

### Air Pollution - 1940s, 1950s

1940s: Smog severe in Los Angeles  
1947: Los Angeles Air Pollution Control District forms  
1949: National symposium on air pollution in Los Angeles  
mid-1950s: Ozone levels in Los Angeles reach 650 ppbv  
1955: Eisenhower asks Congress to examine air pollution  
By 1960: 17 statewide air pollution agencies existed

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### U.S. Air Pollution Laws 1950s

U.S. Air Pollution Control Act of 1955  
Federal technical assistance to state air pollution control  
Funding of Public Health Service for studies of air pollution  
Amended 1960 to study health effects of automobile exhaust  
Did not impose regulations on air pollution  
Delegated regulation to state and local level  
1959  
California Motor Vehicle Control Board set first automobile emission standard worldwide. 1963 model cars required to reroute crankcase hydrocarbon emissions back to manifold for re-burning.

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### U. S. Air Pollution Laws 1960s

Clean Air Act of 1963  
Gave federal government authority to regulate interstate pollution  
Emission standards for stationary sources (power plants, steel)  
No automobile controls  
Motor Vehicle Air Pollution Control Act of 1965  
First regulation of automobiles at federal level  
Emission standards to reduce tailpipe HCs 72%, CO(g) 56%  
For 1968 model cars; patterned after California for 1966 cars  
More than half of 1968 and 1969 cars did not meet standards  
Air Quality Act of 1967  
U.S. divided into Air Quality Control Regions (AQCR)  
Required publication of Air Quality Criteria (AQC) reports  
Science reports about effects of pollutants on health/welfare  
Provide suggestions about acceptable levels of pollution  
States required to set own air quality standards based on AQC  
State Implementation Plans (SIP)  
State plan for regulation submitted to federal government  
If no state enforcement, federal government could sue state

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### Clean Air Act Amendments of 1970

Creation of U. S. Environmental Protection Agency (USEPA) – under President Nixon

Clean Air Act of 1970:

**National Ambient Air Quality Standards (NAAQS)**

Primary: to protect public health (e.g., asthmatics, elderly)

Secondary: to protect public welfare (e.g., visibility, buildings)

**Criteria Air Pollutants**

Originally: CO(g), NO<sub>2</sub>(g), SO<sub>2</sub>(g), TSP (total suspended particulates), hydrocarbons, oxidants

Lead added in 1976

Oxidants change to O<sub>3</sub>(g) in 1979

Hydrocarbons removed in 1983

TSP changed to PM<sub>10</sub>, a PM<sub>2.5</sub> standard added in 1997

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### Clean Air Act Amendments of 1970

**Attainment areas**

Regions where primary standards met

**Nonattainment areas**

Regions where primary standards were not met

**New Source Performance Standards (NSPS)**

Set by USEPA to limit emission from new stationary sources

**National Emission Standards for Hazardous Pollutants (NESHAPS)**

For pollutants causing mortality, severe illness

Initially, for, asbestos, beryllium, mercury. List expanded in 1984

**Congressional control of automobile emissions**

Required 90% reduction HCs, CO(g) by 1975 and NO<sub>x</sub> by 1976

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### Air quality regulation agencies

**U.S. Environmental Protection Agency**

→Federal Clean Air Act; National Ambient Air Quality Standards

**Washington State Department of Ecology**

→Emission testing/air monitoring

→overseeing WA local state agencies

**Puget Sound Clean Air Agency** (~50% of WA population)

→adopting and enforcing air quality regulations;

→sponsoring voluntary initiatives to improve air quality.

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### Clean Air Act Amendments of 1977

Prevention of Significant Deterioration (PSD) in areas already under attainment. Three classes of regions designated:

- Class I: Pristine areas (parks, wilderness) no new sources
  - Class II: Moderate changes allowed but regulations desired
  - Class III: Major growth allowed if NAAQS not exceeded
- PSD permit needed for growth in region allowing growth  
New source must use Best Available Control Technology (BACT)

Computer modeling mandated to check whether new pollution sources might result in standard exceedence

Control of Chlorofluorocarbons (CFCs)

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### Clean Air Act Amendments of 1990

1990: 96 cities still in violation of ozone NAAQS  
--> nonattainment areas divided into six categories  
"Extreme:" Los Angeles: must attain by 2010  
"Severe:" Baltimore, New York: must attain by 2007  
"Severe:" Chicago, Houston,....: must attain by 2005

New sources in nonattainment areas must achieve  
Lowest Achievable Emissions Rate (LAER) by  
adopting Reasonably Achievable Control  
Technology (RACT)

Hazardous Air Pollutants (HAPs)  
Emission limits for 189 toxic chemicals using  
Maximum Achievable Control Technologies  
(MACTs)

More control of CFCs

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### Clean Air Act Revision of 1997

Change in ozone standard  
0.08 ppmv over 8-hour average instead of  
0.12 ppmv over 1-hour average

Addition of PM<sub>2.5</sub> standard

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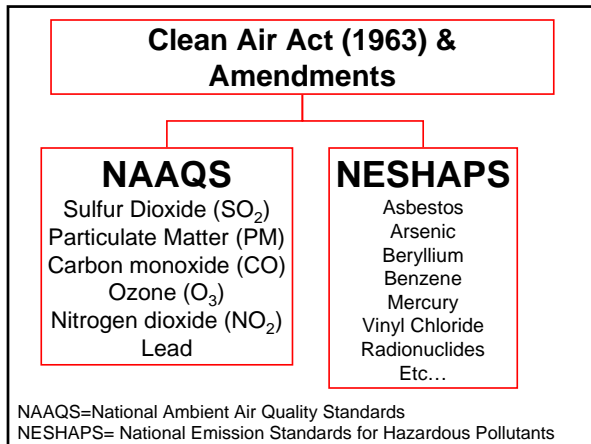
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**National Ambient Air Quality Standards (NAAQS) for 6 Criteria Air Pollutants**

Pollutant	Primary Standards		Secondary Standards	
	Level	Averaging Time	Level	Averaging Time
Carbon Monoxide (CO)	9 ppm (10 mg/m <sup>3</sup> )	8-hour <sup>111</sup>	None	
	35 ppm (40 mg/m <sup>3</sup> )	1-hour <sup>111</sup>		
Lead	1.5 µg/m <sup>3</sup>	Quarterly Average	Same as Primary	
Nitrogen dioxide (NO <sub>2</sub> )	0.053 ppm (100 µg/m <sup>3</sup> )	Annual (Arithmetic Mean)	Same as Primary	
	150 µg/m <sup>3</sup>	24-hour <sup>112</sup>	Same as Primary	
Particulate matter (PM <sub>10</sub> )	15.0 µg/m <sup>3</sup>	Annual <sup>112</sup> (Arithmetic Mean)	Same as Primary	
Particulate matter (PM <sub>2.5</sub> )	35 µg/m <sup>3</sup>	24-hour <sup>112</sup>	Same as Primary	
	0.075 ppm (2008 std)	8-hour <sup>112</sup>	Same as Primary	
Ozone (O <sub>3</sub> )	0.08 ppm (1997 std)	8-hour <sup>112</sup>	Same as Primary	
	0.12 ppm	1-hour <sup>112</sup> (Applies only in limited areas)	Same as Primary	
	0.03 ppm	Annual (Arithmetic Mean)	0.5 ppm (1300 µg/m <sup>3</sup> )	3-hour <sup>112</sup>
Sulfur dioxide (SO <sub>2</sub> )	0.03 ppm	Annual (Arithmetic Mean)	0.5 ppm (1300 µg/m <sup>3</sup> )	3-hour <sup>112</sup>
	0.14 ppm	24-hour <sup>112</sup>		

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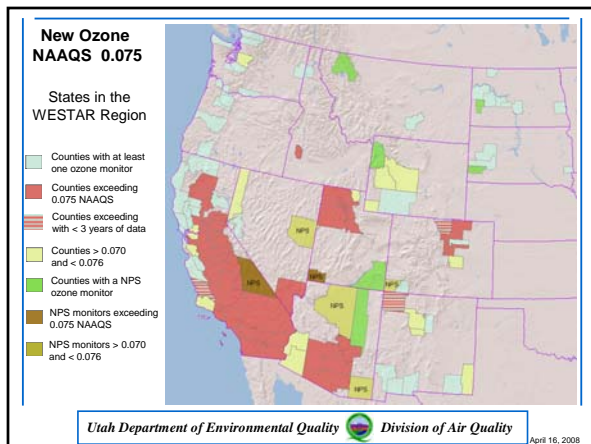
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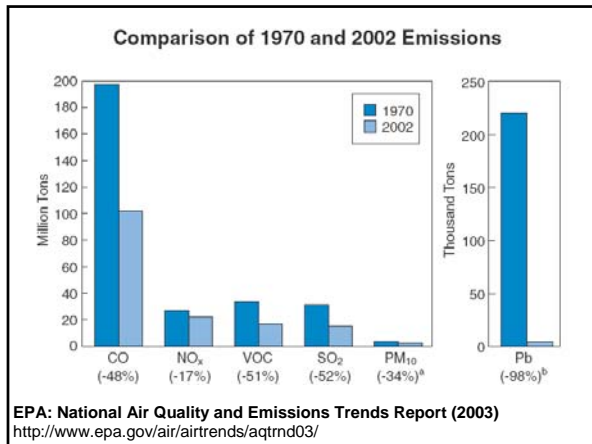
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### Non-Attainment Areas for NAAQS Pollutants

Pollutants	1990	1996	2002
CO	42	31	16
Pb	12	10	3
NO <sub>2</sub>	1	1	0
O <sub>3</sub>	98	68	56
PM-10	70	81	67
SO <sub>2</sub>	51	43	24

# of Counties

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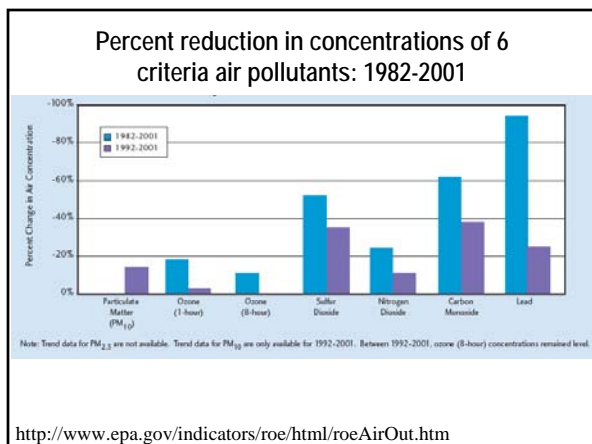
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### Tightening of motor vehicle emission federal standards

*grams per mile*

	<u>HC</u>	<u>CO</u>	<u>NO<sub>x</sub></u>	<u>Particles</u>
PRE-CONTROL	10.6	84.0	4.1	
1970	4.1	34.0		
1975	3.0	28.0	3.1	
1980	0.41	7.0	2.0	
1985	0.41	3.4	1.0	
1990	0.41	3.4	1.0	0.2
1995	0.25	3.4	0.4	
2005	0.125	1.7	0.2	? < 0.1

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### Air Quality Standards Around the World today

	O <sub>3</sub> , ppbv	PM10, µg/m <sup>3</sup>	CO, ppmv	SO <sub>2</sub> , ppmv
US	75 (8h)	150 (24h)	35 (1h)	0.14 (24h)
WHO	60 (8 h)	/	26 (1h)	0.125 (24h)
Canada	50 (1h)	30	30 (1h)	0.06 (24h)
Mexico	110 (1 h)	150 (24h)	11 (8h)	0.13 (24h)
Europe	60 (8 h)	50 (24h)	35 (1h)	0.04 (24h)
China	60 (1 h)	50 (24h)	3.5 (24h)	0.019 (24h)

WHO = World Health Organization

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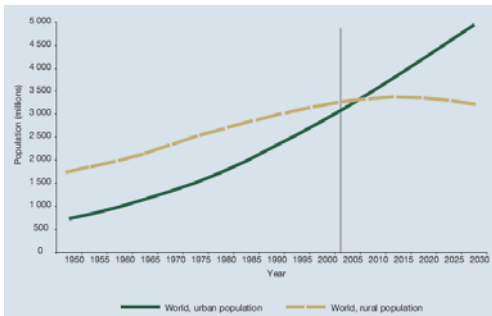
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### The urban and rural populations of the world: 1950-2030



World Urbanization Prospects: The 2003 Revision

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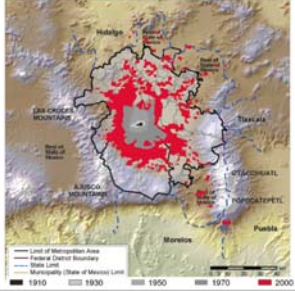
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## Mexico City

Mexico City is one of the cities with the worst pollution worldwide. Sits in a basin surrounded by mountains and under influence of Pacific high pressure → frequent inversions: trapping of pollutants



Population:  
1950: 3 million  
2000: 18 million

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## Mexico City

Pollution sources: industry + cars (2.5 million vehicles = 44% of energy consumption)

Tropical latitudes: plenty of sunshine → ozone air pollution problem year-round

Effects of high altitude (2250 m)?  
more air needs to be inhaled to get same O<sub>2</sub> → higher dose of pollutants



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## China

- Contains 7 out of 10 most polluted cities worldwide
- Two-thirds of 338 cities monitored are polluted
- Largest producer/consumer of coal
- Coal-fired power-plants = 2/3 of China's energy; 1 powerplant built each day
- Indoor burning of coal and biomass a major problem
- Pollution levels could triple or quadruple within 15 years if the country does not curb its rapid growth in energy consumption and automobile use.



Song Yang/Imaginechina; NY Times  
Smog hovers over Urumchi, of the Xinjiang Uighur Autonomous Region.

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## Beijing

- 11 million people, surrounded by heavy industry.
- Ozone > standard for 100 days (1998)
- Observed levels of particulates are very high:  
Daily averages: PM10 = 190  $\mu\text{g}/\text{m}^3$ ; PM2.5=136  $\mu\text{g}/\text{m}^3$  (compare to US standards: 150 and 65  $\mu\text{g}/\text{m}^3$ );  
Annual averages: PM10= 230  $\mu\text{g}/\text{m}^3$ ; PM2.5=106  $\mu\text{g}/\text{m}^3$  (compare to US standards: 50 and 15  $\mu\text{g}/\text{m}^3$ )

- Measures: Relocate industry and people into 20 towns outside Beijing; tougher standards on cars



Greg Baker/Associated Press, NY Times

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## Ozone and Oxygen

Oxygen Atom (O)



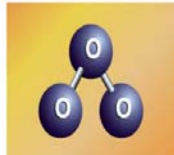
Very Reactive

Oxygen Molecule (O<sub>2</sub>)



Very Un-reactive

Ozone Molecule (O<sub>3</sub>)



Reactive

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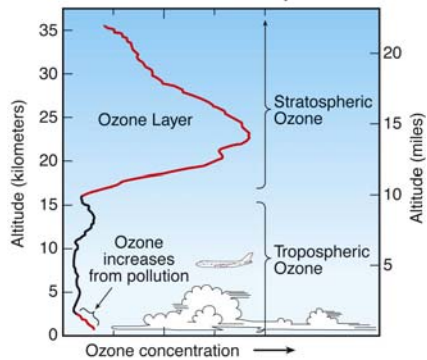
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## Vertical Distribution of O<sub>3</sub>

Ozone in the Atmosphere




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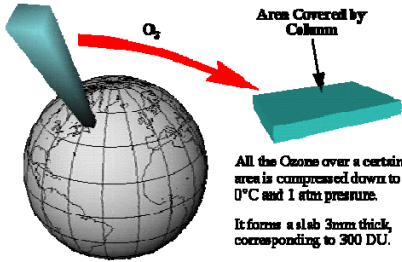
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### Dobson Units



All the Ozone over a certain area is compressed down to 0°C and 1 atm pressure.  
 It forms a slab 3mm thick, corresponding to 300 DU.  
 If you were to bring all O<sub>3</sub> molecules to the surface

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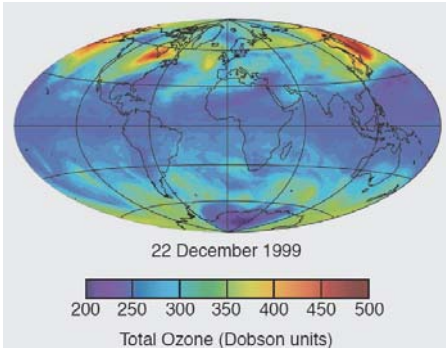
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### Global ozone column abundance



WMO, 2002, 20 questions

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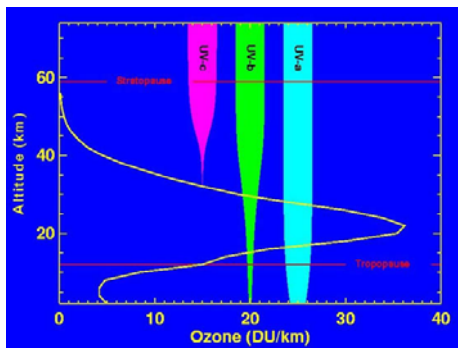
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### UV Protection by the Ozone Layer




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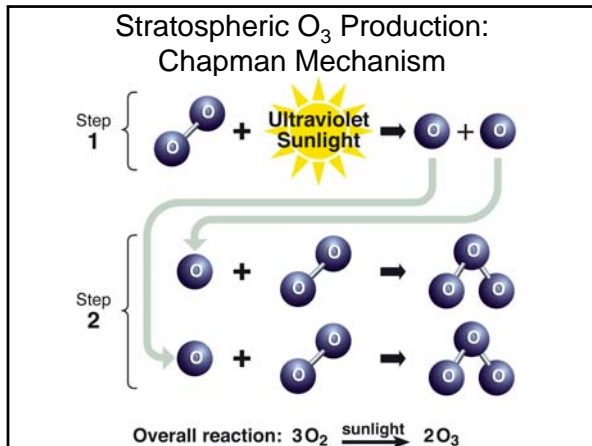
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**Ozone formation animation**

[http://earthobservatory.nasa.gov/Library/Ozone/Anim/ozone\\_creation\\_final.mov](http://earthobservatory.nasa.gov/Library/Ozone/Anim/ozone_creation_final.mov)

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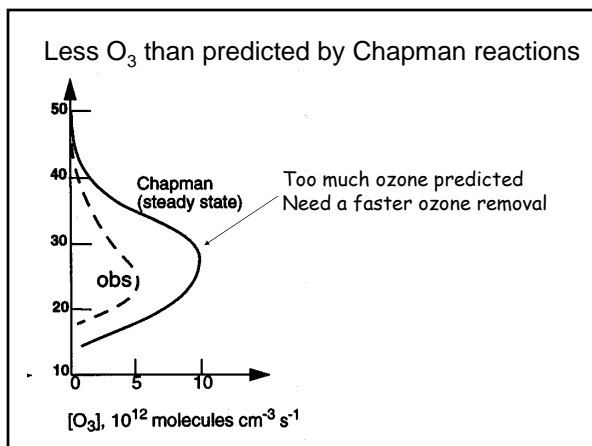
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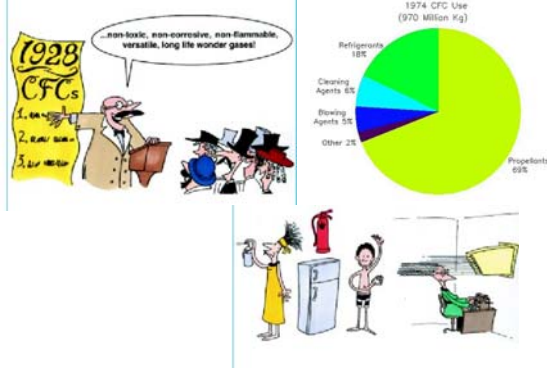
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## Use of CFCs increases rapidly




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## Early Warning Signs

### Stratospheric sink for chlorofluoromethanes : chlorine atom-catalyzed destruction of ozone

Mario J. Molina & F. S. Rowland

Department of Chemistry, University of California, Irvine, California 92664

*Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.*

photolytic dissociation to  $\text{CFCl}_2 + \text{Cl}$  and to  $\text{CF}_2\text{Cl} + \text{Cl}$  respectively, at altitudes of 20–40 km. Each of the reactions are two odd-electron species—one Cl atom and one free radical. The dissociated chlorofluoromethanes can be traced to their ultimate sinks. An extensive catalytic chain reaction leads to the net destruction of  $\text{O}_3$  and O occurs in the stratosphere.

$$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$$

$$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$$

This has important chemical consequences. Under normal conditions in the Earth's atmospheric ozone layer, (2) is slower of the reactions because there is a much lower concentration of atomic oxygen.

Nature, June 28, 1974

Molina, Rowland, and Crutzen win Nobel Prize in 1994

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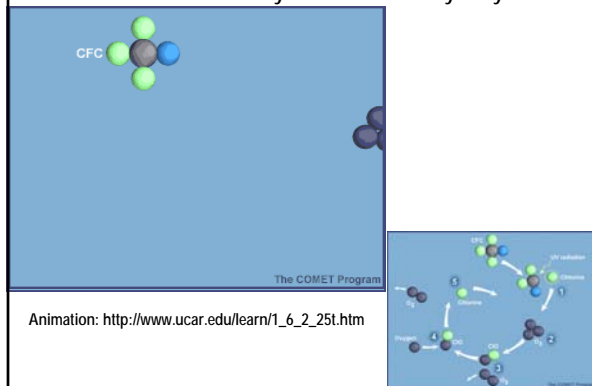
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## Destruction of ozone by the chlorine catalytic cycle




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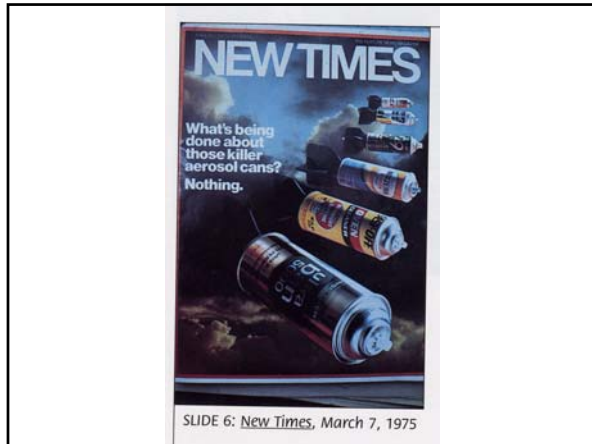
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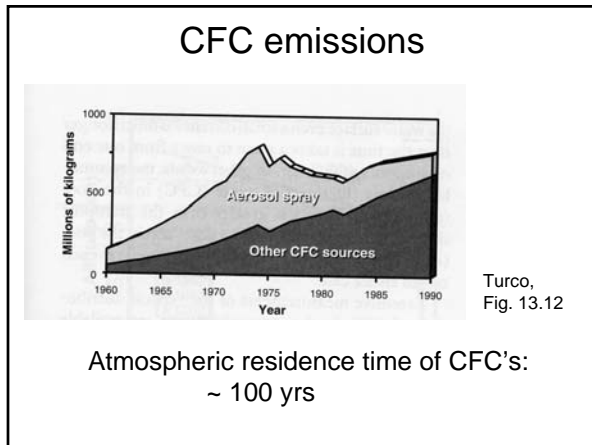
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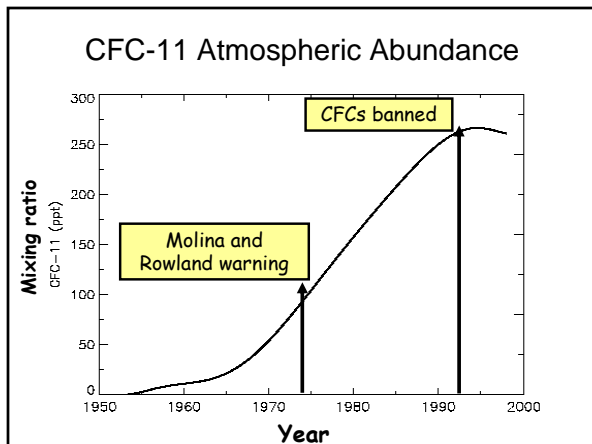
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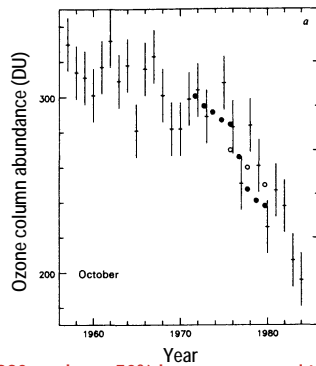
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## What is the ozone hole?



Farman et al. published 1985 this picture that shows that the total ozone column over Antarctica was decreasing each October (Spring)

1980s column 50% lower compared to 1960s values!

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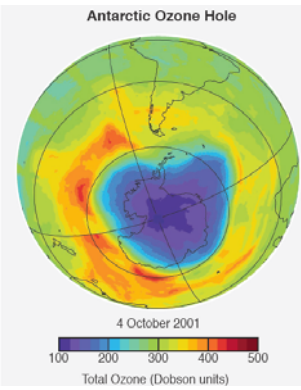
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## The Ozone Hole



The ozone hole covers an area larger than the Antarctic continent

<http://www.epa.gov/ozone/science/unepSciOandA.pdf>

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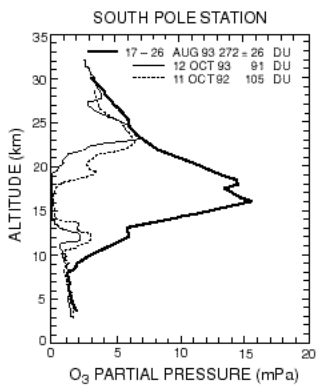
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## Vertical Structure of Antarctic Ozone Hole



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### Antarctic Ozone Hole Conundrum

- What is the cause?
- Why only in springtime between 15 – 25 km ?
- Why primarily in the Antarctic?

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### Antarctic Ozone Hole Theories



Also a scientific debate

- chemistry versus meteorology
- human versus natural
- solar cycles

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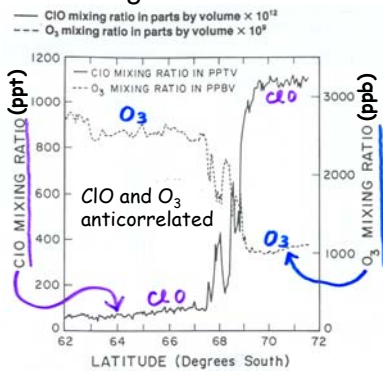
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### “Human Finger Prints”: Chlorine



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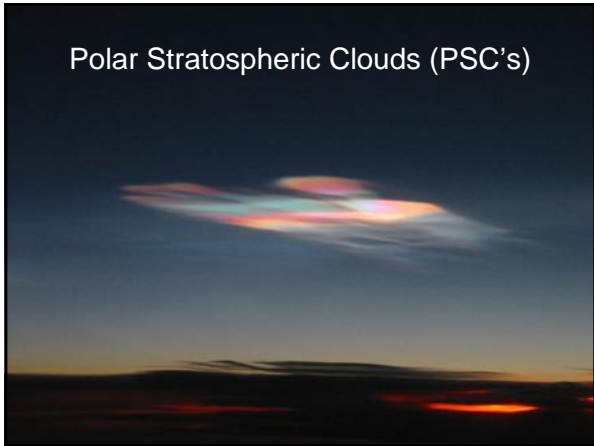
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# Polar Stratospheric Clouds (PSC's)




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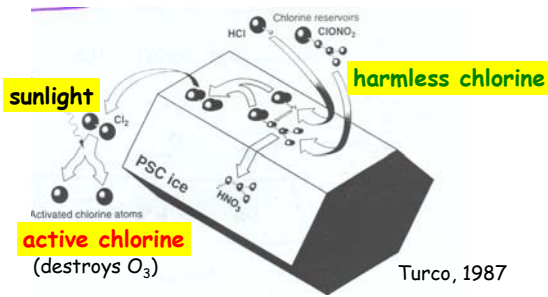
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## Chemistry on Polar Stratospheric Clouds

PSCs allow "inactive" chlorine to become "active"




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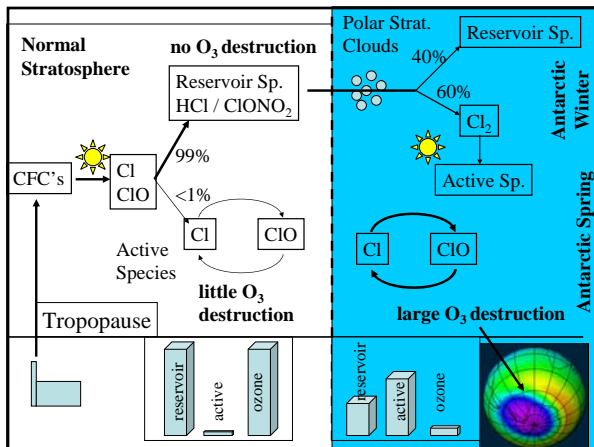
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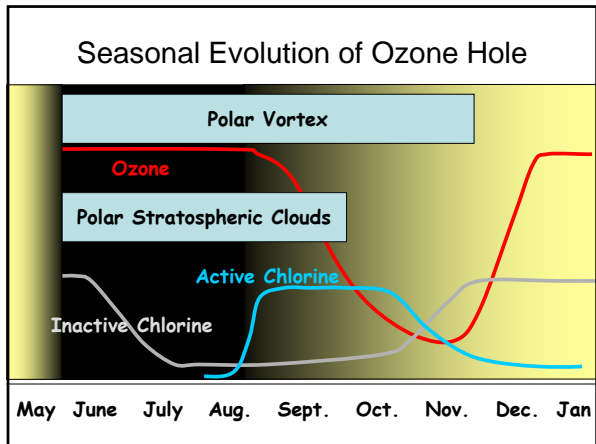
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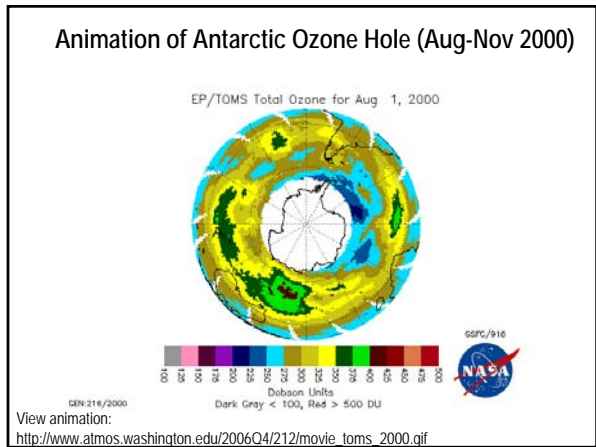
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## Ozone Watch Web page

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

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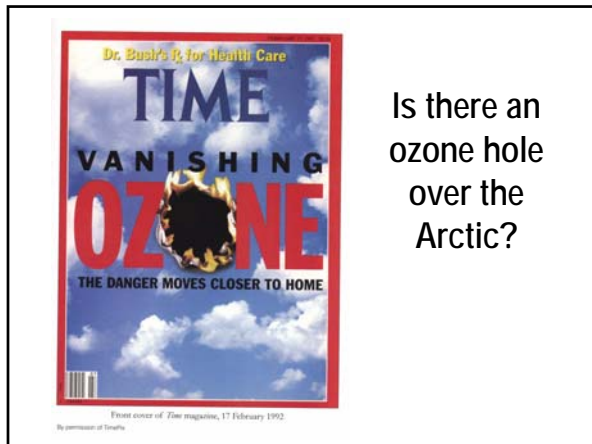
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Is there an ozone hole over the Arctic?

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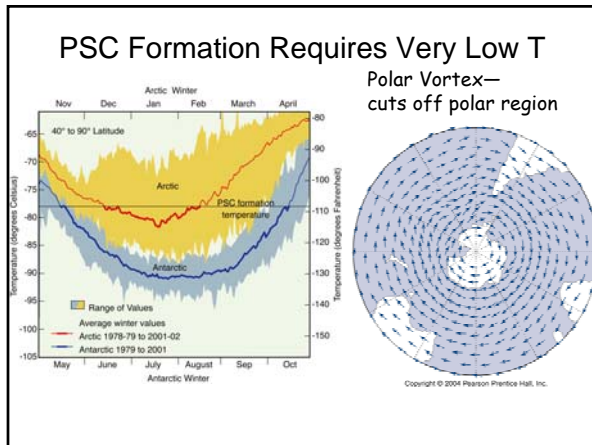
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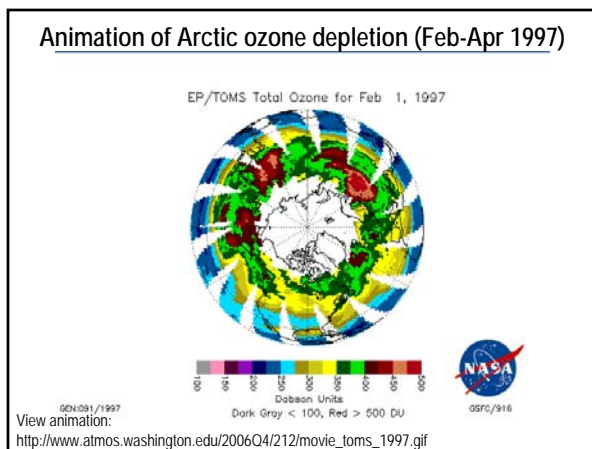
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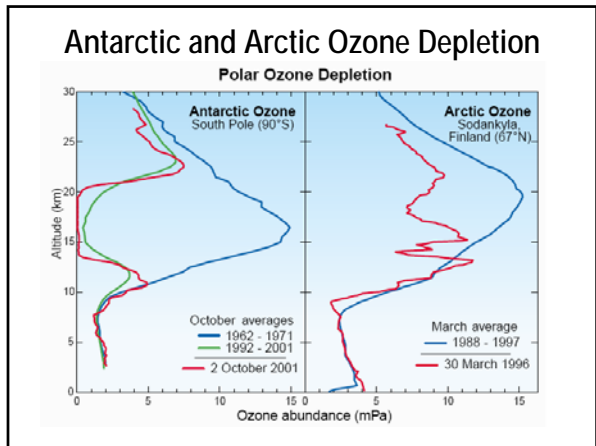
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## Antarctic and Arctic Ozone Depletion




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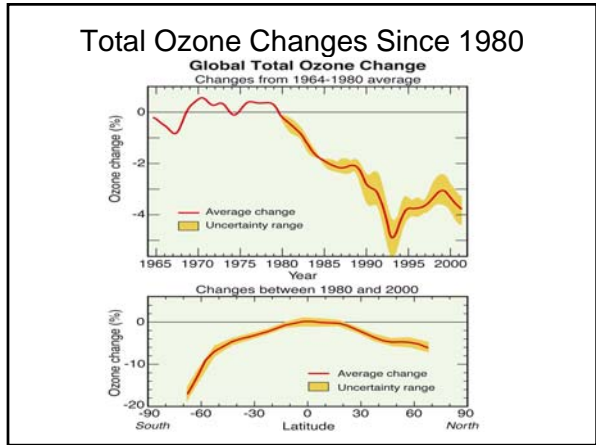
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## Total Ozone Changes Since 1980




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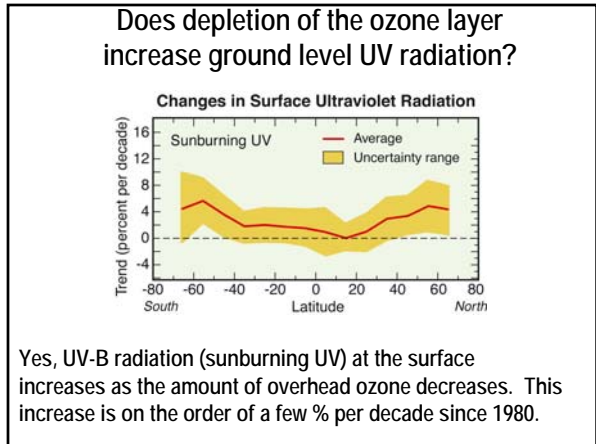
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## Does depletion of the ozone layer increase ground level UV radiation?



Yes, UV-B radiation (sunburning UV) at the surface increases as the amount of overhead ozone decreases. This increase is on the order of a few % per decade since 1980.

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### Effects of enhanced UV-B radiation

Attack molecules in cells, particularly DNA → cellular dysfunction / mutation / formation of toxic species

**Skin:**

- sunburn,
- premature aging of skin,
- skin cancer (basal cell carcinomas ; squamous cell carcinomas; melanoma (dark tumor-like growth))

**Eyes:** Affects cornea (covers iris+lens)

- Snow blindness
- Cataract (loss of transparency of cornea)

**Immune system:** UV-B kills cells which fight infections on skin

Affects crops, plants (slower growth, photosynthesis), animals, and microorganisms.

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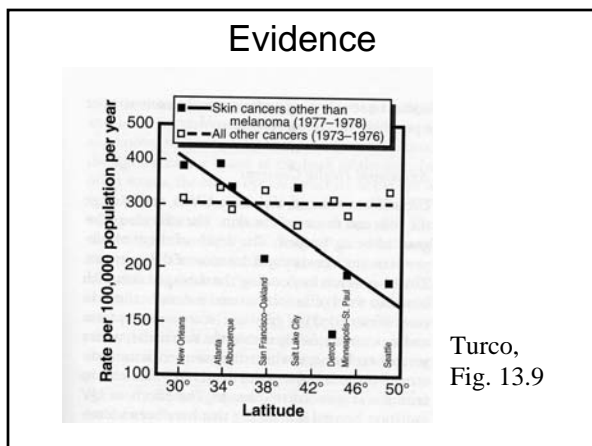
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## Regulations on the production of CFCs

- **Vienna convention (1985):** "Convention for the Protection of the ozone layer" signed by 20 nations (research, future protocols)
- **Montreal Protocol (1987):** "Protocol on substances that deplete the ozone layer" ratified in 1989. Legally binding controls freezing production to 1985 levels.
- **London Amendment (1990):** phaseout of production by 2000 for developed nations and by 2010 for developing nations.
- **Copenhagen Agreement (1992):** Phaseout for developed nations by 1996.
- HCFC production allowed as short-term substitutes for CFCs. HCFC production to be phased out by 2030 (developed nations), 2040 (developing nations).

First environmental problem solved on an international basis!

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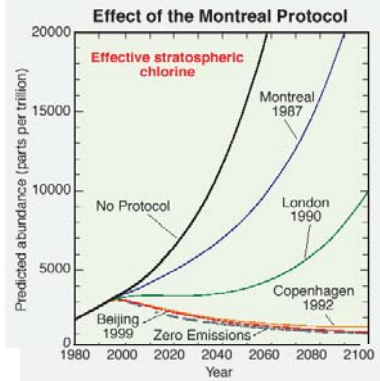
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## Projected Evolution of Tropospheric Chlorine




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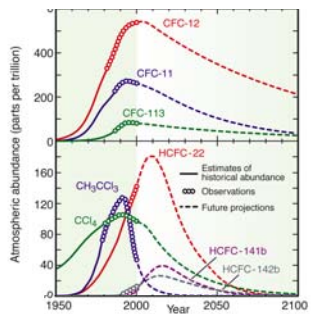
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## Has the Montreal Protocol been successful in reducing ozone-depleting gases in the atmosphere?



Yes!

WMO, 2002, 20 questions

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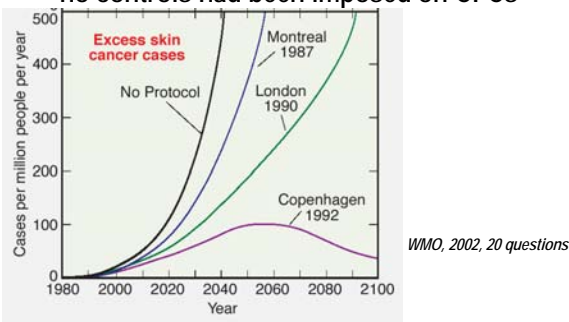
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### Estimated excess cases of skin cancer if no controls had been imposed on CFCs



2050 no protocol: U.S. 33,000 excess skin cancer cases/year  
Europe 14,000 excess skin cancer cases/year

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### The Montreal Protocol is Working!

- Without the Montreal Protocol, ozone depletion in 2050 would be at least 50% at midlatitudes in the Northern Hemisphere and 70% at midlatitudes in the Southern Hemisphere, about 10 times larger than today.
- Surface UV-B radiation in 2050 would at least double at midlatitudes in the Northern Hemisphere and quadruple at midlatitudes in the Southern Hemisphere compared with an unperturbed atmosphere. This compares to the current increases of 5% and 8% in the Northern and Southern Hemispheres, respectively, since 1980.

*WMO 1998 Scientific Assessment of Ozone Depletion*

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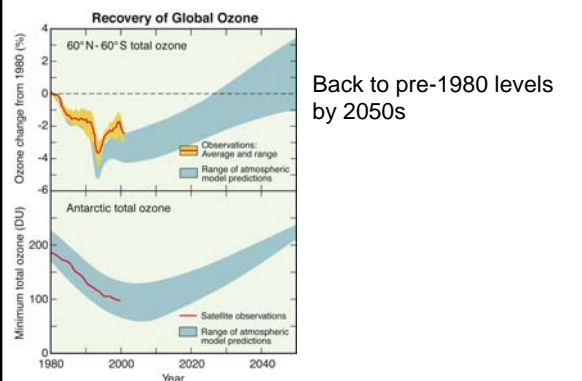
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### When is the ozone layer expected to recover?



Back to pre-1980 levels by 2050s

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