Ozone Depletion: Part 2

Antarctic Ozone Hole: Each spring, the ozone layer thins over the poles.

- Regional *and* seasonal
- No CFC production and very limited regional pollutants
- Special winter weather conditions:
  - Severe cold and isolated air flow: circumpolar vortex
  - North pole vortex breaks down before sunlight returns: smaller ozone hole
  - Formation of polar stratospheric clouds (PSC)
    - Crystals of $HNO_3 \cdot 3H_2O$ and larger crystals form in cold
    - Reservoir gases formed outside polar regions drift in and undergo reaction on surface of crystal: surface catalysis

$$HCl(s) + ClONO_2(g) \xrightarrow{\text{surface}} Cl_2(g) + HNO_3(s)$$

    - HNO_3 forms more crystals with H_2O
    - Released Cl_2 builds up in polar night: Photolysed in arctic morning sunlight.
    - $HOCl$ also formed in surface catalysis reactions
    - Photo-initiation reactions:

$$\begin{aligned} Cl_2 &\xrightarrow{h\nu} 2Cl \\ HOCl &\xrightarrow{h\nu} OH + Cl \end{aligned}$$

    - Rapid destruction of ozone via catalytic cycle: Under cold conditions, dimers $ClO - OCl$ form which are unstable in light.
    - Once concentration of ozone drops, reservoir reactions dominate and HCl and $ClONO_2$ reformed.
    - In antarctic spring, rise in temperature melts PSCs, liberating HNO_3

$$\begin{aligned} HNO_3 &\xrightarrow{h\nu} NO_2 + OH \\ NO_2 + ClO &\longrightarrow ClONO_2 \end{aligned}$$

    - Vortex breakdown replenishes ozone layer from outside: mixes air

Effects of UV radiation

1. Photosynthetic plants: UV B rays make photosynthesis less efficient
   - Plants sensitive to spectrum: Less leaf, seeds and fruit
   - Photoplankton near surface of seas may be affected: Severe repercussions on marine food chain
2. Drop in populations of amphibians (like frogs): Effects of UV radiation on genetic material during development
3. Systematic immunosupression in humans
   - Conformational change in compound in skin triggered by UV B absorption: $\pi \rightarrow \pi^*$ electronic transition
     - Trans urocanic acid transforms to cis-urocanic acid under UV radiation
   - Cis-urocanic acid believed to hinder Langerhans cells' ability to recruit killer T-cells: weakens immune response
4. Cancer caused by mutations in genetic material
   - Amino acids tryptophan and tyrosine $\pi \rightarrow \pi^*$ transitions: protein damage through production of reactive free radicals
   - Thymine and pyrimidine dimerisation in DNA: mutations and cancer
     - Distortions in DNA caused by linkages (dimerisation) between successive Thymine or pyrimidine bases
     - Natural repair mechanisms:
       (a) DNA photolase: binds to pyrimidine dimer and gains UV absorption band; UV absorption cuts dimer link
           * UV light utilized to fix UV damage!
       (b) UV r-ABC enzyme recognizes pyrimidine dimer and excises it; DNA polymerase builds complementary strand and DNA ligase attaches it
     - Repair not 100% efficient: mutations eventually result
     - Mutations to gene which regulate cell division can lead to cancers

Skin Cancer and UV Radiation

- Almost all skin cancers due to overexposure to UVB light (290 nm)
- 1% decrease is ozone layer $\Longrightarrow$ 2% increase in ground UVB intensity
- Predict a $1-2\%$ increase in cancer for 1% decrease in ozone layer
  - 1979-1992: 6.6% decrease in ozone level in southern Canada; expect a $15-20\%$ increase in skin cancer in the long run
  - Australia: estimated that 75% of skin cancers due to exposure
    * Leading the CFC control movement
- Research indicates that sunscreens can *increase* rate of cancer
  - Sunscreens that filter out only UVB rays and not UVA rays (315 nm) can lead to false sense of security: longer exposure times and bad times of day

Sunscreens and sunburns:

- Melanin in melanocytes absorbs UV radiation
  - Production of melanin stimulated by radiation
  - Stops UV damage to underlying tissue
  - People differ not in number of melanocytes but in amount of melanin produced per melanocyte
- Sunburn characterised by erythema-reddening of skin
  - Function of energy of photon and not total energy absorbed: UVC and UVB most energetic
- Melanin scatters UV light-Zinc oxide
- Some sunscreens absorb UV light but undergo no harmful photochemical reaction
  - Phototoxic: photochemical reactions which are toxic
  - Philosophy: Absorb UV radiation via an electronic excitation; either a harmless internal chemical reaction occurs or energy is transferred into vibrational excitations and heat
  - Examples: PABA and O-Hydroxybenzophenone

CFCs and Controls

- Problem: Catalytic destruction of ozone by Cl and Br in stratosphere
- Source: CFCs like CFC-12 (refrigerant) and CFC-11 (blowing agent)
- Goal: Replace CFCs with environmentally safe alternatives
- Strategy: short-term use of hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) in existing technology
  - Contain $C-H$ bonds which can be attacked by OH radical in troposphere: converted into water soluble gases and rained out of atmosphere
  - Shorter lifetimes in atmosphere so don't diffuse into stratosphere
  - Example: HFC-134a (refrigerant, air-conditioners) has similar properties to CFC-12 but has 1/10 lifetime in atmosphere: not very short life since Fluorine atoms stabilize $C-H$ bond

$$OH + CH_3CF_3 \longrightarrow H_2O + CH_2CF_3 \longrightarrow CO_2 + HF$$

- Best idea: alternative technology or replacements for all CFCs, HCFCs, HFCs
  1. Aerosol propellants: isobutane or dimethyl ether
  2. Hydrocarbon blowing agents (in styrofoam production)
     - Old styrofoam has residual CFCs from blowing process that gradually leak into atmosphere
  3. Refigerants: more challenging
     - Propane-butane mixture made in Germany: "Greenfreeze"
     - New mechanisms avoiding compressors
  4. Halons: used to smother fires
     - CF_3Br, CF_3I possible, but toxicity questions

History of CFC Controls

- 1974: Sherwood Rowland and Mario Molina at U.C. Irvine demonstrate chlorine catalytic ozone destruction mechanism and predict depletion on ozone layer: no expermimental evidence at time
- Late 70s: North America and some Scandanavian counties ban use of CFCs
- Early 80s: Increasing evidence and awareness of ozone depletion
- 1987: "Montreal Protocol"-international conference in Montreal: reach agreement to reduce and phase out CFC production and usage on a timetable
- 1990 London and 1992 Copenhagen conferences lead to amendments to
  1. Cease all CFC and Halon production by 1995
  2. Phase out all chlorinated compounds (HCFCs) by 2040
- Canada's role in ozone depletion
  - Active in ozone research since 1930: part of studies of upper atmosphere and impact on weather forecasting
  - Published ozone level data under United Nations World Meteorological Organisation (UNWNO)
  - High arctic ozone observatory in Ellesmere Island in 1993 established by Canadian government
    * Designed two ozone measureing devices; sunphotometer and Brewer ozone spectrometer

Outlook? Not bad if controls observed

- Ozone hole may start to fill in by 2050 if 1992 Copenhagen revisions to Montreal protocol observed: Uncertainty due to global warming and climate modelling