# Fundamentals of Atmospheric Gas-Phase Chemistry

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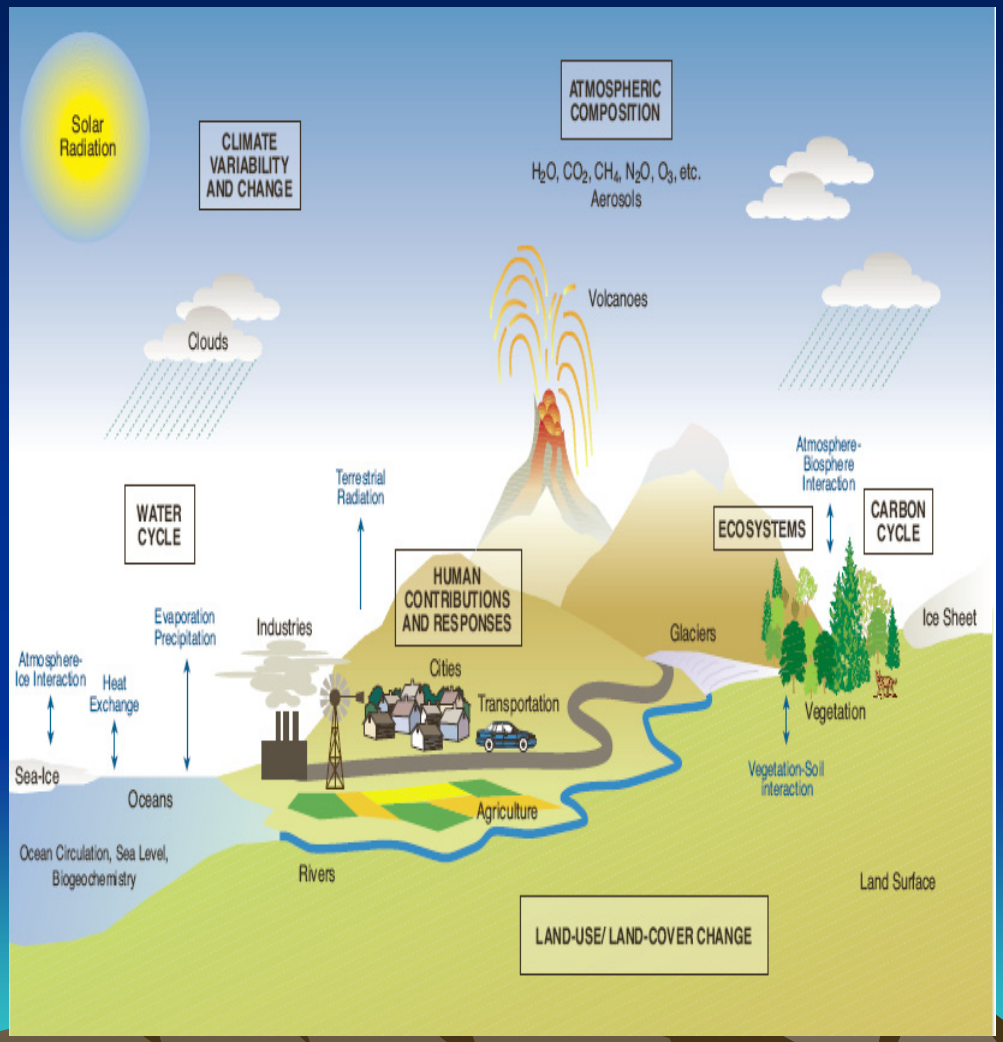
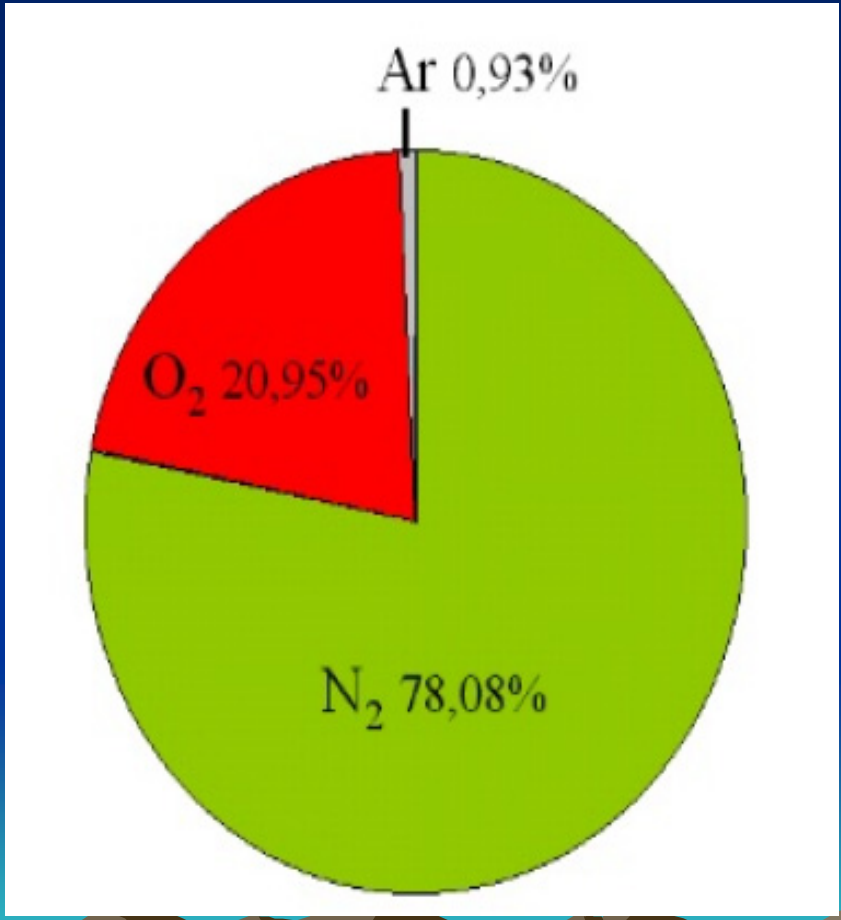
# Atmospheric chemistry and global change




- Many of the global environmental changes forced by human activities are mediated through the chemistry of the atmosphere:
  - Degradation of air quality: Global pollution resulting from industrial combustion and biomass burning
  - Increase in the abundance of tropospheric oxidants including ozone and related impacts on the biosphere and human health
  - Changes in the self-cleaning capability of the atmosphere and in the residence time of anthropogenic trace gases
  - Climatic and environmental impact of changes in land use including deforestation, wetland destruction, etc.
  - Perturbations of biogeochemical cycles of carbon, nitrogen, phosphorus, and sulfur
  - Acidic precipitation
  - Climatic changes (global warming) resulting from increasing emissions of CO2 and other greenhouse gases
  - Climatic impacts (regional cooling) of sulfate aerosols resulting from anthropogenic SO2 emissions
  - Depletion of stratospheric ozone, related increase in the level of UV-B solar radiation at the surface, and impacts on the biosphere and human health

# Trace Gases

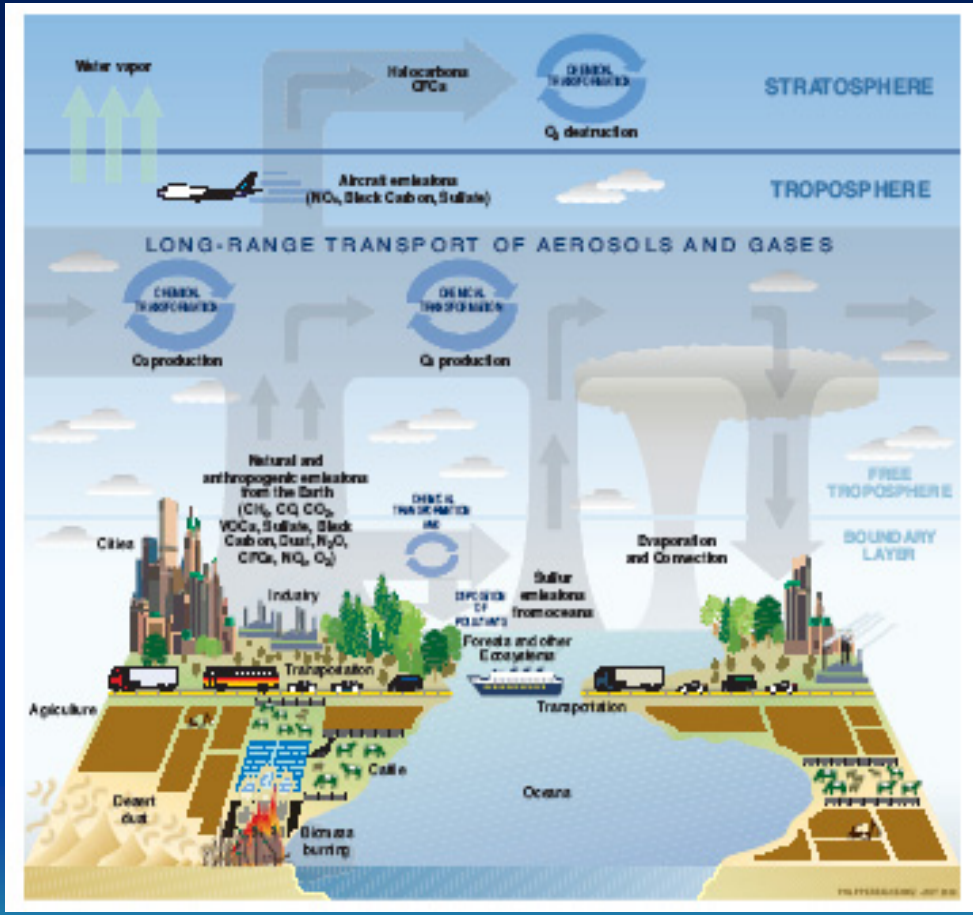



- There are thousands of gases in the troposphere.
- Some of the gases are evenly spread all over the world, whereas the concentrations of others depends strongly on sources, local conditions and on the time of day.
- A gas in the atmosphere can be:
- a) a major component of the air (oxygen, nitrogen, argon)
  b) a major trace gas (carbon dioxide, methane, ozone, nitrogen dioxide)
  c) a minor trace gas (organic gases such as butane, ethanol, CFCs)
- Trace gases are gases which make up only a tiny fraction of the air. Levels of these trace gases can be as low as one molecule in one billion or even one trillion air molecules.

# What is Atmospheric Chemistry

Atmospheric chemists are interested in understanding the chemical composition of the natural atmosphere, the way gases, liquids, and solids in the atmosphere interact with each other and with the earth's surface and associated biota, and how human activities may be changing the chemical and physical characteristics of the atmosphere. There are a number of critical environmental issues associated with a changing atmosphere, including photochemical smog, global climate change, toxic air pollutants, acidic deposition, and stratospheric ozone depletion. A great deal of research and development activity is aimed at understanding and hopefully solving some of these problems is underway. Much of the anthropogenic (human) impact on the atmosphere is associated with our increasing use of fossil fuels as an energy source - for things such as heating, transportation, and electric power production. Photochemical smog/tropospheric ozone is one serious environmental problem associated with burning fossil fuels.

# Toxic Air Pollutants

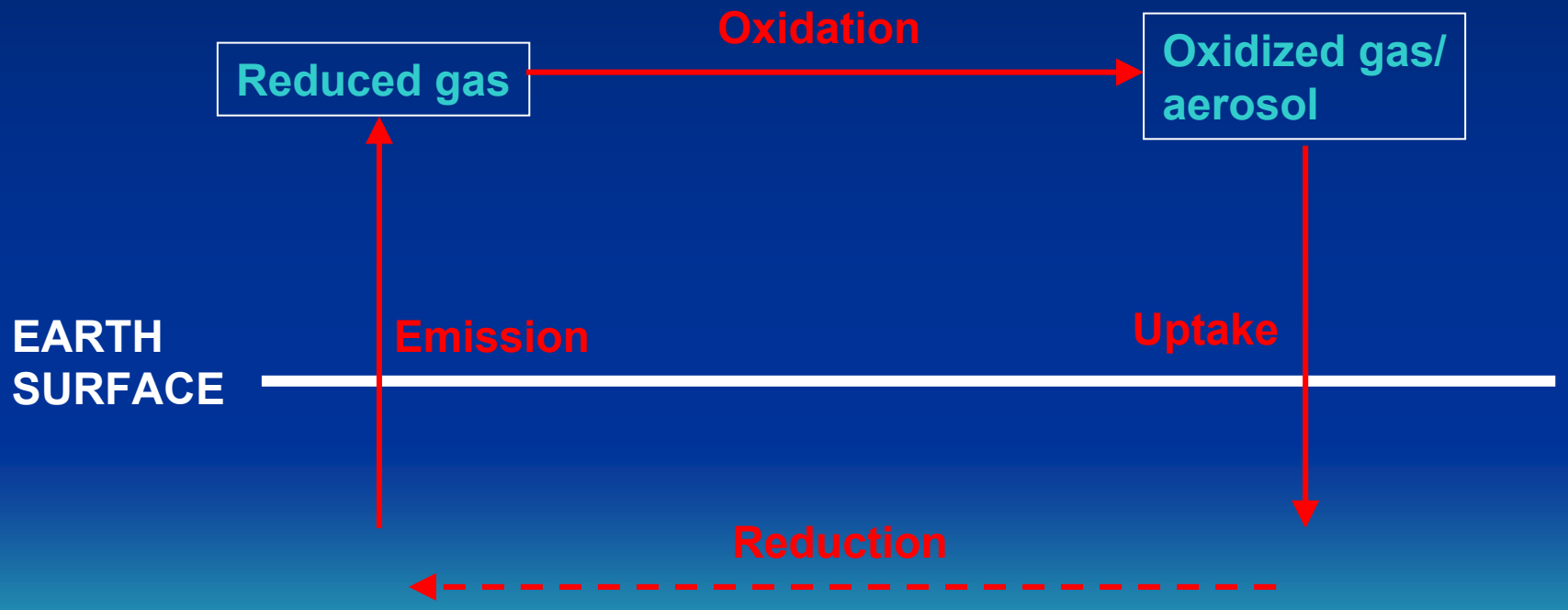



- As a result of a variety of human activities (e.g., agriculture, transportation, industrial processes) a large number of different toxic pollutants are emitted into the atmosphere. Among the chemicals that may pose a human health risk are pesticides, PCBs, polycyclic aromatic hydrocarbons (PAHs), dioxins, and volatile organic compounds (e.g., benzene, carbon tetrachloride). Many of the more environmentally persistent compounds (e.g., PCBs) have been measured in Arctic wildlife and, for example, in tissues of the local Innuit population. Because of the enormous variety of toxic pollutants present in the air that we breathe, it is an enormously challenging task to determine the human health risks from exposure to this mixture. Scientists are needed in this field to measure the atmospheric concentrations of these species, to identify and quantify the sources of these pollutants, and to determine their environmental fate.

# OXIDIZING MEDIUM IN GLOBAL BIOGEOCHEMICAL CYCLES

**Atmospheric oxidation is critical for removal of many pollutants, e.g.**

- **methane (major greenhouse gas)**
- **CO (toxic pollutant)**
- **HCFCs ($Cl_x$ sources in stratosphere)**

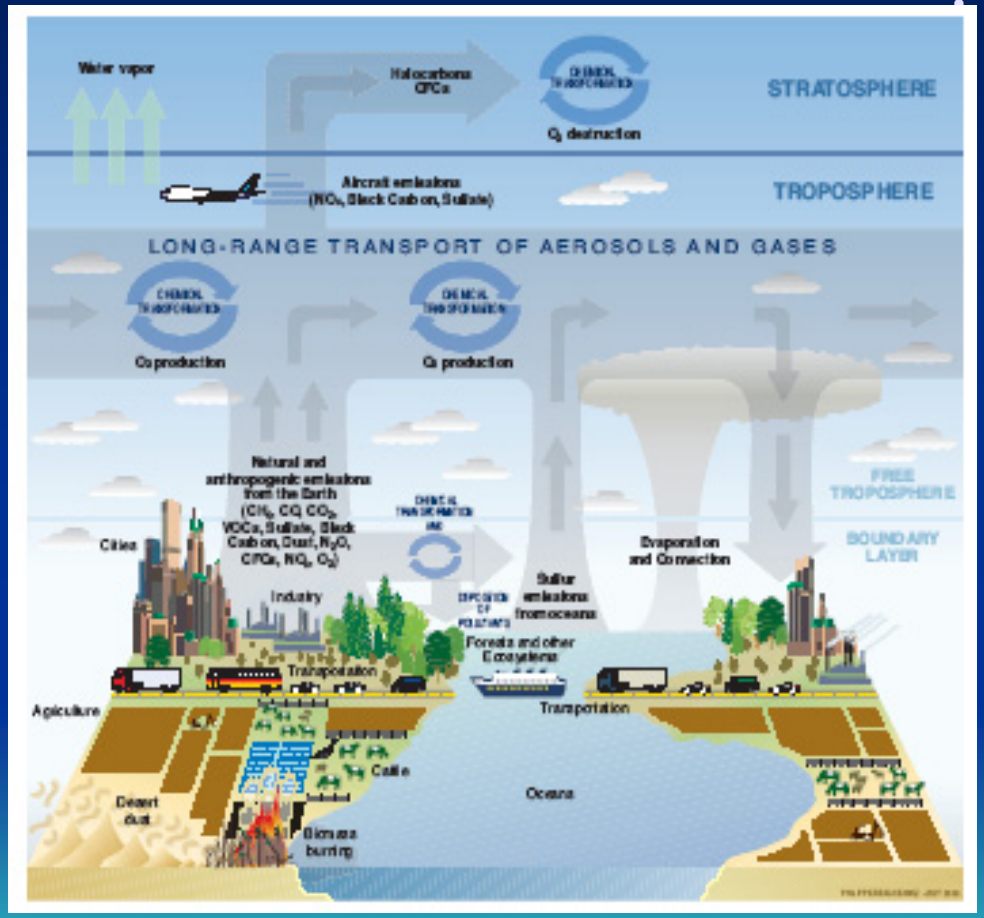


# Acidic Deposition

**Acidified forest near Most, Czechoslovakia (1987)**

- When fossil fuels, and particularly coal, are burned, the sulfur in the fuel is emitted into the atmosphere as sulfur dioxide (SO2). In the atmosphere this SO2 can be oxidized to sulfuric acid (H2SO4) which exists as an aerosol, i.e., in small droplets. This sulfuric acid aerosol ultimately falls back to the surface, with a variety of environmental consequences. At sufficiently high concentrations these aerosols can cause severe respiratory problems in humans. However, most of the sulfur falls in unpopulated regions where it can cause damage to vegetation, and can release metals from the soil into lakes and streams where these metals can be toxic to fish. Acidic pollutants in rainwater also cause substantial damage to building materials. As a result of deposition of acidic pollutants, thousands of lakes have suffered serious losses of aquatic life. Atmospheric chemists are needed to study the chemical processes responsible for SO2 oxidation and the environmental and human health impacts of the acidic aerosols that are produced.

# Global Warming

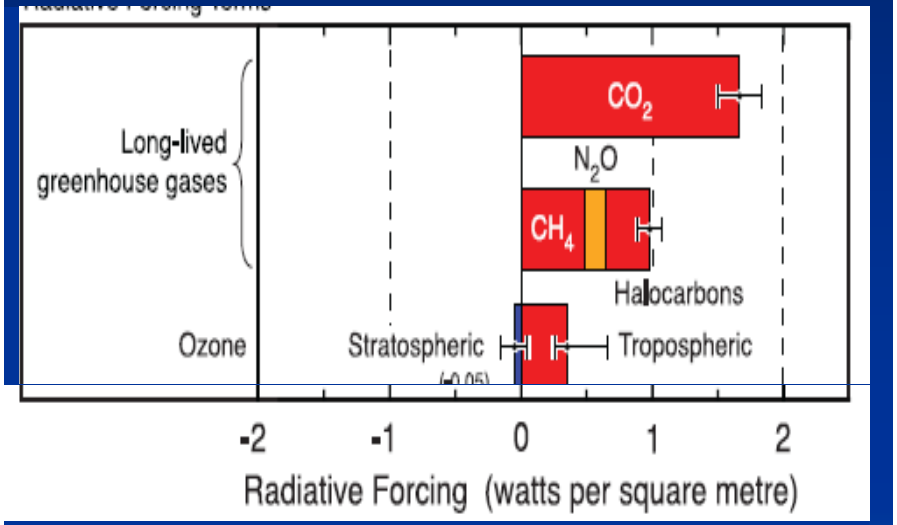



Fossil fuels are composed mostly of carbon. When they are burned this carbon is released into the atmosphere, mainly in the form of carbon dioxide, CO2. We currently emit roughly 5 billion tonnes of carbon into the atmosphere each year. As a result, there has been a steady increase in global atmospheric levels of CO2. This increase in CO2 (along with other gases including methane, ozone, and CFCs) presents a problem, because these gases are "greenhouse" gases, that is they absorb infrared radiation (i.e., "heat") that is radiated out from the earth. Thus, heat that would otherwise be lost to space is trapped in the atmosphere, leading to increased temperatures. Climatologists have predicted that, as a result of increasing concentrations of greenhouse gases in the atmosphere, the earth's temperature will increase by about 3 C by the year 2030. This will result in significant changes in local climate, in some areas leading to loss of arable land, and an increase in sea level with associated coastal flooding. In addition, global warming may exacerbate the photochemical smog problem. Hundreds of atmospheric scientists are employed worldwide to study the magnitude and implications of this problem, and potential solutions.

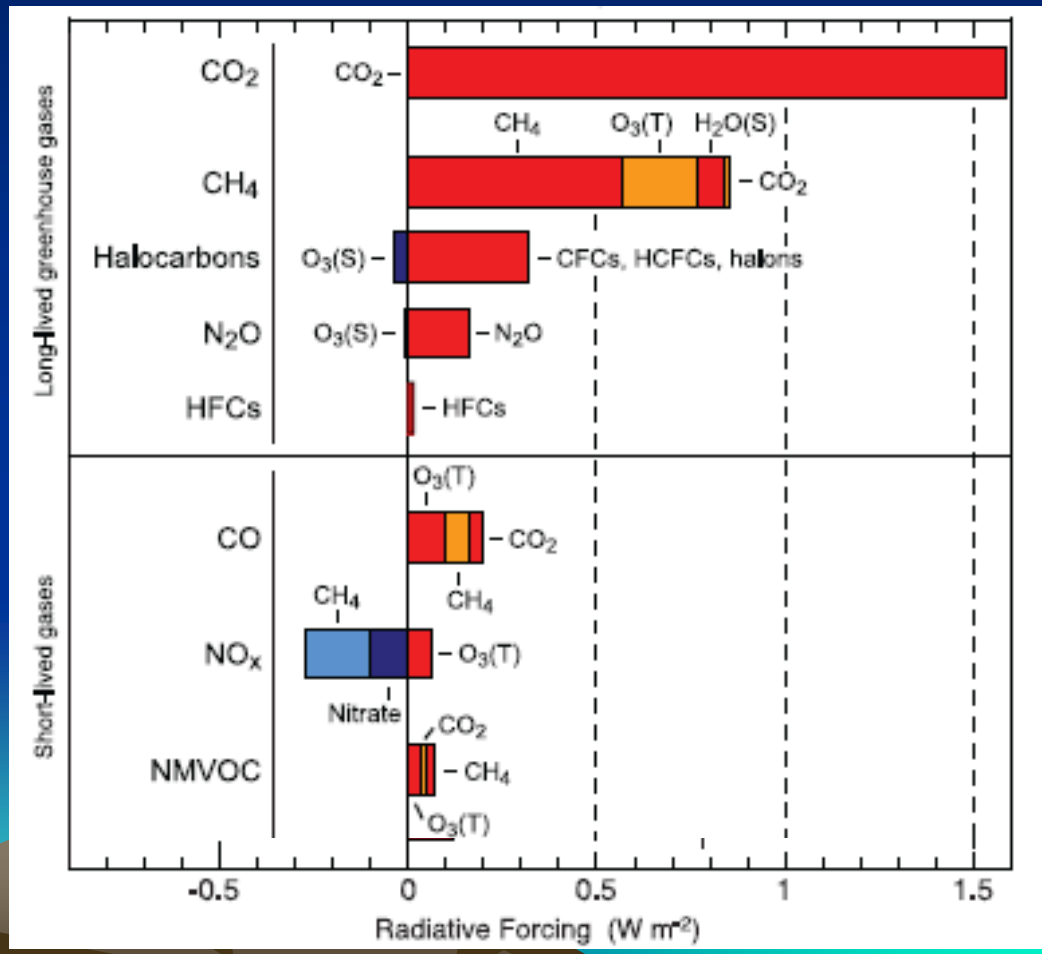
# CHEMICAL GREENHOUSE GASES

**Greenhouse radiative forcing of climate between 1750 and 2005 [IPCC, 2007]**

**Referenced to concentration**



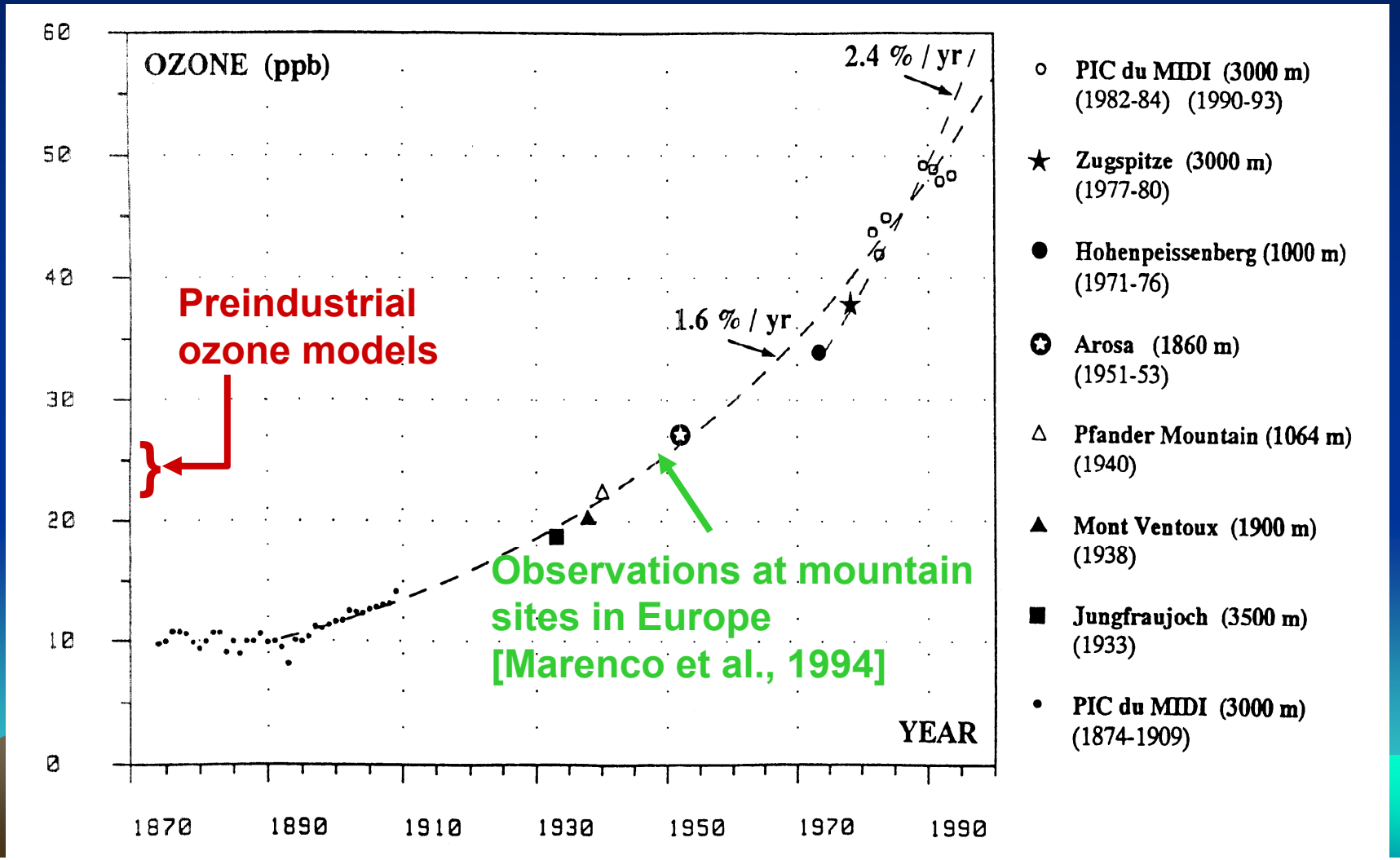

**Referenced to emission**



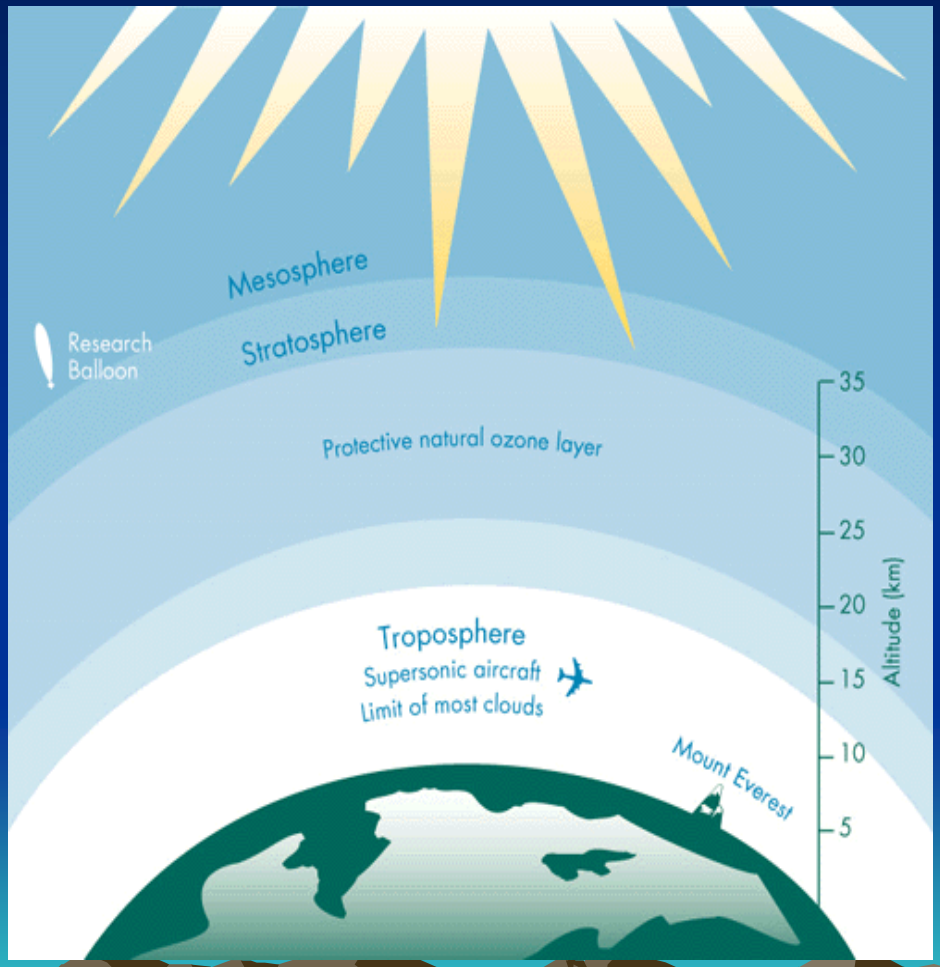
# IPCC RADIATIVE FORCING ESTIMATE FOR TROPOSPHERIC OZONE (0.35 W $m^{-2}$)

**…but these underestimate the observed rise in ozone over the 20th century**

**Fitting to observations would imply a radiative forcing of 0.8 W $m^{-2}$**



# Stratospheric Ozone Depletion

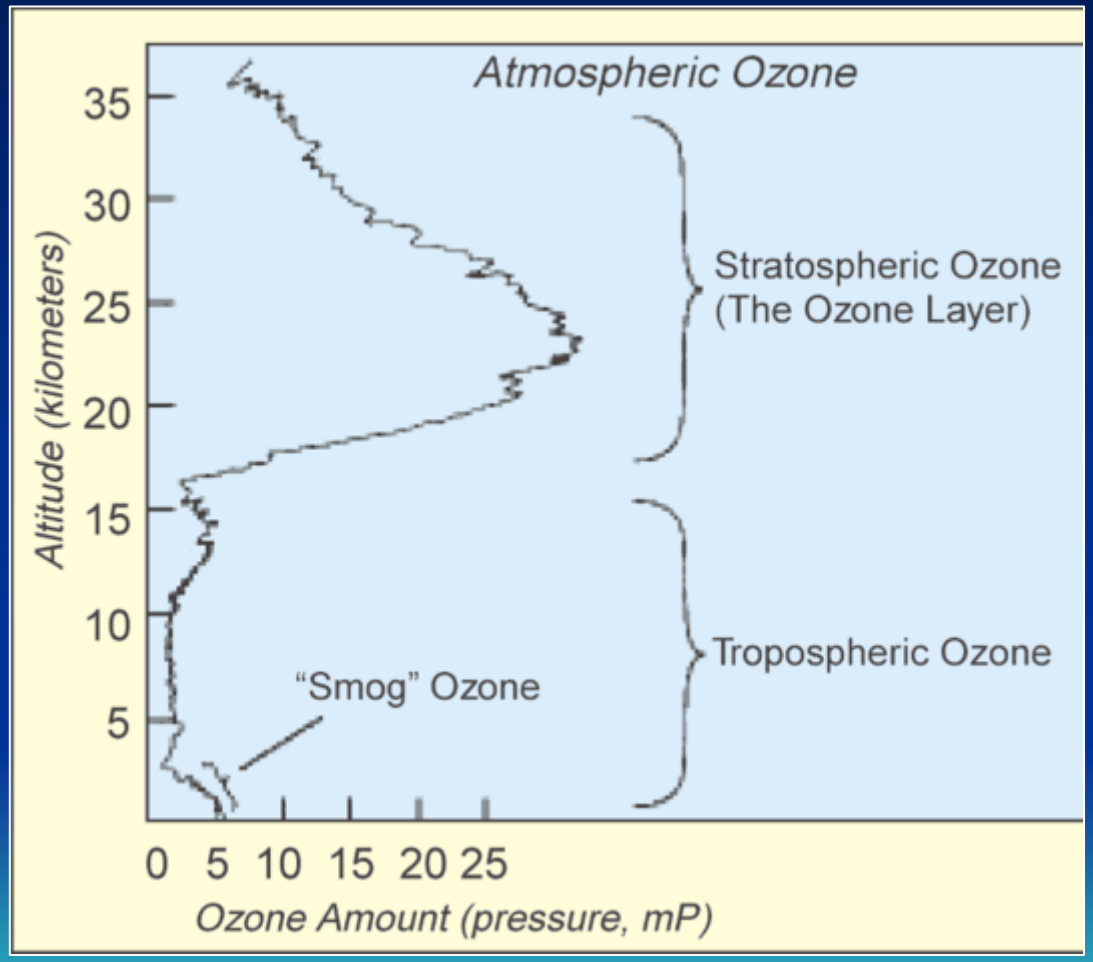



- The "ozone layer" is a region of relatively high ozone concentration (at about 25 km altitude) in the stratosphere, which is a layer of the atmosphere between 15 and 50 km. The ozone is produced from interactions between the energetic ultra violet (UV) light reaching the stratosphere and molecular oxygen. The presence of the ozone layer in the stratosphere is vital to life at the surface since the ozone layer absorbs UV light that would otherwise reach the surface and cause damage to both animal and plant life. However, the ozone layer is becoming chemically perturbed due to the presence of chlorofluorocarbons (CFCs) in the stratosphere. CFCs are used in air conditioners and as cleaning and blowing agents in the chemical industry. These compounds are chemically inert, and they ultimately diffuse upward to the stratosphere. In the stratosphere, because of the presence of the higher energy UV light, these compounds can absorb the light and decompose to produce chlorine atoms which then participate in a chain reaction in which ozone in the ozone layer is destroyed. In 1985 an "ozone hole" was discovered over Antarctica which appears every year in October. The amount of ozone in the stratosphere over Antarctica has decreased to only half the natural level. This large decrease is localized over Antarctica due to the very cold temperatures, but there appears to have been a global decrease in the "natural" abundance of stratospheric ozone of 3-5%. This problem of stratospheric ozone depletion is a very complex and challenging problem, that will likely have a significant impact on human activities for decades to come. Atmospheric chemists are needed to study the processes that occur in the stratosphere, and to study the atmospheric impact of the candidate replacement compounds (e.g., HCFCs).

# Photochemical Smog/Tropospheric Ozone

- When fossil fuels (e.g., gasoline) are burned, a variety of pollutants are emitted into the earth's troposphere, i.e., the region of the atmosphere in which we live - from ground level up to about 15 km. Two of the pollutants that are emitted are hydrocarbons (e.g., unburned fuel) and nitric oxide (NO). When these pollutants build up to sufficiently high levels, a chain reaction occurs from their interaction with sunlight in which the NO is converted to nitrogen dioxide ($NO_2$). $NO_2$ is a brown gas and at sufficiently high levels can contribute to urban haze. However, a more serious problem is that $NO_2$ can absorb sunlight and break apart to produce oxygen atoms that combine with the $O_2$ in the air to produce ozone ($O_3$). Ozone is a powerful oxidizing agent, and a toxic gas. In North America elevated levels of tropospheric ozone cause several billion dollars per year damage to crops, structures, forests, and human health. It is believed that the natural level of ozone in the clean troposphere is 10 to 15 parts-per-billion (ppb). Because of increasing concentrations of hydrocarbons and NO in the atmosphere, scientists have found that ozone levels in "clean air" are now approximately 30 ppb. A principal activity of atmospheric chemists is to study and determine how we might reverse this trend.

# GOOD AND BAD OZONE




**Stratosphere:**

$O_2$ + UV sunlight = O + O

O + $O_2$ → $O_3$

**Troposphere:**

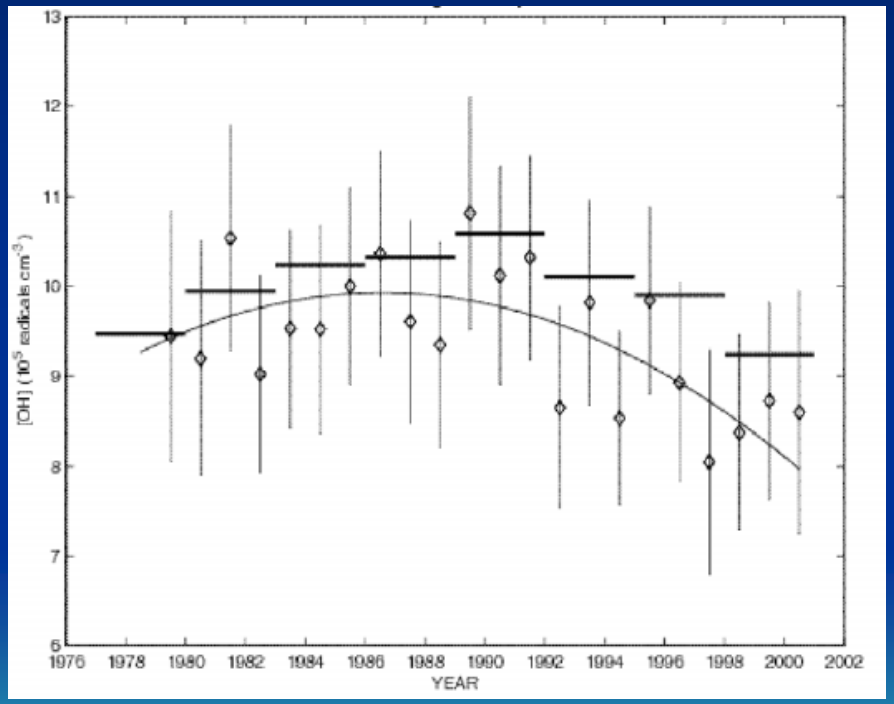
CO, VOCs + NOx + sunlight → $O_3$

# THE TROPOSPHERE WAS VIEWED AS CHEMICALLY INERT UNTIL 1970

- "*The chemistry of the troposphere is mainly that of of a large number of atmospheric constituents and of their reactions with molecular oxygen…Methane and CO are chemically quite inert in the troposphere*" [Cadle and Allen, Atmospheric Photochemistry, 1970]
- Lifetime of CO estimated at 2.7 years (removal by soil) leads to concern about global CO pollution from increasing car emissions [Robbins and Robbins, Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants, *SRI report*, 1967]
- Oxidation in the troposphere is of key importance because the troposphere contains the bulk of atmospheric mass (85%) and because gases are generally emitted at the surface.
- The most abundant oxidants in the Earth's atmosphere are O2 and O3. These oxidants have large bond energies and are hence relatively unreactive except toward radicals (O2 only toward highly unstable radicals).
- With a few exceptions, oxidation of non-radical atmospheric species by O2 or O3 is negligibly slow.

# OH Radical is a Strong Oxidant in the Troposphere

OBSERVED TRENDS IN TROPOSPHERIC OH




- OH reacts rapidly with most reduced non-radical species, and is particularly reactive toward H-containing molecules due to H-abstraction reactions converting OH to H2O.
- Its role in stratospheric oxidation is well known
- Tropospheric OH concentrations of the order of $10^6$ molecules $cm^{-3}$, resulting in a tropospheric lifetime for CO of only a few months and allaying concerns that CO could accumulate to toxic levels.

# OH Production in the Atmosphere

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$

$$O(^1D) + M \rightarrow O + M$$

$$O(^1D) + H_2O \rightarrow 2OH$$

- Critical to the generation of OH is the production of O(1D) atoms by *(R1)*.
- Until 1970 it was assumed that production of O(1D) would be negligible in the troposphere because of near-total absorption of UV radiation by the O3 column overhead.
- It was thought that oxidation of species emitted from the Earth's surface, such as CO and CH4, required transport to the stratosphere followed by reaction with OH in the stratosphere

# O(1D) Production in the Atmosphere

$$O_3 + h\nu \rightarrow O(^3P) + O_2, \quad \lambda < 800 \text{ nm}$$

$$O_3 + h\nu \rightarrow O(^1D) + O_2, \quad \lambda < 320 \text{ nm}$$

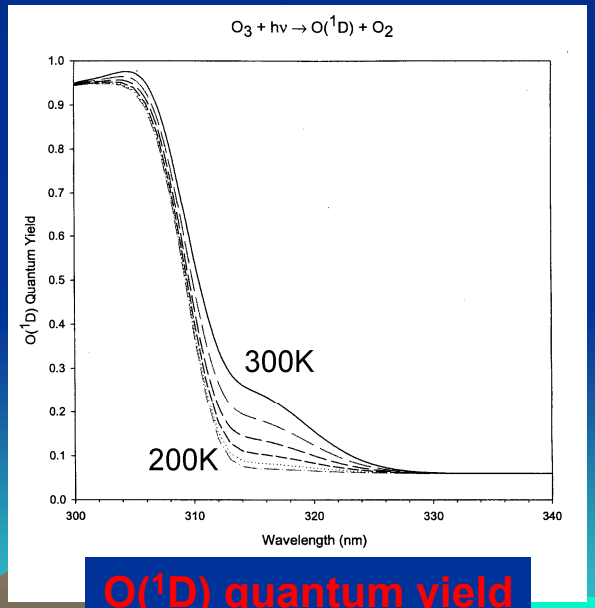
$O(^1D)$ formation is important for the formation of OH, which is the cleansing agent of the atmosphere:

$$O(^1D) + H_2O \rightarrow 2\ OH$$

Only a fraction of the O(1D) radicals react with water vapour, because:

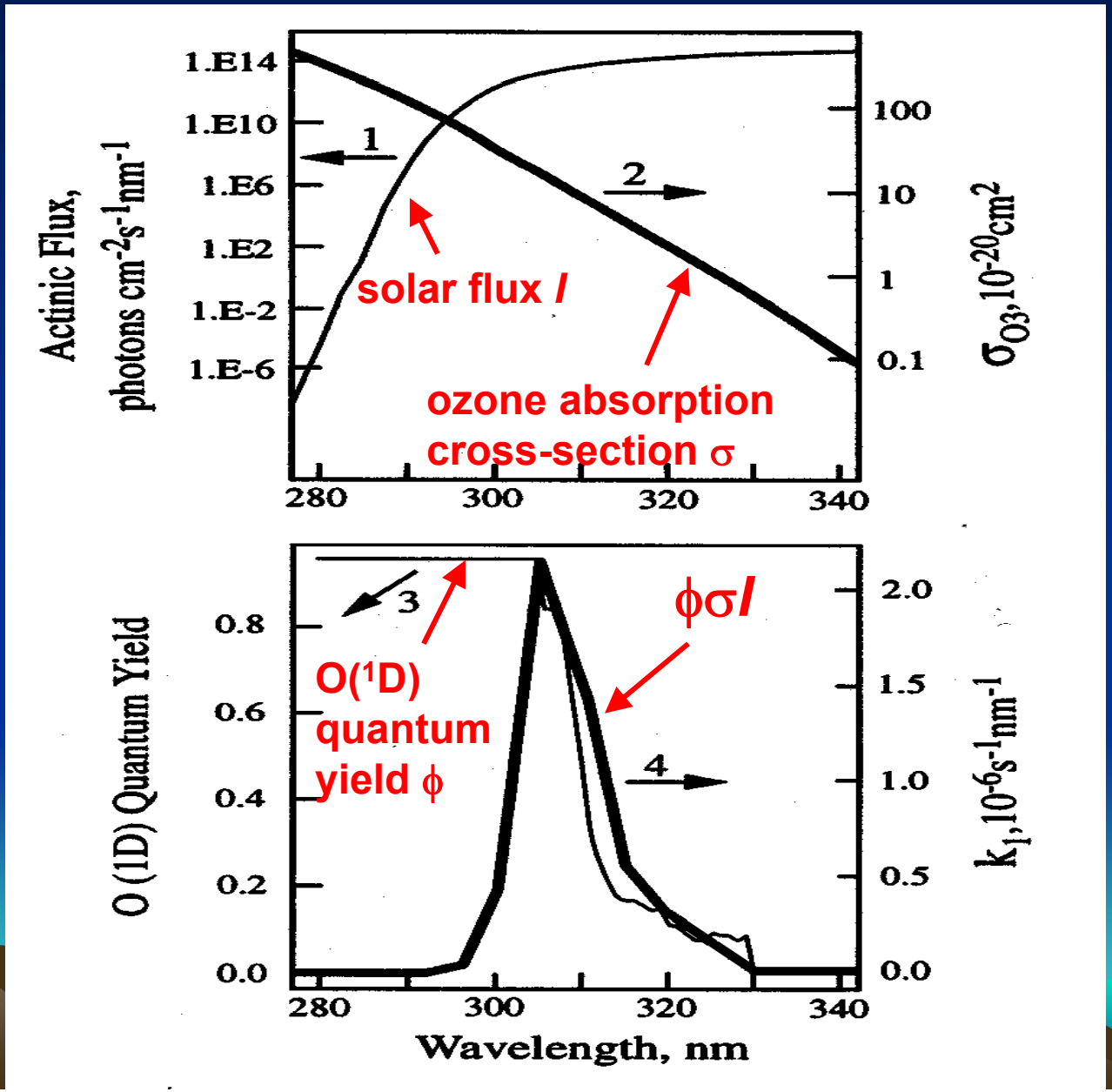
$$O(^1D) + M \rightarrow O(^3P)$$

and $$O(^3P) + O_2 \rightarrow O_3$$




$O(^1D)$ quantum yield

# O(1D) Production in the Troposphere



# OH Tropospheric Sinks

$$CO + OH \rightarrow CO_2 + H$$

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

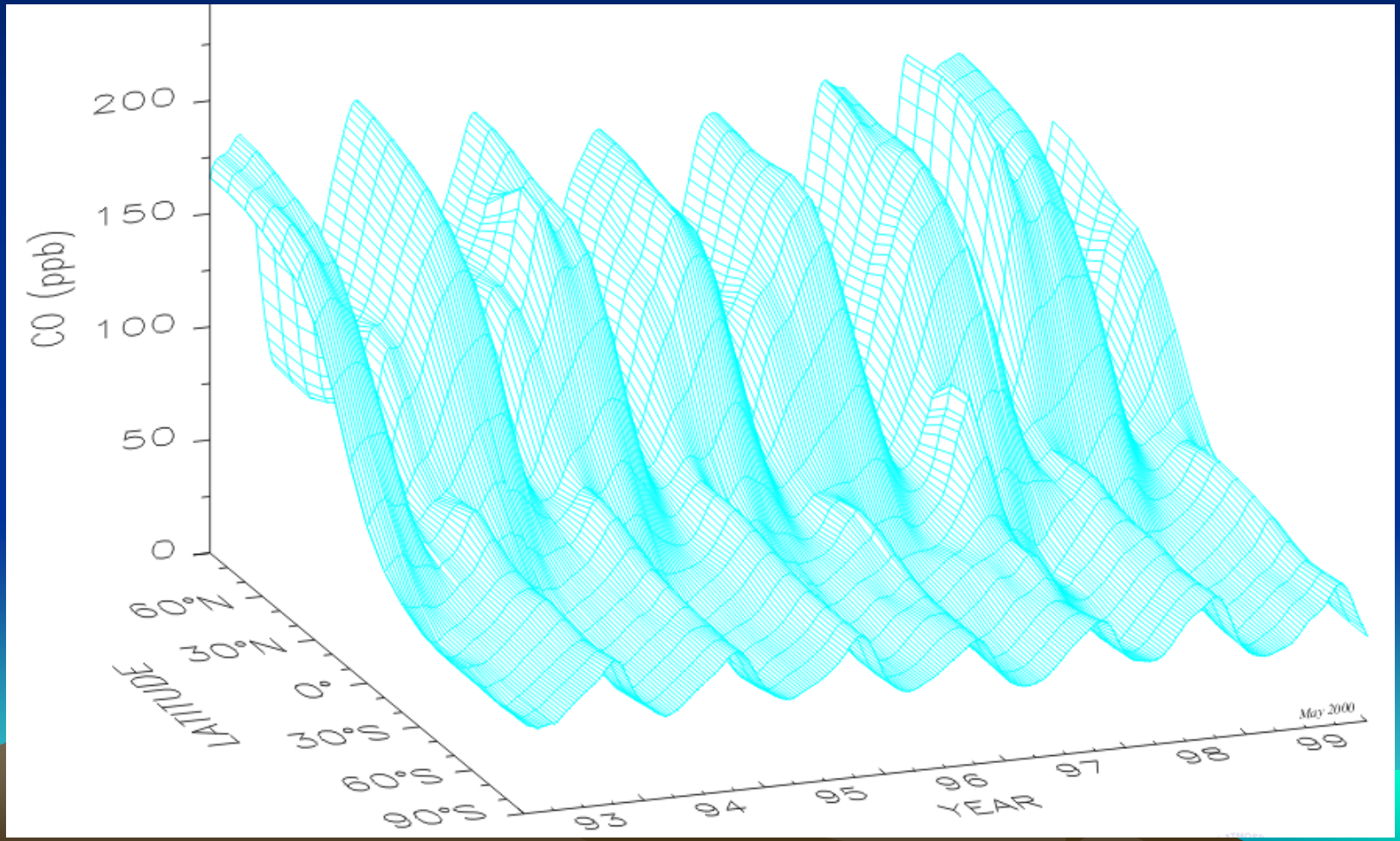
- Carbon monoxide and methane are the principal sinks for OH in most of the troposphere.
- These two gases play therefore a critical role in controlling OH concentrations;
- and more generally in driving radical chemistry in the troposphere.

# CARBON MONOXIDE IN ATMOSPHERE

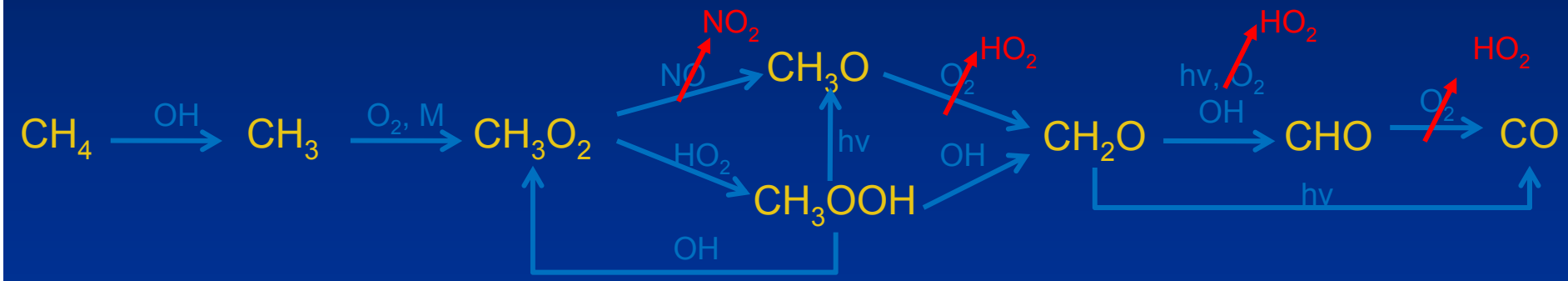
**Source: incomplete combustion**
**Sink: oxidation by OH (lifetime of 2 months)**

| | *Range of estimates (Tg CO yr$^{-1}$)* |
|---|---|
| Sources | 1800–2700 |
| Fossil fuel combustion/industry | 300–550 |
| Biomass burning | 300–700 |
| Vegetation | 60–160 |
| Oceans | 20–200 |
| Oxidation of methane | 400–1000 |
| Oxidation of other hydrocarbons | 200–600 |
| Sinks | 2100–3000 |
| Tropospheric oxidation by OH | 1400–2600 |
| Stratosphere | ~ 100 |
| Soil uptake | 250–640 |

# GLOBAL DISTRIBUTION OF CO
## NOAA/GMD surface air measurements



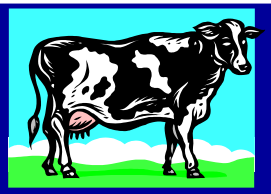
# METHANE OXIDATION SCHEME




**In clean troposphere, ~70% of OH reacts with CO, 30% with $CH_4$**

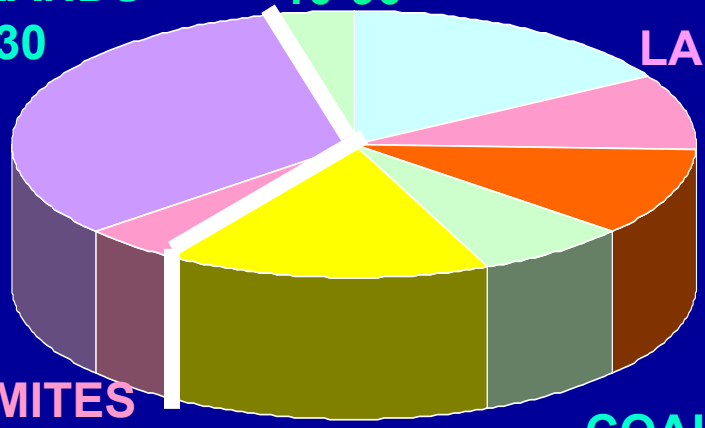
# GLOBAL METHANE SOURCES, Tg $a^{-1}$ [IPCC, 2007]

BIOMASS BURNING 10-90



ANIMALS 80-90

WETLANDS 100-230



LANDFILLS 40-70

GAS 50-70

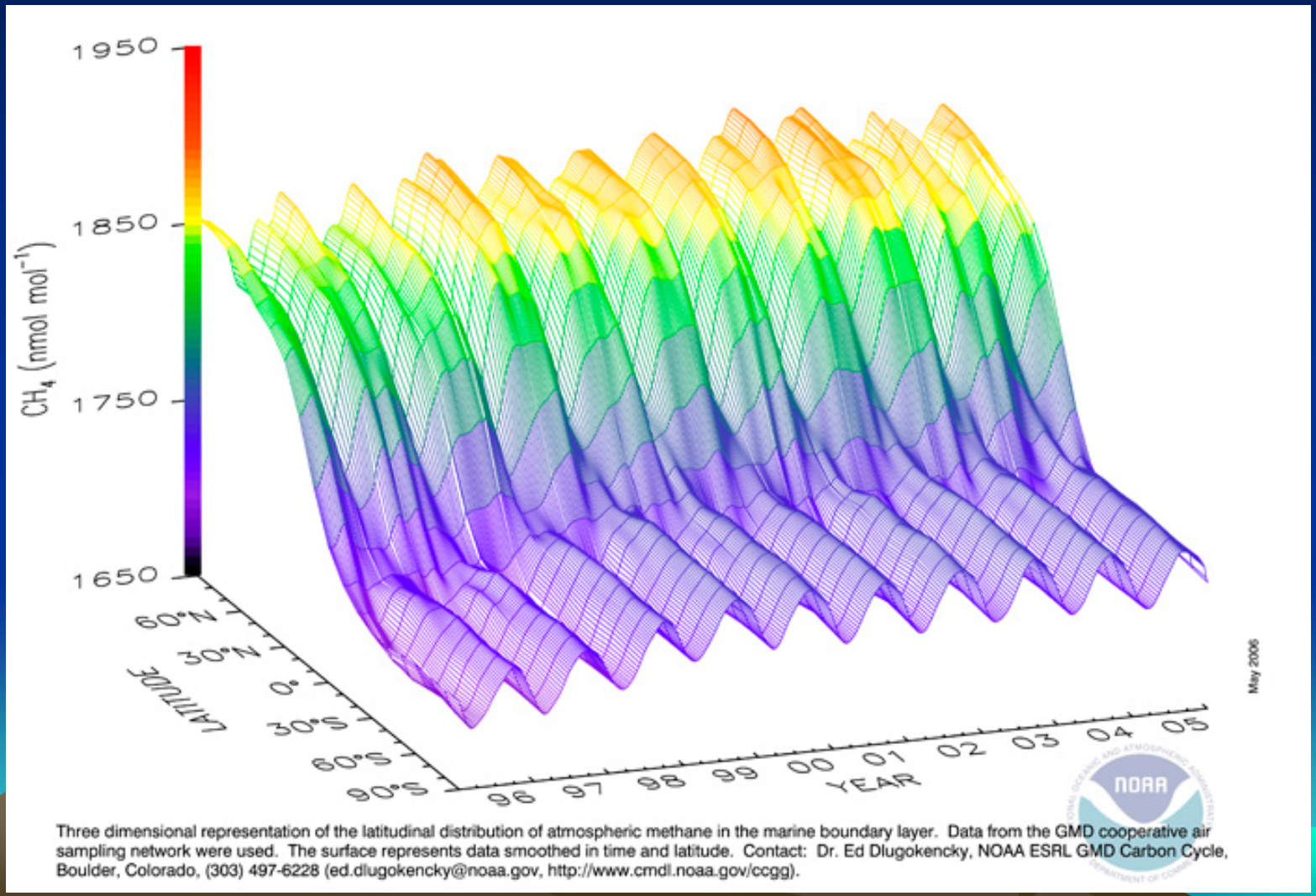
TERMITES 20-30

RICE 30-110

COAL 30-50

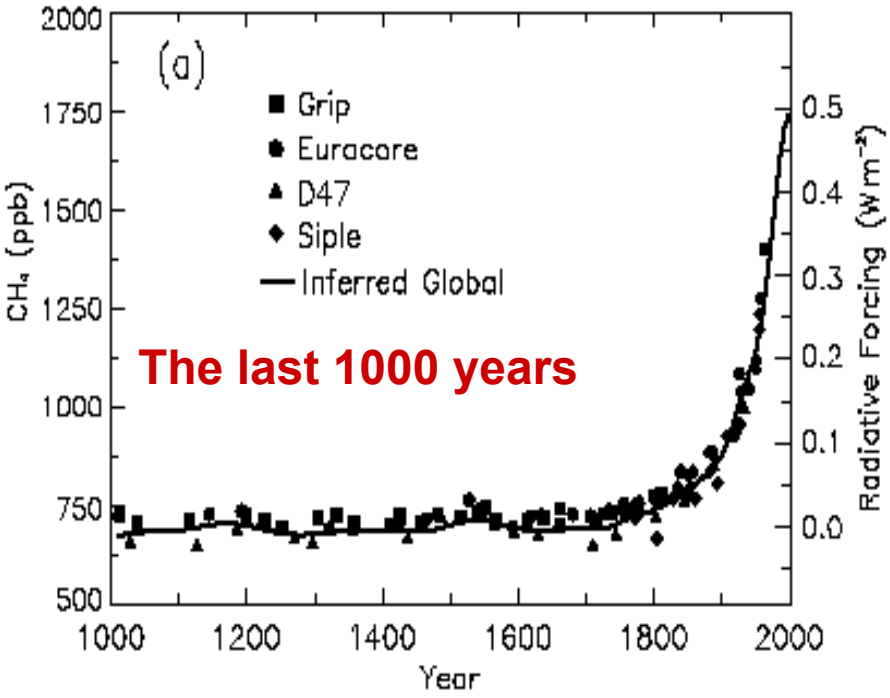
# GLOBAL DISTRIBUTION OF METHANE

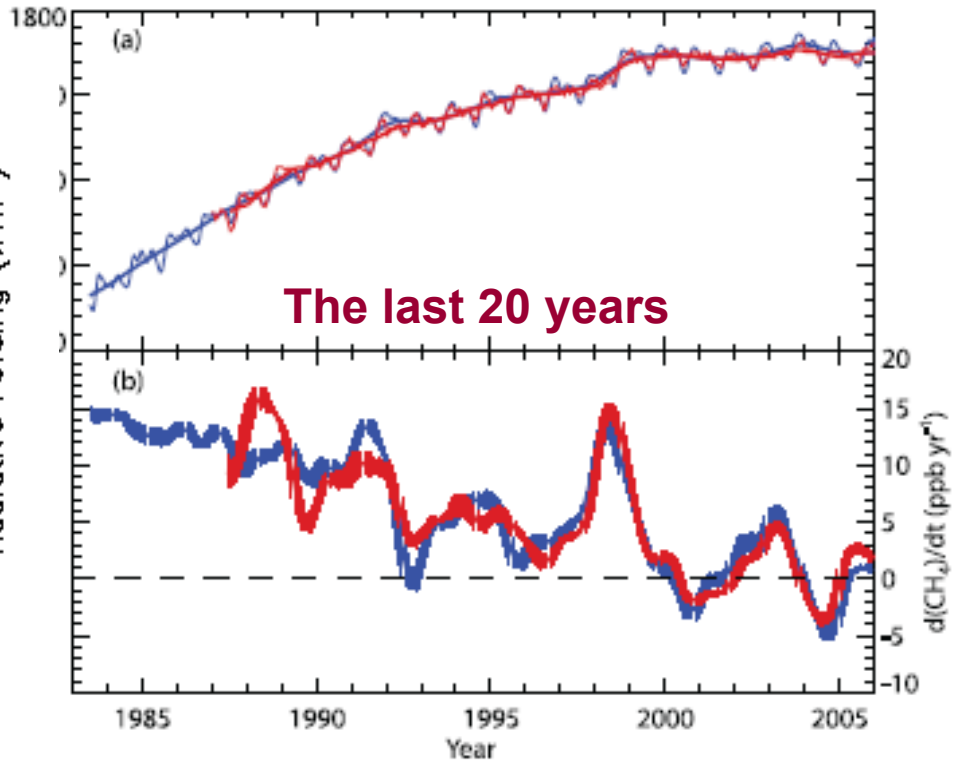
**Sink: oxidation by OH (lifetime of 10 years)**




Three dimensional representation of the latitudinal distribution of atmospheric methane in the marine boundary layer. Data from the GMD cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Contact: Dr. Ed Dlugokencky, NOAA ESRL GMD Carbon Cycle, Boulder, Colorado, (303) 497-6228 (ed.dlugokencky@noaa.gov, http://www.cmdl.noaa.gov/ccgg).

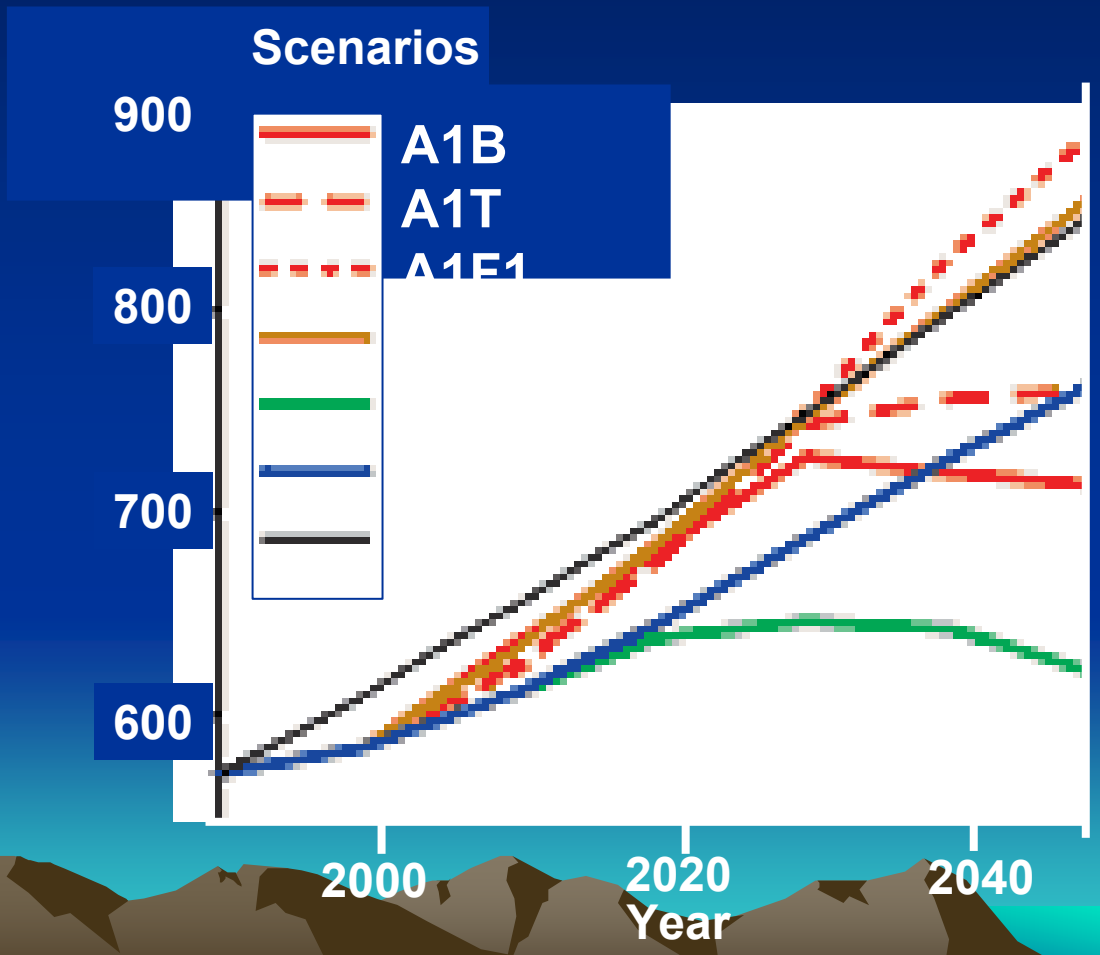
# HISTORICAL TRENDS IN METHANE

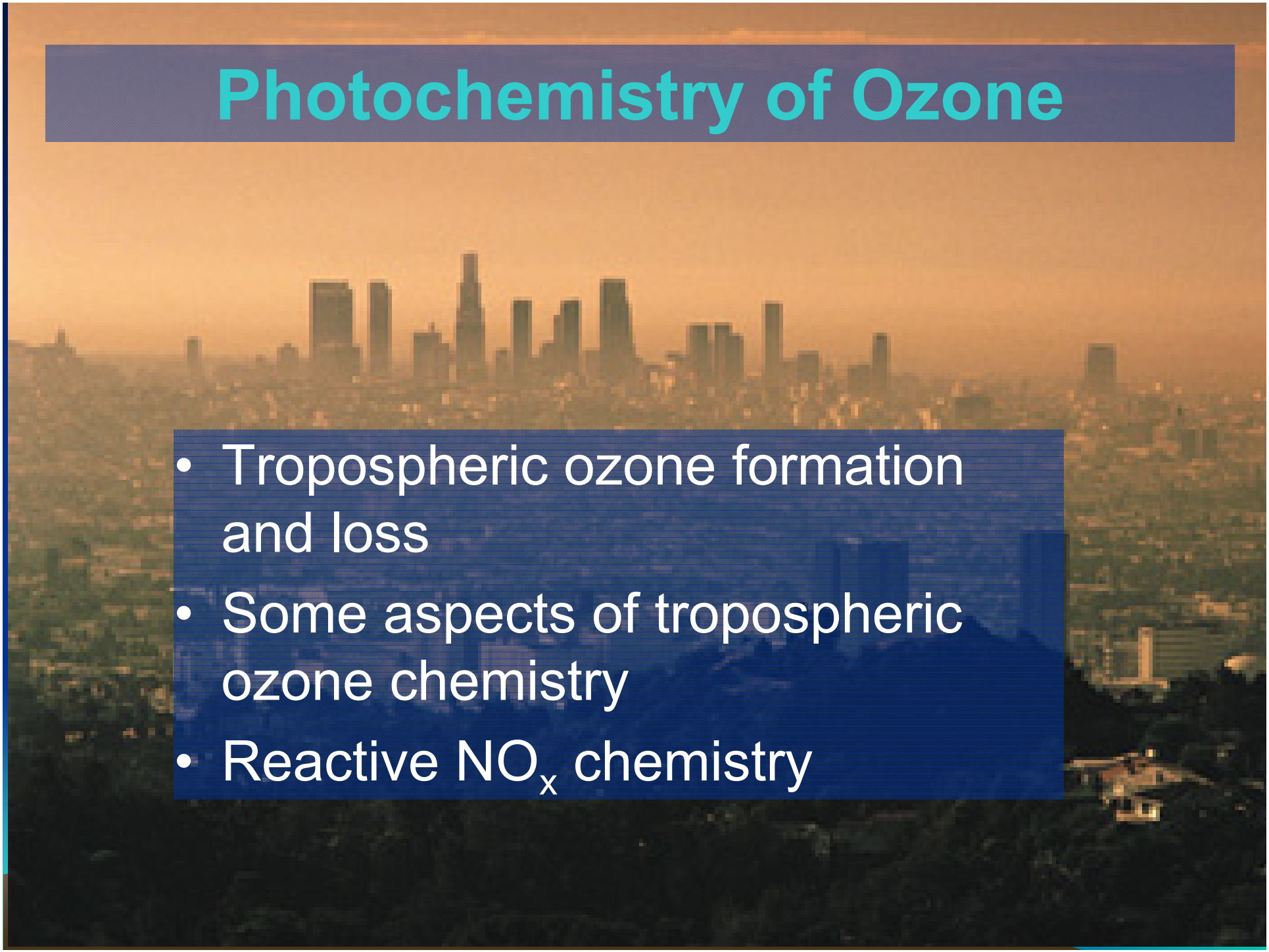


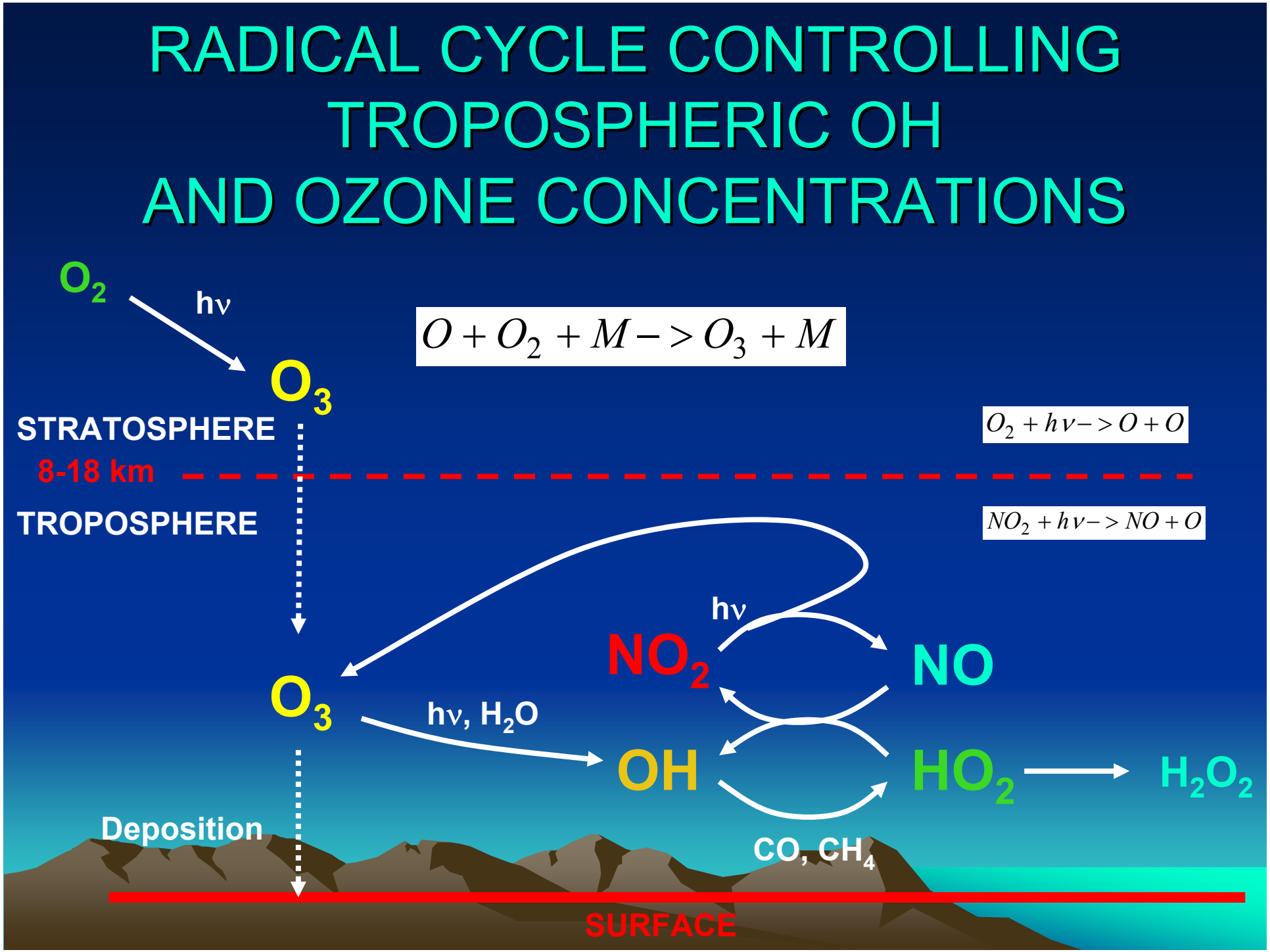

IPCC [2007]

# Projections of Future $CH_4$ Emissions (Tg $CH_4$) to 2050

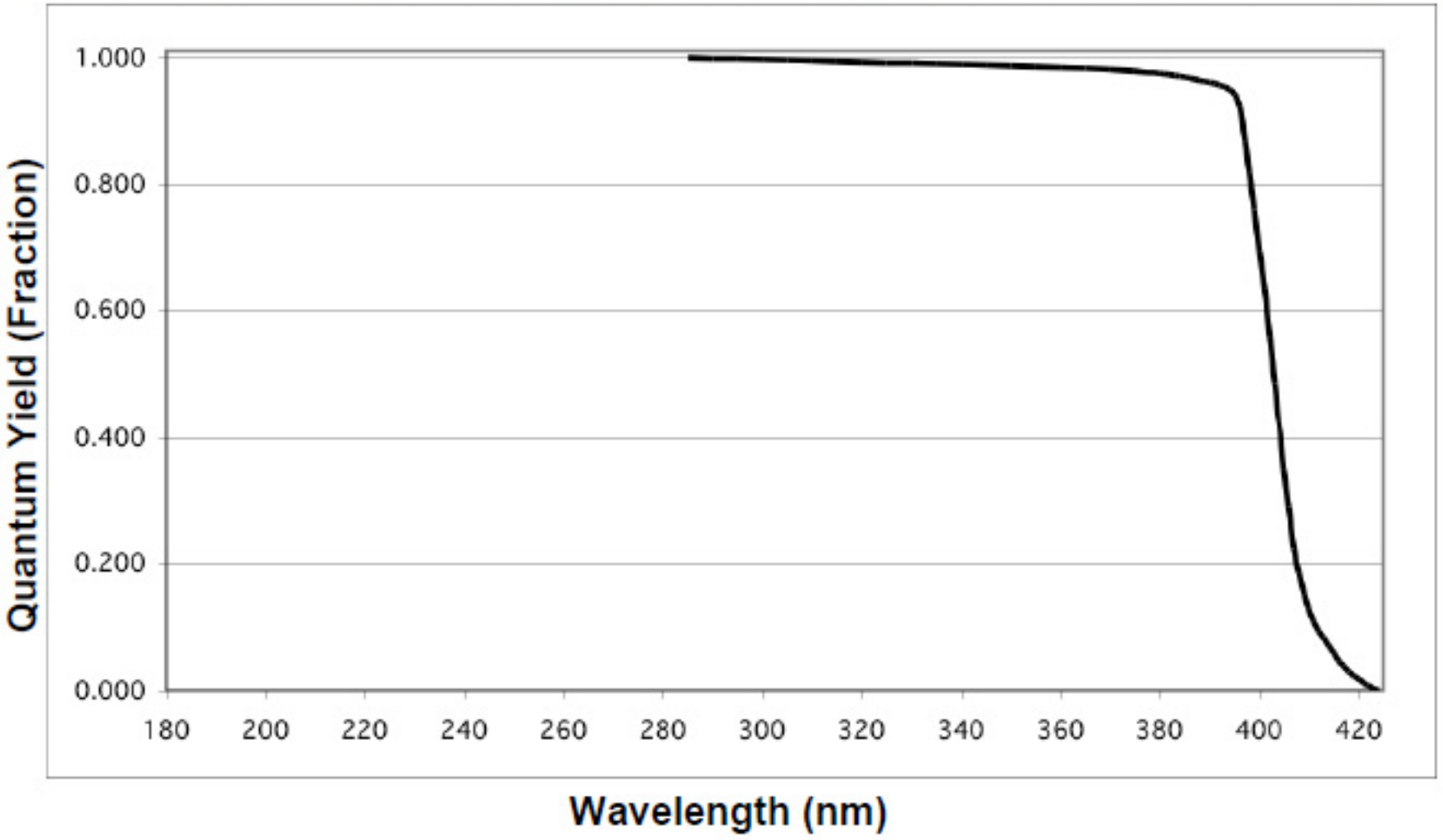



Photochemistry of Ozone
• Tropospheric ozone formation and loss
• Some aspects of tropospheric ozone chemistry
• Reactive $NO_x$ chemistry

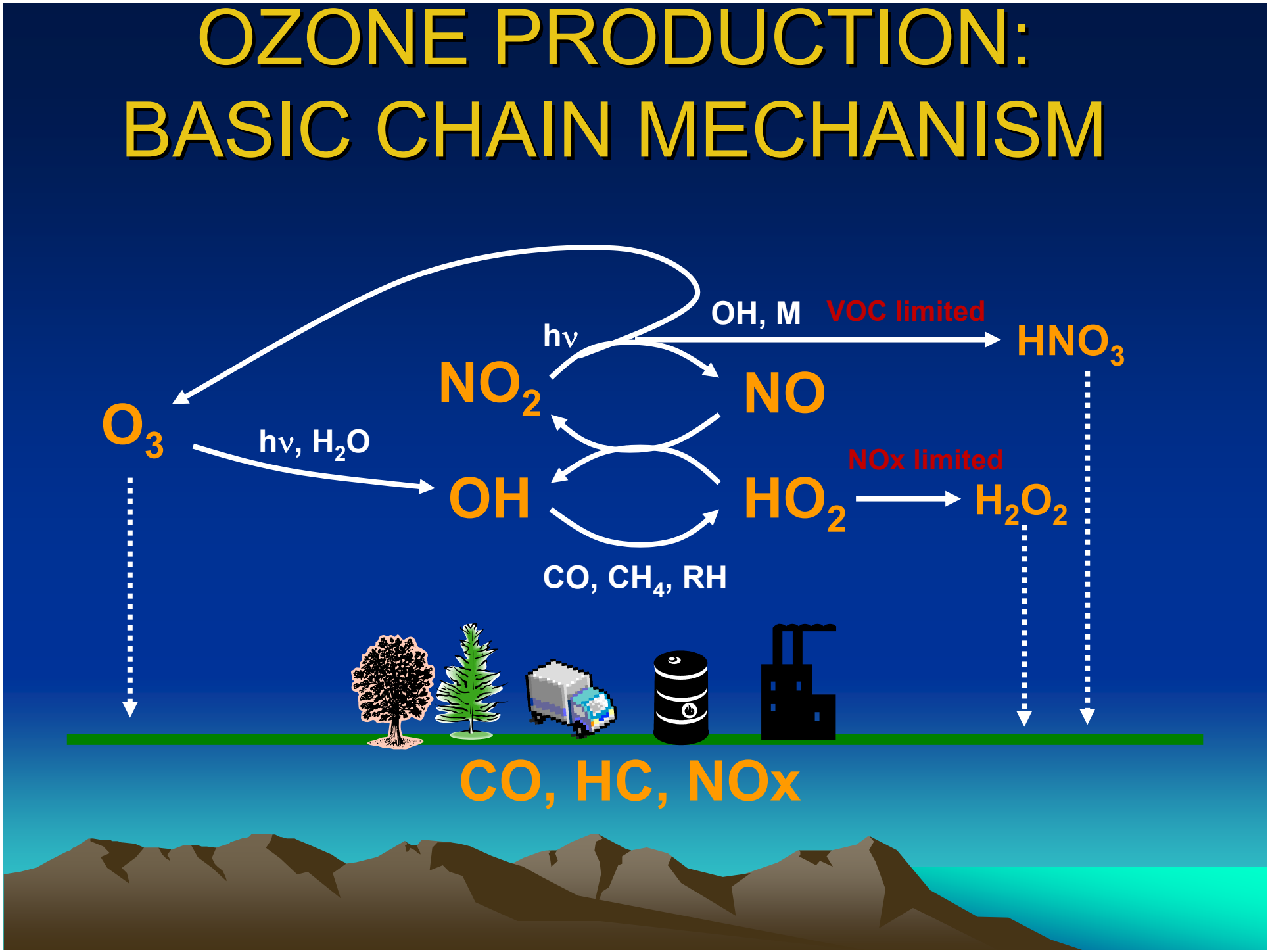
# RADICAL CYCLE CONTROLLING TROPOSPHERIC OH AND OZONE CONCENTRATIONS



# QUANTUM YIELD: $NO_2 + h\nu \rightarrow NO + O(^3P)$



# OZONE PRODUCTION: BASIC CHAIN MECHANISM



# CHAIN MECHANISM FOR $O_3$ PRODUCTION: CO OXIDATION

**Initiation:** **source of HOx (OH production)**

**Propogation:**

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu\ (+O_2) \rightarrow NO + O_3$$
$$\text{NET: } CO + 2O_2 \rightarrow CO_2 + O_3$$

**Termination:** **by loss of HOx (self reaction of $HO_2$)**

→Propagation efficiency of the chain determined by the abundance of NOx

**NOTE**: HOx and NOx catalyze $O_3$ production in the troposphere, and $O_3$ destruction in the stratosphere! The key difference is that $[O_3]$ and [O] are much lower in the troposphere, thus $NO_2$ does not react with O, and OH is far more likely to react with CO, HC, etc. than with $O_3$

# CHAIN MECHANISM FOR $O_3$ PRODUCTION: $CH_4$ OXIDATION

**Initiation:** source of HOx (OH production)

**Propogation:**

$CH_4 + OH \rightarrow CH_3 + H_2O$

$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$

$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$CH_3OOH + OH \rightarrow CH_2O + OH + H_2O$

$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$

$CH_3OOH + hv \rightarrow CH_3O + OH$

$CH_3O + O_2 \rightarrow CH_2O + HO_2$

$CH_2O + OH \rightarrow CHO + H_2O$

$CH_2O + hv + O_2 \rightarrow CHO + HO_2 + O_2$

$CH_2O + hv \rightarrow CO + H_2$

$CHO + O_2 \rightarrow CO + HO_2$

(…then CO oxidation…)

Oxidation from C(-IV) in $CH_4$ through to C(+IV) in $CO_2$

Ozone production from $NO_2$ photolysis following peroxy+NO rxns (where peroxy radicals generated by reactions above)

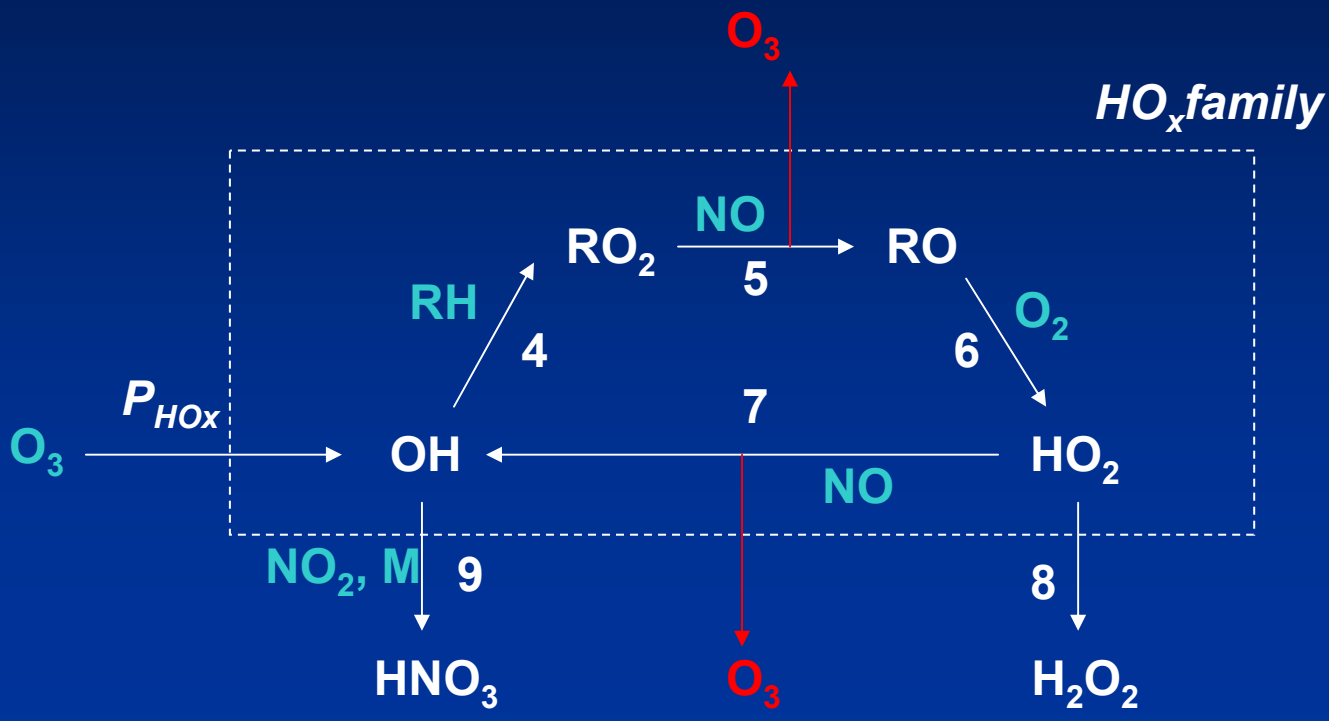
**High NOx:** $CH_3O_2$ and $HO_2$ react only with NO, and $CH_2O$ removed only by photolysis

$CH_4 + 10O_2 \rightarrow CO_2 + H_2O + \mathbf{5O_3} + 2OH$

**Low NOx:** $CH_3O_2$ reacts with $HO_2$, $CH_3OOH$ reacts with OH and $CH_2O$ reacts with OH

$CH_4 + 3OH + 2O_2 \rightarrow CO_2 + 3H_2O + HO_2$

# DEPENDENCE OF OZONE PRODUCTION ON $NO_x$ AND HYDROCARBONS

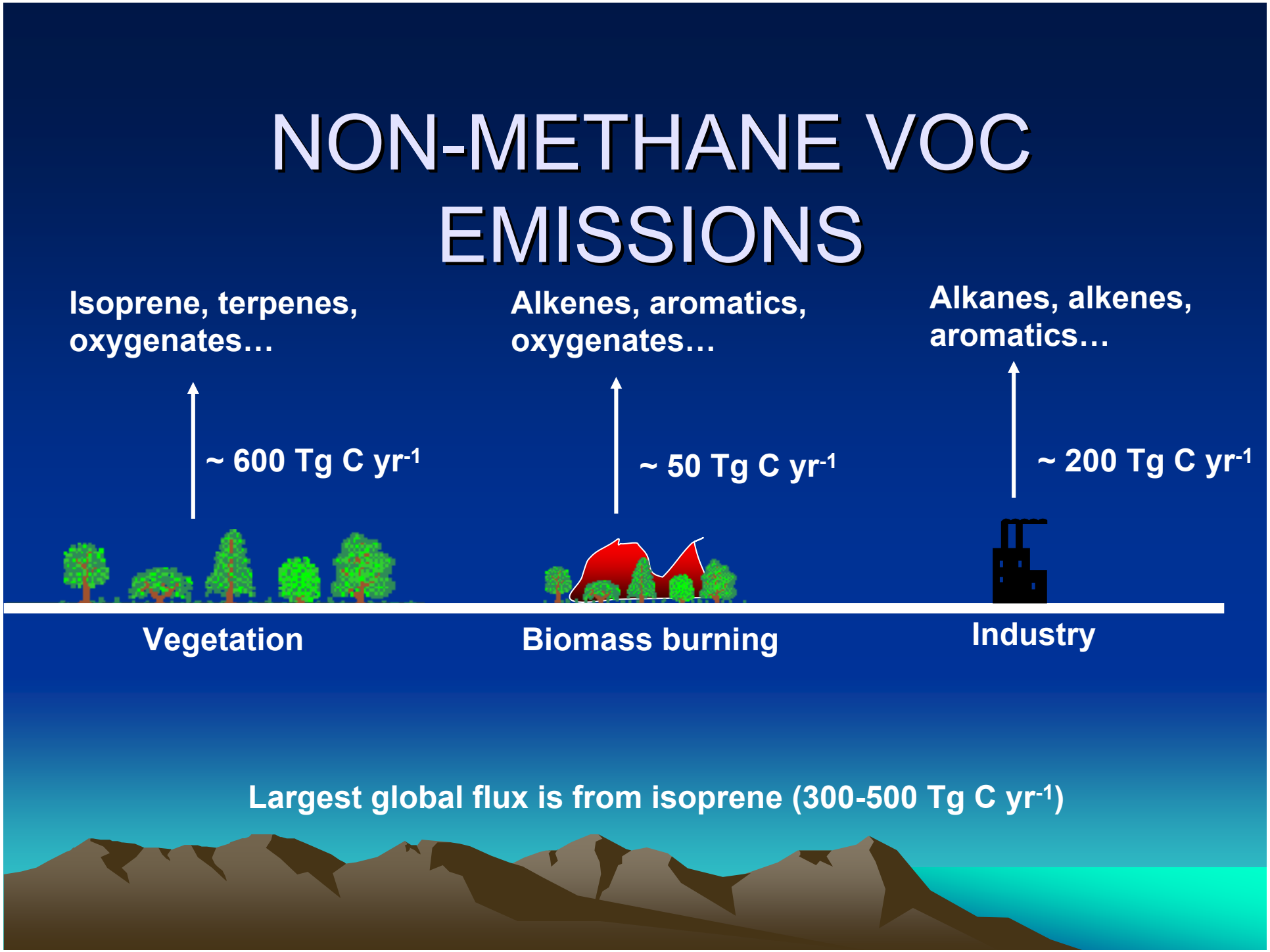



NET: $RH + 4O_2 \rightarrow R'CHO + 2O_3 + H_2O$

"$NO_x$- saturated" or "hydrocarbon-limited" regime

"$NO_x$-limited" regime

# NON-METHANE VOC EMISSIONS

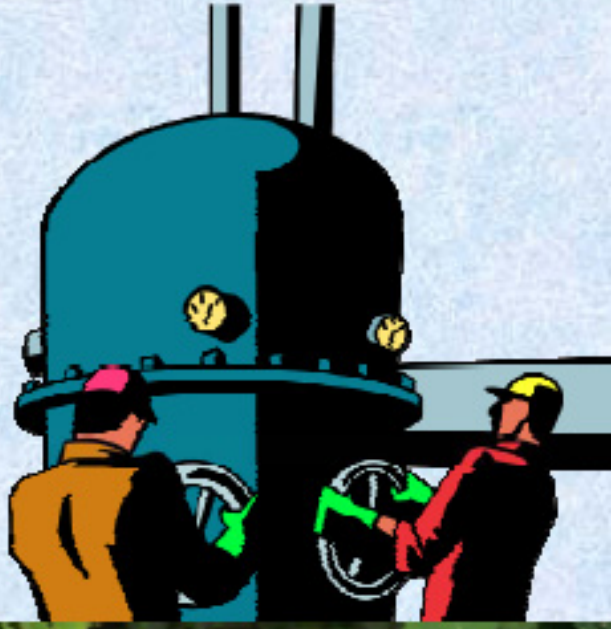


# Sources of Volatile Organic Compound (VOC) Emissions

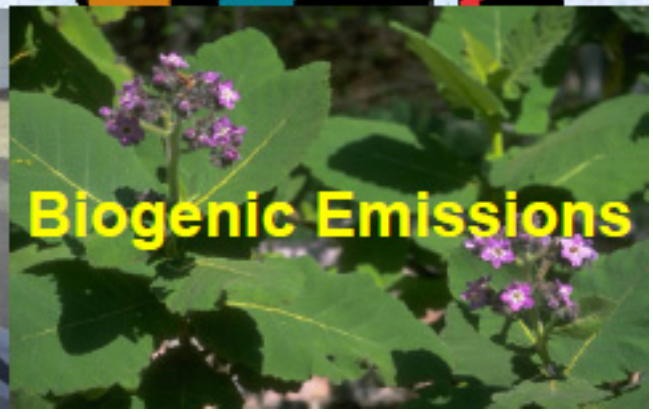
VOC

Refinery Operations and Chemical Production

Coatings



Transportation



Biogenic Emissions

## Photochemical oxidation of CO and volatile organic compounds (VOCs) catalyzed by hydrogen oxide radicals ($HO_x$) in the presence of nitrogen oxide radicals ($NO_x$)

$HO_x = H + OH + HO_2 + RO + RO_2$

$NO_x = NO + NO_2$

### Oxidation of CO:

$$CO + OH \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow OH + NO_2$$

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

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

$$\text{Net: } CO + 2O_2 \rightarrow CO_2 + O_3$$

### Oxidation of VOC:

$$RH + OH \rightarrow R + H_2O$$

$$R + O_2 + M \rightarrow RO_2 + M$$

$$RO_2 + NO \rightarrow RO + NO_2$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3$$

$$RO + O_2 \rightarrow R'CHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$\text{Net: } RH + 4O_2 \rightarrow R'CHO + 2O_3 + H_2O$$

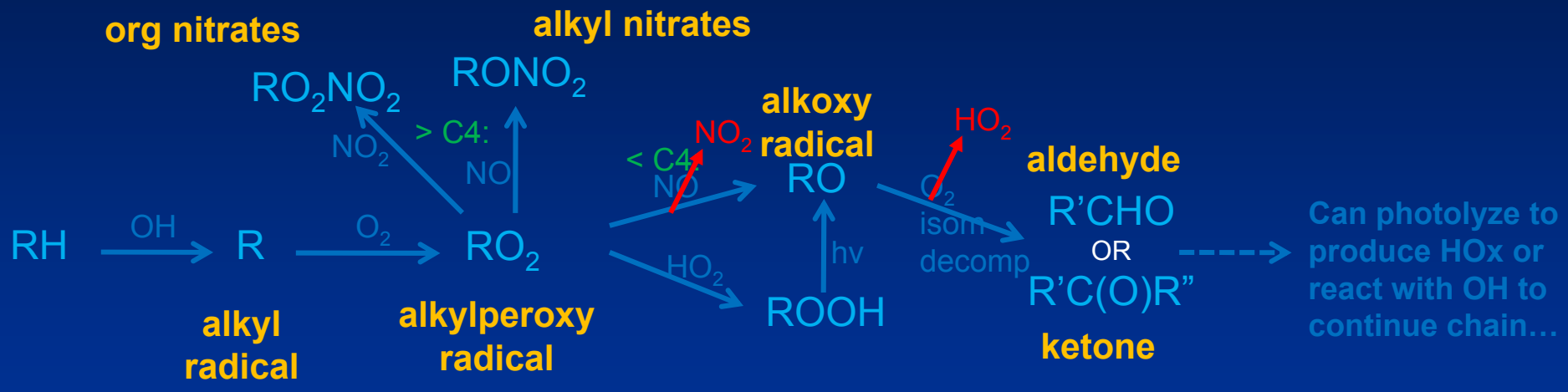
OH can also add to double bonds of unsaturated VOCs

RO can also decompose or isomerize; rang carbonyl produ

Carbonyl products can react with OH to produce additional ozone, or photolyze to generate more $HO_x$ radicals (branching reaction)

# OXIDATION OF HYDROCARBONS CONTRIBUTE TO OZONE FORMATION IN POLLUTED AIR

**Generic Alkane OH Oxidation Scheme (no longer just CO and $CH_4$!)**




Additional oxidation by $NO_3$ (but only at night!)

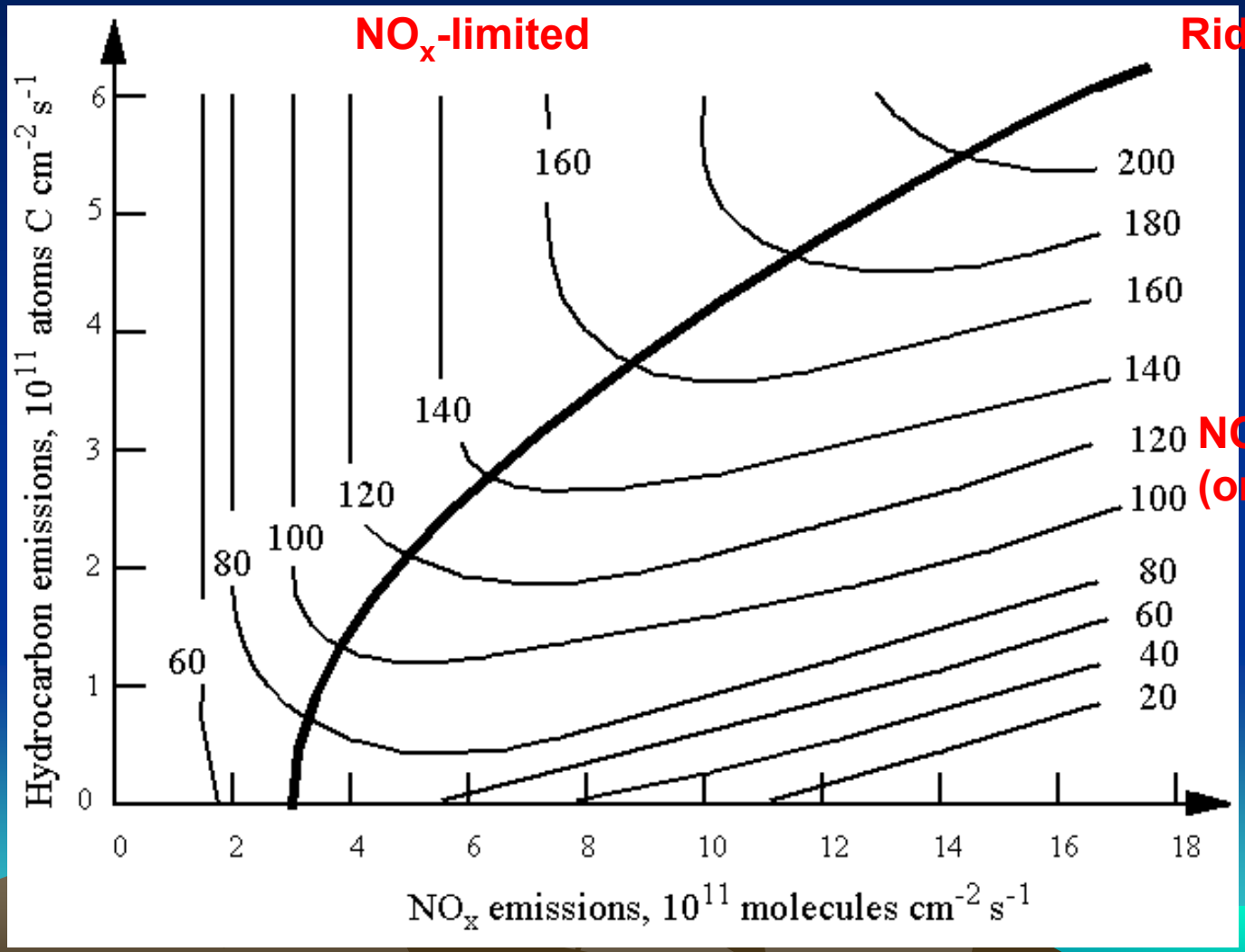
**Alkenes:** OH oxidation adds to double bond (does not abstract H as with alkanes). With double bond, alkenes can also be oxidized by ozone

**Aromatics (with benzene rings):** reactive with OH, via either addition or abstraction

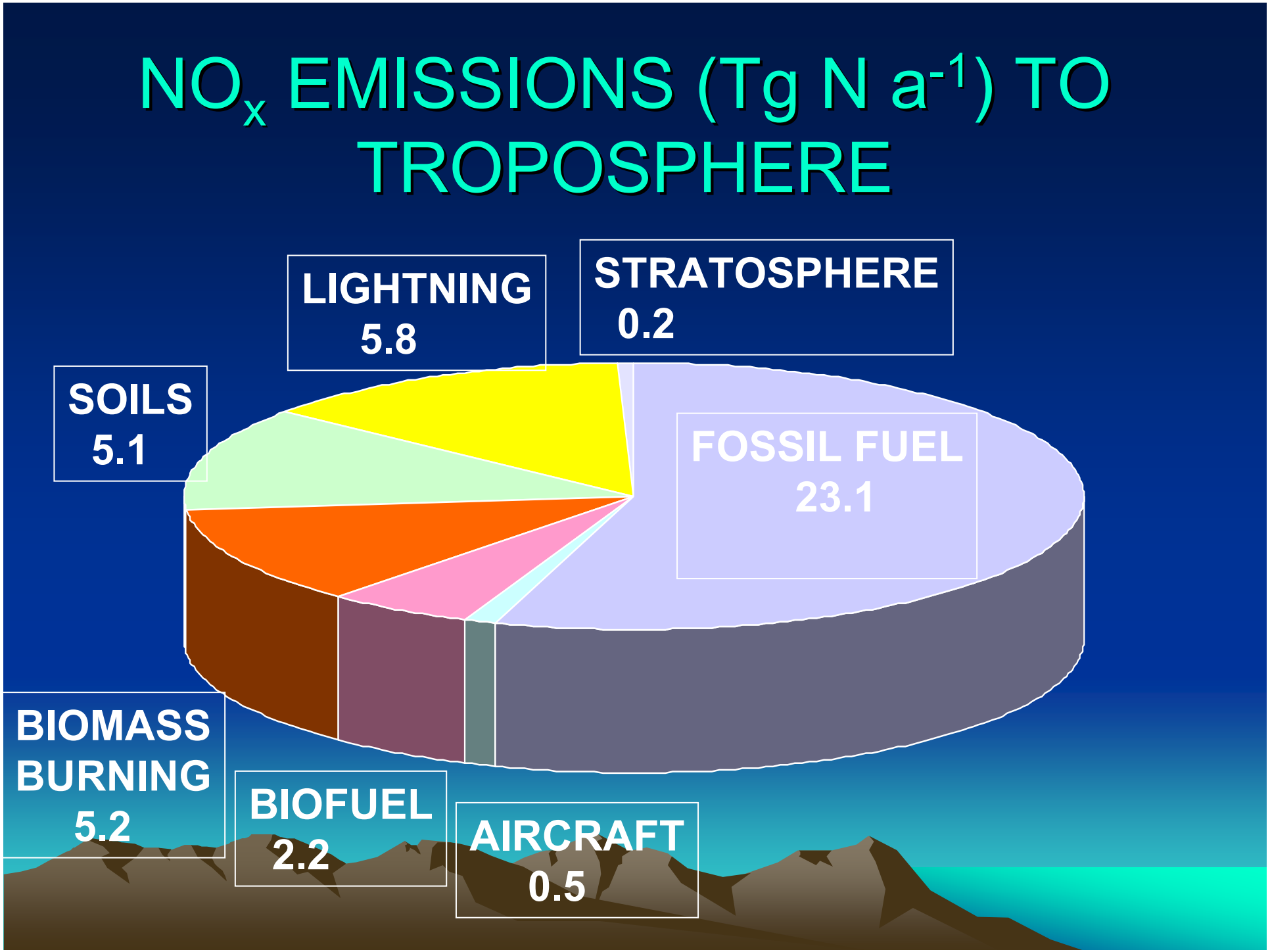
→ *source of secondary organic aerosol (SOA)*

# The crucial role of $NO_x$

# OZONE CONCENTRATIONS vs. $NO_x$ AND VOC EMISSIONS



# $NO_x$ EMISSIONS (Tg N $a^{-1}$) TO TROPOSPHERE



# $NO_x$ EMISSIONS (Tg N $yr^{-1}$) TO TROPOSPHERE

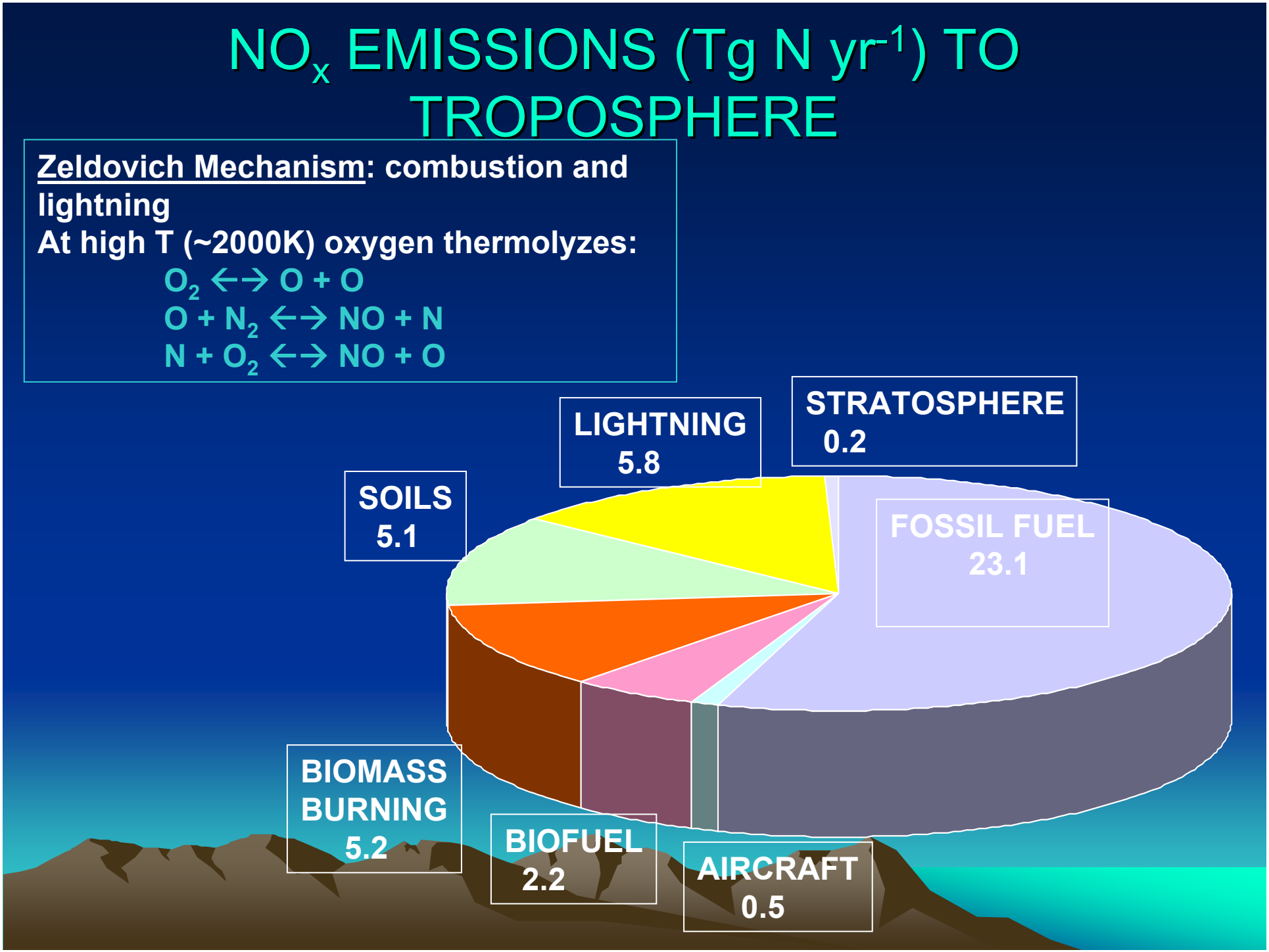
**Zeldovich Mechanism: combustion and lightning**

**At high T (~2000K) oxygen thermolyzes:**

$$O_2 \leftrightarrow O + O$$

$$O + N_2 \leftrightarrow NO + N$$

$$N + O_2 \leftrightarrow NO + O$$



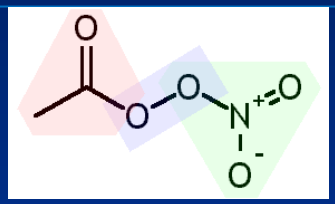
# $NO_X$ CYCLING

**Example of PAN formation from acetaldehyde:**

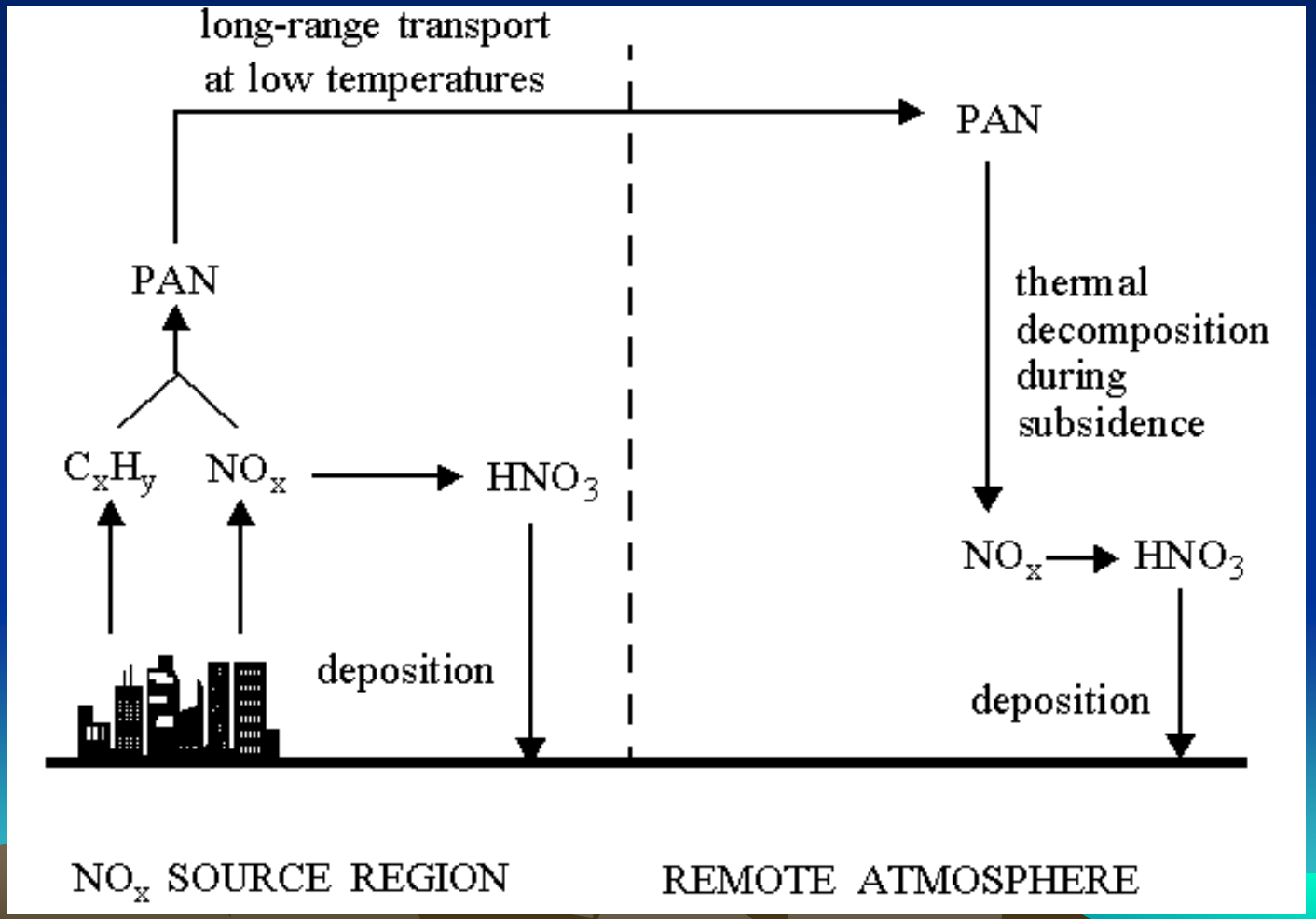
$CH_3CHO + OH \rightarrow CH_3CO + H_2O$

$CH_3CO + O_2 + M \rightarrow CH_3C(O)OO + M$

$CH_3C(O)OO + NO_2 + M \rightarrow CH_3C(O)OONO_2 + M$



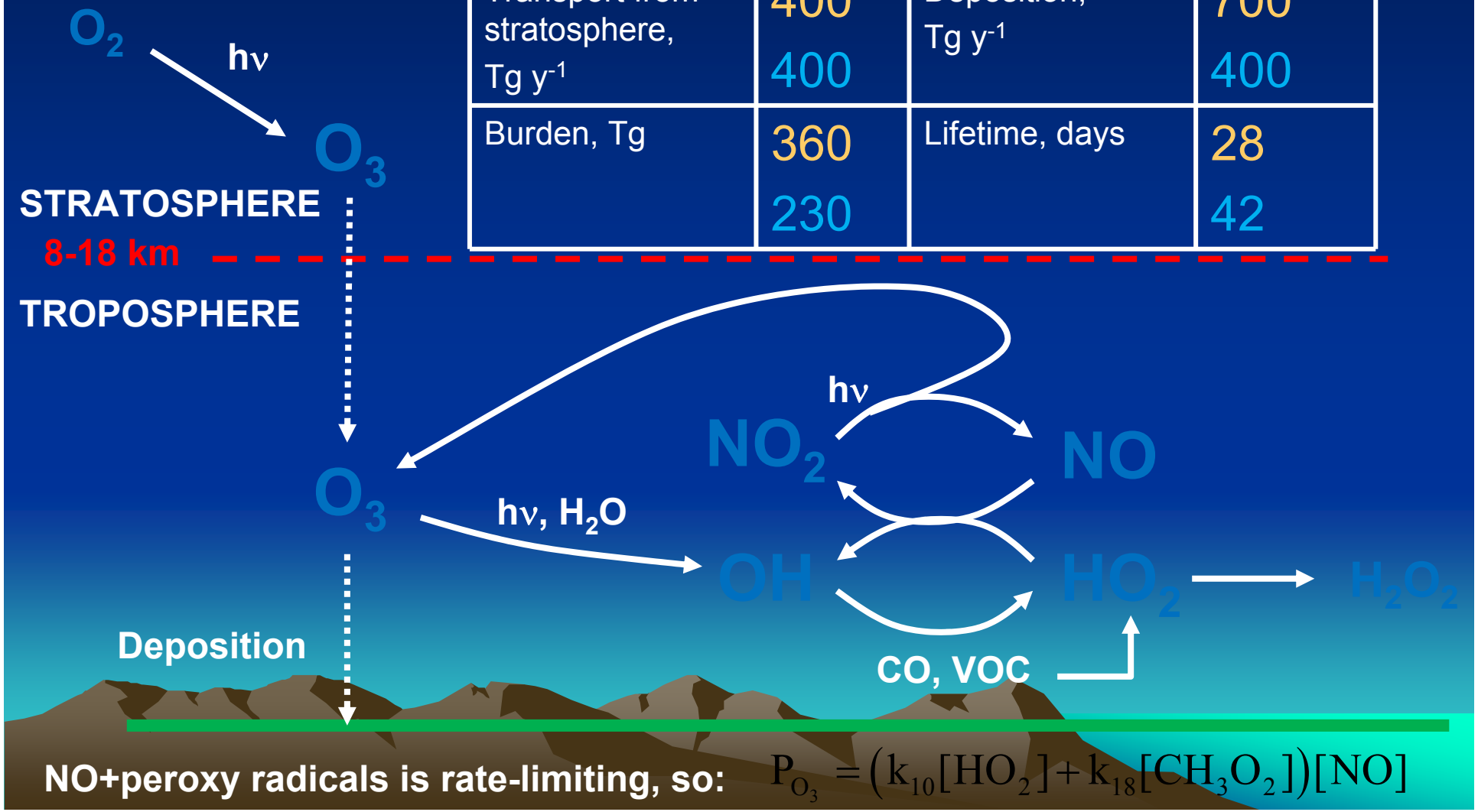
# PEROXYACETYLNITRATE (PAN) AS RESERVOIR FOR LONG-RANGE TRANSPORT OF $NO_x$



# GLOBAL BUDGET OF TROPOSPHERIC OZONE

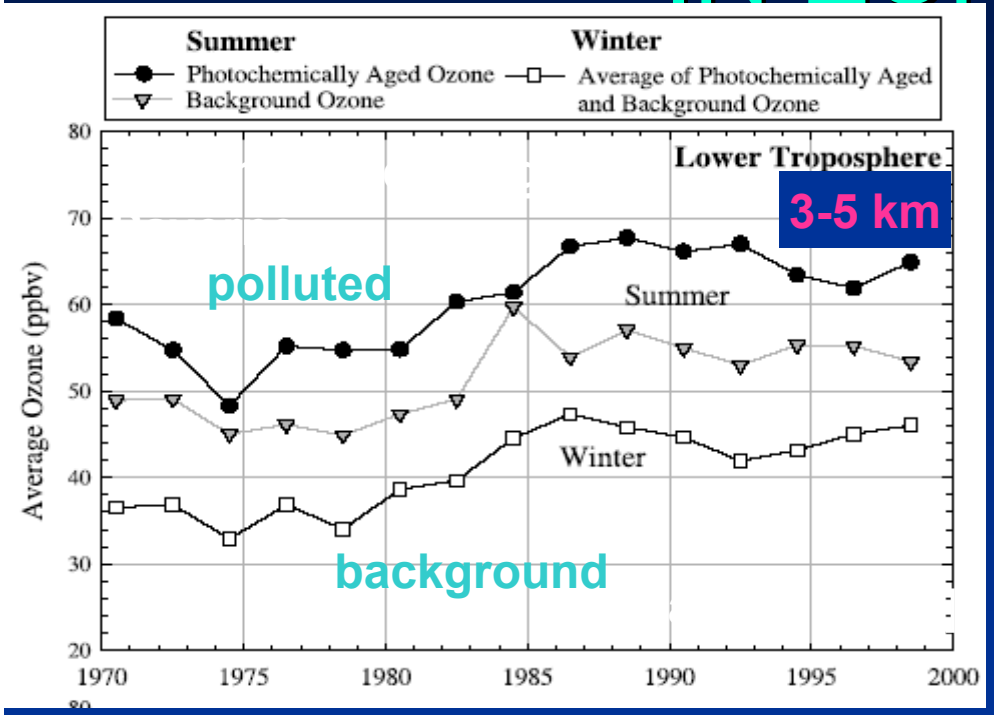
**Present-day**
**Preindustrial**

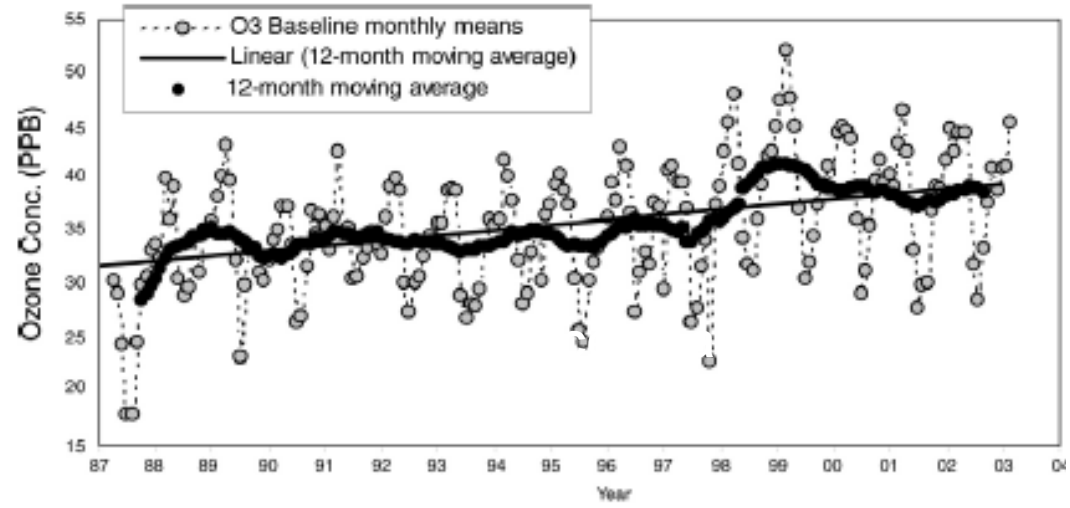
| | | | |
|---|---|---|---|
| Chem prod in troposphere, Tg $y^{-1}$ | 4300<br>1600 | Chem loss in troposphere, Tg $y^{-1}$ | 4000<br>1600 |
| Transport from stratosphere, Tg $y^{-1}$ | 400<br>400 | Deposition, Tg $y^{-1}$ | 700<br>400 |
| Burden, Tg | 360<br>230 | Lifetime, days | 28<br>42 |

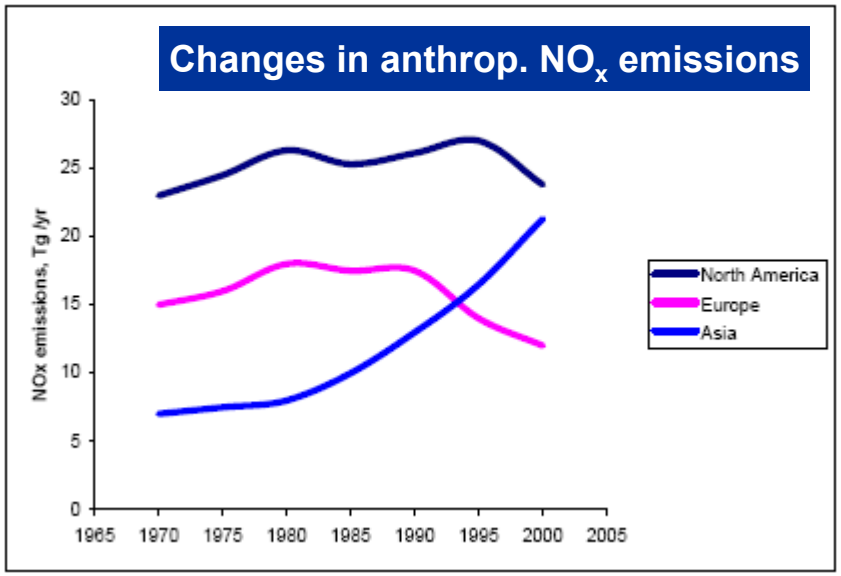



NO+peroxy radicals is rate-limiting, so: $P_{O_3} = \left(k_{10}[HO_2] + k_{18}[CH_3O_2]\right)[NO]$

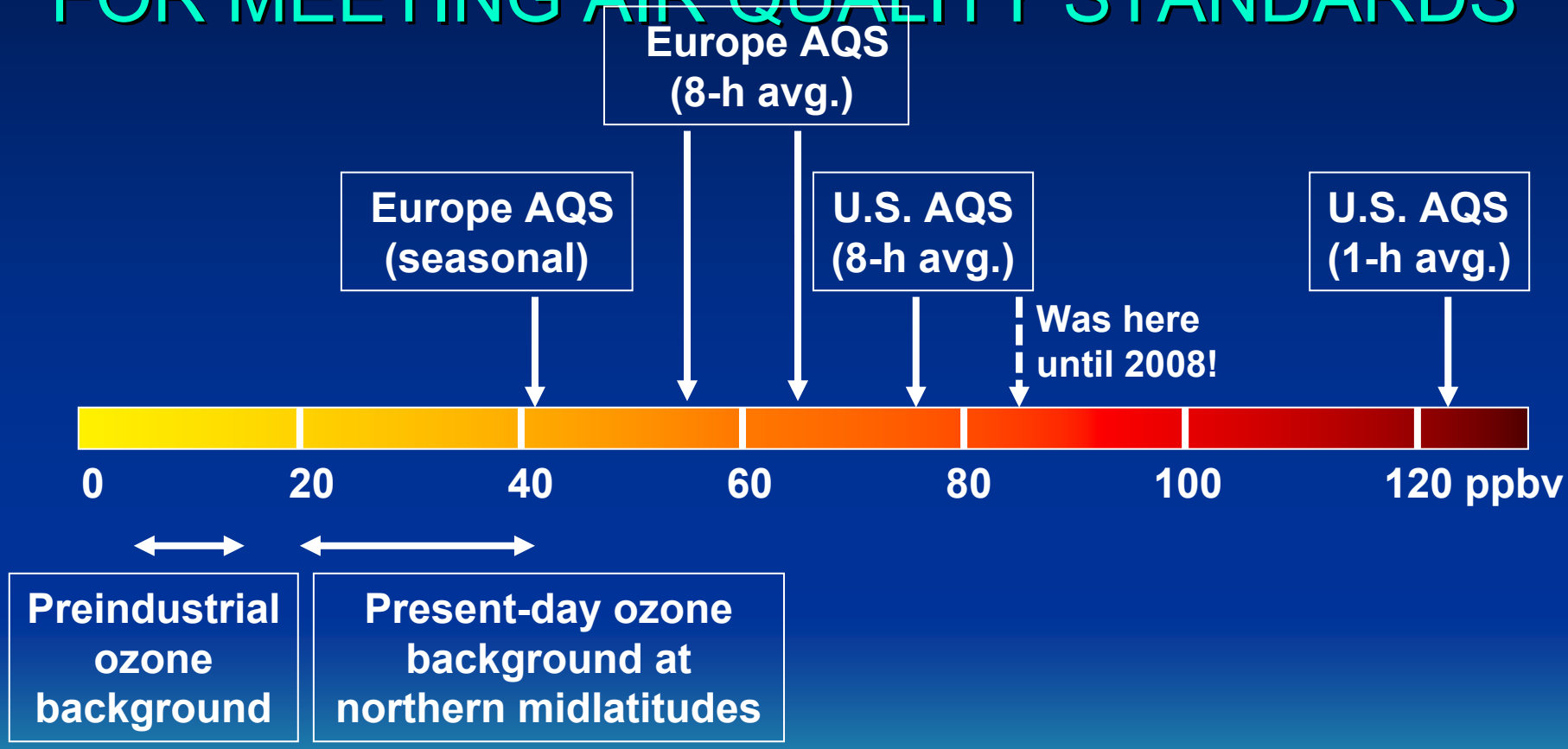
# RISING OZONE BACKGROUND IN EUROPE



# HEMISPHERIC OZONE POLLUTION: IMPLICATIONS OF ENHANCED OZONE BACKGROUND FOR MEETING AIR QUALITY STANDARDS



# General rules for atmospheric oxidation of hydrocarbons

- Attack by OH is by H abstraction for saturated HCs (alkanes), by addition for unsaturated HCs (alkenes)
- Reactivity increases with number of C-H bonds, number of unsaturated bonds
- Organic radicals other than peroxy react with $O_2$ (if they are small) or decompose (if they are large); $O_2$ addition produces peroxy radicals.
- Organic peroxy radicals ($RO_2$) react with NO and $HO_2$ (dominant), other $RO_2$ (minor); they also react with $NO_2$ but the products decompose rapidly (except in the case of peroxyacyl radicals which produce peroxyacylnitrates or PANs)
- $RO_2$+$HO_2$ produces organic hydroperoxides ROOH, $RO_2$+NO produces carbonyls (aldehydes RCHO and ketones RC(O)R')
- Carbonyls and hydroperoxides can photolyze (radical source) as well as react with OH
- Unsaturated HCs can also react with ozone, producing carbonyls and carboxylic acids
- $RO_2$+$R'O_2$ reactions produce a range of oxygenated organic compounds including carbonyls, carboxylic acids, alcohols, esters…

# Further reading

- **This lecture is based on the materials of the following books that are recommended for further reading**
- J.H.Seinfeld and S.N.Pandis. ATMOSPHERIC CHEMISTRY AND PHYSICS: From Air Pollution to Climate Change. JOHN WILEY & SONS, INC. 2006.
- MARK Z. JACOBSON. Fundamentals of Atmospheric Modeling. Cambridge University Press 2005.
- Daniel J. Jacob. INTRODUCTION TO ATMOSPHERIC CHEMISTRY. Princeton University Press. 1999.

# T H A N K S

FOR

YOUR ATTENTION !!!