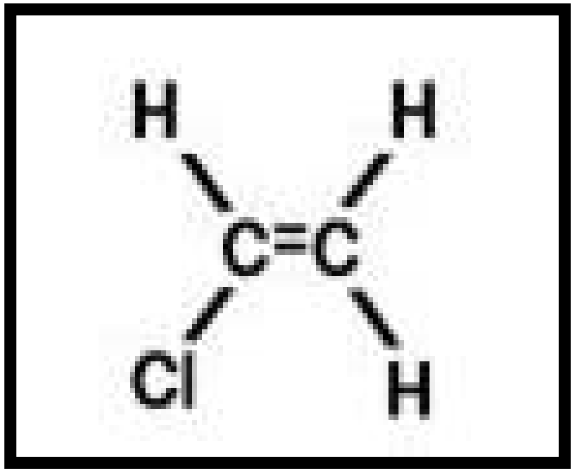
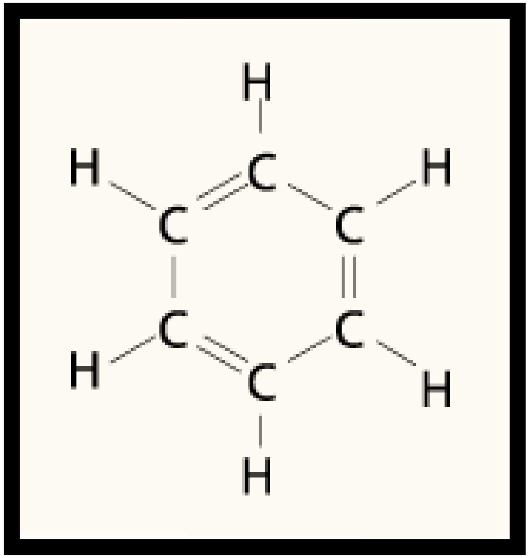




Pollutant Definitions

Significant Pollutants of Interest

Key air pollutants for which ambient air quality standards are being established by some countries:

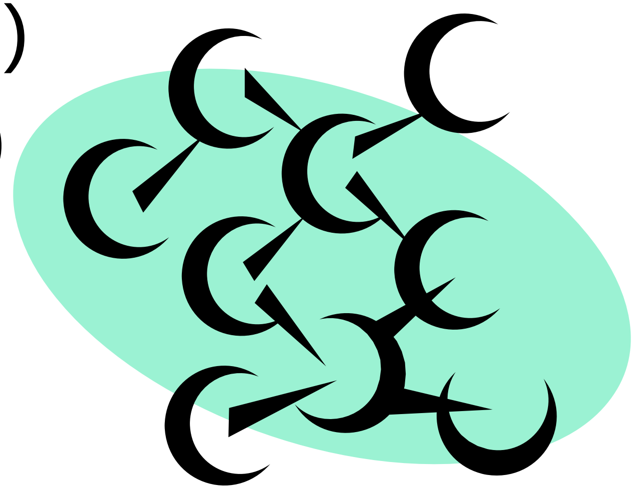
- **CAPs:** Criteria Air Pollutants - Air pollutants for which air quality criteria have been issued in the U.S.
  - Carbon monoxide (CO)
  - Nitrogen oxides (NO_x)
  - Sulfur dioxide (SO_2)
  - Lead (Pb)
  - Particulate matter (PM)
  - Ozone (O_3)
- **Air Toxics – Hazardous Air Pollutants (HAPs)**
  - Section 112b
- **Mercury (Hg)**
  - Mercury is a HAP in Section 112b list

Primary and Secondary Pollutants

- Primary pollutants
  - Emitted directly from a source
  - Examples: Carbon monoxide (CO), nitrous oxide (N_2O), lead (Pb), sulfur dioxide (SO_2), particulate matter (PM), volatile organic compounds (VOC), ammonia (NH_3)
- Secondary pollutants
  - Formed in the atmosphere by chemical reaction
  - Examples: Ozone (O_3), nitrogen dioxide (NO_2), PM, Formaldehyde
- Pollutants can be both primary and secondary
  - Examples: Formaldehyde, PM

U.S. CAPs

- Air pollutants for which air quality criteria have been issued in the U.S.
  - Particulate matter (PM)
  - Carbon monoxide (CO)
  - Nitrogen oxides (NOx)
  - Sulfur dioxide (SO_2)
  - Lead (Pb)
  - Ammonia (NH_3)
  - Ozone (O_3)



International Comparison of Air Quality Standards

Pollutant	Duration of Exposure	WHO Guidelines	United States Standards	European Union Standards	China Standards		
					Class I	Class II	Class III
CO (ppm)	24-hour				3.49	3.49	5.24
	8-hour	8.73	9[a]	8.73			
	1-hour	26.2	35[a]		8.73	8.73	17.47
NO_x (μg/m^3)	Annual		100	40	50	50	100
	24-hour				100	100	150
	1-hour	200		200[i]	150	150	300
Ozone (ppm)	8-hour	0.06	0.08[e]	20			
	1-hour		0.12[f]	50[h]	0.06	0.08	0.10
PM_{10} (μg/m^3)	Annual		50[b]	20	40	100	150
	24-hour		150[a]	50[h]	50	150	250
SO_2 (μg/m^3)	Annual	0.017	0.030		0.007	0.021	0.035
	24-hour	0.044	0.140[a]	0.044[j]	0.017	0.052	0.087

Footnotes

a) Not to be exceeded more than once per year
b) The expected annual arithmetic mean PM10 concentration at each monitor within an area must not exceed 15 μg/m^3.
e) The 3-year average of the 4th-highest daily maximum 8-hr average ozone concentrations measured at each monitor within an area must be <=0.08 ppm.
f) The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12ppm is <=1.
g) Allowed <26 days of exceedances
h) Allowed <8 exceedances
i) Allowed <19 exceedances
j) Allowed <4 exceedances

Particulate Matter (PM)

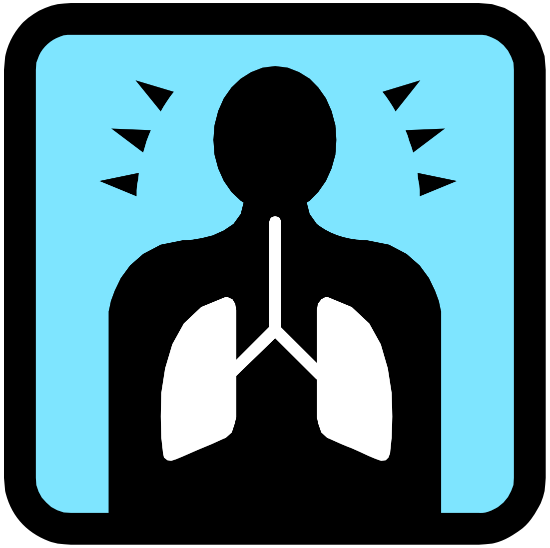
- Primary PM is directly emitted by dust and soot sources
- Secondary PM is formed by gas conversion reactions of NO_x, SO_x, VOCs, and NH_3
- PM size is an important property
  - Total suspended particulate (TSP) = 30 µm and larger
  - Respirable particulate = 10 µm and smaller (PM_{10})
  - Fine particulate = 2.5 µm and smaller ($PM_{2.5}$)

Primary Particulate Matter Sources

- Industrial processes
- Industrial, commercial,
- Residential fuel combustion
- Windblown dust (e.g., from mines)
- Re-entrained dust from vehicle traffic on public and industrial roads
- Open burning, agricultural burning
- Natural sources (sea salt, volcanoes)

Effects of Particulate Matter

- Regional haze, visibility degradation
- Smog
- Soiling of buildings and property
- Alteration of local weather
- Health effects
  - Respiratory problems
  - Lung diseases
  - Premature death
  - Chronic bronchitis



Carbon Monoxide (CO)

- Created by incomplete combustion of carbonaceous fuel
- Sources
  - Automobiles
  - Residential heating and cooking
  - Industrial processes
  - Open burning
  - Prescribed or agricultural burning

Effects of Carbon Monoxide

- Global warming potential
- Health effects
  - Heart diseases
  - Limits the oxygen-carrying ability of blood
  - Respiratory problems
  - Affects the central nervous system
  - Death at higher concentrations

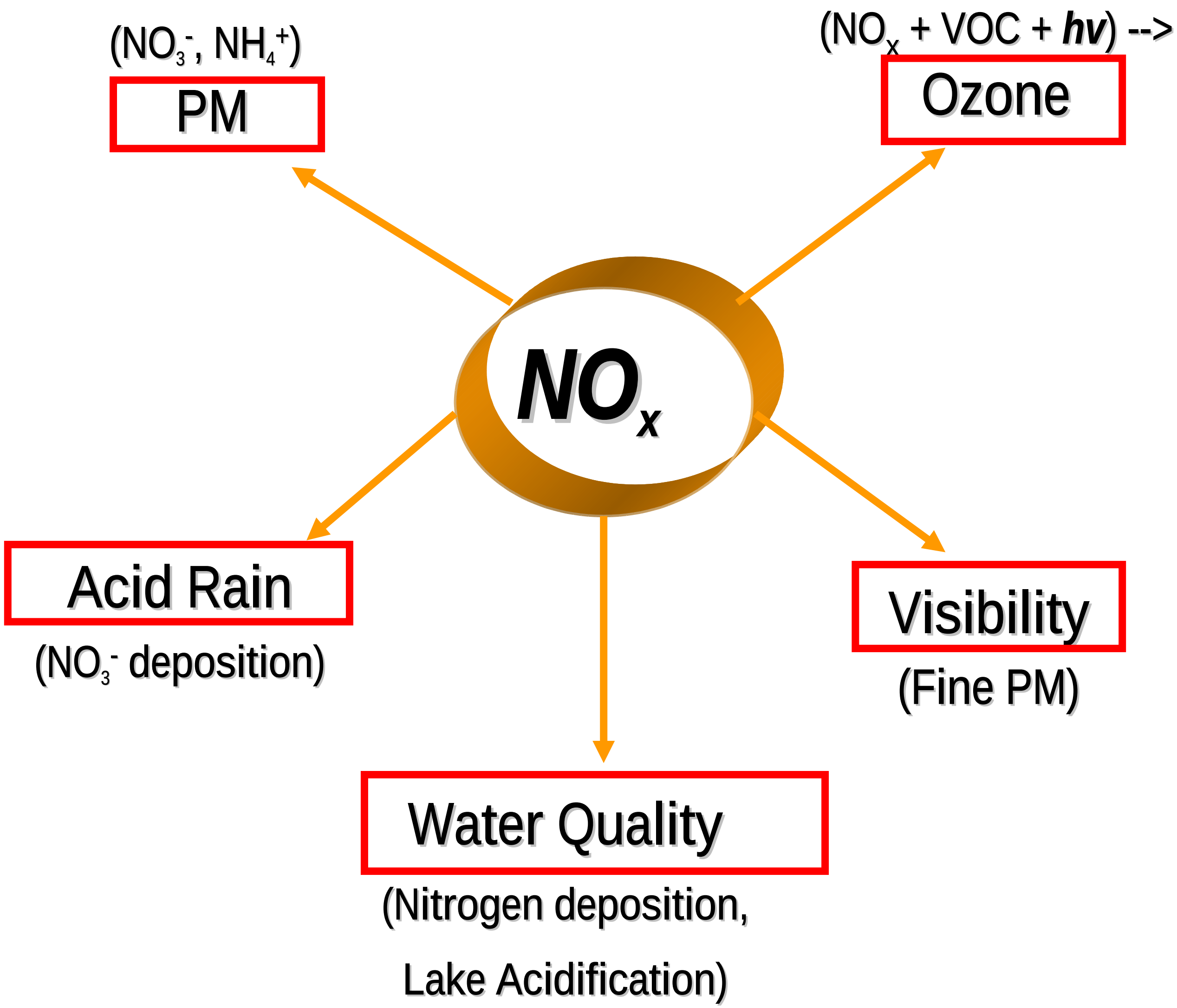
Nitrogen Oxides (NO_x)

- NO_x includes two primary species
  - Nitric oxide (NO)
  - Nitrogen dioxide (NO_2)
- Formed when fuel is burned
  - Nitrogen and oxygen in air => NO_x
  - Organically bound nitrogen in fuels form NO_x
- NO_x is highly reactive and a major ozone precursor

Effects of Nitrogen Oxides

- Photochemical smog
- Ozone formation
- Visibility degradation
- Acid deposition
- Secondary particulate matter precursor
- Eutrophication
  - Nutrient buildup in water
- Human health effects
  - Respiratory problems
  - Lung diseases

NO_x-Related Air Quality Issues



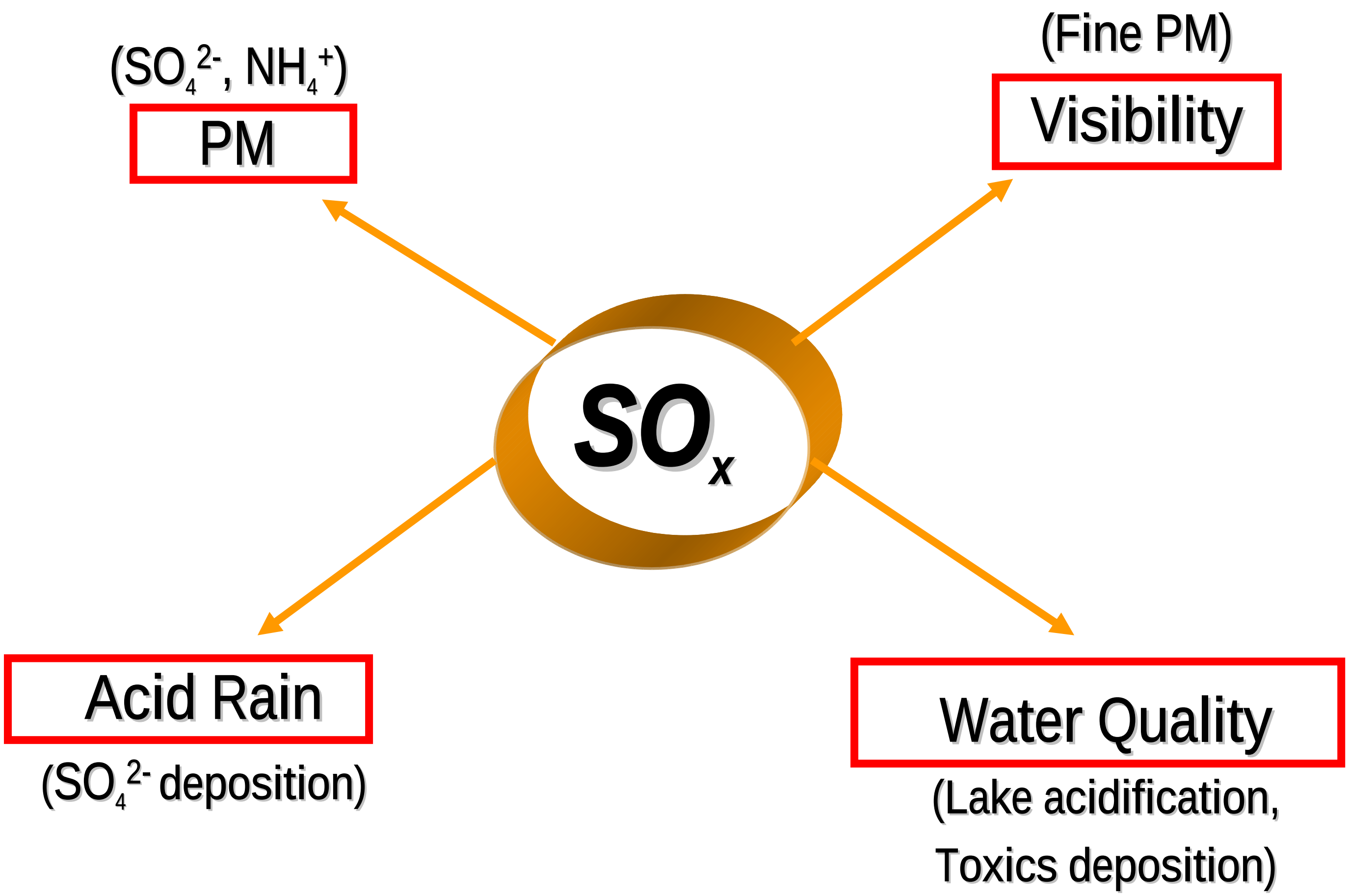
Sulfur Dioxide (SO_2)

- Produced from combustion of sulfur-containing materials (e.g., coal)
- SO_x used to categorize SO_2 and SO_3
- Sources
  - Fossil-fuel combustion
  - Industrial processes
  - Volcanoes

Effects of Sulfur Dioxide

- Visibility degradation
- Acid deposition
  - Damage to vegetation
  - Damage to crops
  - Damage to animals
  - Damage to monuments
  - Damage to drinking water
- Secondary particulate matter precursor
- Corrosion
- Human health effects
  - Respiratory problems
  - Lung diseases
  - Aggravation of existing cardio-vascular diseases

SO_x-Related Air Quality Issues



Lead (Pb)

- A metal found naturally in the environment
- Used in manufactured products
- Sources of lead emissions in the air
  - Metal processing
  - Fuel combustion
  - Waste incinerators
  - Lead-acid battery manufacturing
  - Aircraft

Effects of Lead

- Slowing of vegetative growth
- Elevated levels in water causing reproductive damage to some aquatic and animal life
- Health effects in humans
  - Damage to kidneys, liver, brain, and nerves
  - Leads to osteoporosis and reproductive disorders
  - Causes high blood pressure and increased risk of heart attacks

Ozone

- Formed by free radical reactions of reactive VOCs and NO_x in the presence of sunlight

- Temperature inversions (warm air is trapped near the surface) promotes smog formation

- NO_x limited versus VOC limited

Volatile Organic Compounds (VOCs)

- VOC species are part of the broad group of compounds called total organic gases (TOG)
- VOC species do not include organic compounds with limited or no photochemical reactivity
- VOCs are a significant contributor to ground-level ozone formation

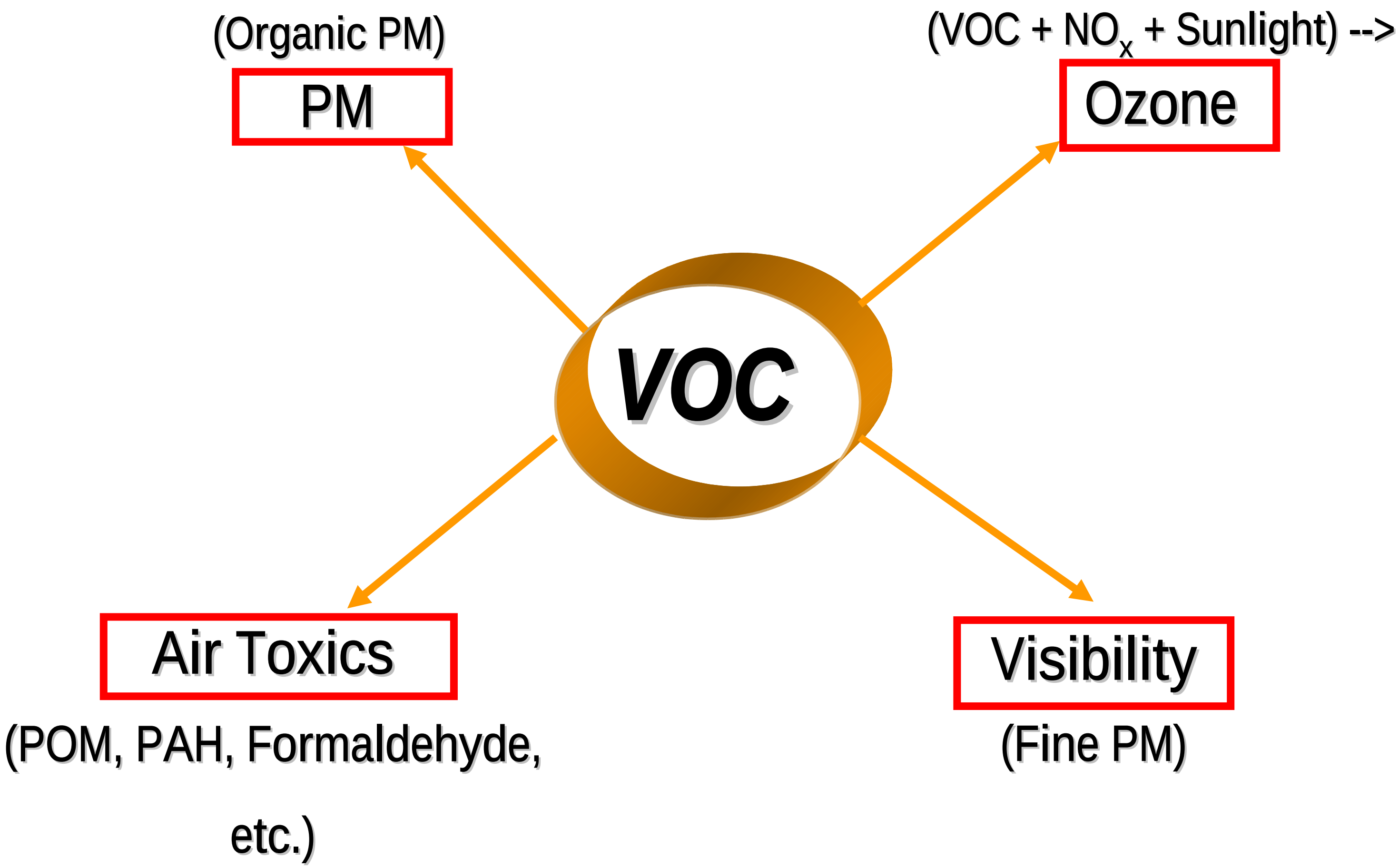
Common VOC Sources

- Combustion sources
  - Stationary fuel combustion
  - Vehicular traffic
- Evaporative sources
  - Surface coatings and paints
  - Petroleum product storage and distribution (e.g., at refineries, fuel stations)
  - Solvents (consumer products, industrial uses)

Effects of VOC

- Secondary aerosol formation (haze and particulate matter precursor)
- Photochemical smog, ground-level ozone formation
  - Damage to vegetation
  - Haze
- Health effects
  - Respiratory problems
  - Nose and throat infections
  - Skin allergies
  - Cancer
  - Kidney, liver, and brain damage
  - Damage to nervous, reproductive and immune systems

VOC-Related Air Quality Issues

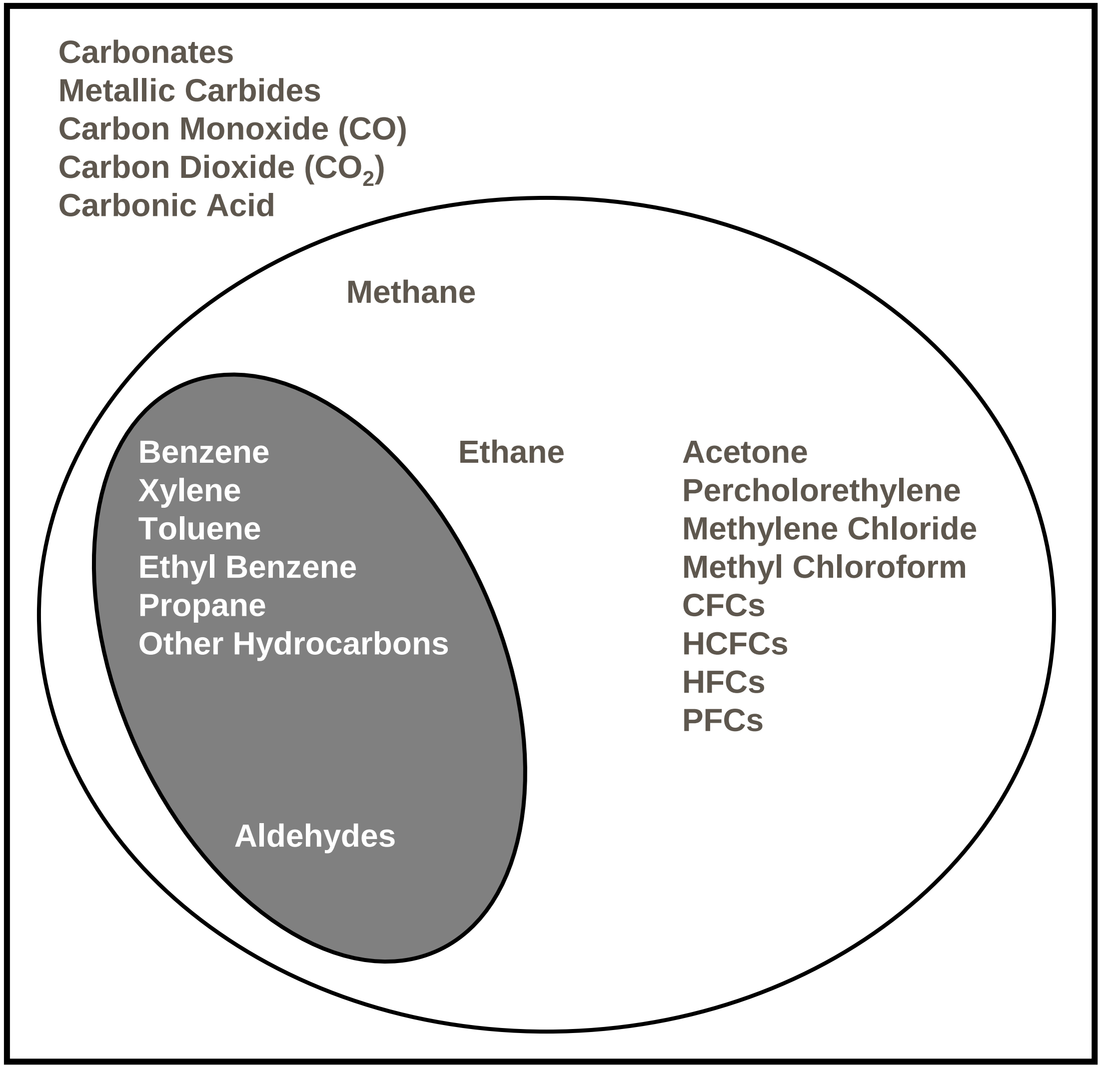


Visual Representation of VOC Definition

Box includes all carbonaceous compounds

Circle includes total organic gases (TOG), also known as total organic compounds (TOC)

Shaded area includes VOC



Air Toxics

- Pollutants capable of causing serious illnesses (e.g., cancer, birth defects) or even death
- Health effects are typically irreversible
- Health effects generally associated with years of exposure rather than hours or days
- Some persist in the environment, either remaining in the air or depositing on soil and in waterways
- Some bioaccumulate in the environment
- Toxic in small amounts

Air Toxics

- Includes:
  - Volatile Organic compounds
  - Metals
  - Semivolatiles
  - Other

- We often incorrectly think of air toxics and PM and VOCs as being separate
  - Air toxics comprise a significant percentage of volatiles and metals
  - Most urban toxic “hot spots” are in same areas as where VOC and PM are emitted
    - Air toxics affect the same populations as VOC and PM

- Thousands of new chemicals being introduced into our environment each year

Issues to Consider With Air Toxics

- Important to use Chemical Abstract Services (CAS) number to describe specific air toxics compound because of chemical synonyms
- Keep in mind that toxicity varies by chemical
  - Carcinogens
  - Non-carcinogens
- Need to assess persistence and bioaccumulation in the environment – multi-pathway modeling of PB-HAPs
- HAP Groups in the CAA and Diesel PM

Pollutant Definitions – Identifying HAPs

- Clean Air Act list of 188 HAPs
  - Handouts 1, 2 and 3
- Clean Air Act Section 112(k) 33 Urban HAPs
  - Handout 3
- Persistent Bioaccumulative HAPs (PB-HAPs)
  - Handout 3

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) – defined as 7-PAH
Propylene dichloride
Quinoline
1, 1, 2, 2-Tetrachloroethane
Trichloroethylene
Vinyl chloride

PB-HAPs: Persistence Bioaccumulative HAPs

Why are PB-HAPs of global interest?

- Persistence: Persist in the environment
- Bioaccumulation: Bioaccumulate in the food chain
- Toxicity: Toxic to humans and wildlife
  - Linked to reproductive, behavioral, developmental, endocrine disruption, & other health effects
  - Exposure through:
    - production and use
    - consuming foods contaminated with persistent pollutants
- Long-Range Transport: Capable of traveling long distances in the air and water

PB-HAPs

- Cadmium
- Chlordane
- Chlorinated dibenzodioxins and furans
- DDE
- Heptachlor
- Hexachlorobenzene
- Hexachlorocyclohexane
- Lead compounds including Alkyl-lead
- Mercury and compounds
- Methoxychlor
- Polychlorinated biphenyls (PCBs)
- Polycyclic Organic Matter (POM)
- Toxaphene
- Trifluralin

(EPA, 2004.Air Toxics Risk Assessment Reference Library, Volume 1, Exhibit 14-1.)

Chemical Abstracts Service (CAS) #s

- EPA’s Office of Environmental Information Substance Registry System www.epa.gov/srs/

Carcinogens

- Chemical or physical agents capable of causing cancer
- Risks are usually reported as lifetime chances that a certain number of people in 1 million will contract cancer after continuous lifetime exposure
- The Unit Risk Estimate is the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 µg/m3 in air

Non-carcinogens

- Capable of causing damage to immune system, neurological, reproductive, developmental, and respiratory health problems
- Risks can be reported relative to a Reference Concentration (RfC), where there is no appreciable risk of effects after continuous lifetime exposure

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

$1x10^{-6}$ $1x10^{-4}$

Risk →

1989

Toxicity Information

- http://www.epa.gov/ttn/fera/risk_atoxic.html
- NATA uses “Chronic Inhalation” to prioritize HAPs and quantify effects
  - URE: cancer
    - Higher URE means higher risk at same dose
  - RfC: noncancer
    - Lower RfC means response can be caused by smaller dose

Toxicity Weighting Emission Inventories

- Methodology
  1. For all NEI poll except 136 and 7440473: Multiply emissions by Metal_CN Speciation Factor to **extract metal and cyanide mass for tox weighting**. Some NEI HAPs are speciated into more than one metal or into a metal and cyanide.

  2. For NEI poll 136 and 7440473: Use **chromium speciation file** to speciate source category emissions into Cr(VI) and Cr(III) emissions. Emissions by source category are needed in order to use Cr speciation file.

  3. **Cancer Tox weighting**: Multiply emissions generated from steps 1 and 2 by URE. Cancer risks between pollutants are additive. Cancer and NonCancer risks are not additive.

  4. **NonCancer Tox weighting**: Divide emissions generated from steps 1 and 2 by RfC for each target organ. NonCancer risks between pollutants are additive by target organ. Cancer and NonCancer risks are not additive.

- Files needed:
  - Toxicity Weighting Factors (Handout 4)
  - Chromium Speciation (Handout 5)

HAP Groups in the CAA

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

Modeling Considerations for HAPs that are part of groups

- Group multiple inventory species into a single pollutant category Example: group lead oxide, lead nitrate, lead sulfate, etc. into lead group)
- Partition inventory species into multiple pollutant categories with different particulate size classes,

  Example: apportion lead chromate to:

  1) lead compounds, fine particulate;
  2) lead compounds, coarse particulate;
  3) chromium compounds, fine particulate and
  4) chromium compounds, coarse particulate
- Adjust the emissions of an inventory species to partition it among multiple pollutant categories, account for a particular portion of it (e.g., the lead portion of lead sulfate), or adjust its potency to determine a toxics or reactivity equivalency
- Speciate compounds based on the type of source if exact compound is not given

  Example: speciate chromium into hexavalent and trivalent forms using assumptions about the process emitting the chromium

Polycyclic Organic Matter

- "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

POM – NEI Groups

- POM
  - POM as 7-PAH
  - POM as 15-PAH – includes 7 PAH compounds
  - Total POM
  - POM Toxicity Groups

Handout 6

Grouping of POM for Risk Assessments

POM GROUP	URE used in Risk Assessment	Basis
POM, Group 1: unspeciated	5.5 * 10 -5	Same URE as was assumed for total POM group in NATA 1996: 5% of risk from Benzo(a)pyrene
POM, Group 2: No URE data	5.5 * 10 -5	Same as 71002
POM, Group 3 5e-2<URE<5e-1	1 * 10 -1	Midpoint of range
POM, Group 4: 5e-3<URE<5e-2	1 * 10 -2	Midpoint of range
POM, Group 5: 5e-4<URE<5e-3	1 * 10 -3	Midpoint of range *this group contains benzo(a) pyrene
POM, Group 6: 5e-5<URE<5e-4	1 * 10 -4	Midpoint of range
POM, Group 7: 5e-6<URE<5e-5	1 * 10 -5	Midpoint of range
POM, Group 8: Unspeciated 7-PAH	2 * 10 -4	Same as was used for 7-PAH from 1996 NATA: 18% of risk from Benzo(a)pyrene

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)
- Handout 7

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"
  - E.g., To quantify how much hydrogen cyanide emissions would result from silver cyanide (CAgN):
    - Molecular Weight of CAgN is 133.8857
    - Molecular Weight of HCN is 27.0256
    - Factor = 27.0256/133.8857= 0.2019
    - Equivalent emissions of CAgN= CAgN 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/
- See Handout 9 for list of compounds mistaken as glycol ethers

Xylenes and Cresols

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

Note: For NATA, we're not currently using the isomers.

Diesel PM

- Mixture of particles that is a component of diesel exhaust
- Cancer and noncancer health effects
- Noncancer health effects not aggregated with other HAPs in NATA
- Diesel PM is not in 1999 NEI for HAPs
- Diesel PM modeling inventory (coarse and fine diesel PM) is created from PM inventory from diesel engines (onroad and nonroad only)

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

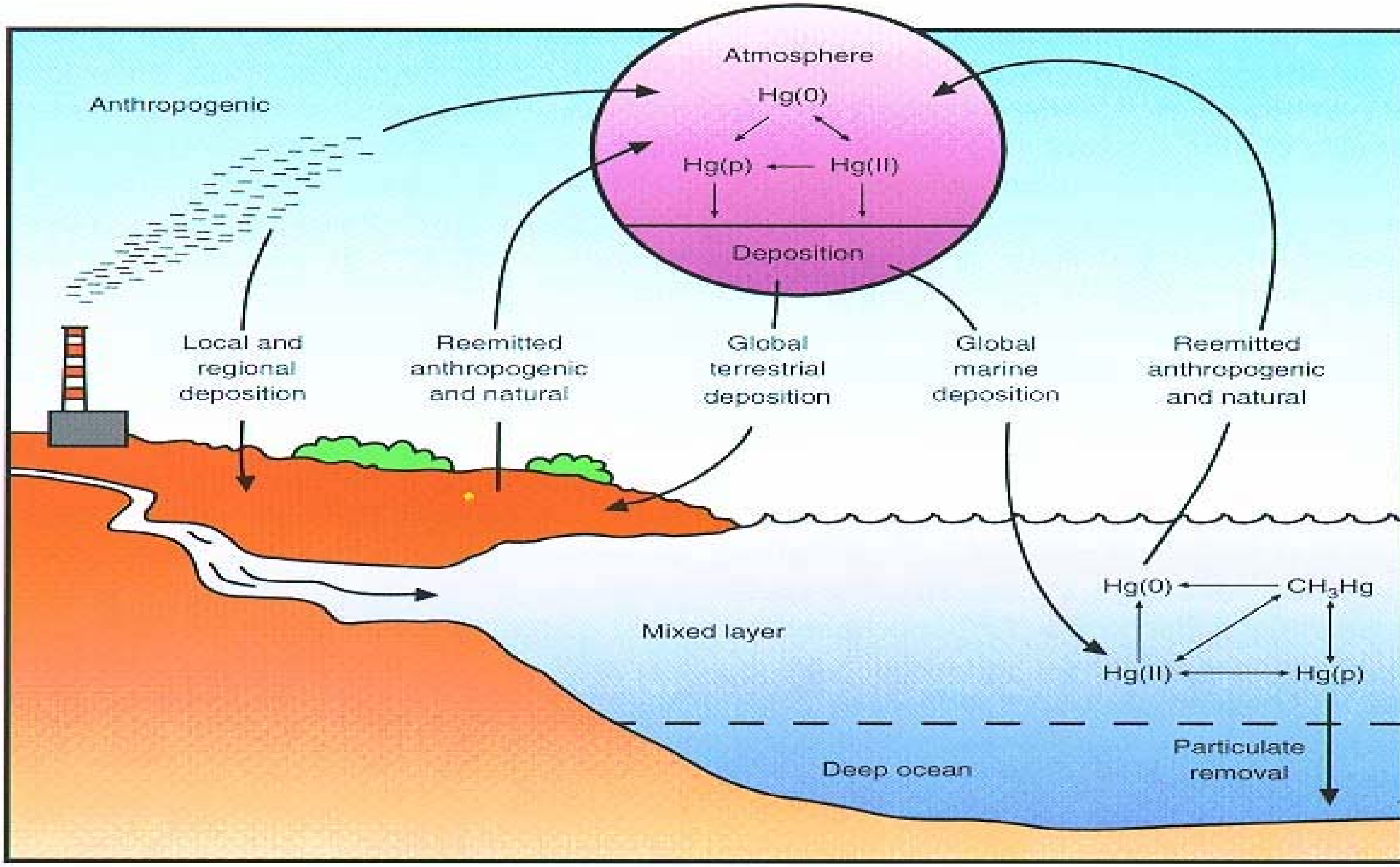
Modeling Metal Compounds

- Specific metal HAPs should be reported in the inventory, if available
- Model mass of metal only
  - E.g. emission modelers compute the mass of manganese in manganese oxide
- Specific compound may be needed for risk assessment or chemistry considerations in model
  - E.g., to determine whether it is hexavalent chromium or trivalent chromium, is it nickel subsulfide?
- For mercury, if exact chemical compounds not known, provide amount of mass as “divalent particulate,” “divalent gas,” and “elemental”
  - These three are “model species” in numerous grid models (e.g., REMSAD, CMAQ)
  - Ideally, emissions should be broken out by specific chemical and by specific form (gas vs particulate)
- Use Mercury Speciation File, Handout 8

Mercury (Hg)

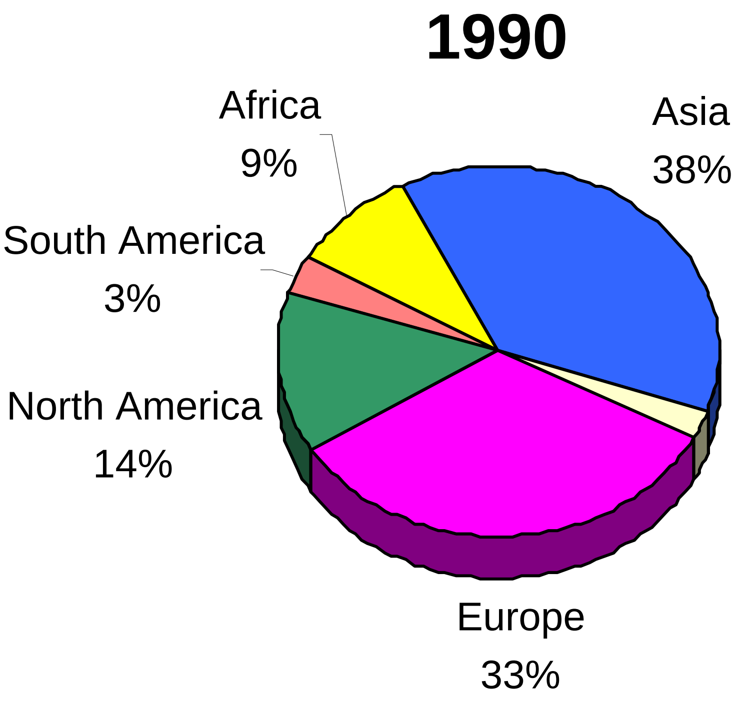
- Mercury is toxic, persistent, and bioaccumulates in food chains
- Global problem
  - Cycled globally - transported great distances through air and oceans
  - Nations with minimal releases, and remote areas (such as the Arctic) are adversely affected
- Current releases add to the “global pool”.....

Global Mercury Cycle

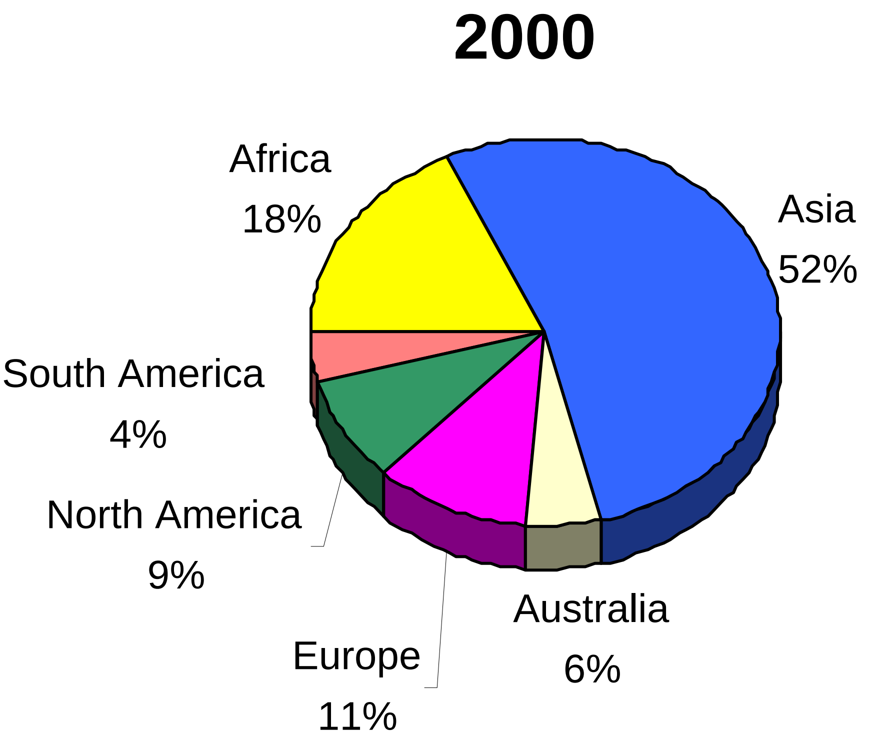


Courtesy of Rita Schoeny U.S. EPA. Adapted from U.S. Dept. of Interior's Report on Hg in the Florida Everglades

Estimated Anthropogenic Emissions of Mercury by Region in 1990 and 2000



Total: 1,881 metric tons/yr

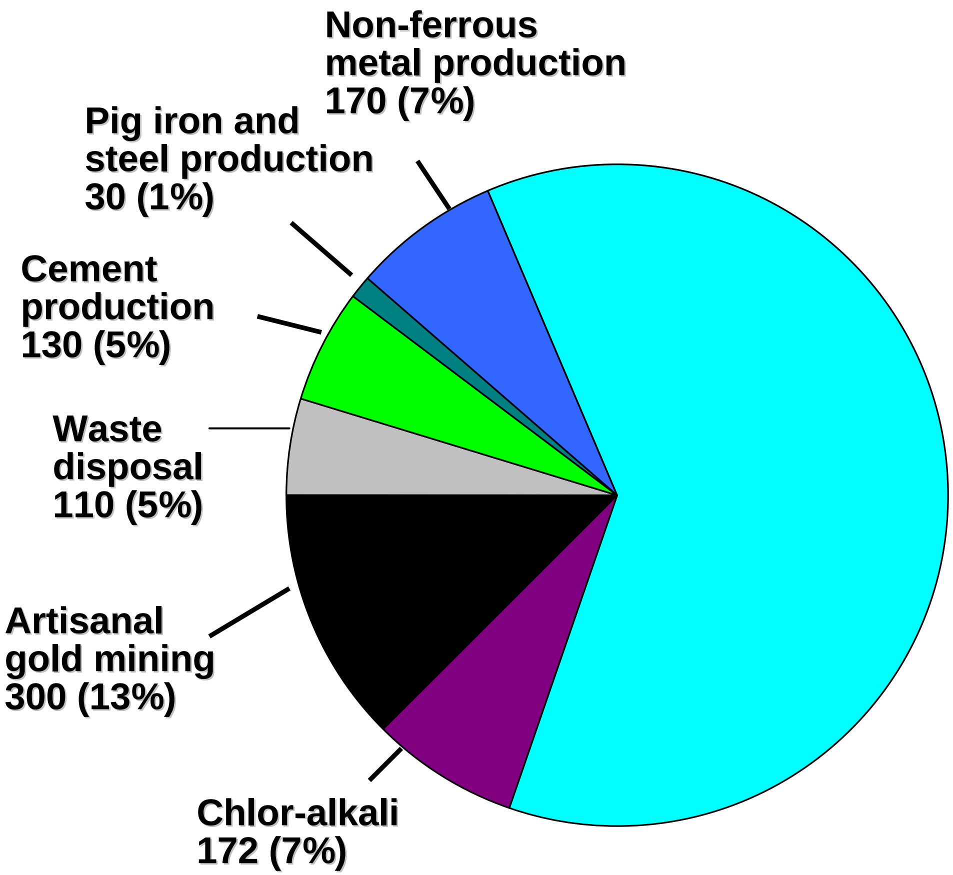


Total: 2,269 metric tons/yr

Note: Significant emissions also occur due to natural sources, and re-emissions from historic anthropogenic sources.

Based on Pacyna, J., Munthe J., Presentation at Workshop on Mercury: Brussels, March 29-30, 2004

Global Mercury Cycle



Estimates are uncertain; most countries do not have Hg inventories

Total: 2,382 metric tons

Source: Estimates derived from data in the 2002 UNEP Global Mercury Assessment

Major Exposure Pathways for Mercury

Humans are exposed to 2 main mercury forms:

- Methylmercury (MeHg):
  - Ingestion of fish - main route of exposure
- Elemental mercury (Hg^0) vapours:
  - Inhalation - main route of exposure

Methylmercury (MeHg) Toxicity

- **MeHg is highly toxic, especially to developing nervous system**
  - Evidence of toxicity to cardiovascular, immune, and reproductive systems
  - Severe poisoning events occurred in 1960s-70s in Minamata Bay, Japan; and in Iraq:
    - Effects on adults included: death, tremors, ataxia, hearing and vision impairment, and balance and speech disturbances
    - Children born to mothers exposed during pregnancy exhibited: cerebral palsy, delayed walking/talking, deficits in learning, and other effects

Exposures to Methylmercury (MEHg)

- Levels of MeHg are generally much higher in fish (and marine mammals) compared to other foods
  - Typically about 0.05 to 1.4 ppm (or mg/kg) in fish
  - Levels vary by species, size, and age of fish
  - Also, vary by characteristics of water body (pH, redox potential, local contamination, and other factors)
  - Highest in large predatory marine species, such as shark, swordfish, large tuna, some whales
  - Levels can also be high in predatory freshwater fish, such as pike, perch, tilapia
- >90% of Hg in fish is in the form MeHg
  - About 95% of ingested MeHg in fish is absorbed through the gastrointestinal tract
    - MeHg is distributed throughout the body and easily passes the placenta and blood brain barrier
    - Half-life in body has been measured to be 35 to 190 days (average = 72 days)

Elemental mercury (Hg^0) vapours

- Inhalation main route of exposure
  - Readily crosses blood brain barrier and placenta
  - Nervous system is primary target of toxicity
  - Neurological effects include tremors, insomnia, memory loss, headaches
  - Also toxic to kidney
  - High exposures can cause death
  - In body, Hg^0 is oxidized to inorganic mercury (Hg^{+2}), which accumulates in kidney
- Long-term Exposure:
  - Long-term occupational exposures to air levels of 25-30 ug/m^3 has resulted in adverse effects on nervous system + kidney
  - U.S. EPA "reference concentration" = 0.1 ug/m^3 (safe exposure level for all humans over a lifetime)
  - E.U. recommends that average annual exposure should not exceed 0.05 ug/m^3
- Short-term Exposure:
  - Short-term exposure to high concentrations can cause serious adverse effects
  - Various Governments have established limits for worker exposures:
    For example, in India short-term (15 minutes) air levels can not exceed 30 ug/m^3

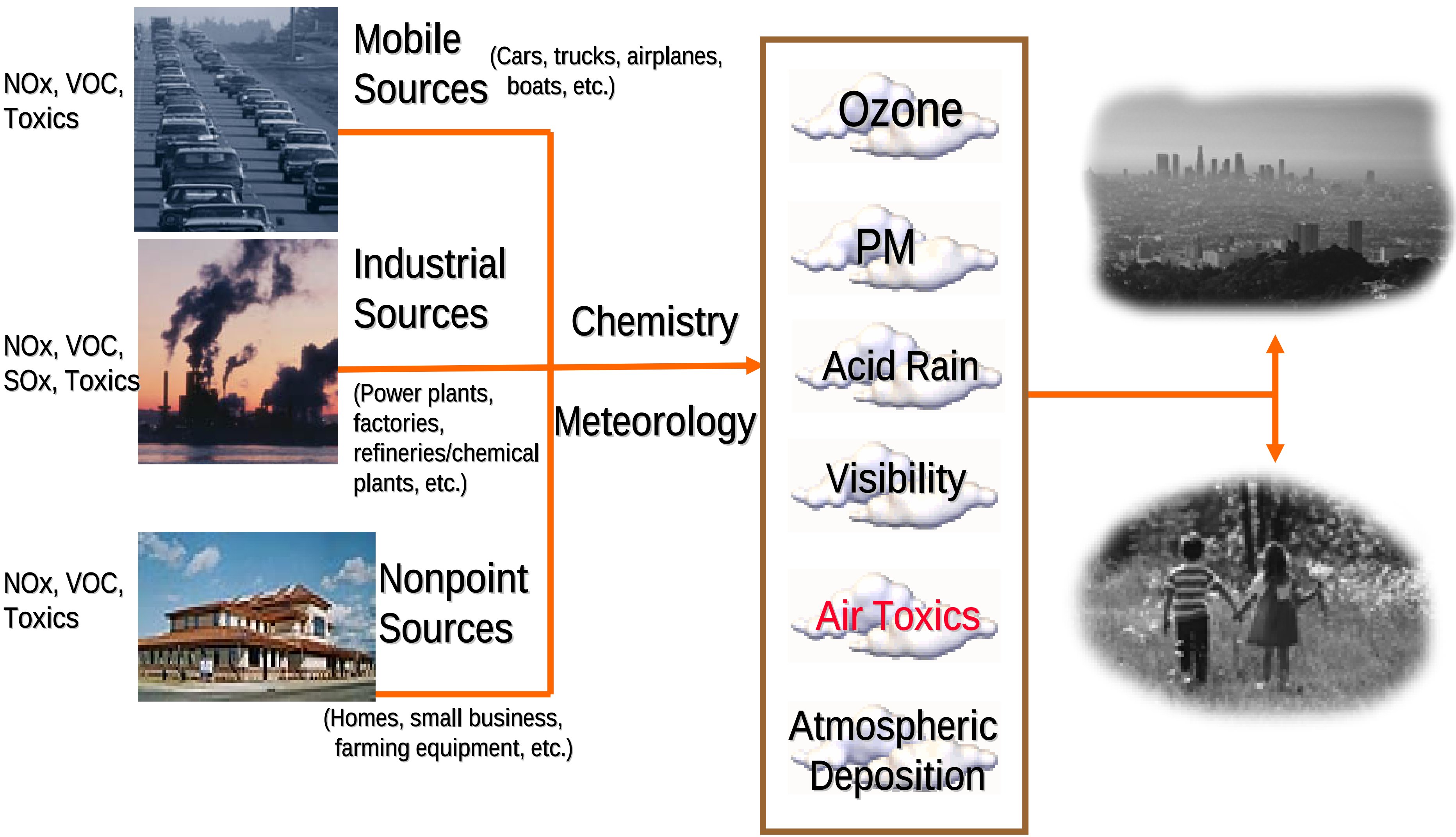
U.S. EPA's "One-Atmosphere" Modeling and Management"

- **"One-Atmosphere" Approach :**

  An integrated approach to address various air quality issues collectively under one modeling and management system.

- **Why "One-Atmosphere" ?**
  - Regulated sources perspective
  - Emitted pollutants perspective
  - Atmospheric chemistry perspective

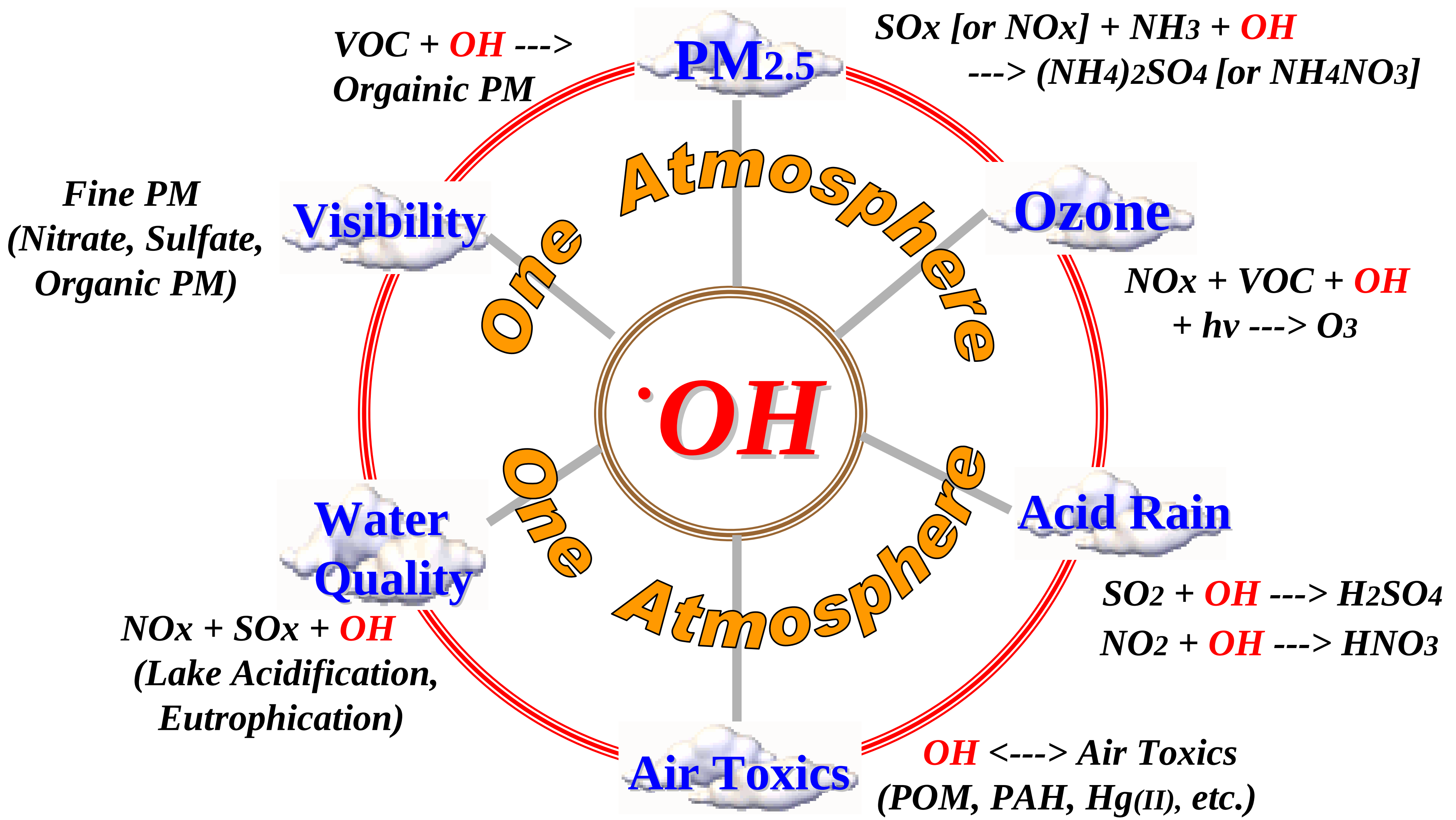
Regulating Air Pollution : One-Atmosphere Approach



One-Atmosphere" Approach (cont.)

- "One-Atmosphere" approach includes HAPs:
  - HAPs can be constituents of CAPs or precursors of CAPs such as VOC
  - HAPs are emitted by same sources as CAPs
  - HAPs impact health and the environment
- Like some CAPs, some HAPs are emitted directly (e.g., benzene) and others are formed by chemical reaction (e.g., formaldehyde and acrolein from photochemical reactions)

·OH Role in Pollutants Formation : One-Atmosphere



EIS Draft Pollutant Code Table

- Handout 10 lists proposed EIS pollutant codes
- Many Changes:
  - Addition of GHGs
  - HAP changes are significant for metals, POM and dioxin/furans
  - CAP changes - minor

HAP Toxicity Exercises

Questions or Comments?