Atmospheric Chemistry
Lecture 2: Tropospheric Chemistry and Aerosols

Jim Smith
Atmospheric Chemistry Division / NCAR
jimsmith@ucar.edu

Outline for Second Lecture

Tropospheric Chemistry and Aerosols

- ⇨ Primary and secondary pollutants
- ⇨ Sulfur chemistry
- ⇨ Nitrogen chemistry
- ⇨ Acid rain
- ⇨ Chemistry of the background troposphere:
  - CO
  - Methane
  - Formaldehyde
- ⇨ Urban Air Pollution
  - Hydrocarbon oxidation
  - Ozone Isopleth plots
  - Smog meteorology

Primary and Secondary Pollutants and their impacts

⇨ **Primary pollutants** are those emitted directly from sources

- CO: affects oxygen-carrying capacity of blood (but not at urban concentrations)
- NO: secondary reactions
- NO_2: 5% in urban, much higher for biomass burning
- SO_2: respiratory constriction (asthma, bronchitis)
- NH_3: aerosol formation
- soot: visibility reduction, PAH is carcinogen
- isoprene: emitted from plants, leads to ozone and makes a certain President think the ozone problem is caused by trees.
- vanillan: yummy smell from Ponderosa Pine

⇨ **Secondary pollutants** are those formed in the atmosphere by chemical interactions among primary pollutants and normal atmospheric constituents.

- NO_2 (95%): lung damage
- H_2SO_4: Aerosol formation, visibility reduction and acid rain
- PAN: hurts your eyes, damage to plants
- O_3: damage to plants & plastics, lung damage (only short-term?)

Tropospheric Chemistry

Sulfur Cycle

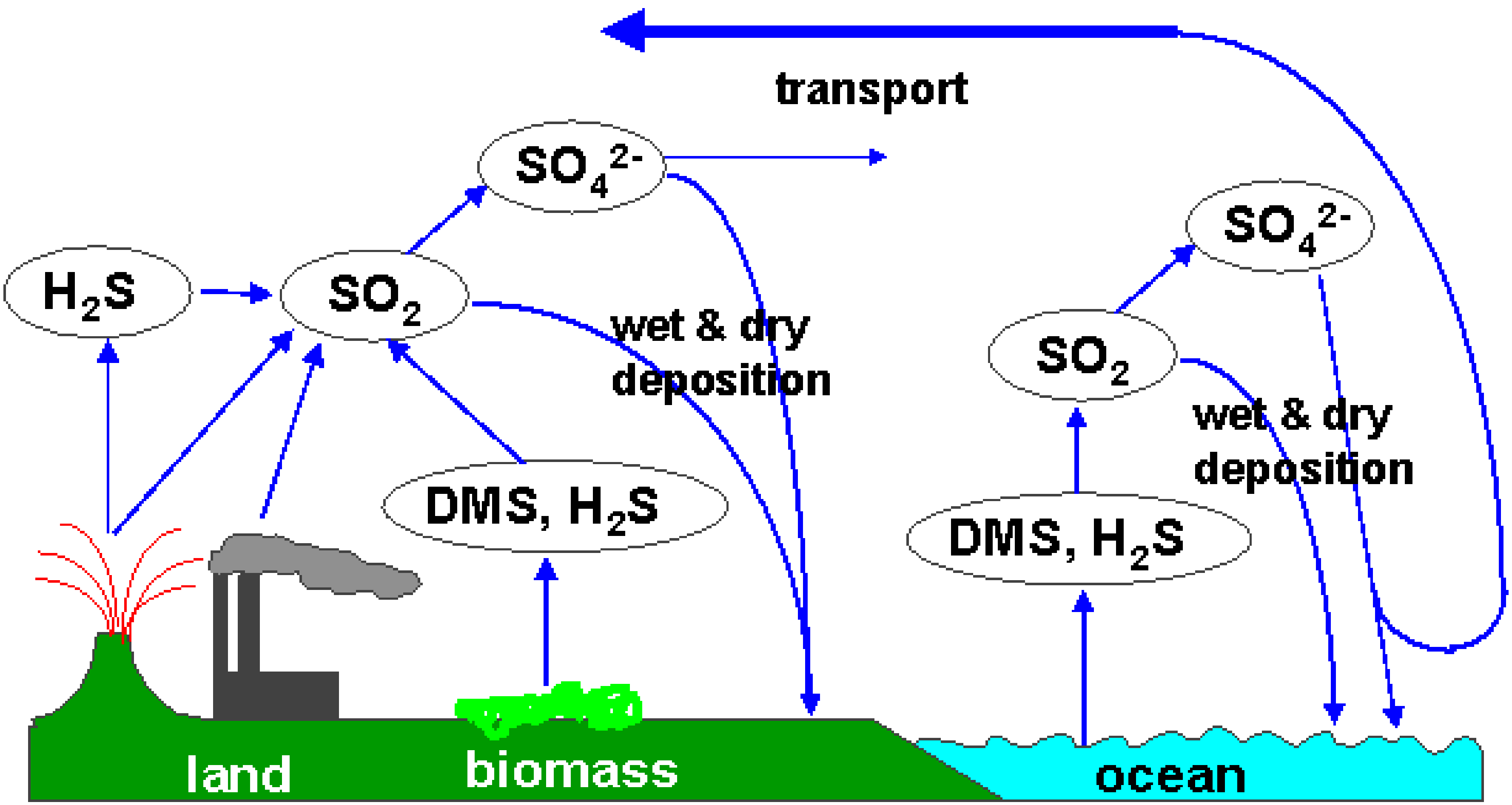


Image courtesy of Hugh Powell, Univ. of Durham, UK

Sulfur Cycle

- ⇨ SO_2 can be converted to H_2SO_4 in the gas phase or in aqueous solution (in clouds or fogs)
- ⇨ Gas phase oxidation involves … OH attack!

$$SO_2 + \bullet OH + M \longrightarrow HSO_3\bullet + M$$

$$HSO_3\bullet + O_2 + M \longrightarrow SO_3 + HOO\bullet + M$$

- ⇨ SO_3 is highly soluble in water, producing sulfuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4(aq)$$

- ⇨ Gaseous SO_2 dissolves in water giving sulfurous acid:

$$SO_2 + H_2O \longrightarrow HSO_3^-(aq) + H^+(aq)$$

- ⇨ Once in solution, there are several oxidation pathways:
  - by dissolved ozone or hydrogen peroxide:

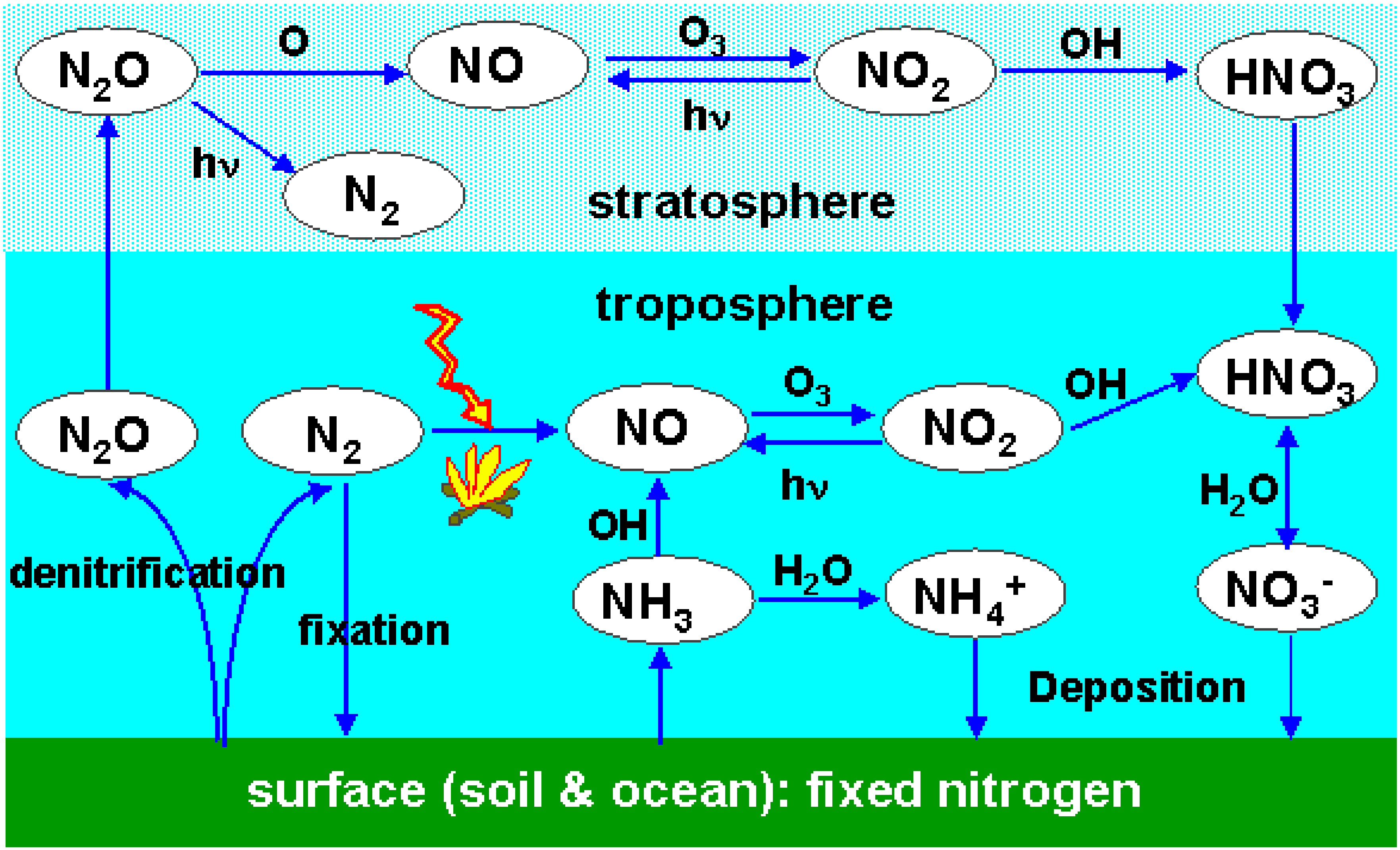
e.g., $$HSO_3^- + H_2O_2 \longrightarrow SO_2OOH^- + H_2O$$

$$SO_2OOH^- + H^+ \longrightarrow H_2SO_4 \qquad \text{(pH dependent)}$$

  - by dissolved oxygen, catalyzed by iron and/or manganese

$$HSO_3^- + \tfrac{1}{2} O_2 \longrightarrow HSO_4^-$$

Nitrogen Chemistry



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Nitrogen Chemistry

- Nitrogen chemistry is actually quite complicated!
- NO and NO_2 can be absorbed in water droplets:

$$2NO_2 + H_2O \longrightarrow 2H^+ + NO_3^- + NO_2^-$$

- NO_2 can be oxidized by OH in the gas phase:

$$NO_2 + \bullet OH + M \longrightarrow HNO_3 + M$$

- In the stratosphere, NO plays a starring role in the catalytic cycle for ozone destruction (Crutzen's contribution!)
- NH_3 is absorbed in water droplets, and is the most important aqueous base in the atmosphere
- At nighttime, NO_2 can be oxidized by O_3 to form NO_3, a strong atmospheric oxidant which can go on to form N_2O_5:

$$NO_3 + NO_2 + M \longrightarrow N_2O_5 + M$$

In the morning, both compounds rapidly photolyze to give the troposphere a morning boost of NOx:

$$N_2O_5 + h\nu \longrightarrow NO_3\bullet + NO_2$$

$$NO_3\bullet + h\nu \longrightarrow \begin{cases} NO + O_2 \\ NO_2 + O \end{cases}$$

Acid Rain

⇨ Normal, unpolluted rainwater has a typical pH of ~5-5.6:

$CO_2 + H_2O \longrightarrow H_2CO_3(aq)$

$H_2CO_3(aq) \longrightarrow H^+(aq) + HCO_3^-(aq)$

$HCO_3^-(aq) \longrightarrow H^+(aq) + CO_3^-(aq)$

⇨ Rain with pH < 4.5 is termed "acid rain"
Term used for both dry acid deposition and acid precipitation

⇨ Acids found in rainwater:
$\mathbf{H_2SO_4}$, $\mathbf{HNO_3}$, HCl, H_2CO_3, H_2SO_3, organic acids

⇨ H_2SO_4 and HNO_3 are main anthropogenic pollutants responsible for acidification, resulting from fossil fuel combustion.

⇨ Emissions of these compounds are decreasing in most industrialized countries, however with residence times of several days, acid rain can affect areas 1000s of km from the emission source.

⇨ Problems caused by acidity:

- damage to vegetation
- acidification of surface waters, esp. lakes.

The primary photochemical cycle of NOx and ozone

- ⇨ NO is a primary pollutant formed by combustion, in the atmosphere it oxidizes to form NO_2:

$$2NO + O_2 \longrightarrow 2\ NO_2$$

- ⇨ Ozone then occurs as a result of photolysis of NO_2:

$$NO_2 + h\nu \longrightarrow NO + O \qquad (1)$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad (2)$$

- ⇨ Note that there are no other significant sources of ozone in the atmosphere other than reaction 2. Once formed, ozone can regenerate NO_2:

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (3)$$

- ⇨ Let's consider the system of reactions 1-3. The rate of change of O_3 is:

$$\frac{d[\mathrm{O_3}]}{dt} = -k_3[\mathrm{O_3}][\mathrm{NO}] + k_2[\mathrm{O}][\mathrm{O_2}][\mathrm{M}]$$

- ⇨ Similarly, the rate of change of O is:

$$\frac{d[\mathrm{O}]}{dt} = k_1[\mathrm{NO_2}] - k_2[\mathrm{O}][\mathrm{O_2}][\mathrm{M}]$$

The primary photochemical cycle of NOx and ozone

$$NO_2 + h\nu \longrightarrow NO + O \quad (1)$$
$$O + O_2 + M \longrightarrow O_3 + M \quad (2)$$
$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (3)$$

$$\frac{d[\mathrm{O}]}{dt} = k_1[\mathrm{NO_2}] - k_2[\mathrm{O}][\mathrm{O_2}][\mathrm{M}]$$

- In reality, reaction 2 is so fast that the oxygen atom disappears as soon as it's formed by reaction 1. The result is that d[O]/dt is always very nearly zero …this is called the "pseudo-steady state approximation" (PSSA):

$$k_1[\mathrm{NO_2}] = k_2[\mathrm{O}][\mathrm{O_2}][\mathrm{M}]$$

- The steady-state ozone concentration was given by:

$$\frac{d[\mathrm{O_3}]}{dt} = -k_3[\mathrm{O_3}][\mathrm{NO}] + k_2[\mathrm{O}][\mathrm{O_2}][\mathrm{M}] = 0$$

- Substituting the result of the PSSA into the above equation gives:

$$[\mathrm{O_3}] = \frac{k_1[\mathrm{NO_2}]}{k_3[\mathrm{NO}]}$$

- **The steady-state ozone concentration is proportional to [NO2] / [NO]**

Chemistry of the background troposphere

- The key species involved are:
  - methane (CH_4)
  - carbon monoxide (CO)
  - formaldehyde (HCHO)
  - ozone (O_3)
  - NOx (NO and NO_2)
  - nitric acid (HNO_3)
  - hydrogen peroxide (H_2O_2)
- The initiation step that starts it all is the photolysis of ozone to generate two OH radicals ("the atmosphere's detergent"):

$$O_3 + h\nu \longrightarrow O_2 + O^*$$

$$O^* + H_2O \longrightarrow 2 \bullet OH$$

CO chemistry

- ⇨ Chemical lifetime of 30-90 days
- ⇨ Primary natural source is oxidation of methane (20-50%), with the remainder from oxidation of other hydrocarbons and from oceans.
- ⇨ Primary sink is OH radical attack:

$$\bullet OH + CO \longrightarrow CO_2 + \bullet H \qquad (1)$$

$$\bullet H + O_2 + M \longrightarrow HOO\bullet + M \qquad (2)$$ the hydroperoxyl radical

$$HOO\bullet + \mathbf{NO} \longrightarrow \mathbf{NO_2} + \bullet OH \qquad (3)$$

- ⇨ If NOx concentrations are low, the following reaction competes with (3):

$$HOO\bullet + O_3 \longrightarrow \bullet OH + 2O_2 \qquad (4)$$

- ⇨ So the photolytic oxidation of CO to CO_2, catalyzed by OH, leads to a net production of ozone in the presence of NOx since:

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]}$$

or to the net destruction of O_3 if NOx concentrations are low via (4)

Chemistry of the Background Troposphere

CH_4 and HCHO chemistry

- ⇨ Chemical lifetime of 8-10 years
- ⇨ Primary natural source is biogenic (swamps, tropical rainforests, livestock)
- ⇨ In urban air, methane oxidation is slower than other hydrocarbons
- ⇨ Primary sink is OH radical attack:

$$\bullet OH + CH_4 \longrightarrow \bullet CH_3 + H_2O$$

$$\bullet CH3 + O_2 + M \longrightarrow CH_3OO\bullet + M$$ methylperoxy radical

$$CH_3OO\bullet + \mathbf{NO} \longrightarrow \mathbf{NO_2} + CH_3O\bullet$$ methoxy radical

$$CH_3O\bullet + O_2 \longrightarrow HCHO + HOO\bullet$$ formaldehyde

$$(HOO\bullet + \mathbf{NO} \longrightarrow \mathbf{NO_2} + \bullet OH)$$

- ⇨ HCHO is further attacked by OH to form CO:

$$HCHO + \bullet OH \longrightarrow HCO\bullet + H_2O$$

$$HCO\bullet + O_2 \longrightarrow HOO\bullet + CO$$

$$(HOO\bullet + \mathbf{NO} \longrightarrow \mathbf{NO_2} + \bullet OH)$$

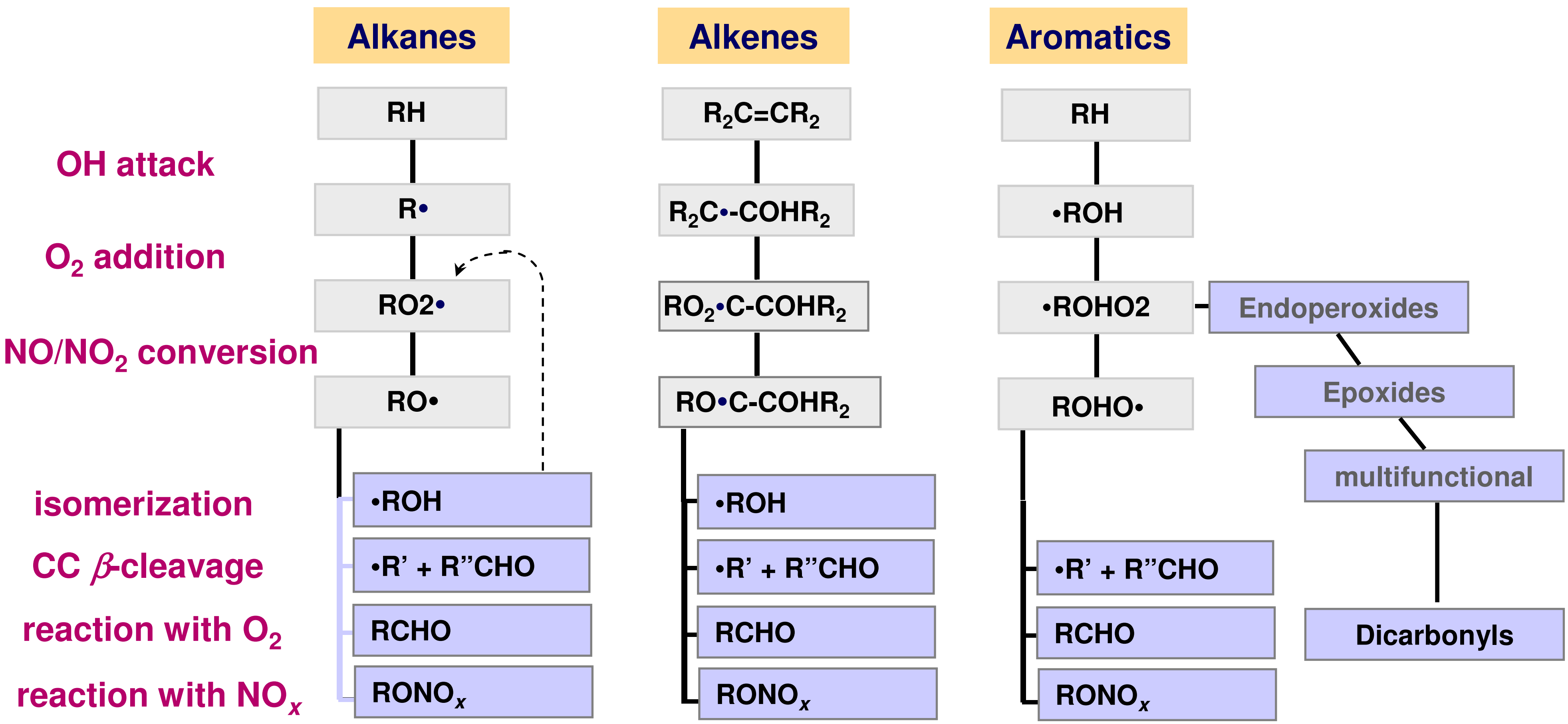
- ⇨ As we saw before, CO is oxidized to CO_2:

$$CO + 2O_2 + h\nu \longrightarrow CO_2 + O_2$$

- ⇨ So methane is oxidized photolytically to CO_2 via OH attack, with formaldehyde and CO as intermediates and net production of ozone.

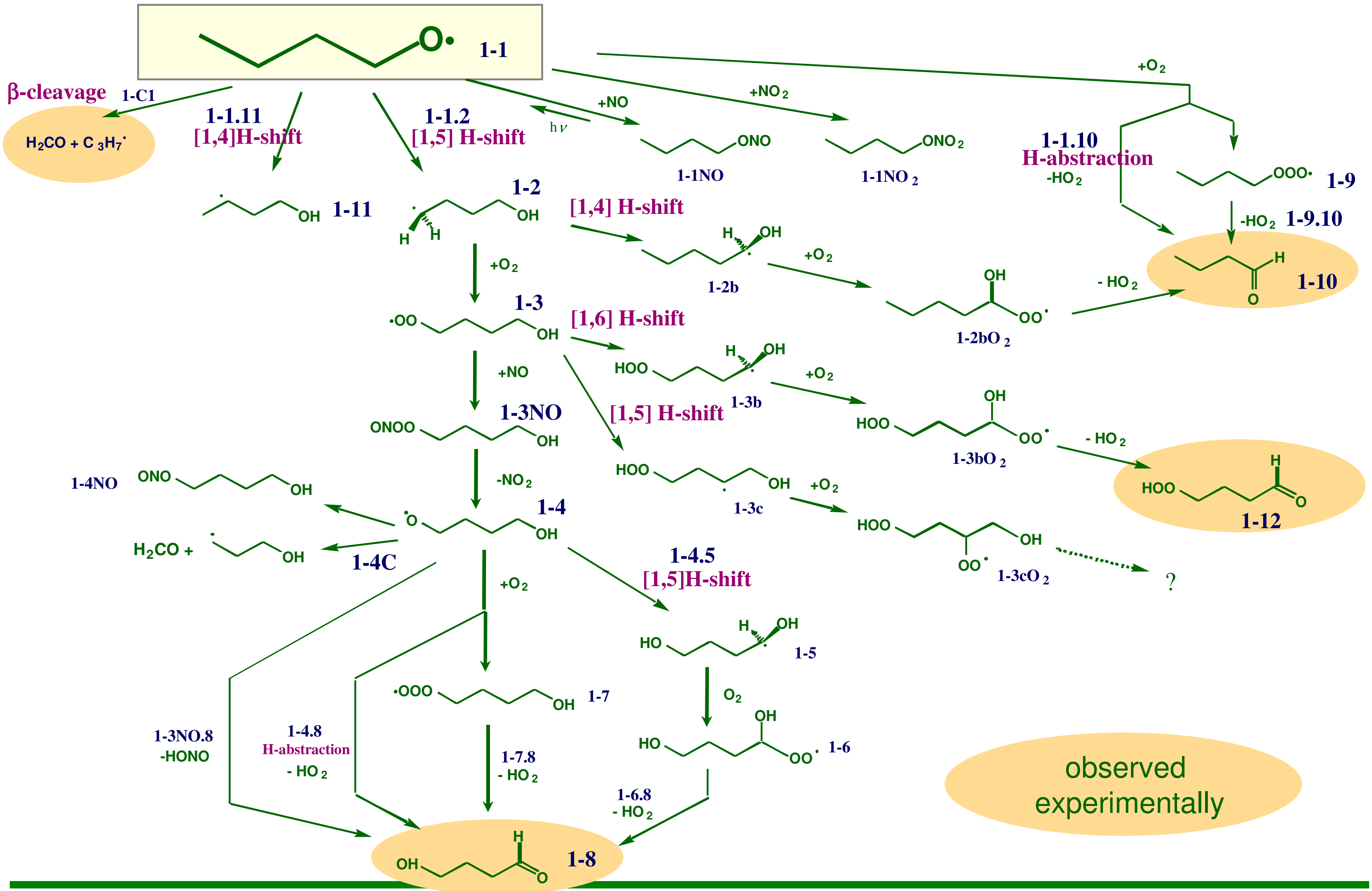
Chemistry of Urban Air Pollution

Key Steps in Atmospheric Hydrocarbon Oxidation



Chemistry of Urban Air Pollution

Butane Oxidation (even simple molecules have complicated chemistry!)



Chemistry of Urban Air Pollution

Formation of peroxyacetyl nitrates (PAN) from oxidation of acetaldehyde

⇨ Ozone has received much attention as a urban pollutant, yet there are many other compounds that, though present at trace levels, can have a profound effect on human health and welfare. Carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAHs), a common constituent in diesel exhaust is one such example. PAN is another.

⇨ The peroxyacetyl nitrates (PAN) are formed by reaction of aldehydes with OH, followed by reaction with NO_2:

$$CH_3CHO + \bullet OH \longrightarrow CH_3CO\bullet + H_2O$$

$$CH_3CO\bullet + O_2 \longrightarrow CH_3C(O)OO\bullet$$

$$CH_3C(O)OO\bullet + NO_2 \longrightarrow CH_3C(O)O_2NO_2\bullet \qquad \text{PAN!}$$

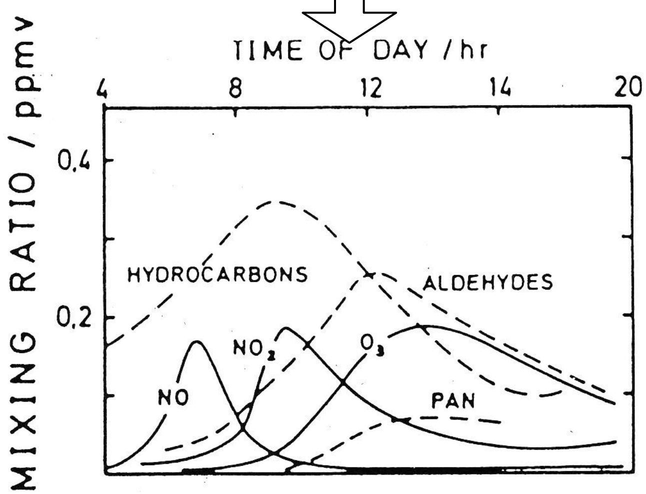
⇨ PAN and related compounds are important eye irritants

⇨ Since the last reaction is reversible, they are important reservoirs of NO_2.

Dynamics of pollutant formation

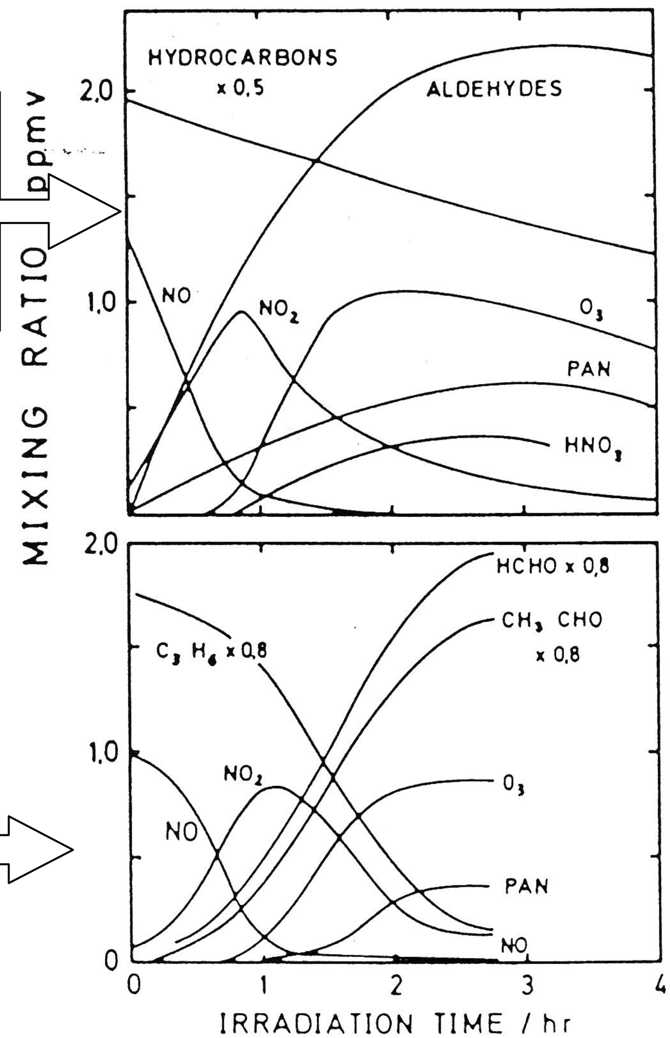
- The oxidation of volatile organic compounds (VOCs) causes ozone to peak late in the day

Downtown LA



Irradiation of car exhaust in smog chamber

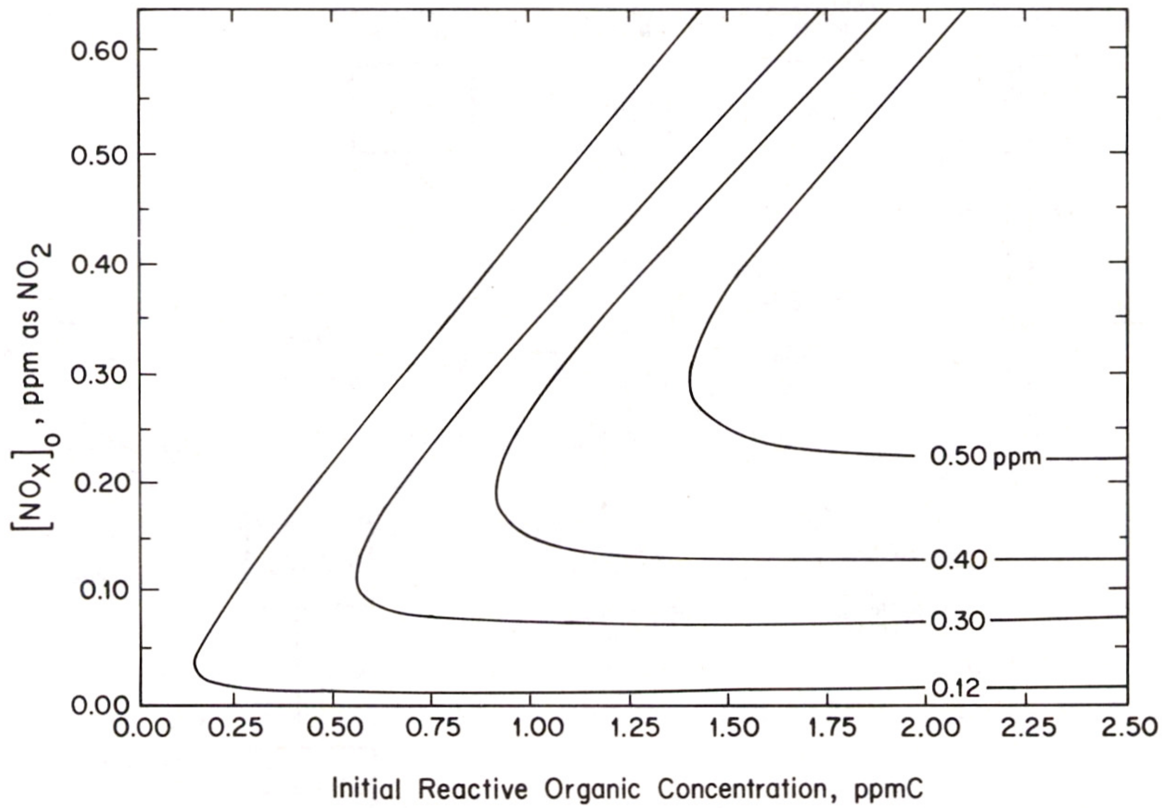
Irradiation of Propene, NO and air in smog chamber



Urban Air Pollution Chemistry

Why is ozone sometimes worse on the weekend?

- At low [Organic]/[NOx] ratios (1-2), there are not organics around to generate radicals needed to convert NO to NO2
- At high [Organic]/[NOx] ratios (>20), ozone cannot accumulate because:
  - it is consumed by reaction with alkenes
  - NO2 is removed by reactions with free radicals produced by organics
  - radical-radical reactions competes with NO-NO2 conversion.

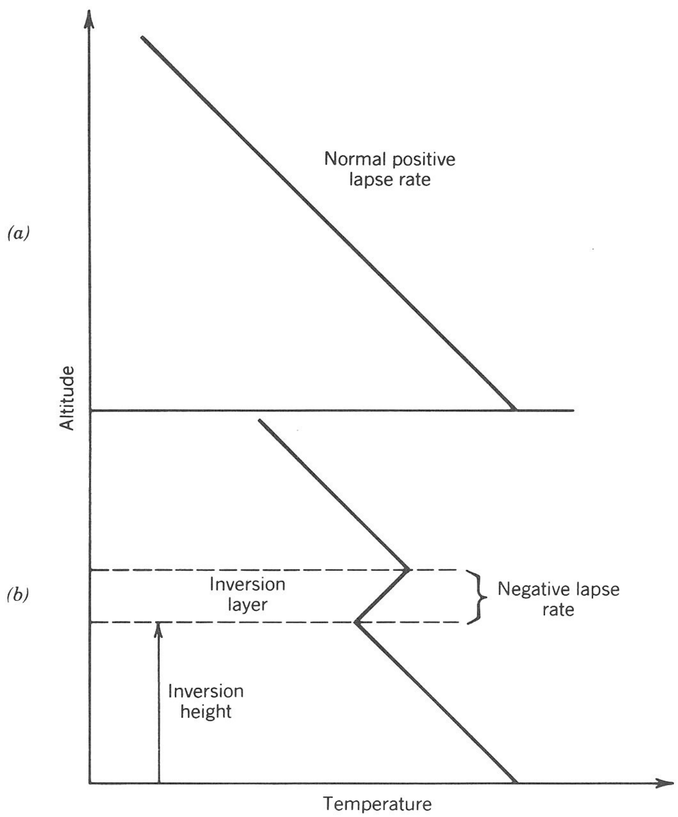


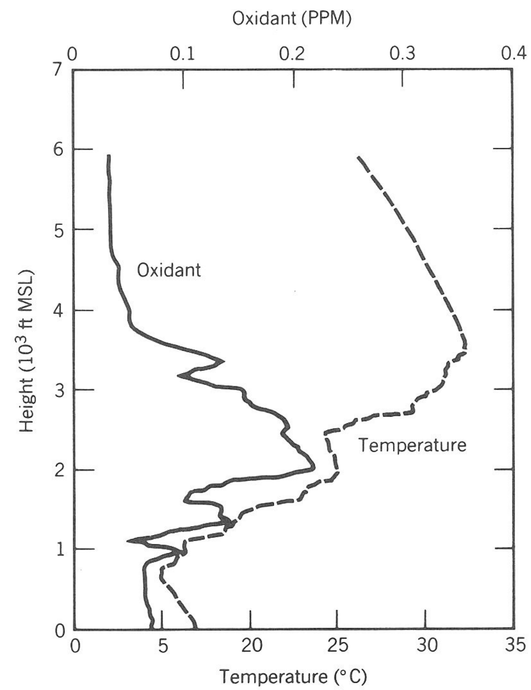
So there is an ozone maximum!

On weekends the primary NOx source (cars) is reduced so ozone may go up as a result!

Smog Meterology: Why is ozone worse in Los Angeles?

- The worst urban pollution incidents are associated with aggravating meteorological conditions, especially fogs and temperature inversions.
- A common way for an inversion to form is by cooling of the surface layer at night. This cool layer is trapped under warmer air during the day.





Biomass burning in Southern Africa

In this animation, multiple fires are burning across the southern part of the African continent in September 2000. The fires were observed by the AVHRR instrument. The fires generated large amounts of aerosols (the dark haze), which were observed with the TOMS instrument.

View this movie at:

http://visibleearth.nasa.gov/cgi-bin/viewrecord?6472

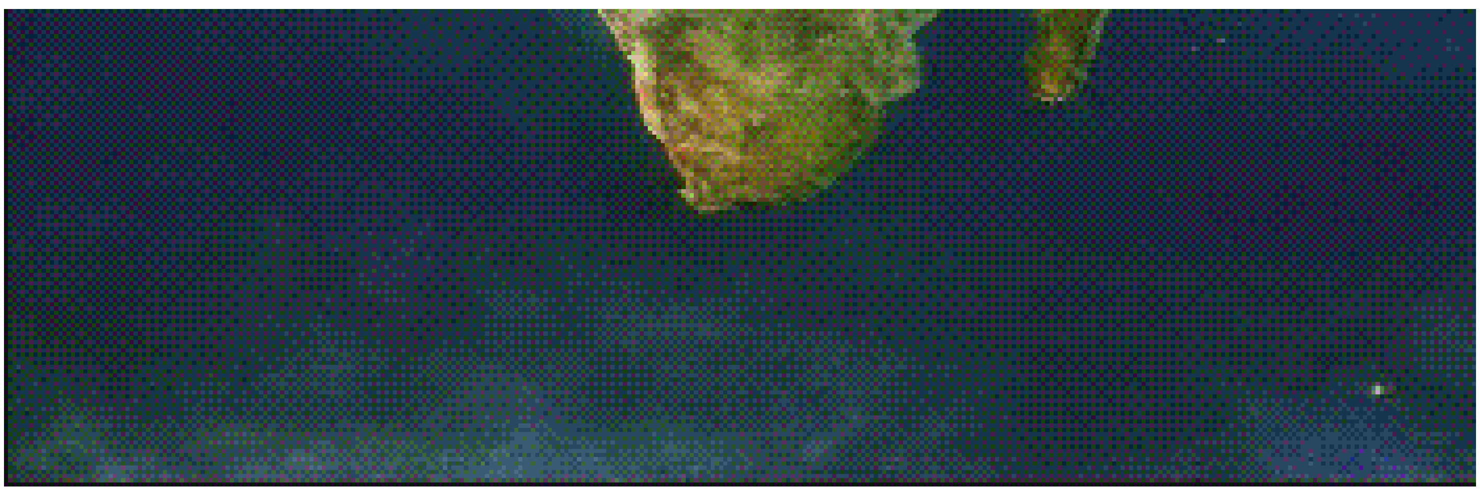
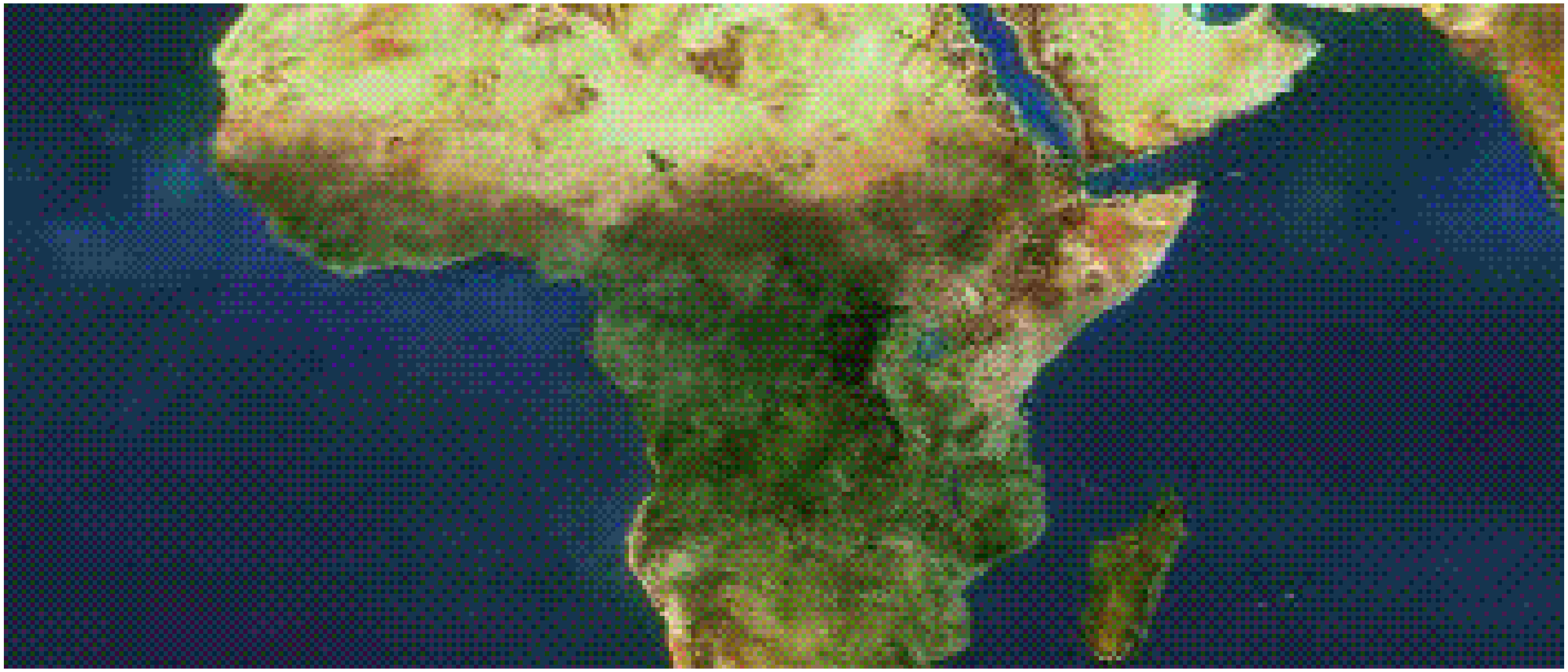


Image courtesy of NASA Goddard Space Flight Center, Science Visualization Studio

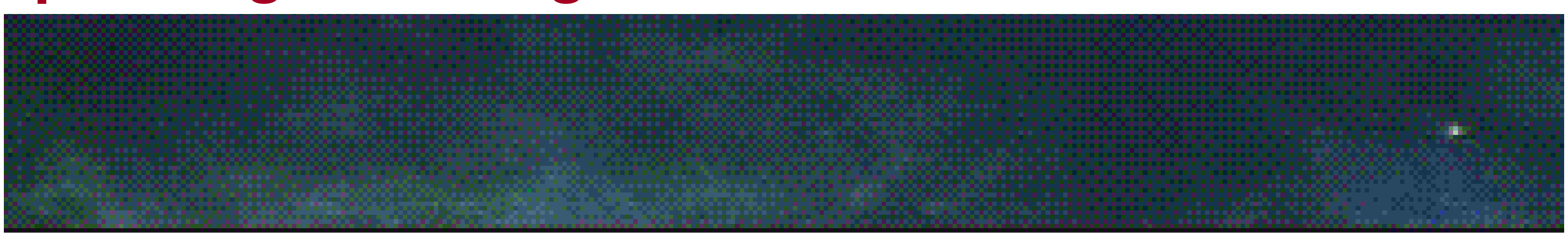
Ozone formation from biomass burning

Tropospheric Ozone over Southern Africa from 9/5/2000 to 9/25/2000 as measured by TOMS



View this movie at:

http://svs.gsfc.nasa.gov/vis/a000000/a002000/a002018/



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