EAS 309/B3090
Fall 2019
Lecture #15

Chapter 5:
Atmospheric
Chemistry

Sections you should read:
5.1
5.2
5.3.1 (OH-)
5.3.5 ($O_3$)
5.4.1 (Aerosols)

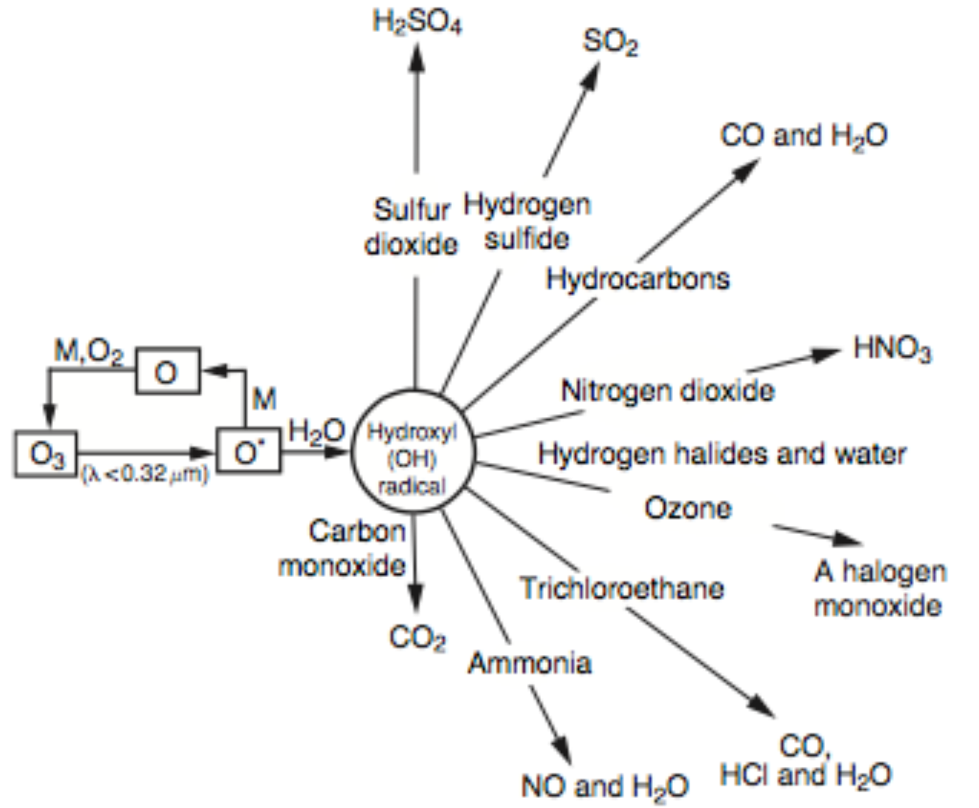



**Fig. 5.4** Illustration of the central role of the OH radical in the oxidation of tropospheric trace gases. Little escapes oxidation by OH. [Adapted from *Global Tropospheric Chemistry*, United States National Academy Press, 1984, p. 79.]

# Terminology

***Sources:***

where (or how) chemicals are added to the atmosphere

***Sinks:***

where (or how) chemicals are removed from the atmosphere

***Photochemical Reaction:*** reaction that involves sunlight, e.g.,

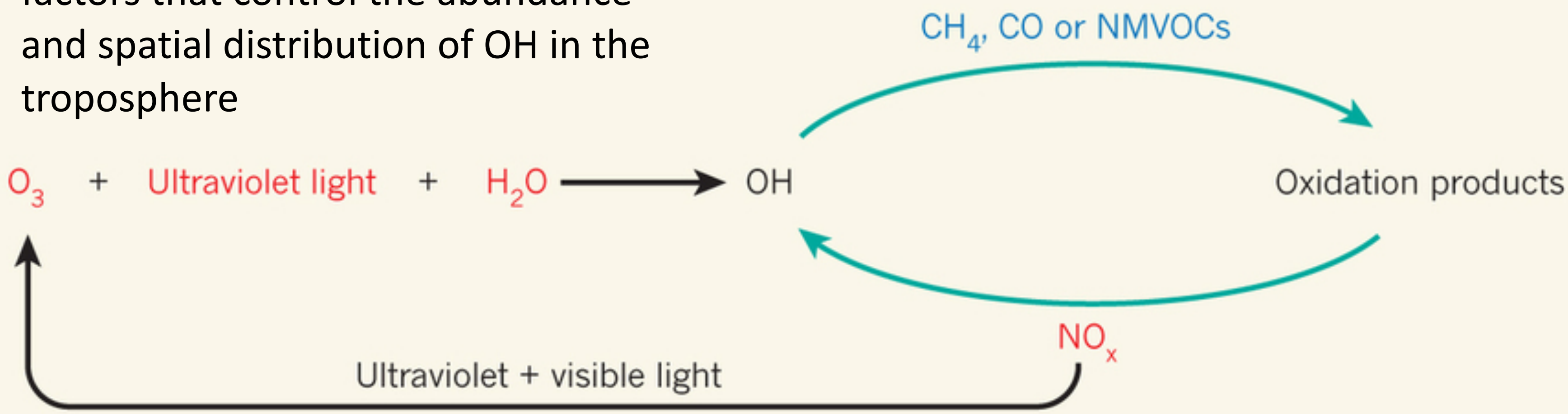
$O_3 + hv \rightarrow O_2 + O$-

***VOCs***: volatile organic compounds; **organic compounds** that easily become vapors or gases. Along with carbon, they contain elements such as hydrogen, oxygen, fluorine, chlorine, bromine, sulfur or nitrogen.

***Oxidation Products:***

when an oxygen is added to a certain product or an electron or hydrogen was removed from it.

This highly simplified scheme depicts factors that control the abundance and spatial distribution of OH in the troposphere

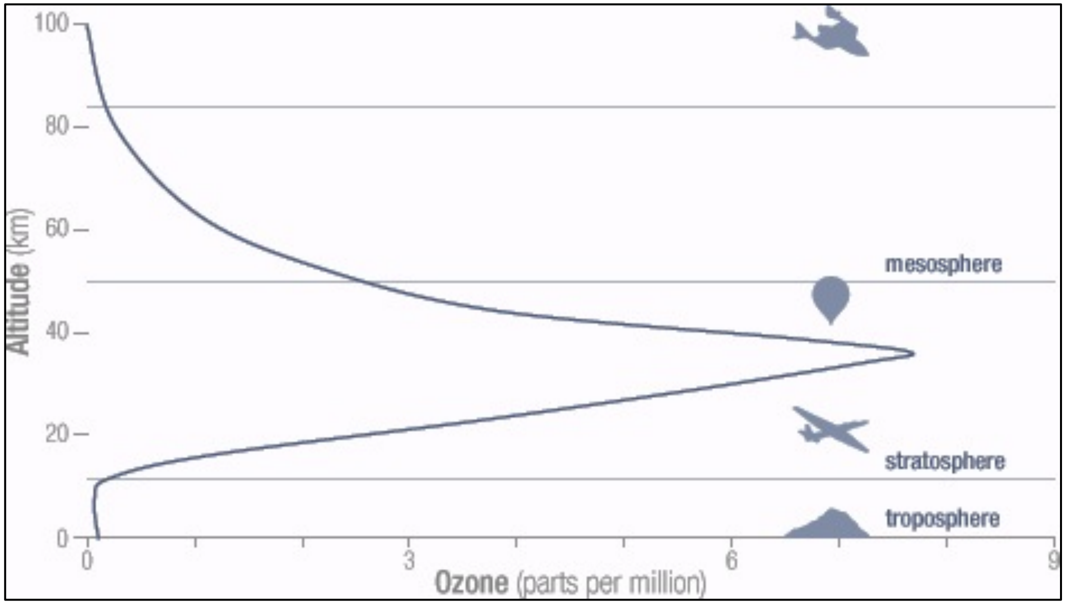



- <u>Sources of OH are shown in red, and sinks in blue.</u>
- Main pathway for OH formation is the absorption of ultraviolet light by tropospheric ozone (O3) and its subsequent break-up in the presence of water vapour.
- OH radicals may then react with compounds such as methane (CH4), carbon monoxide (CO) and non-methane volatile organic compounds (NMVOCs) to form oxidation products.
- Some of those products serve as extra sinks for OH before their eventual loss from the atmosphere.
- Others can react with nitrogen oxides (NO*x*) in the presence of sunlight to produce more OH and O3.
- The relative importance of each source or sink varies spatially and temporally.

Fiore, Nature, 2014

# Ozone chemistry

- The natural ozone layer
- Human threats to the ozone layer
- Tropospheric Ozone

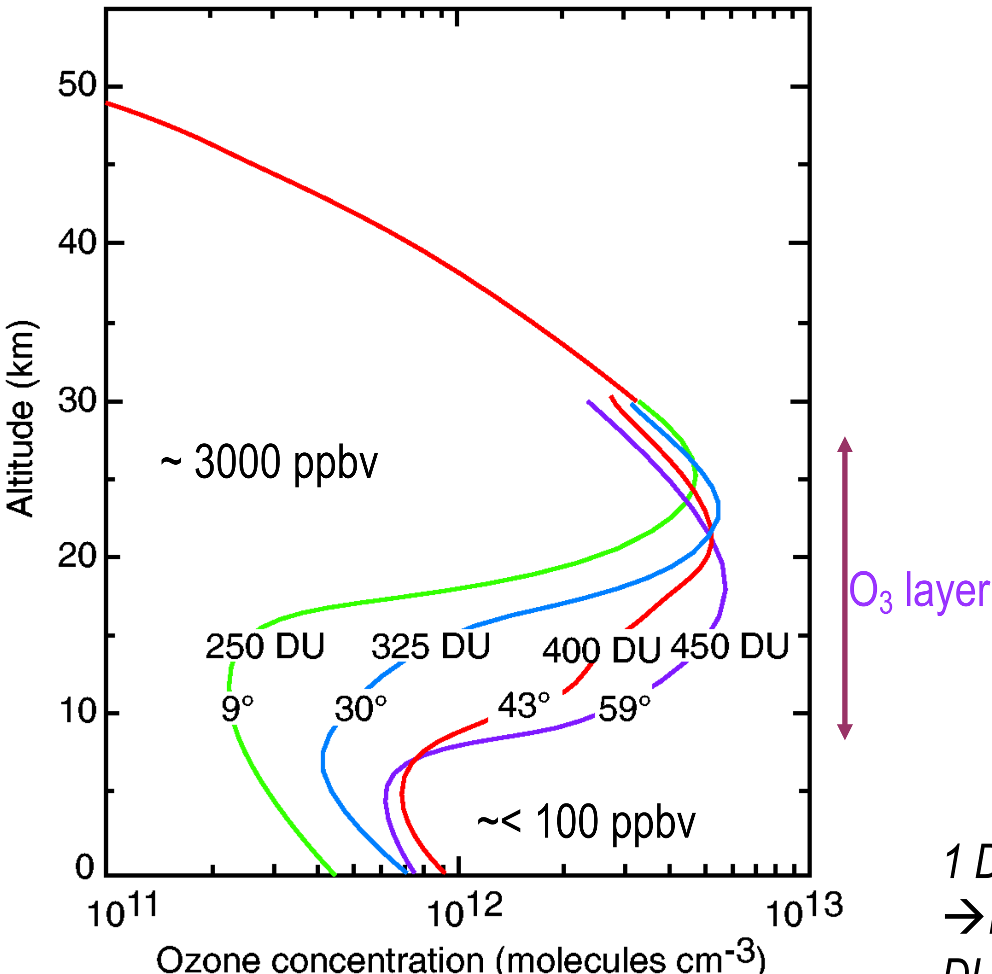



**Stratospheric "good" ozone**

- 90% of the ozone in the atmosphere sits in the stratosphere,
- Ozone in the stratosphere is a result of a balance between sunlight that creates ozone and chemical reactions that destroy it.
- Ozone is created when $O_2$ is split apart by sunlight into single oxygen atoms. Single oxygen atoms can re-join to make $O_2$, or they can join with $O_2$ molecules to make ozone ($O_3$).
- Ozone is destroyed when it reacts with molecules containing nitrogen, hydrogen, chlorine, or bromine. Some of the molecules that destroy ozone occur naturally, but people have created others.

http://ozonewatch.gsfc.nasa.gov/

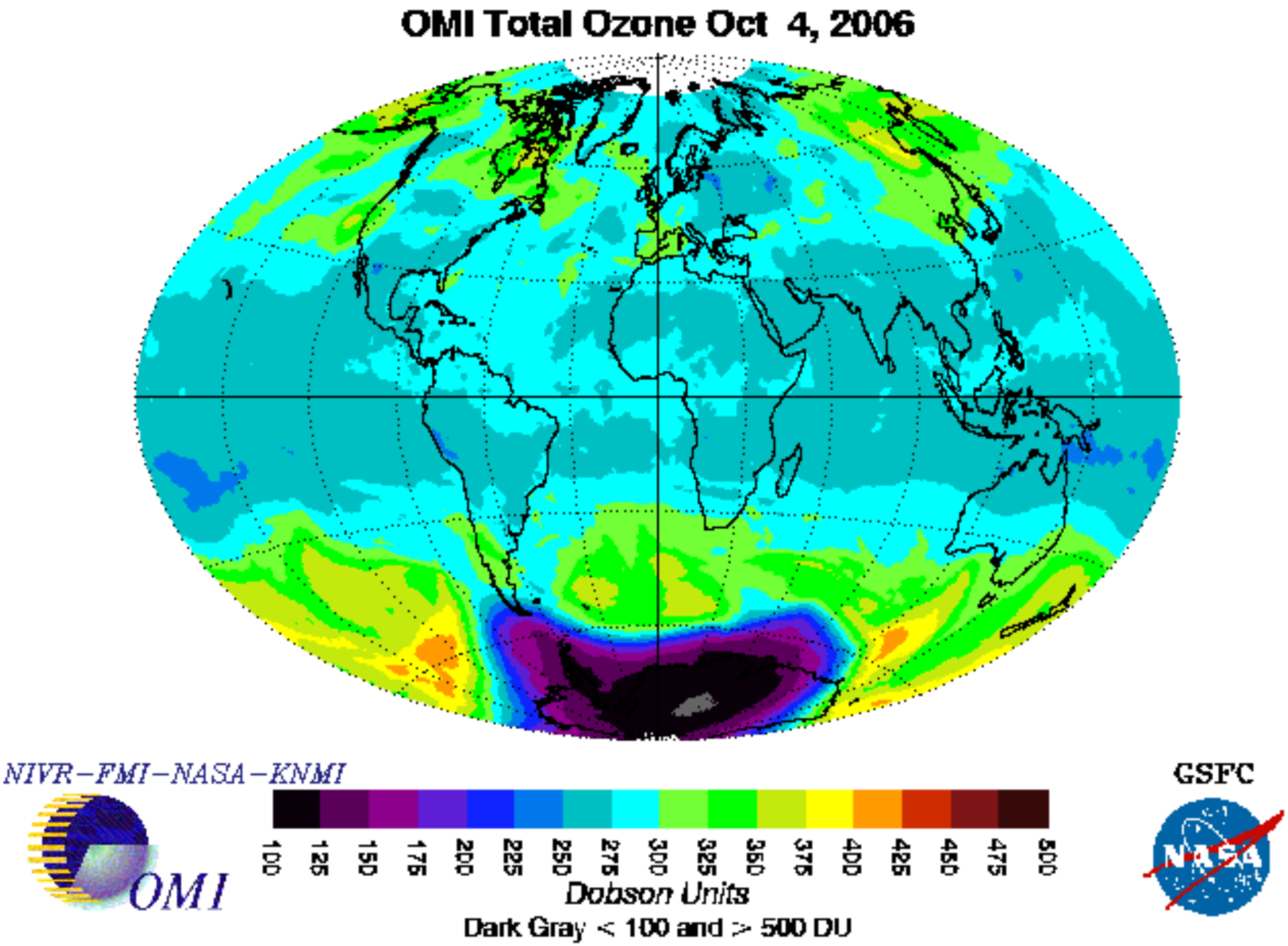
# Stratospheric ozone (1970's profile)



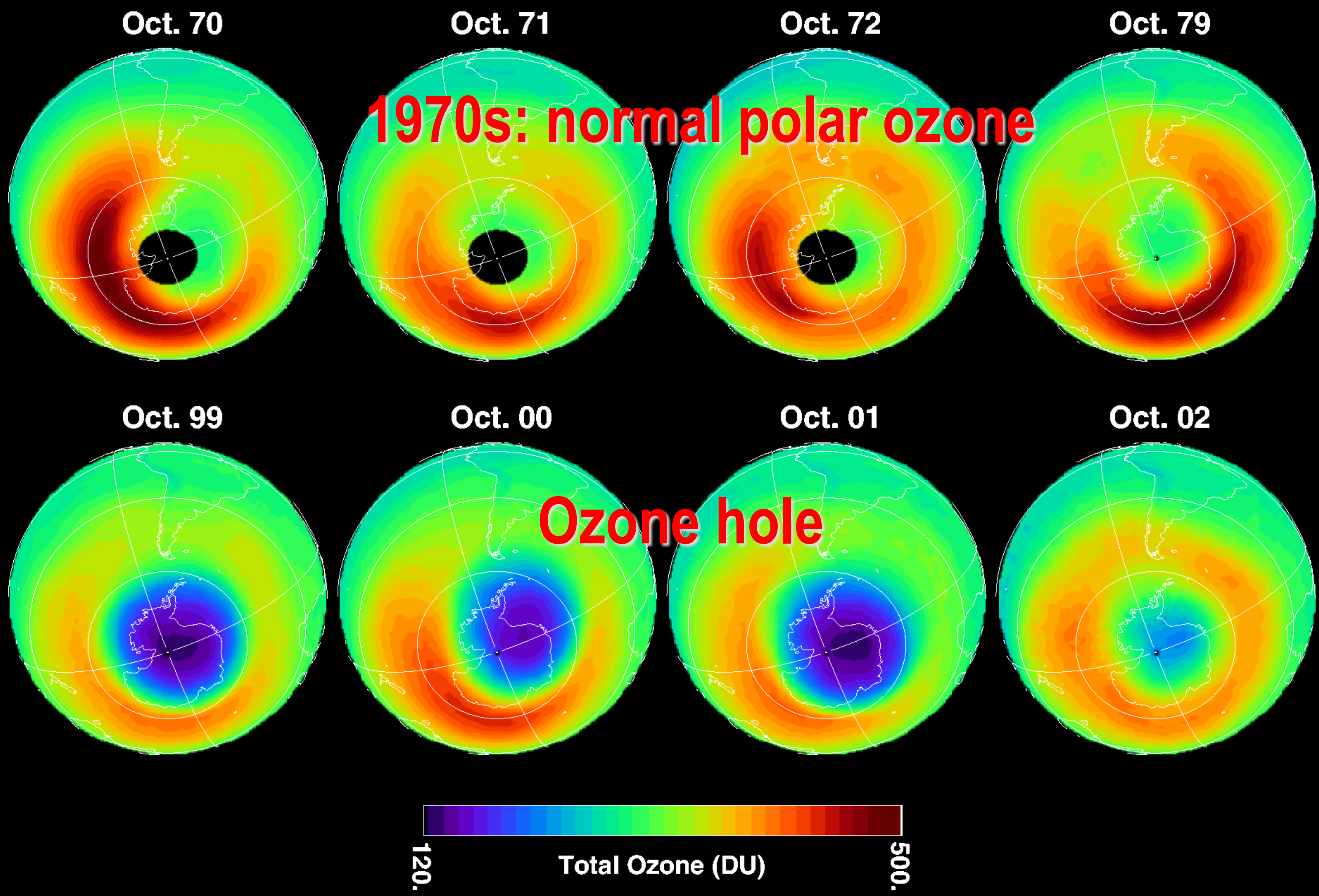

- Protective shield reducing UV radiation (230-320 nm) reaching Earth's surface
- Vertical profile of temperature in stratosphere
- Vulnerable to anthropogenic emissions

*1 DU = 2.6 x $10^{16}$ molecules $O_3$ $cm^{-2}$*
*→Bring all ozone to the ground (0°C 1 atm) 300 DU = 3 mm thick layer*

Figure 5.16 from Wallace and Hobbs


OMI Total Ozone Oct 4, 2006
NIVR–FMI–NASA–KNMI
OMI
100 125 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500
Dobson Units
Dark Gray < 100 and > 500 DU
GSFC
NASA

# The Antarctic ozone hole viewed from space



# Rapid ozone destruction mechanisms

Polar sunrise: $Cl_2 + h\nu \rightarrow Cl + Cl$

Molina and Molina (1987): ClO dimer catalytic cycle

$$2(\,Cl + O_3 \rightarrow ClO + O_2)$$
$$ClO + ClO \rightarrow Cl_2O_2$$
$$Cl_2O_2 + h\nu \rightarrow ClOO + Cl$$
$$ClOO + M \rightarrow Cl + O_2 + M$$

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$$\text{Net:} O_3 + O_3 \rightarrow 3O_2$$

**~75 % of ozone removal in ozone hole**

**Take home:**

**This cycle of reactions destroys ozone and leaves Cl free to repeat.**

***(you do not need to know this cycle, just understand the concept)***

M is some semi-stable gas, e.g., $N_2$ or $O_2$

See section 5.7 for exact details.

## Tropospheric “bad” ozone

- Although ozone high up in the stratosphere provides a shield to protect life on Earth, direct contact with ozone is harmful to both plants and animals (including humans).

- Ground-level ozone forms when nitrogen oxide gases from vehicle and industrial emissions react with volatile organic compounds (carbon-containing chemicals that evaporate easily into the air, such as paint thinners).

- According to the Environmental Protection Agency, exposure to ozone levels of greater than 80 parts per billion for 8 hours or longer is unhealthy. Such concentrations occur in or near cities during periods where the atmosphere is warm and stable.

- The harmful effects can include throat and lung irritation or aggravation of asthma or emphysema.

# The Urban Smog Problem


**Smog – "Smoke" + "Fog"**

•Coined due to reduced visibility associated with pollution episodes

**Major components:**

•"invisible": $O_3$, CO, $SO_2$

CO: carbon monoxide

$SO_2$: surfur dioxide

•"visible": PM (particulate matter, i.e., aerosols) + some gases ($NO_2$)

$NO_2$: nitrogen dioxide

Ingredients to Make Smog

•Sun (photochemistry)

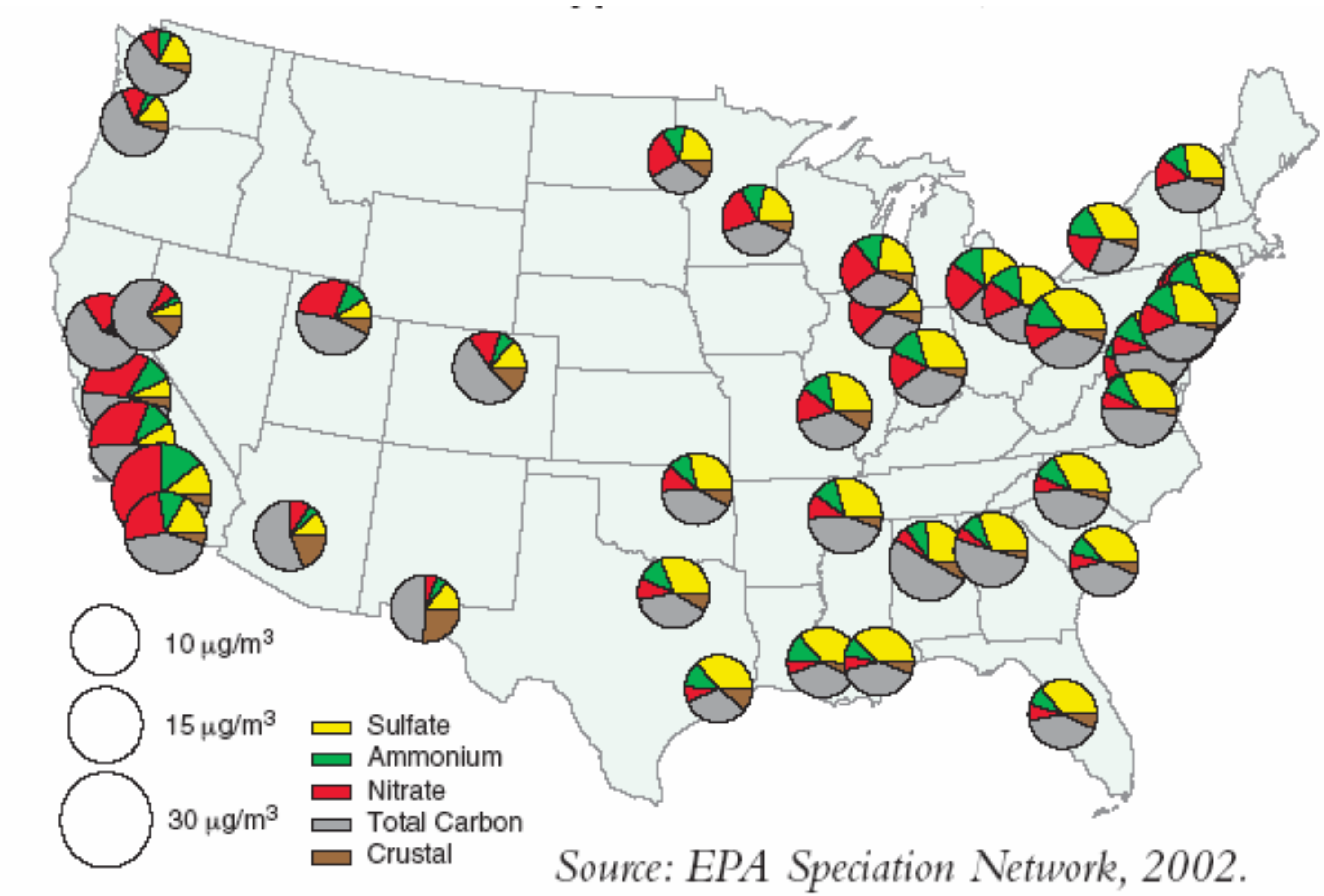
•Stagnation

•Sources of NO, $NO_2$, $SO_2$, PM and VOC (volatile organic compounds)

e.g., formaldehyde

Slide adapted from J. Thornton UW

# Annual Average $PM_{2.5}$ in Urban Areas: Mass and Composition




Slide prepared by J. Thornton UW

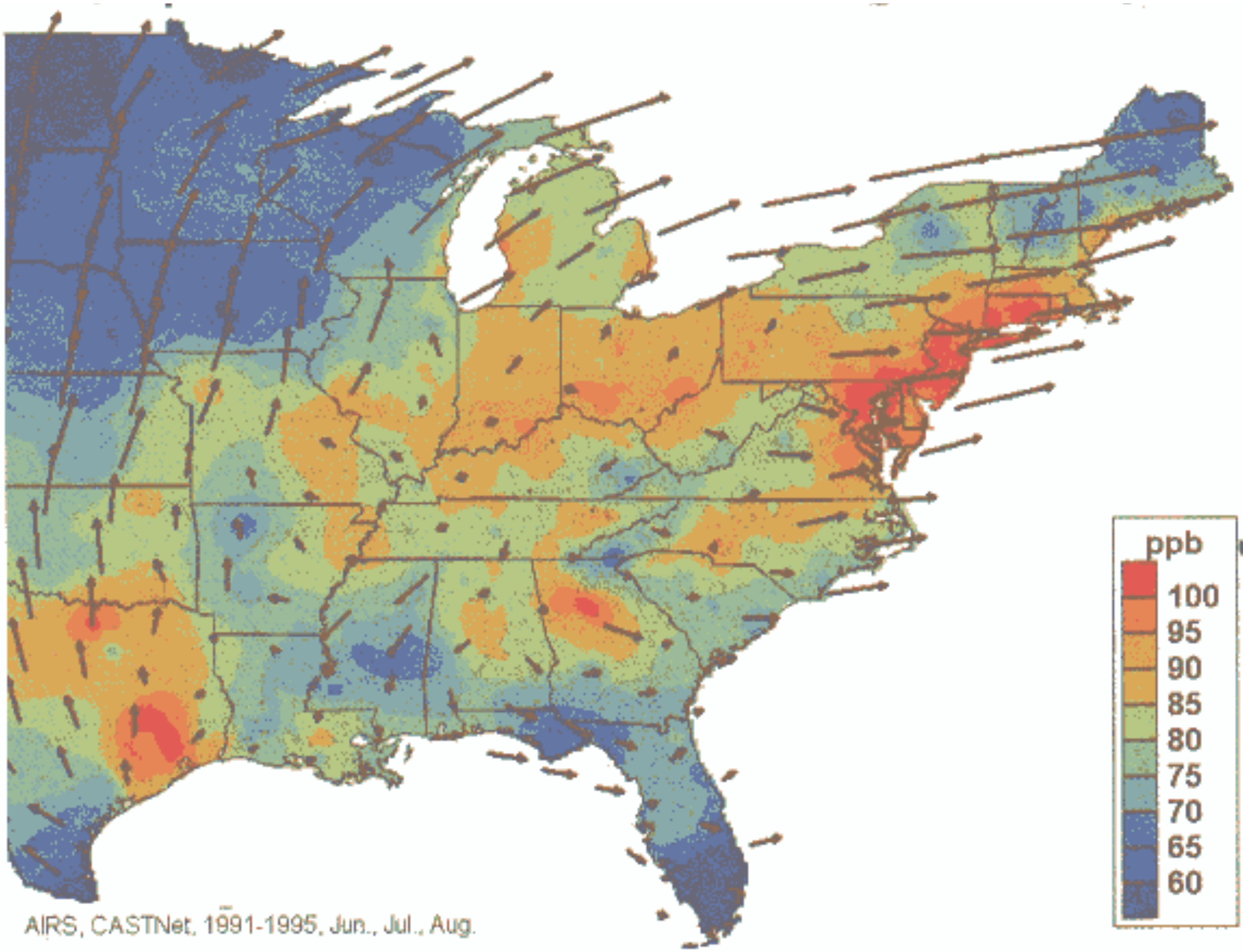
# Surface $O_3$ and Transport

**90th percentile $O_3$ concentrations for summers 1991-1995 and mean 850hPa winds on days when $O_3$ > 90th percentile**

- Large regions with high $O_3$ tend to have low wind speed
  - stagnation enhances impact of local chemistry

- Persistent stagnation and/or poor vertical mixing (LA, Mexico City, Athens) causes the worst air quality

- Air Pollution is not just an urban problem




Slide prepared by J. Thornton UW

# Chemical Production of $O_3$: Main Ingredients

Fossil Fuel Combustion and Use

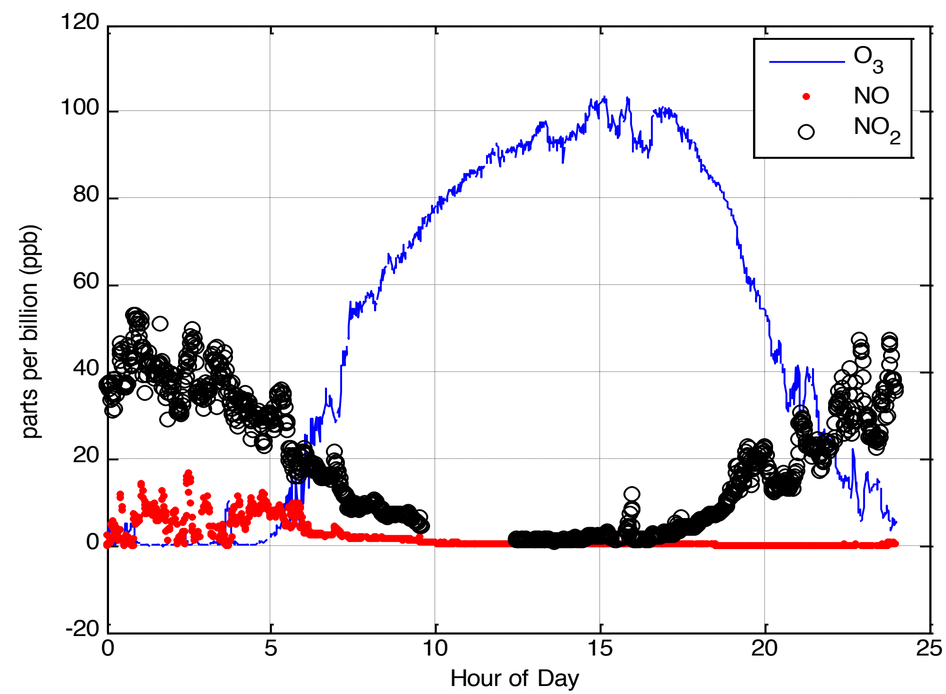
$NO_x$ = NO and/or $NO_2$

VOC = Volatile Organic Compounds

hν = uv-vis radiation

Biogenic Activity

Evolution of $NO_x$ and $O_3$ in Nashville, TN

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