Overview of Global Warming, Ozone Depletion, and Air Quality

AOSC 433/633 & CHEM 433

Ross Salawitch

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

Notes:

- **Ross, Austin, & Tim are co-teaching this class; please include all of us on class related email unless you are writing to set up a meeting with one of us**
- **Lectures are the "glue" that hold this class together: therefore, attendance is strongly encouraged**
- **We like to "ask questions" for many reasons: to get to know you, to keep you engaged, etc. Please participate at your own level of comfort**
- **Problem sets tend to be quantitative and exams tend to be qualitative: Problem Set #1, due 2 weeks from today, *will be posted* over the weekend**

We encourage students to start working on Problem Set #1 soon and not wait until the night before due date to get started

Lecture 2

29 January 2015

Overview of Global Warming, Ozone Depletion, and Air Quality

Course theme: effect of human activity on atmospheric composition

- climate change
- air quality
- stratospheric ozone depletion and recovery

Today's goals:

1) Overview of climate change, air quality, and ozone depletion

2) We'll provide lots of "detail" today … we do not expect all of these details to "stick". We do expect, however, that when you review this lecture at the end of semester, details will be understandable

3) Linkages between these topics, which are often thought of as "disparate", but actually are linked in profoundly important manners

Please complete the Learning Outcome quiz following lecture to review salient "take away" messages from today

Motivational Words: 12 Nov 2014

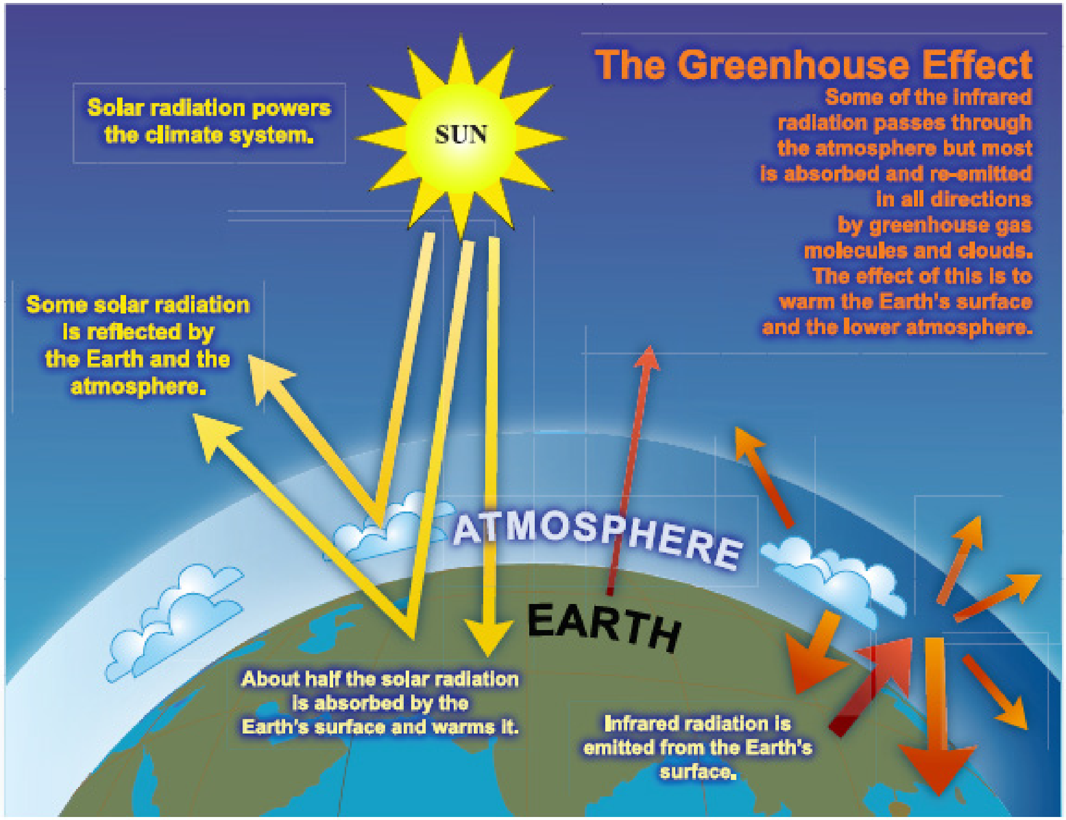
• The Presidents of the United States and China announced their respective post-2020 actions on climate change, recognizing that these actions are part of the longer range effort to transition to low-carbon economies, **mindful of the global temperature goal of 2°C**. The **U.S.** intends to achieve an economy-wide target of **reducing emissions by 26%-28% below its 2005 level in 2025** ; **China** intends to achieve **peaking of CO_2 emissions around 2030** and make best effort to peak early & intends to increase share of non-fossil fuels in primary energy consumption to ~20% by 2030.

• The United States and China hope that by announcing these targets now, they can inject momentum into the global climate negotiations and inspire other countries to join in coming forward with ambitious actions as soon as possible, preferably by the first quarter of 2015 … to reach a successful global climate agreement in Paris in late 2015.

• The two sides have among other things:
- established the U.S.-China Climate Change Working Group (CCWG), under which they have launched initiatives on vehicles, smart grids, carbon capture, energy efficiency, GHG data management, forests and industrial boilers;
- agreed to work together towards the global phase down of **hydrofluorocarbons (HFCs)**, very GHGs'
- created the U.S.-China Clean Energy Research Center, which facilitates collaborative work in carbon capture and storage technologies, energy efficiency in buildings, and clean vehicles; and
- agreed on a joint peer review of inefficient fossil fuel subsidies under the G-20.

Text: http://www.whitehouse.gov/the-press-office/2014/11/11/us-china-joint-announcement-climate-change
Image: http://www.asianews.it/news-en/China-and-the-United-States-agree-to-climate-agreement-by-2030-32676.html

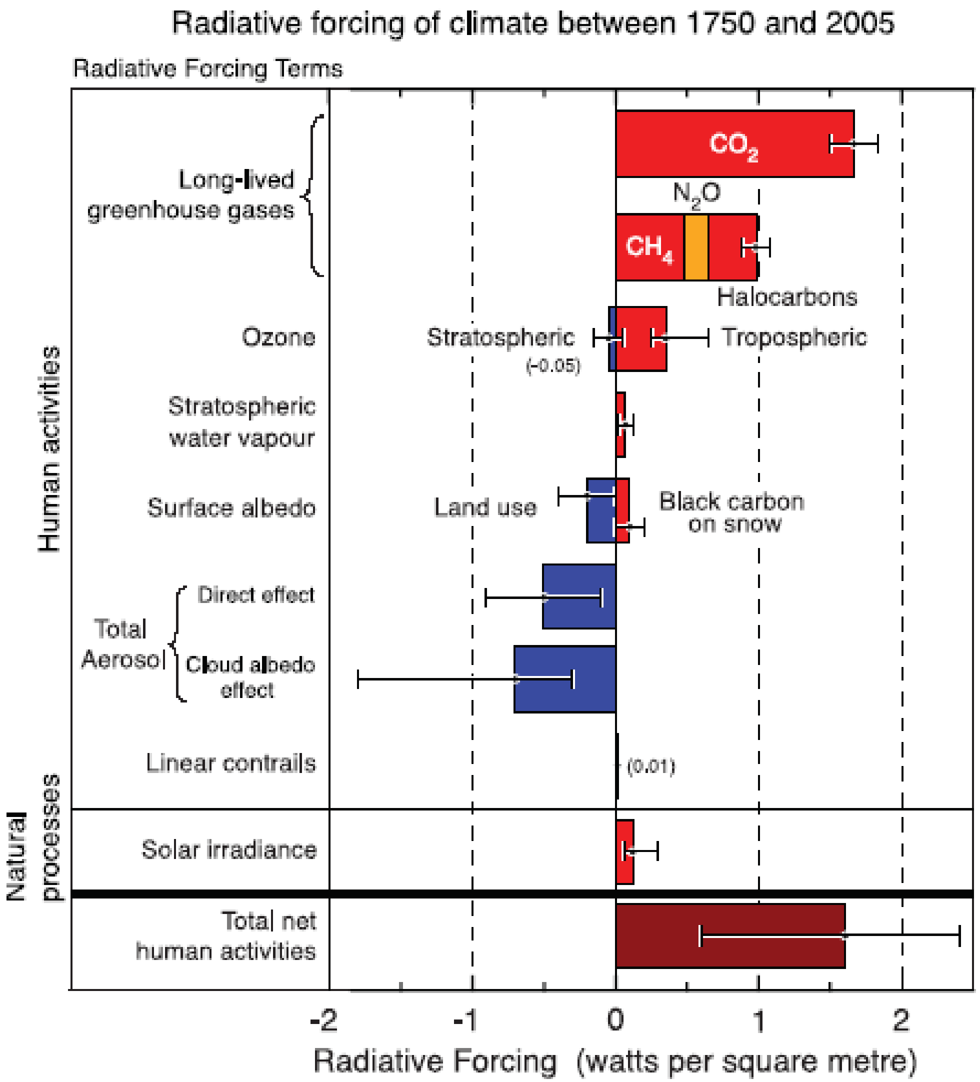
Greenhouse Effect



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

Question 1.3, IPCC, 2007

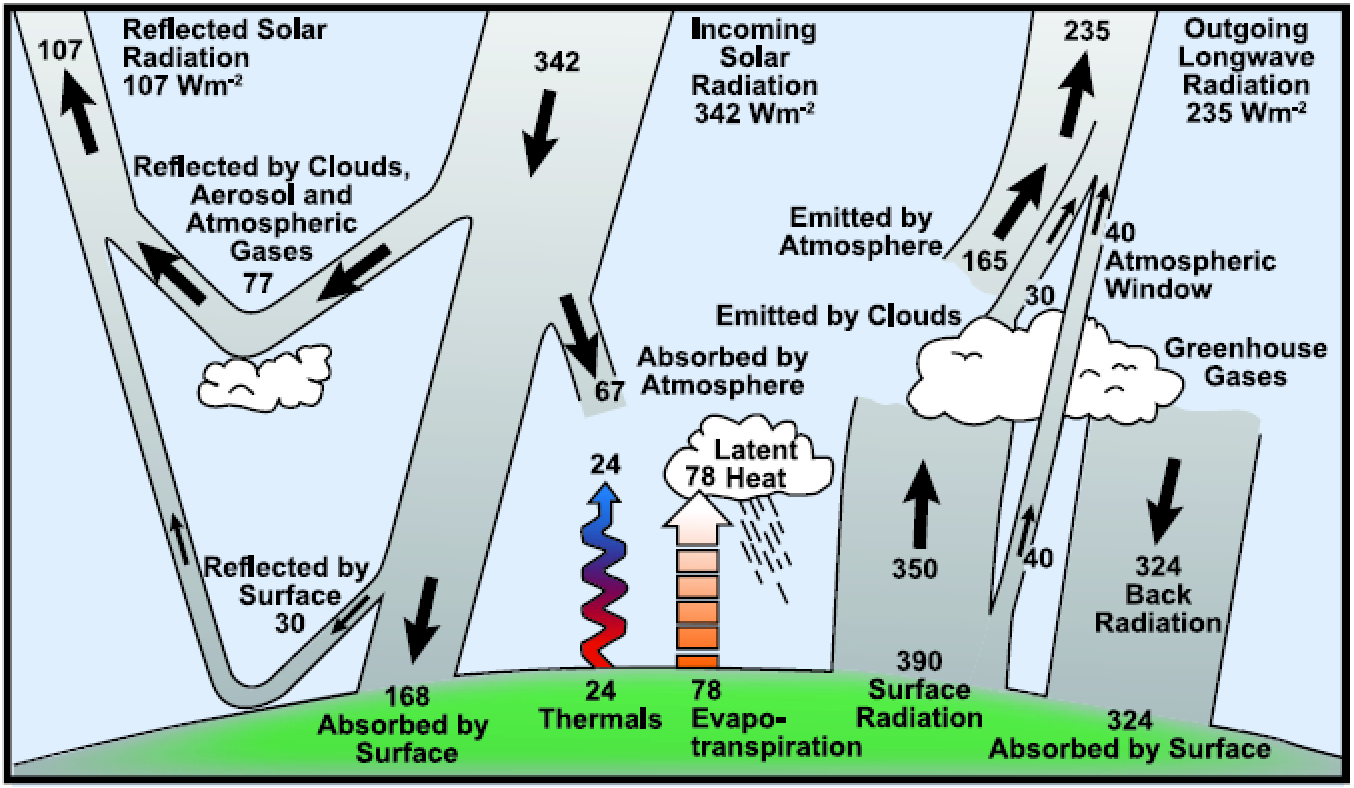
Radiative Forcing of Climate, 1750 to 2005



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

Question 2.1, IPCC, 2007

Radiative Forcing



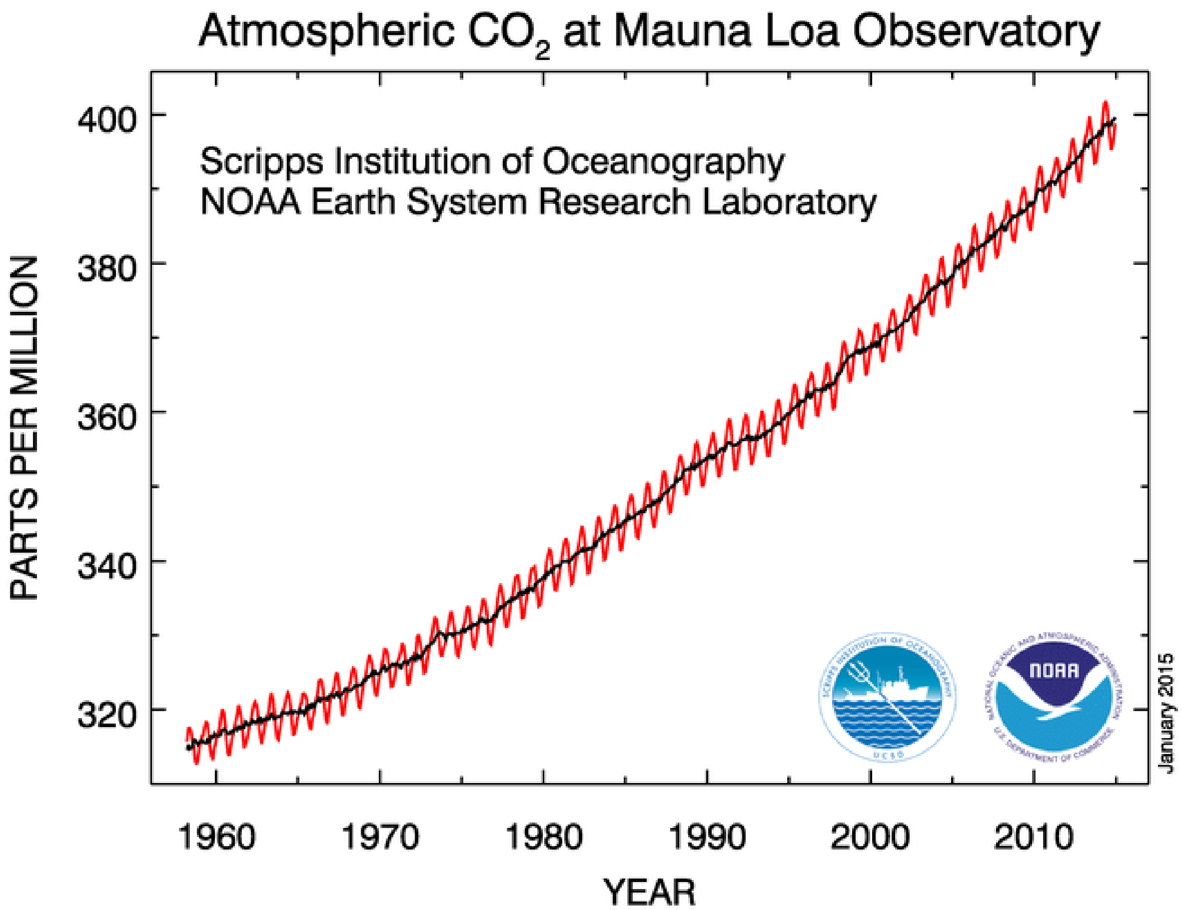
FAQ 1.1, Figure 1. *Estimate of the Earth's annual and global mean energy balance. Over the long term, the amount of incoming solar radiation absorbed by the Earth and atmosphere is balanced by the Earth and atmosphere releasing the same amount of outgoing longwave radiation. About half of the incoming 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.

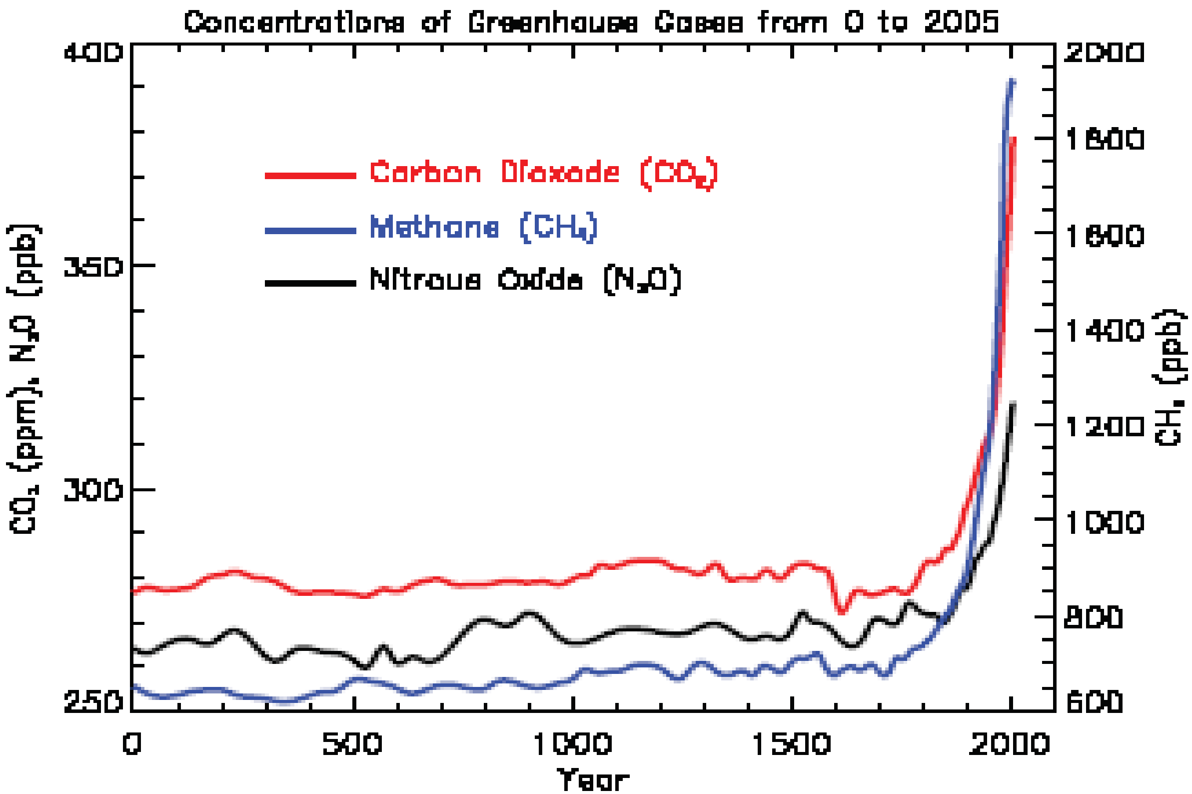
Modern CO_2 Record

Global average CO_2 in Dec 2014: 398.78 parts per million (ppm) and rising !



Legacy of Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
http://www.esrl.noaa.gov/gmd/ccgg/trends

GHG Record Over Last Several Millennia



FAQ 2.1, Figure 1. *Atmospheric concentrations of important long-lived greenhouse gases over the last 2,000 years. Increases since about 1750 are attributed to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb).*

Question 2.1, IPCC, 2007

GWP – Global Warming Potential

$$\text{GWP}(CH_4) = \frac{\int_{\text{time initial}}^{\text{time final}} a_{CH4} \times [CH_4(t)]\, dt}{\int_{\text{time initial}}^{\text{time final}} a_{CO2} \times [CO_2(t)\, dt]}$$

where:

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

a_{CO2} = Radiative Efficiency (W m^{-2} kg^{-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

GWP – Global Warming Potential

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.

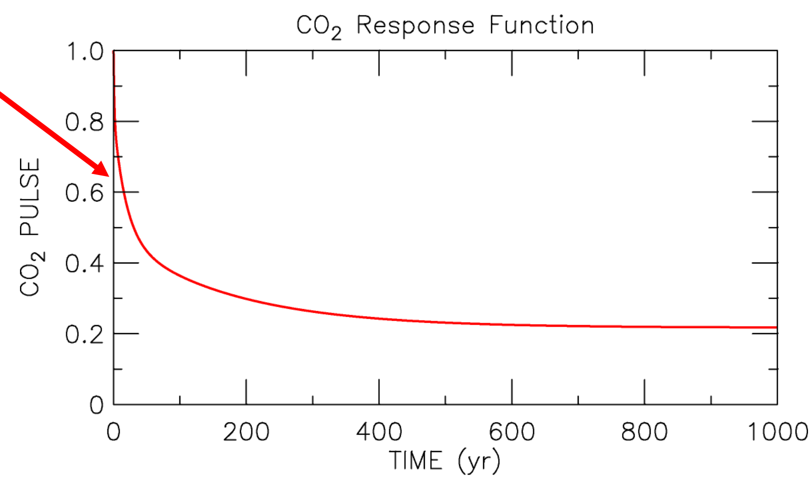
[a] The CO_2 response function used in this report is based on the revised version of the Bern Carbon cycle model used in Chapter 10 of this report (Bern2.5CC; Joos et al. 2001) using a background CO_2 concentration value of 378 ppm. The decay of a pulse of CO_2 with time t is given by

$a_0 + \sum_{i=1}^{3} a_i \cdot e^{-t/\tau_i}$ 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.

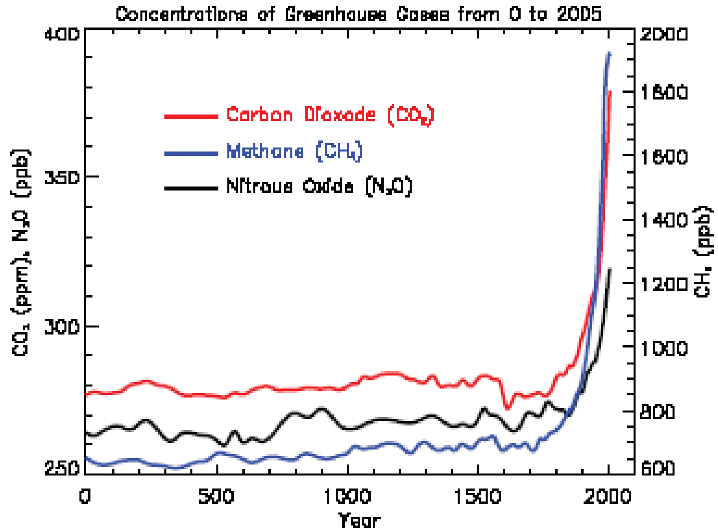
[b] The radiative efficiency of CO_2 is calculated using the IPCC (1990) simplified expression as revised in the TAR, with an updated background concentration value of 378 ppm and a perturbation of +1 ppm (see Section 2.10.2).

[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"



GWP – Global Warming Potential



FAQ 2.1, Figure 1. *Atmospheric concentrations of important long-lived greenhouse gases over the last 2,000 years. Increases since about 1750 are attributed to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb).*

Over the time horizon of ~1750 to 2005:

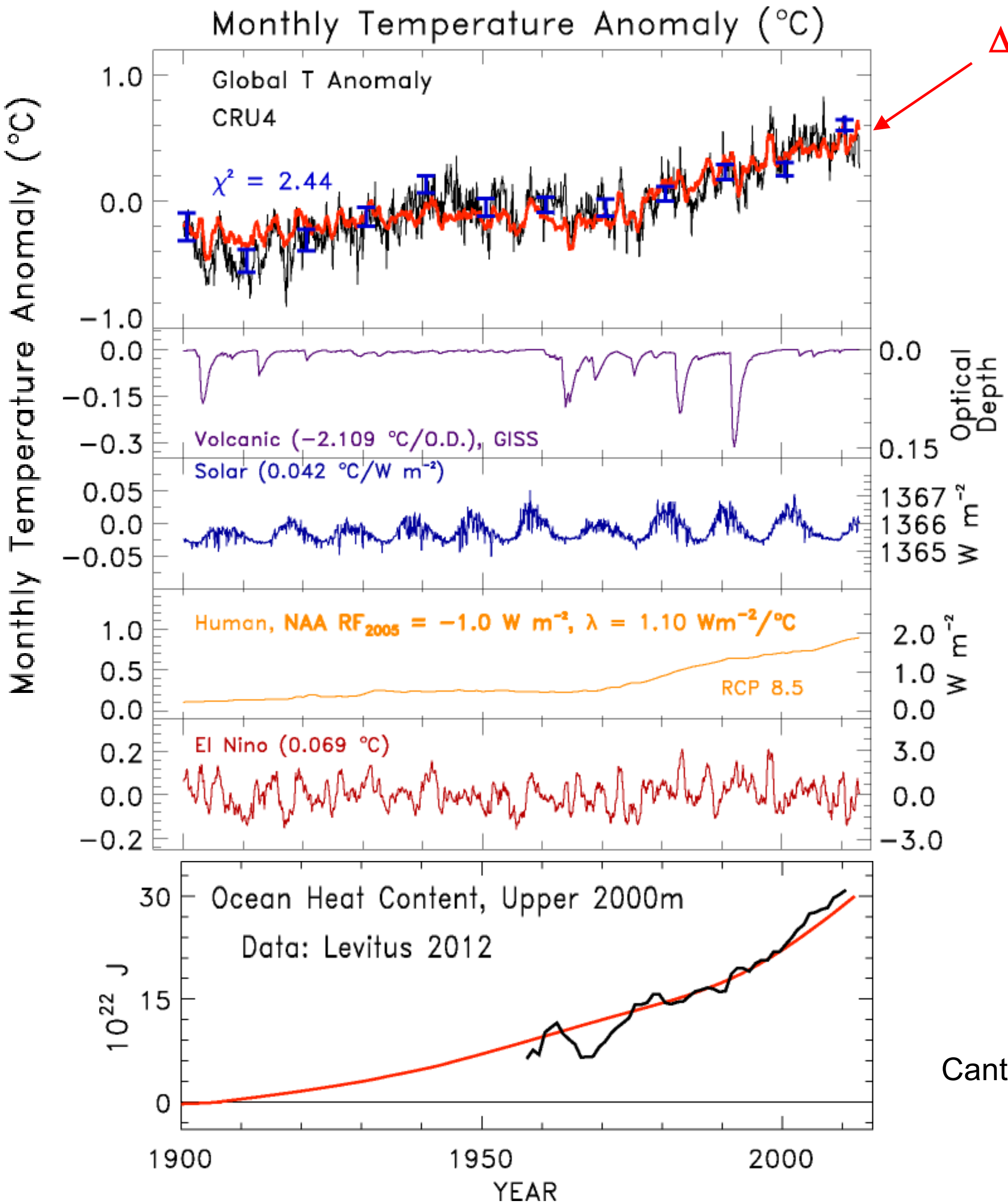
RF CH_4 relative to $CO_2 \approx 26.4 \times 1250$ ppb / 100 ppm = $26.4 \times 0.0125 = 0.33$

RF N_2O relative to $CO_2 \approx 216 \times 50$ ppb / 100 ppm = $216 \times 5{\times}10^{-4} = 0.11$

Total RF $CH_4 + N_2O$ relative to $CO_2 \approx 0.44$

This rough estimate is not too different than the RF of $CH_4 + N_2O$ relative to RF of CO_2, **~38%,** from FAQ 2.1, Figure 2

Are humans responsible?



$$\Delta T_{MDL\,i} = (1+\gamma)\,(GHG\,RF_i + NAA\,RF_i)\,/\,\lambda_P + C_0 + C_1\times SOD_{i-6} + C_2\times TSI_{i-1} + C_3\times ENSO_{i-2} - Q_{OCEAN\,i}\;/\,\lambda_P$$

where

$\lambda_P = 3.2\ W\ m^{-2}\,/\,°C$

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

NAA RF = net RF due to anthropogenic aerosols

SOD = Stratospheric optical depth

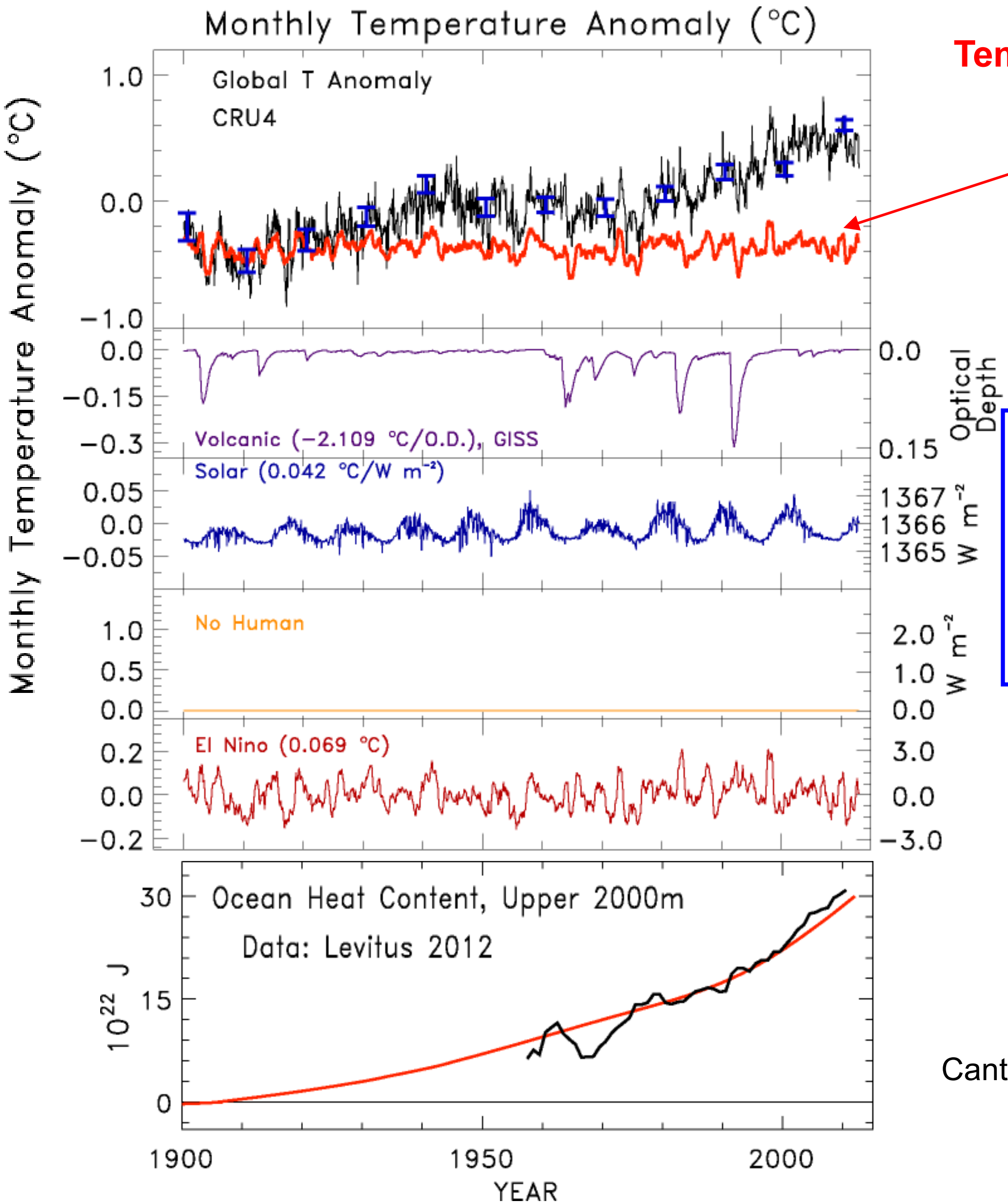
TSI = Total solar irradiance

ENSO = Multivariate El Niño South. Osc Index

Q_{OCEAN} = Ocean heat export

Canty et al., *ACP*, 2013

Are humans responsible?



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

Global warming is caused by CO_2 greatest waste product of modern society as well as other GHGs.

Temperature will continue to rise until human emission of GHGs is curtailed

Canty et al., *ACP*, 2013

Are humans responsible?

Orbital variations: drive the ice ages but too small to drive modern warming

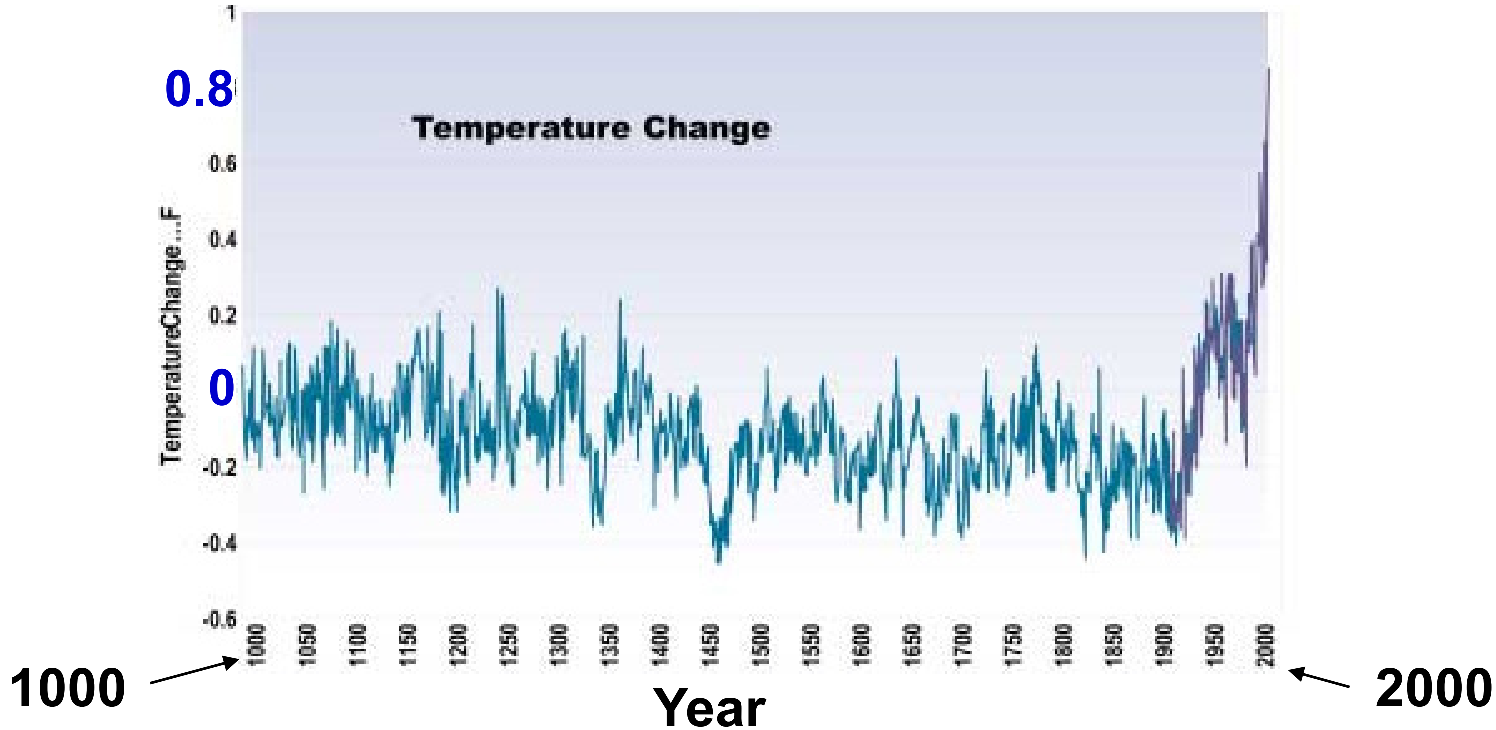
Volcanoes: no sustained forcing

Solar variability:

- Perhaps dominant forcing of Medieval Warming and Little Ice Age
- Small effect since ~1860

Internal variability (eg, El Niño / La Niña) :

- Climate record from 1000 to 1850 shows nothing like sustained, present rate of warming



Are humans responsible?

Orbital variations: drive the ice ages but too small to drive modern warming

Volcanoes: no sustained forcing

Solar variability:

Perhaps dominant forcing of Medieval Warming and Little Ice Age
Small effect since ~1860

Internal variability (eg, El Niño / La Niña) :

Climate record from 1000 to 1850 shows nothing like sustained, present rate of warming

***IPCC Climate Change 2013* concludes:**

It is extremely likely* human activity has been the dominant cause of the observed warming since the mid-20th century

*** At least a 95% chance of being correct**

IPCC ⇒ Intergovernmental Panel on Climate Change

See http://www.ipcc.ch/publications_and_data/ar4/syr/en/mainssyr-introduction.html for definitions of high confidence, extremely likely, etc.

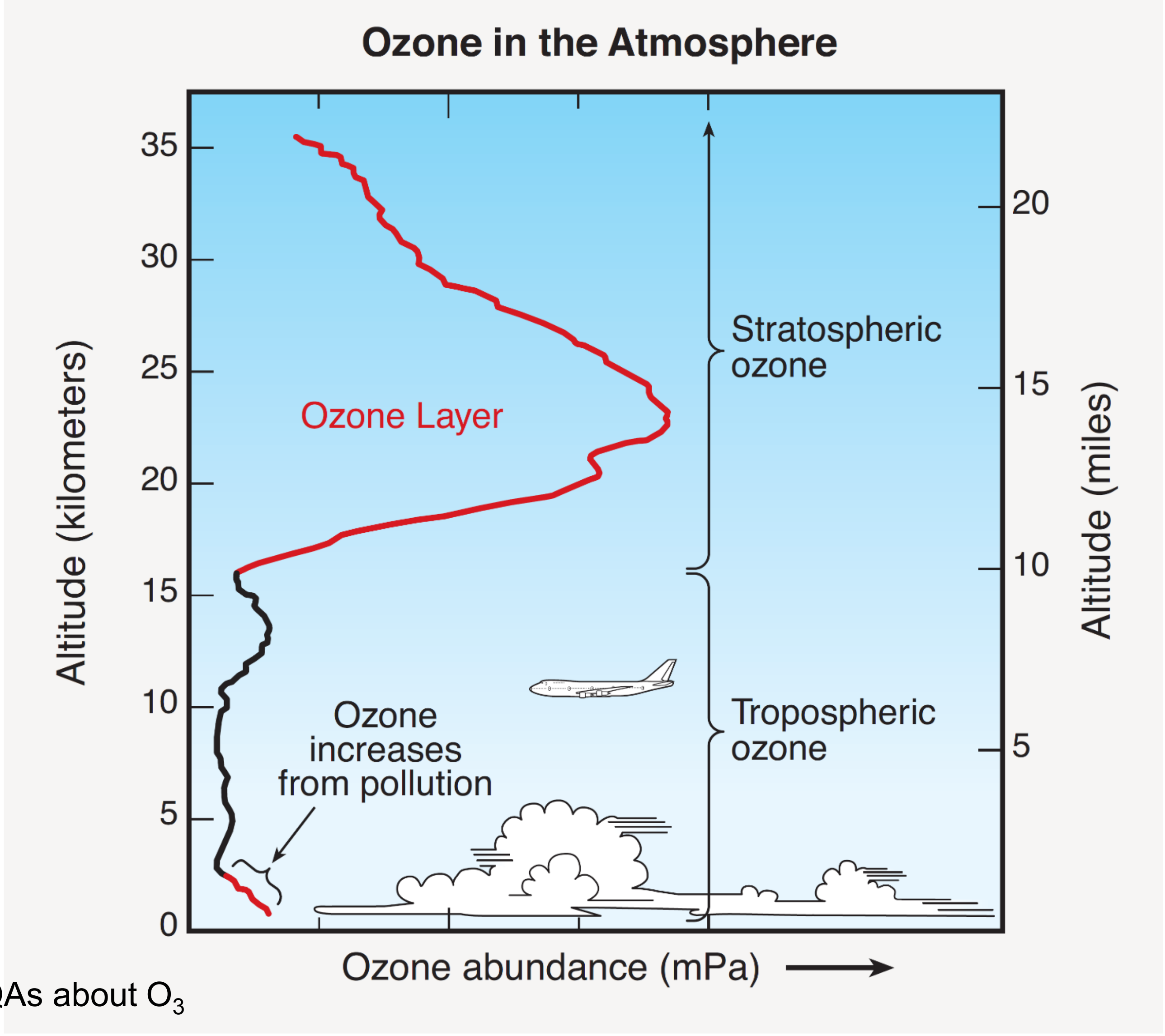
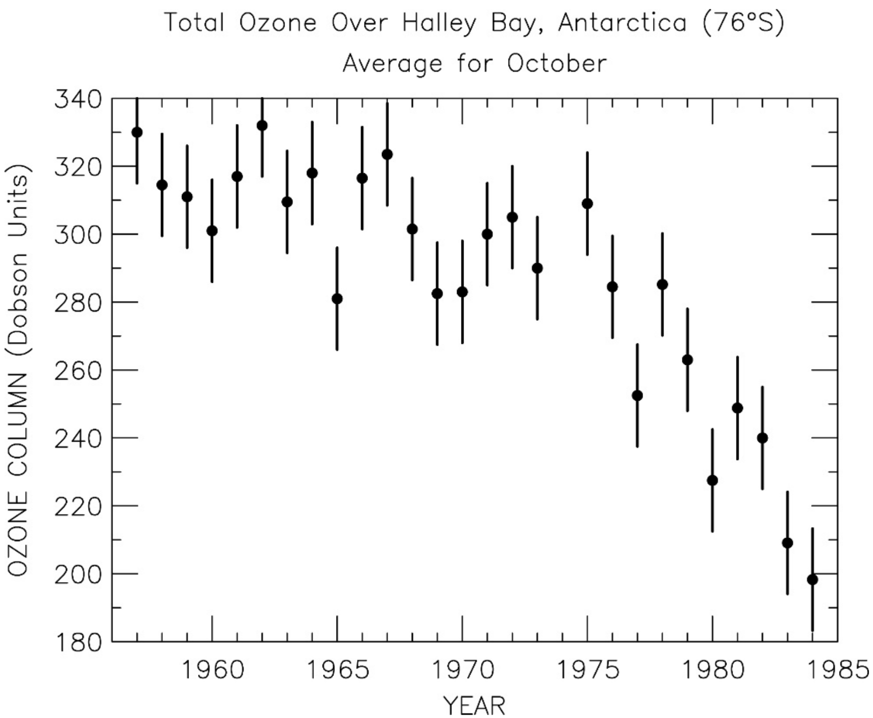


Fig. Q1-2, 20 QAs about O_3

It is incredible that human activity both destroys stratospheric ozone (so-called good ozone) and produces tropospheric ozone (so-called bad ozone)

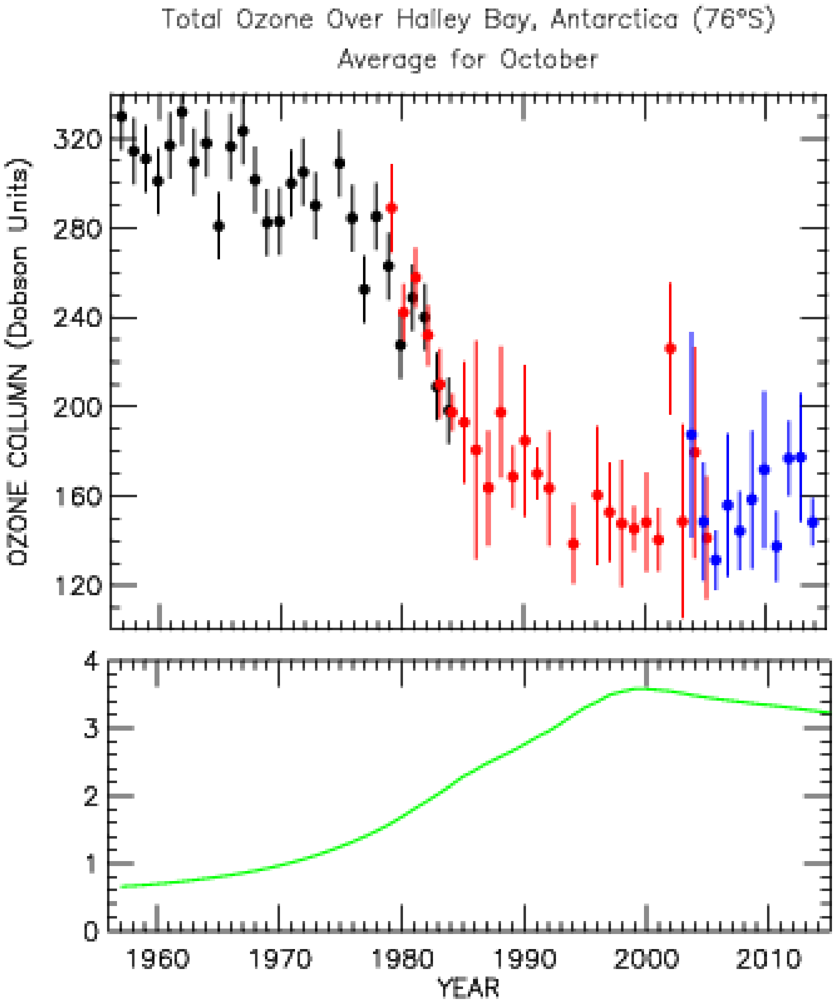
Earth's Atmosphere – Effect of Humans

Stratospheric Ozone – shields surface from solar UV radiation

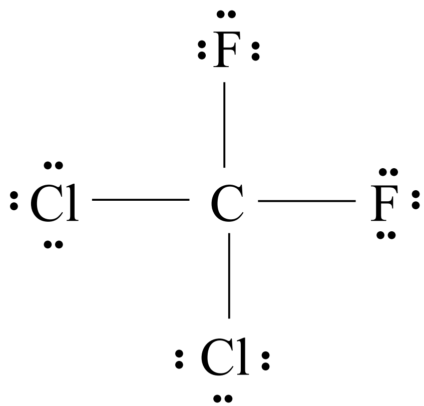


After Farman *et al*., Large losses of total ozone in Antarctica reveal Seasonal ClOx/NOx interaction, Nature, 315, 207, 1985.

Update



What is this compound?



How is it eventually removed from the atmosphere ?

What does it produce upon its removal ?

Measurements of Reactive Chlorine From Space

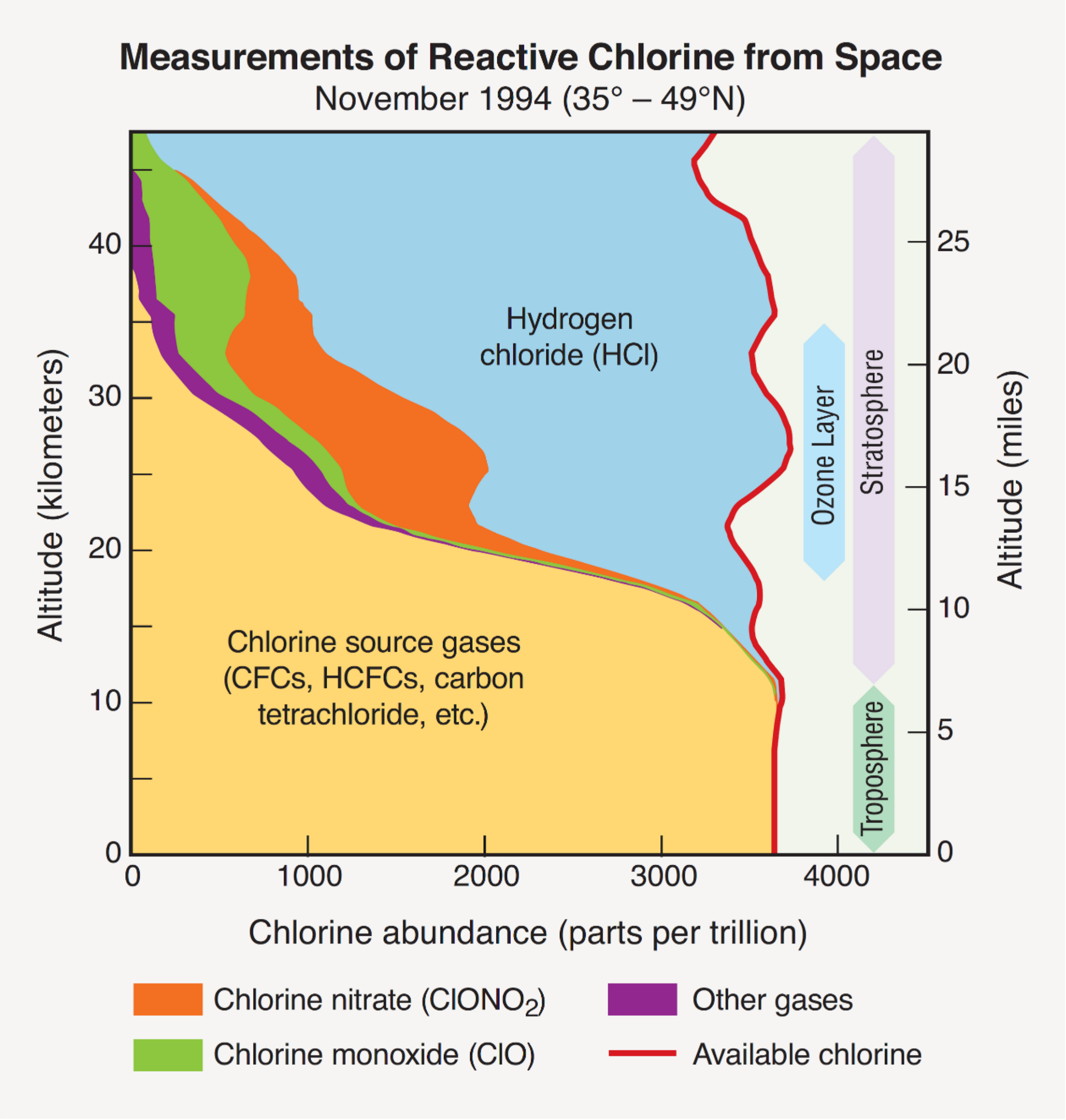
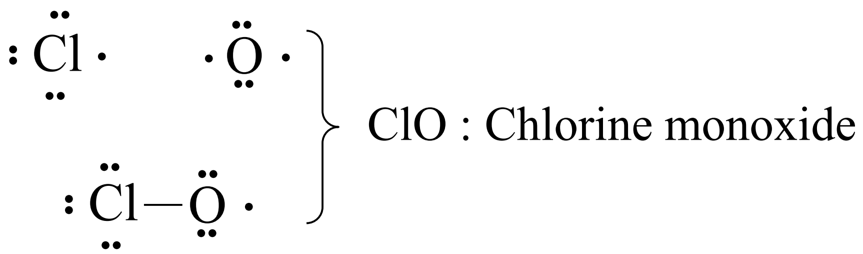


Fig. Q8-2, 20 QAs about O_3

ClO (Chlorine Monoxide) is a Radical

Radicals

- Odd number of electrons - unpaired electron in outer valence shell
- Go to great lengths to pair off lone electron
- Exceptionally reactive



See pages 71 to 75, Ch 2, Chemistry in Context, for description of Lewis Dot Structures of atmospherically important species

Chlorine Radicals Lead to Ozone Loss

$$ClO + ClO + M \rightarrow ClOOCl + M$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClOOCl + h\nu \rightarrow ClOO + Cl$$
$$ClOO + heat \rightarrow Cl + O_2$$

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

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

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

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

Montreal Protocol Has Banned Industrial Production of CFCs and Halons

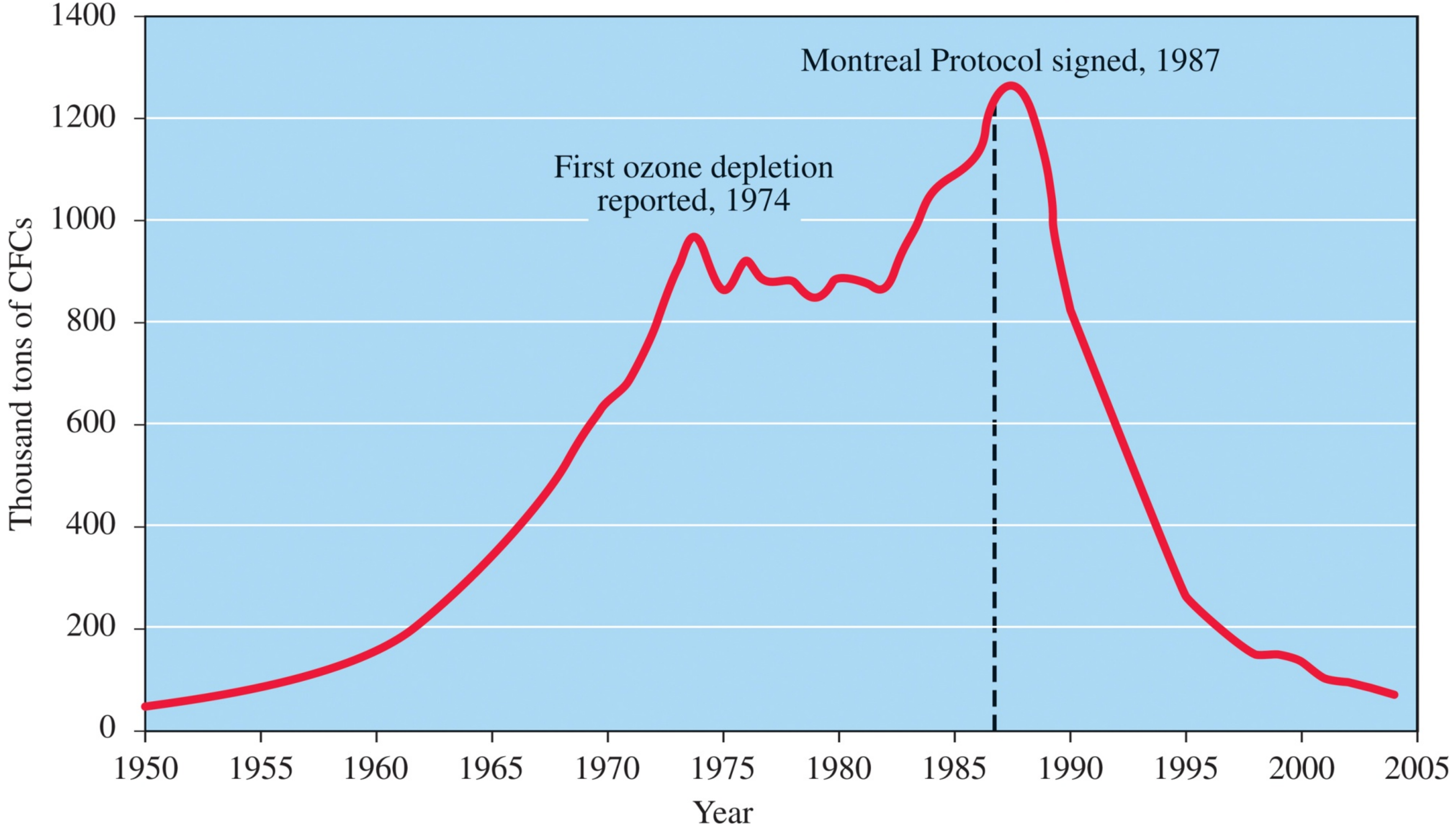


Fig. 2.19, Chemistry in Context

And Atmospheric Levels of these Pollutants are Declining

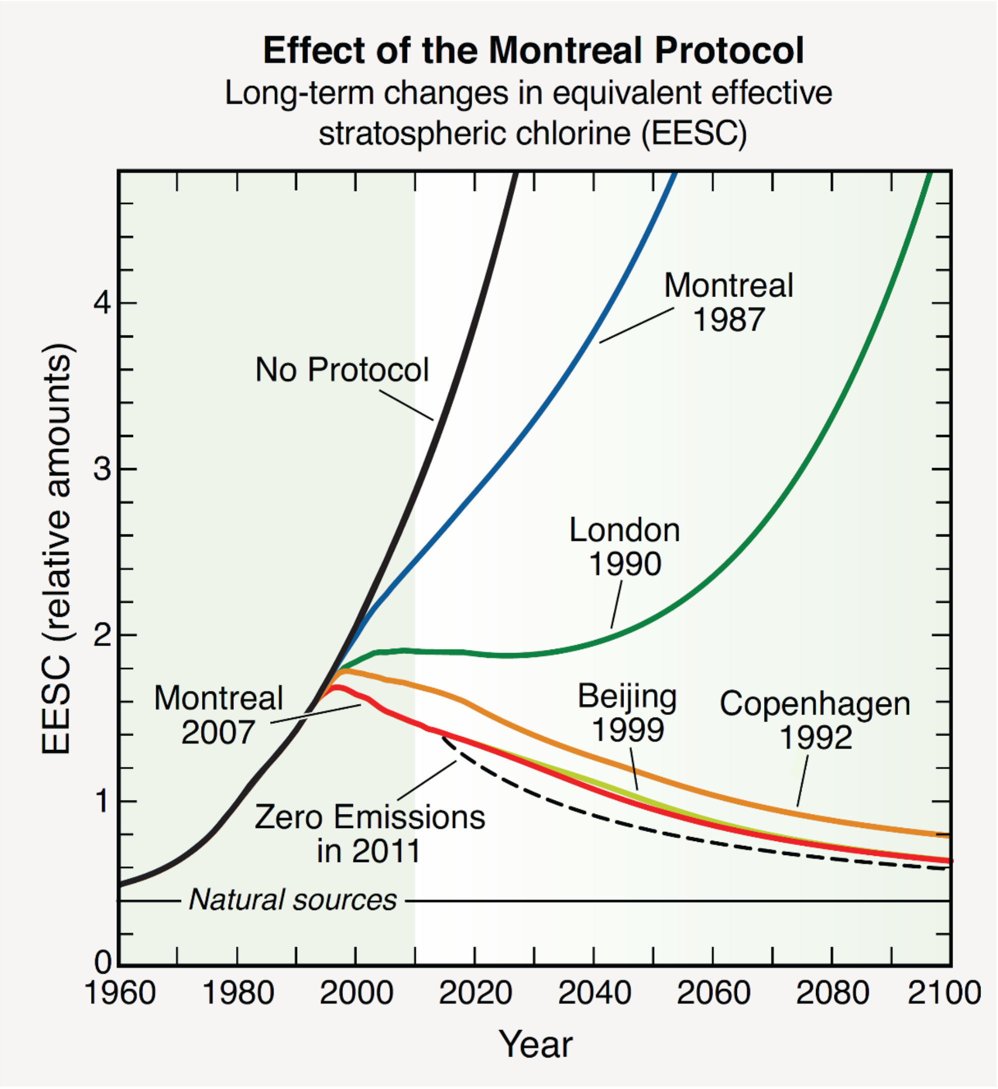
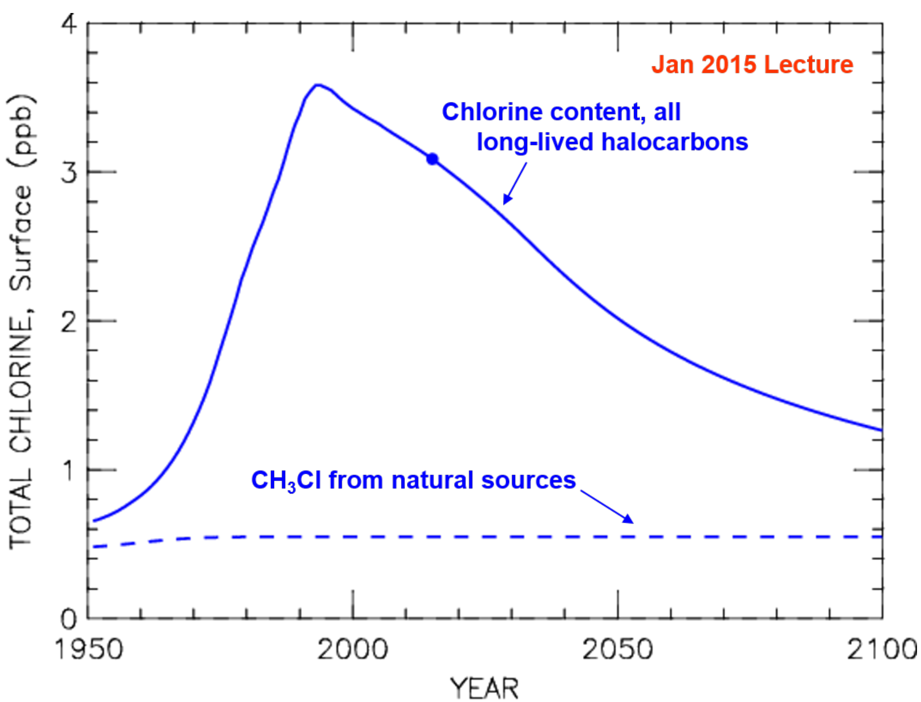
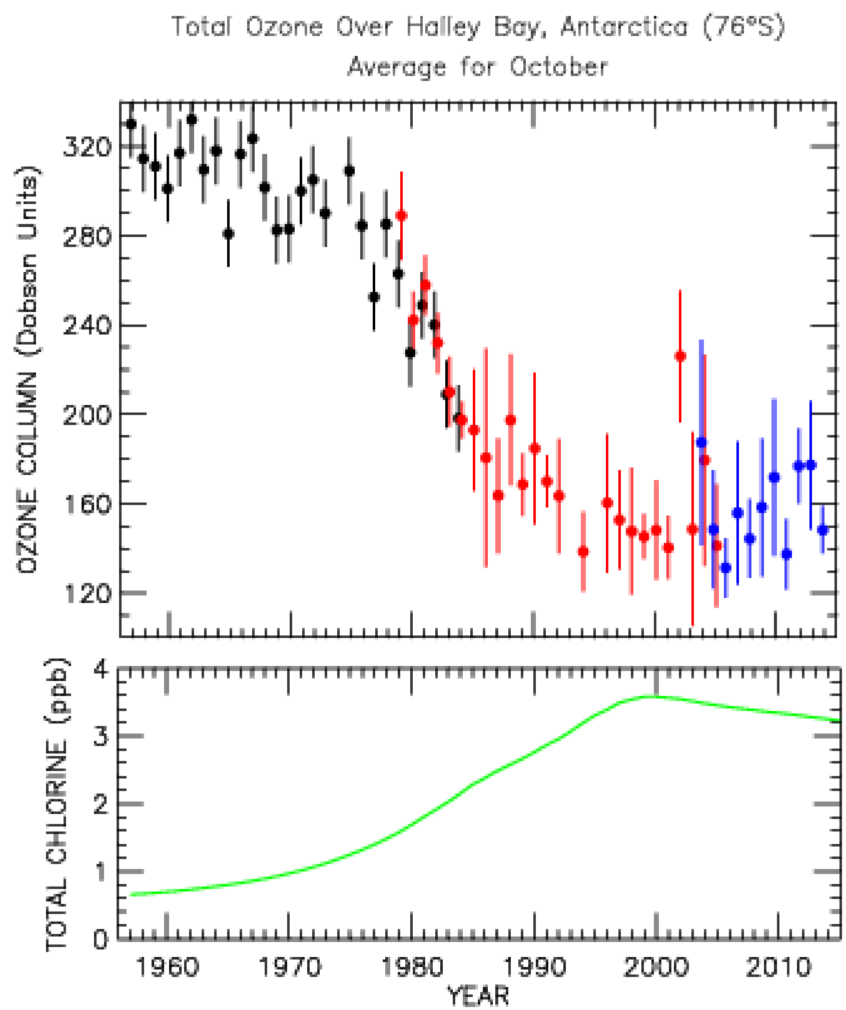


Figure Q15-1, 20 QAs about O_3

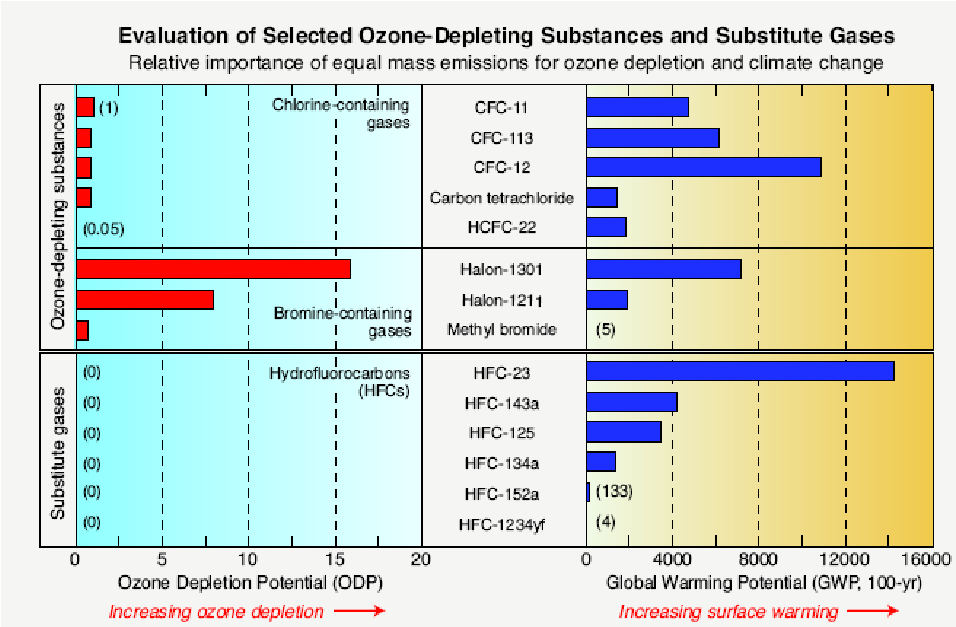
Montreal Protocol Has Banned Most Industrial Production of CFCs and Halons





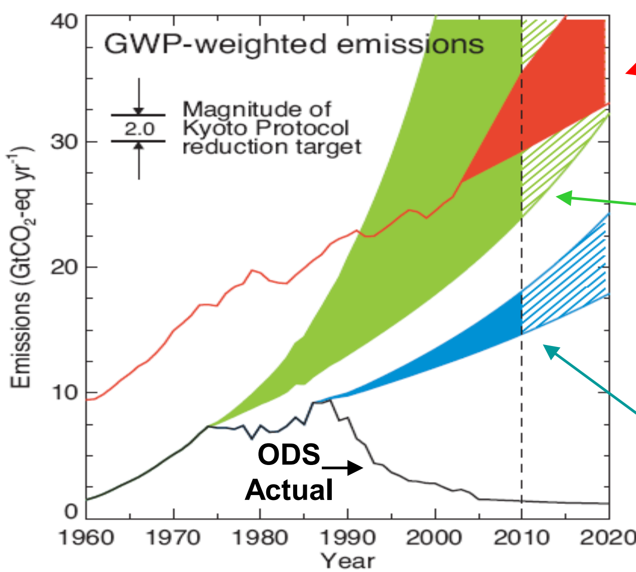
and the ozone layer is perhaps in initial phase of "recovery"

Link Between Ozone-Depleting Substances (ODS) and Climate Change



Twenty Questions and Answers About The Ozone Layer: 2010 Update (WMO, 2010)

Most ozone depleting substances have a significant "GWP"



GWP weighted emissions of CO_2

GWP weighted emissions of CFCs, without early aerosol propellant ban (i.e., no ban on CFCs)

GWP weighted emissions of CFCs, without Montreal Protocol

Velders *et al.*, *PNAS*, 2007

Air Quality Index

Table 1.4 **Levels for the Air Quality Index**

Air Quality Index (AQI) Values	Levels of Health Concern	Colors
When the AQI is in this range:	*...air quality conditions are:*	*...as symbolized by this color.*
0–50	Good	Green
51–100	Moderate	Yellow
101–150	Unhealthy for sensitive groups	Orange
151–200	Unhealthy	Red
201–300	Very unhealthy	Purple
301–500	Hazardous	Maroon

- Computed for each criteria pollutant even though many newspapers only give a single value (usually for worse index)
- In the U.S. health officials are generally concerned about elevated O_3, $PM_{2.5}$, and ultra-fine particles

Tropospheric Pollutants (The Air We Breathe)

Criteria Pollutants

Table 1.2 U.S. National Ambient Air Quality Standards

Pollutant	Standard (ppm)	Approximate Equivalent Concentration ($\mu g/m^3$)
Carbon monoxide		
8-hr average	9	10,000
1-hr average	35	40,000
Nitrogen dioxide		
Annual average	0.053	100
Ozone		
8-hr average	0.075	147
1-hr average	0.12	235
Particulates*		
PM_{10}, annual average	—	50
PM_{10}, 24-hr average	—	150
$PM_{2.5}$, annual average	—	~~15~~ ← Lowered to 12 $\mu g/m^3$ Dec 2012
$PM_{2.5}$, 24-hr average†	—	35
Sulfur dioxide		
Annual average	0.03	80
24-hr average	0.14	365
3-hr average	0.50	1,300

*PM_{10} refers to all airborne particles 10 μm in diameter or less. $PM_{2.5}$ refers to particles 2.5 μm in diameter or less.

—The unit of ppm is not applicable to particulates.

†$PM_{2.5}$ standards are likely to be revised after 2011.

Source: U.S. Environmental Protection Agency. Standards also exist for lead, but are not included here.

Note: A standard also exists for lead, but lead does not appear in this table since U.S. localities are in compliance

Chapter 1
Chemistry in Context

Criteria pollutant: identified as being common-place and detrimental to human welfare (i.e., ubiquitous pollutant)

Tropospheric Ozone Production

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

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

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

NO & NO_2 : Emitted by fossil fuel combustion & biomass burning

$$N_2 + O_2 \xrightarrow{\text{High T}} 2\ NO$$

CO: Emitted by fossil fuel combustion & biomass burning

Tropospheric Ozone – oxidant, lung irritant, harmful to crops

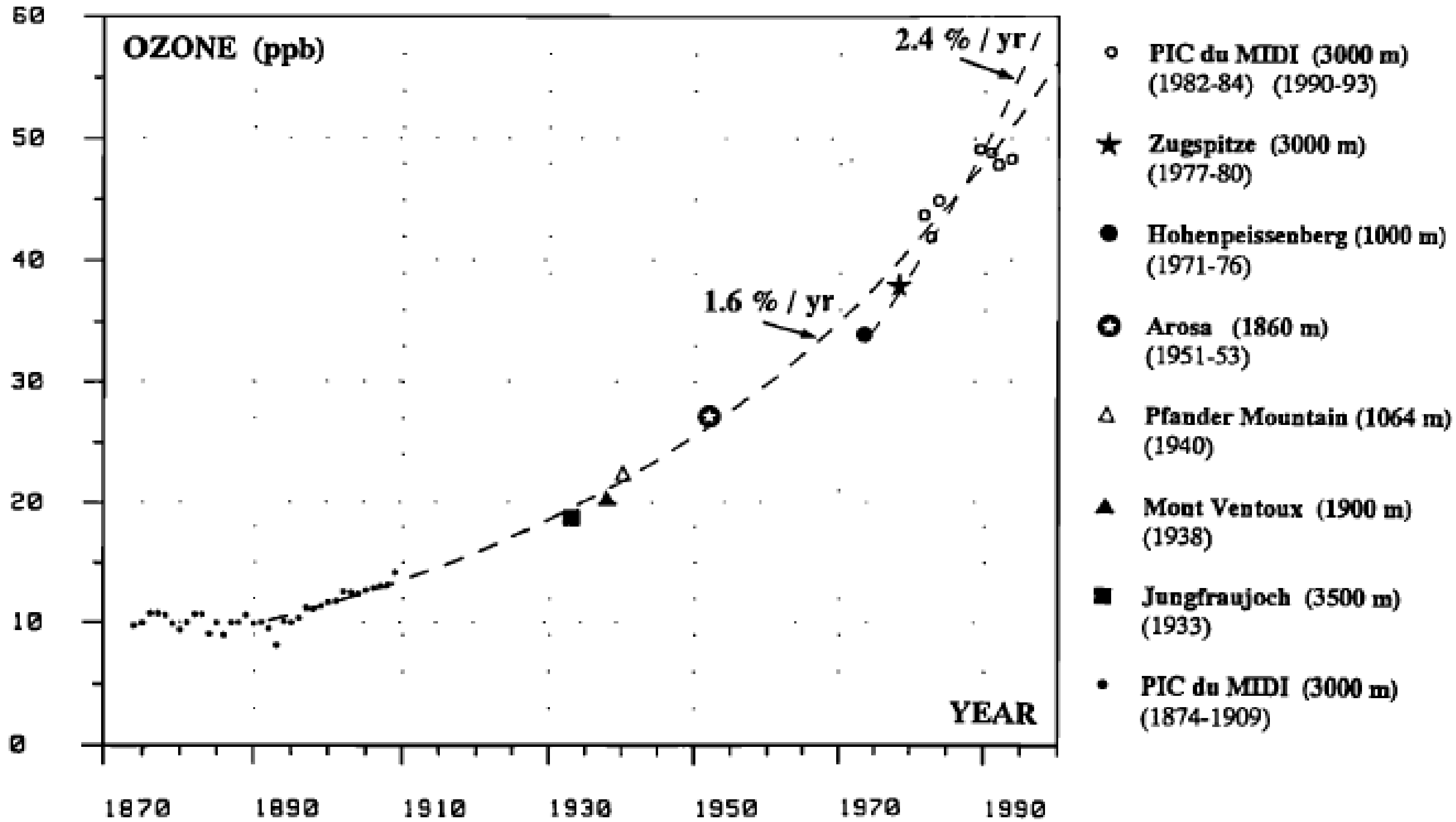
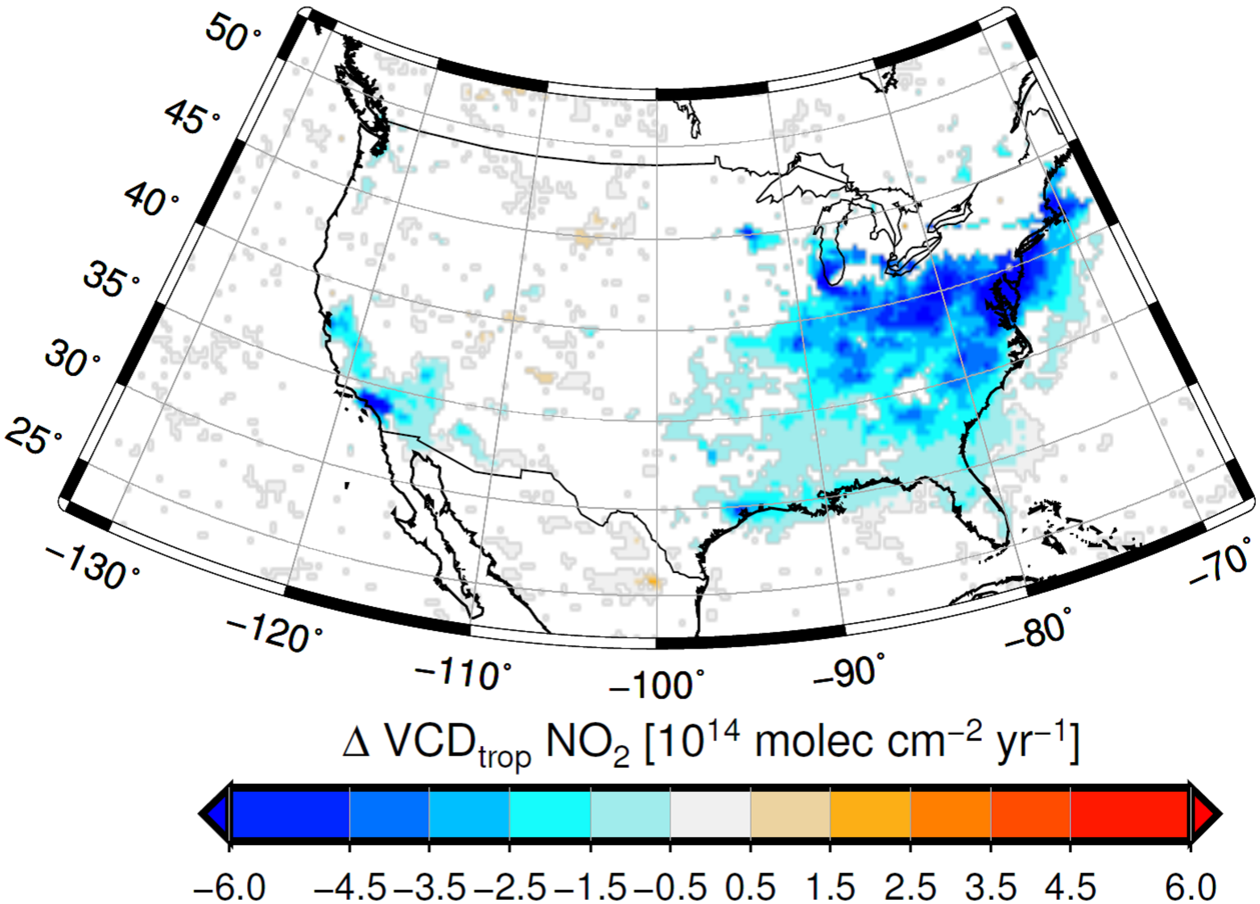


Figure 5. Ozone evolution in the free atmosphere over western Europe, from measurements at the Pic du Midi and in various European stations at high altitudes (see text).

Marenco *et al.*, *JGR*, 1994

Nitrogen Dioxide (NO_2): Combustion product that leads to formation of tropospheric ozone

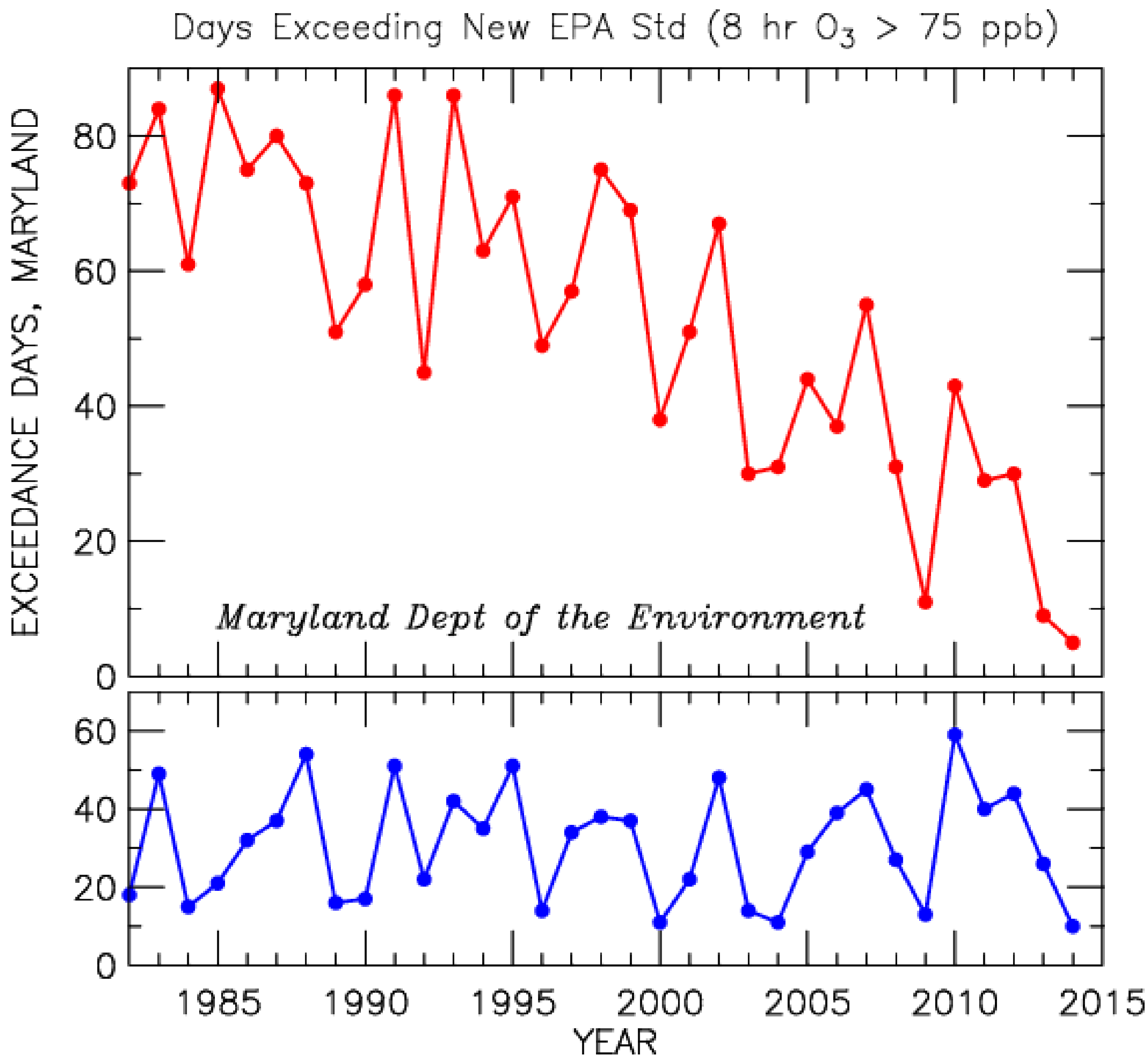
Value in 2011 minus value in 2006



VCD_{trop} = Vertical Column Density in the Troposphere

Hilboll *et al*., *ACP*, 2013

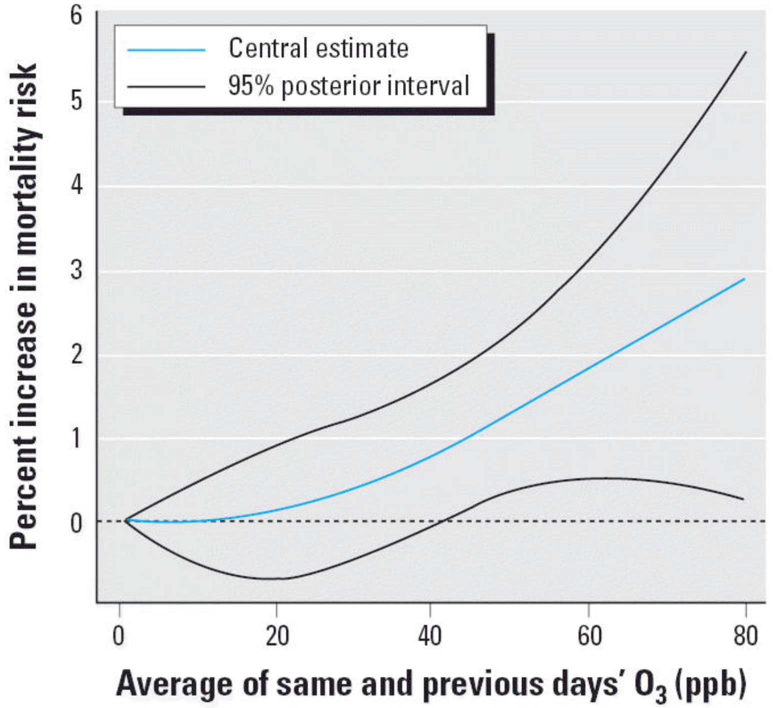
Significant Improvements in *Local* Air Quality since early 1980s



Air Quality Standards and Why We Care

Year	Averaging Period	EPA Surface Ozone Standard
1979	1 hr	125 ppb
1997	8 hr	85 ppb
2008	8 hr *	75 ppb
2015#	???	???

* The 8 hr standard is met when the 3-yr average of the annual 4th highest daily maximum 8 hr O_3 is less than 75 ppb



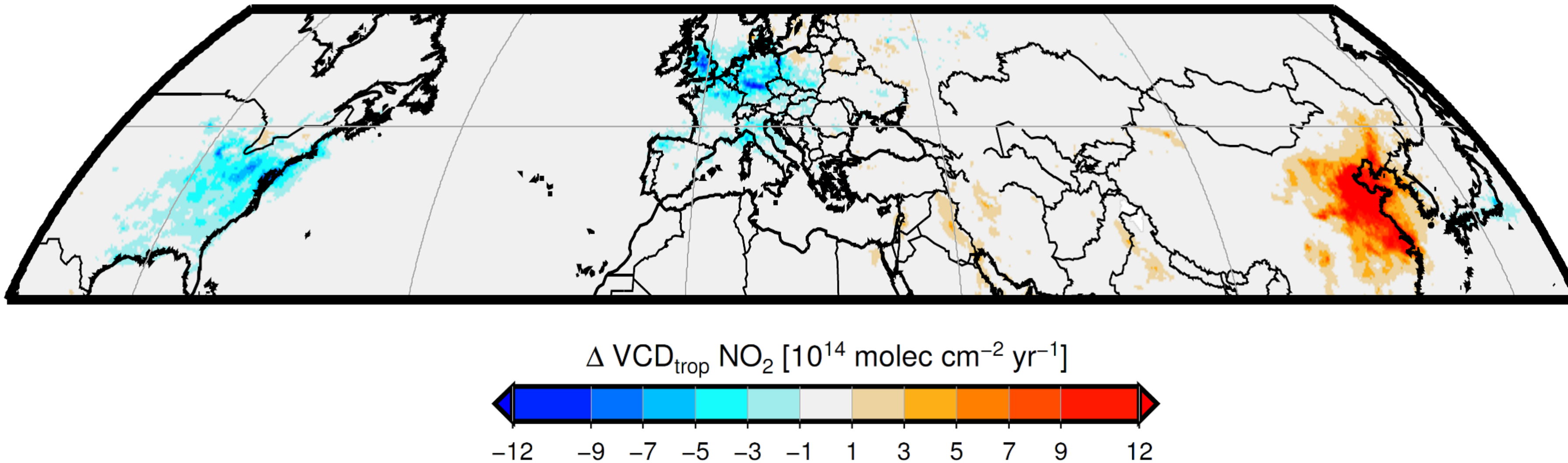
Increased risk of premature mortality for even low levels of surface O_3; further reductions will benefit public health

Bell et al., 2006
http://www.ncbi.nlm.nih.gov/sites/ppmc/articles/PMC1440776

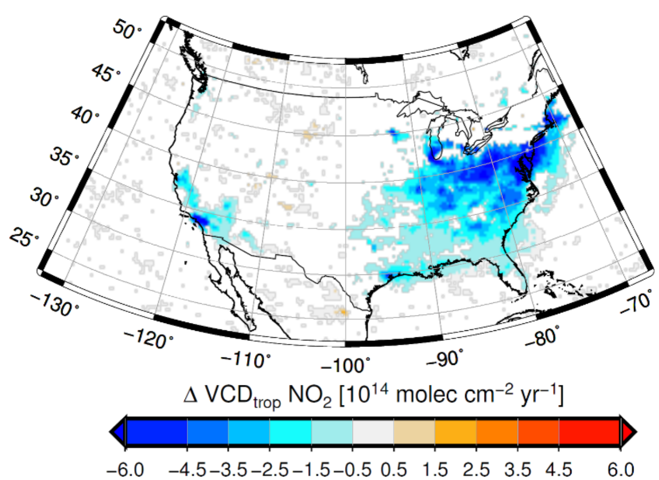
On November 25, 2014 the EPA proposed to lower the NAAQS for ground-level ozone to "a level within the range of 65 to 70 ppb, based on extensive scientific evidence about the harmful effects of ozone; written comment on the proposed new rule is due 17 March 2015 http://www.epa.gov/groundlevelozone/actions.html

Nitrogen Dioxide (NO_2): Combustion product that leads to formation of tropospheric ozone

Value in 2011 minus value in 2006



Value in 2011 minus value in 2006



Hilboll *et al.*, *ACP*, 2013

Next Lecture: Fundamentals of Earth's Atmosphere

Reading:

Chemistry in Context, Secs 1.0 to 1.2,1.5 to 1.8, 1.14, 2.1, 3.6 & 3.7 (~28 pgs) as well as 7 pages from Atmospheric Environment by McElroy

Admission Ticket for Lecture 3 is now posted at:

http://www.atmos.umd.edu/~rjs/class/spr2015/admission_tickets/ACC_2015_admis_ticket_lecture_03.doc

Please bring a calculator to class on Tuesday