Smog and Photochemical Pollution

- First observed in Los Angeles
  - Transportation emissions trapped in air basin
  - Characterized by reddish-brown haze and toxic chemicals: Ozone
  - Hot weather
  - Introduction of NO and hydrocarbons (RH) shifts natural balance of NO_x/O_3 and OH cycles

Daily Cycle

1. Cars start in morning: provide heat

$$N_2 + O_2 \xrightarrow{\Delta} 2NO \tag{1}$$

2. Oxidation of NO later in morning

$$NO + O - O - R \longrightarrow NO_2 + OH \tag{2}$$

3. Photolysis of NO_2

$$NO_2 \xrightarrow{h\nu} NO + O \tag{3}$$

4. Formation of ozone

$$O + O_2 \xrightarrow{M} O_3 \tag{4}$$

5. Photolysis of ozone to form OH

$$O_3 \xrightarrow{h\nu} O_2^* + O^* \xrightarrow{H_2O} 2\ OH \tag{5}$$

6. Formation of hydrocarbon radicals $\Longrightarrow$ interaction with 2

- Late in day, 3 slows down toxic compounds such as aldehydes, peroxyacetylnitrate (PAN) build up.

Formation of PAN: aldehyde breakdown in presence of NO_2 radical

$$CH_3COH \ + \ OH \longrightarrow CH_3 - C = O \ + \ H_2O$$
$$CH_3C = O \ + \ O_2 \longrightarrow CH_3CO_3$$

then either

$$CH_3CO_3 \ + NO \longrightarrow NO_2 \ + \ CH_3CO_2 \tag{6}$$
$$CH_3CO_2 \overset{\text{many steps}}{\longrightarrow} CO_2 + H_2O$$

or

$$CH_3CO_3 \ + \ NO_2 \longrightarrow CH_3CO_3NO_2 \qquad \text{(PAN)} \tag{7}$$

can be important.

- During day, photolysis of NO_2 keeps $[NO_2]$ small, so path (6) dominates.
- Late in day, $[NO_2]$ builds up and less NO is present (shift in equilibrium), so path (7) becomes significant.

Summary of Smog Cycle

Early in day:

- Peak production of NO and RH early in morning: morning commute
- Peroxy radical oxidation of NO to form visible NO_2

Noon-early afternoon:

- Hydrocarbons converted to aldehydes, then broken down to CO_2 and H_2O
- Ozone production from NO_2 photolysis

Late daylight hours:

- Fewer UV rays for photolysis, O_3 and NO_2 build up
- Less NO and more NO_2, so aldehyde oxidation less dominant
- NO_2 radical combines with organic radicals in a termination reaction to make toxic compounds like PAN
- Toxic compounds stable until morning sunlight photolyses them: reservoir gases for NO_2 and organic radicals.

Measurement of pollution levels: Concentrations of toxic compounds like aldehydes and *ground-level ozone* are measured.

- Set standards: World Health Organization (WHO)
  - WHO standard for “safe” air: 100 ppb (parts per billion)
  - USA standard: 120 ppb
  - Canadian standard: 82 ppb
- Peak ozone level in L.A. in 1970’s: 680 ppb
  - Typically around 300 ppb now: How?
- Problem worst in Mexico City: Exceed WHO standards 310 days/yr
  - Thousands of premature deaths annually in Mexico City due to respiratory problems: Oxidation of tissues and lung disease
  - Also very bad in Athens and Rome
- Transport of pollutants affects rural areas
  - Ex. Southwestern Ontario farmland pollution from Lake Erie industry.

What to do?

Photochemical pollution requires:

1. Heat-little can be done
2. Hydrocarbons
3. NO_x

Mimimisation of role of Hydrocarbons:

1. Reduce concentrations of very active hydrocarbons:
   - Large hydrocarbons with weak $C-H$ bonds: H-abstraction
   - Unsaturated RH such as alkenes: OH addition
   - Aromatic compounds: stabilization effects
2. Major problem: gasoline and petroleum products
   - Home furnaces, power plants, industry

- Vapor locks on gas station and limit industrial leakages
- Natural sources: Terpenes (unsaturated) from trees and plants
  - Conifers: pinene (in needles) and limonene account for 70% of RH in Atlanta
  - Deciduous trees and shrubs: isoprene (rubbery sap)
- Best approach: avoid petroleum fuels: alternative energy sources like *biodiesel*
  - Biodiesel: rape methyl ester (RME) produced from rapeseed oil (vegetable oil) can be used directly in diesel engines. Also sunflower oil or Soya oils can be converted to fuel.
    * Reduces RH and CO emissions by 50%, NO_x by 10%.
    * Fewer deposits and less wear on engine
    * Accounts for 15% of Austian diesel market
    * Used in taxi fleets and buses in Berlin, Zurich, Bologna and Lake Como
    * Used as a heating fuel in the German parliament building (Reichstag): provides enough heat for $50,000$ homes
    * Growing rapeseed plant provides CO_2 sink
- Reformulate fuels to minimize photochemical pollution

Formulations of gasoline:

- Burning fuel involves radical chemistry: O_2 combines with radicals created by spark from spark plug
  - Compression of air/fuel also heats mixture which can produce radicals: called pre-ignition or "knocking"
  - Temperature of radical generation depends on mixture of compounds in gasoline
    * Branched chain hydrocarbons more resistant to radical generation: iso-octane (octane rating)
    * Companies tried lead additives which pollutes and dirties engine, and aromatic compounds (carcinogenic)
  - New attempt: "oxygenates" additives like methyl-tertiary-butyl-ester (MTBE)
    * Clean burning leads to less CO and unburned RH, but leads to more NO due to hotter engine

NO_x emissions and emissions controls: Key

- 3-way catalytic converter: Large effect in California

- Surface catalysis on Rd and Pt/Pd surfaces greatly limits NO_x, CO and RH emissions
- Releases CO_2, N_2, H_2O and O_2: mainly benign products