Topic # 14
OZONE DEPLETION IN THE STRATOSPHERE

see pp 75-79 in Class Notes

“[The Ozone Treaty is] the first truly global treaty that offers protection to every single human being.”

~ Mostofa K. Tolba,
Director of the UN Environment Programme

International Day for the Preservation of the Ozone Layer

SEPTEMBER 16th

The United Nations' (UN) International Day for the Preservation of the Ozone Layer is celebrated on September 16 every year. This event commemorates the date of the signing of the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987.

The earth's ozone layer plays an important role in protecting human health and the environment. ©iStockphoto.com/Stephen Strathdee

http://www.timeanddate.com/holidays/un/international-ozone-layer-preservation-day

The real answer:

The ozone hole is:

-- a depletion of ozone in the lower stratosphere

-- that has occurred with increasing severity each spring (since measurements begin in 1970s)

NOTE: the "Key Concepts" are all provided on p 79

OZONE STORY = A very interesting illustration of the scientific process!

The THEORY that the ozone layer in the stratosphere might be damaged by human intervention PRECEDED the actual OBSERVATION of the ozone hole.

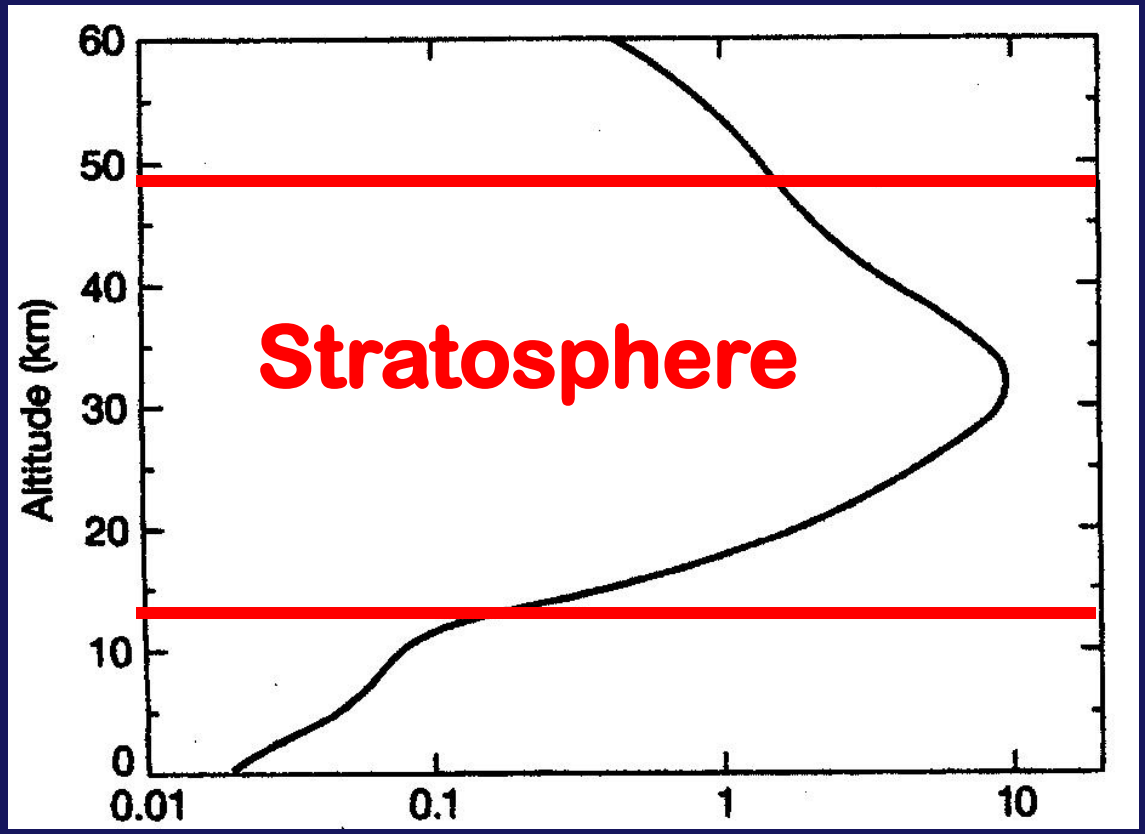
Yet, when the hole WAS observed (via satellite) it was almost "missed" because it wasn't expected . . .

But let's begin with the stratospheric ozone layer itself . . . . . .

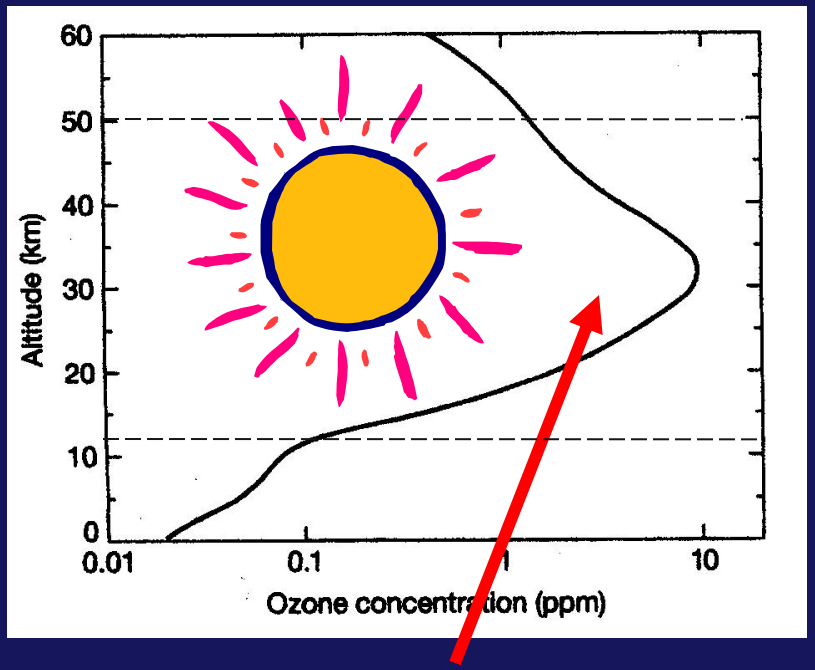
Key Concept

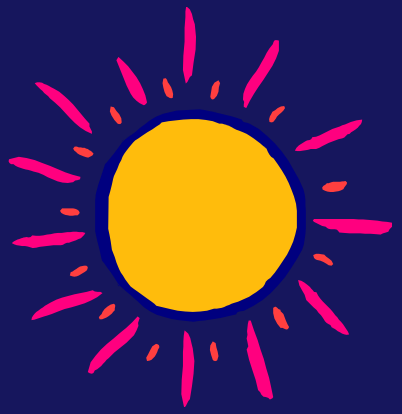
WHERE IS THE OZONE LAYER?

SGC
Fig. 3-11



OZONE: Sources





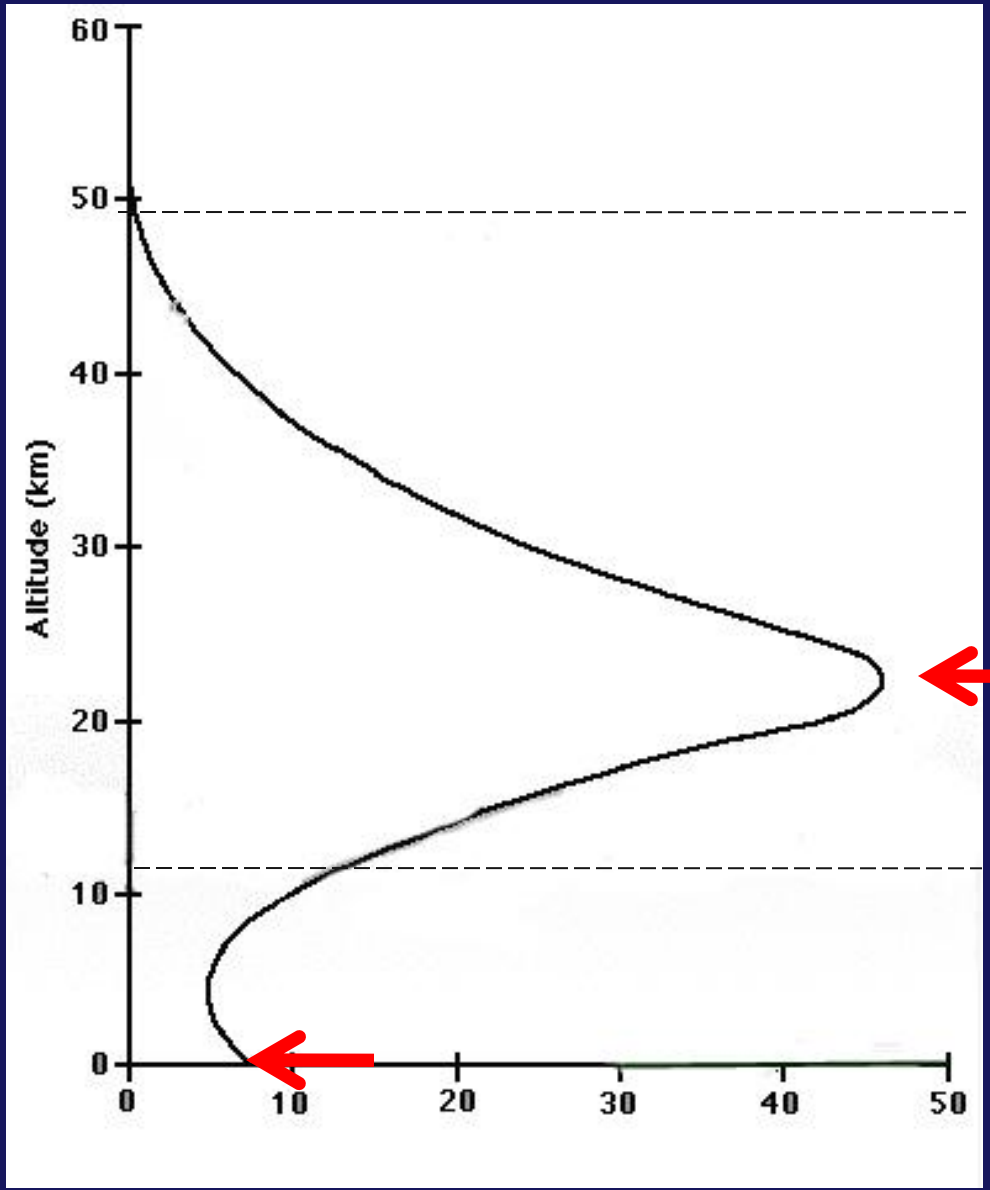
Ozone is produced naturally in photochemical reactions in the stratospheric ozone layer --"good ozone" -- is <u>decreasing</u>!

However, ozone has <u>*increased*</u> in troposphere due to photochemical smog reactions -- "bad ozone"

review

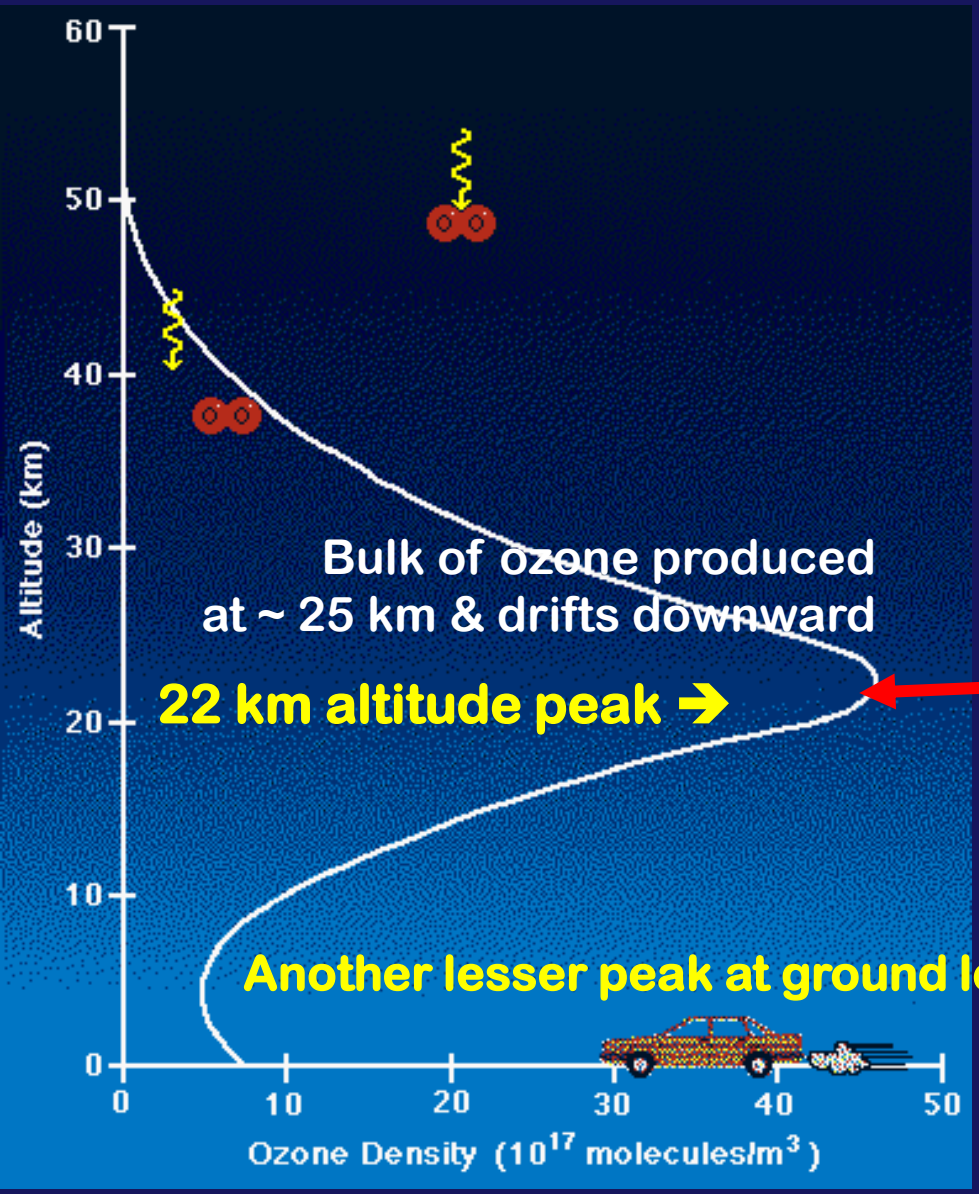
Here's a different version of the figure ➔

Shows 2 peaks, a major peak in O_3 density in the **stratosphere**, a smaller secondary peak in the **lower troposphere**



Ozone Density

(10^{17} molecules / m^3)



First we'll focus on the "GOOD" ozone located in the STRATOSPHERE (the ozone that is being depleted leading to an ozone "hole")

THE OZONE LAYER IN THE STRATOSPHERE -- WHY IT'S THERE

Due to: the natural "Chapman Mechanism"

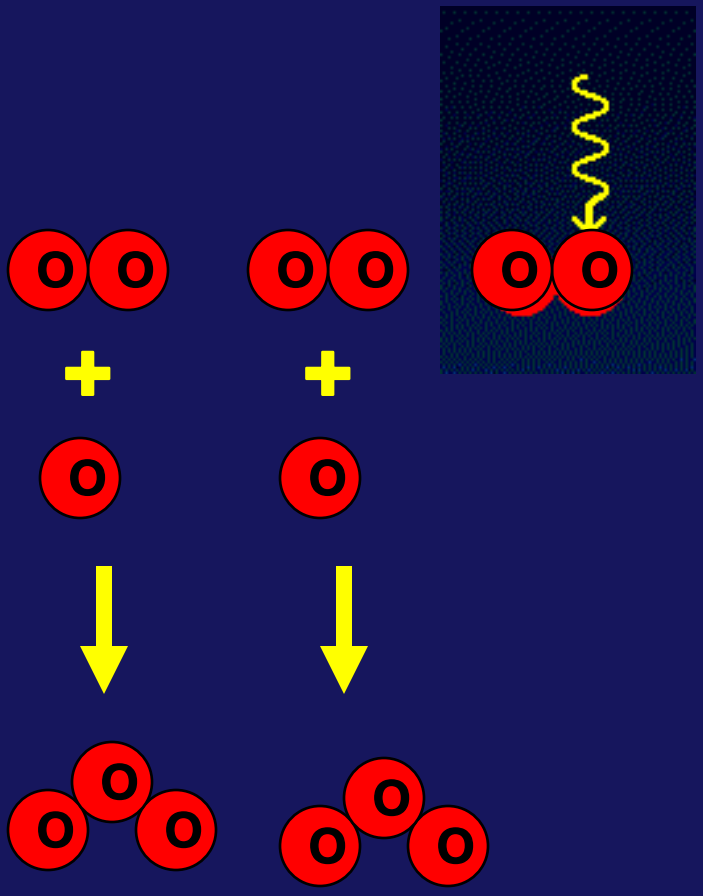
(a series of photochemical reactions)

THE CHAPMAN MECHANISM

(first proposed in 1930s)

- ozone is continuously produced and destroyed
- through **PHOTOCHEMICAL REACTIONS** in the stratosphere
- involves oxygen (O_2), molecular oxygen (O), photons of UV radiation, and OZONE (O_3).

Key Concept



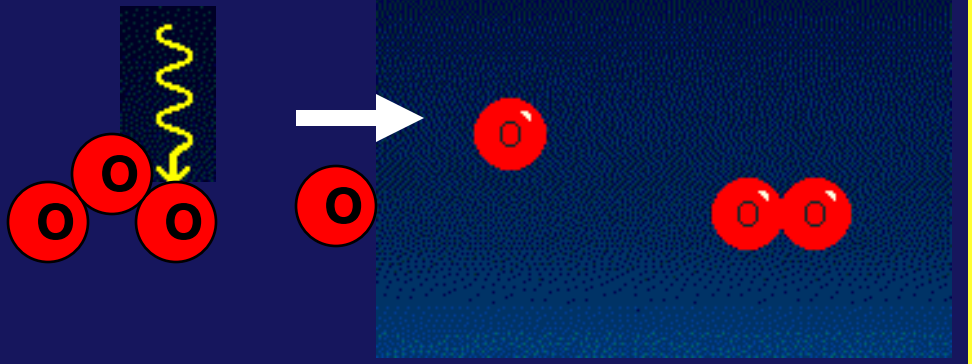
The Chapman Mechanism

Ozone exists in the upper atmosphere as a consequence of photochemical reactions between molecular oxygen and sunlight:

$$O_2 + O_2 + O_2 + \text{sunlight}$$

$$\rightarrow O_2 + O + O + O_2$$

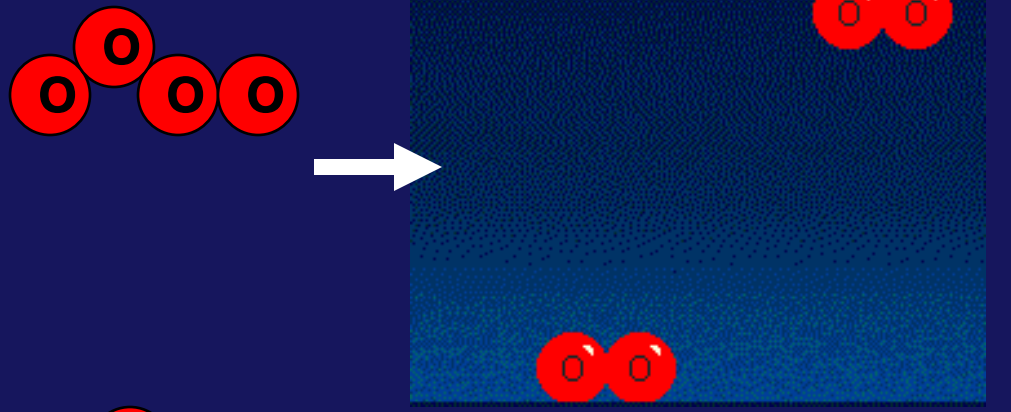
$$\rightarrow O_3 + O_3$$



Ozone is destroyed naturally by reaction with ultraviolet radiation:

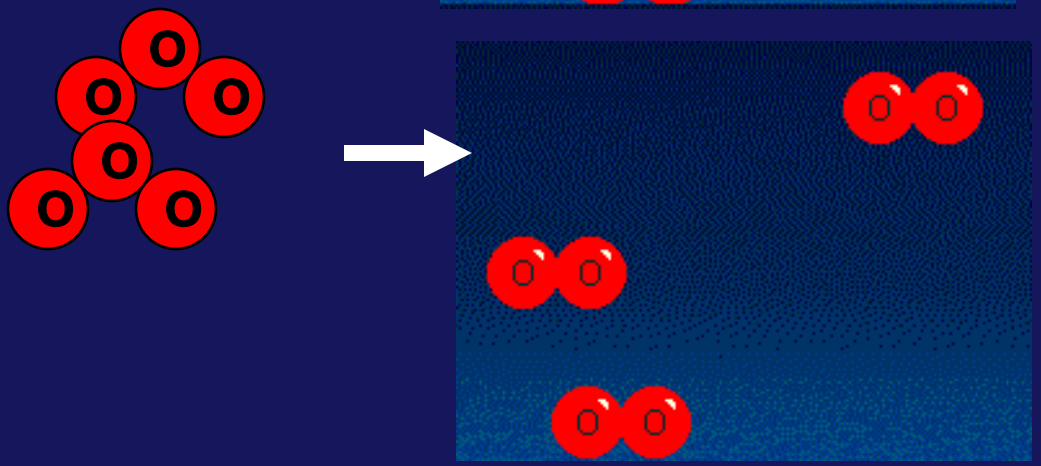
$$O_3 + UV \rightarrow O_2 + O$$

This is part of how the ozone layer protects the earth's surface from ultraviolet radiation.



Ozone is also destroyed naturally by reactions promoted by collisions with atomic oxygen:

$$O_3 + O \rightarrow 2\,O_2$$

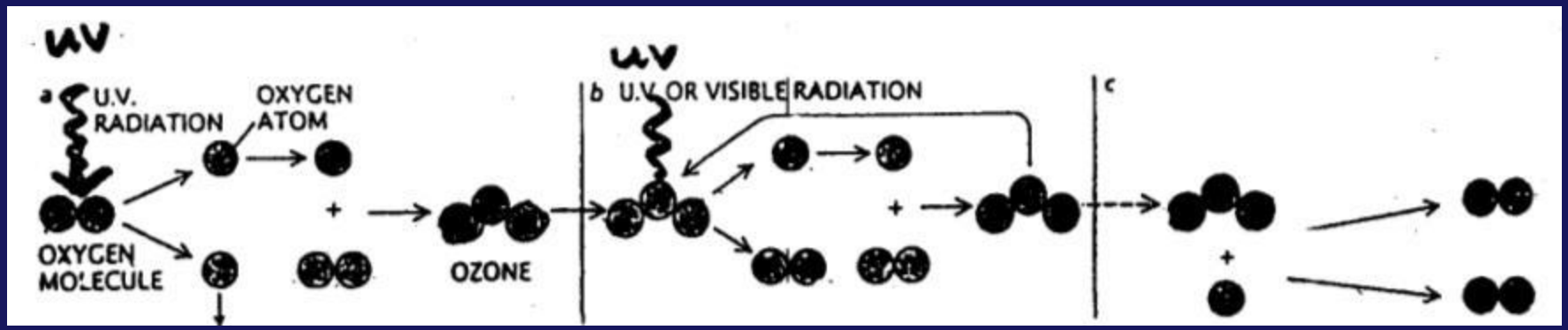


As well as being destroyed by collisions with itself:

$$O_3 + O_3 \rightarrow 3\,O_2$$

The Chapman Mechanism

(another view)



Ozone being formed naturally

Ozone being destroyed naturally

Ozone being formed naturally

Ozone being destroyed naturally

[Go to movie clip]

In theory:

- **a balance of ozone is established over time**

- **prevents much of the harmful UV radiation from reaching the earth's surface.**

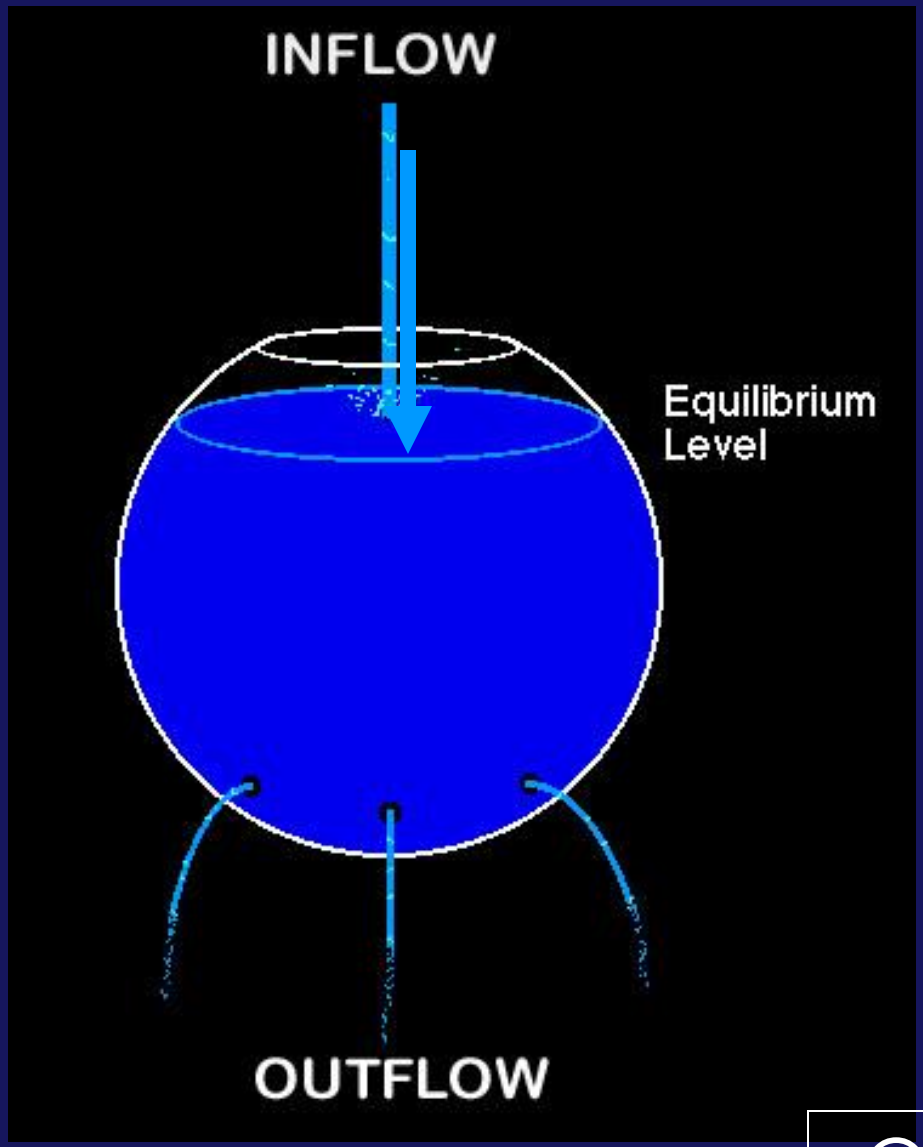
Leads to an "Equilibrium" or "Steady State"

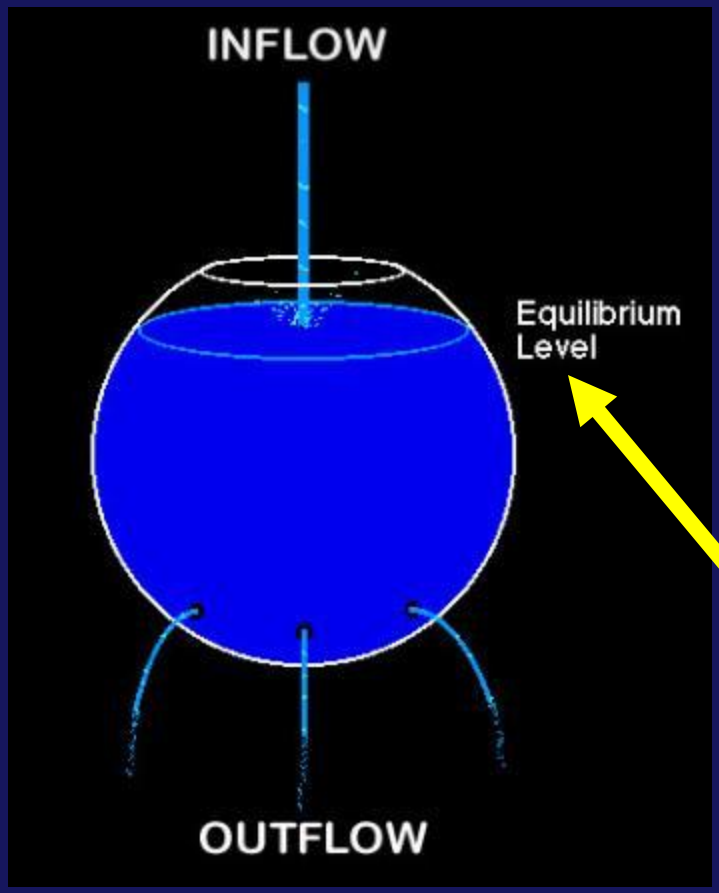
Key Concept

STEADY STATE =

a condition in which the STATE of a system component (e.g. reservoir)

is CONSTANT over time.





Steady state can be achieved in a reservoir:

a) if there are no inflows or outflows, *or*

b) if the rate of inflow = the rate of outflow.

Any imbalance in these rates leads to a change in the level of the reservoir.

FLOW DIAGRAM OF A STEADY STATE

Inflow

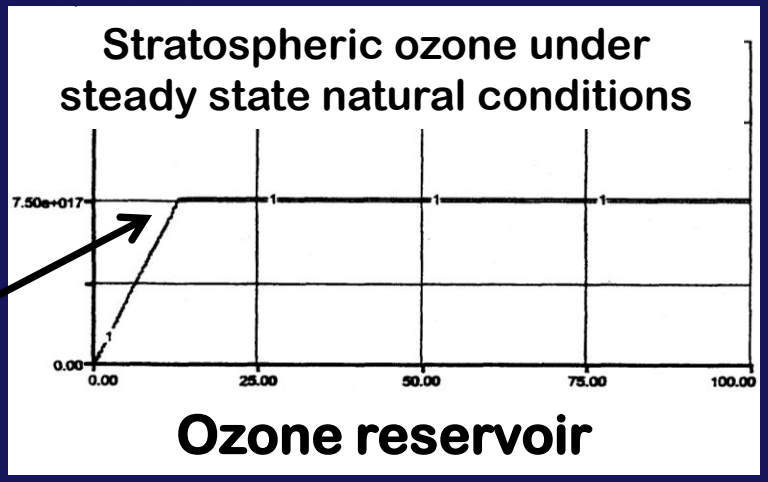
Ozone being formed via natural Chapman mechanism

Reservoir of STRATOSPHERIC OZONE

Outflow

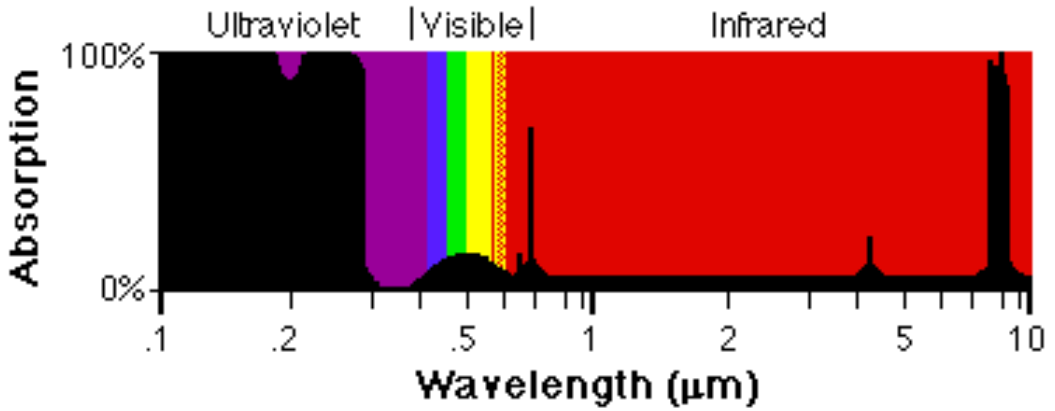
Ozone being destroyed via natural Chapman mechanism

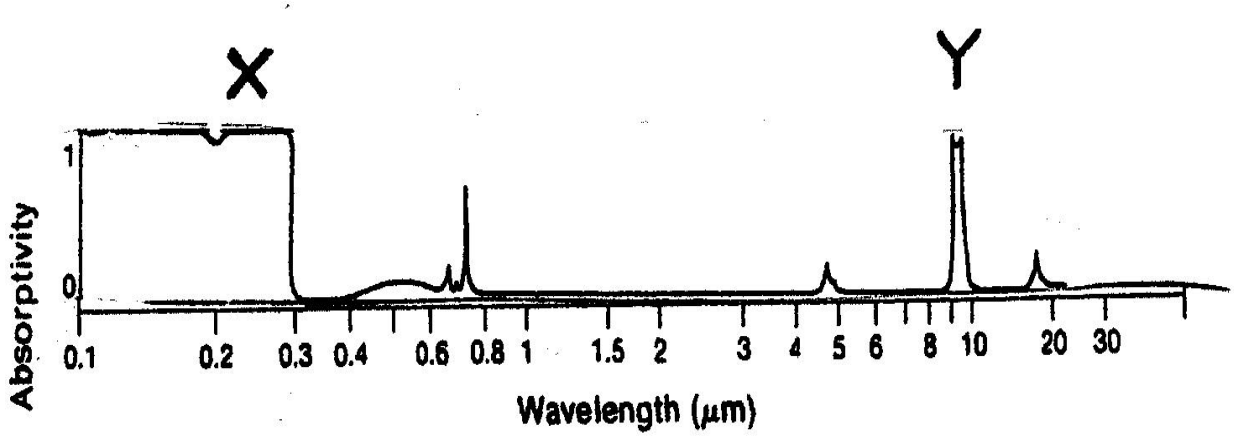
After an initial period of adjustment a steady state is reached ➔ as a horizontal line



Review: Why stratospheric ozone is "Good":

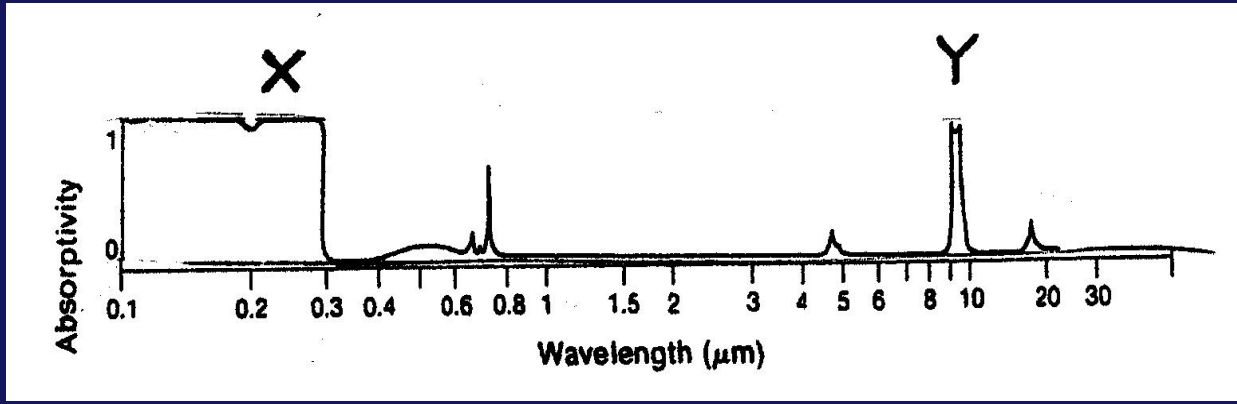
Black areas = radiation absorbed





Ozone has the property of being a very strong absorber of ultraviolet radiation → **nearly total absorption of wavelengths less than 0.3 µm**

← remember this figure?

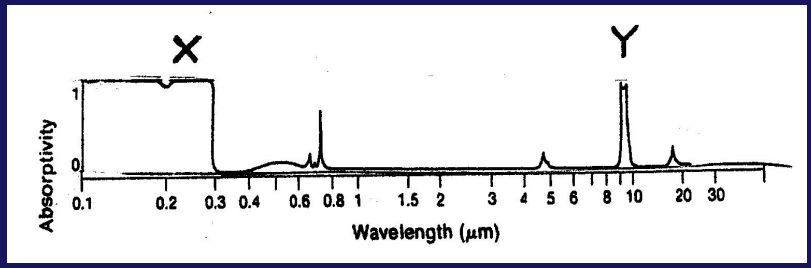


Circle the CORRECT completion to this sentence:

The global change issue usually referred to as Stratospheric Ozone Depletion is related to the part of the absorption curve that is labeled ____.

X or Y

Ok, X is right, but Why?



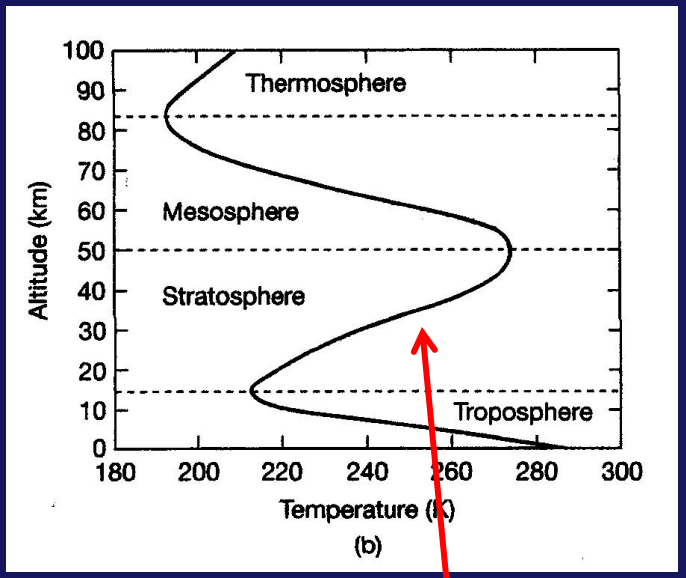
1. . . . because X represents UV radiation being absorbed -- hence if ozone is depleted, MORE ultraviolet radiation will reach the Earth's surface.

2. . . . because X represents *terrestrial longwave* radiation being absorbed -- and hence serves as a catalyst in the Chapman mechanism.

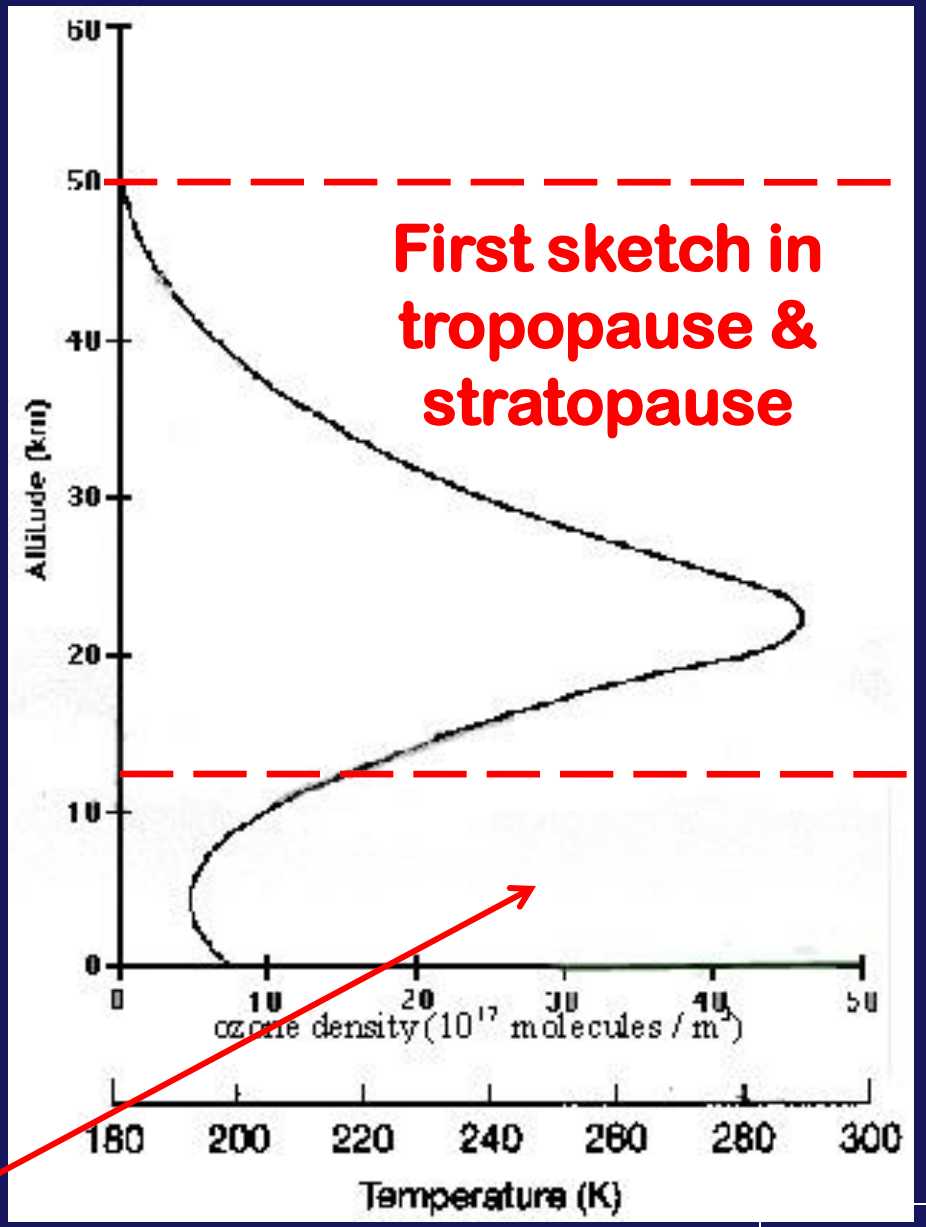
3. . . .because X represents *easy transmission of wavelengths of terrestrial longwave radiation out to space* which then disappear through the "atmospheric window" also known as the ozone hole.

p. 38 in Class Notes:

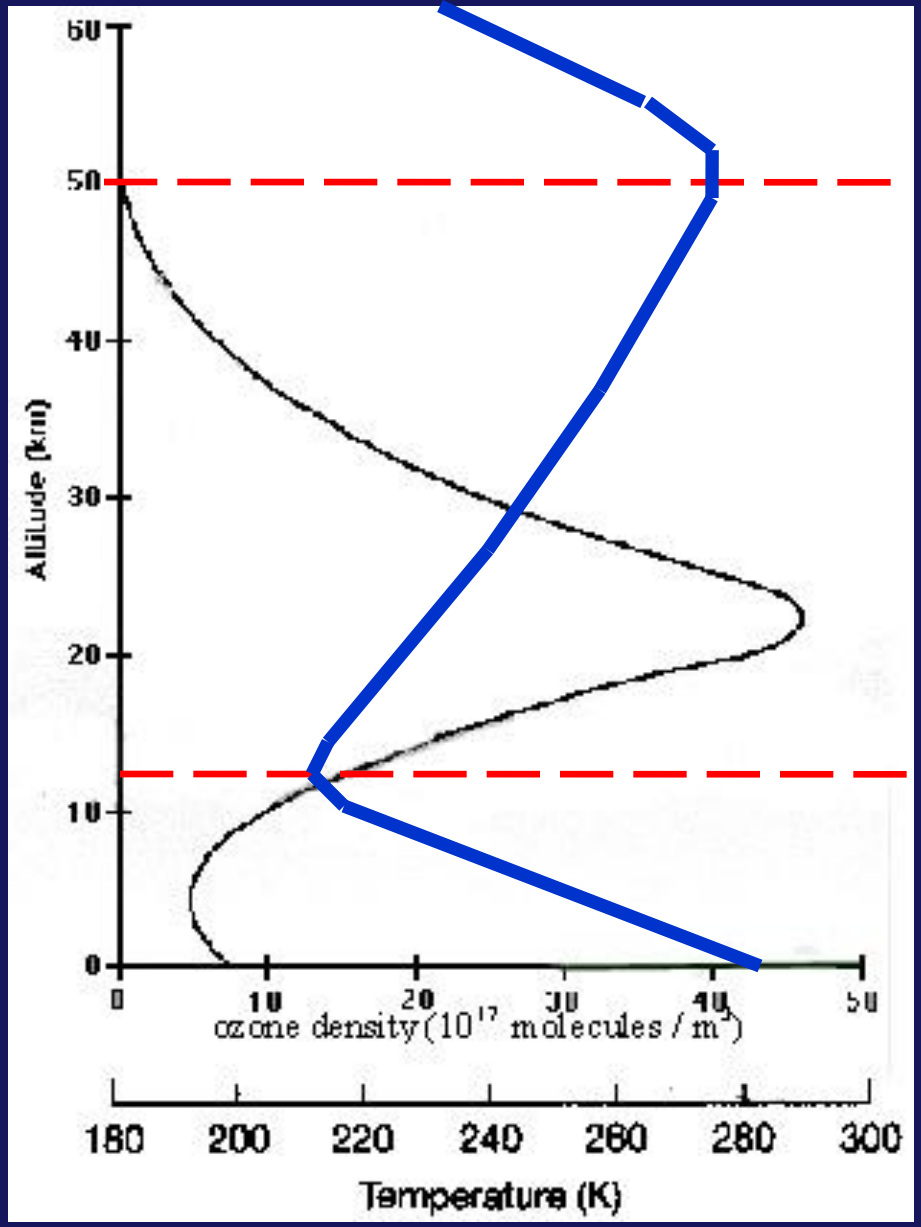
Temperature graph



Ozone Density graph



Now roughly sketch the <u>temperature</u> line from this graph onto the ozone graph



TEMPERATURE

[increases / decreases]

with increasing altitude in the stratosphere

WHY???

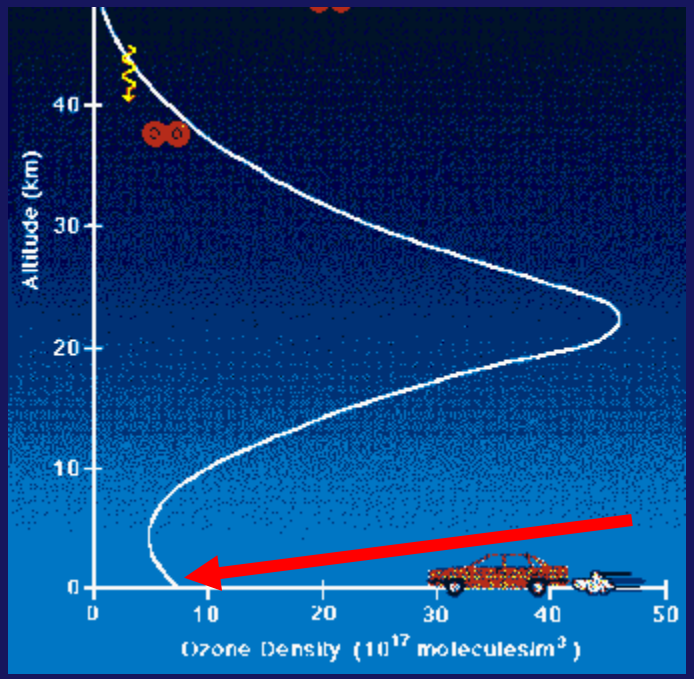
Why is there an increase in temperature with altitude in the STRATOSPHERE?

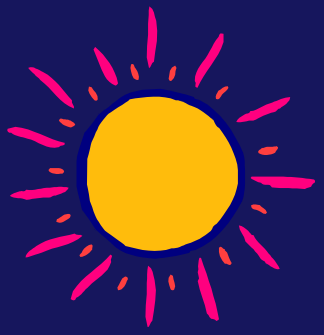
1. It is the **closest layer to the sun,** hence it is closest to the solar "heat source."

2. It receives **large amounts of UV radiation** from the sun PLUS it has a **high concentration of ozone** to absorb this UV.

3. It is the layer which **contains most of the GH gases that absorb IR radiation** emitted by the Earth's surface.

What about the "BAD" ozone located in the troposphere?





Ozone has *increased* in troposphere due to photochemical smog reactions ➔ "bad ozone"

HEALTH AND ENVIRONMENTAL EFFECTS OF GROUND-LEVEL OZONE

Why are We Concerned about Ground-Level Ozone?

➔ **Ozone is the prime ingredient of smog in our cities and other areas of the country.**

http://www.epa.gov/ttn/oarpg/naaqsfin/o3health.html

➔ When inhaled, even at very low levels, ozone can:

- cause acute respiratory problems
- aggravate asthma
- cause significant temporary decreases in lung capacity
- cause inflammation of lung tissue
- lead to hospital admissions & emergency room visits
- impair the body's immune system defenses

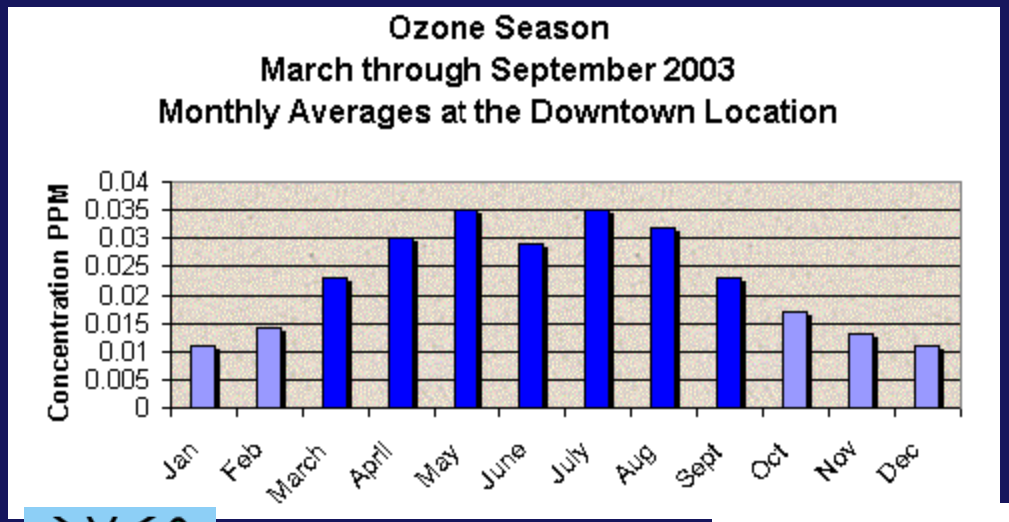
http://www.epa.gov/ttn/oarpg/naaqsfin/o3health.html

"BAD" OZONE

Ground-level ozone is a form of pollution created when:

nitrogen oxides in auto emissions
+ **hydrocarbons** from plant matter
+ **solvents** and **gasoline fumes**

. . . . mix and bake in stagnant heat and sunlight!



Tucson data

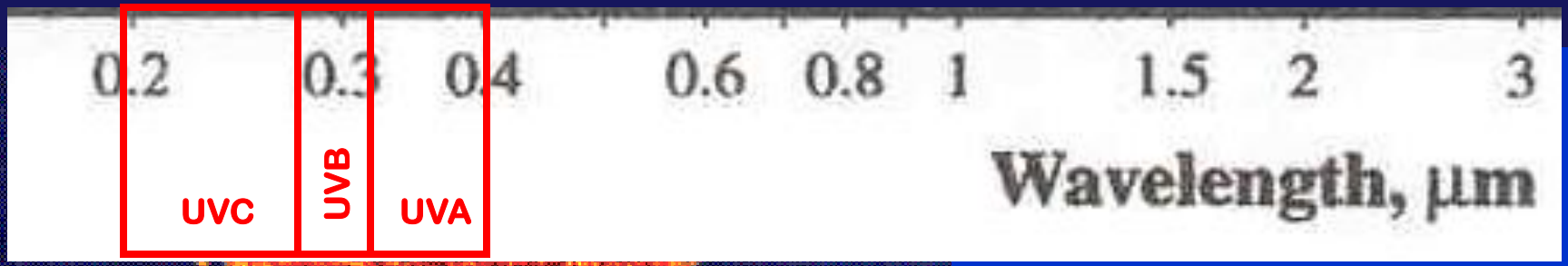
AIR INFO NOW

http://www.airinfonow.org/html/ozoneMC.html

☺

ANOTHER LINK TO EVERYDAY LIFE:

SUN SAFETY!



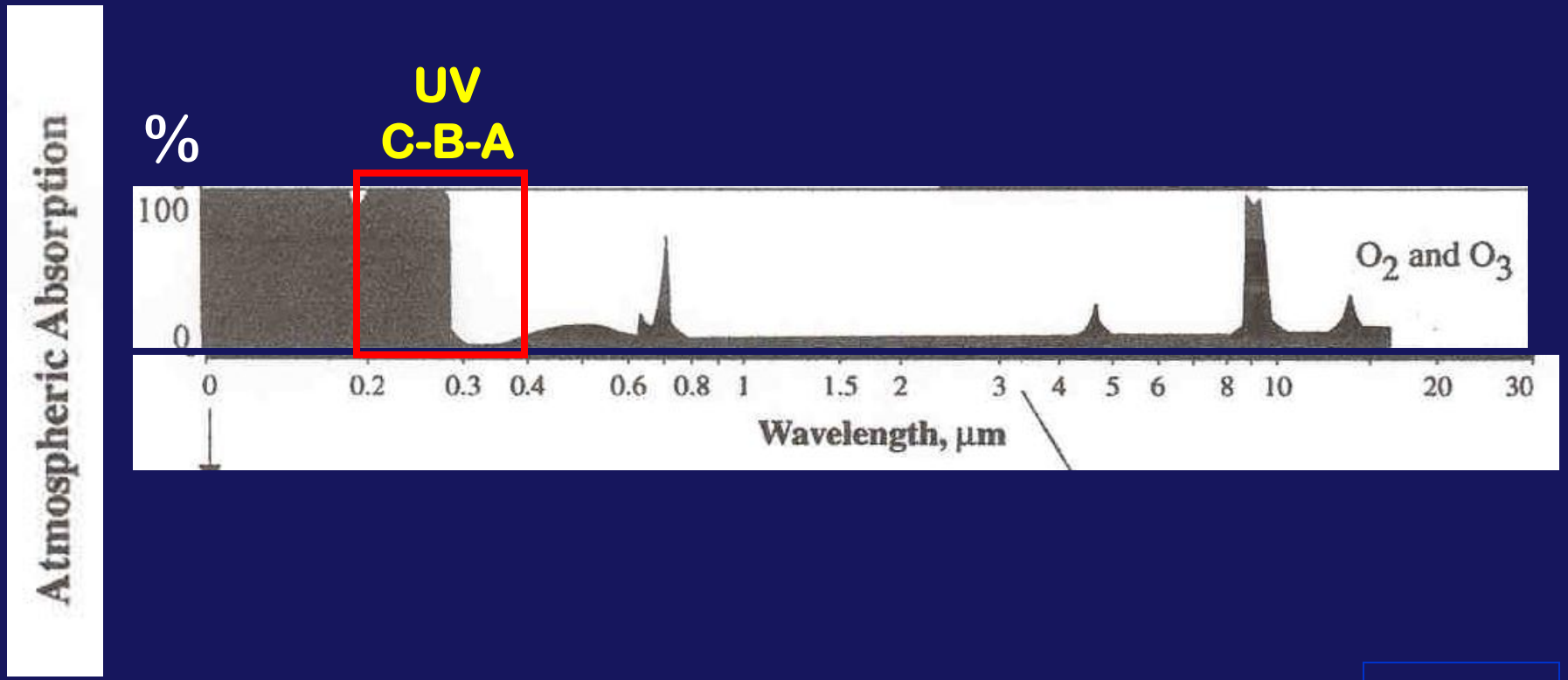
Turn to p 75

UVA = .32 to .4 µm
(once thought to be relatively harmless, BUT causes wrinkles, premature aging and associated sun-related skin damage; new research indicates possible skin cancer link)

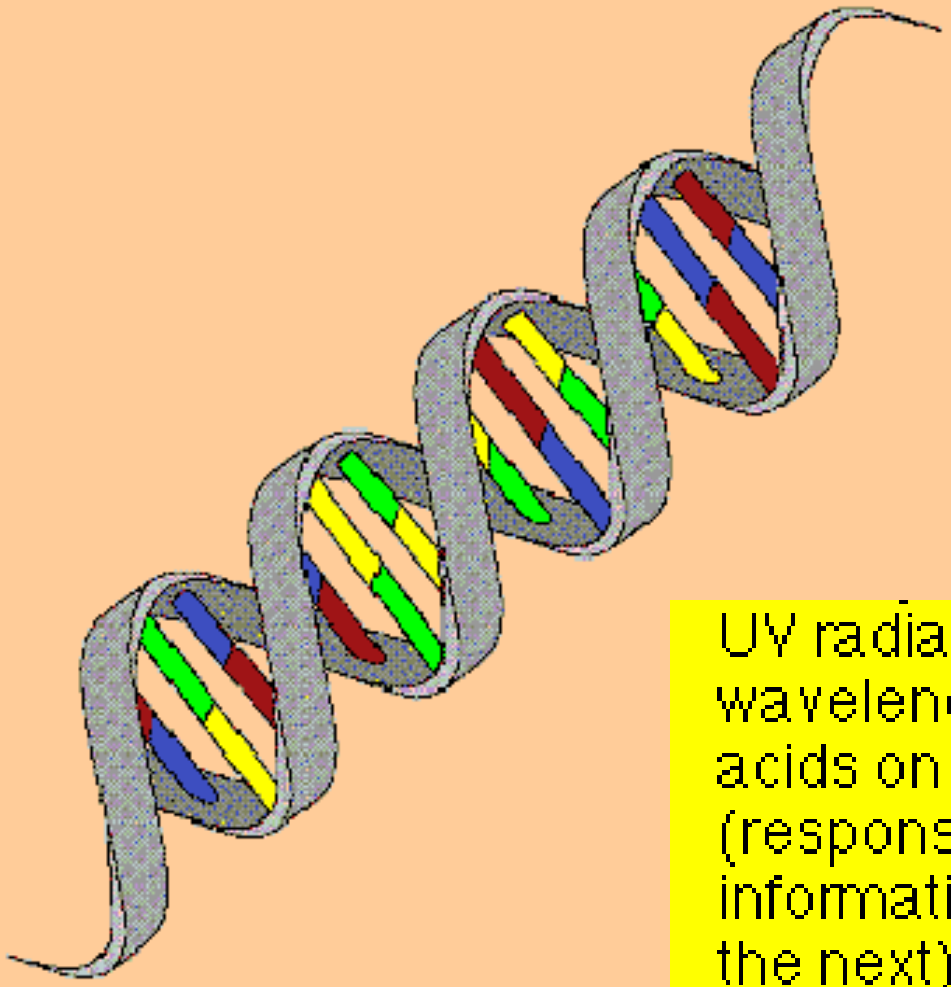
UVB = .29 to .32 µm
(harmful, sunburn, skin cancer)

UVC = .20 to .29 µm
(extremely harmful, damages DNA)

OZONE / Oxygen Absorption Curve



UV-C wavelengths are the most harmful



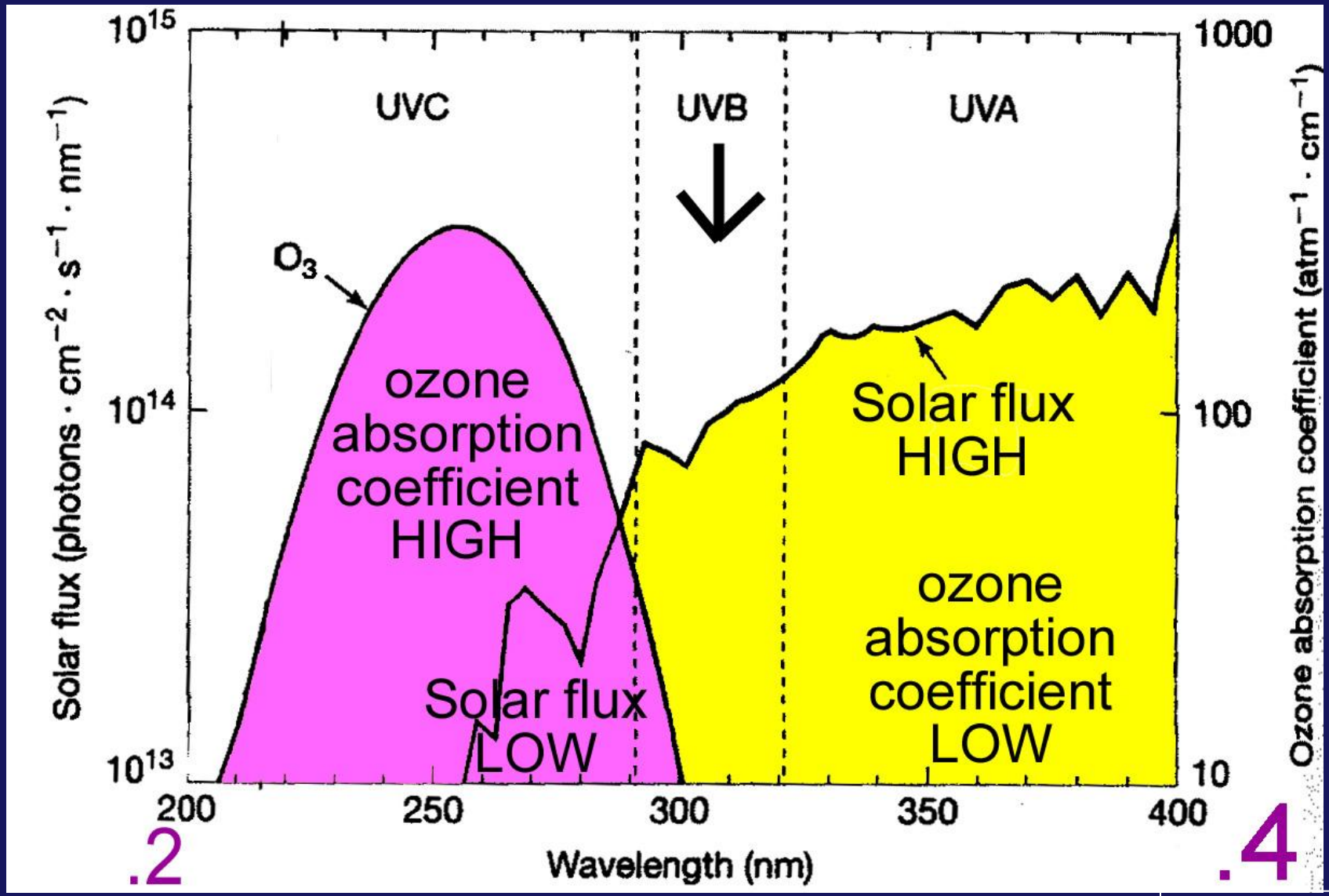
Segment of a DNA Molecule

UV radiation, at ultraviolet wavelengths of about .26 µm, the acids on the DNA molecule (responsible for transmitting genetic information from one generation to the next) are destroyed.

Wavelength Range	Name	Biological Effect
.32 to .4 μm (320-400 nm)	**UVA** **(SPF doesn't rate UVA protection!)**	once thought to be relatively harmless, BUT causes wrinkles, premature aging and associated sun-related skin damage; new research indicates possible skin cancer link
.29 to .32 μm (290-320 nm)	**UVB** **(see SPF for protection)**	harmful, causes sunburn, skin cancer, and other disorders
.20 to .29 μm (200 - 290 nm)	**UVC** **(almost completely absorbed by O3)**	extremely harmful, damages DNA -- but almost completely absorbed by ozone

p 75

OZONE absorbs harmful UVC & most harmful UVB



GC Savvy Link : Sunscreen Topic
The Skin Care Scoop

http://fp.arizona.edu/kkh/nats101gc/sun_essentials.htm

Updated table:

UV wavelength bands	UVC	UVB	UVA
wavelength band range in nanometers according to IGC, Table 17-1 p 344	200-290 (100-280 in other sources)	290-320 (280-315 in other sources)	320-400 (315-400 in other sources)
Padimate O, 290-315 nanometers		(X)	
Benzophenones, 250-350 nanometers	(X)	X	(X)
Octyl methoxycinnamate, 290-320 nanometers		X	
Avobenzone, 320-400 nanometers			XX
Oxybenzone 270 to 350 nanometers	(X)	X	(X)
Titanium dioxide, 290-700 nanometers		X	XX
Zinc oxide, 290-700 nanometers		X	XX
NEW! Ecamsule (Mexoryl SX) *** max absorption 345 nm		X	XX

X means the ingredient protects over the entire band,
(X) means the ingredient protects over part of the band
XX means the ingredient protects over the longer wavelength UVA band, now known to be harmful

Check the active ingredients:

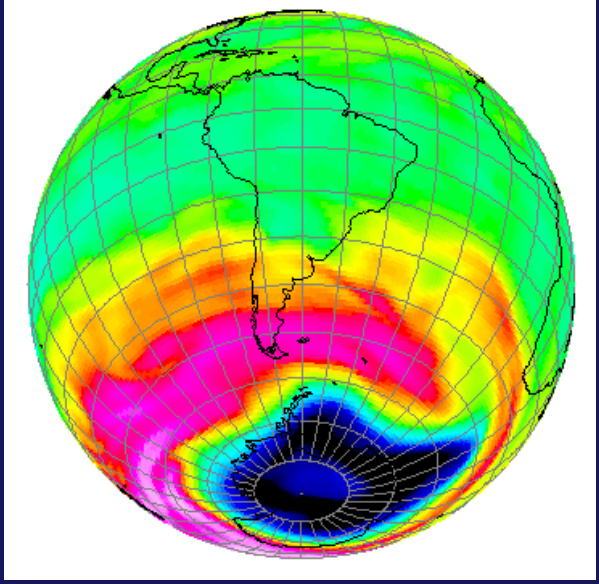
- **titanium dioxide**
- **zinc oxide**
- **avobenzone** (also called butyl methoxydibenzoylmethane)
- Ecamsule (mexoryl sx)

are the KEY ingredients authorized for use in U.S. products that protect you from the entire UVA spectrum.

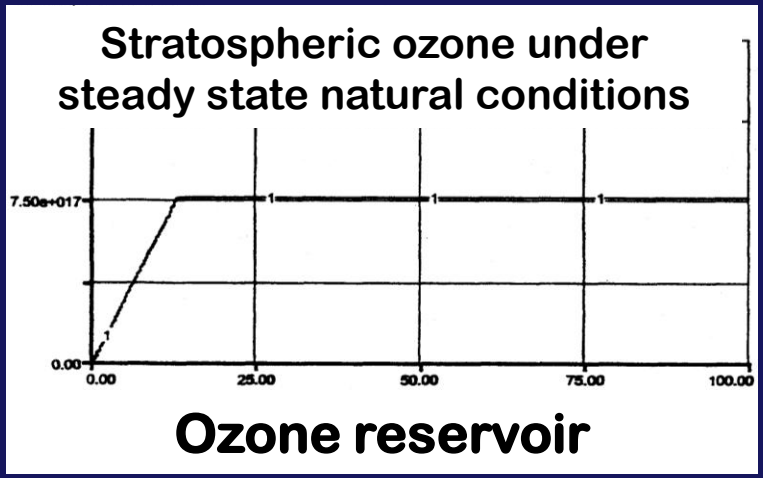
Therefore, if one of those isn't listed as an active ingredient on the label, the product should not be used for sun protection by anyone!

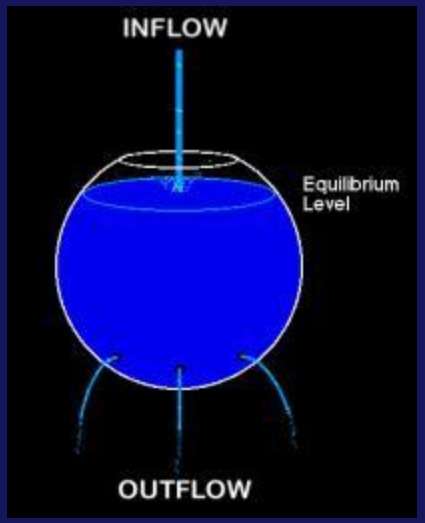
NEXT:

THE DESTRUCTION OF STRATOSPHERIC OZONE



The Chapman Mechansim "balance" is being disrupted by the introduction of CFC's and other similar gases into the stratosphere:





> CFCs are photo-dissociated into **FREE CHLORINE ATOMS (Cl)** and other molecular fragments by UV rays

> **Chlorine** (and other gases such as Nitric oxide, NO) act as **catalysts** in ozone loss reactions

Key Concept

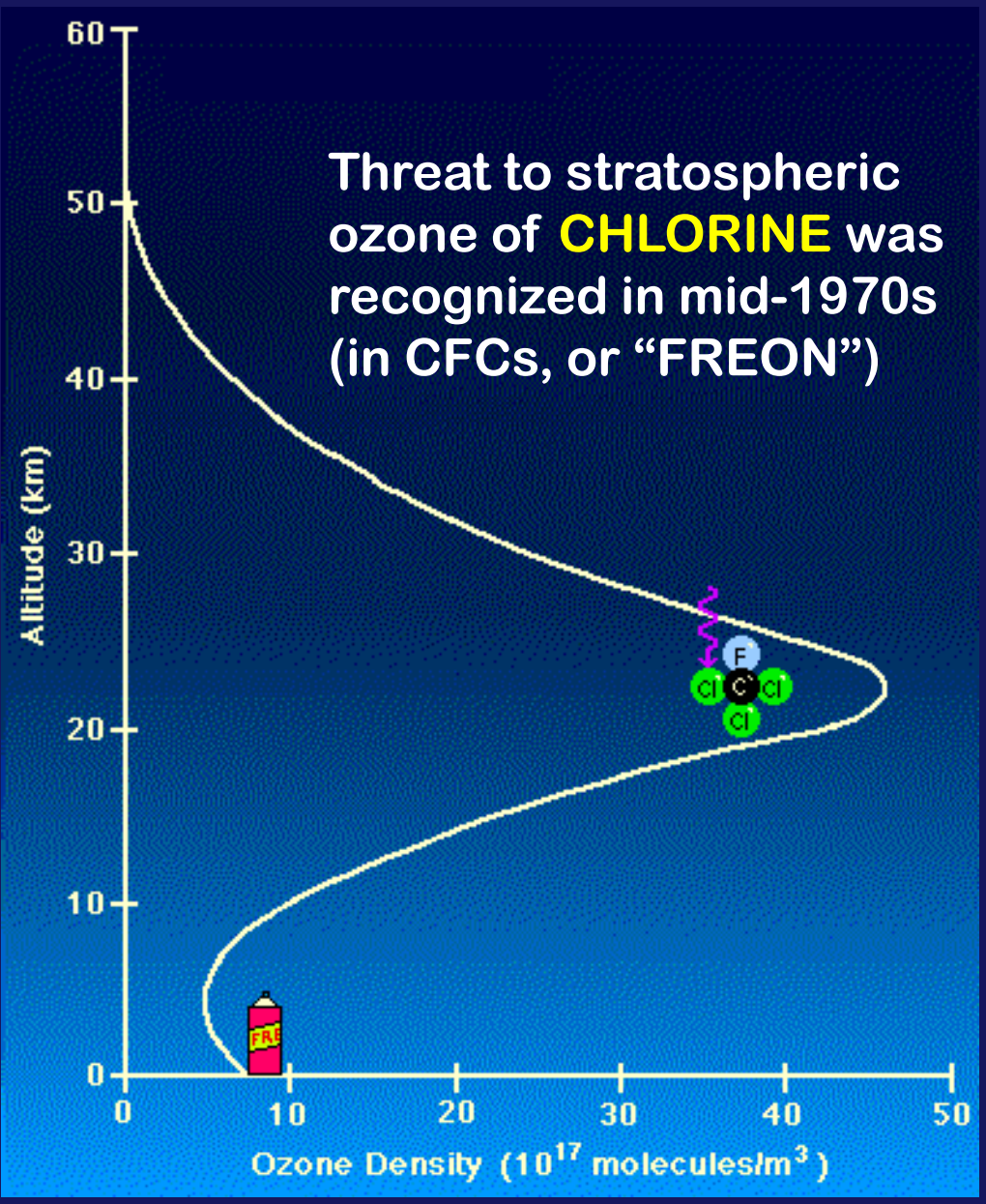
CATALYST =

A compound that increases the rate of a chemical reaction and is itself unchanged by the reaction

Through chemical reactions:

- **the chlorine removes ozone from the stratosphere**
- **and also frees more chlorine atoms to begin the process all over again**

Key Concept



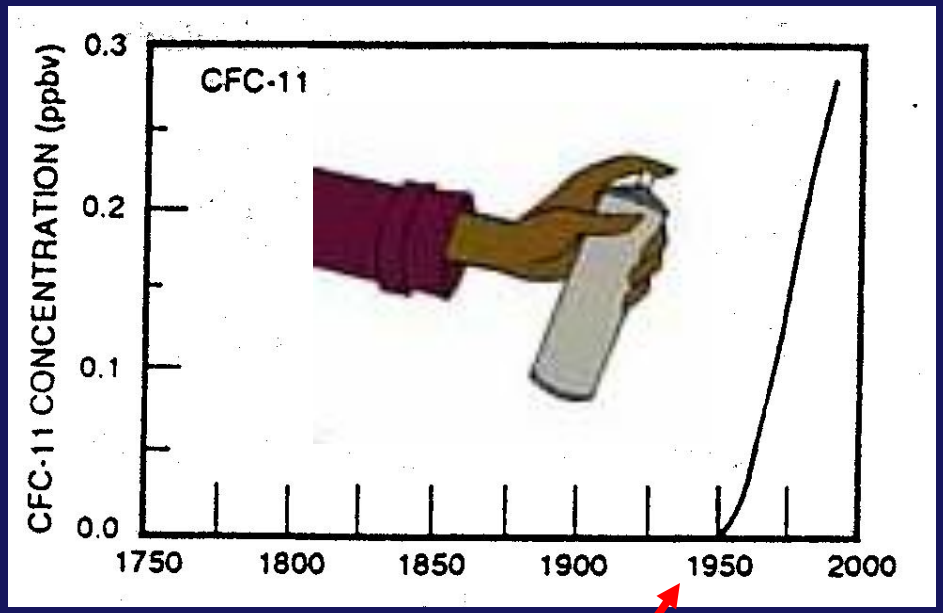
CFC compounds

Chlorofluorocarbons

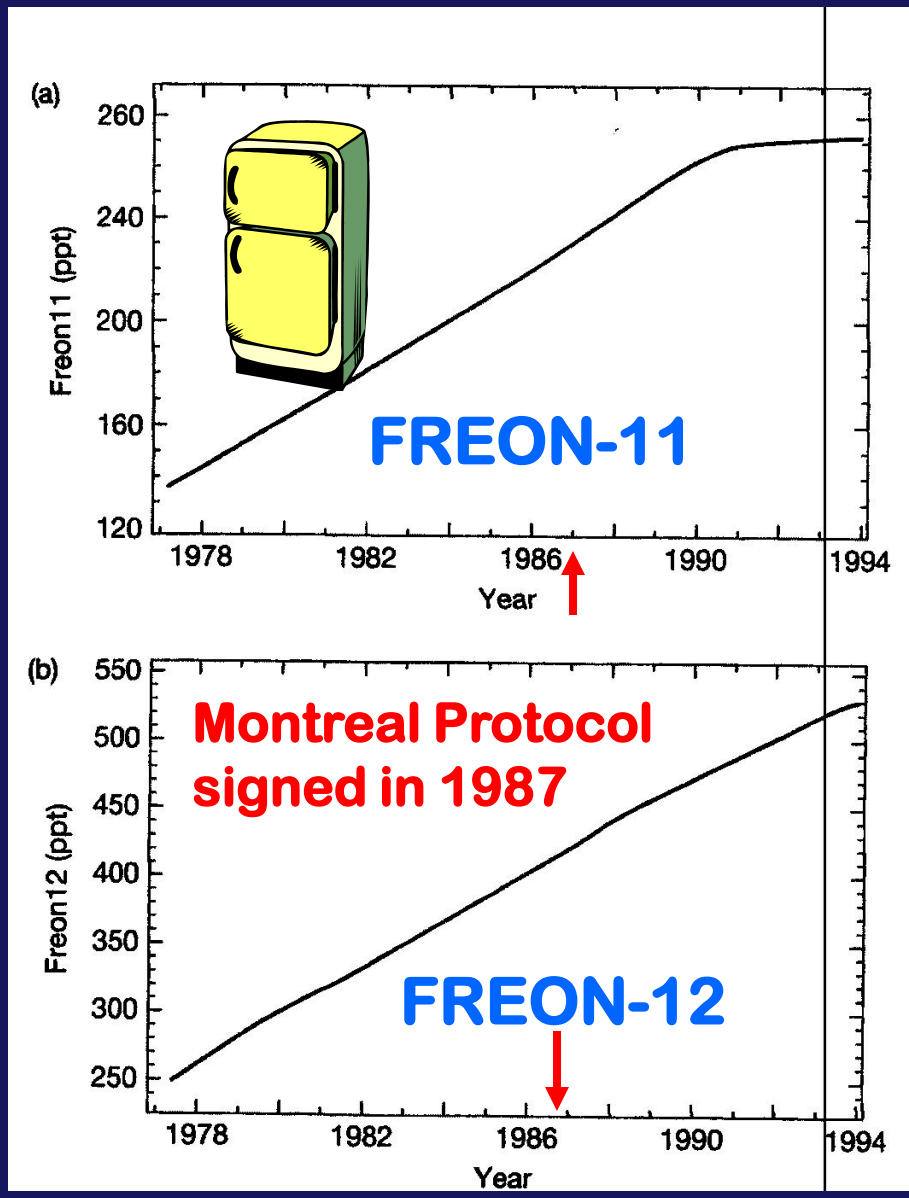
are unreactive at Earth's surface,

but if they get into the stratosphere, they can be broken down by high energy UV radiation ➔ leads to release of highly reactive **CHLORINE atoms (Cl)**

CFCs: Trends



Human-made -- didn't exist before 1950!



review

CFC's & the CHLORINE CATALYST

A single chlorine atom may destroy hundreds of thousands of ozone molecules during its residence in the stratosphere!

[Go to movie clip]

This chemical theory of ozone destruction by CFC's was first proposed in 1974 – but no observations existed!

(Atmospheric chemists Crutzen, Molina, Rowland were later given Nobel prize for this theory)

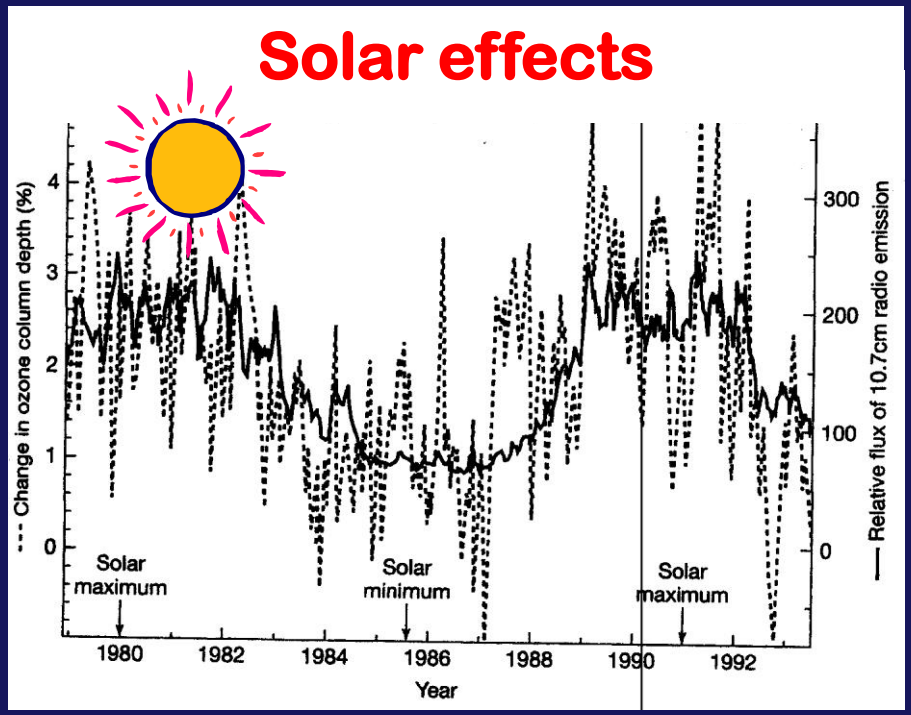
Key Concept

Other theories to explain the hole have included:

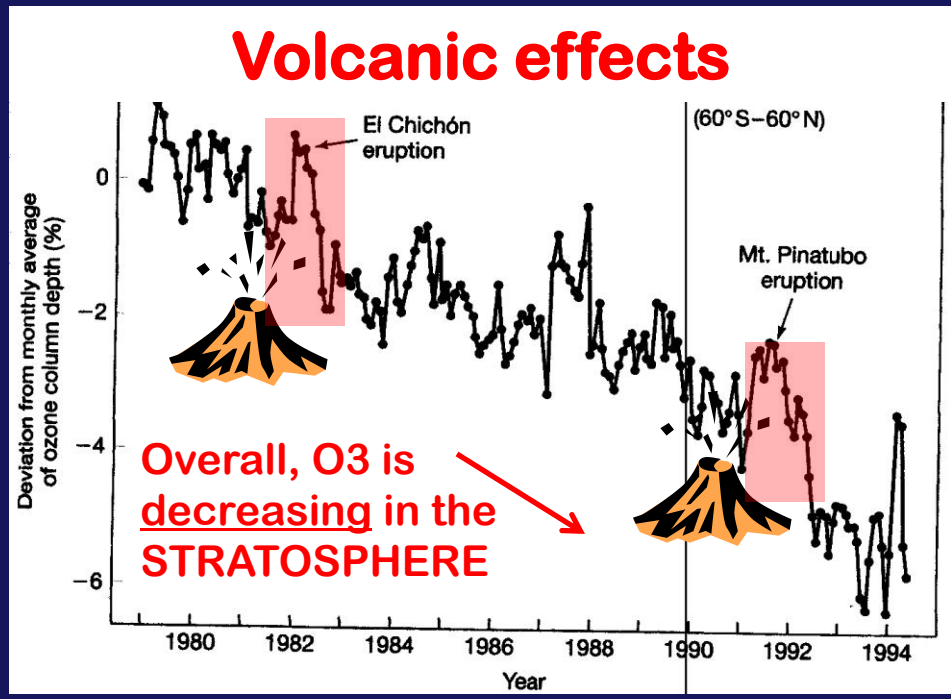
- solar variability (sunspot cycle)
- dynamical air motion
- volcanic eruptions

Key Concept

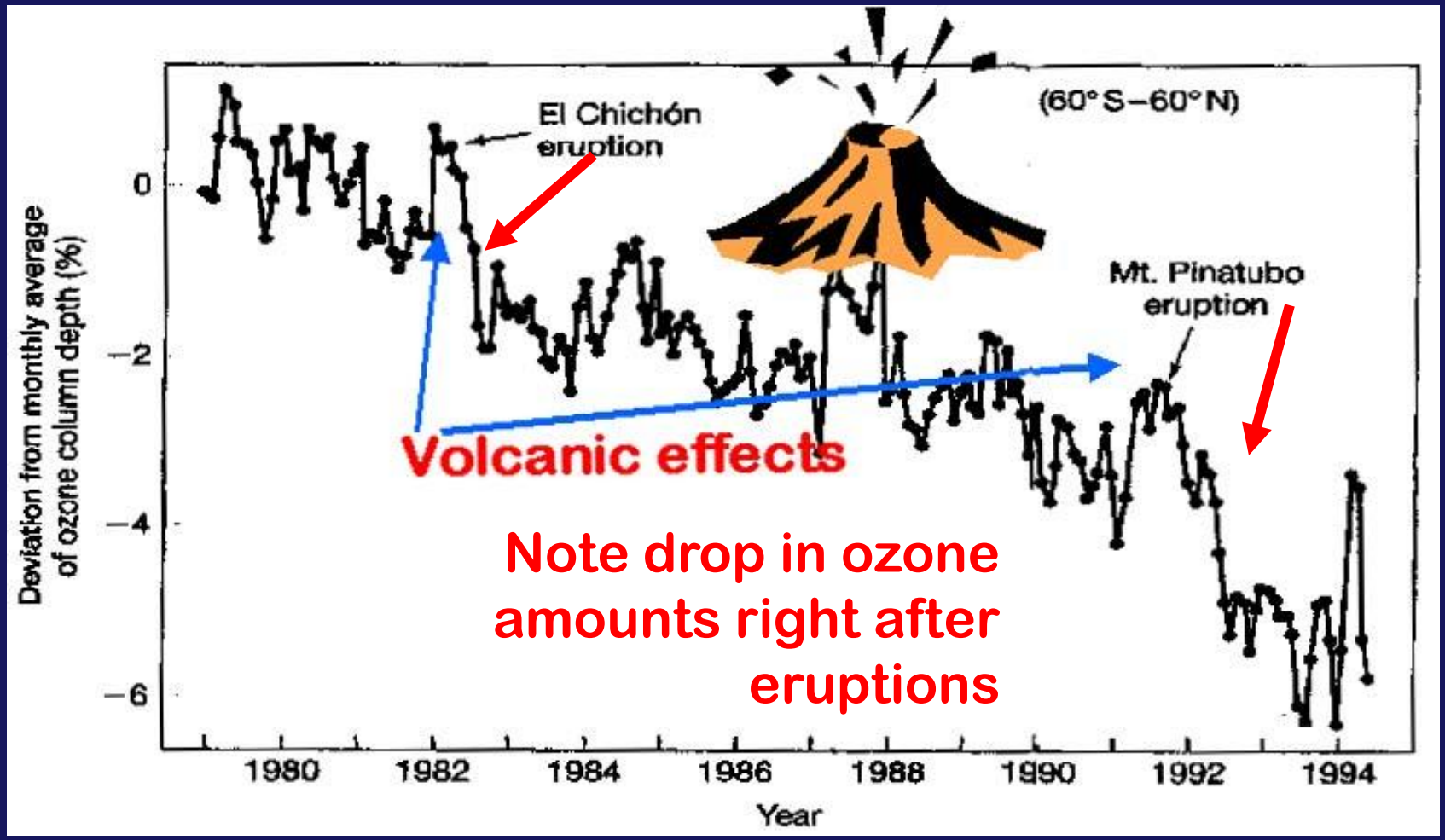
Solar effects



Volcanic effects



OZONE & ERUPTIONS



Stratospheric ozone is destroyed by photochemical reactions that take place on the surfaces of the sulfate aerosols

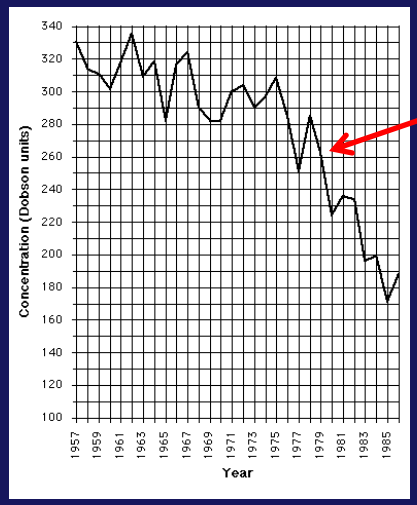
DISCOVERY OF THE OZONE HOLE:

"A Misadventure of Science?"

CHAPTER 1

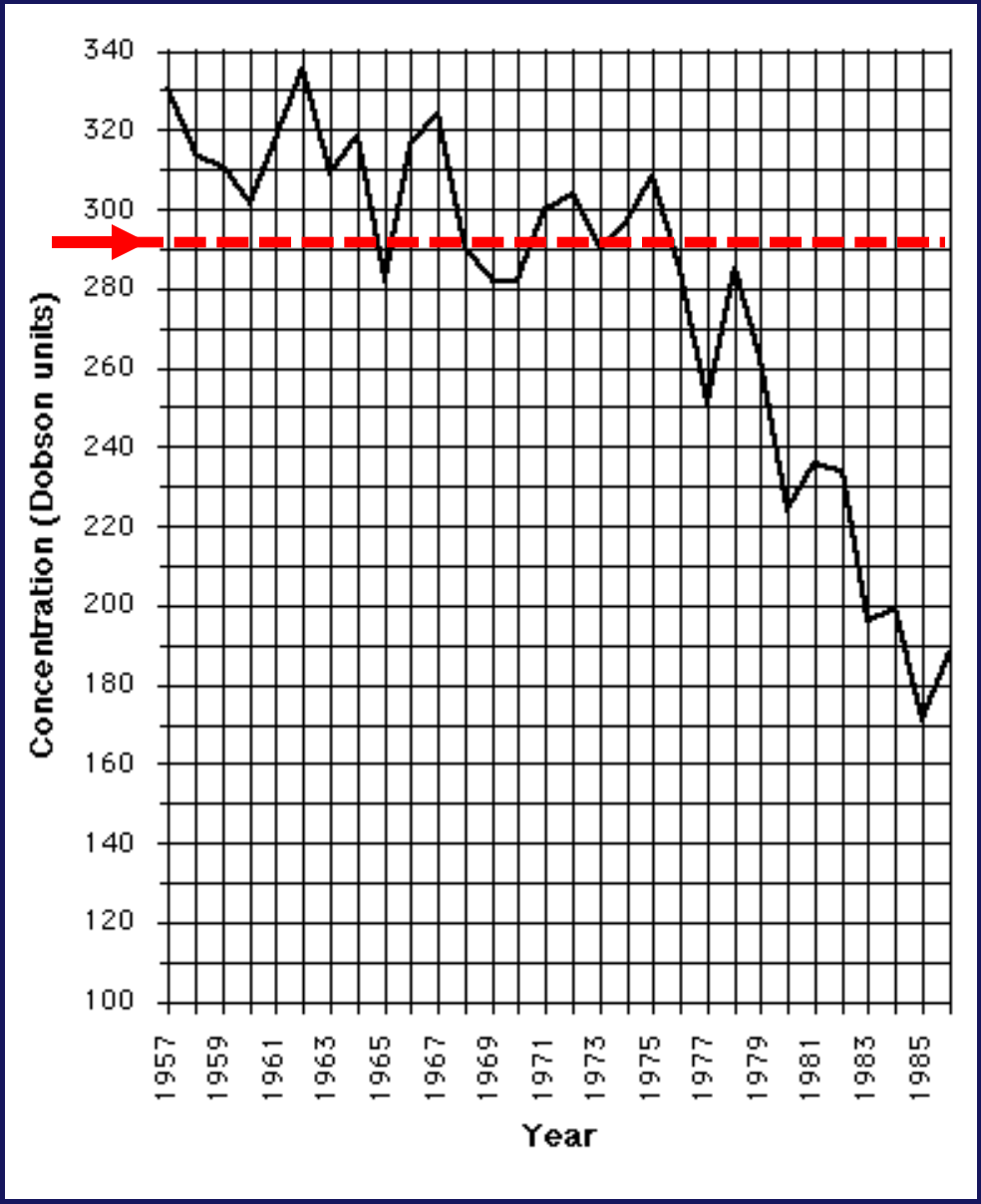
- **Ground-based** ozone measurements since **1956**. (British survey team)

- They observed a new trend of decreasing ozone concentrations beginning in **1977**



- Didn't believe their measurements & delayed publication for several years while rechecking data & instruments.

Finally published in **1985**; greeted with skepticism!



Declining OZONE CONCENTRATIONS

(in Dobson units)

(over Antarctica)

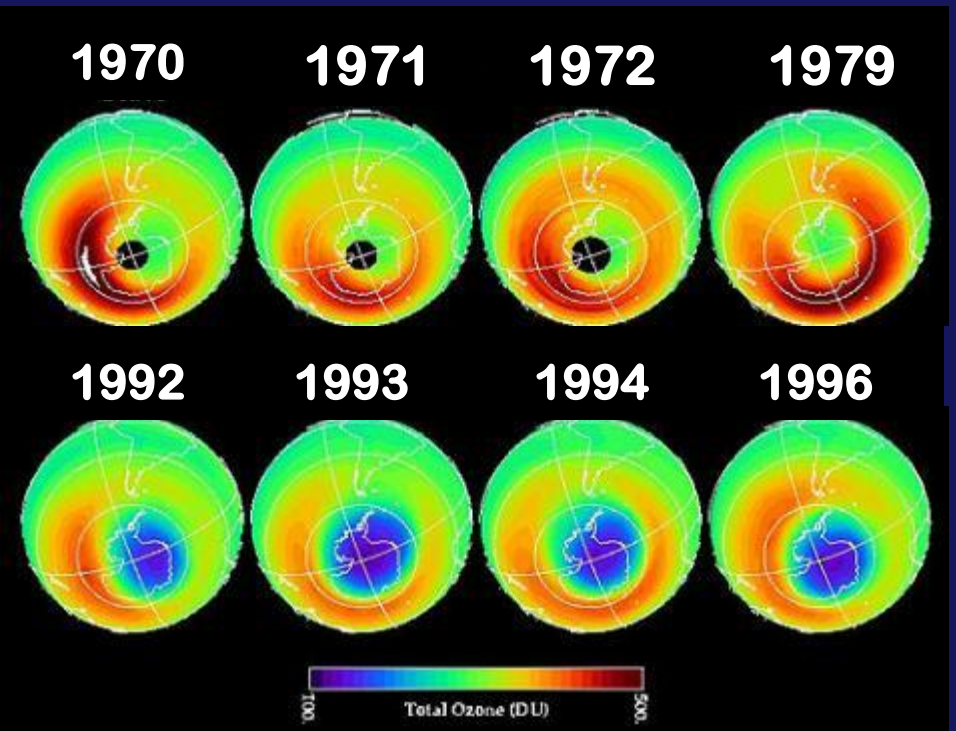
1957-1986

Early data from ground measurements of British survey team

DISCOVERY OF THE OZONE HOLE (cont.)

CHAPTER 2

- Meanwhile, satellites had been launched to observe ozone from above via the **TOMS** instrument on the satellite



Total Ozone in October (DU)

- TOMS detected the developing hole, but the anomalously low readings were rejected as "noise" by the computer program set up to process the data !!

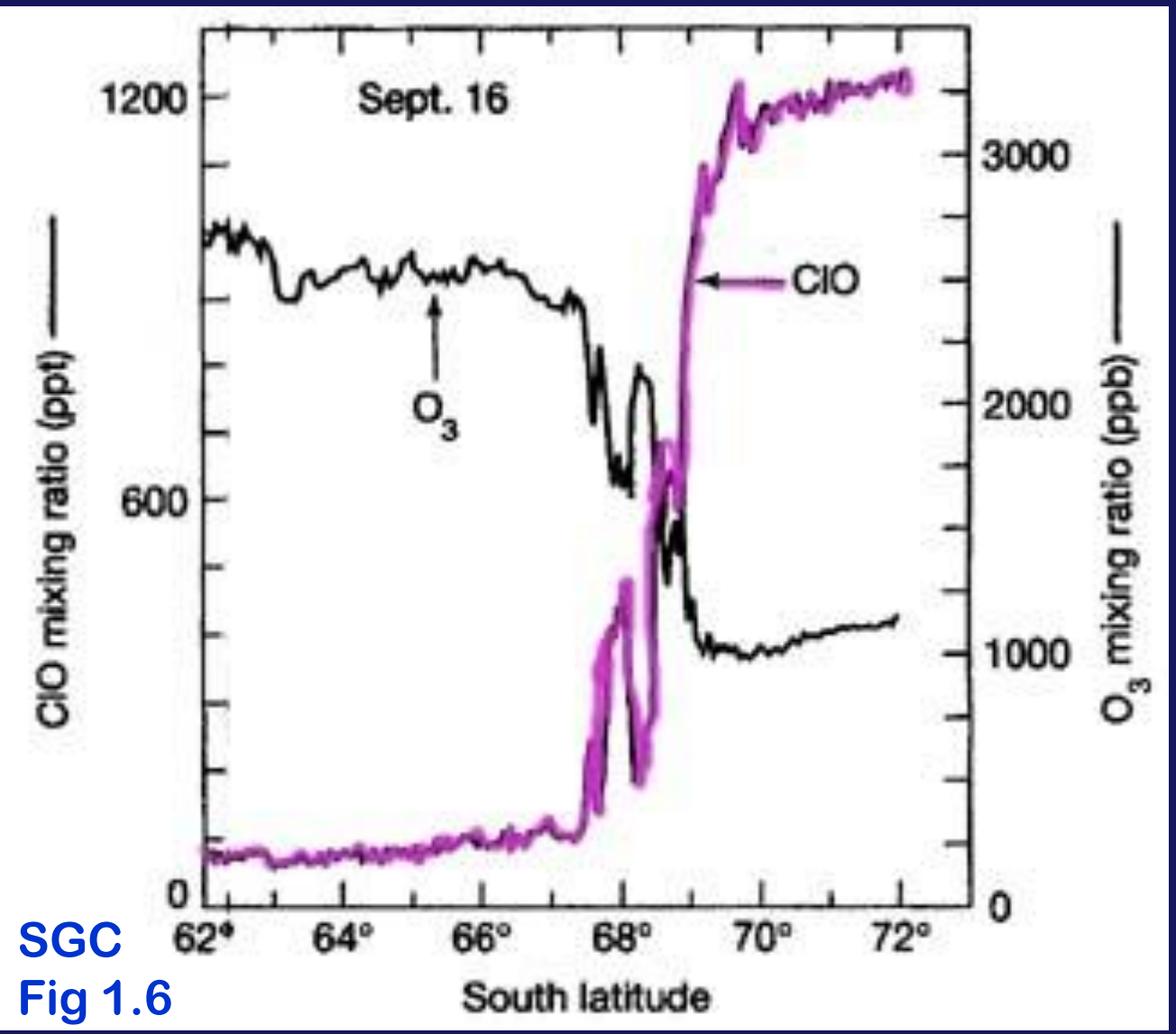
DISCOVERY OF THE OZONE HOLE

(cont.)

CHAPTER 3

- In **1986** Dr. Susan Soloman's expedition to Antarctica ➔ identified chlorine increase

- She devised the theory that correctly explained the destruction of ozone by chlorine compounds



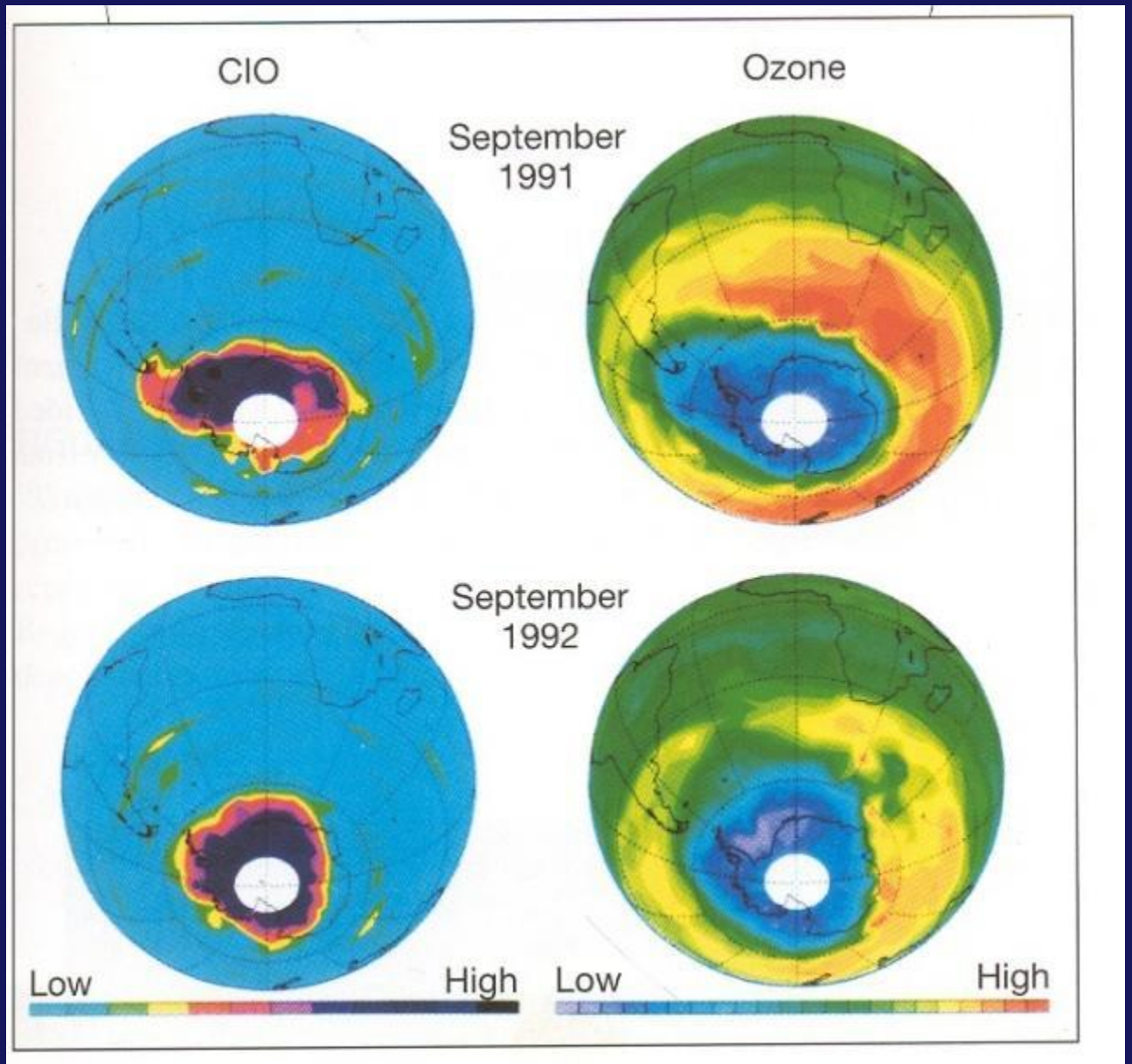
SGC
Fig 1.6

ClO (chlorine monoxide) from the chlorine catalytic cycle = **THE evidence of chemical reactions** occurring in hole region during time of greatest O_3 depletion (in September, spring in Southern Hemisphere)

ANTARCTIC LAND MASS

To the South Pole

Simultaneous measurements of ozone (O3) and chlorine monoxide (ClO)



Color version of SGC Fig 1.6

The chemical reaction theory – catalyzed by chlorine from CFCs -- is almost universally accepted as conclusive at present.

The prominent scientists involved in developing the chemical reaction theory were awarded the Nobel Prize for Physics in 1995.

Key Concept

WHY ANTARCTICA?

The ozone "hole(s)" have a unique REGIONALITY and SEASONALITY :

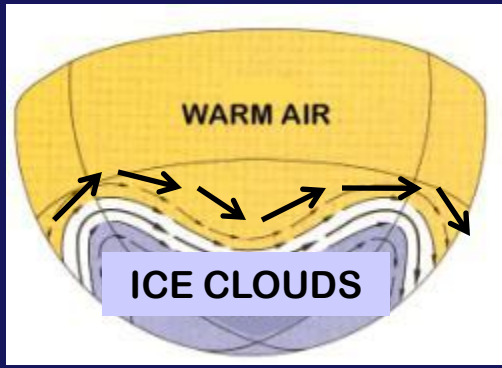
> it is most severe over Antarctica in S.H. spring (Sep, Oct);

> a less severe depletion (not a true hole) occurs over the Arctic in N.H. spring (Feb, Mar)

Key Concept

The special conditions that make ozone depletion most severe over polar regions (esp. Antarctica) are:

(1) the unique **CIRCUMPOLAR CIRCULATION PATTERN** over Antarctica in winter which isolates the stratosphere inside a vortex and acts like a "containment vessel" in which chemical reactions may occur in near isolation;



(2) The presence of **POLAR STRATOSPHERIC ICE CLOUDS** -- on the surfaces of these extremely cold cloud particles certain chemical reactions are more efficient and faster.

Key Concept

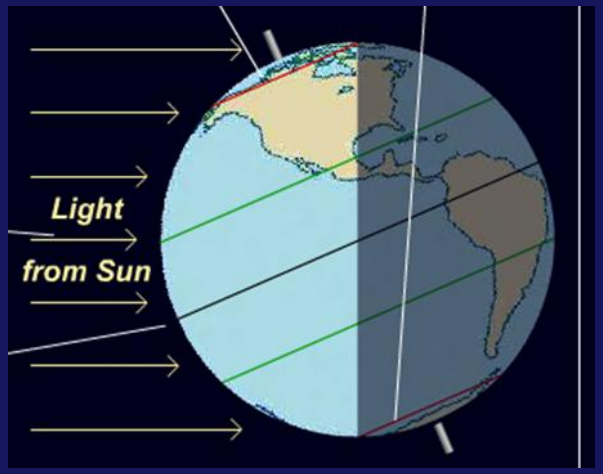
POLAR STRATOSPHERIC CLOUDS OVER ANTARCTICA

[Go to movie clip]

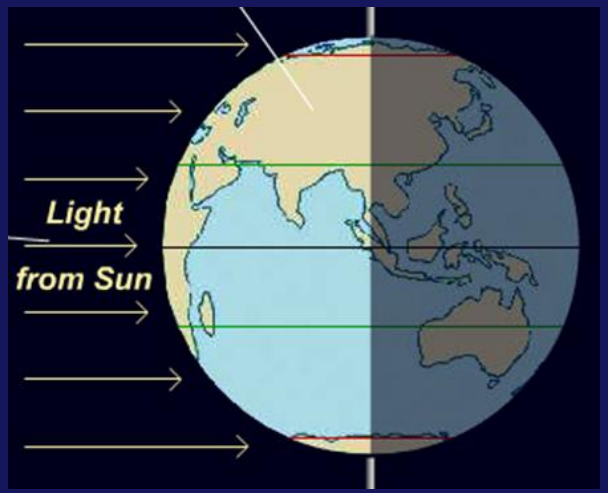
LAST INGREDIENT:

SUNLIGHT + UV PHOTONS

June



Sept



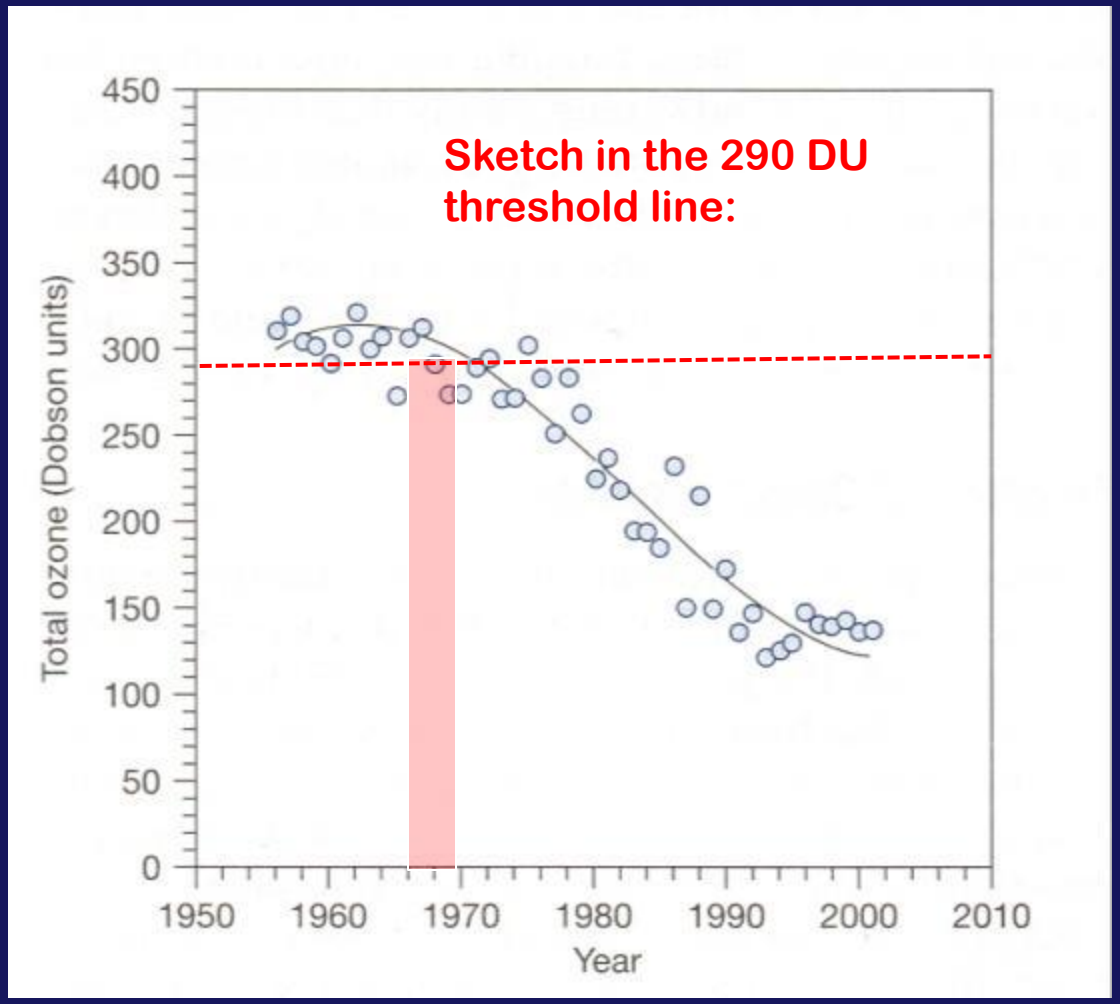
Only after well after the June Solstice and esp. the September Equinox, does the South Pole & Antarctic Circle receive sufficient sunlight!

RATE OF OZONE DEPLETION

in DOBSON UNITS (DU)

When did the Hole begin forming?

Hole generally defined as < 290 DU



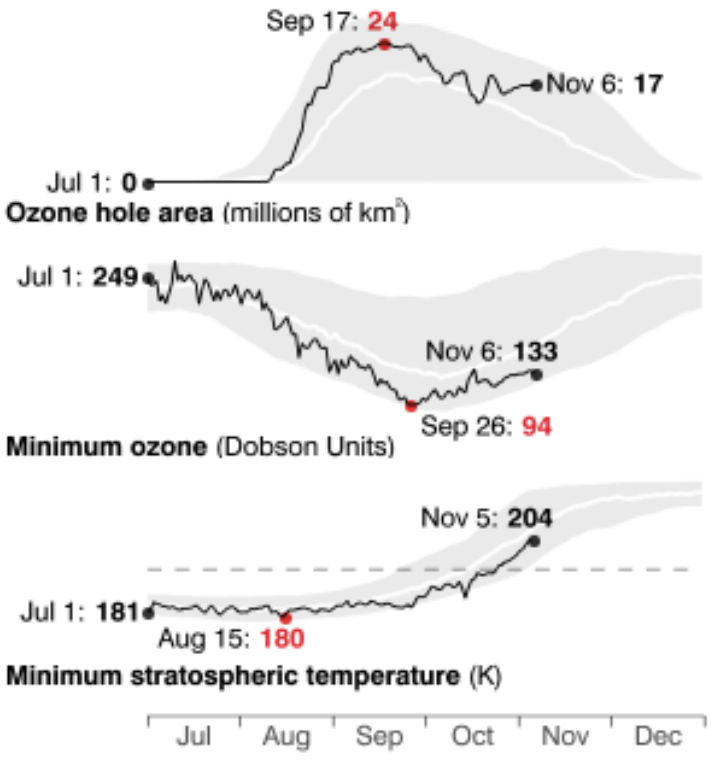
~ 1969 to 1970

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

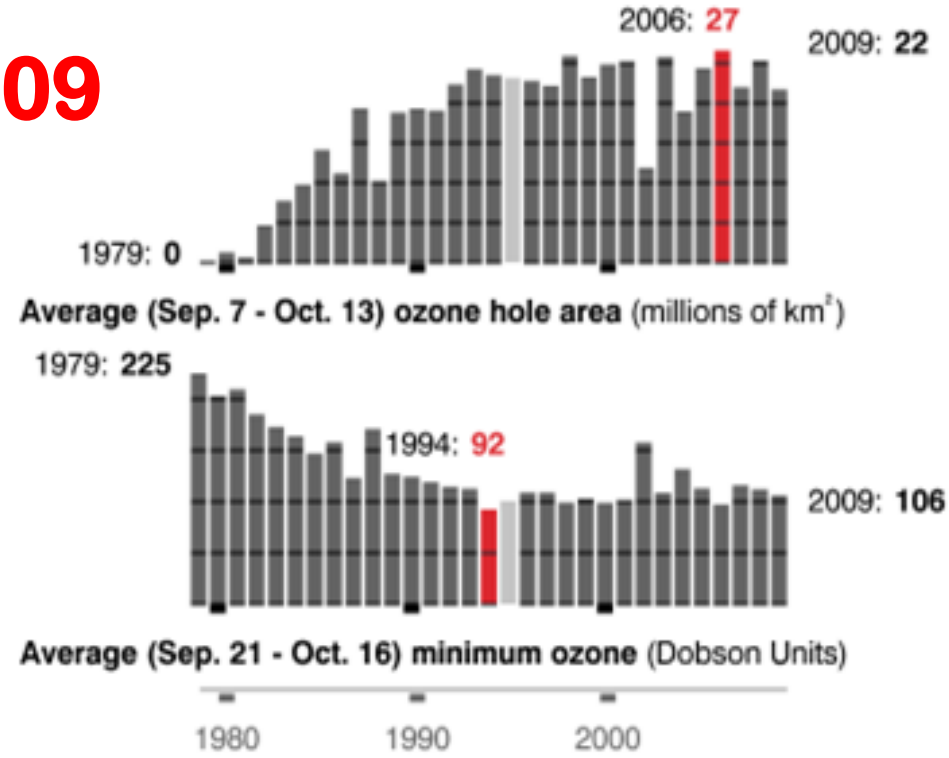
Update of graphs on p 77 in Class Notes

↓

OZONE HOLE WATCH
images, data, and information; updated daily



2009



see also: http://macuv.gsfc.nasa.gov/

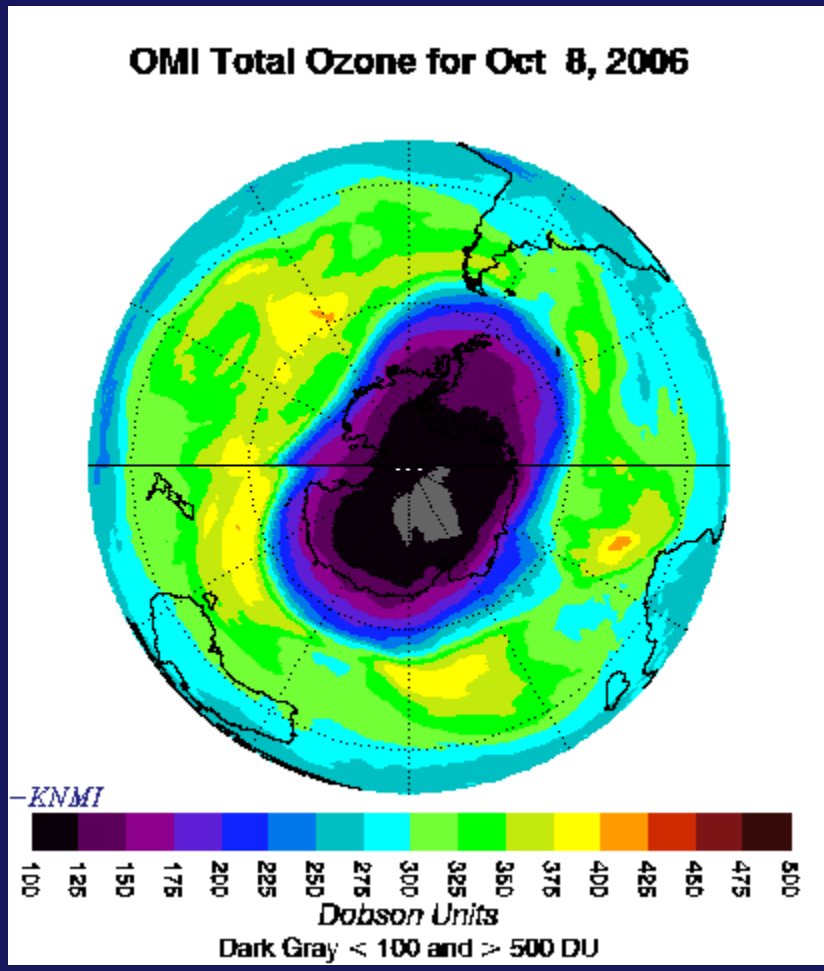
HOW DEEP DOES THE HOLE GET?

The intensity of ozone depletion varies from year to year.

The value of **85 Dobson Units** on October 8, 2006 was the second lowest ever recorded by satellite measurements.

Nearly ALL of the ozone in the layer 8-13 miles above the Earth's surface was destroyed!

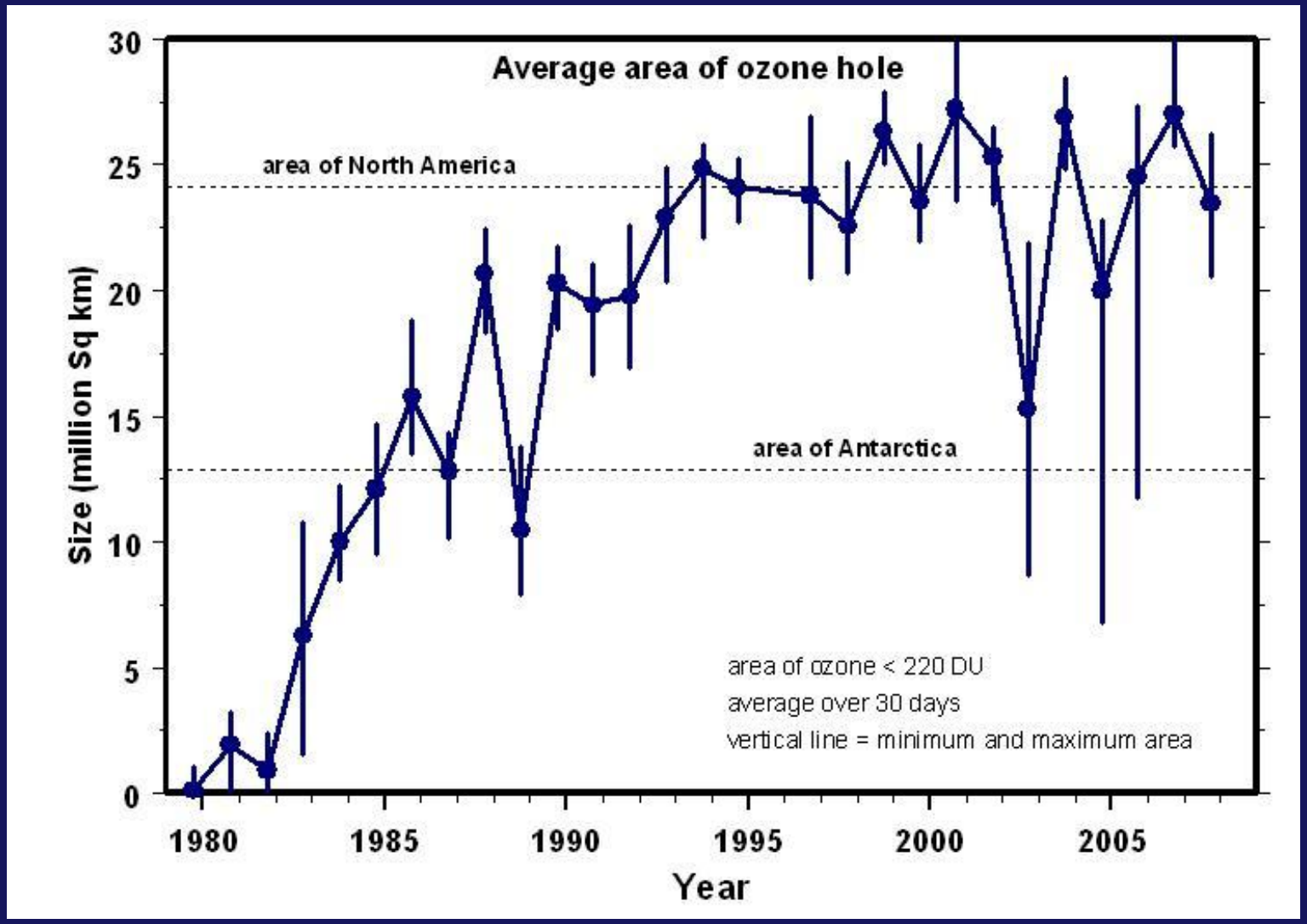
In this critical layer, the instrument measured a record low of only 1.2 DU!



2006 also saw the second LARGEST sustained ozone hole.

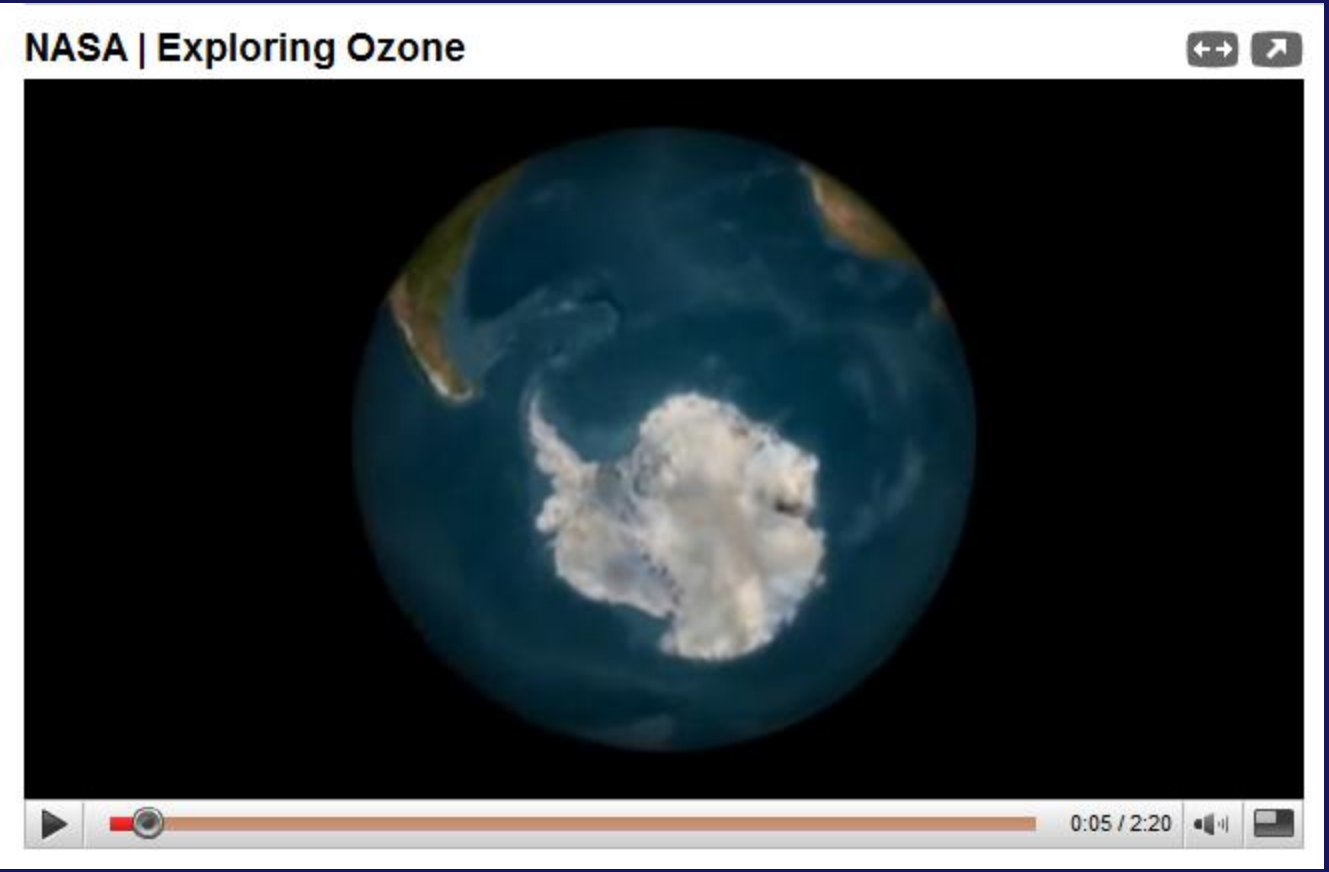
http://www.sciencedaily.com/releases/2006/10/061019162053.htm

Over time, the AVERAGE SIZE OF THE HOLE has gotten LARGER:



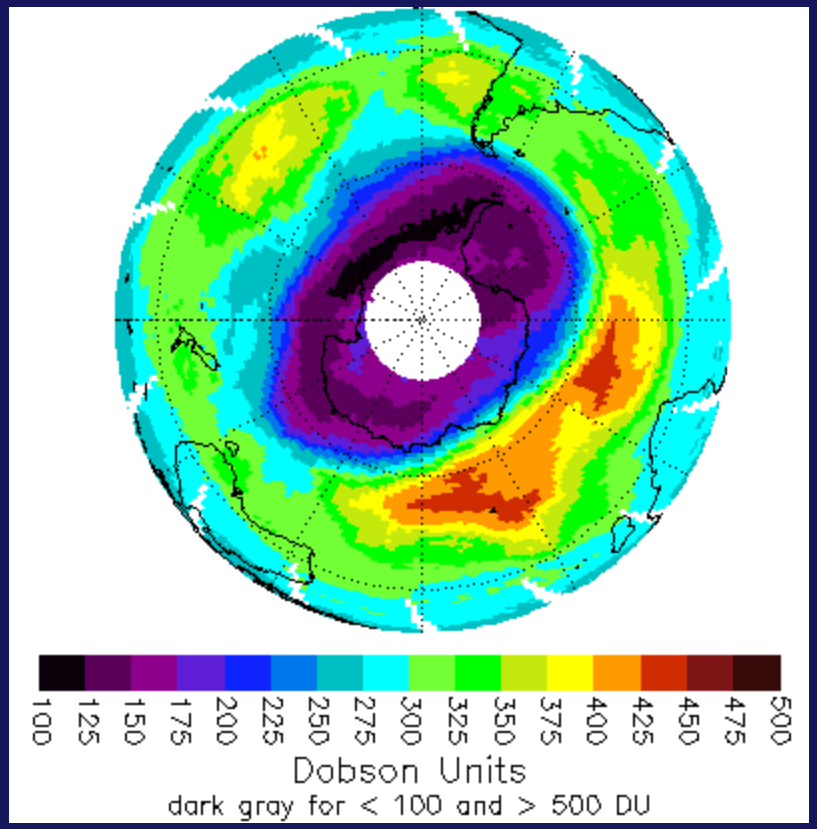
http://toms.gsfc.nasa.gov/eptoms/dataqual/oz_hole_avg_area_v8.jpg

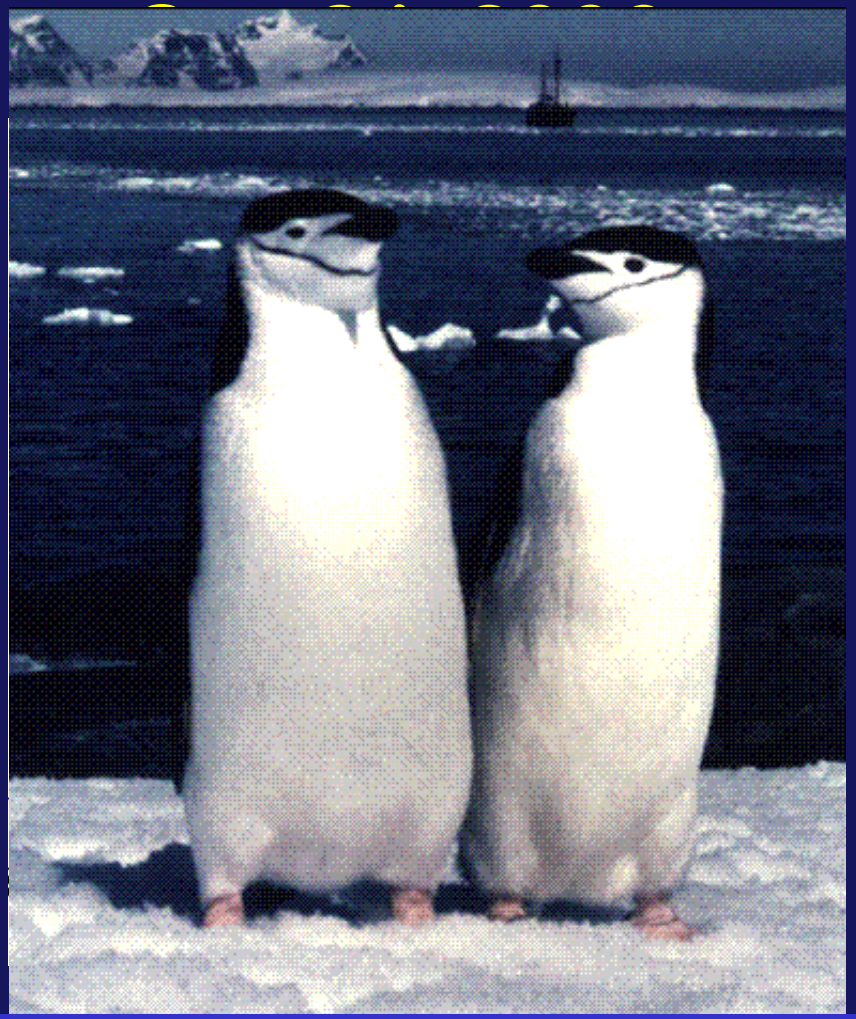
Recap:



http://www.youtube.com/watch?v=qUfVMogIdr8&feature=player_embedded

Sep 9, 2000





Here are some inhabitants with strong cause for concern about the Ozone Hole!

But what about the rest of us?

HOLE IN OZONE LAYER EXPOSED A CITY

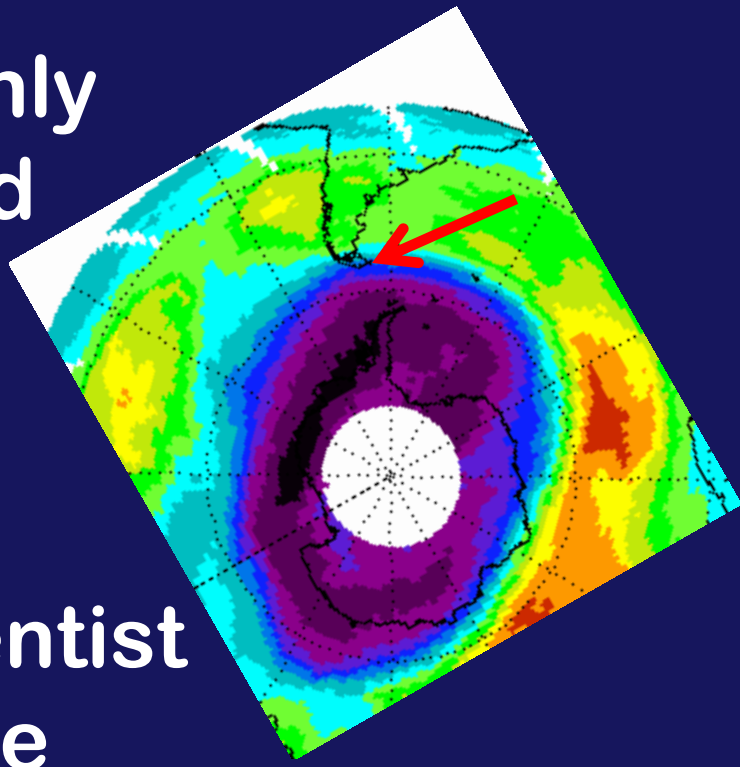
THE ASSOCIATED PRESS 10-6-00

WELLINGTON, New Zealand –

"The hole in the ozone layer over Antarctica stretched over a Chilean city when it ballooned to a record size last month, the first time it has reached a population center, scientists said yesterday. . . .

In an Upside-Down World, Sunshine Is Shunned
(New York Times 12-27-2002)

“Previously, the hole had only opened over Antarctica and the surrounding ocean.



“Citing data from NASA, atmospheric research scientist Stephen Wood said the hole covered **11.4 million square miles** - an area more **than three times the size of the United States** - on Sept. 9 and 10.

A "solar stoplight" in Punta Arenas announces an orange alert, the second highest of four levels, and warns people to limit their exposure to the sun between noon and 3 p.m. to a maximum of 21 minutes.

a woman and her child are bundled up against the sun

"For those two days, the hole extended over Punta Arenas, a southern Chilean city of about 120,000 people, exposing residents to very high levels of ultraviolet radiation.

" . . . findings showed a city being exposed to the ozone hole for the first time."

What about other parts of the globe?

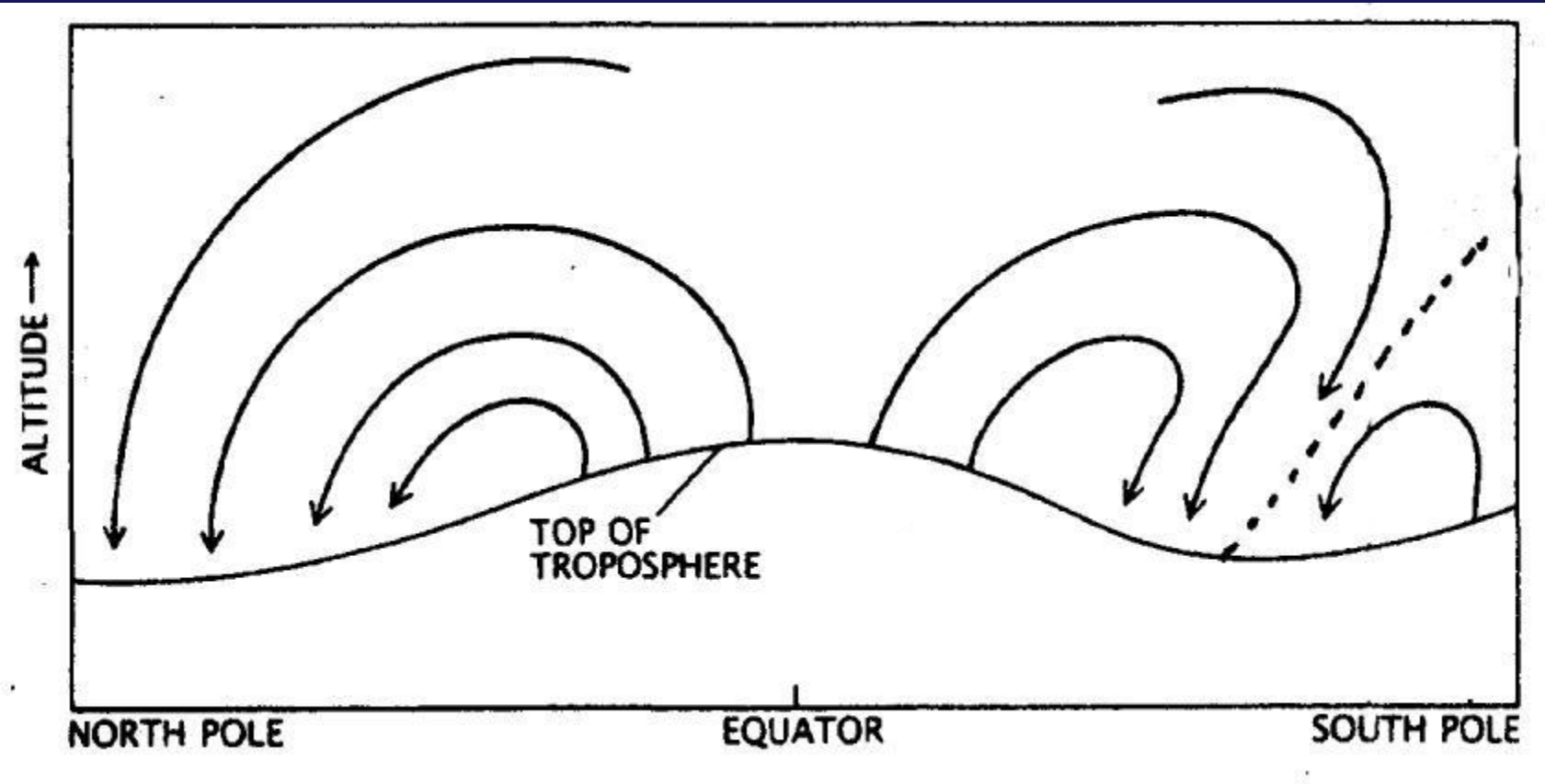
> Decreases have been observed in nearly all latitude zones:
(1.1 - 9% in S.H. & 1.1 - 3.7% in N.H.)

> Mid-latitude ozone has been decreasing by ~ 4% per decade in both hemispheres, whereas tropical ozone has remained more or less constant.

http://www.theozonehole.com/arcticozone.htm

Key Concept

Stratospheric Atmospheric Circulation Determines this Distribution



Ozone production highest in tropics but stratospheric circulation distributes it poleward

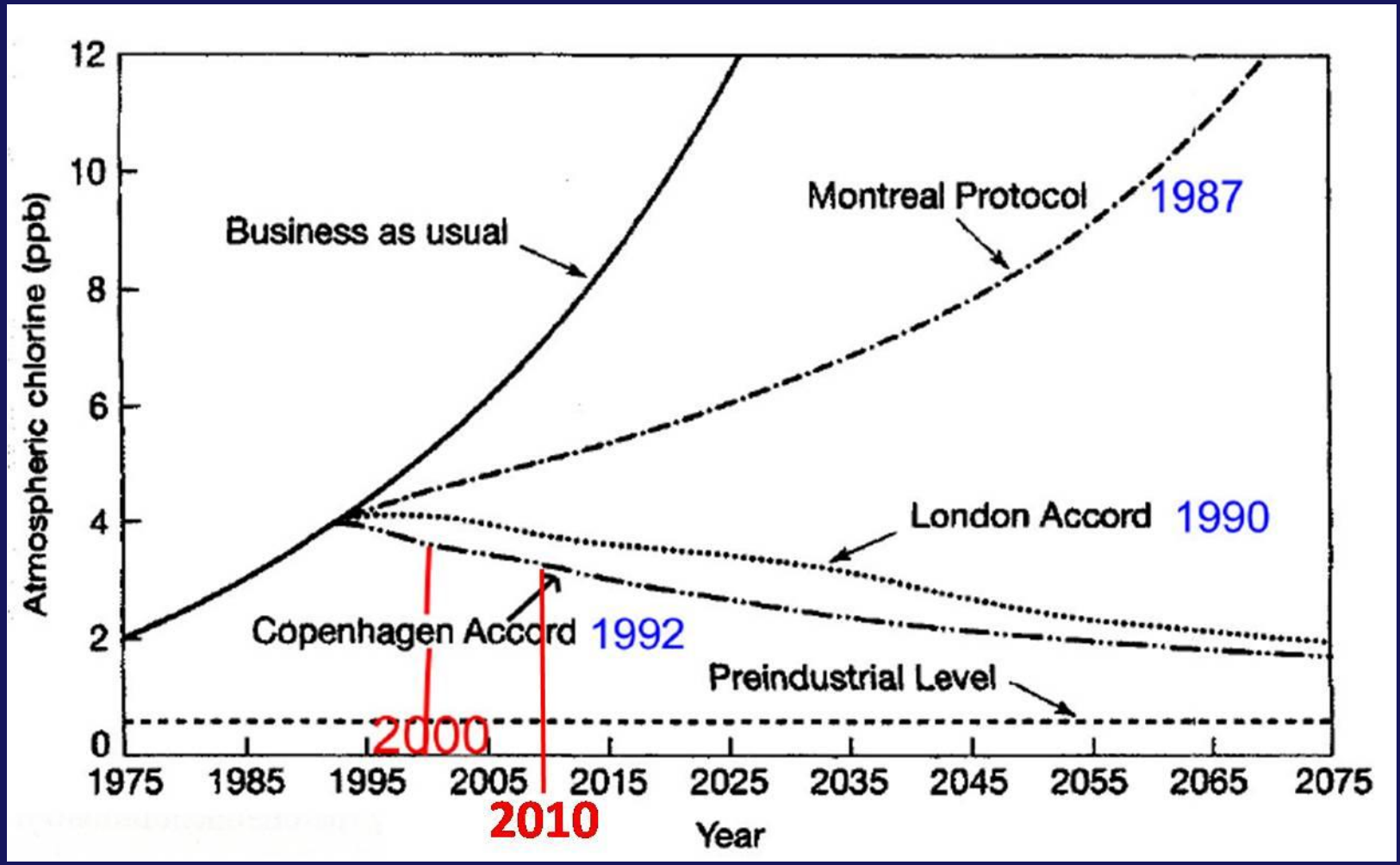
Arctic ozone depletion also takes place!

There are concerns that an "Arctic Ozone Hole" may develop that is similar to the severe Antarctic Hole

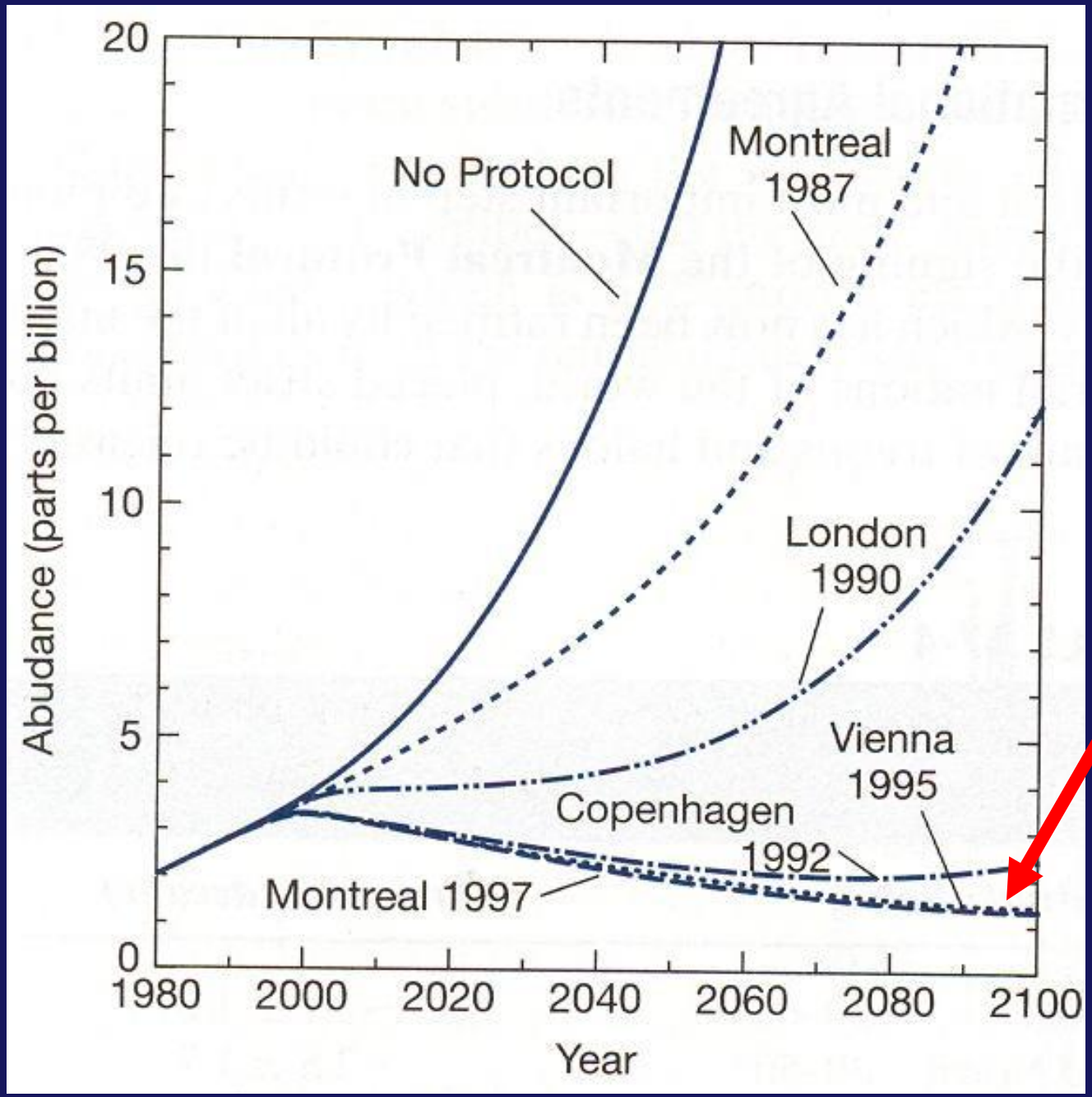
"An Arctic Ozone Hole, if similar in size to the Antarctic Ozone Hole, could expose over 700+ million people, wildlife and plants to dangerous UV ray levels.

The likely hood of this happening seems inevitable based on the deterioration of ozone layer caused by the effects of global warming on the upper atmosphere."

http://www.theozonehole.com/arcticozone.htm



Very long residence time of CFCs!



Model results based on more recent agreements:

Vienna 1995 & Montreal *(again)* 1997

The world is "making do" with freon substitutes, but some concern over long-term effects of substitutes remains . . .

Why can't we just ship the "bad ozone" in the troposphere up to the stratosphere to 'fill the hole'?

> Ozone is *increasing* in the troposphere due to car exhaust, etc ("bad ozone"), but only at the rate of about 1% per year,

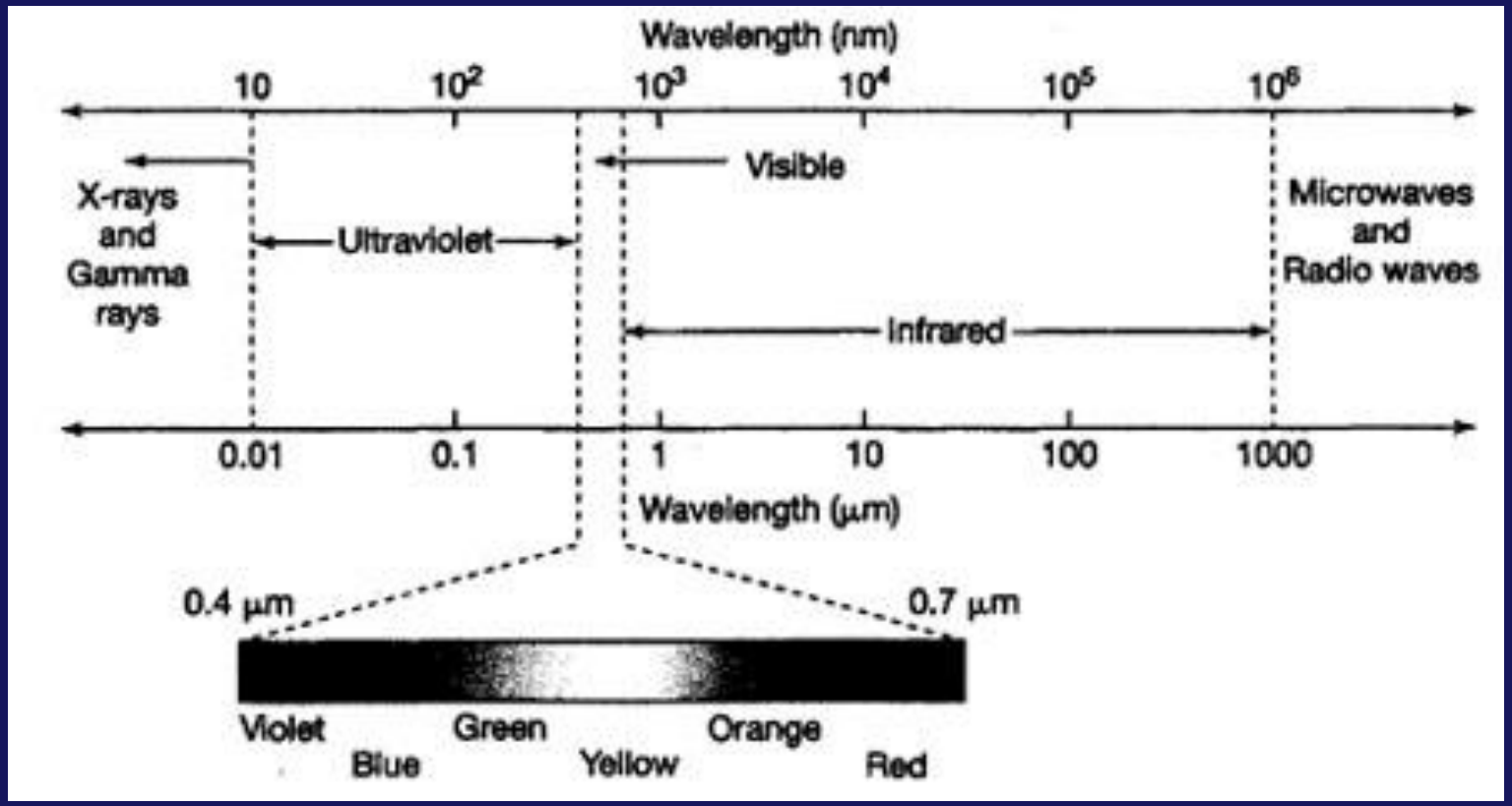
> hence stratospheric levels of "good ozone" are going down at a rate faster than ozone is being added in the troposphere.

Key Concept

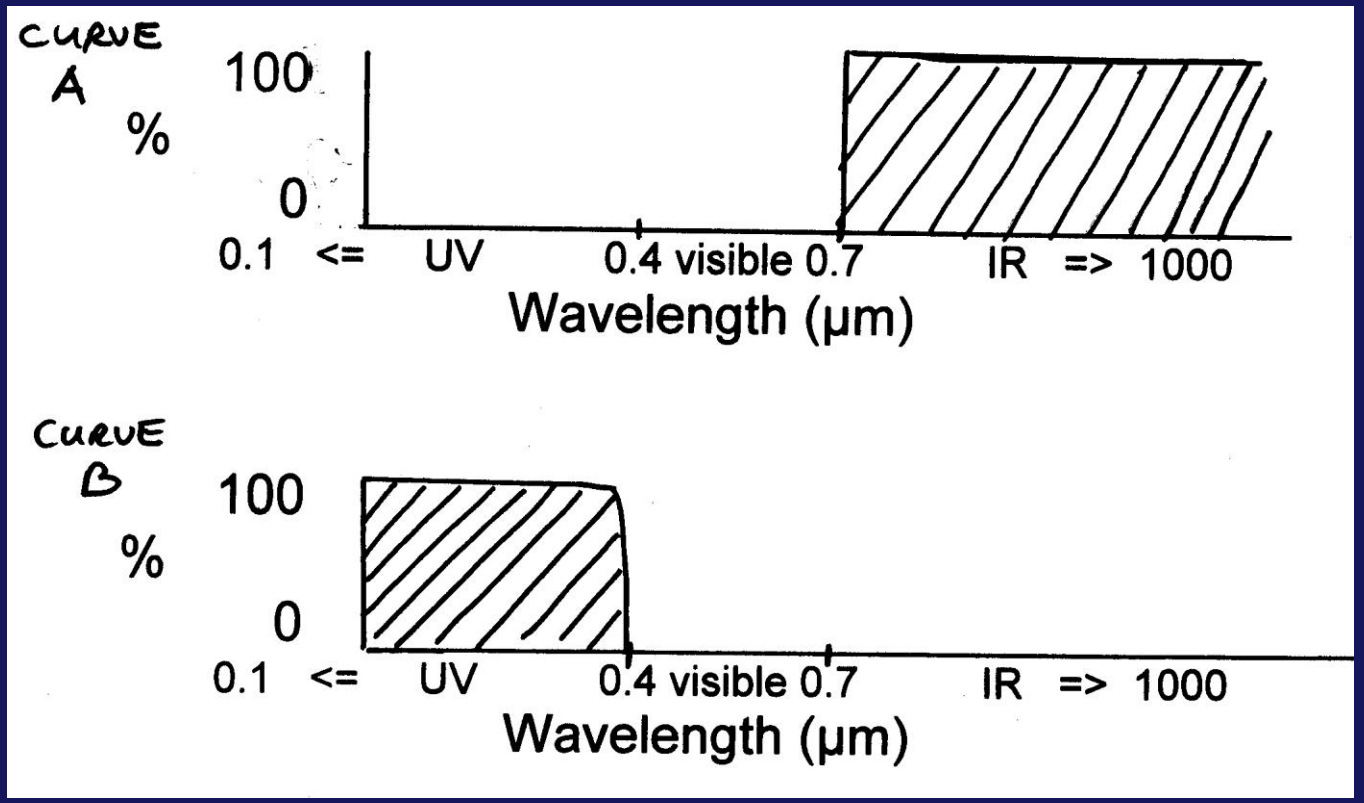
THE OZONE DEPLETION STORY TIES TOGETHER MANY OF THE CONCEPTS YOU'VE LEARNED IN THE COURSE THUS FAR:

- the nature of matter, e.g., chemical reactions and photon interaction with atoms

> the electromagnetic spectrum --especially the wavelengths of UV radiation

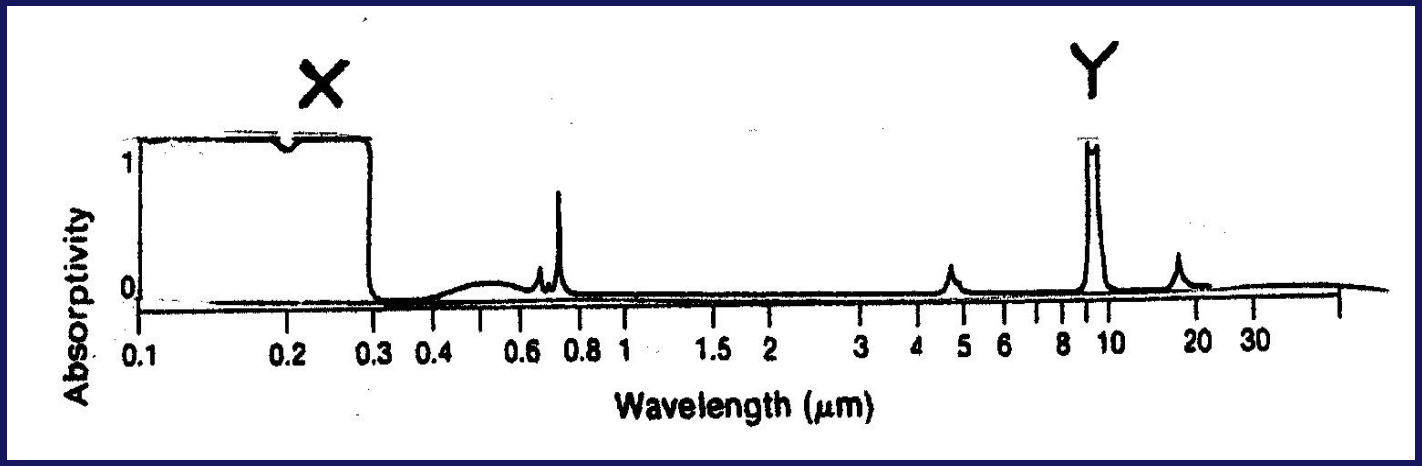


> absorption curves, especially the absorption curve for ozone

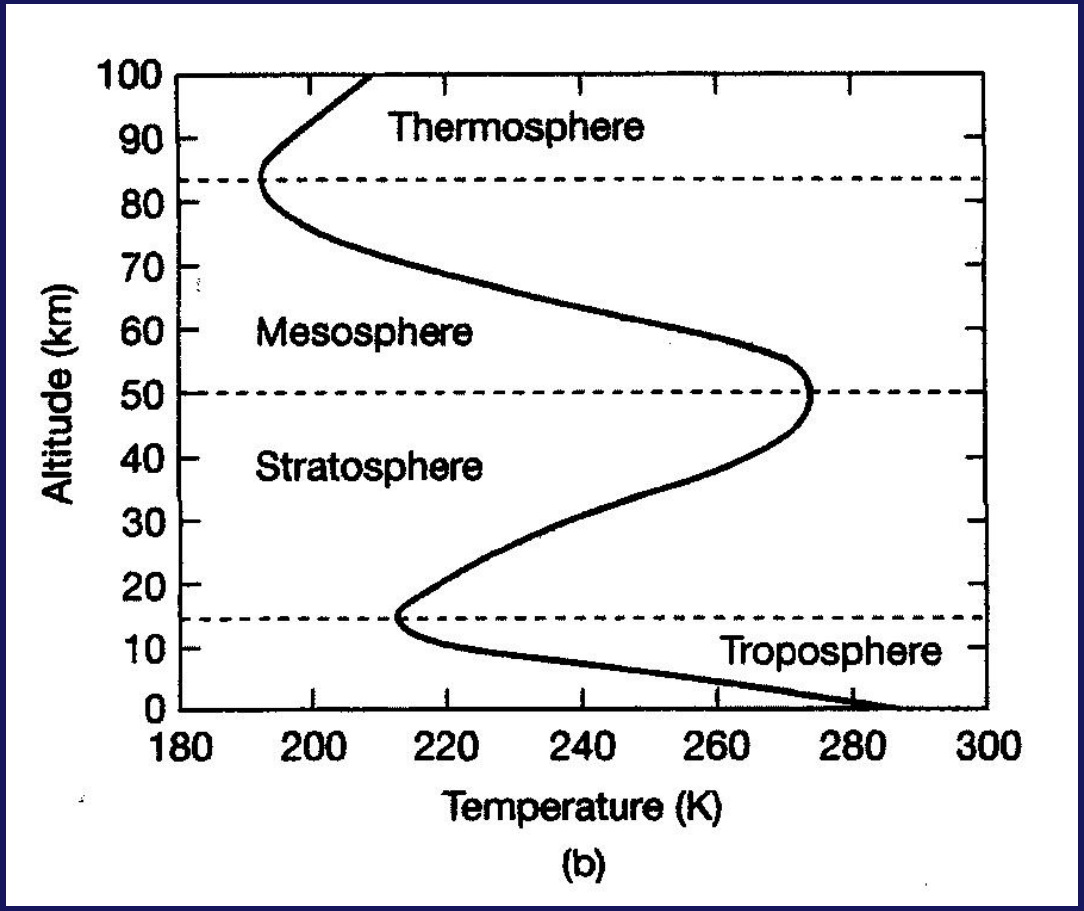


> Effect of clouds -- in this case the importance of Polar Stratospheric Clouds (PSCs)

> Greenhouse gases (ozone is also a greenhouse gas but this affects IR radiation, not UV radiation)



> the vertical structure of the atmosphere (troposphere, stratosphere)



> the ever-changing nature of science; early theory right for wrong reason

> Preconceived ideas influencing one's observations

. . . and the surprise of discovery!

The OZONE & THE MONTREAL PROTOCOL

http://www.youtube.com/watch?v=Dn3KvZ_Xyqs&eurl=http://www.theozonehole.com/discoverer.htm

The Discover of the Ozone Hole issues a warning

http://www.theozonehole.com/discoverer.htm

MOVIE TIME !

ENJOY YOUR VETERAN'S DAY BREAK ON WED & I'LL SEE YOU ON THURSDAY –

DON'T FORGET
Deliverable #1
or RQ-8