Chemistry of troposphere

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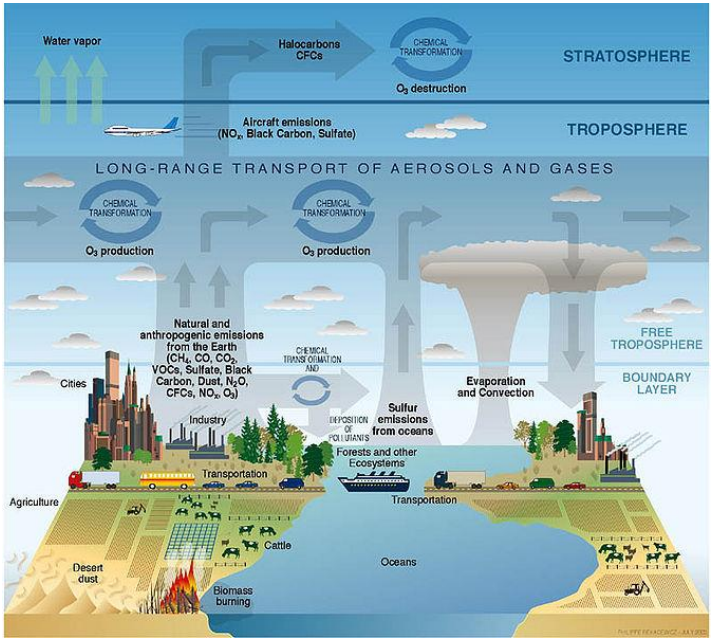
Why is atmospheric chemistry important?

- Human activity is changing the composition of the atmosphere
- Regulatory policy requires an understanding of pollutant impact
- Atmospheric pollutants impact living organisms
  - ✓ Health
  - ✓ Vegetation (e.g., farming) & animals
  - ✓ Climate change
- Atmospheric pollutants & their subsequent chemistry are responsible for:
  - ✓ Acid rain
  - ✓ Photochemical smog (e.g., arctic haze)
  - ✓ Ozone hole



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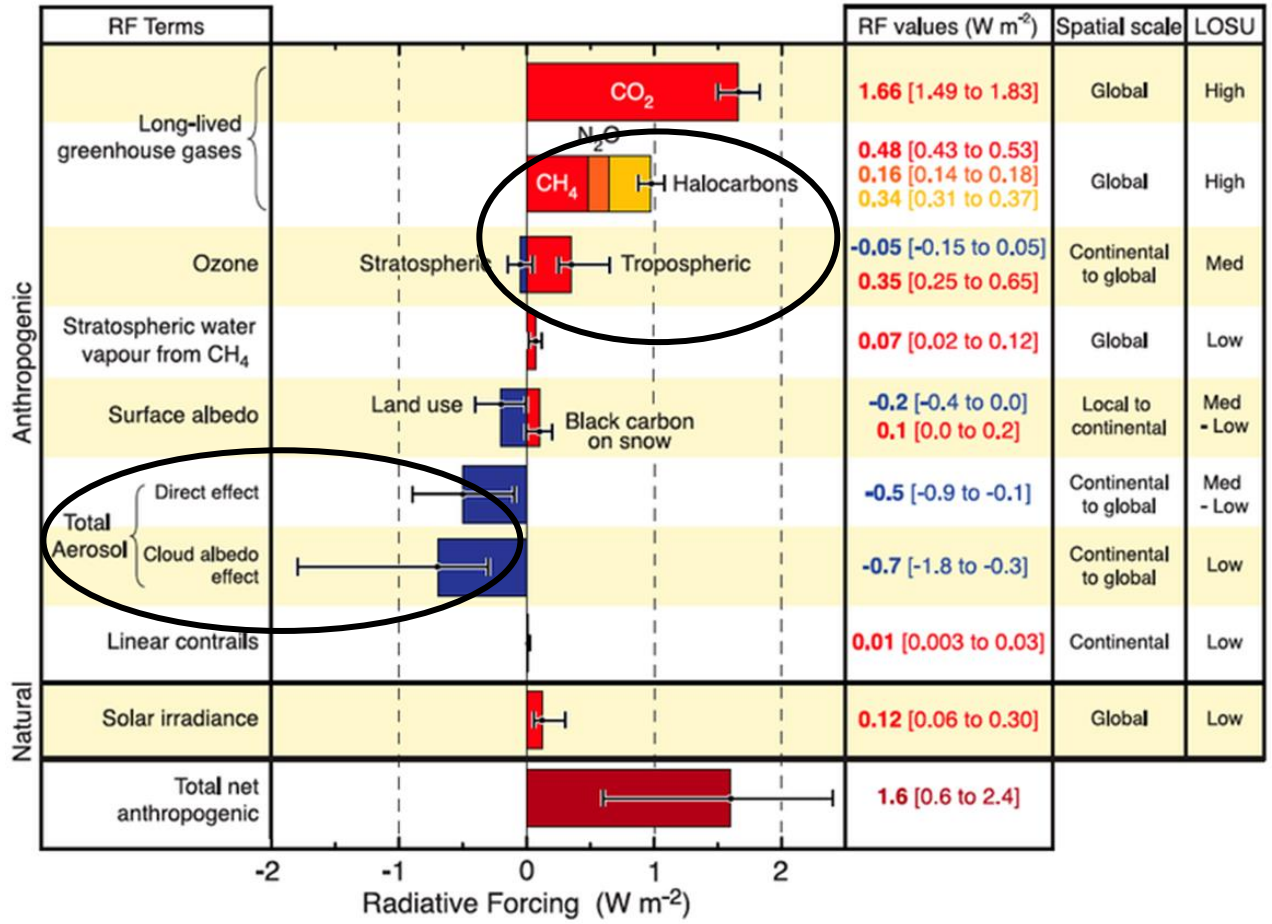
Atmospheric chemistry and climate change

- Atmospheric chemistry plays an important role in radiative forcing processes



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General scheme of reactivity in the troposphere

Major reactions occurring in the troposphere

LIGHT

(a particular ultraviolet component)

Radical HO• (basically)

Also: O_3, H_2O_2, NO_3•

PHOTOCHEMICAL REACTIONS

- O_3 photolysis
- NO_2 photolysis
- Aldehydes and ketones photolysis

OXIDATION REACTIONS

- Hydrocarbons oxidation
- NO oxidation
- NO_2 and SO_2 oxidation

Important Atmospheric Chemical Species

- Inorganic oxides: CO, CO_2, NO_2, SO_2
- Oxidants: O_3, H_2O_2, HO• radical, HO_2• radical, ROO• radicals, NO_3 radical
- Reductants: CO, SO_2, H_2S
- Hydrocarbons: Natural CH_4, pollutant alkanes, alkenes, aromatics
- Oxidized organics: Aldehydes, ketones, acids, organic nitrates
- Photochemically active species: NO_2, formaldehyde
- Acids: H_2SO_4, H_2SO_3, HNO_3
- Bases: NH_3
- Salts: NH_4HSO_4
- Unstable reactive species: Electronically excited nitrogen dioxide (NO_2*), HO•
- Solid and liquid particles in aerosols and clouds
  - ✓ Sources and sinks for gas-phase species
  - ✓ Sites for surface reactions on solids
  - ✓ Aqueous phase reactions in water droplets

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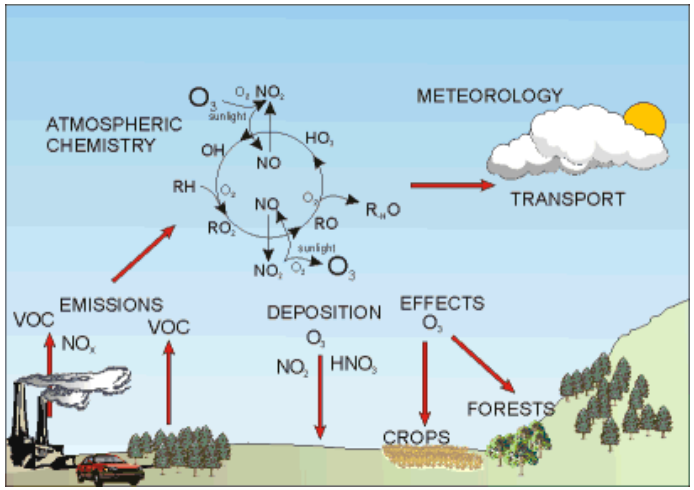
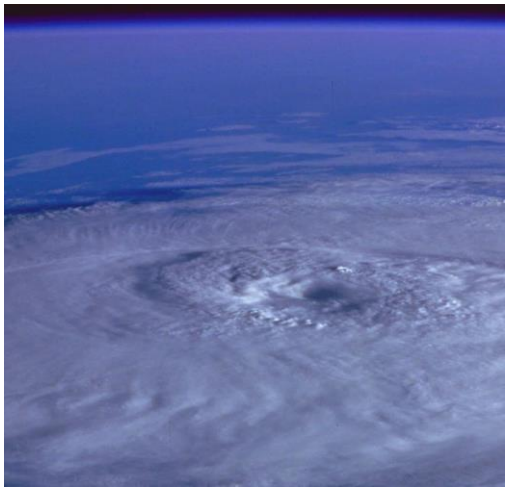
Tropospheric Chemistry

- Can be described as low temperature combustion system
- Overall reaction:

$$CH_4 + 3O_2 \leftrightarrow CO_2 + 2H_2O$$

- Obviously not a **thermal** process, but a radical mediated process initiated **photochemically**



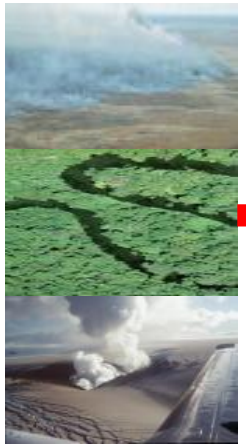


Tropospheric Chemistry

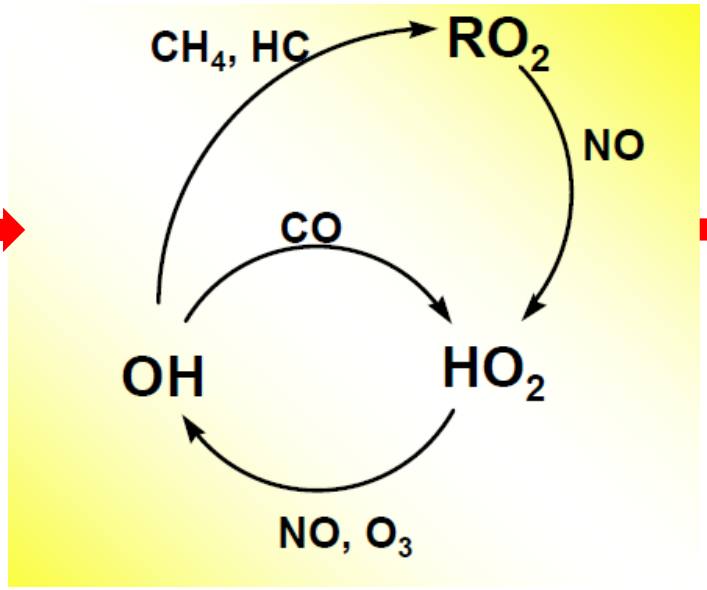
Sources

Anthropogenic

Biogenic

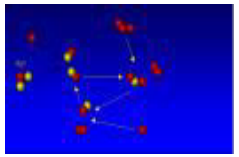


Chemical Processing



Impacts

Aerosols



NO_x

O_3

Oxidants

Primary Emissions

POPs

Hg
Heavy metals

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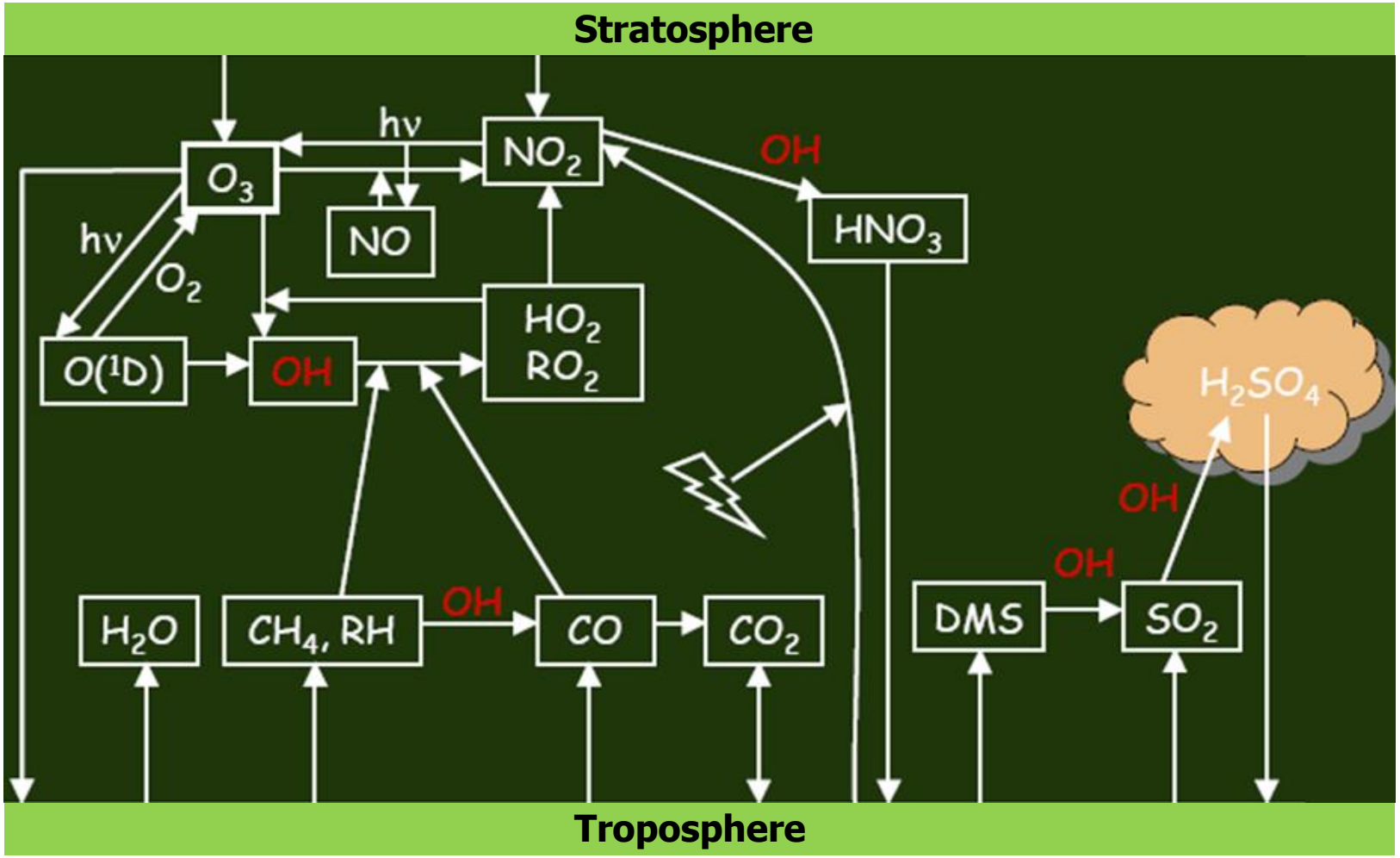
Tropospheric Chemistry



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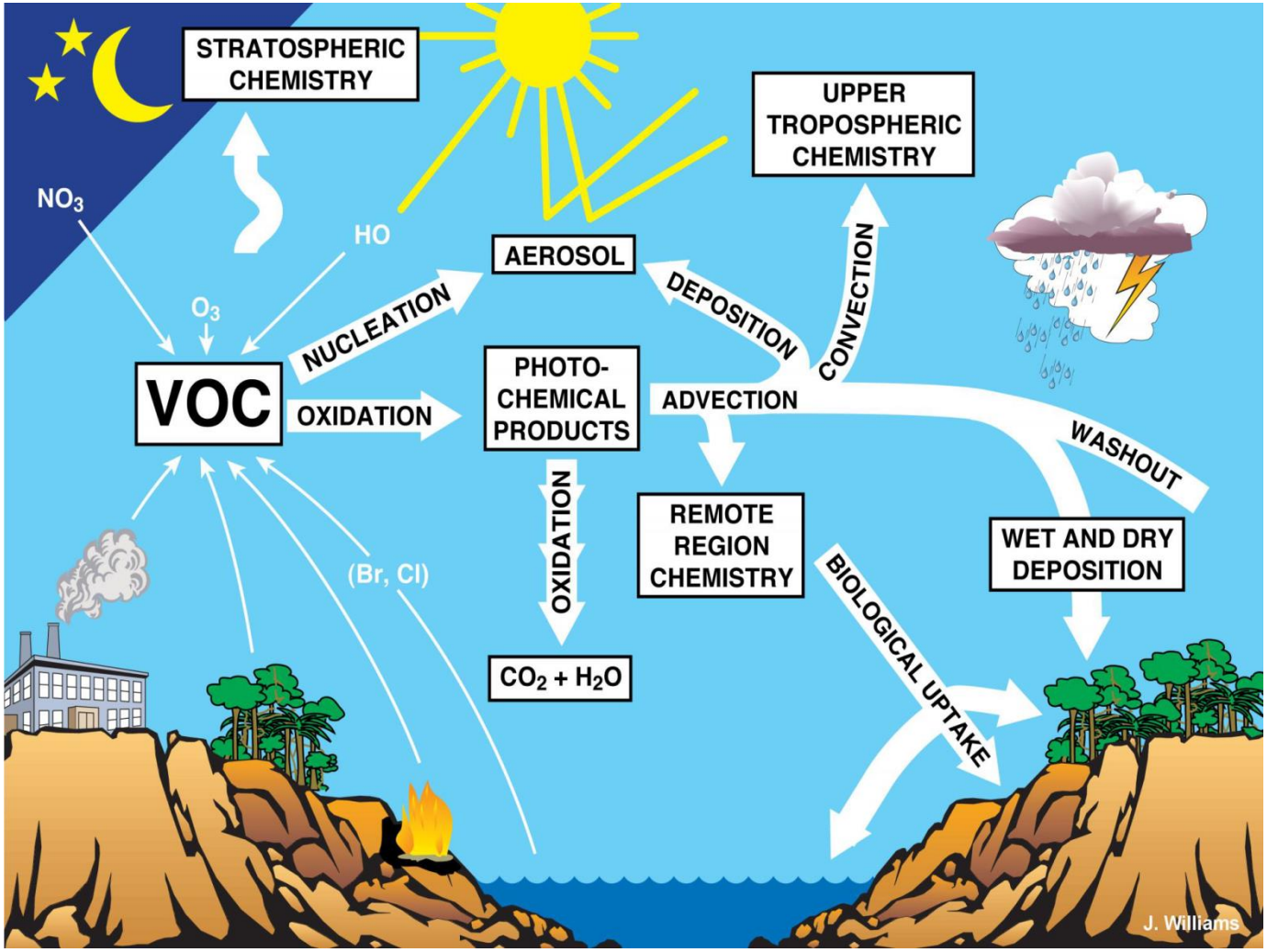
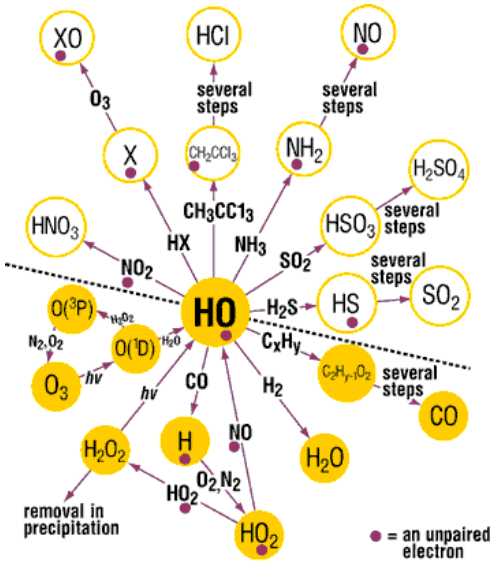
Tropospheric Chemistry



Oxidation Chemistry

- The three most important oxidizing species in the air are:
  - ✓ Hydroxyl radical: HO•
  - ✓ Nitrate radical: NO_3•
  - ✓ Ozone molecule: O_3
- *Free radicals* are atoms or molecules with unpaired electrons
- They are highly chemically reactive because of the strong pairing tendency of their unpaired electrons
  - ✓ Undergo series of chain reactions generating more free radicals
  - ✓ *Chain termination* such as $H_3C• + H_3C• \rightarrow C_2H_6$



Oxidation Chemistry

• The major route for the formation of the hydroxyl radical in the troposphere ozone photolysis:

$$NO_2 + h\nu \ (\lambda < 400 \text{ nm}) \rightarrow NO + O\bullet$$

$$O\bullet + O_2 + M \rightarrow O_3$$

$$O_3 + h\nu \ (\lambda < 320 \text{ nm}) \rightarrow O_2 + O^*$$

$$O^* + H_2O \rightarrow 2\ HO\bullet$$

$$NO_2 + H_2O \rightarrow NO + 2\ HO\bullet$$

• It is extremely reactive and able to oxidize most of the chemicals found in the troposphere, and is therefore known as the **detergent of the atmosphere**

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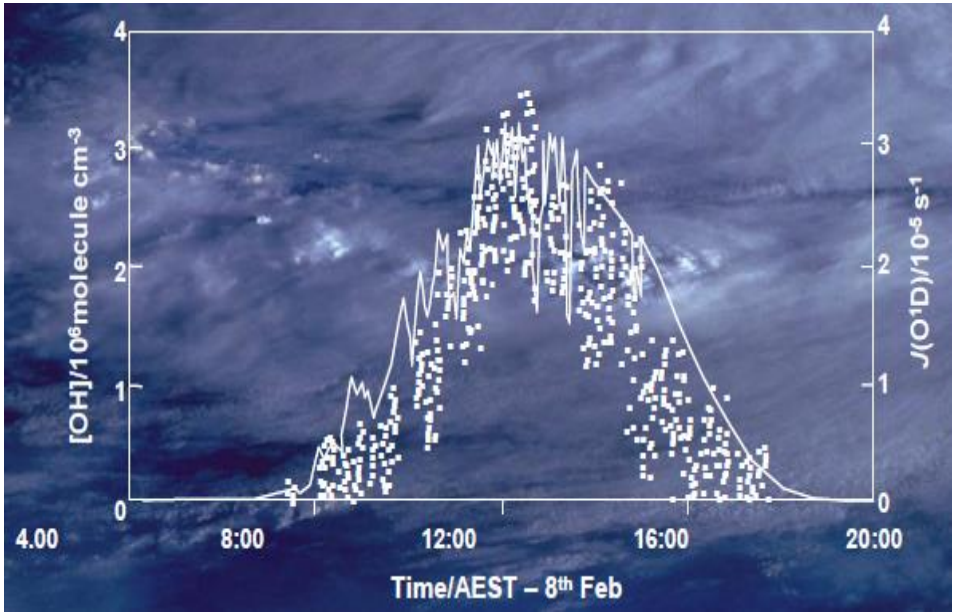
Oxidation Chemistry

- Only a few compounds in the troposphere do not react with HO•
  - ✓ Chlorofluorocarbons (CFC's)
  - ✓ Nitrogen (N_2)
  - ✓ Carbon dioxide (CO_2)
- Concentrations of HO• are extremely low: range of $1x10^5$-$2x10^7$ molecules cm^{-3}



HO• measurements

HO• detection instrument (Antarctica)

Oxidation Chemistry

- Hydroxyl radical reacts with many electron rich (multiple bonded) species in the atmosphere, but no with N_2 and CO_2
- It can react by abstraction of hydrogen, e.g.

$$CH_4 + HO\bullet \rightarrow \bullet CH_3 + H_2O$$
$$NH_3 + HO\bullet \rightarrow \bullet NH_2 + H_2O$$
$$H_2S + HO\bullet \rightarrow \bullet SH + H_2O$$
$$CH_3Cl + HO\bullet \rightarrow \bullet CH_2Cl + H_2O$$

- Hydroxyl radical is commonly removed by reaction with CO or CH_4

$$HO\bullet + CO \rightarrow CO_2 + H\bullet$$
$$HO\bullet + CH_4 \rightarrow H_3C\bullet + H_2O$$

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Oxidation Chemistry

- Other important radicals are:
  - ✓ Hydroperoxyl radical: HOO•/HO_2•
  - ✓ Methyl radical: CH_3OO•
- These peroxy radicals are less reactive than other ones
- Main reactions:
  - ✓ Peroxy radical production

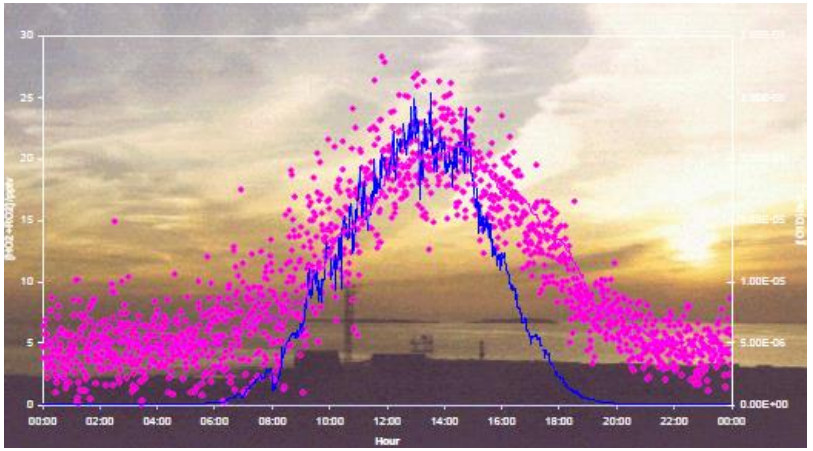
$$HO\bullet + CO \rightarrow HO_2\bullet + CO_2$$

  - ✓ Ozone destruction

$$HO_2\bullet + O_3 \rightarrow OH + 2O_2$$

  - ✓ Peroxy radical recombination

$$HOO\bullet + HOO\bullet \rightarrow H_2O_2 + O_2$$



HOO• measurements

Oxidation Chemistry

- Reactions mediated by radicals

$H_2 + O_2$	→ $HO_2\bullet + H\bullet$	Start
$H_2 + HO_2\bullet$	→ $OH\bullet + H_2O$	Propagation
$H_2 + OH\bullet$	→ $H\bullet + H_2O$	
$H\bullet + O_2$	→ $OH\bullet + O\bullet$	Branching
$O\bullet + H_2$	→ $OH\bullet + H\bullet$	
$OH\bullet + HO_2\bullet$	→ $H_2O + O_2$	Termination

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Formation of tropospheric ozone

• In an non-polluted atmosphere (absence of VOCs) ozone is formed only through the photochemical cycle of the nitrogen oxides and its concentration is proportional to the quotient $[NO_2]/[NO]$. A maximum of this ratio implies a peak of ozone concentration

• In urban polluted environment this is different and the maximum ozone occurs some time later. There are other factors involved

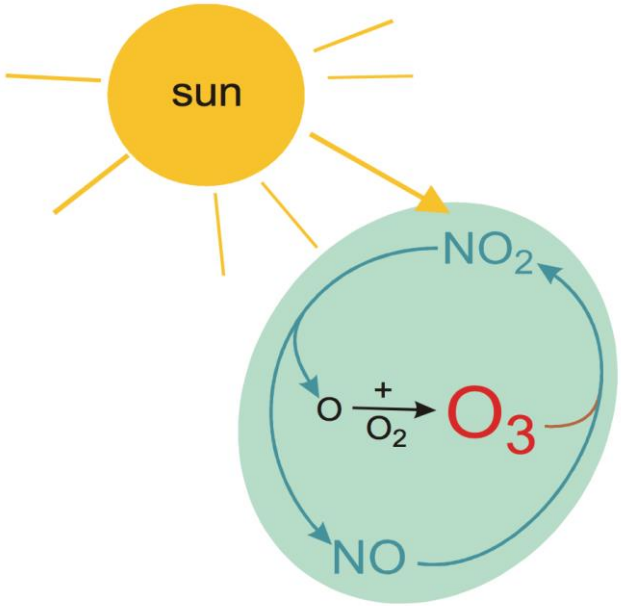
Photochemical cycle of NO_2, NO and O_3

- When NO and NO_2 are present in sunlight O_3 formation occurs by photolysis:

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

Where M represents N_2 or O_2



- Once formed, O_3 reacts with NO:

$$O_3 + NO \rightarrow NO_2 + O_2$$

- The three reactions form (during sunlight) an equilibrium (that depends on the intensity of sunlight), called photostationary state
- The photostationary state does not lead to a photochemical net production of O_3

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Sulfurous and photochemical smog

Sulfurous (or reducing) smog

- Term "smog" is derived from the words "smoke" and "fog"
- Sulfurous smog, also known as "London smog", results from a high concentration of sulfur oxides and soot particles in the air and is caused by the use of sulfur-bearing fossil fuels, particularly coal.

"London, by reason of the excessive coldness of the air hindering the ascent of the smoke, was so filled with the fuliginous steam of the sea-coal, that hardly could one see across the street, and this filling the lungs with its gross particles, exceedingly obstructed the breast, so as one could scarcely breathe"

John Evelyn, 1684

Sulfurous and photochemical smog

Sulfurous (or reducing) smog

- Source: burning of coal (lignite rich in pyrite):

$$4\ FeS\ (s) + 11\ O_2 \rightarrow 8\ SO_2\ (g) + 2\ Fe_2O_3$$

$$SO_2\ (g) + H_2O \rightarrow H^+ + HSO_3^-$$

- In the presence of trace metals (Fe, Mn) or carbon particles the conversion to sulfuric acid is catalyzed:

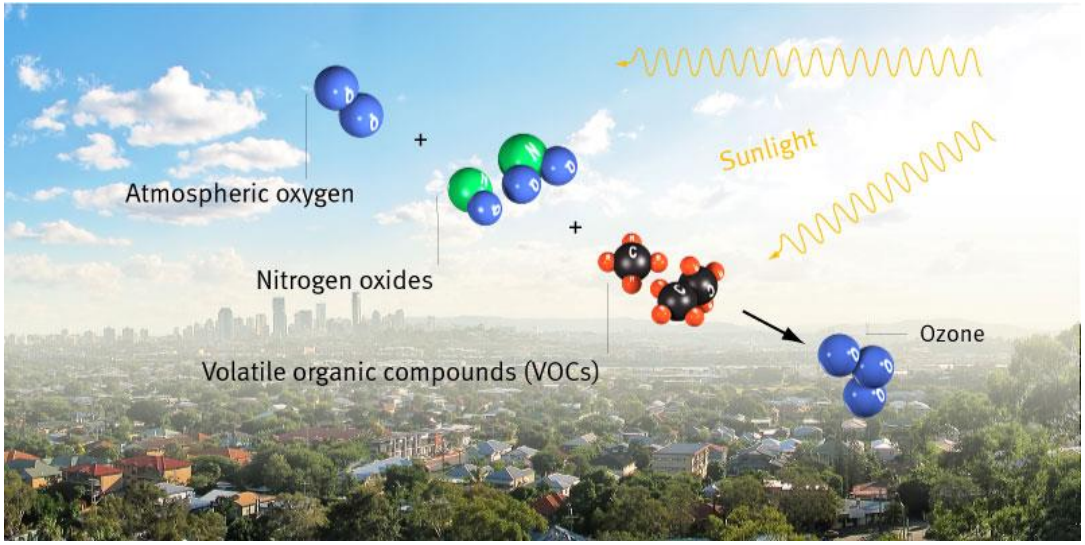
$$2\ HSO_3^-\ (l) + O_2 \rightarrow 2\ H^+ + 2\ SO_4^=$$

- Sulfuric acid is highly hygroscopic and produces large droplets in suspension → "pea soup fog"

Sulfurous and photochemical smog

Photochemical (or oxidant) smog

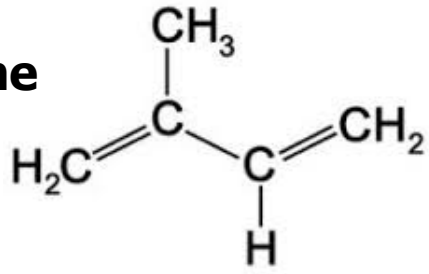
- Also known as "Los Angeles smog"
- Occurs most prominently in urban areas that have large numbers of automobiles, requires neither smoke nor fog
- It is the chemical reaction of sunlight, nitrogen oxides and volatile organic compounds in the atmosphere, which leaves airborne particles and ground-level ozone

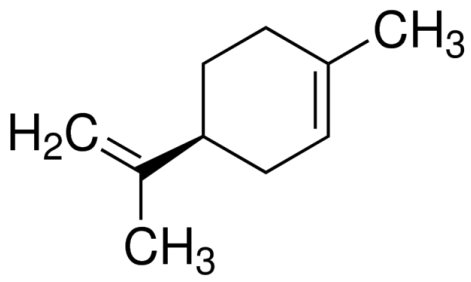


Photochemical smog precursors

- **Nitrogen oxides (NOx):** emitted by combustion sources
- **Volatile organic compounds (VOC):** sources of VOC include emissions from motor vehicles due to either evaporation or incomplete combustion of fuel, and from biomass burning. Vegetation also releases VOCs like isoprene (broadleaves) and limonene (conifers)

isoprene





limonene

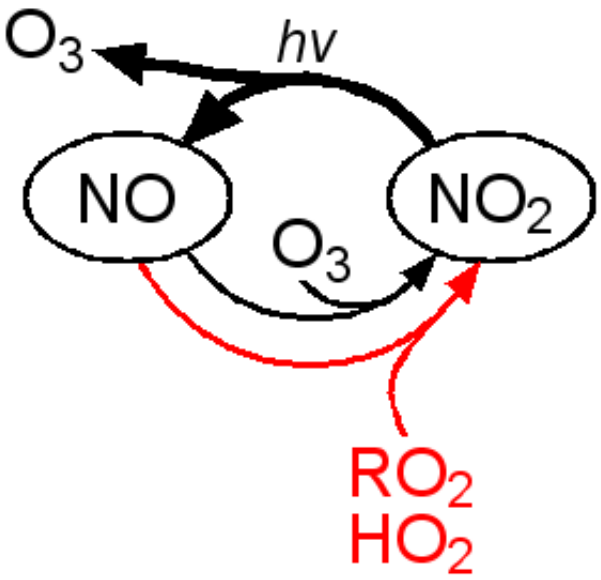
- **Sunlight:** smog pollution is more pronounced in cities with a high solar radiation index (tropical cities), in summer and in the hours of maximum sun exposure

Photochemical smog

- The presence of peroxy radicals, from the oxidation of hydrocarbons, disturbs O_3-NO-NO_2 cycle

$$NO + HO_2\cdot \rightarrow NO_2 + OH\cdot$$
$$NO + RO_2\cdot \rightarrow NO_2 + RO\cdot$$

- Leads to net production of ozone



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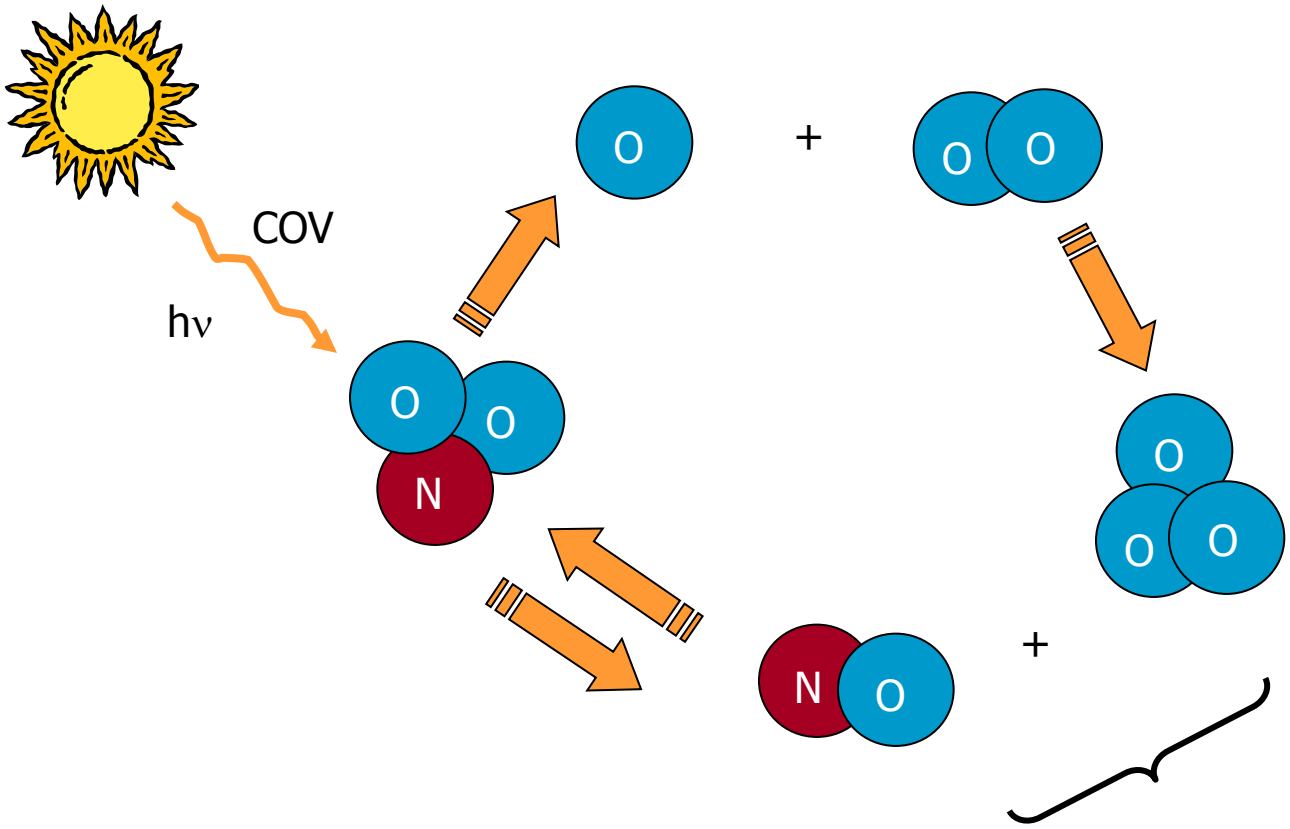
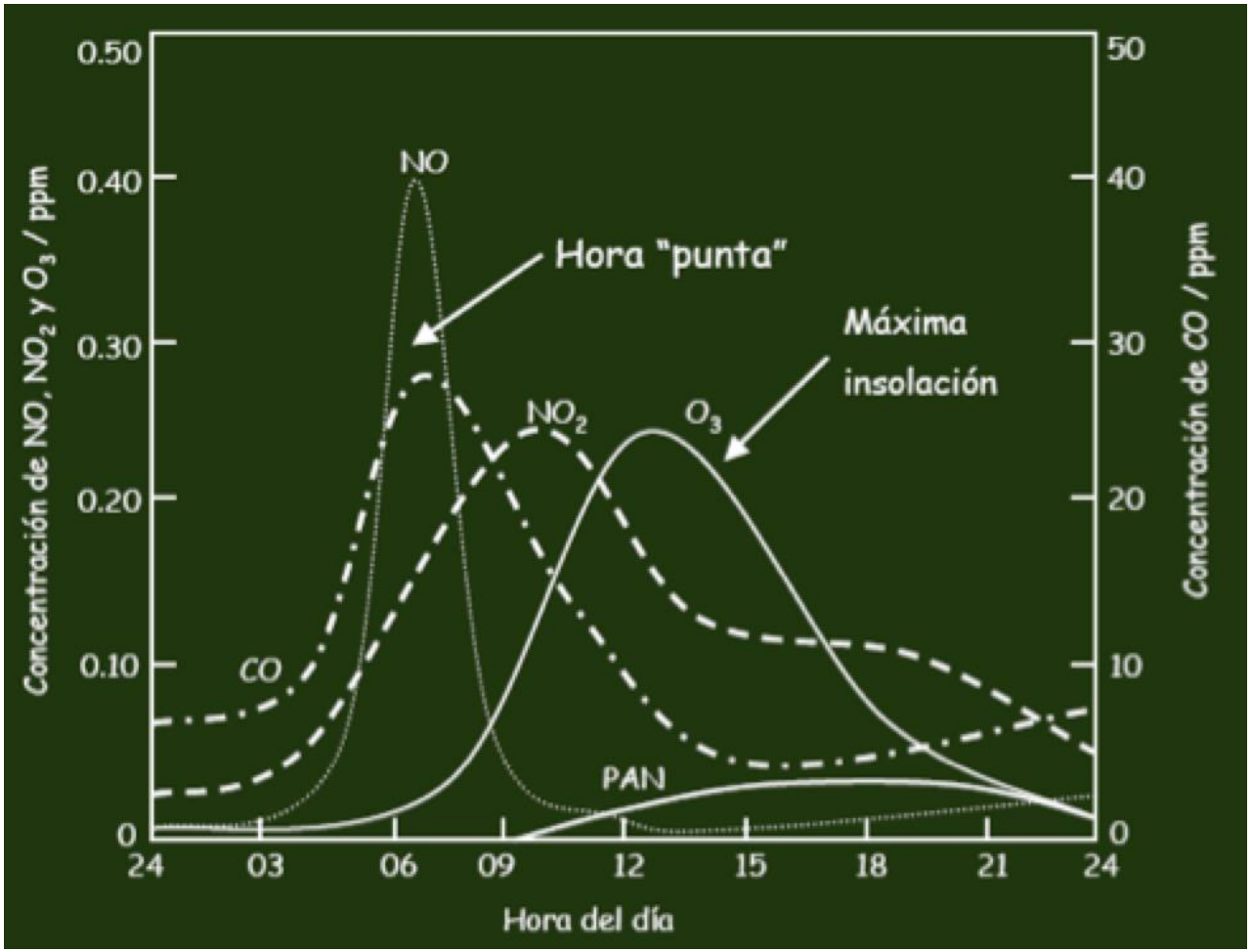
Cycle of formation/destruction of ozone



Formation

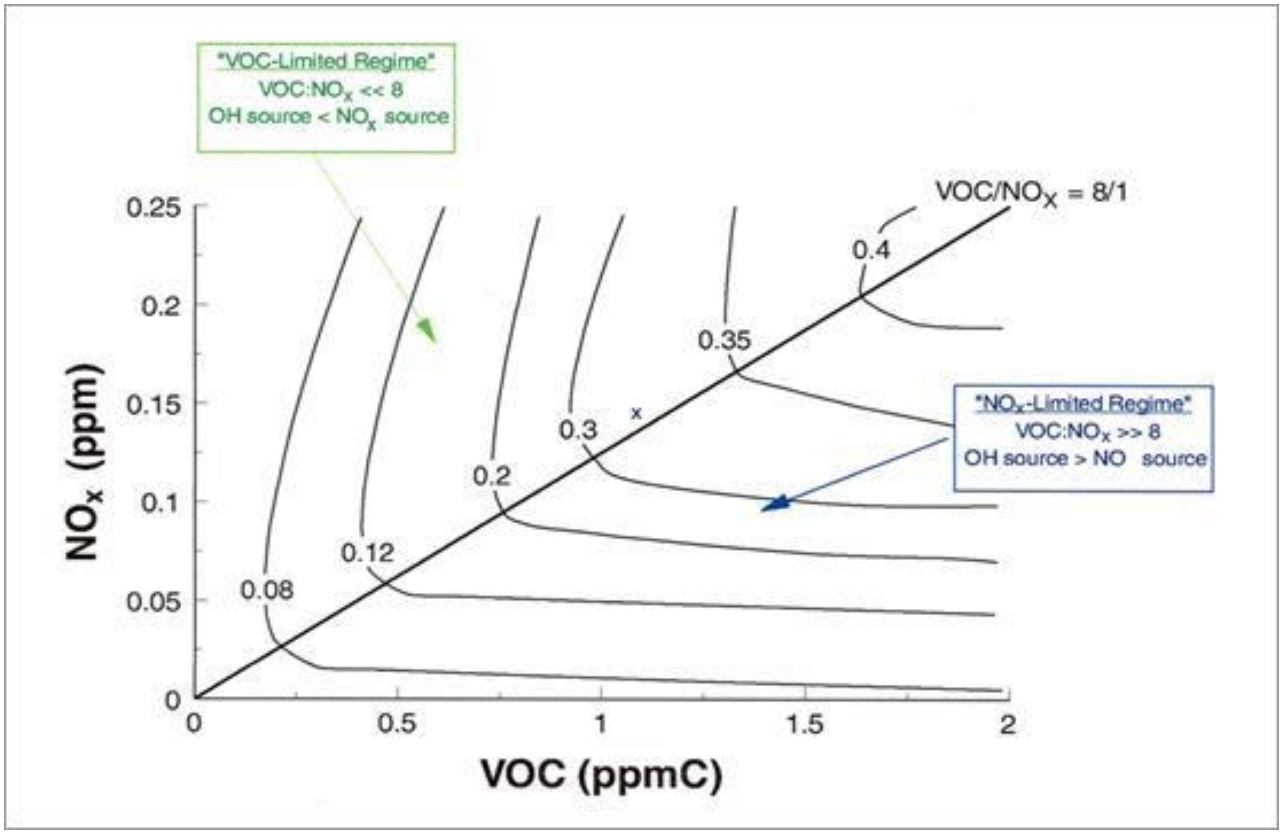
Destruction

Photochemical smog



Strategies to Limit Ozone Production

- In low hydrocarbon high NO_X conditions, reducing NO_X can increase ozone
- Reduction of hydrocarbons will have a limited effect in downwind regions and where natural hydrocarbons are significant



Peroxyacetyl Nitrates (PAN)

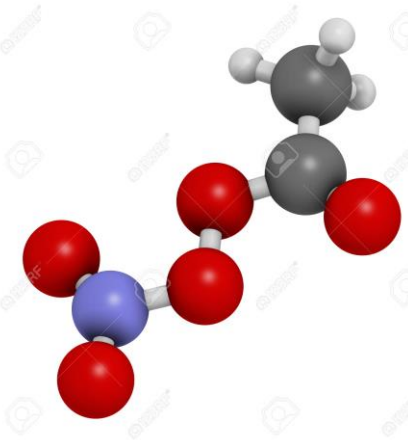
- Are secondary pollutants formed from peroxyacid radicals and NO_2

$CH_3CHO + OH^{\bullet} \rightarrow CH_3C^{\bullet}O + H_2O$

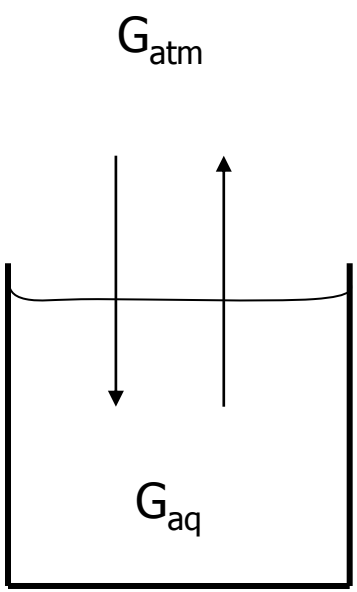
$CH_3C^{\bullet}O + O_2 \rightarrow CH_3C(O)OO^{\bullet}$ (acetylperoxy)

$CH_3C(O)OO^{\bullet} + {}^{\bullet}NO_2 \rightarrow CH_3C(O)OONO_2$ (PAN)

- Effects on human health:
  - ✓ Respiratory and eye irritants
  - ✓ Mutagenic- causing skin cancer



Acid rain



- Solubility of gases in water (law of Henry)

  CO_2 (aq) = K_H PCO_2 , K_H = 3,38 10^{-2} mol/atm L

  PH_2O = 0,0313 atm, [CO_2] = 370 ppm

  PCO_2 = (1-0.0313 atm) (0.00037) = 3,58 10^{-4} atm

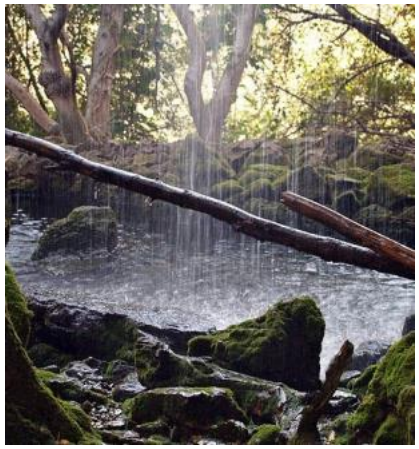
- pH of pure rain water

  CO_2 (aq) = 3.38 10^{-2} 3.58 10^{-4} = 1.18 10^{-5} mol/L

  $H_2CO_3 \leftrightarrow H+ + HCO_3^-$ Ka = $10^{-6.3}$

$$pH = \frac{1}{2}\left(pk_{a_1} + pC_A\right) = 5{,}6$$

Acid rain



- SO_2: rapid dry deposition (not water soluble)
- SO_4^{2-}, H_2SO_4: almost entirely as aerosols (very soluble)
- Gas phase reactions: (1-5% hr):

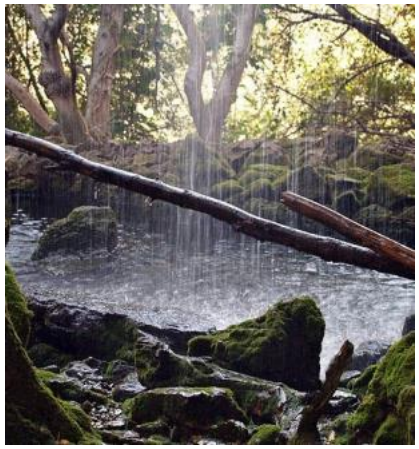
$$SO_2 + \bullet OH \Rightarrow M \Rightarrow HOSO_2$$

$$HOSO_2 + O_2 \Rightarrow SO_3 + HO_2$$

$$SO_3 + H_2O \Rightarrow M \Rightarrow H_2SO_4$$

$$net \ \bullet OH + SO_2 + O_2 + H_2O \Rightarrow H_2SO_4 + HO_2$$

Acid rain



- SO_2: rapid dry deposition (not water soluble)
- SO_4^{2-}, H_2SO_4: almost entirely as aerosols (very soluble)
- Aqueous phase (cloud based reactions): 10%/minute

$$SO_2 + H_2O \Leftrightarrow HSO_3^- + H^+ \Leftrightarrow SO_3^- + 2H^+$$

$$HSO_3^- + H_2O_2 \Rightarrow M \Rightarrow SO_4^{2-} + H^+ + H_2O$$

or

$$HSO_3^- + O_3 \Rightarrow SO_4^{2-} + O_2 + H^+$$

Acid rain

- NOx can be dry deposited to the earth or can be oxidized in the atmosphere
- Gas phase reactions: (hours)

$$NO_x + O_3 \Rightarrow NO_2 + O_2$$

$$NO + HO_2 \Rightarrow NO_2 + OH$$

$$NO_2 + OH \Rightarrow M \Rightarrow HNO_3$$

- Gas/Liquid (cloud based reactions):

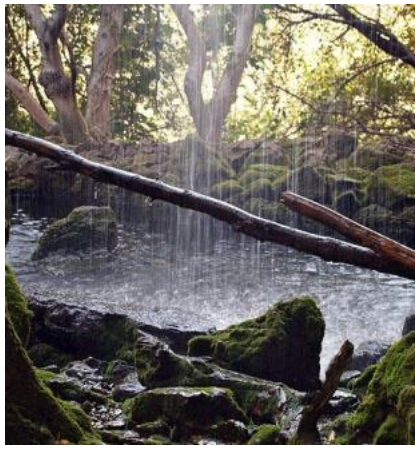
$$NO_2 + O_3 \Leftrightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \Rightarrow M \Rightarrow N_2O_5$$

$$N_2O_5 + H_2O(l) \Rightarrow 2H^+ + 2NO_3^-$$

$$2NO_2 + O_3 + H_2O(l) \Rightarrow 2H^+ + NO_3^- + O_2$$

Acid rain



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