Final Review

AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2015

12 May 2015

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Final Exam

– Monday, 18 May, 10:30 am to 12:30 pm
– This room
– Format similar to prior exams
– ***Please bring a calculator***
– "Virtual conversation"
– Closed book, no notes
– Backbone of course remains the lectures
– ***Entire course*** will be covered on the final exam
– We will be present to answer questions …
  please ask if you think a question requires clarification

– **If you have an exam either right before or right after this exam, please let me know**

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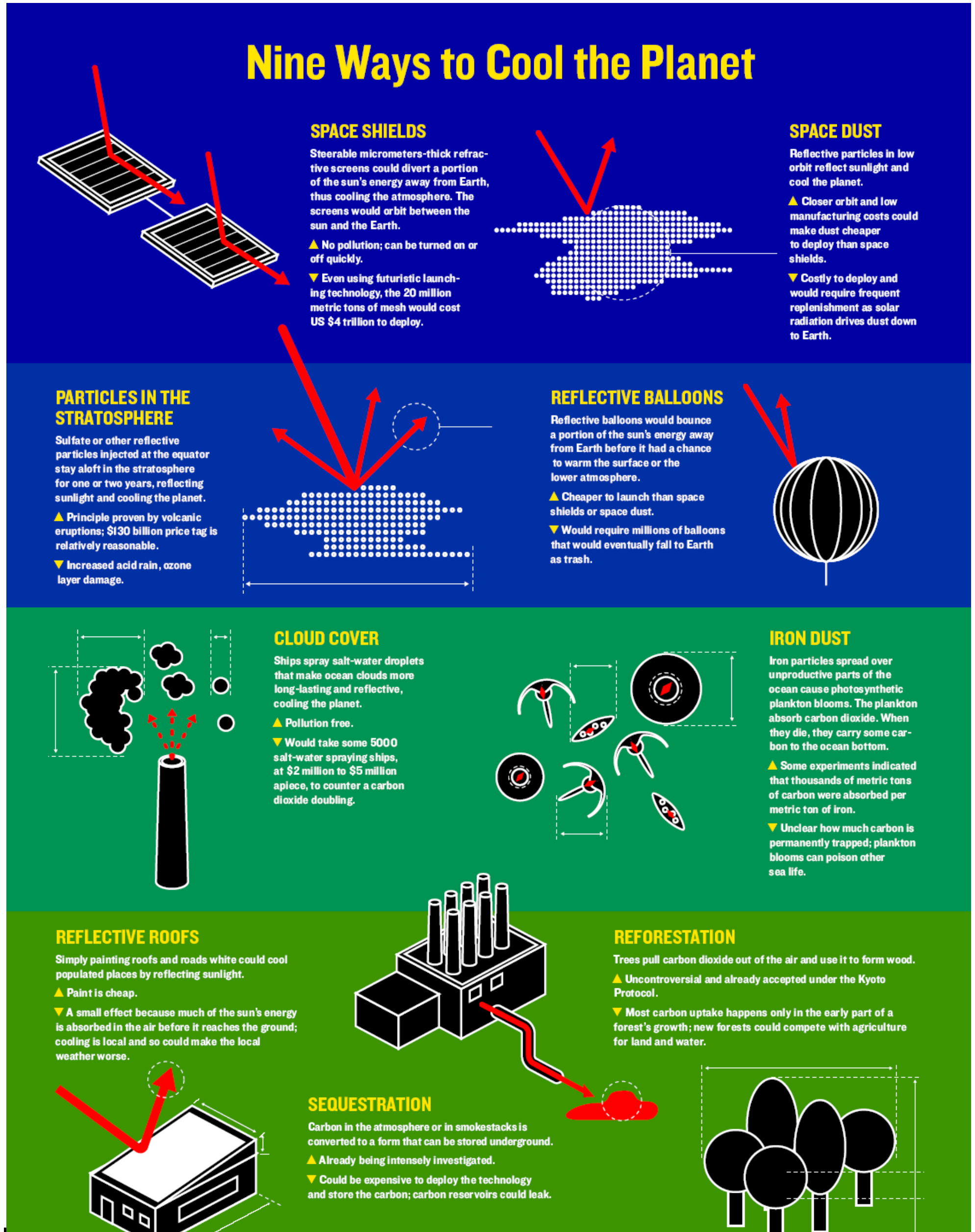
Of the “nine ways to cool the planet” discussed in the IEEE article, which of these seems most appealing to you? Briefly state why.



IEEE Spectrum, May 2007

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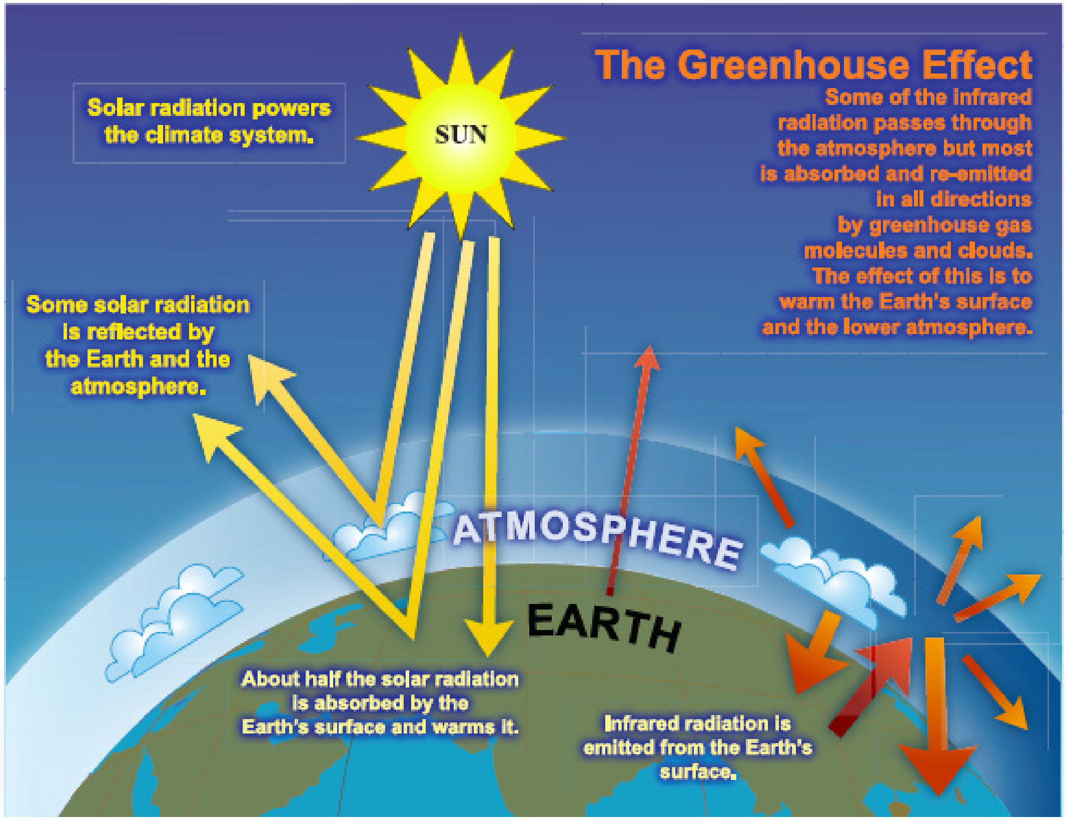
Greenhouse Effect



FAQ 1.3, Figure 1. *An idealised model of the natural greenhouse effect. See text for explanation.*

What is the "most important" GHG?

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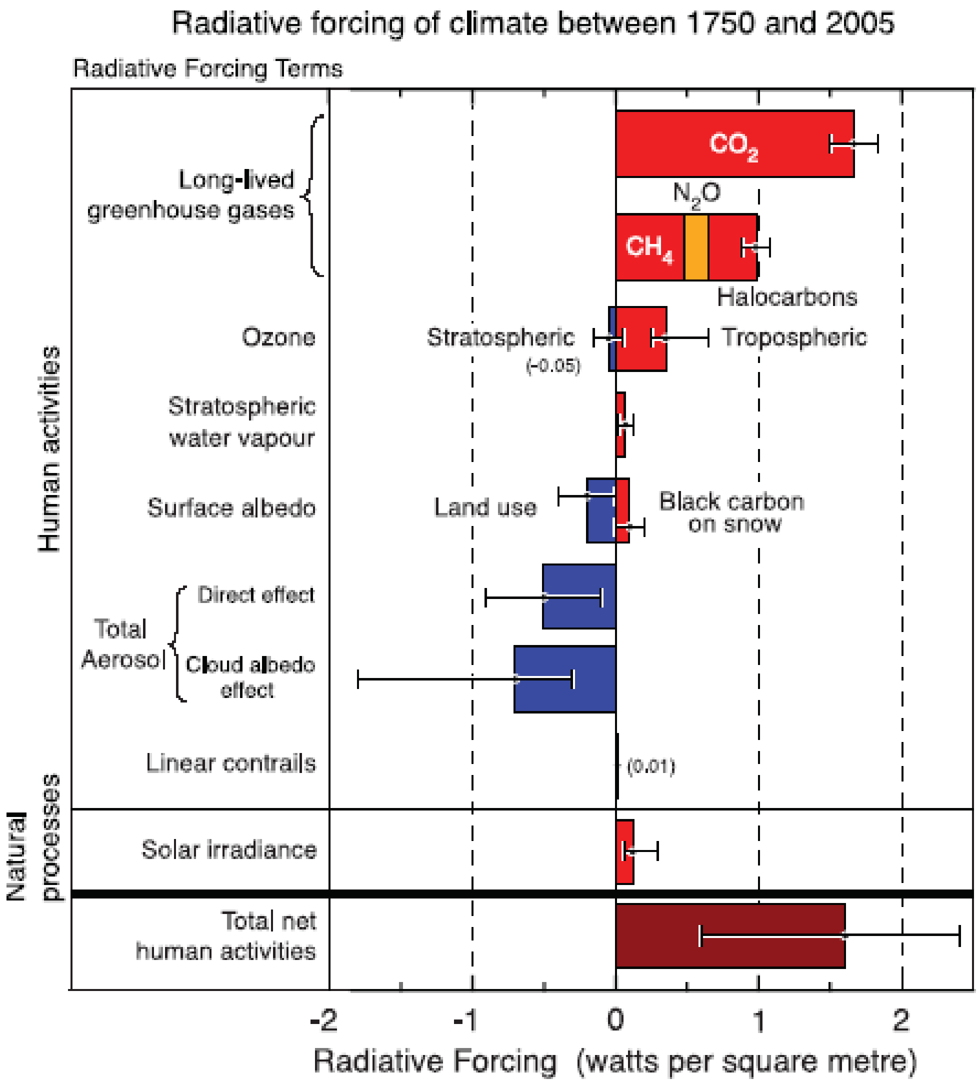
Radiative Forcing of Climate, 1750 to 2005



FAQ 2.1, Figure 2. *Summary of the principal components of the radiative forcing of climate change.*

Question 2.1, IPCC, 2007

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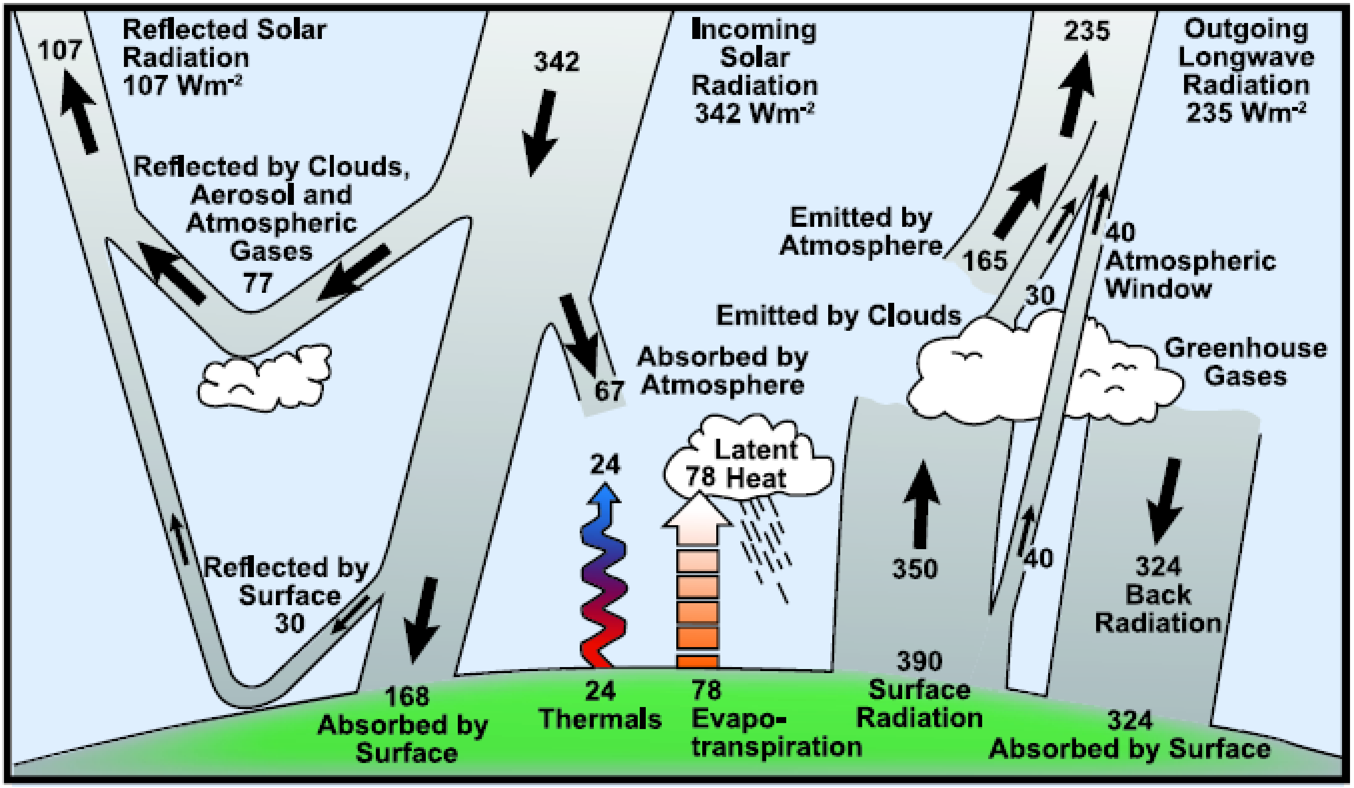
Radiative Forcing



FAQ 1.1, Figure 1. *Estimate of the Earth's annual and global mean energy balance. Over the long term, the amount of incoming solar radiation absorbed by the Earth and atmosphere is balanced by the Earth and atmosphere releasing the same amount of outgoing longwave radiation. About half of the incoming solar radiation is absorbed by the Earth's surface. This energy is transferred to the atmosphere by warming the air in contact with the surface (thermals), by evapotranspiration and by longwave radiation that is absorbed by clouds and greenhouse gases. The atmosphere in turn radiates longwave energy back to Earth as well as out to space. Source: Kiehl and Trenberth (1997).*

Question 1.1, IPCC, 2007

Radiative Forcing of Climate* is *Change in Energy
reaching the lower atmosphere (surface to tropopause) as GHGs rise.
"Back Radiation" is most important term.

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Connection Between GHG Abundance and Surface T

How much does ΔF change when CO_2 changes?

$$\Delta F \approx 5.35 \text{ W/m}^2 \ \ln\left(\frac{CO_2^{\,Final}}{CO_2^{\,Initial}}\right)$$

Changes in ΔF can be caused by changes in chemical composition (GHGs), aerosol loading, as well as surface albedo, H_2O, & cloud feedback

$$\Delta T = \lambda_{BB}(1+f)\ (\Delta F_{CO2} + \Delta F_{CH4+N2O} + \Delta F_{ALBEDO} + \Delta F_{AEROSOLS})$$

where $\lambda_{BB} = 0.3 \text{ K} / \text{W m}^{-2}$,

and $f =$ represents total feedbacks due to surface albedo, H_2O, & clouds

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GWP – Global Warming Potential

$$\text{GWP}(\text{CH}_4) = \frac{\int_{\text{time initial}}^{\text{time final}} a_{\text{CH4}} \times [\text{CH}_4(\text{t})]\ \text{dt}}{\int_{\text{time initial}}^{\text{time final}} a_{\text{CO2}} \times [\text{CO}_2(\text{t})\ \text{dt}]}$$

where:

a_{CH4} = Radiative Efficiency (W m^{-2} ppb^{-1}) due to an increase in CH_4

a_{CO2} = Radiative Efficiency (W m^{-2} ppb^{-1}) due to an increase in CO_2

CH_4 (t) = time-dependent response to an instantaneous release of a pulse of CH_4

CO_2 (t) = time-dependent response to an instantaneous release of a pulse of CO_2

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GWP – Global Warming Potential

SAR: Second Assessment Report (issued in 1995)

Table TS.2. *Lifetimes, radiative efficiencies and direct (except for CH_4) global warming potentials (GWP) relative to CO_2. {Table 2.14}*

Industrial Designation or Common Name (years)	Chemical Formula	Lifetime (years)	Radiative Efficiency ($W\ m^{-2}\ ppb^{-1}$)	Global Warming Potential for Given Time Horizon: SAR‡ (100-yr)	20-yr	100-yr	500-yr
Carbon dioxide	CO_2	See below[a]	[b]1.4×10^{-5}	1	1	1	1
Methane[c]	CH_4	12[c]	3.7×10^{-4}	21	72	25	7.6
Nitrous oxide	N_2O	114	3.03×10^{-3}	310	289	298	153

Notes:

‡ SAR refers to the IPCC Second Assessment Report (1995) used for reporting under the UNFCCC.

[a] The CO_2 response function used in this report is based on the revised version of the Bern Carbon cycle model used in Chapter 10 of this report (Bern2.5CC; Joos et al. 2001) using a background CO_2 concentration value of 378 ppm. The decay of a pulse of CO_2 with time t is given by

$$a_0 + \sum_{i=1}^{3} a_i \cdot e^{-t/\tau_i}$$ where $a_0 = 0.217$, $a_1 = 0.259$, $a_2 = 0.338$, $a_3 = 0.186$, $\tau_1 = 172.9$ years, $\tau_2 = 18.51$ years, and $\tau_3 = 1.186$ years, for $t < 1{,}000$ years.

[b] The radiative efficiency of CO_2 is calculated using the IPCC (1990) simplified expression as revised in the TAR, with an updated background concentration value of 378 ppm and a perturbation of +1 ppm (see Section 2.10.2).

[c] The perturbation lifetime for CH_4 is 12 years as in the TAR (see also Section 7.4). The GWP for CH_4 includes indirect effects from enhancements of ozone and stratospheric water vapour (see Section 2.10) .

from IPCC 2007 "Physical Science Basis"

Time constant of 172.9 years dominates

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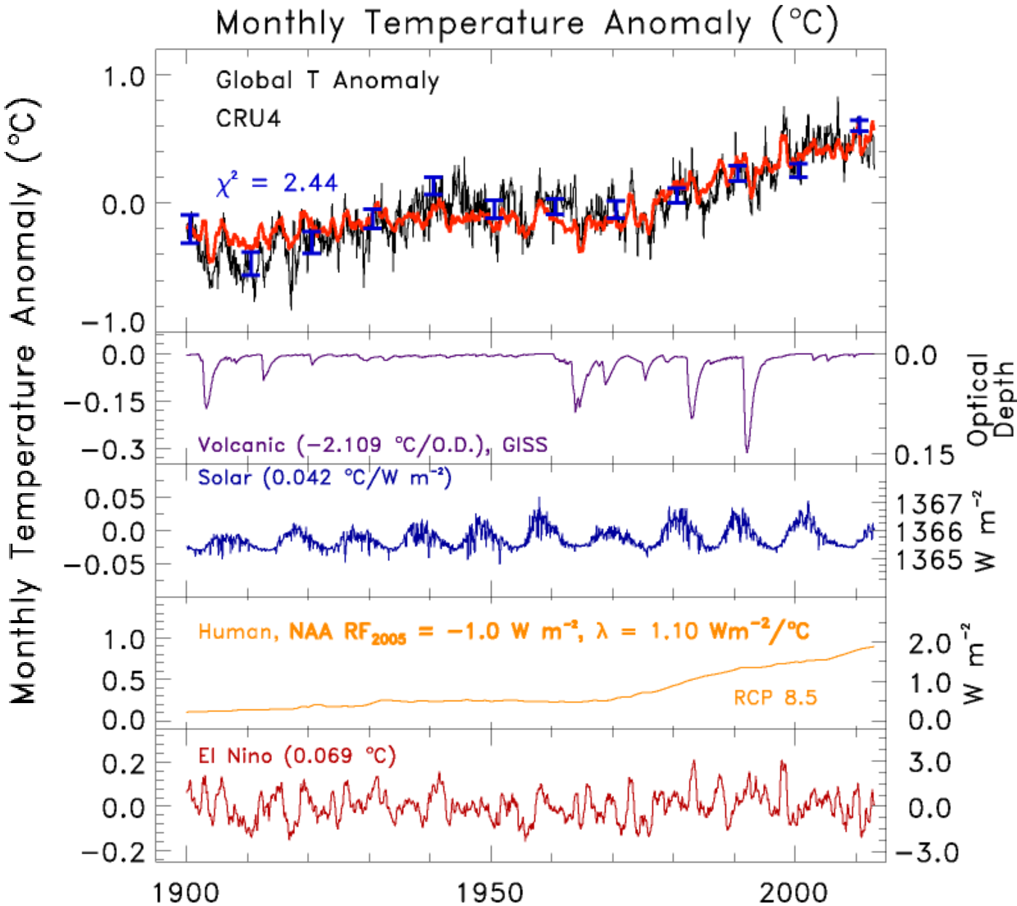

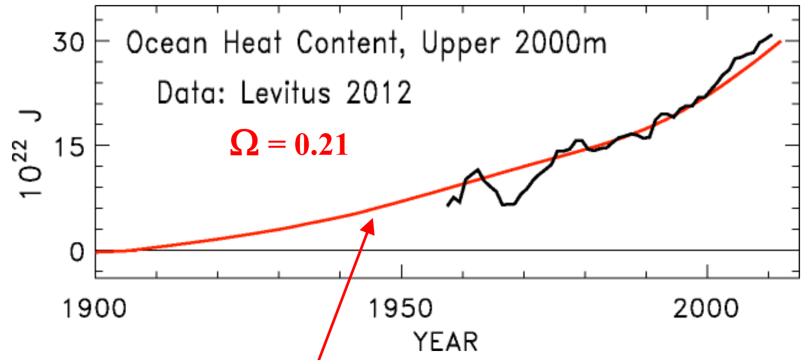

$$\Delta T_{MDL\ i} = (1+\gamma)\,(GHG\ RF_i + NAA\ RF_i)\,/\,\lambda_{BB} + C_o + C_1\times SOD_{i-6} + C_2\times TSI_{i-1} + C_3\times ENSO_{i-2} - Q_{OCEAN\ i}\,/\,\lambda_{BB}$$

where

$\lambda_{BB} = 3.21$ W m^{-2} / °C

$1+\gamma = \{1 - \Sigma(\text{Feedback Parameters})\,/\,\lambda_{BB}\}^{-1}$

NAA RF = net RF due to anthropogenic aerosols

SOD = Stratospheric optical depth

TSI = Total solar irradiance

ENSO = Multivariate El Niño South. Osc Index

Q_{OCEAN} = Export of heat, atmos. to ocean

$= \Omega\,(1+\gamma)\,\{(GHG\ RF_{i-72}) + (NAA\ RF_{i-72})\}$

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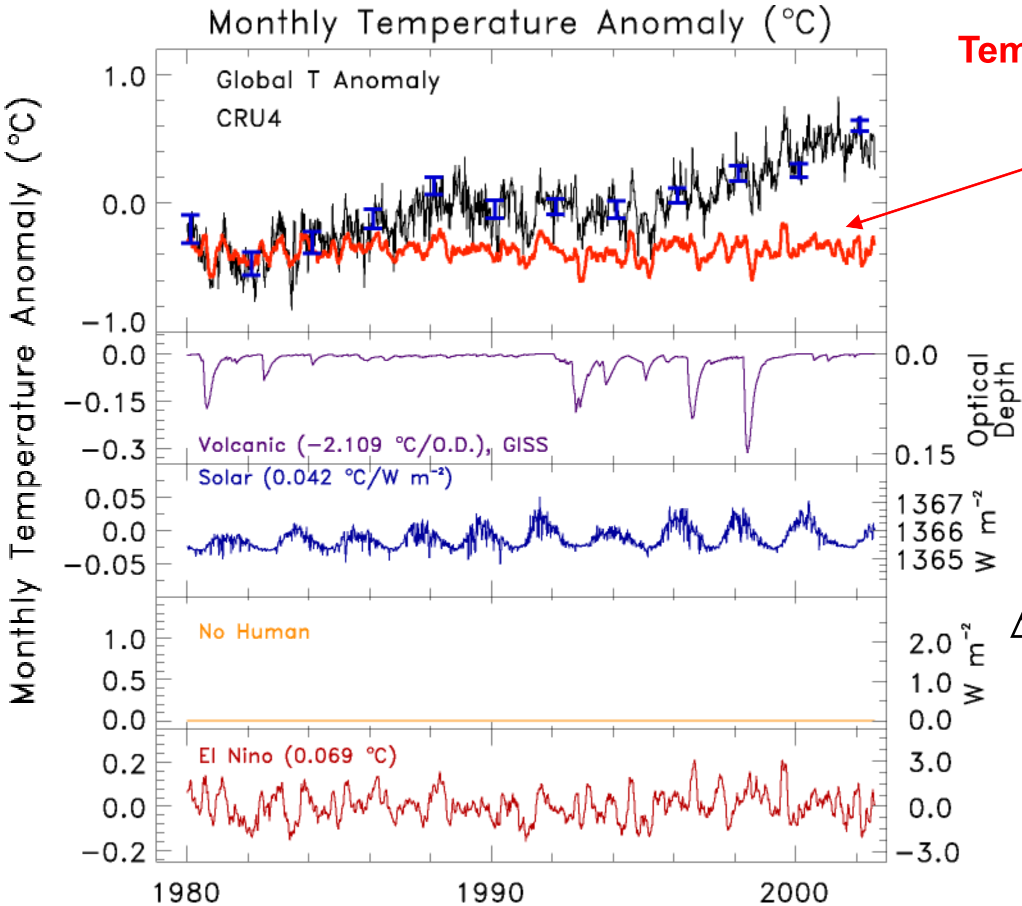

Temperature nearly flat without human influence, i.e., if volcanoes, solar, & ENSO are sole drivers of global climate

$\Delta T_{MDL\ i}$ = ~~(1+ γ) (GHG RF$_i$ + NAA RF$_i$) / λ_{BB}~~

$+ C_0 + C_1 \times SOD_{i-6} + C_2 \times TSI_{i-1} + C_3 \times ENSO_{i-2}$

~~− $Q_{OCEAN\ i}$ / λ_{BB}~~

where

$\lambda_{BB} = 3.21\ W\ m^{-2} / °C$

$1+\gamma = \{ 1 - \Sigma(\text{Feedback Parameters}) / \lambda_{BB} \}^{-1}$

~~NAA RF = net RF due to anthropogenic aerosols~~

SOD = Stratospheric optical depth

TSI = Total solar irradiance

ENSO = Multivariate El Niño South. Osc Index

~~Q_{OCEAN} = Export of heat from atmosphere to ocean~~

Global warming is caused by CO_2, the greatest waste product of modern society, and we should reduce our collective dependence on fossil fuels sooner rather than later

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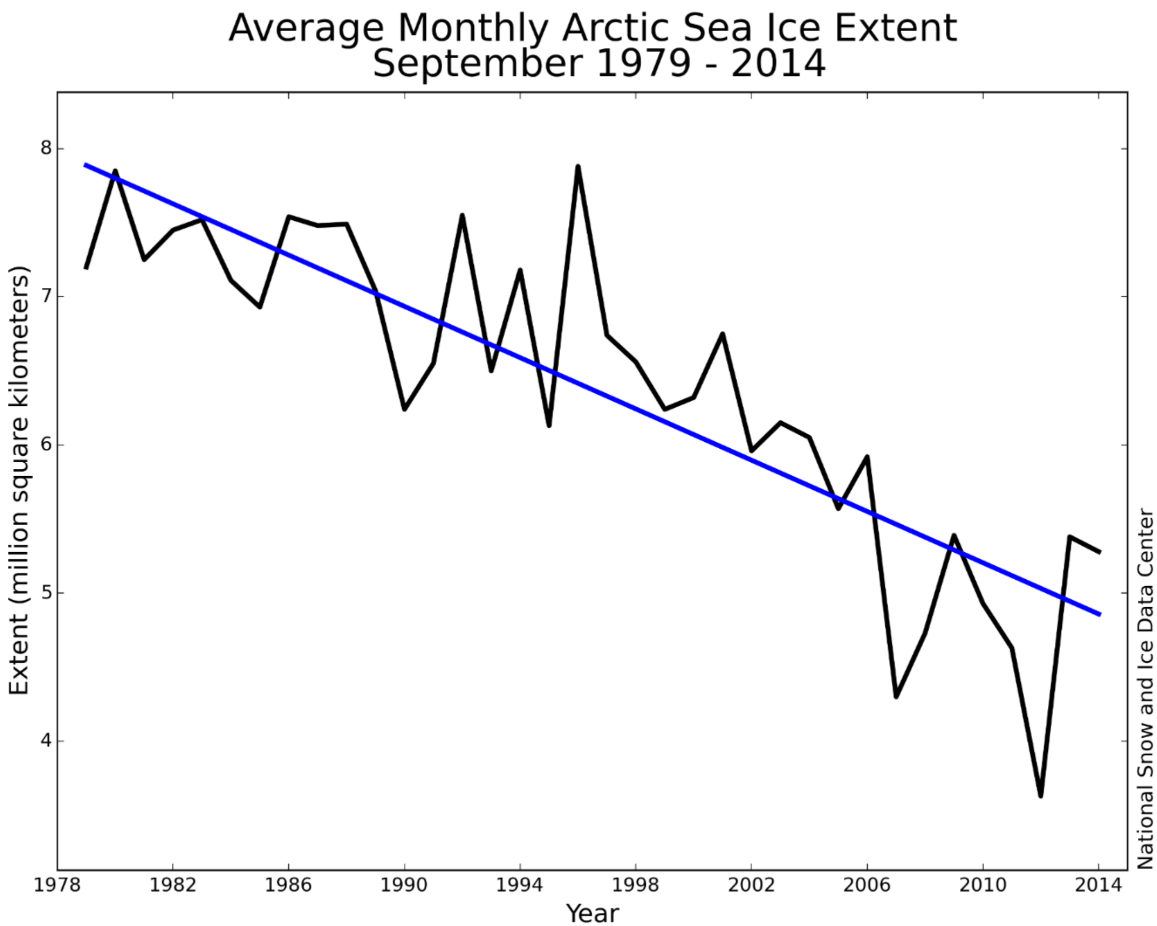
Arctic Sea Ice: Canary of Climate Chnage



http://nsidc.org/arcticseaicenews/files/2014/10/monthly_ice_NH_09.png

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Arctic Sea Ice: Canary of Climate Chnage

http://switchboard.nrdc.org/blogs/dlashof/what_happens_in_the_arctic_doe_1.html

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What about the polar bears?

Polar bear census data:

Location	Polar Bear Population Status	Risk of Future Decline
East Greenland	Data deficient	No estimate
Barents Sea	Data deficient	No estimate
Kara Sea	Data deficient	No estimate
Laptev Sea	Data deficient	No estimate
Chukchi Sea	Data deficient	No estimate
Southern Beaufort Sea	Reduced	No estimate
Northern Beaufort Sea	Not reduced	No estimate
Viscount Melville	Severely reduced	Very Low
Norwegian Bay	Not reduced	Higher

Location	Polar Bear Population Status	Risk of Future Decline
Norwegian Bay	Not reduced	Higher
Lancaster Sound	Not reduced	Higher
M'Clintock Channel	Severely reduced	Very Low
Gulf of Boothia	Not reduced	Lower
Foxe Basin	Not reduced	Lower
Western Hudson Bay	Reduced	Very High
Southern Hudson Bay	Not reduced	Lower
Kane Basin	Reduced	Very High
Baffin Bay	Reduced	Very High

Tables on this website updated frequently:
http://pbsg.npolar.no/en/status/status-table.html

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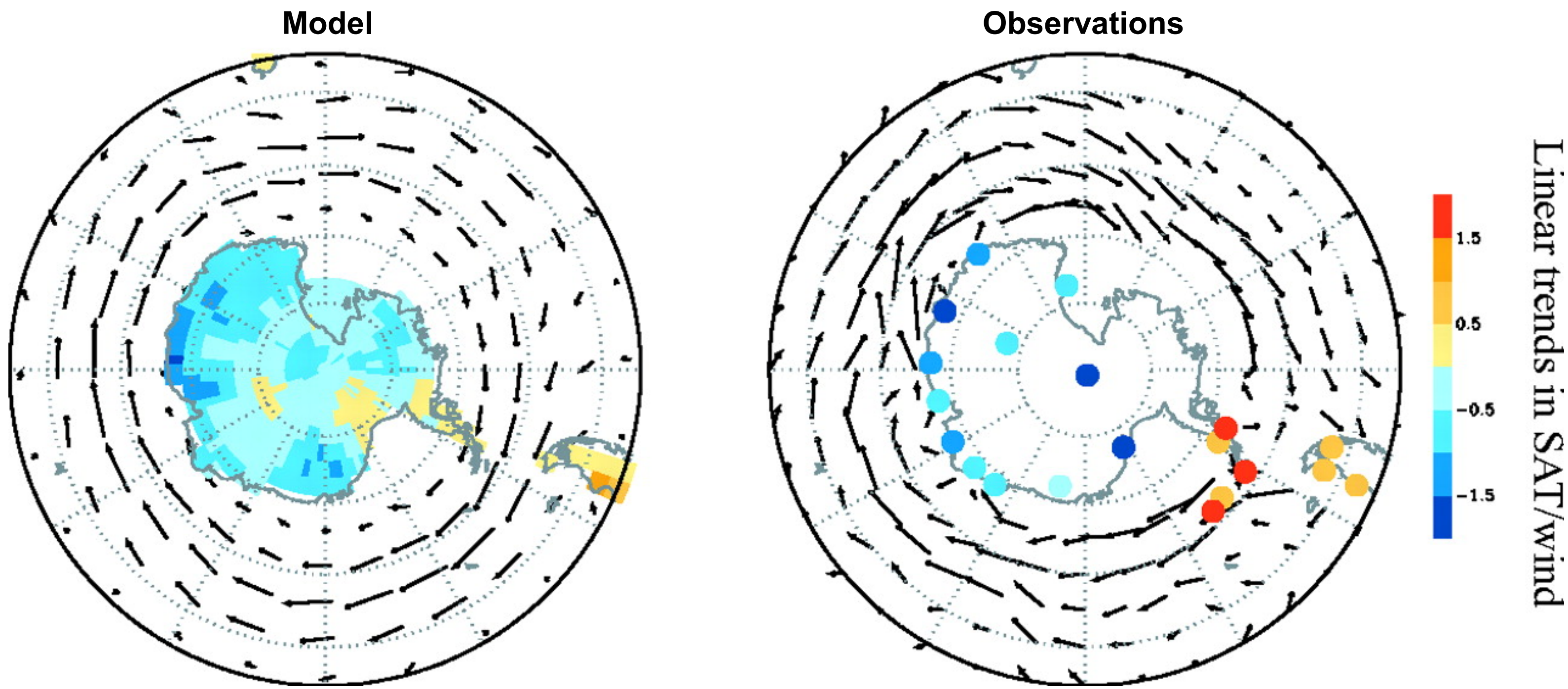
The Ozone Hole may have shielded the Antarctic from warming



Simulated and observed changes in surface temperature (K) and winds from 1969 to 2000, averaged over December to May.

Gillett and Thompson, *Science*, 2003

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Ozone Depletion and Halocarbons

Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases.

Gas	Atmospheric Lifetime (years)	Ozone Depletion Potential (ODP) [c]
Halogen source gases		
Chlorine gases		
CFC-11	45	1
CFC-12	100	0.82
CFC-113	85	0.85
Carbon tetrachloride (CCl_4)	26	0.82
HCFCs	1–17	0.01–0.12
Methyl chloroform (CH_3CCl_3)	5	0.16
Methyl chloride (CH_3Cl)	1	0.02
Bromine gases		
Halon-1301	65	15.9
Halon-1211	16	7.9
Methyl bromide (CH_3Br)	0.8	0.66
Hydrofluorocarbons (HFCs)		
HFC-134a	13.4	0
HFC-23	222	0

Continuous emission

$$\text{ODP (species "}i\text{")} = \frac{\text{global loss of } O_3 \text{ due to unit mass emission of "}i\text{"}}{\text{global loss of } O_3 \text{ due to unit mass emission of CFC-11}}$$

$$\approx (\alpha\, n_{\text{Br}} + n_{\text{Cl}}) \frac{\tau_i}{\tau_{\text{CFC-11}}} \frac{MW_{\text{CFC-11}}}{MW_i} \frac{1}{3}$$

where :

τ is the global atmospheric lifetime

MW is the molecular weight

n is the number of chlorine or bromine atoms

α is the effectiveness of ozone loss by bromine relative to ozone loss by chlorine

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Heterogeneous Chemistry, Mid-Latitude vs Polar Regions

a) What type of aerosol particles are present in the mid-latitude stratosphere?

b) What heterogeneous chemical reaction occurs on the aerosol particles present in the mid-latitude stratosphere and how is ClO affected by this reaction?

c) What type of particles are present in the polar stratosphere during winter?

d) What is the effect of these particles on the chemical composition of the polar stratosphere
Scientists have shown that chemical reactions occurring on the surface of these particles convert species such as and (that do not depleted ozone) and that do not cause harm to the ozone layer in the dark of winter.

e) Following the return of sunlight, significant levels of what radical compound builds up inside the Antarctic stratosphere, leading to rapid loss of ozone?

f) Why does the ozone hole occur only over Antarctica?

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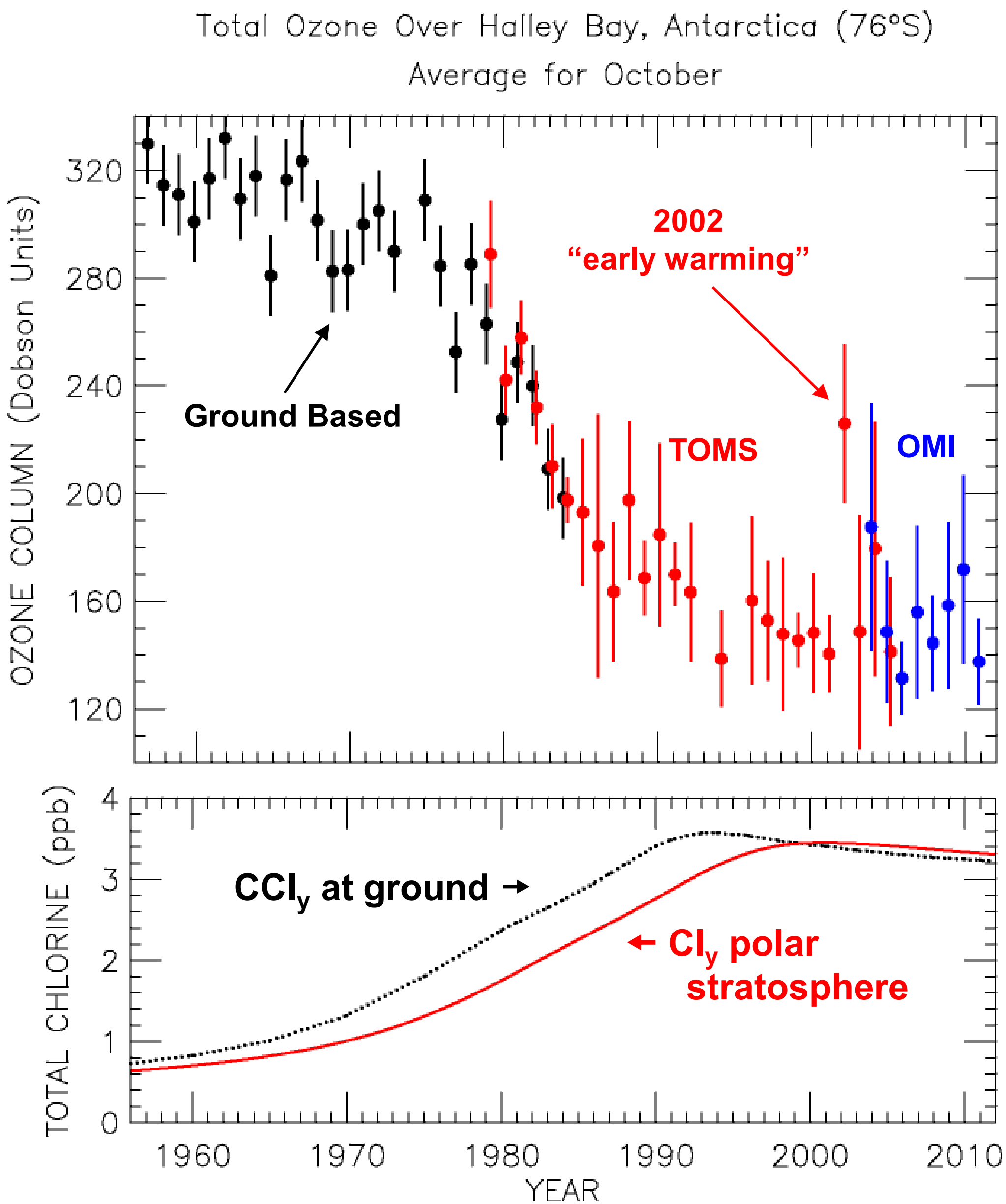
Polar Ozone Loss: Antarctica



Much of this "leveling off" is indeed due to the "leveling off" of halogens

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Climate and Chemistry Coupling

Scientists have long known that rising GHGs leads to cooling of the stratosphere, due to direct radiative effects

The stratosphere has been cooling past several decades in a manner broadly consistent with theory:

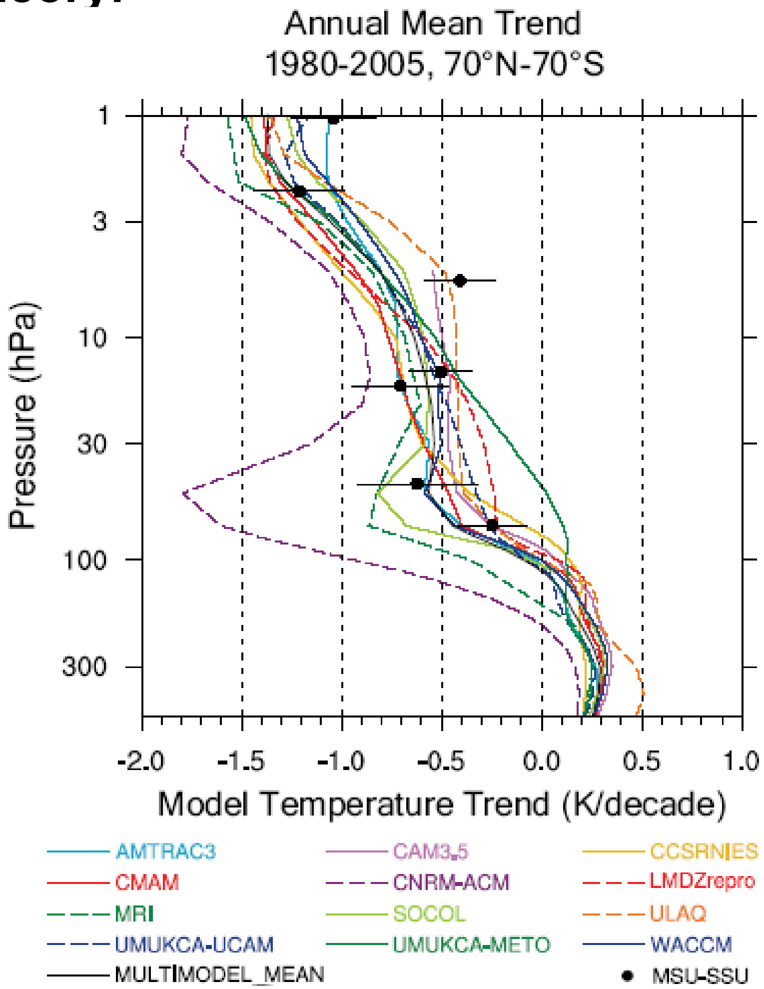

Figure 4−11, WMO/UNEP (2011)

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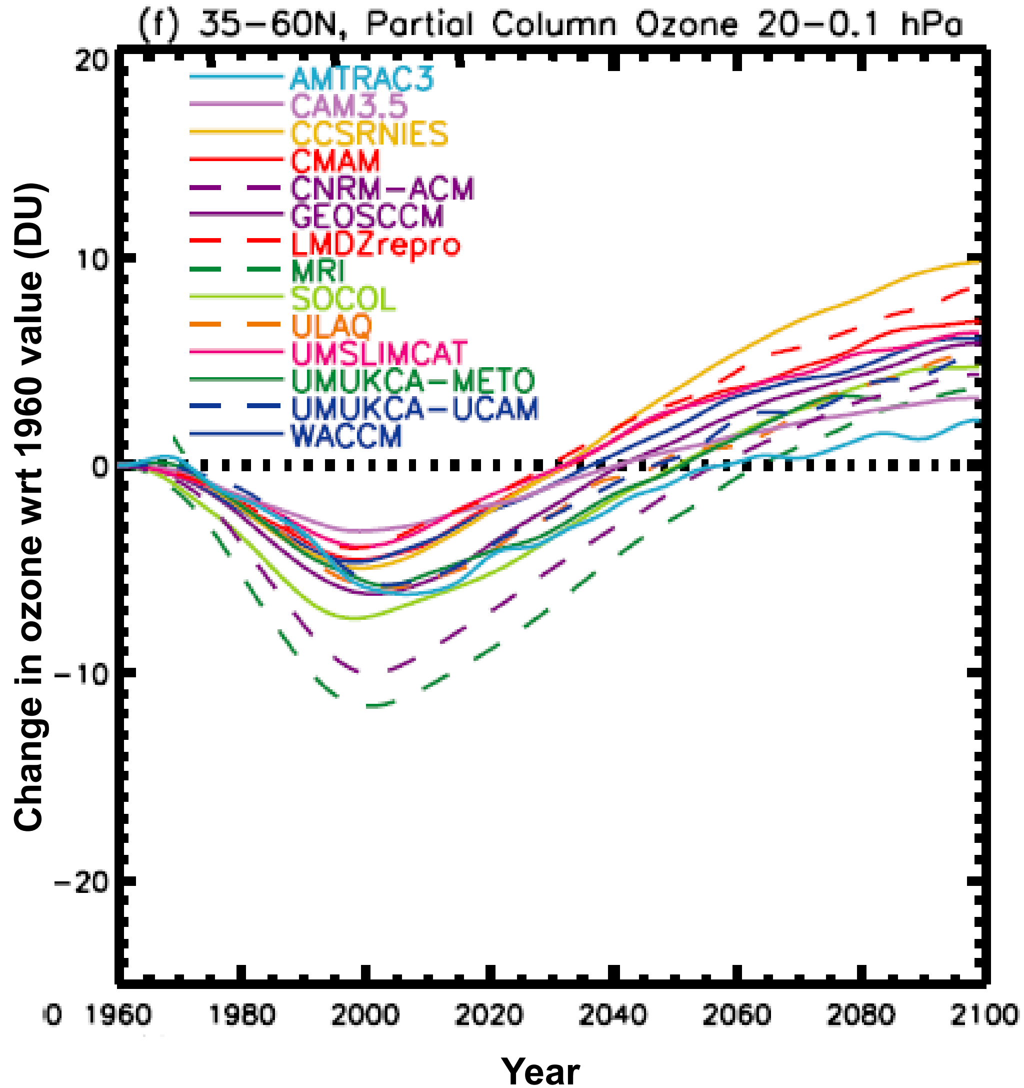
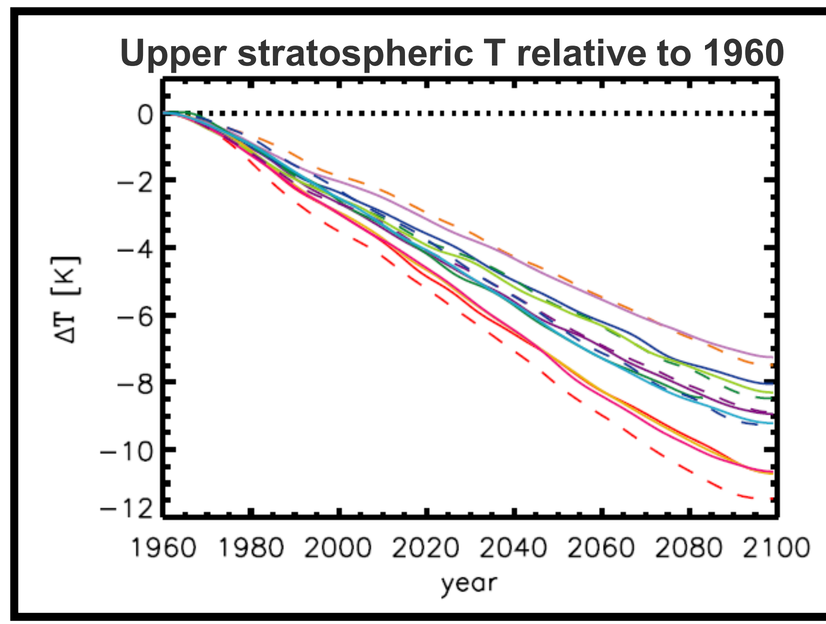
Future Trends, Upper Stratospheric Ozone



14 coupled chemistry climate models (CCMs) predict upper stratospheric ozone in 2100 will exceed upper stratospheric ozone in 1960

Due to stratospheric cooling !

Why this response of ozone to lower T ?



Oman *et al.*, *JGR*, 2010

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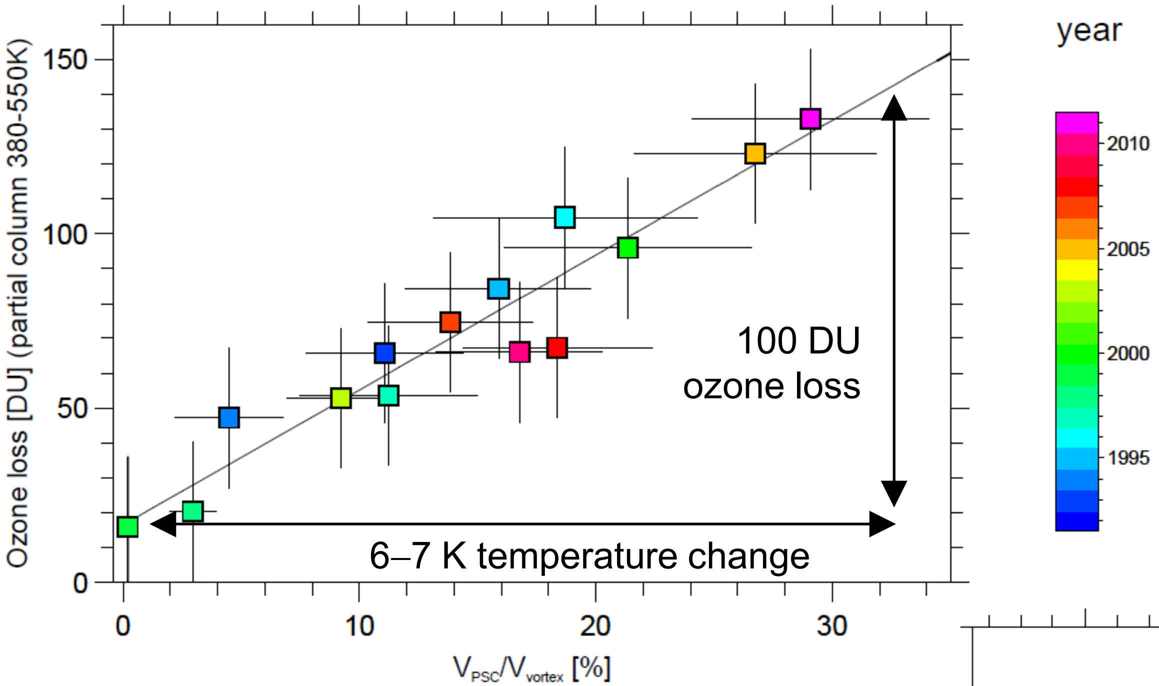
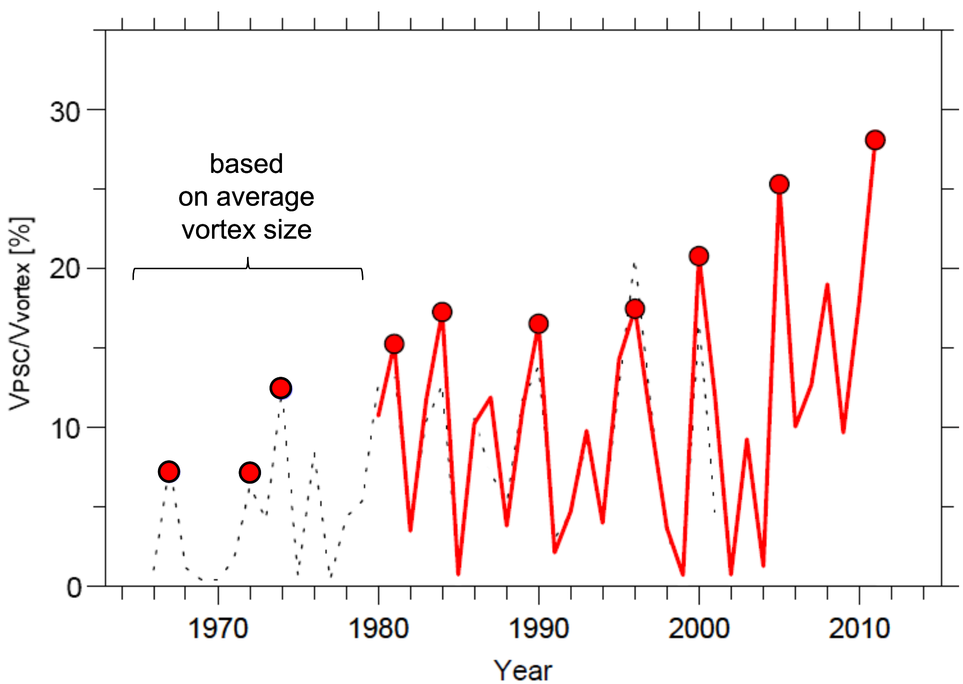
Arctic Ozone 2011 in Context of Prior Years





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One Atmosphere – One Photochemistry

Stratosphere

HO_2 formation:

$$OH + O_3 \rightarrow HO_2 + O_2$$

HO_2 loss:

$$HO_2 + O_3 \rightarrow OH + 2\,O_2$$

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

Troposphere

HO_2 formation:

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2$$

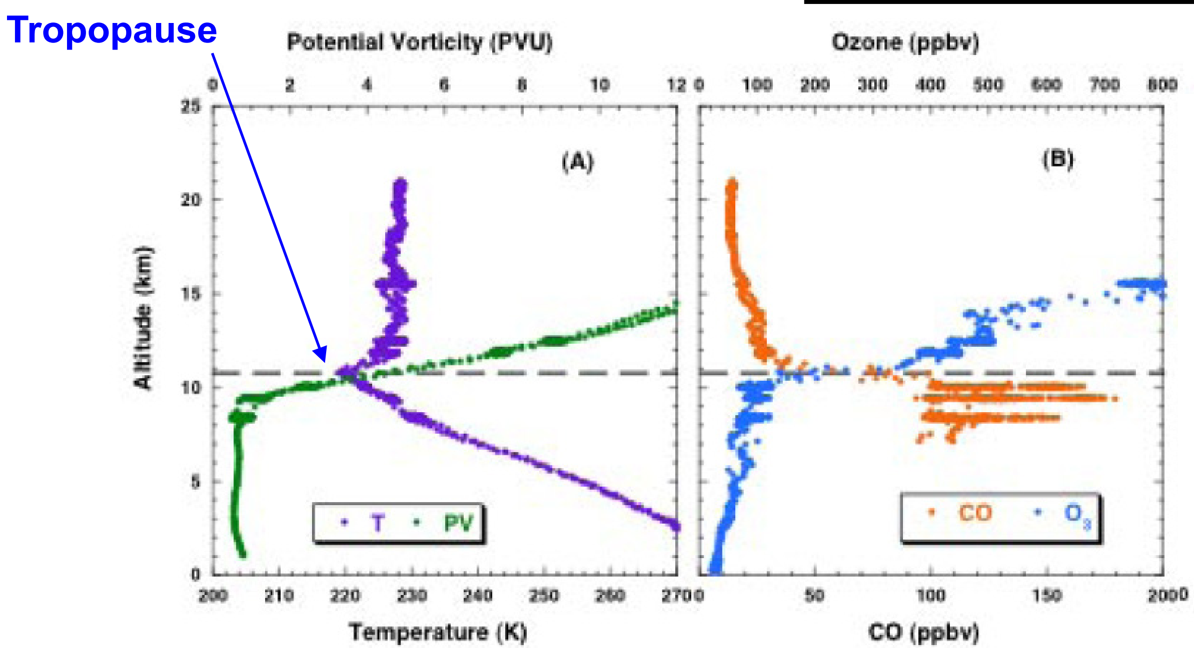
HO_2 loss:

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

Followed by:

$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

Net: $$CO + 2\,O_2 \rightarrow CO_2 + O_3$$



Above Tropopause:
Lots of O_3, little CO

Below Tropopause:
Lots of CO, little O_3

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Laura Pan, NCAR: http://surf.arc.nasa.gov/archive/lpan.pdf

Tropospheric Ozone Production

$$
\begin{aligned}
CO + OH &\rightarrow CO_2 + H \\
H + O_2 + M &\rightarrow HO_2 + M \\
HO_2 + NO &\rightarrow OH + NO_2 \\
NO_2 + h\nu &\rightarrow NO + O \\
O + O_2 + M &\rightarrow O_3 + M
\end{aligned}
$$

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

"Chain Mechanism" for production of ozone

Initiation: O_3 photolysis giving $O(^1D)$, followed by $H_2O+O(^1D) \rightarrow 2OH$ as well as emission of CO & NO_x from combustion of fossil fuels

Termination: $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ or $OH + NO_2 + M \rightarrow HNO_3 + M$

Propagation: $HO_2 + NO$

Ozone Production "limited" by $k[HO_2][NO]$ (propagation term)

High NO_x ($NO+NO_2$) forces termination via production of HNO_3.

In this case, as NO_x rises, OH and HO_2 (HO_x) fall

⇨ what happens to O_3 production ?

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Tropospheric Ozone Production

$$CO + OH \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$

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

Ozone Production "limited" by k[HO_2][NO] (propagation term)

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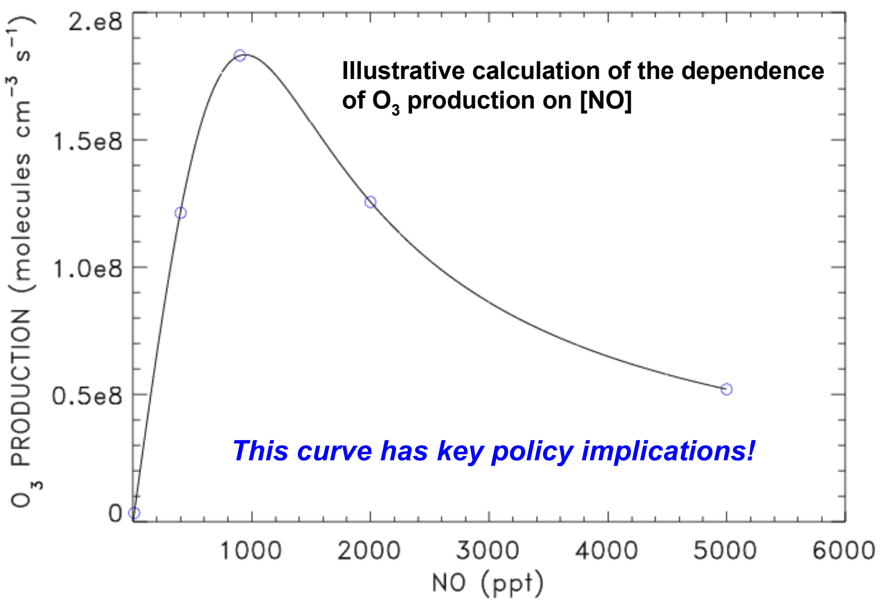

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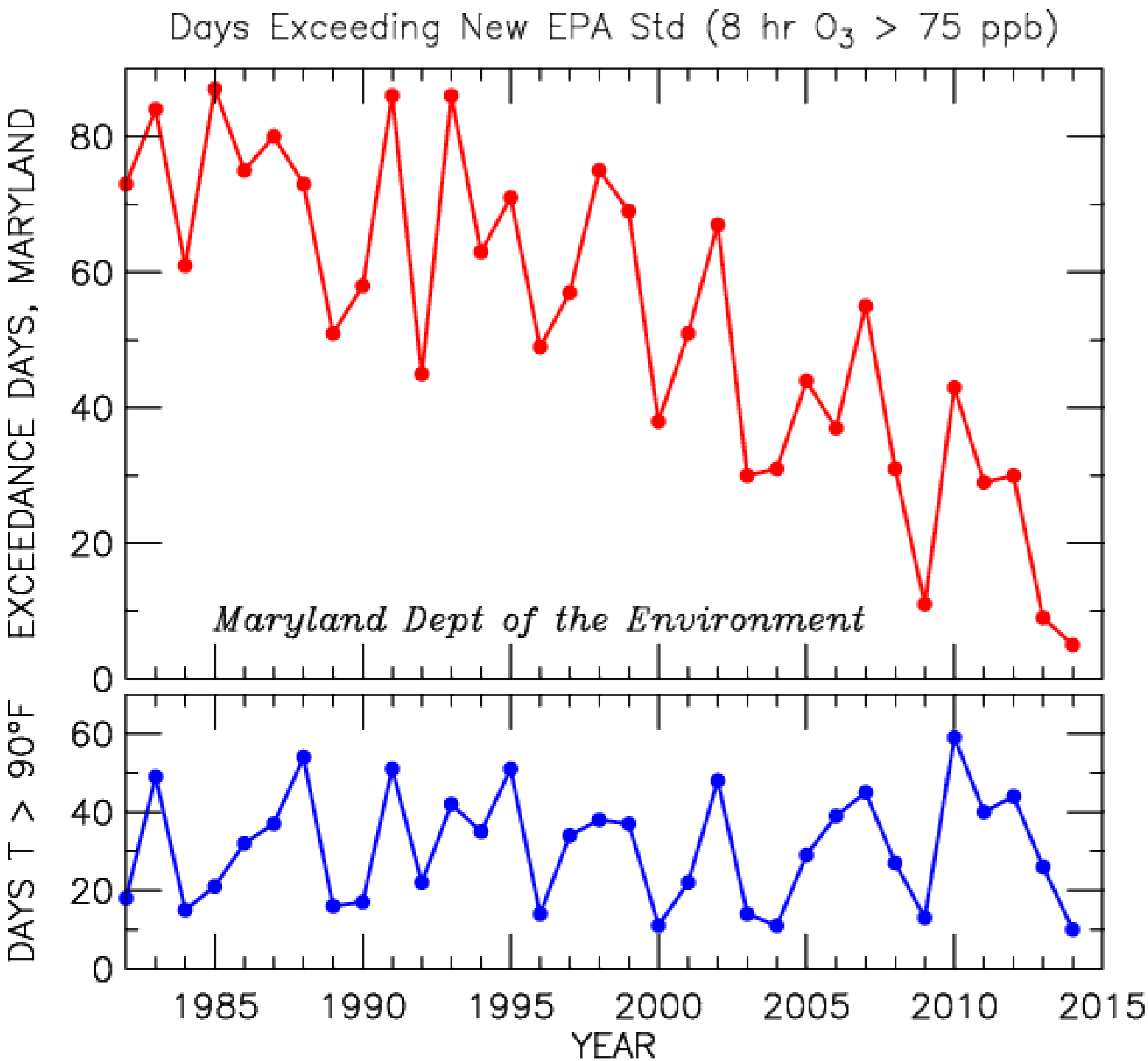
Significant Improvements in *Local* Air Quality since early 1980s



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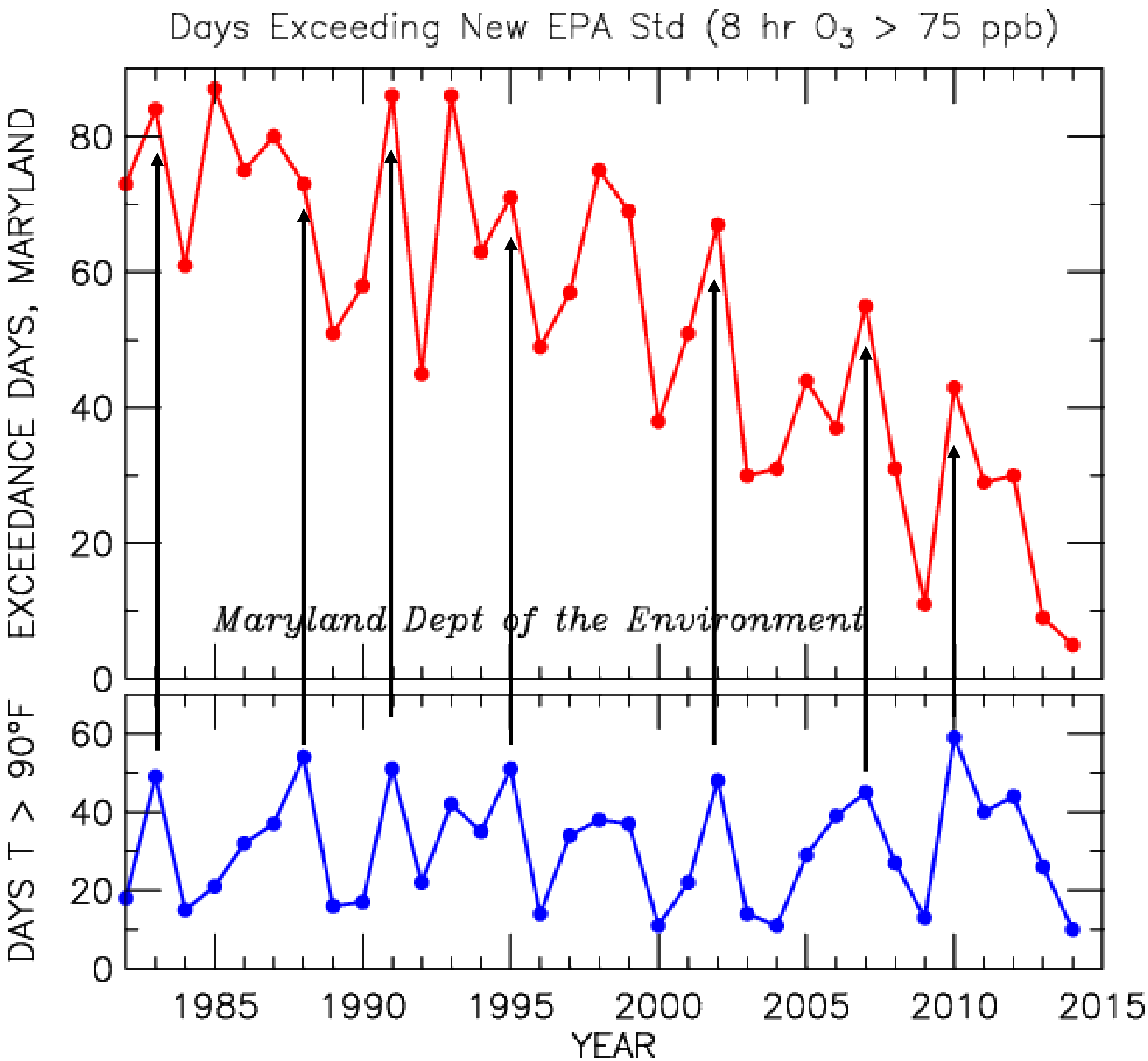
Significant Improvements in *Local* Air Quality since early 1980s



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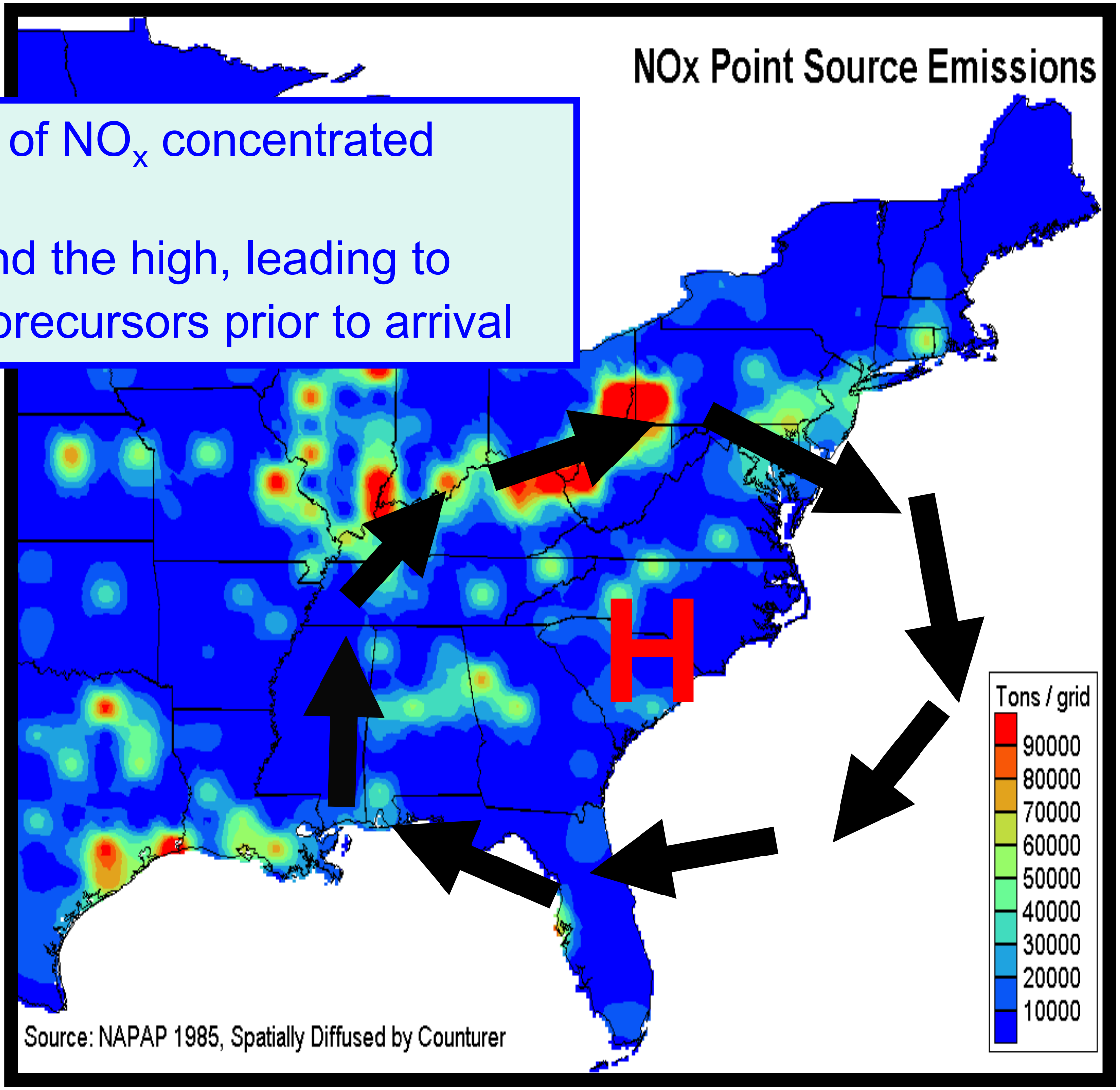
Day-to-day meteorology (weather!) affects severity and duration of pollution episodes

- Large power plant emissions of NO_x concentrated along the Ohio River valley
- Air circulates clockwise around the high, leading to significant build up of ozone precursors prior to arrival



http://www.mde.state.md.us/assets/document/BJH%20-%20Basics%20on%20Ozone%20Transport.ppt

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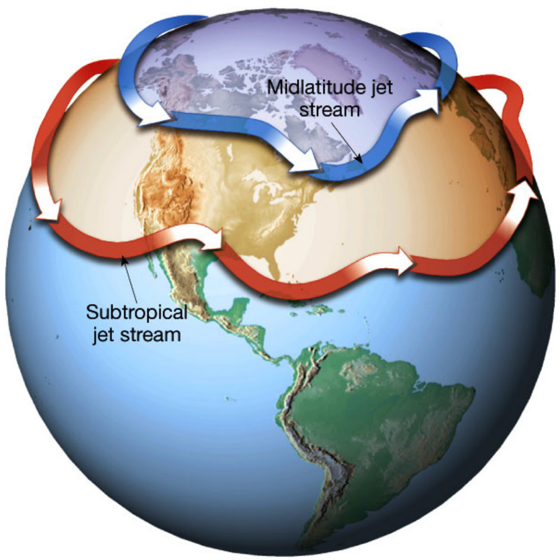
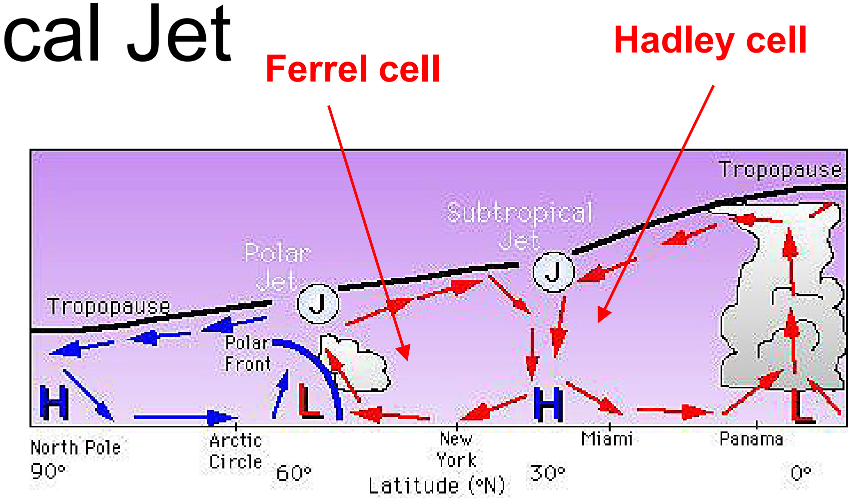
Subtropical Jet



http://www.ux1.eiu.edu/~cfjps/1400/FIG07_014A.jpg



http://www.fas.org/irp/imint/docs/rst/Sect14/jet_stream.jpg

Subtropical Jet: where poleward descending branch of the Hadley Circulation meets the equatorward descending of the Ferrel Cell

Area of high pressure, fair weather, low rainfall: conductive to high ozone

Poleward expansion of the sub-tropical jet:

- Number of days Subtropical Jet within 150 miles of Baltimore has increased by ~50% between 1979 and 2003 due to “frontal movement”
- Driving force: weakening of the equator to pole temperature gradient, caused by more rapid warming at high latitudes compared to tropics

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Our Favorite Air Pollutants ☺

Species	Source	Consequence
CO_2		
CH_4		
N_2O		
NO_x		
SO_2		
Soot		
CFCs		
Halons		
CH_3Br		
HCFCs		

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Final Statements

It is difficult for people living now, who have become accustomed to the steady exponential growth in the consumption of energy from fossil fuels, to realize how transitory the fossil fuel epoch will eventually prove to be when it is viewed over a longer span of human history

M. King Hubbert, Scientific American, 1971
as quoted in foreword of
***When Oil Peaked* by Kenneth S. Deffeyes**

In many ways, fossil fuels should be considered as a gift from nature, which have allowed mankind to reach unprecedented levels of development. They served us well, but now – due to their finite nature – must be replaced by more sustainable sources of energy.

Olah *et al.*, *Beyond Oil and Gas: The Methanol Economy*, 2009.

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Final Statements

I believe that the development of renewable energy will be to students of your generation what the electronics & computer industry were to students of our generation: an opportunity for great innovation, entrepreneurial development, societal benefit, and also a very comfortable lifestyle for those who lead the "green revolution"

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