

Ozone Layer Depletion

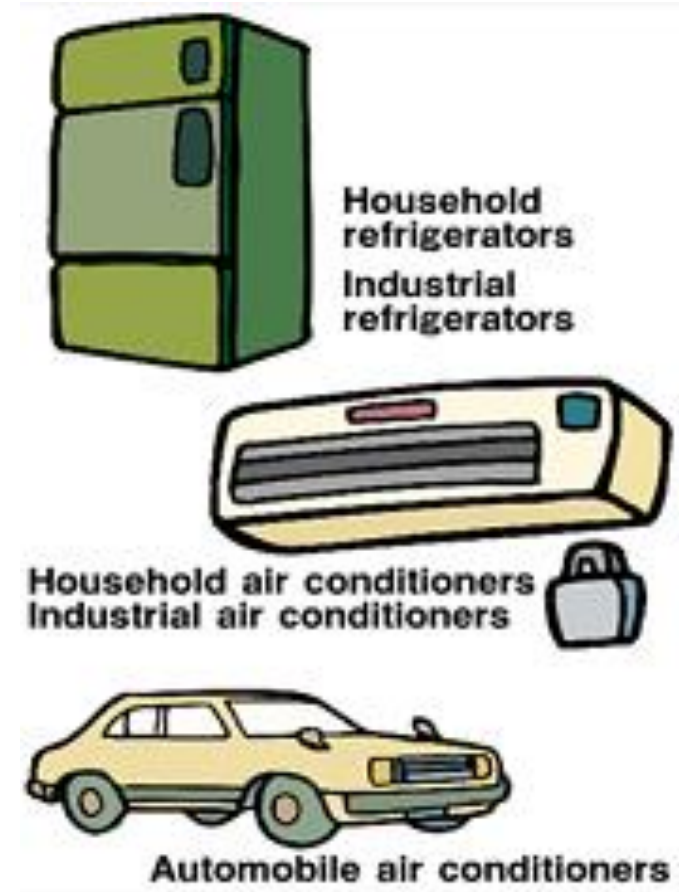
1. Why the hole in the atmospheric ozone layer above us?
2. What has been done about this?
3. Why should we worry about Ozone Layer Depletion?

What is Ozone? Ozone Layer?

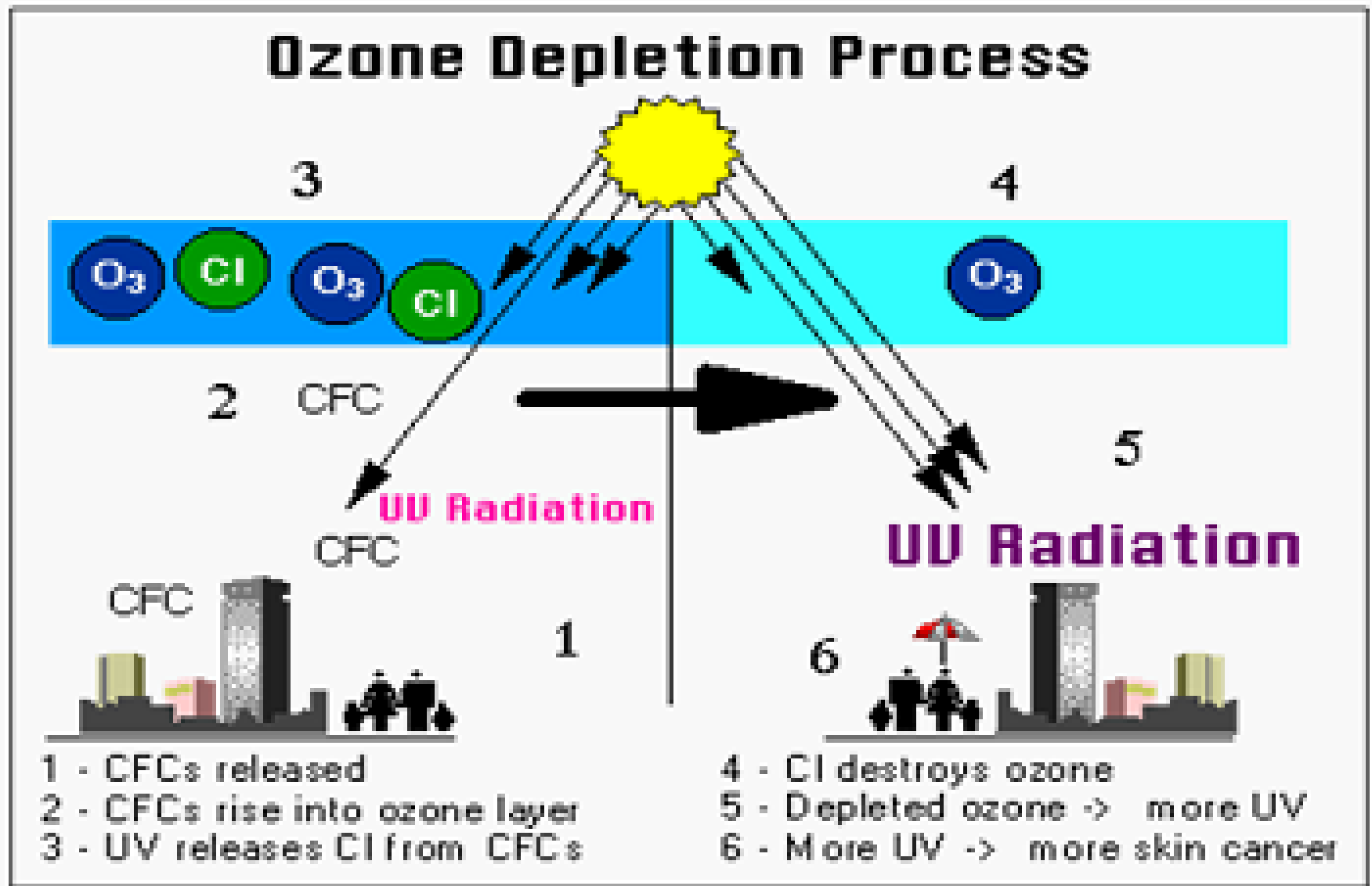
- ✓ Ozone (O_3) is a highly-reactive form of oxygen.
- ✓ Unlike oxygen (O_2), ozone has a strong scent and is blue in color.
- ✓ Ozone exists within both the tropospheric and stratospheric zones of the Earth's atmosphere
- ✓ In the troposphere , ground level ozone is a major air pollutant and primary constituent of photochemical smog
- ✓ In the stratosphere, the ozone layer is an essential protector of life on earth as it absorbs harmful UV radiation before it reaches the earth.

CFC's and ozone depletion

- ✓ Chlorofluorocarbons are created and used in refrigerators and air conditioners.
- ✓ These chlorofluorocarbons are not harmful to humans and have been a benefit to us.
- ✓ Once released into the atmosphere, chlorofluorocarbons are bombarded and destroyed by ultraviolet rays.
- ✓ In the process chlorine is released to destroy the ozone molecules

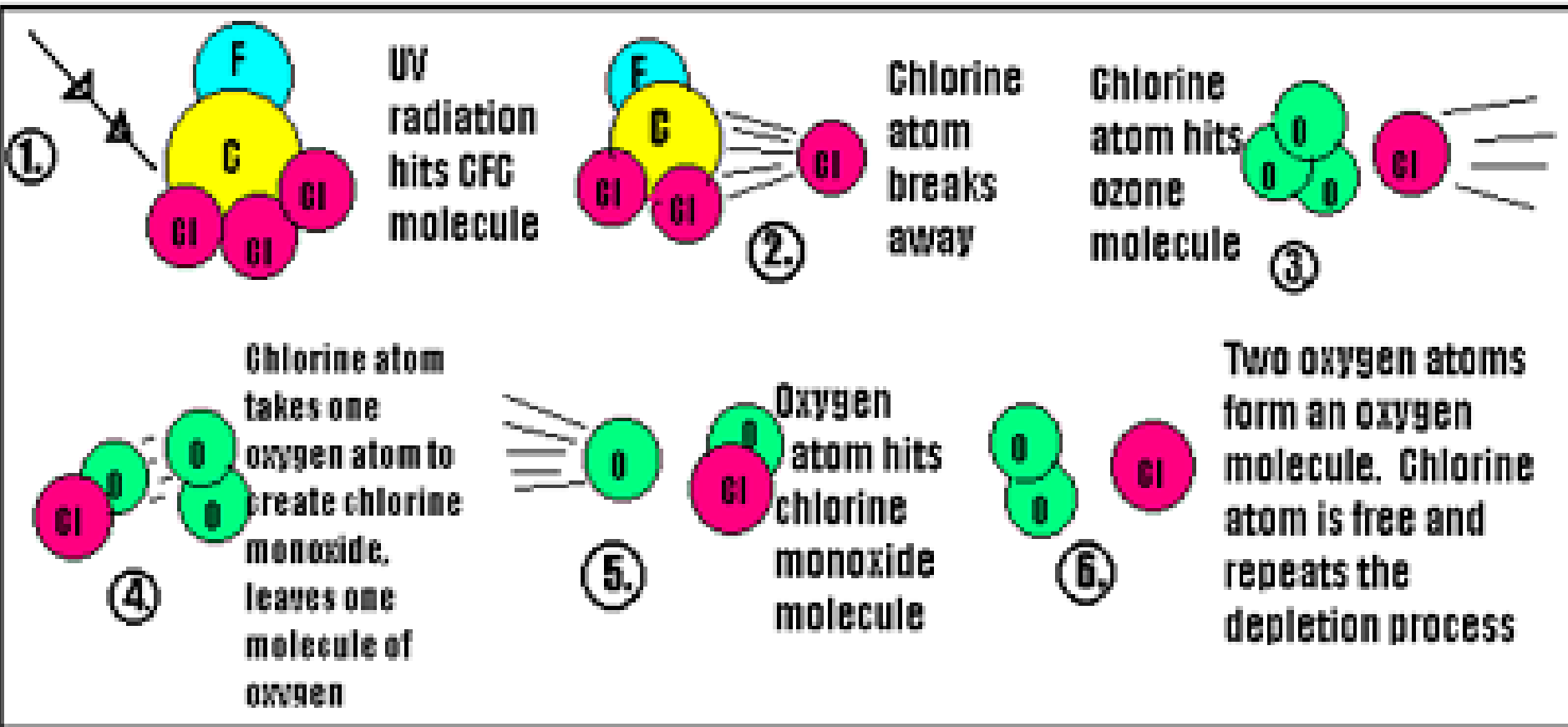


The ozone depletion process



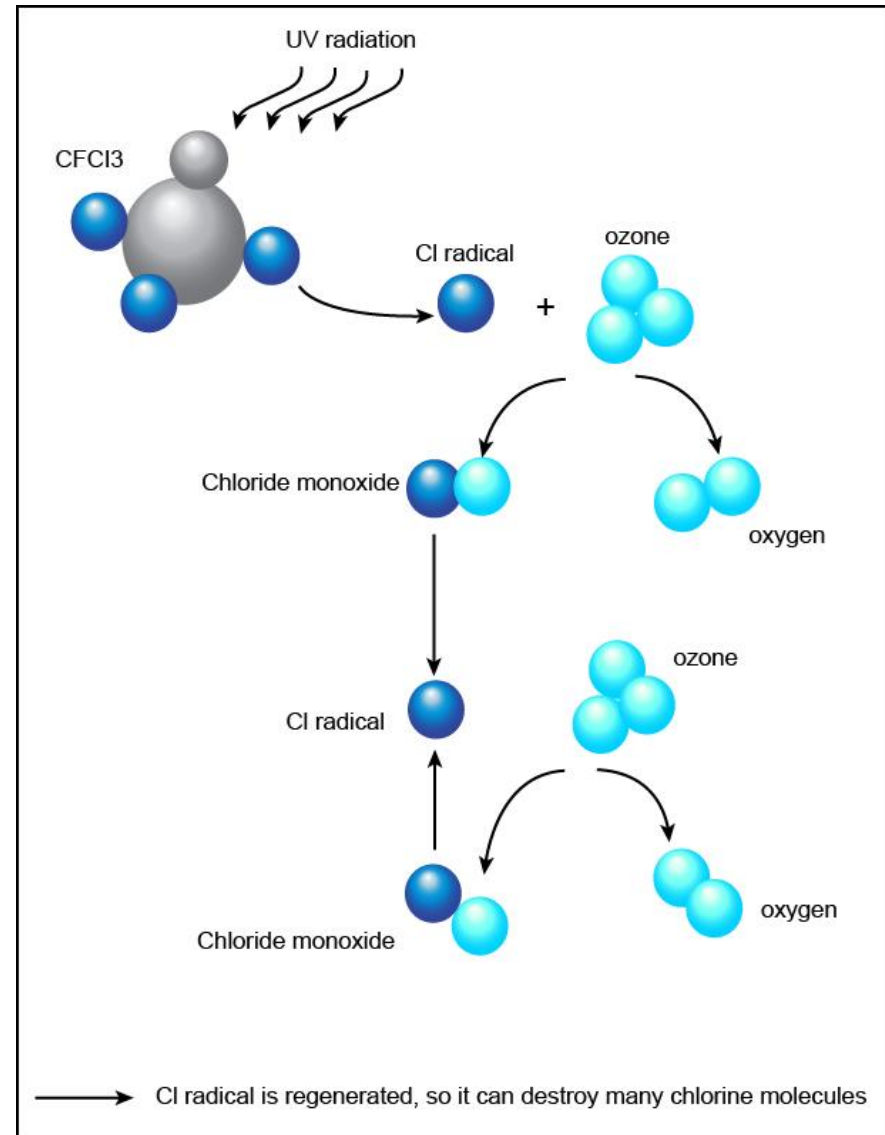
Destruction of ozone by chlorine

✓ The ozone is then destroyed by chlorine atoms.

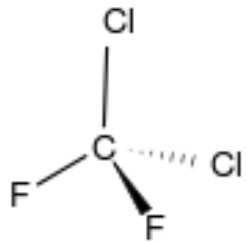
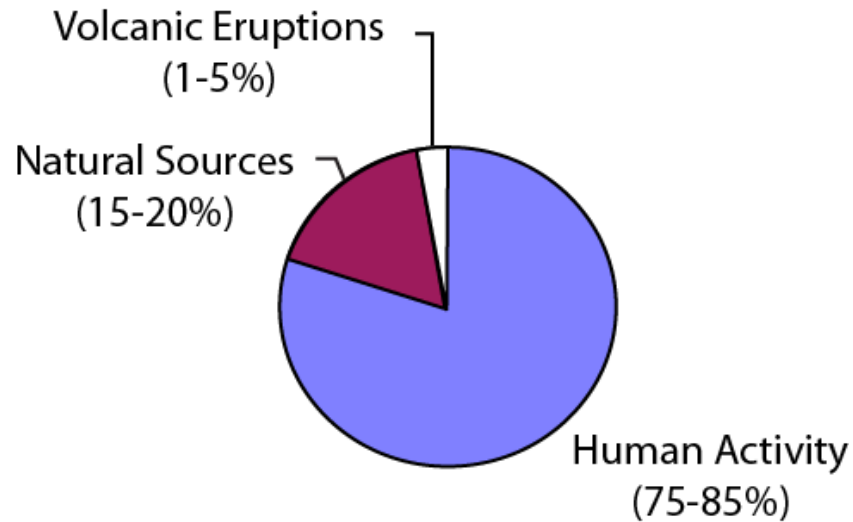


Ozone destruction by UV rays

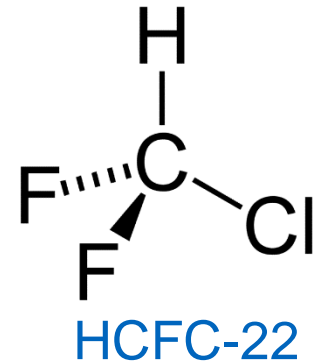
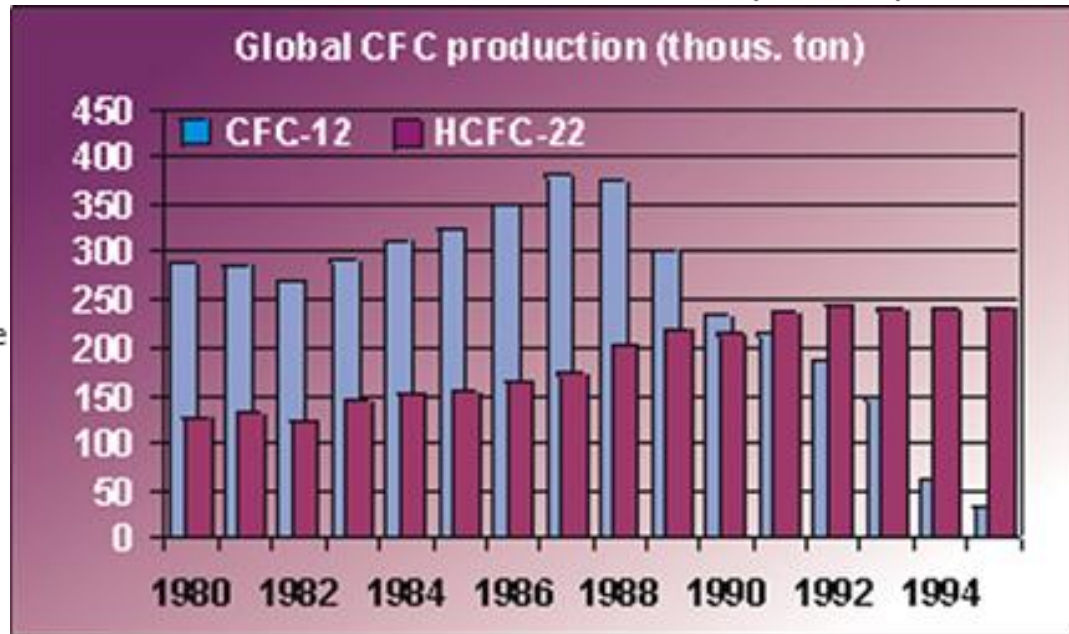
- ✓ UV radiation from the sun releases the radicals Cl and ClO .
- ✓ Ozone is a highly unstable molecule so it readily donates its extra oxygen molecule to free radical species such as hydrogen, bromine, and chlorine.
- ✓ These compound species act as catalysts in the breakdown of ozone molecules.



Responsibility for ozone damage each year



Dichlorodifluoromethane
CFC-12



Effects of UV rays on Aquatic Ecosystems

- ✓ Ozone depletion causes increases in UV rays's effects on aquatic ecosystems by:
 - decreasing the abundance of phytoplankton – affects the food stock for fishes and the absorption of CO₂
 - decreasing the diversity of aquatic organisms – reduces food stock and also destroys several fish and amphibians.



phytoplankton

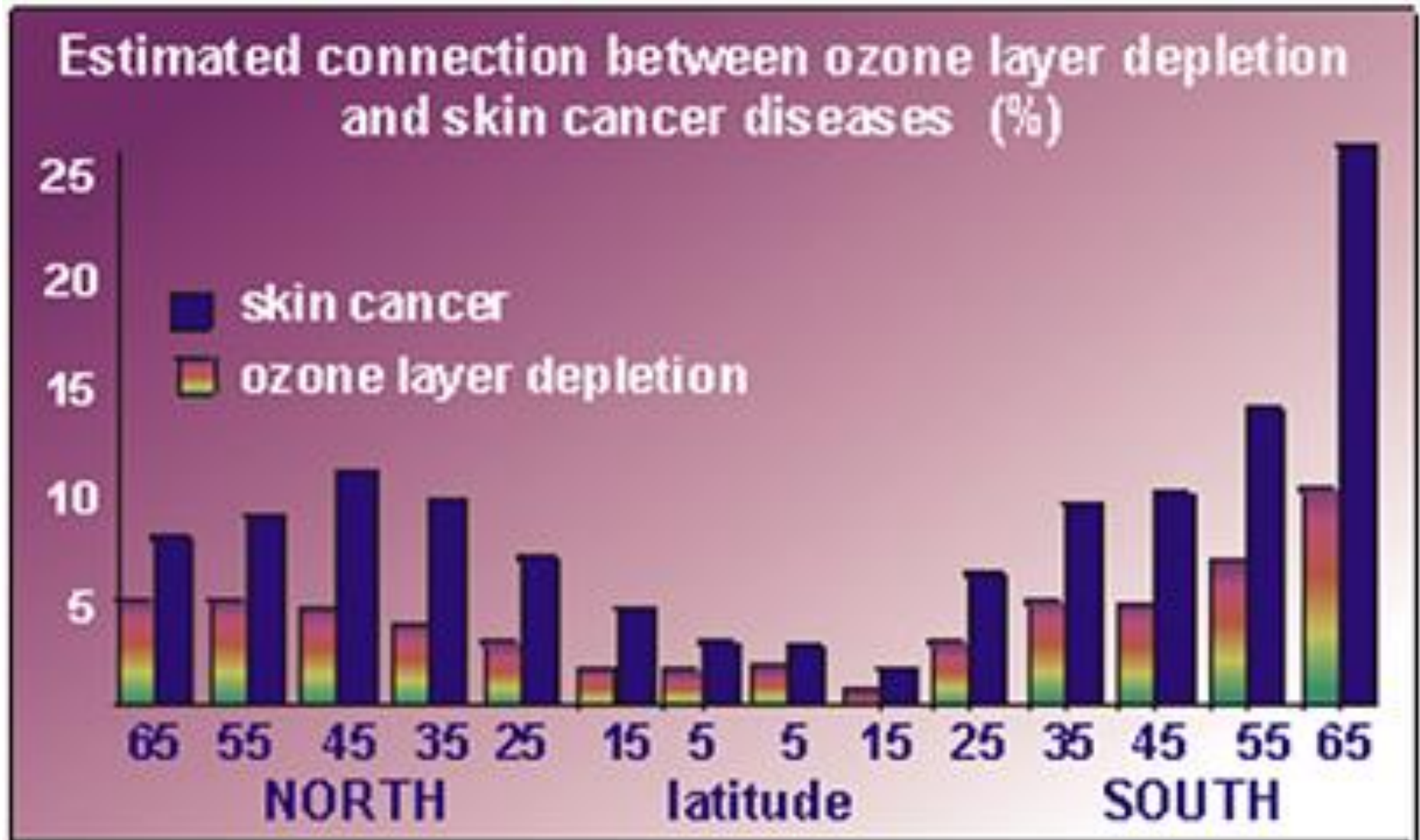
Effects of UV rays on Terrestrial Ecosystems

- ✓ Damage to plant cell DNA molecules - makes plants more susceptible to pathogens and pests
- ✓ Reductions in photosynthetic capacity in the plant - results in slower growth and smaller leaves
- ✓ Causes mutations in mammalian cells and destroys membranes

Harmful effects of UV rays on people

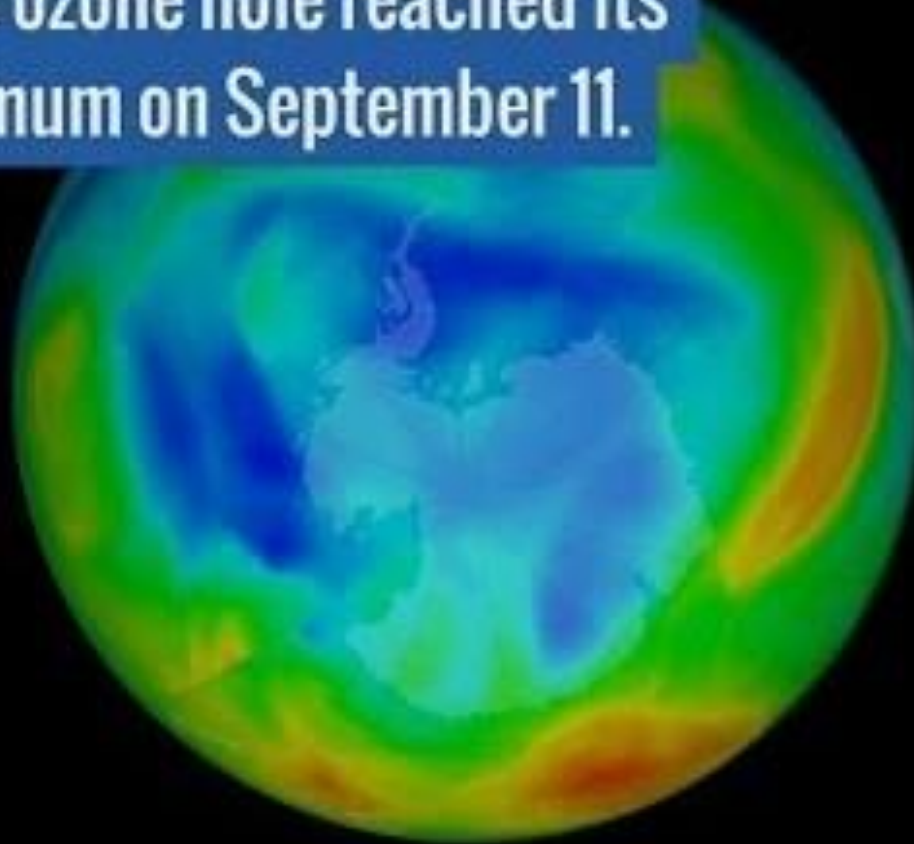
- ✓ Skin cancer
- ✓ Premature aging (photoaging) of the skin (different from normal chronological aging)
- ✓ Cataracts and eye disorders (corneal sunburn and blindness)
- ✓ Immune system damage

Correlation between Ozone depletion and skin diseases



Warm Winter Air Makes for a Small Ozone Hole

This year, the ozone hole reached its annual maximum on September 11.



Aug 12, 2017

The Ultraviolet Exposure Index

✓ INDEX VALUES EXPOSURE

0 – 2 = Minimal

3 - 4 = Low

5 - 6 = Moderate

7 - 9 = High

10 + = Very High

✓ **Factors affecting UV exposure**

- **Clouds cover** - partly cloudy days do little to reduce UV exposure but rainy or substantially overcast days reduce UV exposures
- **The time of day** – peak exposure time is 12:00 noon - 1:00 p.m. UV intensity is reduced by about half at three hours before and three hours after the peak exposure time.

Factors affecting UV exposure...

- ✓ The time of year - more UV is received in the late spring and early summer and much less is received in the late fall and early winter.
- ✓ Lifestyle – determines a person's risk to UV exposure.
 - Skiing, sunbathing, or swimming can lead to extremely high exposures.
 - Use of tanning parlors also increase risk.

Home work

Catalytic destruction of Ozone

Brief discussion about the following cycles and the chemical reactions involved in it.

- ✓ Hydroxy Radical Cycle
- ✓ Nitric Oxide Cycle
- ✓ Chlorine Cycle
- ✓ Null cycles

Table 6.1**Common Names for Regions of the UV Spectrum**

λ (nm)	Name	Species Absorbing	Location
10–240	Far-UV	O_2 , N_2	Thermosphere, mesosphere
250–290	UV-C	O_3	Stratosphere
290–320	UV-B	O_3	Stratosphere, troposphere
320–380	UV-A	NO_2	Polluted troposphere
400–750	Visible	Many	Earth's surface

Pollutants

- ✓ Organic and Inorganic chemicals in environment

- toxicity, polychlorinated hydrocarbons like DDT, polymers, detergents
- their impact on environment

Organic Pollutants

- ✓ Humans are exposed daily to numerous chemicals that can harm their health
- ✓ Many harmful organic compounds are stable in the environment (atmosphere, water, soil, food chain) for long periods → Persistent Organic Pollutants (POPs)
 - Characterised by stability, mobility, and bioaccumulation
 - Harmful to human health and produce ecological damage
- ✓ Stockholm Convention (May 2001): over 90 countries promised to reduce or eliminate the production, use, and release of 12 key POPs – the “dirty dozen”.

Key POPs – the dirty dozen

- ✓ The Dirty Dozen are produced for use as insecticides, fungicides, chemical additives, or are inadvertently produced during combustion. A biocide is a substance toxic to varying degrees to life forms:
 - Either synthesised deliberately to target and kill specific organisms – general name pesticide
 - Or may be inadvertently produced
- ✓ Pesticides: insecticide, bactericide, fungicide, herbicide
- ✓ A pesticide designed to eliminate all types of living organisms is called a fumigant or sterilant

Table of POP

POP	Use
Aldrin	Crop insecticide (corn, cotton)
Chlordane	Crop insecticide (vegetables, citrus, cotton, potatoes)
DDT (dichloro-diphenyl-trichloroethane)	Crop insecticide (cotton)
Dieldrin	Crop insecticide (cotton, corn)
Endrin	Crop insecticide (cotton, grains)
Heptachlor	Insecticide (termites and soil insects)
Hexachlorobenzene	Fungicide for seed treatment

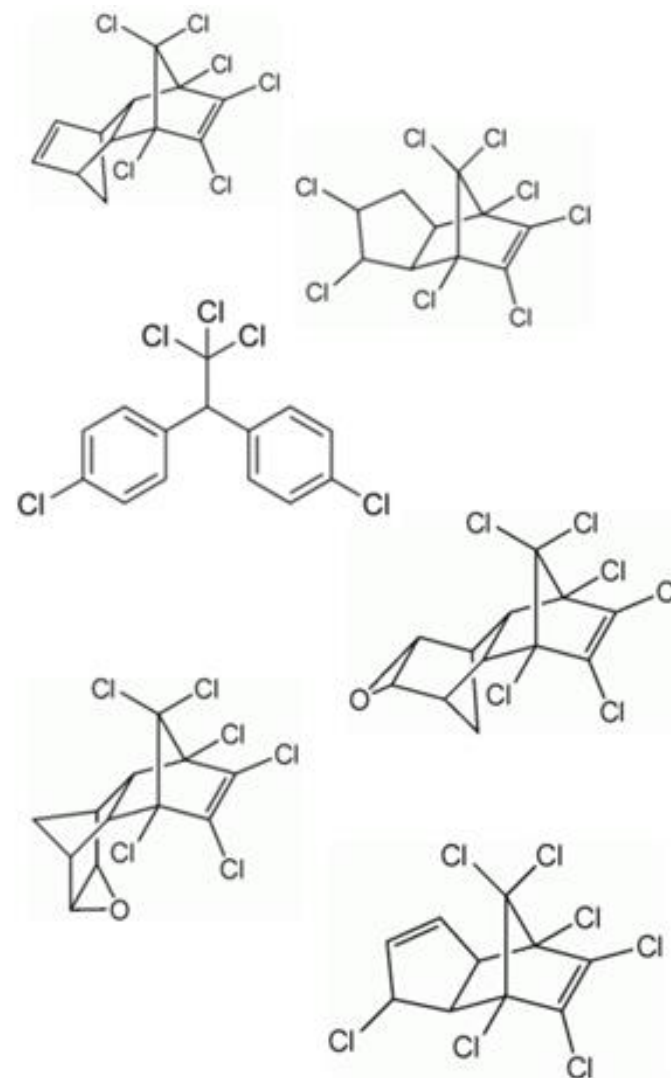
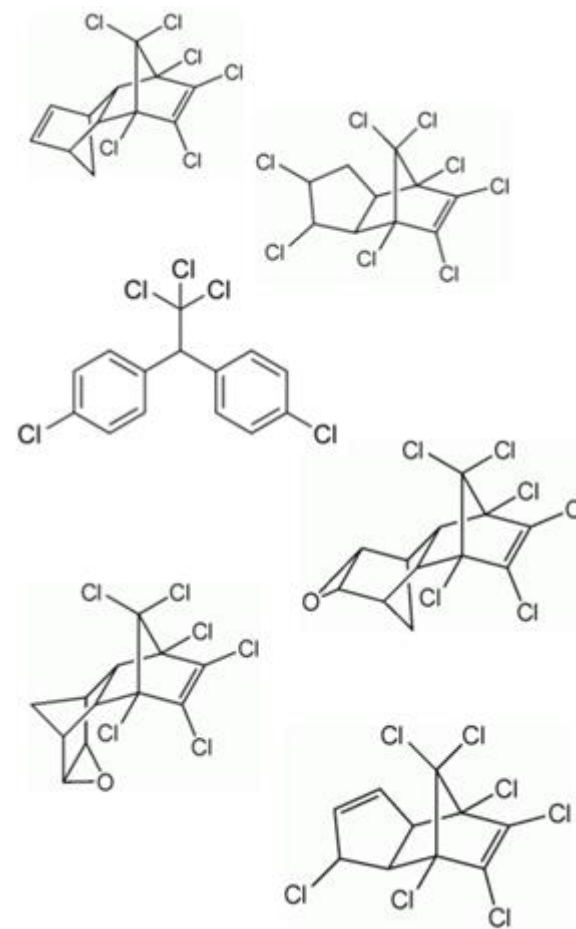


Table of POP

POP	Use
Mirex	Insecticide (termites, fire ants)
Toxaphene	Insecticide (livestock, crops)
PCBs	Industrial chemical (paint and plastic additive)
Dioxins	Unintentionally produced during combustion
Furans	Unintentionally produced during combustion



Organic biocides

- ✓ Fate of biocides in the environment:
 - Chemical stability (rate it degrades to other compounds)
 - Mobility (mechanism and rate of transport)

- ✓ Rapid degradation mobility less of an issue

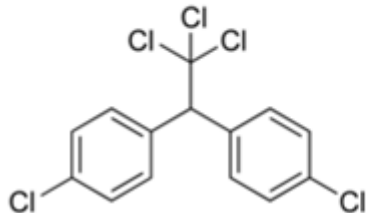
- ✓ Different degradation mechanisms may operate as the pesticide moves to a new environment

- ✓ Degradation products may have biocidal properties:
 - Usually reduced toxicity, but sometimes toxicity is enhanced

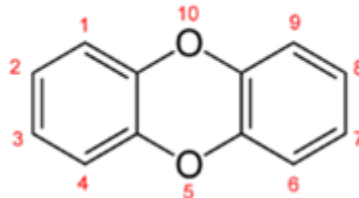
Polychlorinated Hydrocarbons

- ✓ All the Dirty Dozen are polychlorinated hydrocarbons
- ✓ They are stable and do not readily degrade to less toxic forms
 - Persist in the environment for a long time and can bioaccumulate through the food chains
- ✓ Insoluble in water, soluble in fats
- ✓ Polychlorinated hydrocarbons of particular concern are:

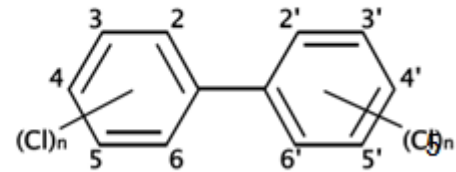
DDT



dioxins



PCBs

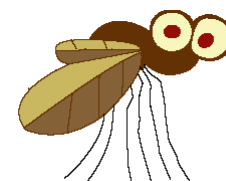
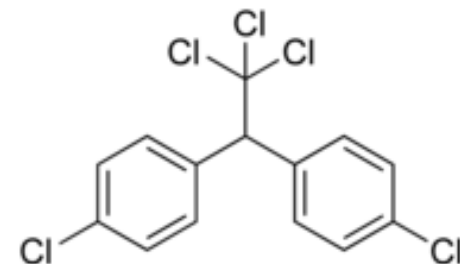


Pesticide production

- ✓ Few pesticides were available before 1940:
 - Some natural insect poisons extracted from plants
 - Early insecticides were nicotine sulfate obtained from tobacco, rotenone from the tropical derris plant and garlic oil
 - A few inorganic compounds of lead and arsenic
- ✓ Large scale use of pesticides began after WWII with the introduction of DDT

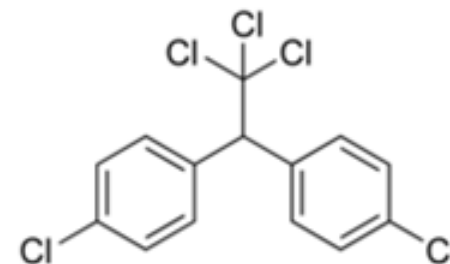
✓ DDT

- ✓ At its introduction it seemed to be an ideal insecticide:
 - Cheap to produce
 - Apparently non-toxic to humans and other mammals
 - Did not breakdown easily → continued to kill insects for a long time after application



DDT – A Short History

- ✓ 1874 – First synthesised by Othmar Zeidler - dichlorodiphenyltrichloroethane (DDT)
- ✓ 1939 – Paul Hermann Müller discovered insecticidal properties of DDT
- ✓ 1940s – Rapid development in WW2 to combat malaria, typhus, and other mosquito-borne diseases in military & civilian populations
 - Following WW2, extensive use of DDT contributed to eradication of malaria in America & Europe
- ✓ 1948 – Müller awarded Nobel Prize
- ✓ 1950s – A WHO campaign to eradicate malaria was based on extensive spraying with DDT – a marked reduction in malaria mortality rate was found
 - → mortality rate dropped from 192 to 7 per 100,000
 - increasing resistance to DDT was found in pests



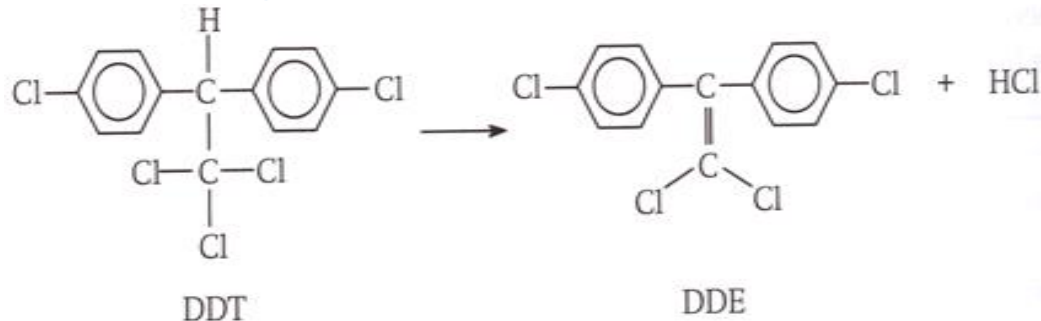
DDT – A Short History

- ✓ 1950s – Marked decline of bird populations, especially raptors like the peregrine falcon, osprey, and eagles, were observed
- ✓ 1962 – Rachel Carson publishes *Silent Spring*, raising American awareness of the ecological effects & health risks of DDT and start of modern environmental movement.
- ✓ 1970s-80s – ban on DDT use in Western countries; recovery of affected bird populations
 - DDT use continued in developing countries, but widespread spraying discontinued. Insecticide impregnated bednets and indoor spraying favoured.
- ✓ 2001 – Stockholm convention, restricting DDT use to health crises



DDT

- ✓ Chemical stability: DDT degrades to DDE (dichlorodiphenyldichloroethene)



- ✓ DDE is less toxic than DDT but more resilient in the environment
- ✓ DDT has a broad spectrum of activity. It was banned in several countries in the 1970s because of ecological considerations
- ✓ Still used extensively to reduce insect-transmitted diseases:
 - yellow fever, sleeping sickness, typhus, malaria and others
- ✓ Persistent in the environment and resistant to complete degradation by microorganisms
- ✓ Readily adsorbed onto sediments and soil
- ✓ Most DDT that enters water becomes firmly attached to soil particles
- ✓ Readily taken up by microorganisms and is therefore passed on through the food chain
- ✓ Normally stored in fatty tissue

DDT – Environmental Levels and Human Exposure

- ✓ **Air:** when DDT is sprayed, any that fails to reach its target can drift away.
- ✓ Vaporisation from treated fields can be detected for more than 6 months after application. It can drift up to 1000 km
- ✓ Environmental levels:
 - Nonagricultural areas: $< 1 - 2.4 \text{ ng m}^{-3}$
 - Agricultural communities: $1 - 22 \text{ ng m}^{-3}$
 - Communities with anti-mosquito programmes: up to $8.5 \text{ } \mu\text{g m}^{-3}$
- ✓ **Water:** highest level recorded 0.84 mg/L (USA: 1964 – 1968)
 - Over 90% of DDT in the general population comes from food
- ✓ **Acute exposure:** Acute toxicity of DDT is high in insects and lower in mammals. Large doses causes focal necrosis of liver cells in several species. It increases liver tumours in mice
- ✓ **Human exposure:** Can affect the nervous system. Acute intoxication by DDT can lead to symptoms such as nausea, vomiting, paraesthesia, dizziness, confusion, tremors and in severe cases convulsions
- ✓ All the symptoms are rare
- ✓ No evidence that DDT has reproductive or teratogenic effects
- ✓ All epidemiological studies in humans have indicated that DDT is not carcinogenic

Pollutant Formation in Combustion Systems

✓ NO_x Formation

- Thermal NO_x
- Prompt NO_x
- Fuel NO_x

✓ Carbon Monoxide (CO)

✓ Volatile Organic Compounds (VOC)

✓ Polycyclic Aromatic Hydrocarbons (PAH), Soot and Submicron Particulates (solid-phase pollutants)

✓ Sulphur Compounds

NO_x formation

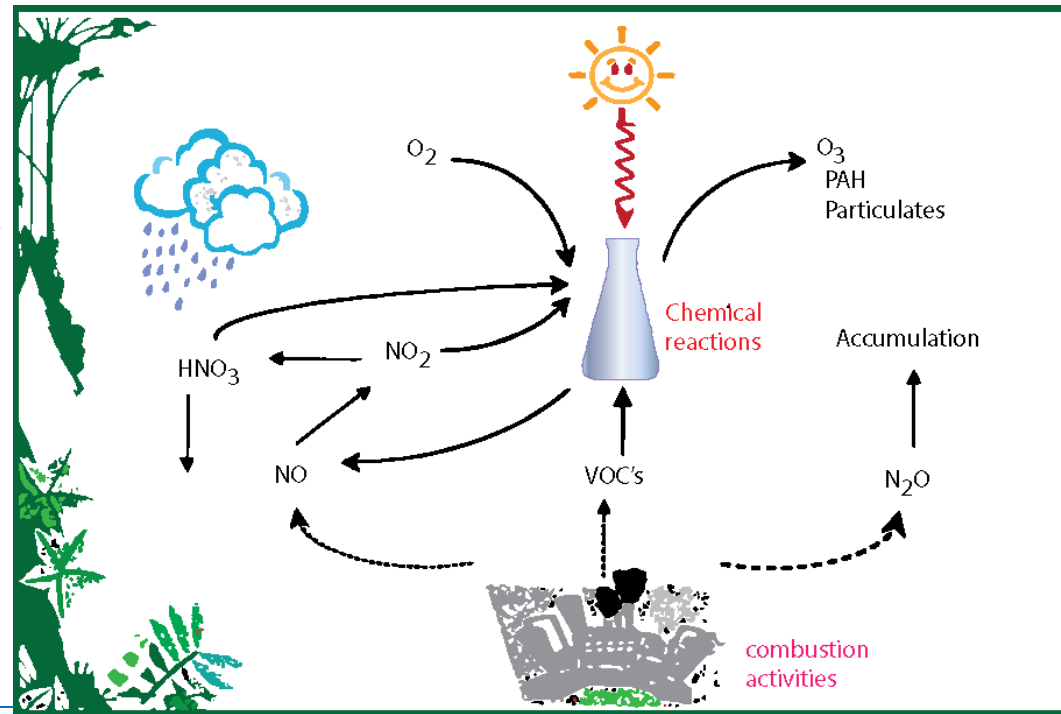
- ✓ What is NO_x?
- ✓ NO_x = Oxides of Nitrogen which are produced by combustion:
 - Nitric Oxide (NO)
 - Nitrogen Dioxide (NO₂)
 - Nitrous Oxide (N₂O)
- ✓ Nitric Oxide (NO)
 - Highly reactive due to lone electron at N atom
 - Not particularly toxic
 - Major precursor of photochemical smog (NO → NO₂)
 - It is produced by most of combustion systems

NO_x formation

- ✓ Nitrogen Dioxide (NO₂)
 - Brown, poisonous gas
 - Emissions of NO₂ from most combustion < 10% of NO_x
 - Adverse health effects include: lung irritation, bronchitis, pneumonia and a lowering respiratory resistance
 - Ambient limit = 120ppb [NEPC, 1998]
- ✓ Significant direct emissions of NO₂ occur from processes involving premixed flames:
 - Indoor gas appliances (20-100% of NO_x)
 - Gas turbines → yellow/brown plumes

Nitrous Oxide (N₂O)

- ✓ Relatively inert
- ✓ Uses: Dental anaesthetic
- ✓ Strong absorber of infrared radiation ($\sim 300 \times \text{CO}_2$)
- ✓ Stability = long atmospheric residence times (~ 150 yrs)
- ✓ Hence, potentially significant greenhouse gas
- ✓ Long life-time also allows its transportation into stratosphere and participates in ozone depletion
- ✓ Only significant from low-temperature processes (eg. Fluidised bed combustion)



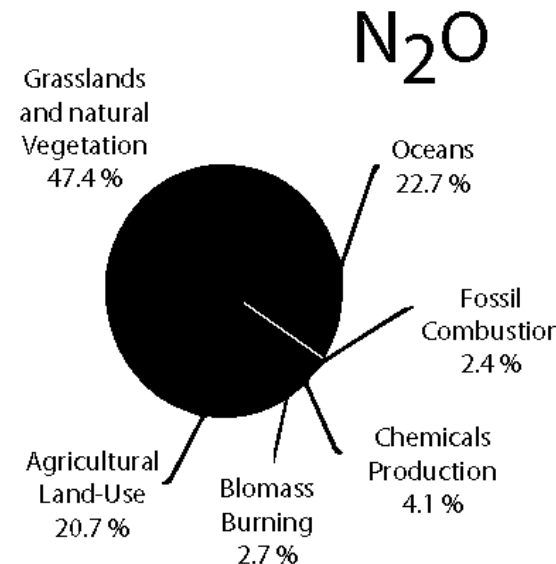
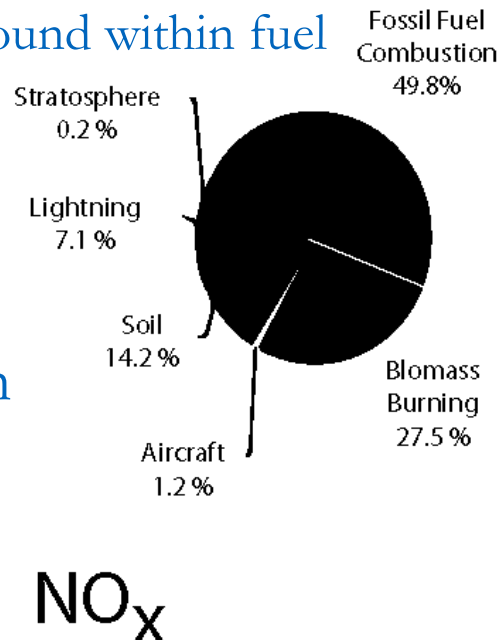
Sources of Nitrogen

✓ Formation of NO_x requires a source of nitrogen

✓ Two sources of nitrogen:

- a. Molecular nitrogen from air ($1/2 \text{N}_2$ (from air) + $1/2 \text{O}_2 \rightarrow \text{NO}$)
- Thermal or Zeldovich Mechanism.
- Prompt-Fenimore Mechanism ($\text{HC} + \text{N}_2$).
- Other minor mechanisms
- b. Nitrogen chemically bound within fuel
- Fuel NO_x ,

✓ Most of NO_x in the form of NO



Thermal NO

- ✓ One of the most important issues for combustion engineers is:
'What are my NO_x emissions?'
- ✓ In most cases, unusually high NO_x emissions are due to NO formed by the Thermal (Zeldovich) mechanism
- ✓ Thermal NO mechanism involves the attack of molecular nitrogen (N₂) and atomic nitrogen (N) by oxygen (O₂) and oxygen-containing radicals (O, OH). This can occur in oxygen rich mixture.
- ✓ First identified by Zeldovich (1946) and extended by Fenimore and Jones (1957)
- ✓ Described by the following reactions:
 - $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$ (R.1)
 - $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$ (R.2)
 - $\text{N} + \text{OH} \rightarrow \text{NO} + \text{H}$ (R.3)

Thermal NO

- ✓ Westenberg (1971) invoked the steady-state approximation and determined that the maximum NO formation rate is given by:

$$\frac{d[\text{NO}]}{dt} = 1.45 \times 10^{17} T^{-1/2} \exp\left[\frac{-69460}{T(\text{K})}\right] \cdot [\text{O}_2]_{\text{eq}}^{1/2} \cdot [\text{N}_2]_{\text{eq}} \text{ mol/cm}^3 \cdot \text{s}$$

- ✓ Hence, [NO] depends on:
 - Temperature (the higher the temp, strongly the higher the NO formed)
⇒ high temp environment
 - O₂ concentration (the higher the oxygen conc, the higher the NO formed)
⇒ oxygen-rich environment
 - Residence time

Prompt NO

- ✓ Fenimore (1971) observed an additional formation of NO which could not be explained by the thermal mechanism
 - NO formed close to the burner (hence - "prompt" NO)
 - Effect is not observed under very fuel-lean conditions or in systems with H₂ or CO as fuel
 - Mechanism involves the attack of N₂ by hydrocarbon fuel fragments, mainly CH radicals and C-atoms.
 - The Prompt-Fenimore mechanism is initiated mainly by R.4 (the formation of HCN) with a lesser contribution from R.5
 - :CH + N₂ → HCN + N (R.4)
 - C + N₂ → CN + N (R.5)
 - HCN is subsequently oxidised to NO (see diagram)
 - Prompt mechanism dominates for hydrocarbon combustion in fuel-rich, in both premixed and diffusion flames

