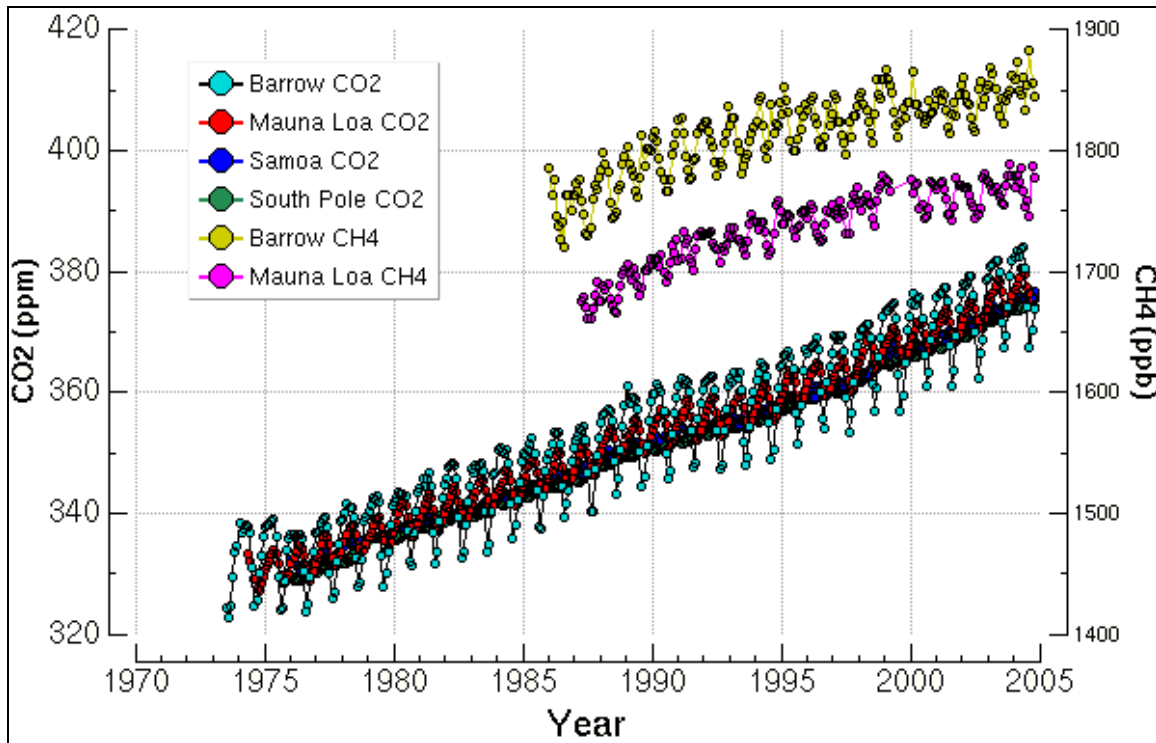


Summary of Issues with CO₂

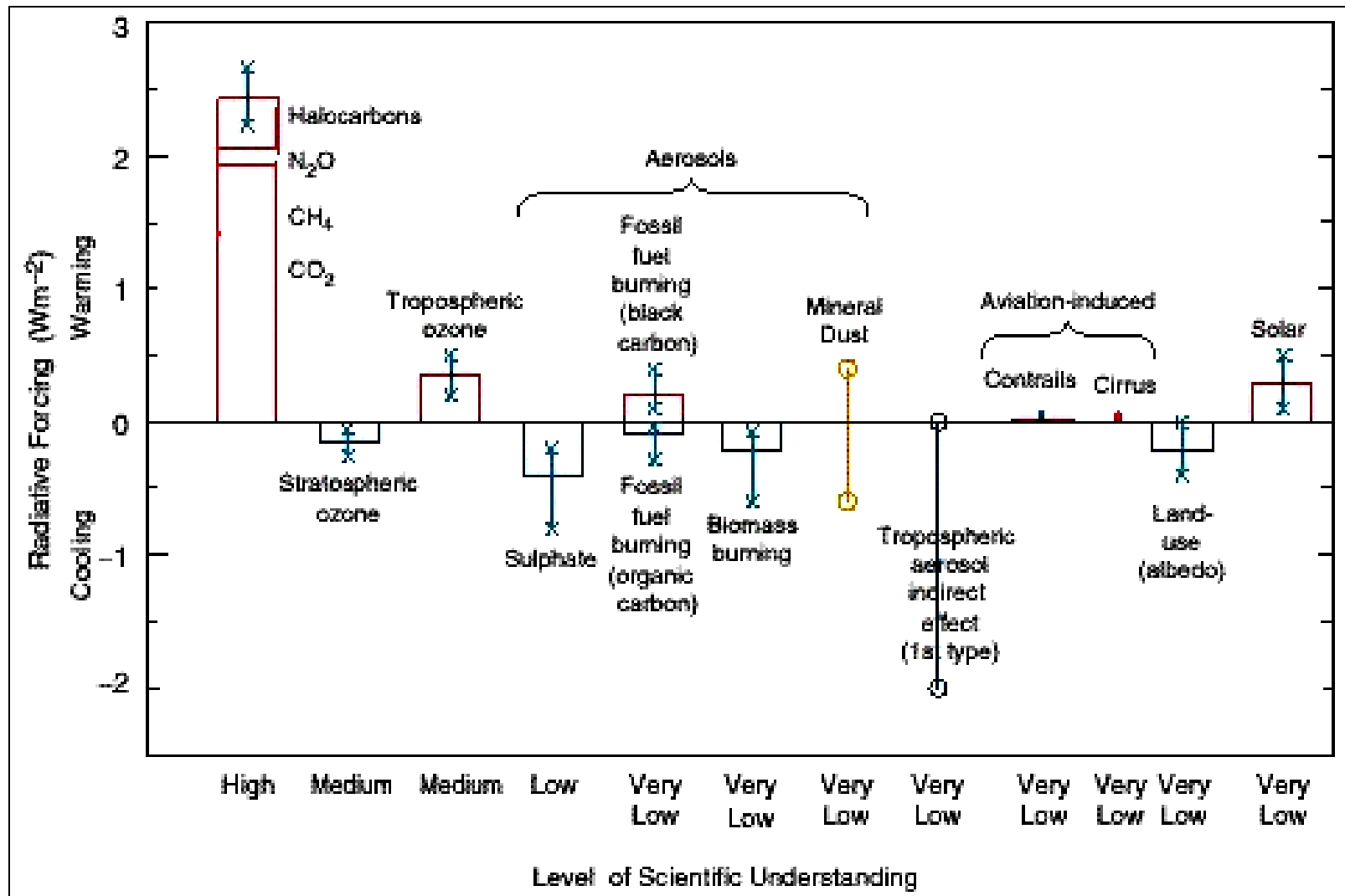
- Complete combustion of organic fuel leads to generation¹, and subsequent release of CO₂
- Decreased levels of forestation are a concern given vegetation is a sink for CO₂
- Increasing water temperature, e.g., ocean water decreases the water solubility of CO₂, therefore decreasing the efficiency of a potential sink for CO₂
 - Please review Henry's Law and its relationship in mass transfer to air from water and temperature of the system (the smaller the H_c, the lower the resistance to mass transfer to air from the water/air interface)
- Acid rain reduces pH of natural water systems thus potentially increasing release of CO₂ from CaCO₃
 - Also, changes the equilibrium (Question: How is the equilibrium changed?)
- Others?

¹ This is hopefully what we realize; usually, incomplete combustion of fossil fuels leads to formation of CO and complex hydrocarbons of various vapour pressures that can create primary air pollution, which can then be followed by secondary air pollution.



<http://www.cmdl.noaa.gov/ccgg/insitu.html>

- (Mauna Loa Observatory is located on the Island of Hawaii at an elevation of 3397 m on the northern flank of Mauna Loa volcano at 200 north).

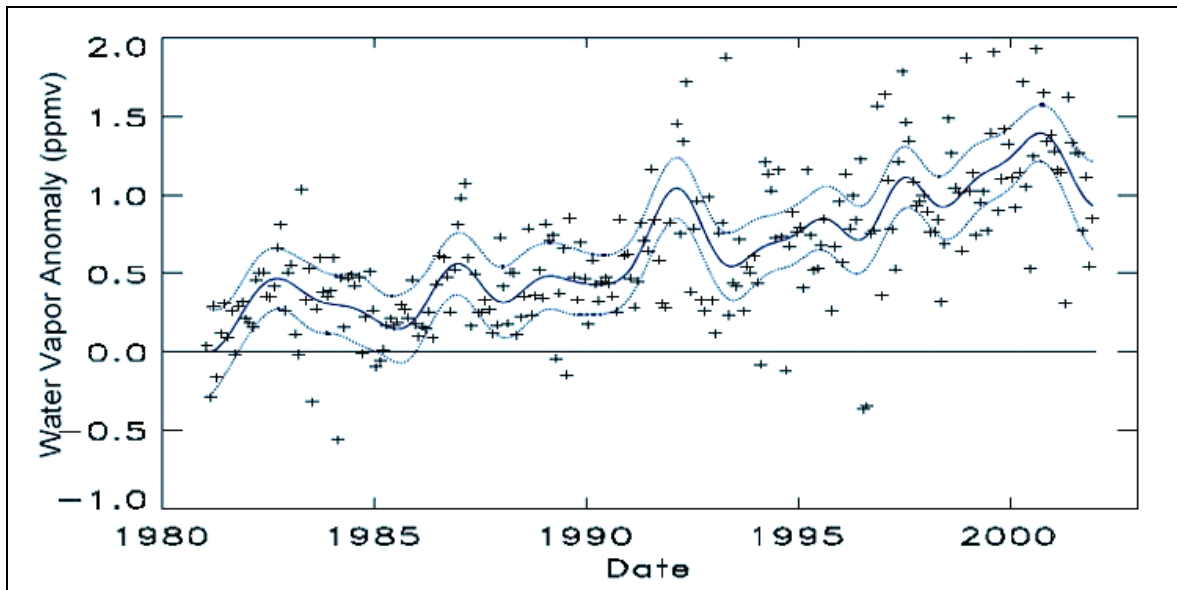


Ozone

- Ozone formation and destruction in the stratosphere
 - The composition of the stratosphere is similar to that of the troposphere, but $T \sim 220 \text{ K}$ and $p(\text{total}) \sim 0.1 \text{ atm}$
 - The “ozone layer” is not really a layer
- “Chapman Mechanism”
 - Ozone formation:
 - $\text{O}_2(\text{g}) + h\nu \rightarrow 2 \text{O}(\text{g})$
($\lambda < 240 \text{ nm}$ not in troposphere)
 - $\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$
 - Ozone destruction:
 - $\text{O}_3(\text{g}) + h\nu \rightarrow \text{O}(\text{g}) + \text{O}_2(\text{g})$
($\lambda < 325 \text{ nm}$ stratosphere and troposphere)
 - $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{O}_2(\text{g})$
- Ozone level is at steady state correspond, where the rate of formation and destruction of ozone is balanced. (solar driven): energetics of these reactions.
- Sunlight (energy) driven reactions
- Rate of ozone destruction increases with some pollutants
- Naturally, over 300,000 t of ozone are made and destroyed **each day** in the atmosphere

- Experimental concentration of ozone is less than the Chapman mechanism predicts, therefore, there are other sinks for ozone loss
- The other sinks are **chain reactions** involving radical species X, where X can be any of NO, Cl, Br, OH, H
 - $X(g) + O_3(g) \rightarrow XO(g) + O_2(g)$
 - $XO(g) + O(g) \rightarrow X(g) + O_2(g)$
- Net reaction is:
 - $O(g) + O_3(g) \rightarrow 2O_2(g)$
 - X is a catalyst that is re-formed in each cycle
- The upper atmosphere contains small concentrations of these “X” substances, and these reactions proceed naturally – they do not necessarily represent pollution
- **What is the significance of stratospheric ozone?**
 - the conversion of solar radiation into heat makes the stratosphere warmer than the upper troposphere
- **Generalization** the warm parts of the atmosphere all have energy deposited in them
 - the absorption of solar radiation < 300 nm in the stratosphere prevents this damaging radiation from reaching the Earth’s surface
 - in the wavelength range 300-325 nm (UV-B) just a little radiation does leak through, and this is enough to dissociate **tropospheric** ozone

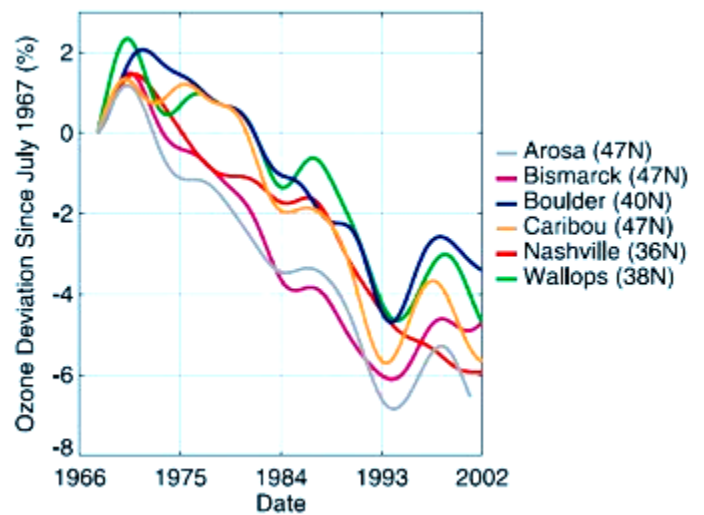
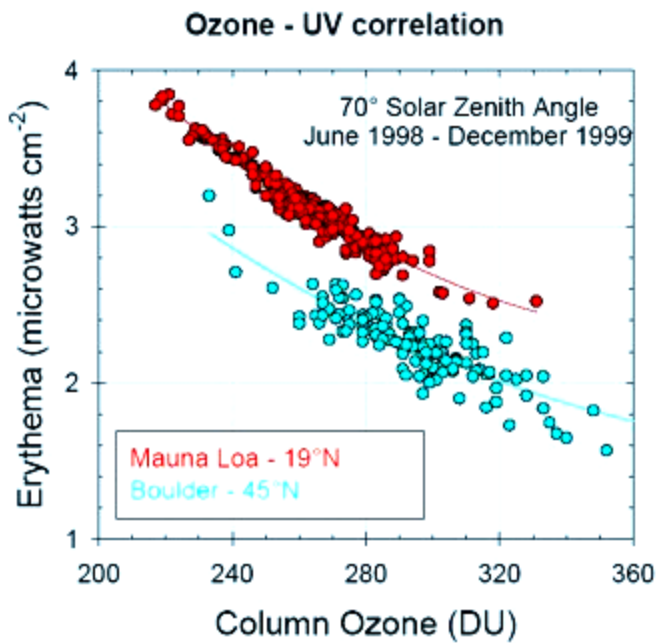
Water Vapour and Ozone

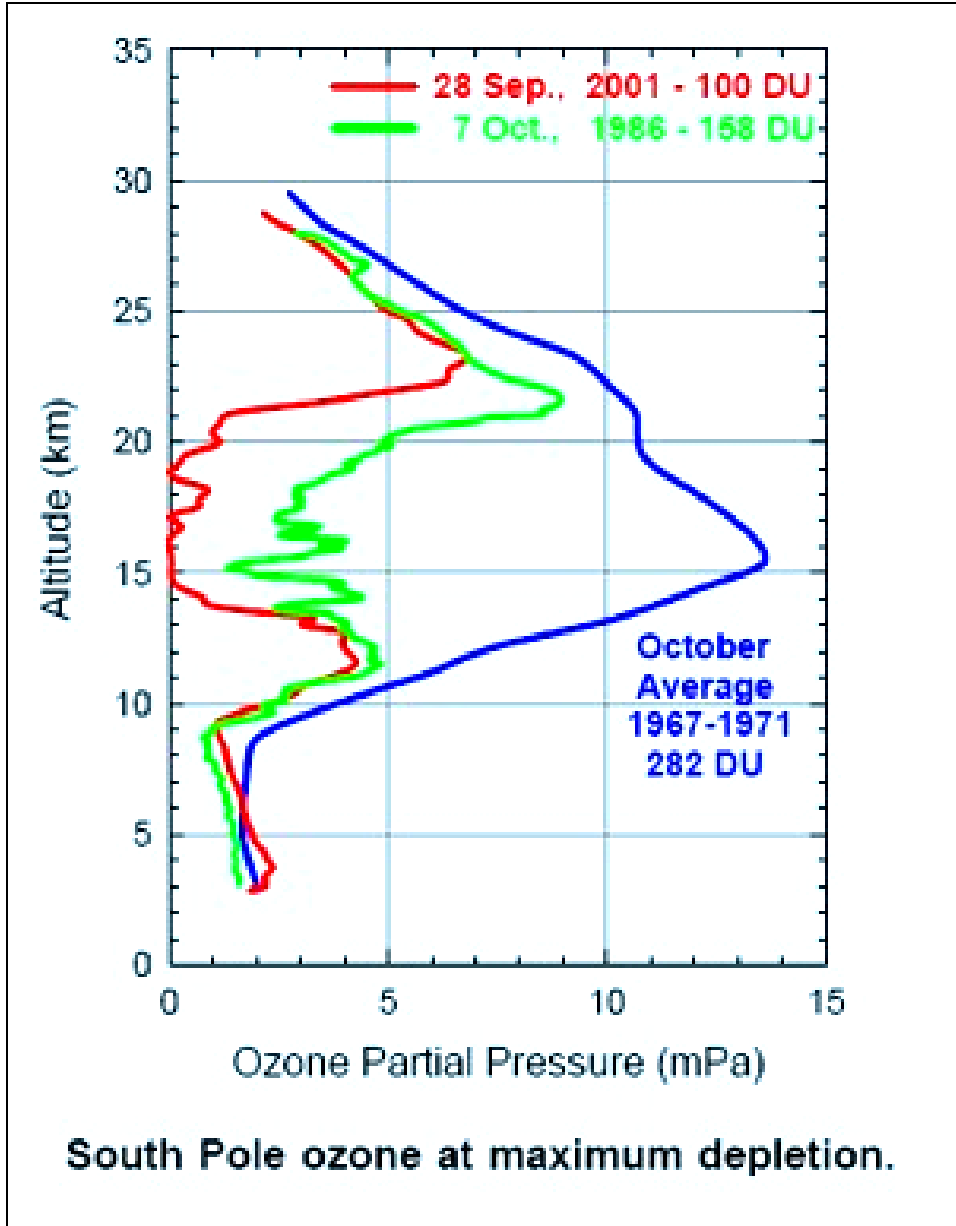


<http://www.cmdl.noaa.gov/ozone.html>

Stratospheric Water Vapor

- “Utilizing balloon-borne frost-point hygrometers, GMD has detected an approximately 1% per year increase in stratospheric water vapor at Boulder, Colorado, since 1980.”
- “Besides implications for climate change, increased water vapor can affect the rate of chemical ozone loss, for example, by increasing the incidence of polar stratospheric clouds.”
- “Satellite measurements of water vapor, although not of adequate length for accurate trend determination, suggest that the increase may extend to other latitudes.”





Chlorofluorocarbons (CFCs)

What were/are CFCs used for?

- Refrigerants
- Propellants for foams
- Propellants for aerosols

CFC Numbering System

- Add 90 to the number; the three digits represent the numbers of C, H, F atoms; make up the rest of the “unused bonds” with Cl.
 - Example: CFC-112 is C₂F₂Cl₄
 - 112+90=202. Therefore, 2 Carbon atoms, 0 Hydrogen atoms, 2 Fluorine atoms, the rest are Chlorine atoms. Same numbering system for HCFCs and HFCs.

Properties of CFCs

- CFCs do not absorb radiation < 250 nm
 - NOT present in the troposphere
- The CFCs are chemically unreactive
 - NO tropospheric sinks
- Slow migration to stratosphere, $t^{1/2} \sim 5$ yr
 - Globally well mixed
- In stratosphere, slow reaction with $t^{1/2}$ many decades:
 - e.g. $\text{CF}_2\text{Cl}_2 + h\nu \rightarrow \text{CF}_2\text{Cl} + \text{Cl}$

- note that the weakest bond breaks first
- CFCs are a source of stratospheric chlorine atoms
 - Chlorine atoms are catalysts for destroying stratospheric ozone
 - “X” in the chain sequence on the previous page
- Photolysis initiates the chain reactions; up to 10^4 cycles per chlorine atom!
- CFCs increase an existing “sink strength”, thereby lowering the steady state concentration of ozone.
 - Originally, it was thought that this was a new sink

The Montreal Protocol

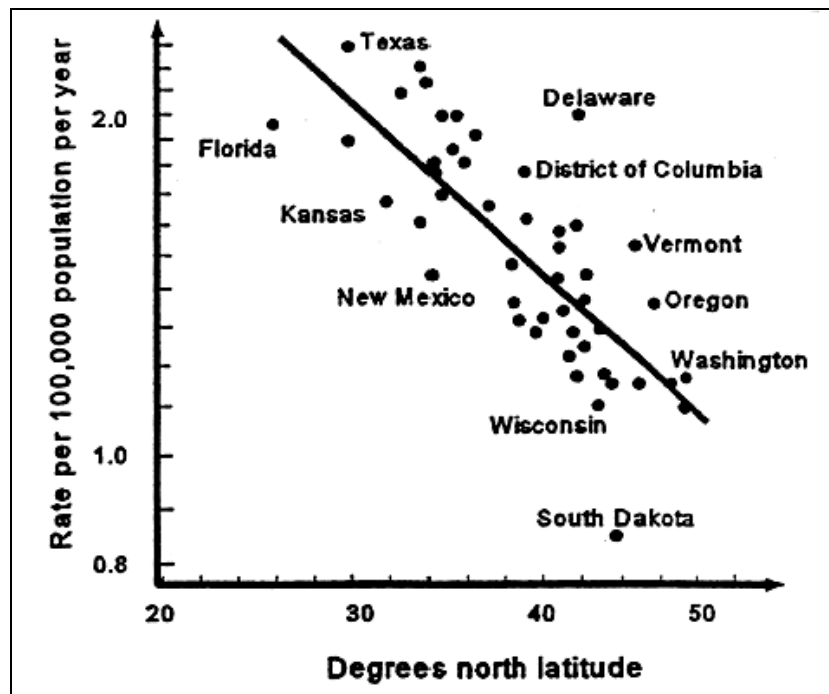
- In 1974, CFCs first discovered in the atmosphere
- Many of them were increasing at a rate of 6%/year in by the late 1970s
- Diffusion to the stratosphere takes ~5 to 10 years
- In 1978, North America and Europe ban on aerosol use of CFCs
- In 1987, The Montreal Protocol
 - A ban on “hard” CFCs + CH_3CCl_3 + CCl_4 to take place January 1, 1996
 - 10 year extension for developing countries (originally by 2010)
 - Halons (e.g., CF_3Br) phased out January 1, 1994

- The Montreal Protocol is historic because it is the first instance of international action on the basis of a future anticipated environmental threat

Mario Molina and Sherwood Rowland received the 1995 Nobel Prize in Chemistry for their seminal work on stratospheric ozone depletion: *Nature*, 1974, 249, 810

Why have CFCs been banned?

- CFC lifetimes 100+ years
 - Photolysis is inefficient
- Loss of stratospheric ozone allows more UV-B radiation to reach the earth's surface
- Relationship between UV radiation and skin cancer
 - (melanoma deaths among white US males)



- High UV at noon, in summer, high altitude, in the tropics.

Ozone-Depleting Gases

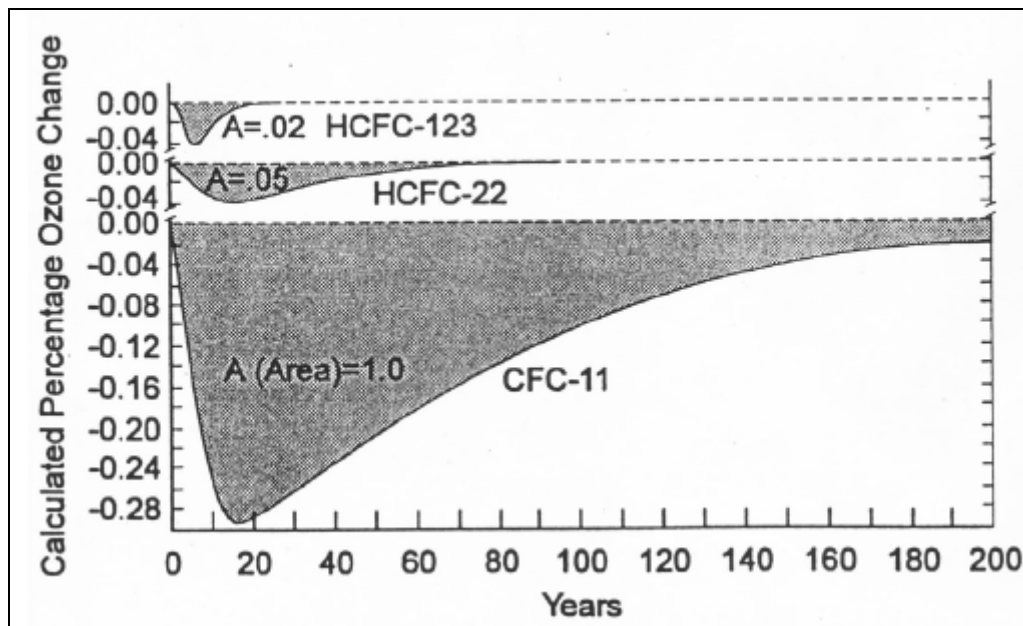
- CFC-11, CFC-12 and N₂O
- Most ozone depleting stratospheric gases are anthropogenic. Some, such as CH₃Br and CH₃Cl, have natural sources.

CFC Replacement Compounds

- HCFCs (hydrochlorofluorocarbons) and HFCs (hydrofluorocarbons)
 - Desired properties
 - **Chemical stability**
 - **Low toxicity**
 - **Boiling point (appropriate)**
- CFC replacements must undergo **tropospheric oxidation**
- Since CFCs deplete stratospheric ozone, replacements should **avoid or minimize Cl atoms**
- Because **hydrocarbons** can be oxidized in the troposphere, replacement compounds should **include H atoms**.
 - HCFCs and HFCs can react with tropospheric OH radicals (Question: What is the source of tropospheric OH radicals?)

- e.g. $\text{CH}_3\text{CHF}_2 + \text{OH} \longrightarrow \text{CH}_3\text{CF}_2 + \text{H}_2\text{O}$
followed by further reactions of CH_3CF_2
- Recall that CFCs and their replacements are also greenhouse gases
 - Polar C-F and C-Cl bonds.
 - Fully fluorinated compounds **must** be avoided
 - No hydrogen atoms are available to react with OH and also the fluorinated compounds have high global warming potentials

Ozone Depleting Potential (ODP)



- The relative areas are ODPs based on equal masses
 - CFC-11 is CFCl_3
 - HCFC-22 is CHF_2Cl
 - HCFC-123 is $\text{C}_2\text{HF}_3\text{Cl}_2$

CFCs, HFCs, HCFCs: ODP vs Global Warming Potential

Compound		ODP (CFC1 ₃ =1)	GWP (CO ₂ =1)
HCFC-22	CHF ₂ Cl	0.05	4300
HCFC-123	CF ₃ CHCl ₂	0.02	300
HCFC-124	CF ₃ CHFCl	0.02	1500
HFC-125	CF ₃ CHF ₂	0.0	5300
HFC-134a	CF ₃ CH ₂ F	0.0	3300
HCFC-141b	CH ₃ CFCl ₂	0.1	4300
HCFC-142b	CH ₃ CF ₂ Cl	0.06	1800
HFC-152a	CH ₃ CHF ₂	0.0	410

Note: HFCs have ODP = zero; GWPs taken from the IPCC

<http://216.239.33.100/search?q=cache:4ApslDfh9poC:tis.eh.doe.gov/oepa/rules/60/60fr52357.pdf+global+warming+potential+HCFC&hl=en> (20 year horizon).

► They are much larger than the values in the text

Response of industry to the phase-out of CFCs (some of the alternatives they came up with)

- Aerosol propellants
 - CO₂
 - CH₃OCH₃—H₂O
 - C₄H₁₀-CH₂Cl₂
- Foam blowing agents
 - [HCFC-22]
 - HCFC-141b
 - Cyclopentane
- Refrigerants
 - HFC-134a
 - Hydrocarbons (in Europe)
- Note concern about CF₃CO₂H as a highly stable breakdown product of several HFCs, including HFC-134a

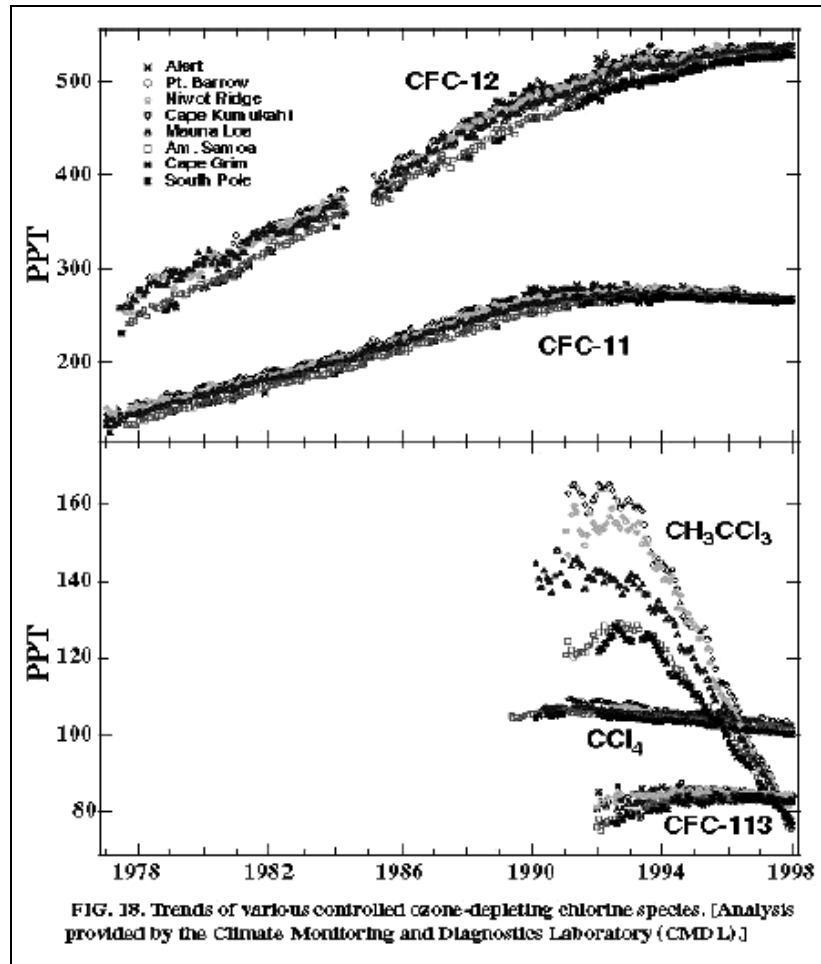
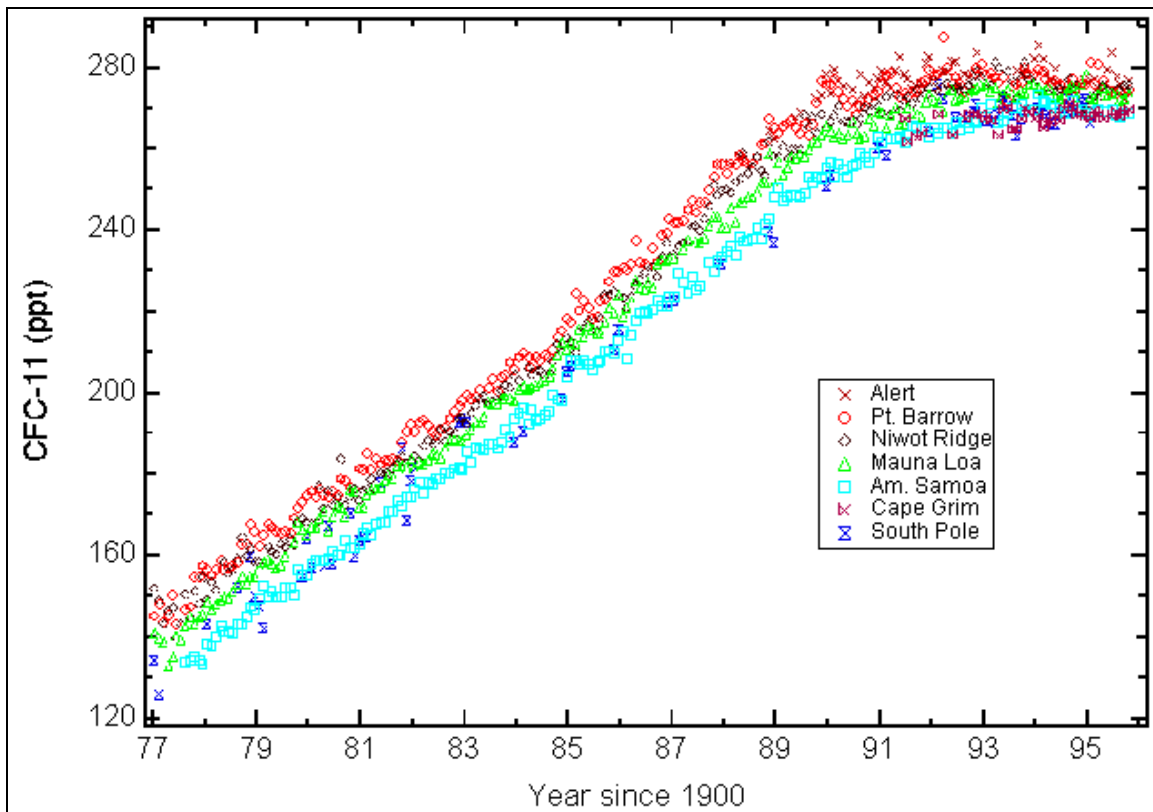


Figure from:

http://www.cpc.ncep.noaa.gov/products/assessments/assess_98/fig18.gif

Note that the CMDL is currently called the Global Monitoring Division (<http://www.cmdl.noaa.gov>)². This is a very useful site to visit for information related to atmospheric issues such as ozone and air quality, not to mention temperature.

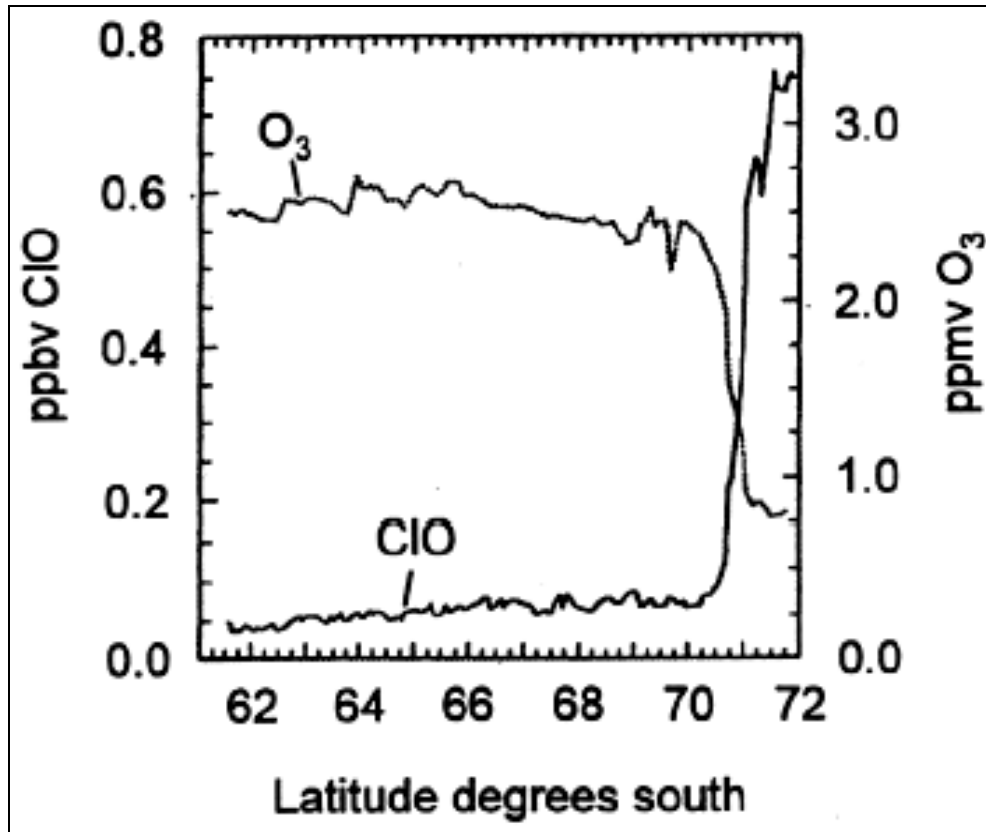
² The Climate Monitoring and Diagnostics Laboratory (CMDL) has merged into the Earth System Research Laboratory (ESRL) as part of its Global Monitoring Division (GMD).



<http://www.cmdl.noaa.gov/noah/publictn/elkins/cfcs.html>

Polar Ozone Holes:

The precipitating event for the Montreal Protocol



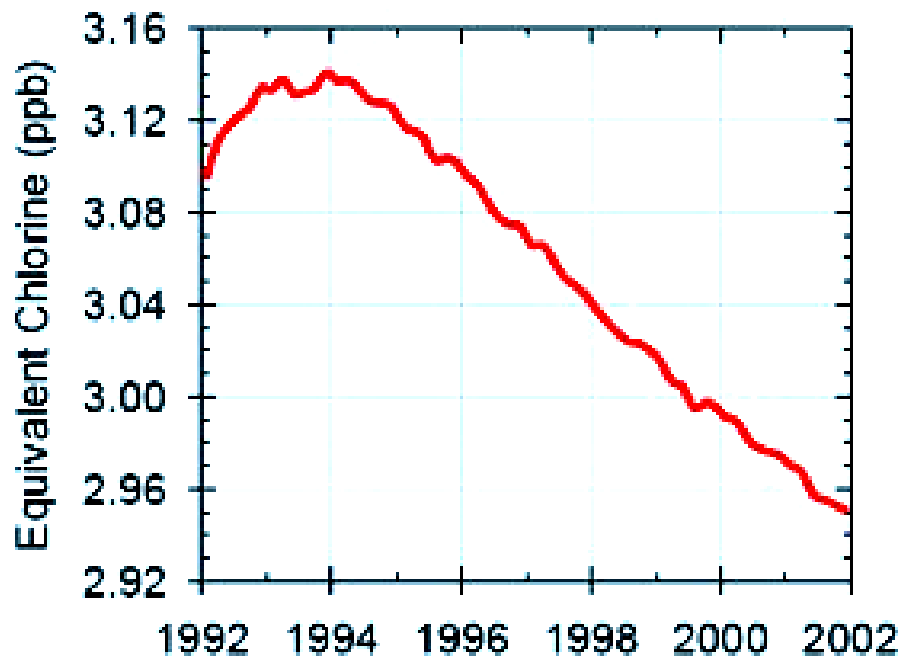
Environ. Sci. Technol., 1991; data of September 21, 1987

- “Polar Sunrise” experiments have shown that this effect is also seen in the Arctic (but not every year)
- The curious effect of the break-up of the Ross Antarctic ice shelf (January-March 2002): D.W.J. Thompson and S. Solomon, *Science*, 2002, 296, 895 attributed to stratospheric **cooling** from the polar ozone hole having two effects:
 - Tropospheric warming;
 - Changing polar vortex → W Antarctic becomes warmer, E Antarctic cooler

The other cycles for ozone depletion: X= Cl, NO, OH, or H

- CH₃Cl
 - Natural source of atmospheric chlorine
 - Marine origin
 - Long tropospheric t^{1/2}
- NO
 - not much transport from the troposphere (short t^{1/2})
 - mostly made in the upper atmosphere, but injection into stratosphere from *e.g.*, volcanic eruptions, supersonic aircraft
 - Another route is photolysis of N₂O
 - N₂O + hν → N₂ + O* (excited oxygen atom)
 - O* + N₂O → 2NO
 - Note: O* also comes from high energy dissociation of ozone
 - O₃ + hν → O* + O₂*
- OH arises from photolytic cleavage of H₂O in the stratosphere (not troposphere) and from reaction of excited state oxygen atoms with water vapour
 - O* + H₂O → 2 OH
- H atom chemistry is most important in the upper stratosphere, where p(O₂) is less:
 - H + O₂ → HO₂ competes in the troposphere

Success Due to the Montreal Protocol



Global equivalent atmospheric chlorine (all chlorine and bromine compounds), now decreasing because of the Montreal Protocol.

Summary:

Measurements of climatically important gases include carbon dioxide (CO₂), nitrous oxide (N₂O), chlorofluorocarbons (CFC's), and ozone (O₃). More compounds have been added including methane (CH₄), carbon monoxide (CO), hydrogen (H₂), hydrochlorofluorocarbons (HCFC's), hydrofluorocarbons (HFC's), methyl halides, and sulfur hexafluoride (SF₆). The intention is to develop correlations between climate change and atmospheric issues related to anthropogenic sources (or increases) of environmental pollutants.