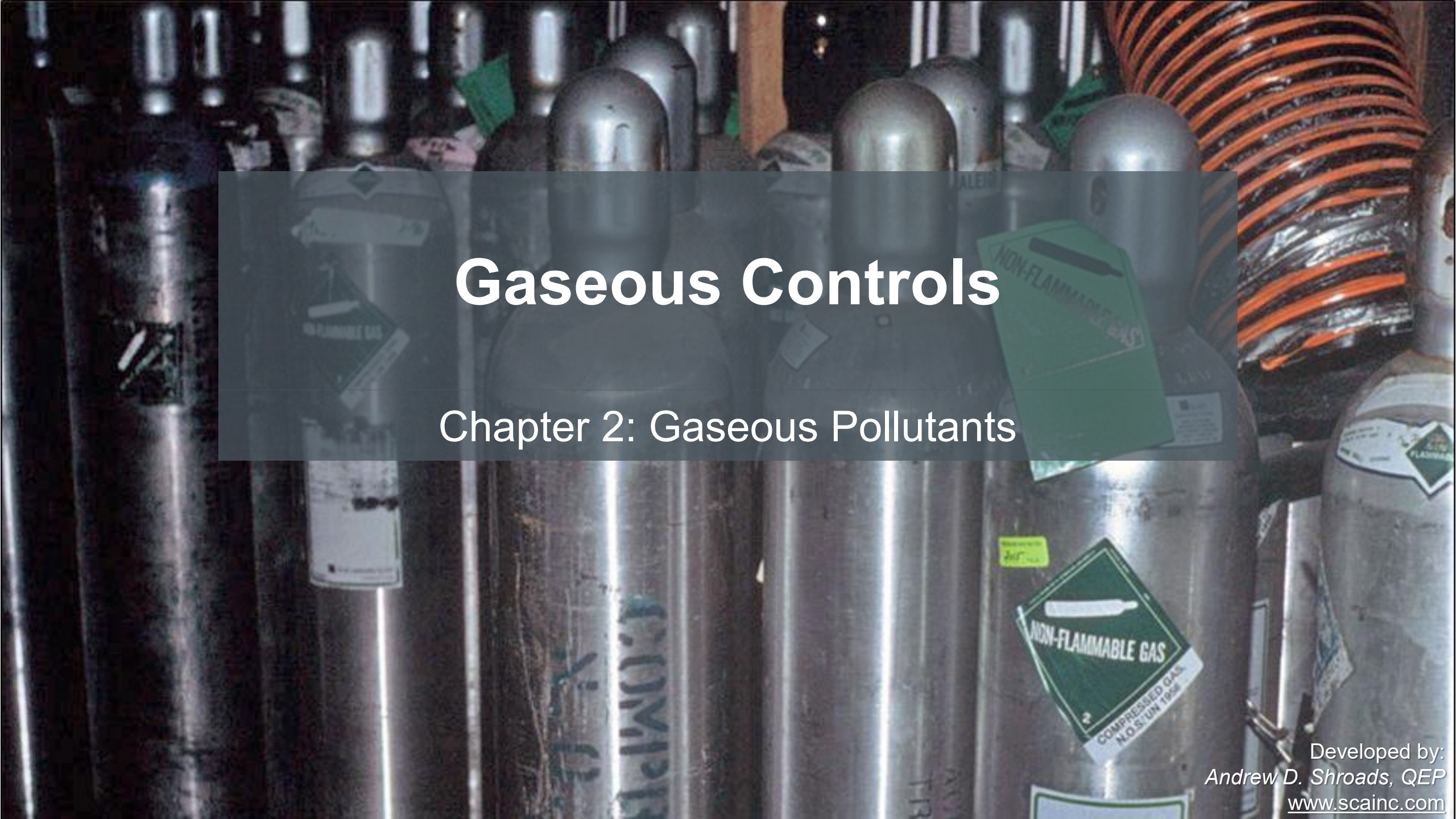
Gaseous Controls

Chapter 2: Gaseous Pollutants



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Chapter 2: Objective

To improve understanding of gaseous air pollutants

- What are the gaseous air pollutants?
- What are some of the environmental and health impacts of gaseous air pollutants?
- How do we regulate gaseous air pollutants?
- What control technologies reduce emissions of gaseous air pollutants?

Gaseous pollutants:

- Airborne pollutants in the gaseous or vapor phase
- Emitted by natural and anthropogenic (human-made) sources
  - Anthropogenic emissions primarily from industry (solvent use) and combustion (stationary sources and transportation)
- Classified as primary and secondary gaseous pollutants
  - Primary: Gaseous pollutants directly emitted from a source
    - Emitted directly to atmosphere via stack or fugitive emissions
  - Secondary: Form in the atmosphere through chemical reactions
    - Primary pollutants react with other compounds to form secondary pollutants

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Primary Pollutants

- Carbon monoxide (CO)
- Nitrogen oxides (NO_X)
- Sulfur dioxide (SO_2)
- Volatile organic compounds (VOC)
- *Ammonia (NH_3)*
- *Acid Gases: Hydrogen fluoride (HF), Hydrogen chloride (HCl), and Sulfuric Acid (H_2SO_4)*
- *Hydrogen sulfide (H_2S) / Reduced Sulfur*
- *Mercury (Hg)*

Secondary Pollutants

- Nitrogen oxides (NO_X)
- Ozone (O_3)
- *Sulfuric Acid (H_2SO_4)*

Carbon Monoxide (CO)



- Colorless, odorless gas that is harmful when inhaled
  - Reduces amount of oxygen that can be transported in blood
- Very insoluble in water
- Carbon monoxide is a result of incomplete combustion (not enough oxygen to form CO_2)
  - $2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$
- Very stable, therefore difficult to oxidize
  - Difficult to oxidize ($2CO + O_2 \rightarrow 2CO_2$), requires high temperatures (>1800°F)

Nitrogen Oxides (NO_X)

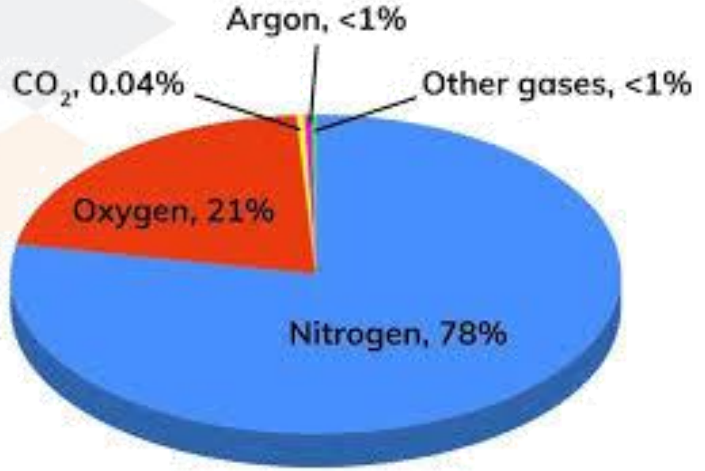




- NO_2 is a reddish-brown gas with pungent, acrid odor
- Primarily formed from combustion
- Irritates the respiratory system
  - Aggravates asthma and increases risk of cardiovascular disease
- Multiple environmental impacts:
  - Contributes to acid (HNO_3) rain, damaging stone and lowering lake pH
  - Contributes to nutrient pollution in coastal waters
  - Reacts in atmosphere to form fine particulates ($PM_{2.5}$) & ozone

NO_X Formation from Combustion

- NO_X is formed when things burn
  - Burning is oxidation reaction (materials gain oxygen and release heat)
  - Nitrogen combines with oxygen during burning
  - Nitrogen makes up majority of air (78%)



- Three sources of NO_X from combustion:
  1. Thermal NO_X – Airborne nitrogen is oxidized
  2. Fuel NO_X – Nitrogen in fuel is oxidized
  3. Prompt NO_X – Airborne nitrogen is oxidized by hydrocarbon radicals in fuel during early combustion

Nitrogen Dioxide (NO_2) vs Nitrogen Oxides (NO_X)

- NO_2 is a national ambient air quality standard pollutant
  - Most prevalent form of NO_X in atmosphere
  - NO is what is usually emitted at stack (soon oxidizes to NO_2)
- NO_X is regulated air pollutant (except N_2O)
  - New Source Performance Standards (NSPS): NO_X or NO_2 equivalent
  - Cross State Air Pollution Rule / Title IV: NO_X
- N_2O is a greenhouse gas (GHG)

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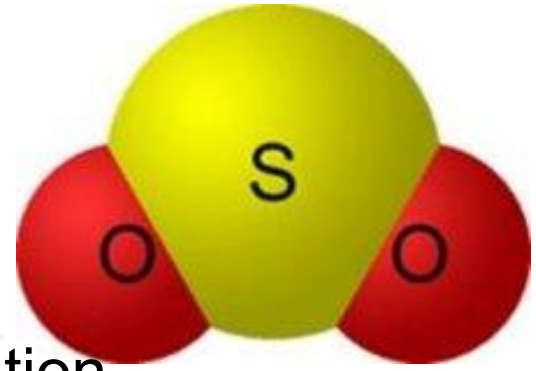
Family of Nitrogen Oxides (NO_X) Compounds				
Name	**Formula**	**Properties**	**Uses**	**Stability**
Nitric Oxide	**NO**	**Colorless Gas**	**Nitric Acid; Oxidizer**	**Intermediate Compound**
Nitrogen Dioxide	**NO_2**	**Red-brown Gas**	**Nitric Acid; Rocket Fuel; Sterilization**	**Stable**
Nitrous Oxide	**N_2O**	**Colorless Gas; Greenhouse Gas**	**Laughing Gas; Engine Horsepower**	**Stable**
Dinitrogen Dioxide	N_2O_2	Colorless Gas	Pharmaceuticals	Intermediate Compound
Dinitrogen Trioxide	N_2O_3	Black Solid	Special Purpose Fuel; Chemistry	Highly Unstable
Dinitrogen Tetroxide	N_2O_4	Colorless Liquid	Nitric Acid; Rocket Fuel	Highly Unstable
Dinitrogen Pentoxide	N_2O_5	White Solid	Rocket Fuel; Explosives	Highly Unstable

Sulfur Dioxide (SO_2)



- Colorless gas with pungent odor
- Irritates the respiratory system
  - Breathing impairment, respiratory illness, and aggravation of existing cardiovascular disease
- In combustion, most of the sulfur in fuel is converted to SO_2
- Multiple environmental impacts:
  - Contributes to acid (H_2SO_4) rain, damaging stone and lowering lake pH
  - Damages foliage and decreases plant growth and crops from deposition
  - Reacts in atmosphere to form fine particulate matter ($PM_{2.5}$)

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Sources of CO

- Fossil fuel combustion
  - Boilers, mobile sources

Sources of NO_X

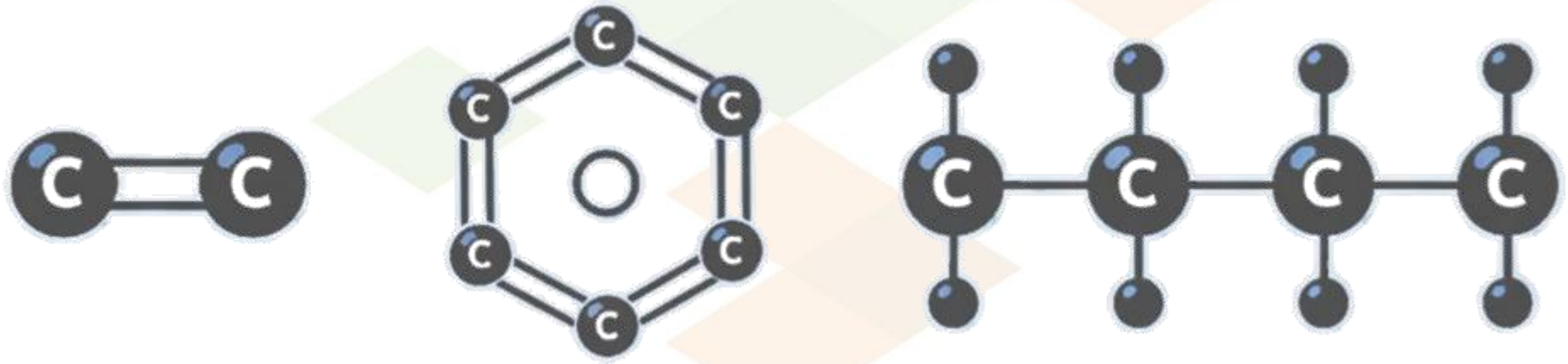
- Fossil fuel combustion
  - Boilers, mobile sources
- Oil & Gas Refining

Sources of SO_2

- Fossil fuel combustion
  - Boilers, mobile sources
- Oil & Gas Refining
- Chemical Manufacturing
- Portland Cement

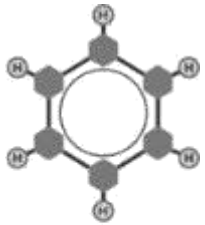
Organic Compounds

- Contain carbon-carbon or carbon-hydrogen bonds
  - Carbon-carbon (C-C) bond can be single, double, or triple bond
  - Carbon bonds can form rings (phenyl / benzene)
  - Carbon bonds can repeat (polymers)



Volatile Organic Compounds (VOC)

1. Organic Compounds
   - Chemical substance that contains carbon with a carbon-carbon bond or carbon-hydrogen bond (hydrocarbon)



2. Volatile (Easily Evaporate)
   - Volatile is any organic compound evaporating at 230ºF (EPA Method 24 for coatings)



3. Photochemically Reactive
   - Participate in atmospheric chemical reaction to form ozone



- Excludes CO, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate

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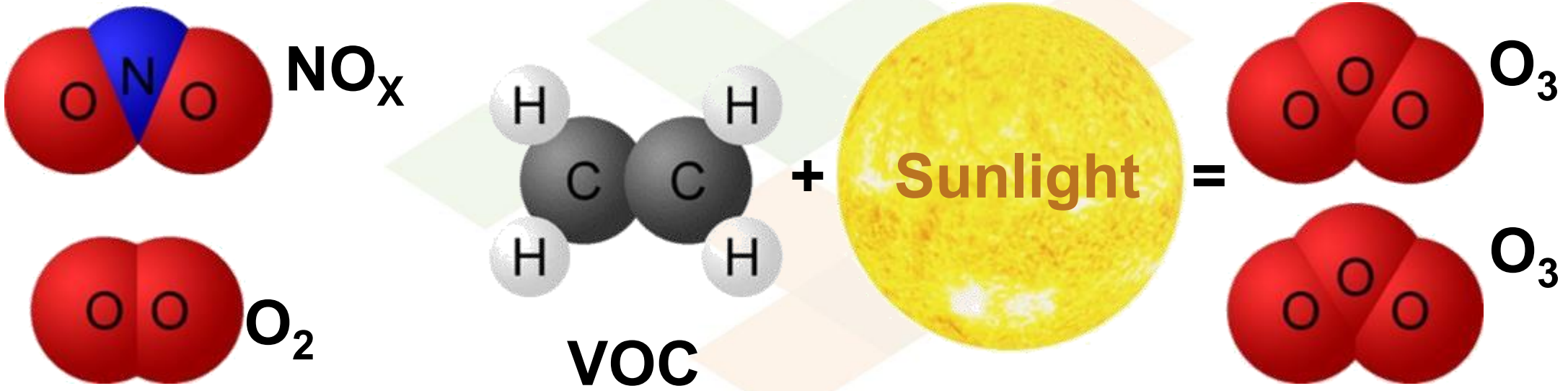
VOCs are defined by **exclusion**: any organic compound **not** exempted in Title 40, Code of Federal Regulations, §51.100(s)

Common VOC-exempt Organic Compounds

Gases / Refrigerants	Industrial Chemicals
Methane (Natural Gas)	Acetone (Solvent)
1,1,1,2-tetrafluoroethane (R-134a)	Methyl Acetate (Solvent)
Chlorodifluoromethane (R-22)	Methylene Chloride (Solvent)
Difluoromethane (R-32)	Perchloroethylene (Dry Cleaning)
Ethane (Chemical Feedstock)	Methyl Chloroform (Degreasing)
	And many more…

Photochemical Reactions

- Ozone (O_3) is formed in an atmospheric photochemical reaction with Oxygen (O_2), VOCs, and NO_X
- Need sufficient amounts of **both** VOC and NO_X to form ozone



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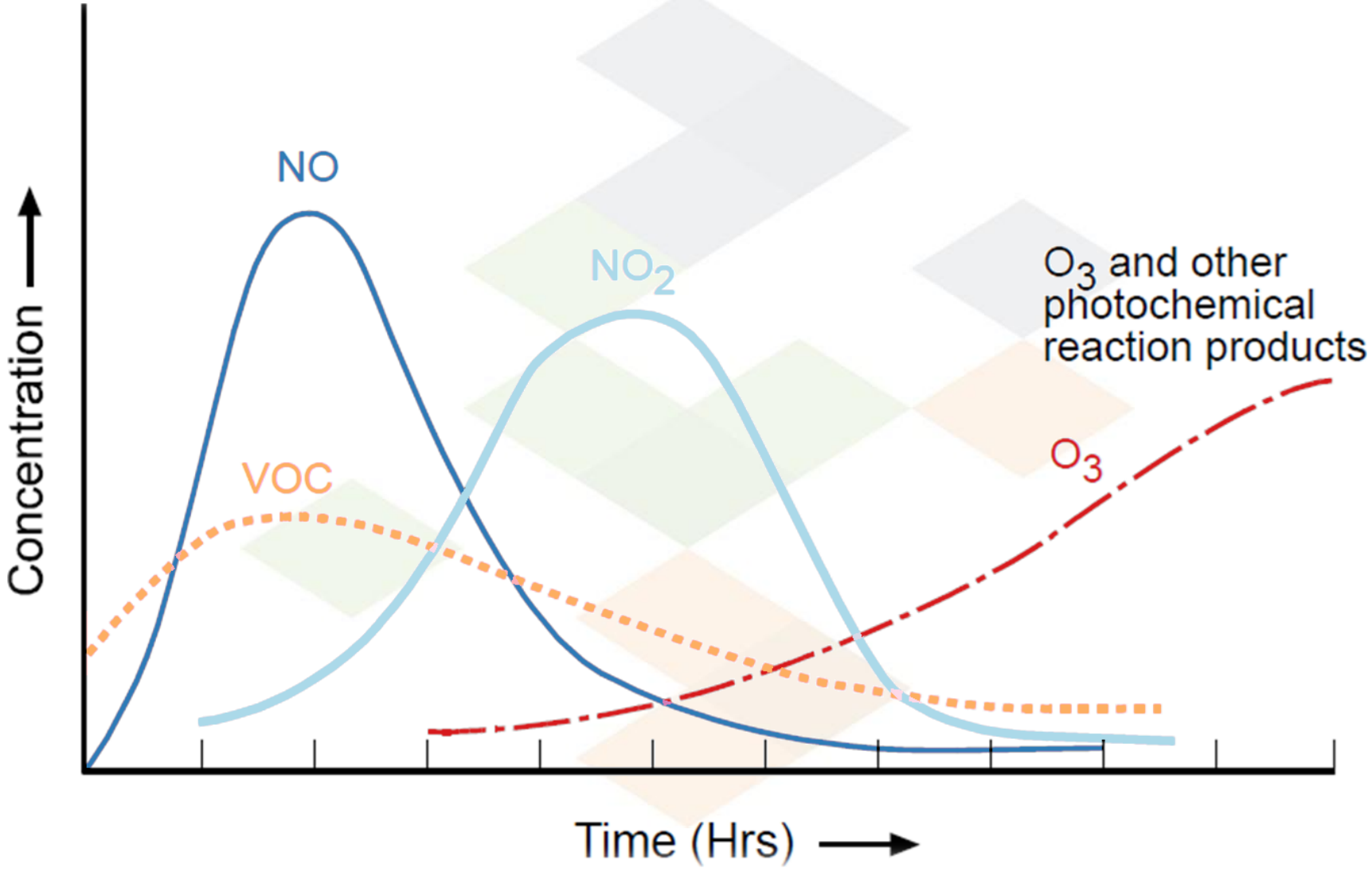

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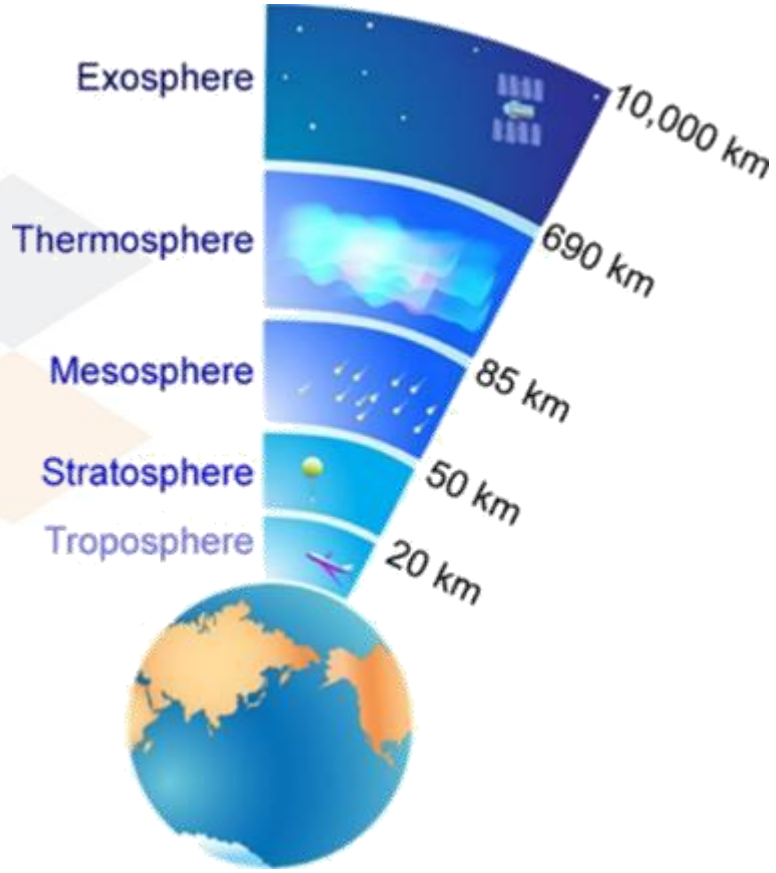
- **Stratospheric (good) ozone**
  - Absorbs ultraviolet (UV) radiation
  - O_3 destroyed by ozone depleting substances (chlorofluorocarbons – CFC)
- **Tropospheric (bad) ozone**
  - Triggers coughing, chest pain, airway inflammation, and throat irritation
  - Damages vegetation, stunts crop growth, and increases risk of disease and insect damage



VOC from evaporation in industrial processes

- Surface coating
- Synthetic organic chemical or pharmaceutical manufacturing
- Mold release (plastic, metal)
- Oil / gas refining, transmission, and distribution
- Solvents

VOC from incomplete combustion

- Engines
- Boilers

Ammonia (NH_3)

- Assists in $PM_{2.5}$ formation with SO_2 & NO_X
- Irritates eyes, ears, nose, throat, and upper airway
- Strong odor
- Commonly used as an additive in some air pollution controls
  - Ammonia reacts with NO_X to form N_2
  - Ammonia improves fly ash resistivity to increase collection efficiency of PM in electrostatic precipitators

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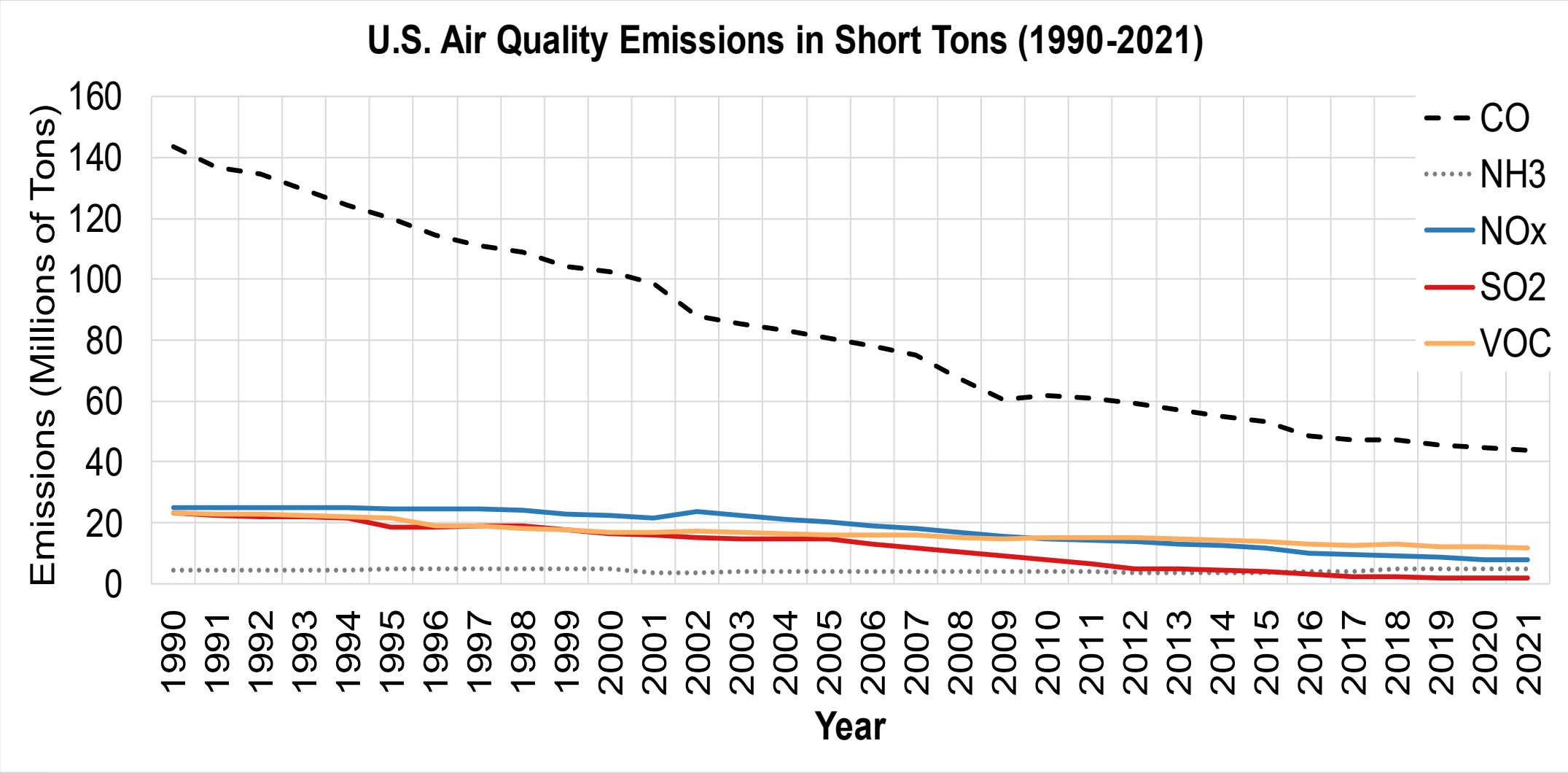
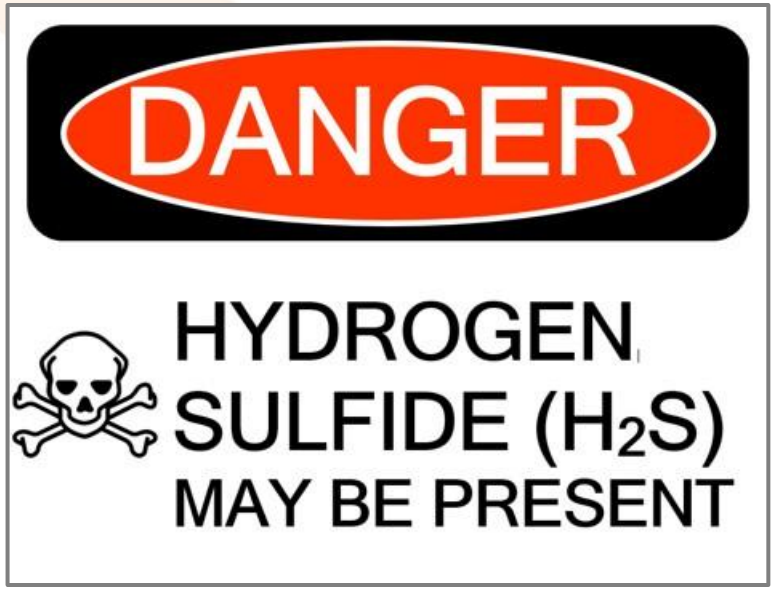


Hydrogen Chloride (HCl) & Hydrogen Fluoride (HF) – HAP

- Combustion of materials containing chlorine or fluorine
  - Incineration of solid wastes containing plastics
- Emitted by mineral ore processing operations
- Very soluble in water and are strong irritants
- Both designated as hazardous air pollutants (HAPs)
  - Both irritate and damage mucous membranes in your nose, throat, and respiratory tract
  - HF also causes deep tissue destruction and life-threatening systemic electrolyte imbalances

Hydrogen Sulfide (H_2S) / Total Reduced Sulfur (TRS):

- H_2S has a strong, rotten egg odor
  - Emitted from: metallurgical, petroleum, and petrochemical processes; sour natural gas wells; wastewater, and landfills
- TRS emitted from Kraft pulp mills, petroleum and natural gas processing, wastewater, and landfills
  - Methyl mercaptan (CH_3SH)
  - Dimethyl sulfide $(CH_3)_2S$
  - Dimethyl disulfide $(CH_3)_2S_2$

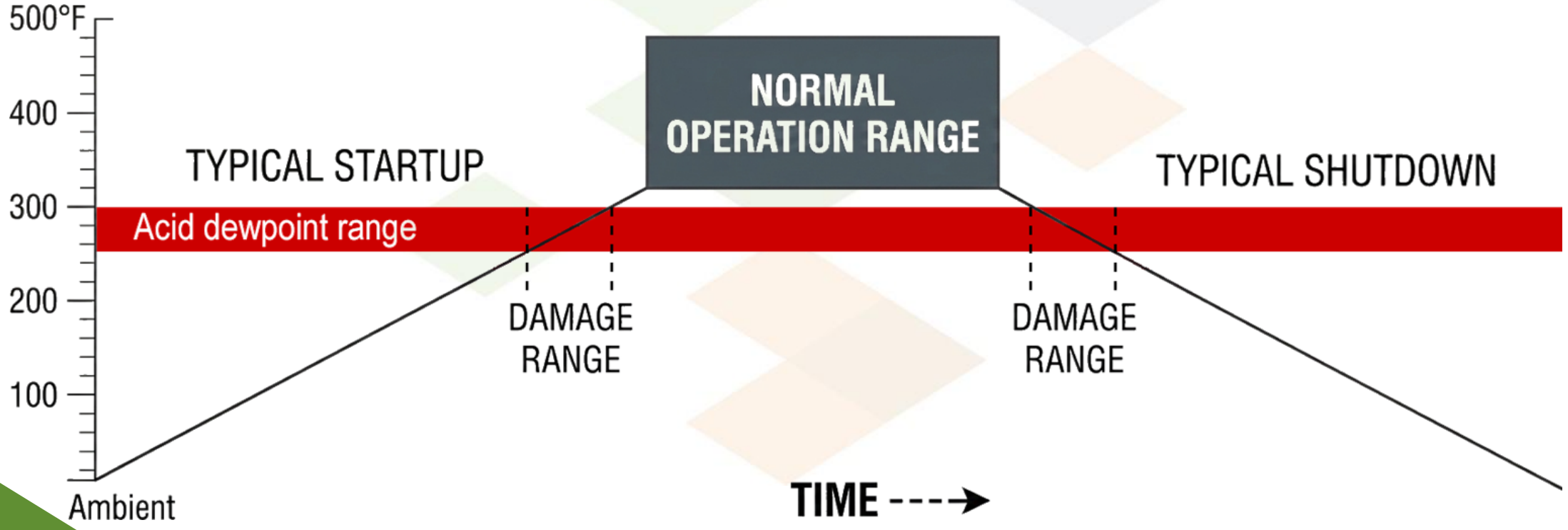


Sulfuric Acid (H_2SO_4) – HAP

- During combustion of sulfur in fuels, 95% of sulfur is converted to SO_2 and 0.5% to 2% is converted to sulfur trioxide (SO_3)
  - At <600°F, SO_3 reacts with water to form H_2SO_4 ($SO_3 + H_2O \rightarrow H_2SO_4$)
- Highly corrosive
  - Damages air pollution control equipment, ductwork, and fans
  - Keep exhaust gas streams above sulfuric acid dew point (250-300ºF)



May have to modify control device startup / shutdown to minimize time in acid dewpoint range



Mercury – HAP

- Potent neurotoxin & vaporizes at ambient temperature
  - Cannot see or smell mercury vapors
- Converted into methylmercury (CH_3Hg+) by microbial action in soils and aquatic sediment
  - Methylmercury bioaccumulates in food chain
- Sources:
  - Chlor-alkali manufacturing processes
  - Mining operations (naturally occurring with other ores)
  - Metal refining (amalgamation)
  - Material combustion containing elemental mercury (coal, solid waste)

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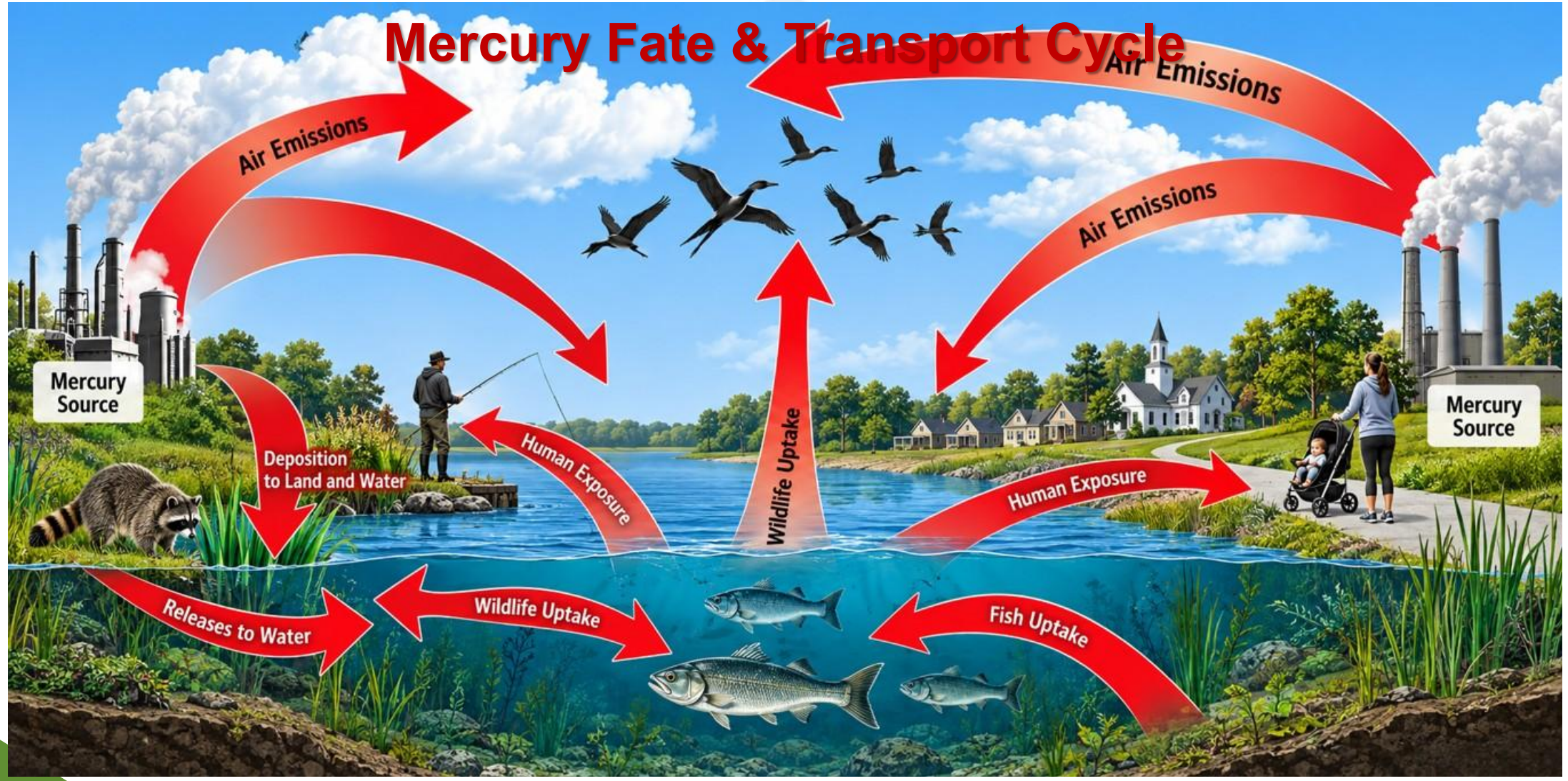

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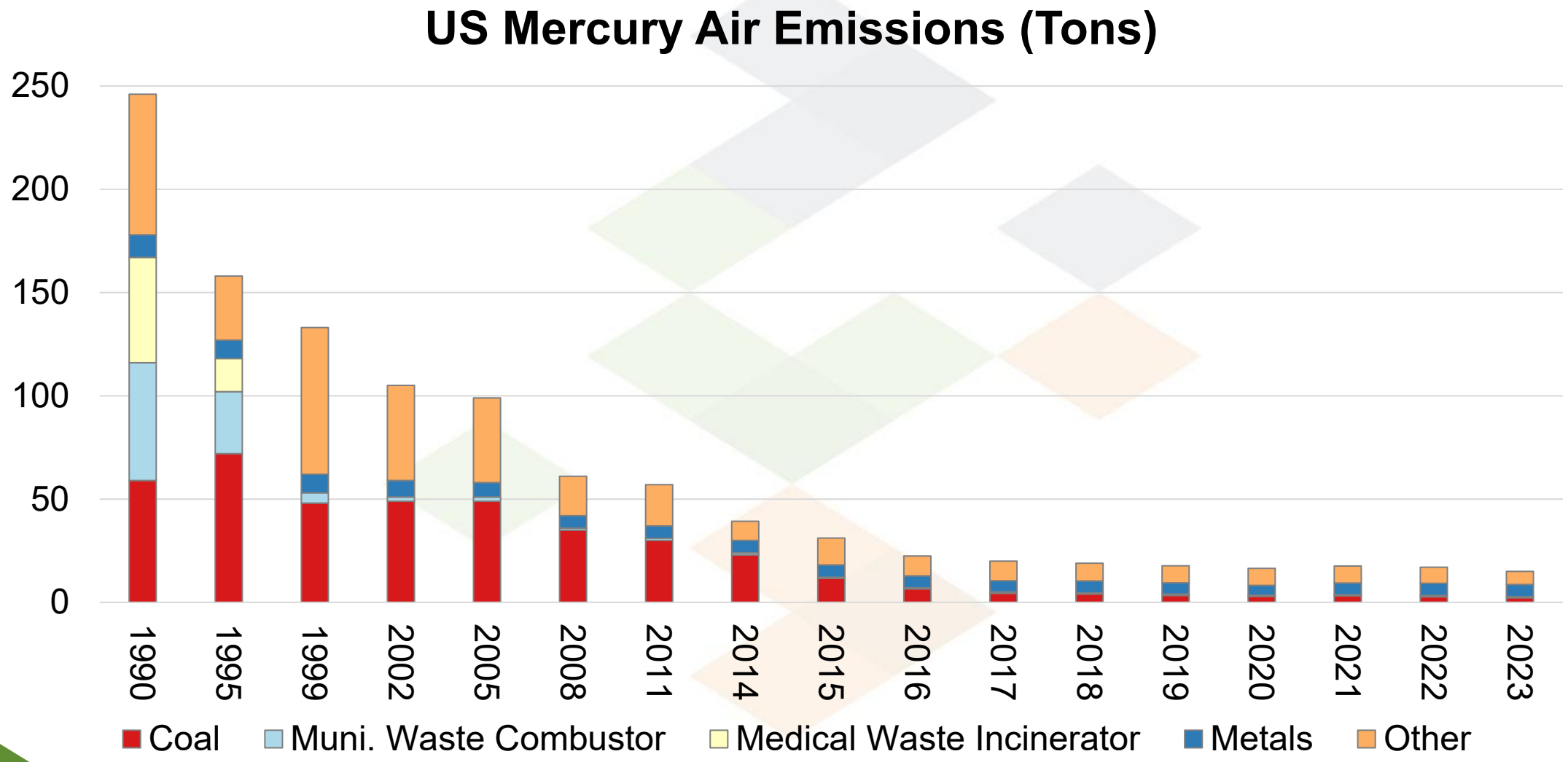
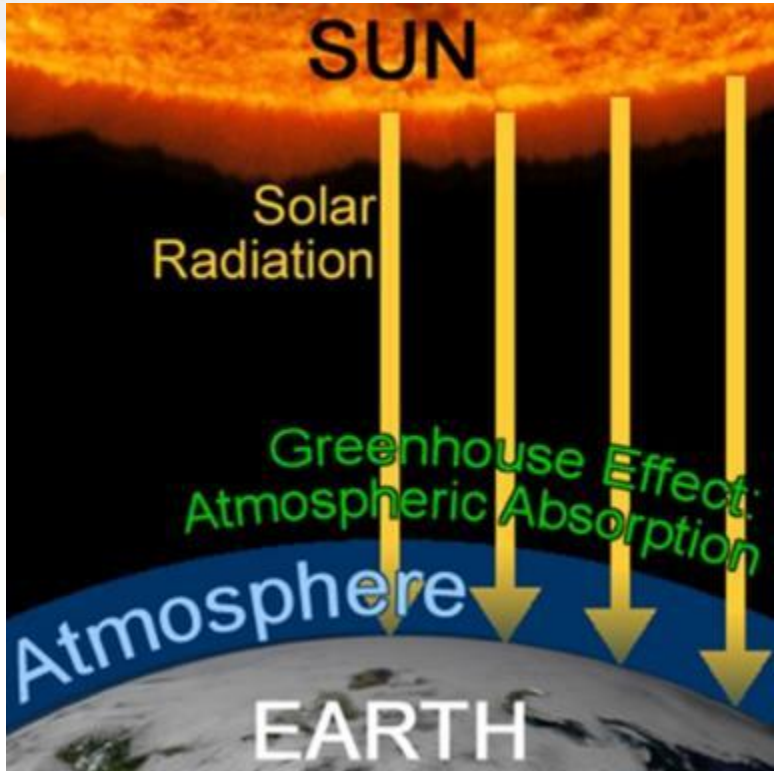


Greenhouse Gases (GHG)

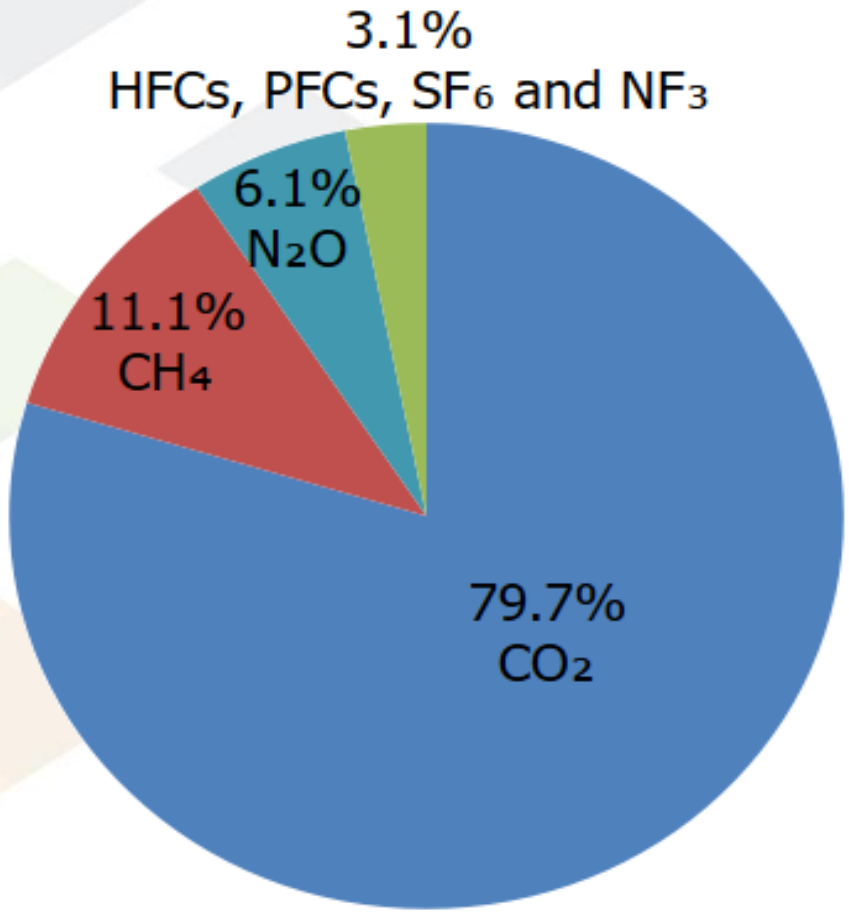
- Air pollutants that absorb solar radiation, warming the atmosphere via the greenhouse effect
- Increase in (GHG) increases atmospheric energy
  - Increases surface temperatures and atmospheric instability
- Instability changes regional climates
  - Increases cloud formation and total precipitation during rain and snow events
  - Amplifies & changes weather



Categories of GHG:

1. Carbon dioxide (CO_2)
2. Methane (CH_4)
3. Nitrous oxide (N_2O)
4. Fluorinated Gases
   - Hydrofluorocarbons (HFC)
   - Nitrogen Trifluoride (NF_3)
   - Perfluorocarbons (PFC)
   - Sulfur Hexafluoride (SF_6)

2022 U.S. GHG Emissions



Sources of GHG

CO_2, CH_4, and N_2O are primarily formed from combusting organic compounds (fossil fuels, wood, and solid wastes)

CO_2 and CH_4 is also emitted from non-combustion sources:

- Organic decay and landfills
- Industrial and agricultural activities
- Oil and gas operations



Fluorinated GHG consist of hundreds of man-made gases emitted from industrial and commercial processes

- HFC and PFC
  - Refrigerants, propellants, fire extinguishers, solvent cleaning, semiconductor manufacturing, foam-blowing, and medicine
  - Developed as alternatives to ozone-depleting substances
- NF_3
  - Semiconductor, flat panel display, and solar cell production
- SF_6
  - Electrical equipment and semiconductor & metal production



Global Warming Potential (GWP)

- Each GHG has a different capacity to absorb solar radiation
- GWP is a measure of the heat trapping ability and atmospheric lifetime for each GHG, measured in carbon dioxide equivalents (CO_2e)

Global Warming Potentials of Select GHG		
GHG	**100-Year GWP**	**Atmospheric Lifetime**
CO_2	1	50-200 years (Reference GHG)
CH_4	25	9-15 years
N_2O	298	120 years
HFC	0.01 - 14,900	1-270 years (1-15 years most common)
PFC	0.4 - 17,700	2,600-50,000 years
SF_6	22,800	800-3,200 years

Example: 1 metric ton (MT) CH_4 is equivalent to 25 MT CO_2 or 25 MT CO_2e

Local / State Regulations

- Air pollution regulations were first developed by local and state air agencies
  - 1881 Chicago City Council passes first smoke ordinance with penalties
  - 1907 Chicago Department of Smoke Abatement requires permit applications for constructing boilers
  - 1967 Federal Air Quality Act encouraged local & state agencies to develop standards and requirements
  - Local and state air agencies continue to regulate air emissions using state laws, administrative regulations, and permits
  - Many states still have state ambient air quality standards

Gaseous Pollutant Regulation

- In 1966, Los Angeles County adopted Rule 66
  - No discharge >15 pounds of organic material in any one day for organic solvents contacting flame or evaporated >200ºF; or
  - No discharge >40 pounds of photochemically reactive materials in any one day; or
  - Employ an air pollution control device to reduce emissions by 85%.
- Many state and local air agencies copied this rule

"Rule 66 is acknowledged to be the most complicated piece of air pollution control legislation conceived." ***– Journal of Paint Technologies***

Federal Regulations

- Federal regulation of air pollution began with 1970 Clean Air Act
  - National Ambient Air Quality Standards (NAAQS)
  - New Source Performance Standards (NSPS)
  - National Emissions Standards for Hazardous Air Pollutants (NESHAP)
  - State Implementation Plans (SIP) for nonattainment areas and existing sources of air pollution
  - Federal Implementation Plans (FIP) for areas without a SIP
- State / Federal partnership
  - Congress recognized that local / state air agencies were already regulating air pollution and incorporated that into the Clean Air Act

NAAQS

- Requirement for atmospheric concentration of air pollution
  - Six standards for CO, NO_X, lead, ozone, PM (PM_{10} & $PM_{2.5}$), and SO_2
  - States must demonstrate via monitoring compliance (attainment) with each standard
  - If state does not comply with standard (nonattainment), it must develop a SIP to attain the standard
- Many local / state air agencies retain ambient air quality standards separate from the NAAQS
  - May be more restrictive standards for a NAAQS pollutant
  - May be for other air pollutants, like ammonia, HF, and H_2S

NSPS

- Requirements for new sources of air pollution
  - New, reconstructed, and modified sources regulated by NSPS
  - Standards developed for specific industries or types of facility (boilers)
  - Title 40 of the Code of Federal Regulations (40 CFR), Part 60
- Existing sources subject to emissions guidelines
  - EPA drafts model rules in 40 CFR, Part 60
  - States incorporate model rules into SIP
  - For states without a SIP, EPA publishes a FIP in 40 CFR, Part 62
  - States can request delegation to enforce a FIP

National Emissions Standards for HAP (NESHAP)

- 1970 Clean Air Requirements for Air Toxics (HAP)
  - Exposure-based standards for HAP control
  - EPA to identify HAP and establish emission limits within 1 year of listing
  - By 1990, EPA had only identified 8 HAP and issued 22 standards in 40 CFR, Part 61 for Arsenic, Asbestos, Benzene, Beryllium, Coke Oven Emissions, Mercury, Radionuclides, and Vinyl Chloride
  - Local & state air agencies can request delegation to enforce NESHAP



NESHAP

- 1990 Clean Air Act Updates
  - Congress identified 189 HAP (H_2S removed in 1991)
  - EPA can add / remove HAP from list (1 added & 4 removed since 1990)
  - Updated air toxic requirements to risk-based standards for HAP control
    - Phase 1: Maximum Achievable Control Technology (MACT) initial standards
    - Phase 2: 8-year review of MACT to evaluate any remaining health or environmental risks and incorporate new technologies
  - Standards are published in 40 CFR, Part 63
  - Original 40 CFR, Part 61 NESHAP retained but no new regulations
  - Local & state air agencies can request delegation to enforce NESHAP

Permits

- ***New Source Review (NSR)***
  - Permit required for new or modified major sources of air pollution
  - Federal NSR program for major sources in nonattainment (NNSR) and attainment areas (Prevention of Significant Deterioration – PSD)
  - Various local & state NSR programs for minor sources
- ***Operating Permits***
  - Applies to all sources (both existing and new / modified sources)
  - Title V of the 1990 Clean Air Act requires a federal operating permit program for major sources
  - Some local & state operating permit programs for non-major sources

Air pollution controls include any equipment or method of operation to reduce emissions of air pollutants

1. **Prevention:** Decreasing the amount of air pollutants formed
2. **Collection**: Removing air pollutants from exhaust air
3. **Conversion:** Changing an air pollutant chemically to another, less harmful (inert) chemical

! Air pollution controls are required by applicable regulation & permit

Three Concepts of Air Pollution Controls		
1. Prevention	**2. Collection**	**3. Conversion**
Process Formulation	Separation / Filtration / Aggregation	Combustion / Oxidation / Incineration
Process Optimization	Absorption / Scrubbers	Reduction / Scrubbers
Alternative Processes	Adsorption	Bioreactors / Biofiltration
	Condenser	
	Sequestration	

Chapter 2:
Recap

In this chapter, we discussed:

- Types of gaseous air pollutants
- Environmental and health impacts of gaseous air pollutants
- Regulation of gaseous air pollutants
- Control technologies for gaseous air pollutants