloropropene methylene chloride tetrachloroethylene trichloroethylene vinyl chloride benzene *	Arsenic * beryllium cadmium hexavalent chromium * chromium (and compounds) lead manganese nickel	Acrolein * Formaldehyde * Acetaldehyde

* 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 <u>not be detected</u> 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.

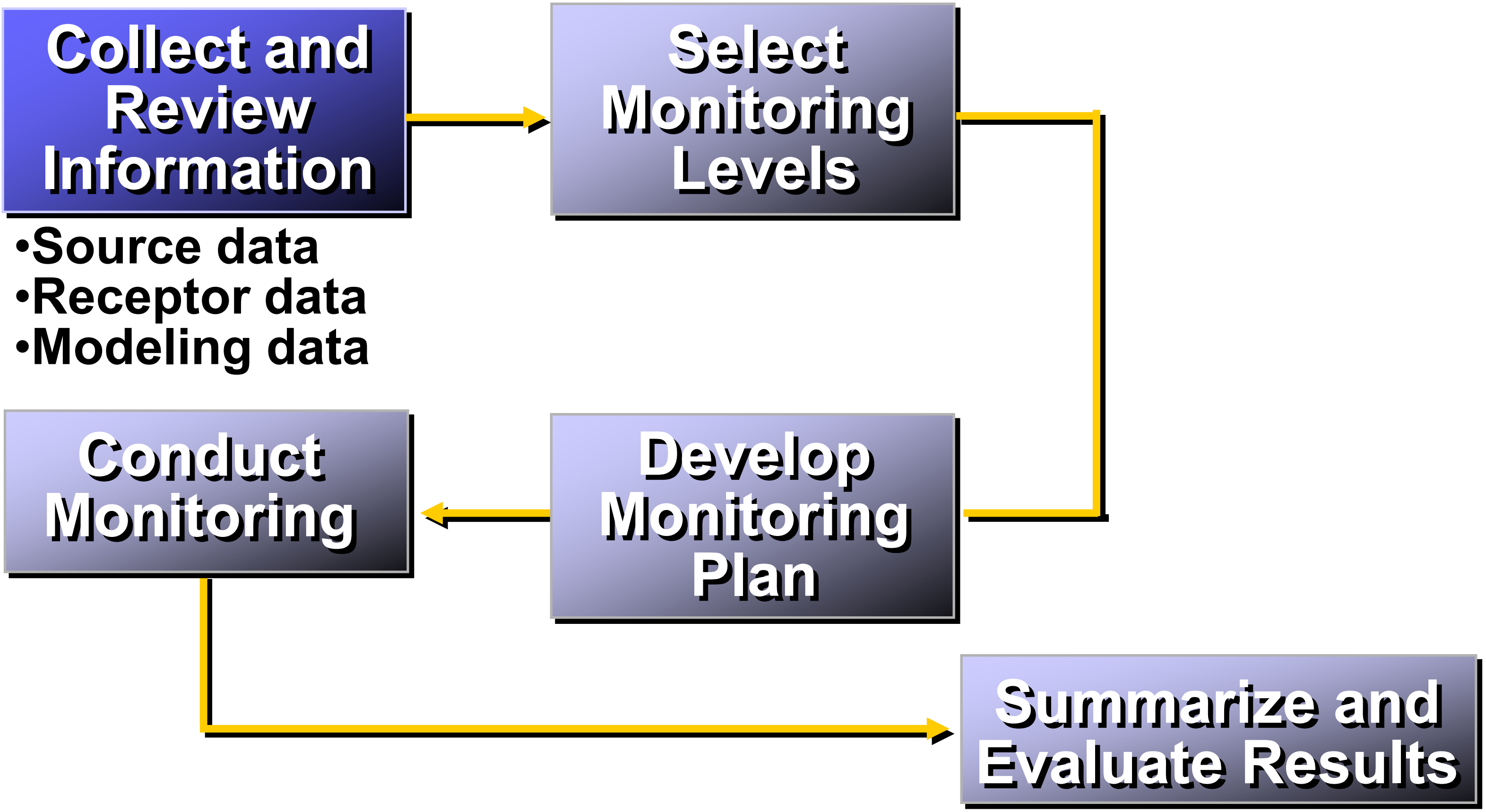
Detection Limits & Limit of Quantification

- 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

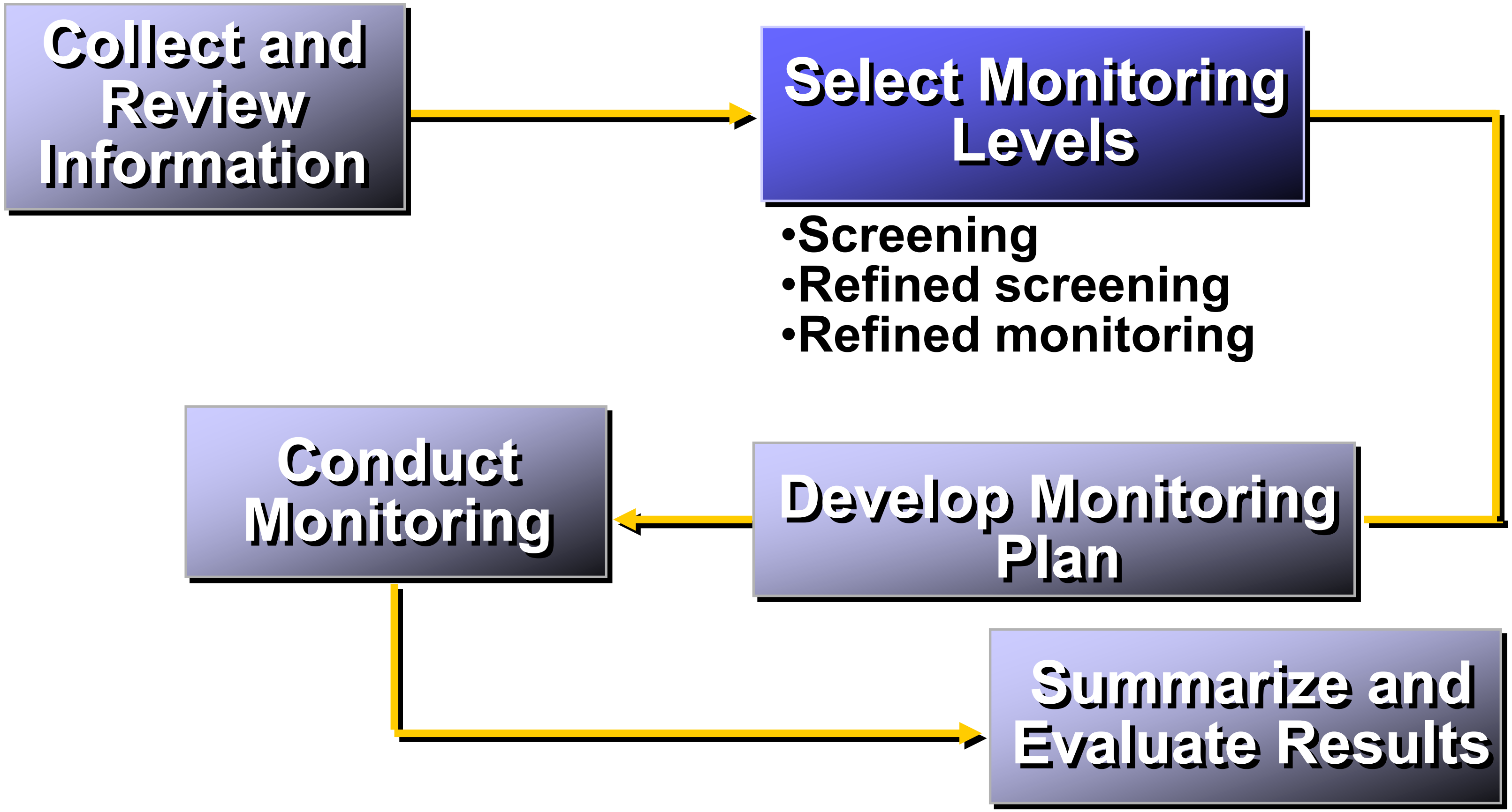
Select Monitoring Levels

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

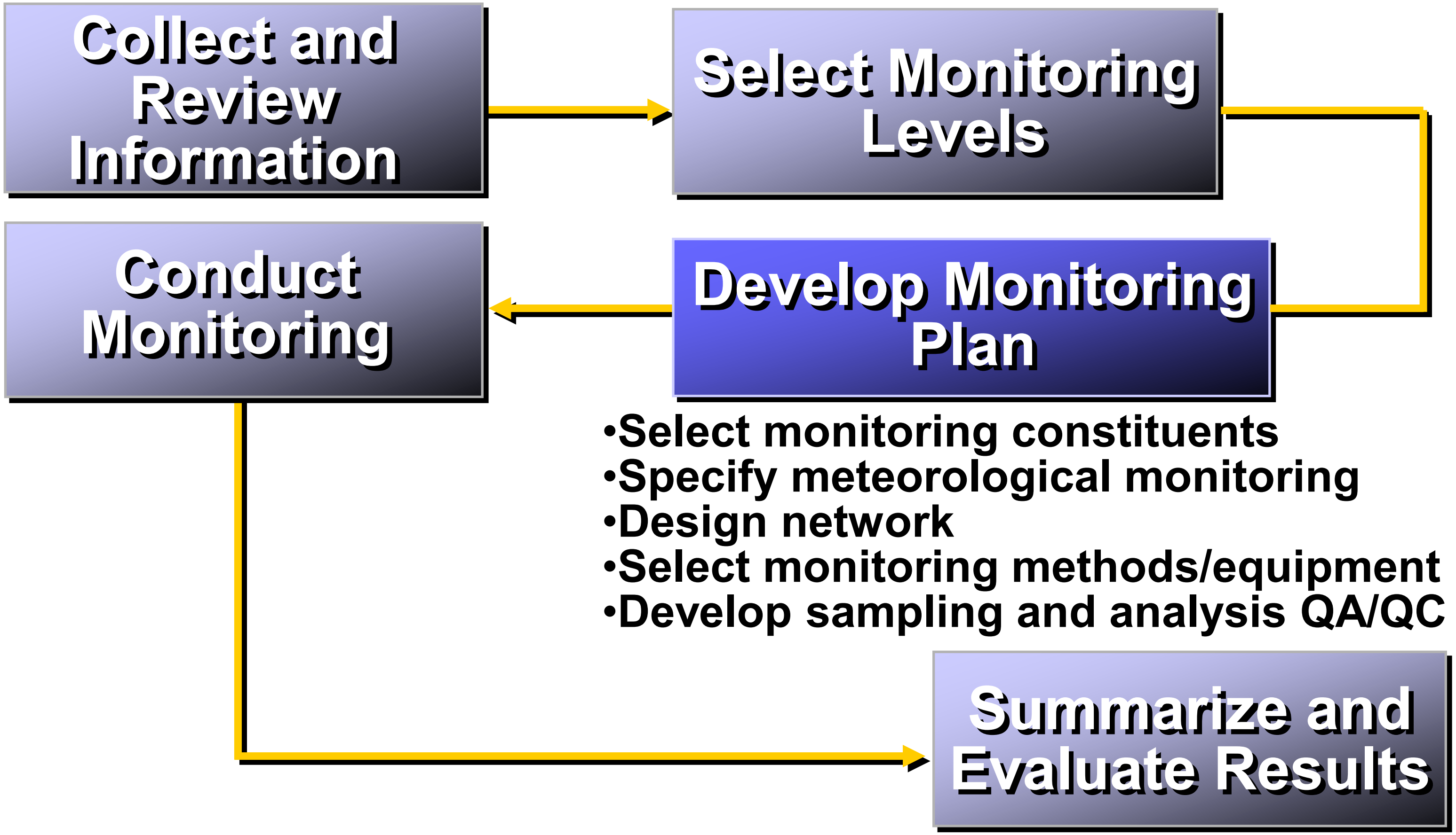
Refined Screening Techniques

- 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

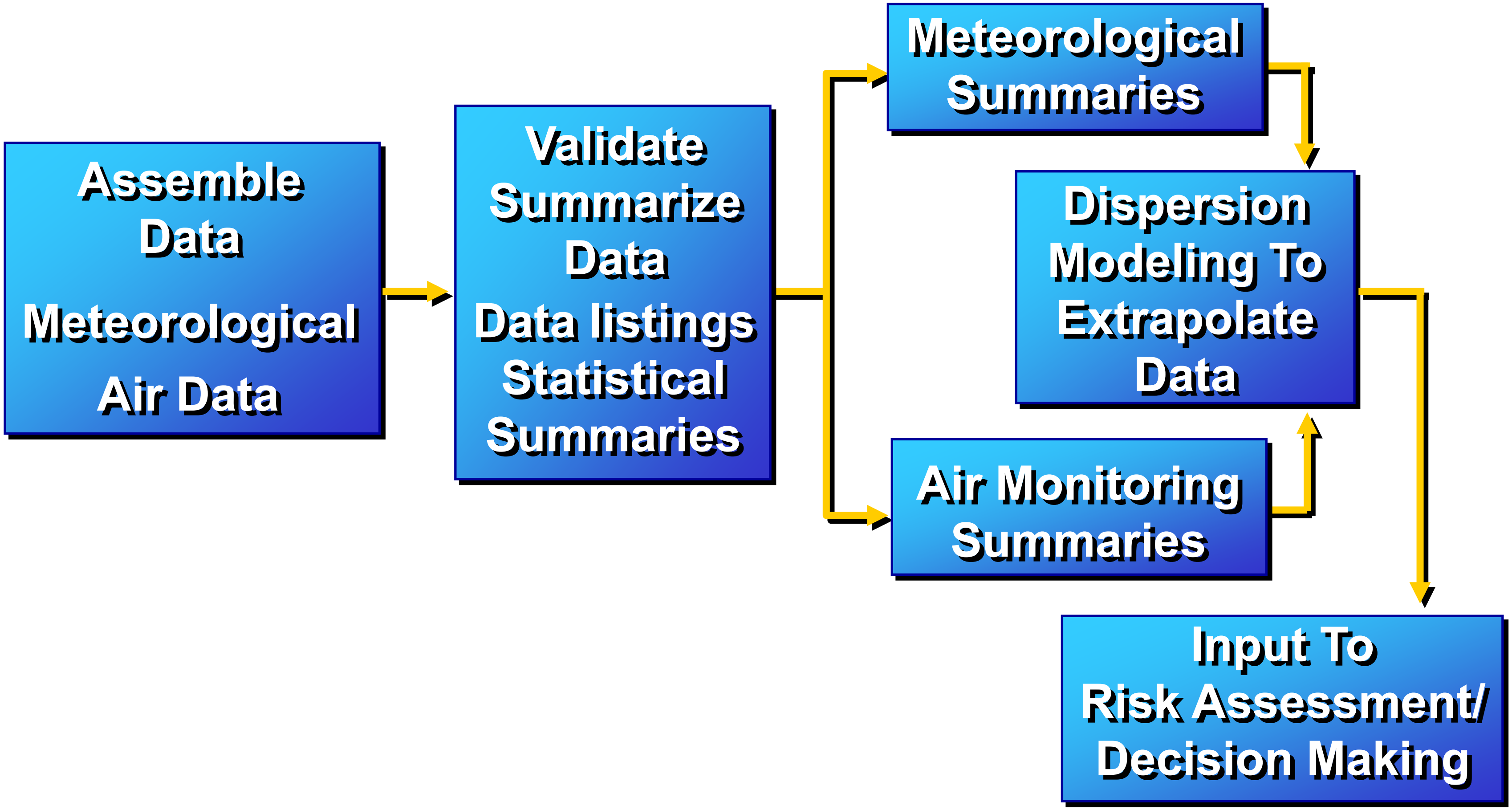
Develop Monitoring Plan

Conduct Monitoring

- Select monitoring constituents
- Specify meteorological monitoring
- Design network
- Select monitoring methods/equipment
- Develop sampling and analysis QA/QC

Summarize and Evaluate Results

Summarize and Evaluate Results



Assemble Data

Meteorological

Air Data

Validate Summarize Data

Data listings

Statistical Summaries

Meteorological Summaries

Dispersion Modeling To Extrapolate Data

Air Monitoring Summaries

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

Organic Compound Classes

- Very Volatile Organic Compounds (VVOC)
- Volatile Organic Compounds (VOC)
- Semi-volatile Organic Compounds (SVOC)
- Nonvolatile Organic Compounds (NVOC)

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

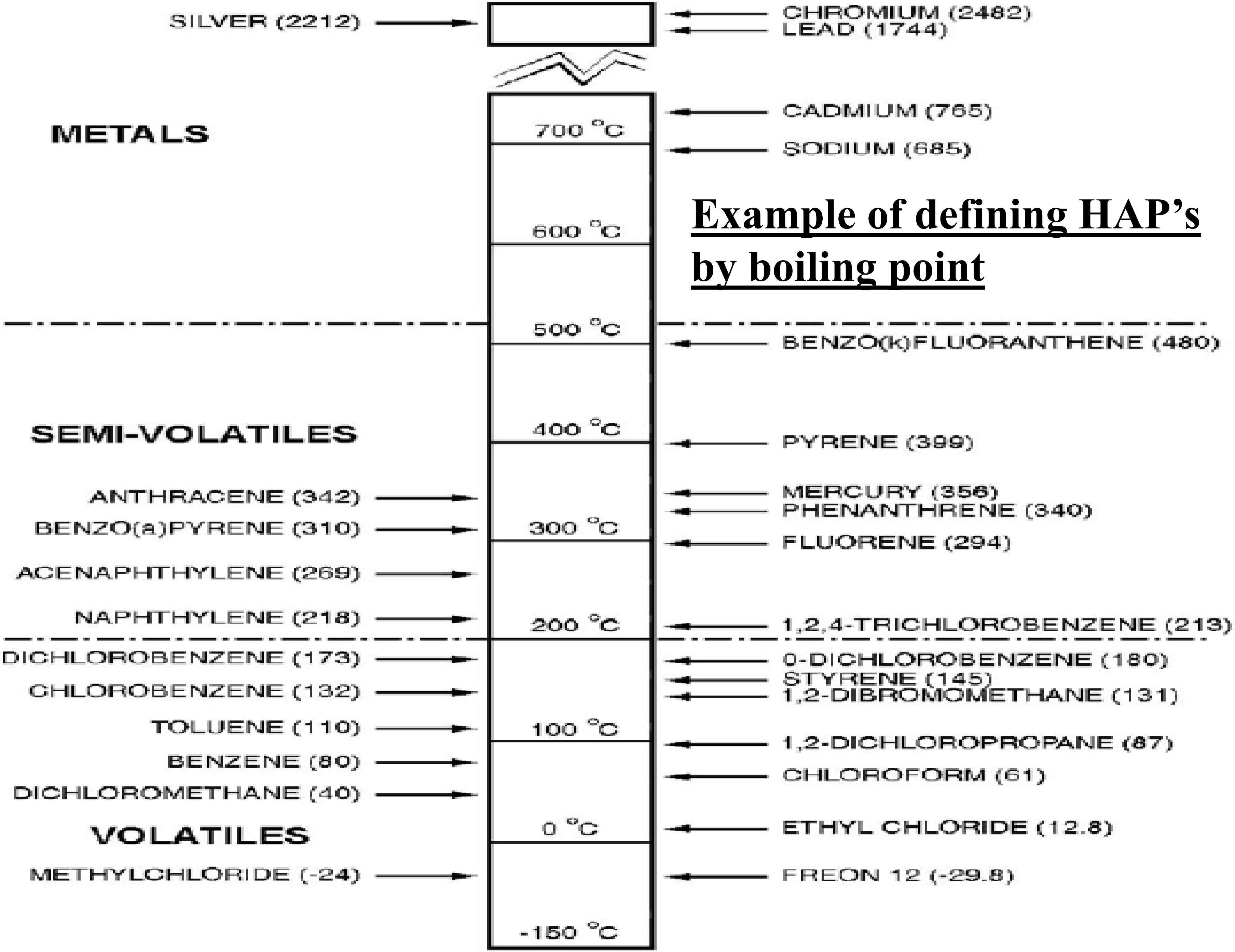
Example of HAPs in each Volatility Class

	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

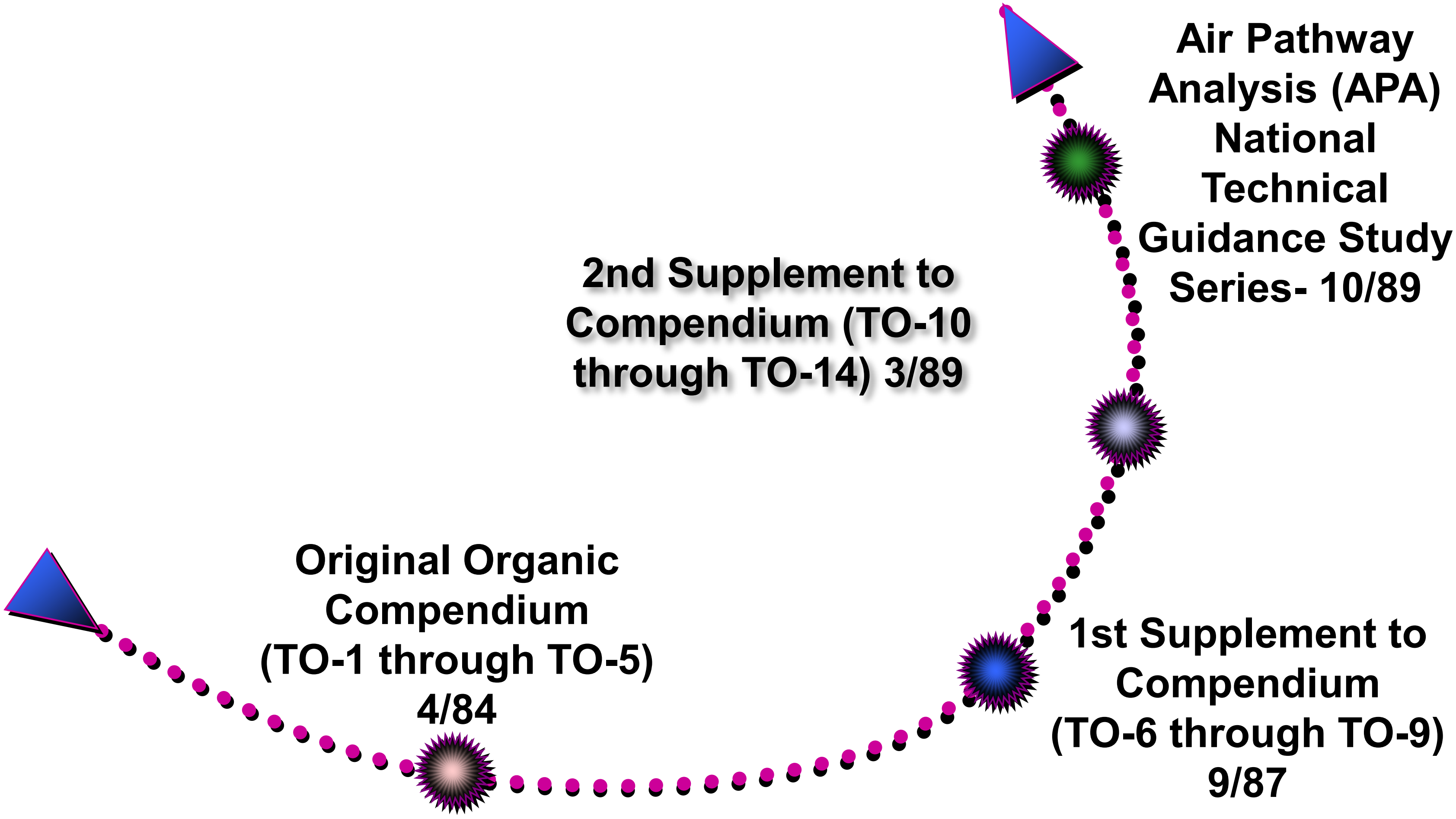
General Classification of HAPs

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



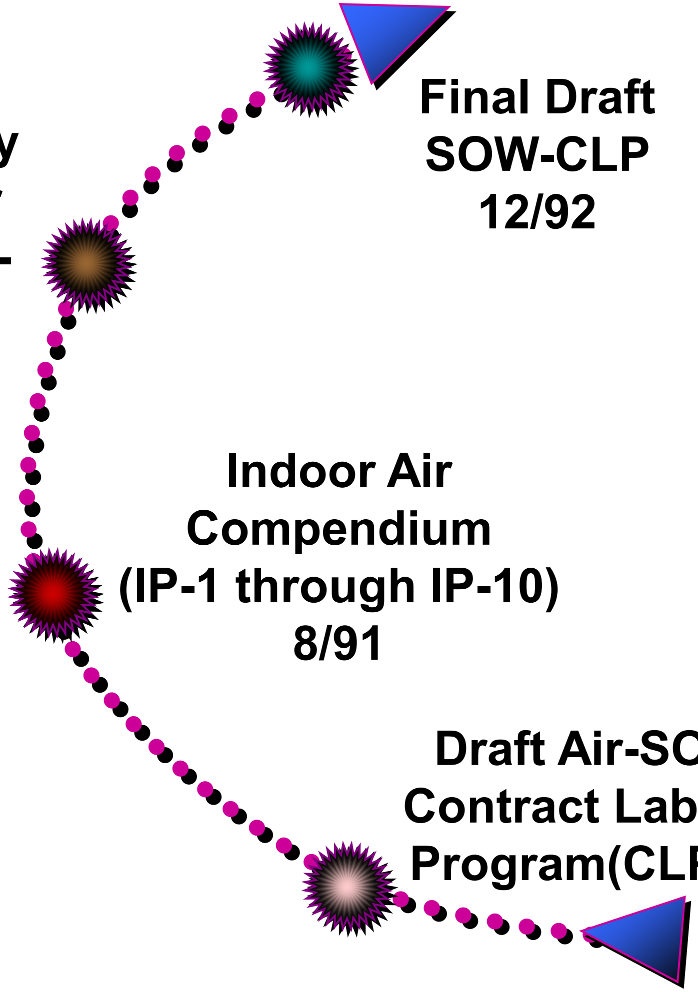
Original Organic Compendium (TO-1 through TO-5) 4/84

1st Supplement to Compendium (TO-6 through TO-9) 9/87

2nd Supplement to Compendium (TO-10 through TO-14) 3/89

Air Pathway Analysis (APA) National Technical Guidance Study Series- 10/89

Indoor HAP/Air Toxics Sampling Progression



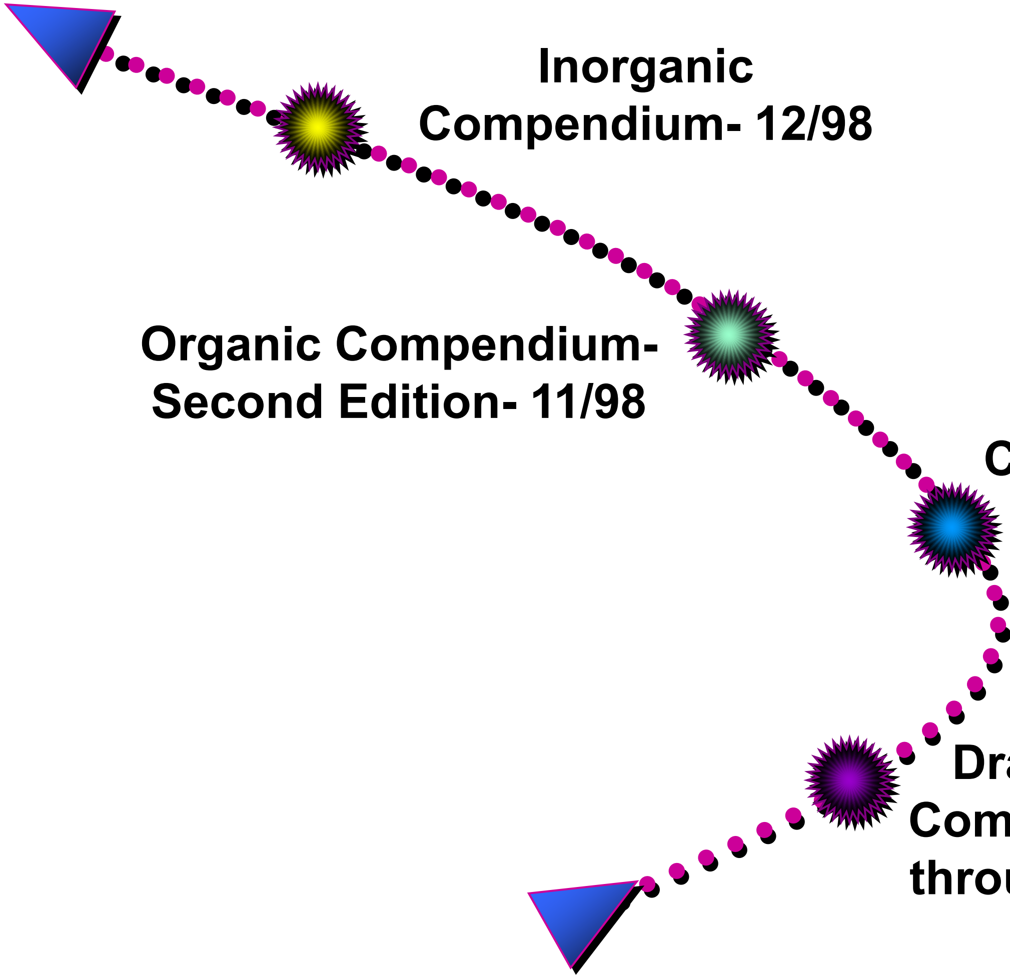
Final Draft
SOW-CLP
12/92

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-96-0l0a, June 1999 (Winberry et al., 1999a)
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition,* EPA/625/R-96-0l0b, 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

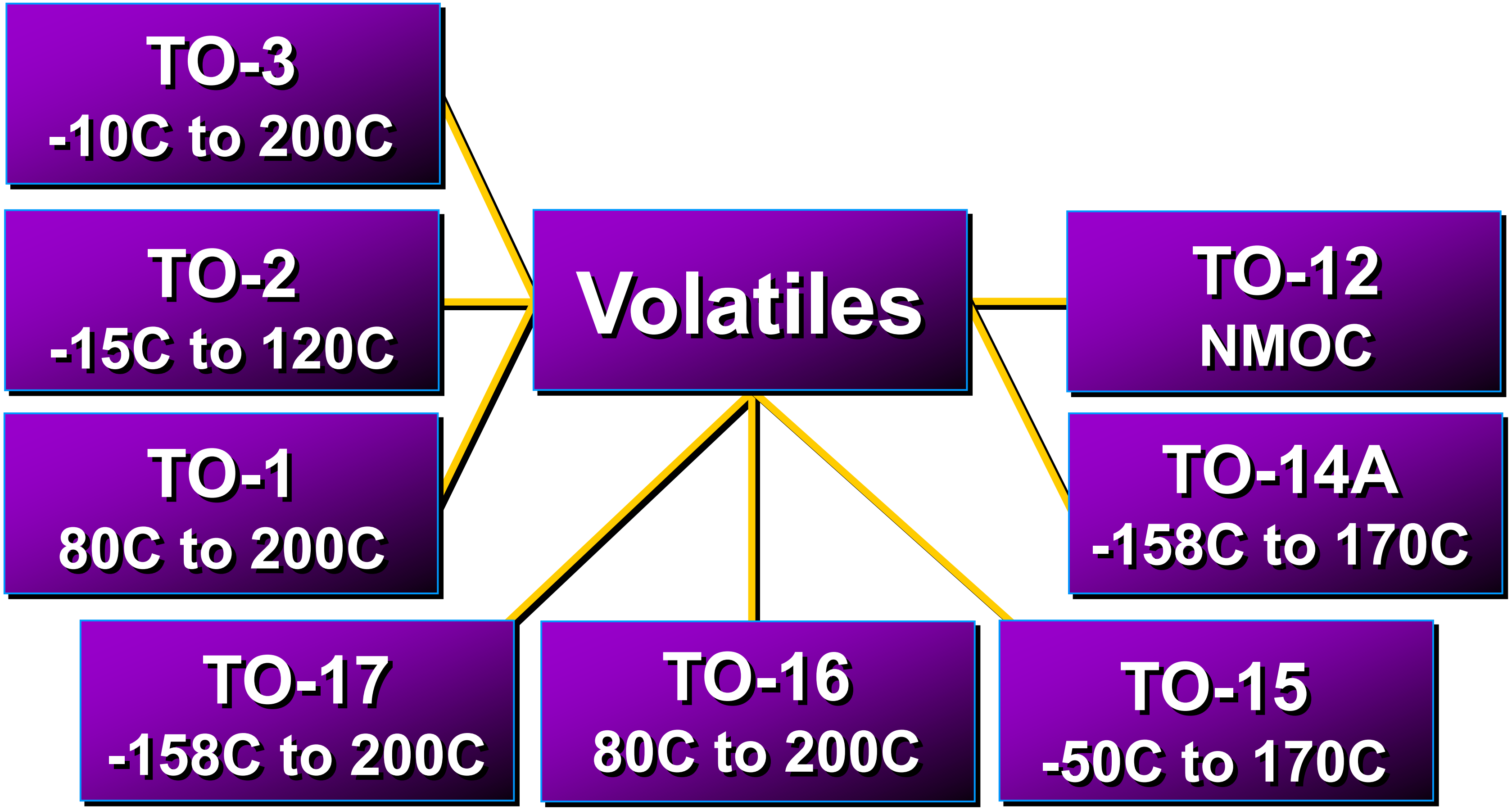
Summary of Toxic Organic Compendium

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

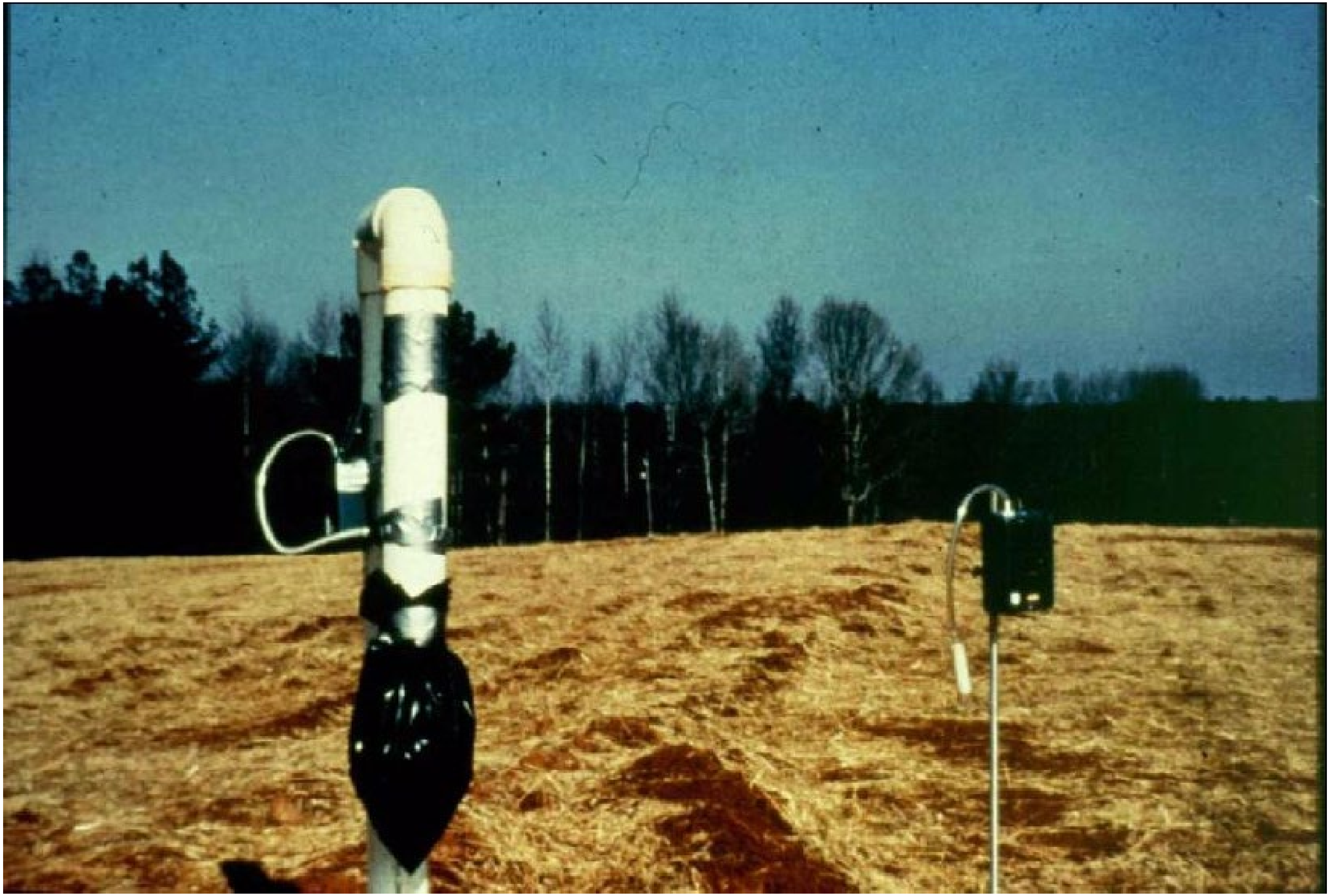
TO-12
NMOC

TO-14A
-158C to 170C

TO-17
-158C to 200C

TO-16
80C to 200C

TO-15
-50C to 170C

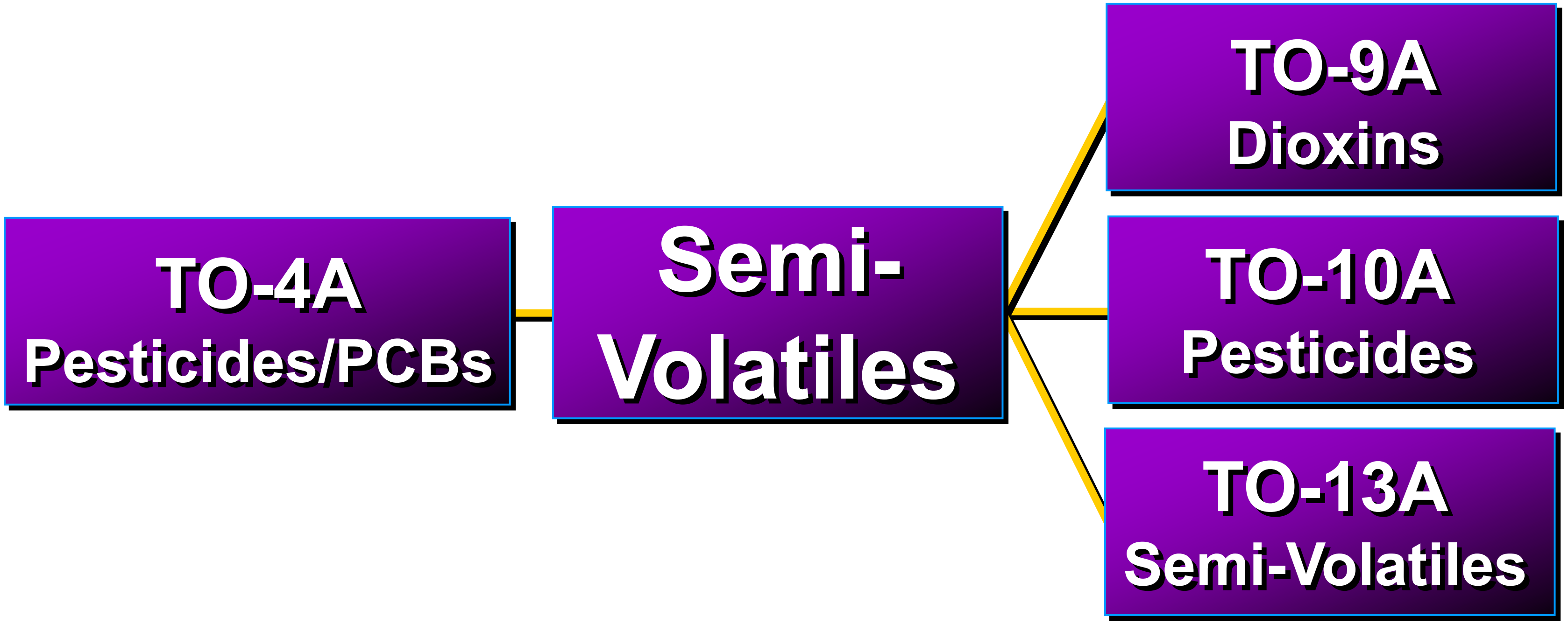


Encapsulated Vent Tube Sampling for PCBs Utilizing EPA Compendium Method TO-10A. (Note Portable Monitor to the Right of the Vent Tube for Ambient Monitoring of Emissions During Normal Vent Tube Emissions.)

Compendium Method TO-15 Application for Monitoring VOCs at the perimeter of a MSW Landfill

Example of Compendium Method TO-15
Application for Landfill COPCs at the Perimeter of the Site.

Compendium of Classification of Analytes



TO-4A
Pesticides/PCBs

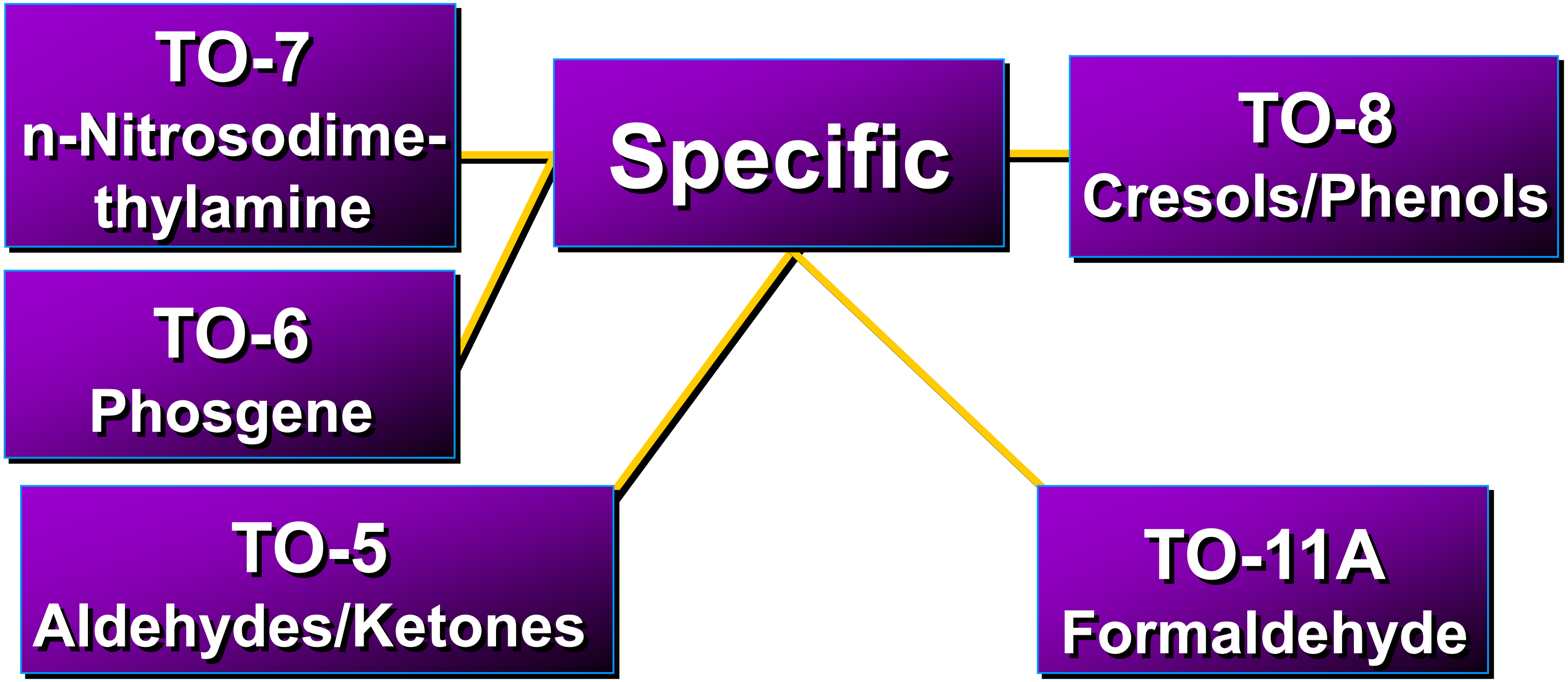
Semi-Volatiles

TO-9A
Dioxins

TO-10A
Pesticides

TO-13A
Semi-Volatiles

Compendium of Classification of Analytes



TO-7
n-Nitrosodimethylamine

TO-6
Phosgene

Specific

TO-8
Cresols/Phenols

TO-5
Aldehydes/Ketones

TO-11A
Formaldehyde


Compendium
of Methods
for the Determination of Toxic
Organic Compounds in Ambient Air
RESTEK

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 <u>without</u> 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 <u>analyzed in the lab</u>, 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 <u>returned to the laboratory</u> for analysis.