Overview of Global Warming, Ozone Depletion, and Air Quality

AOSC 433 & 633

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Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2017

Note:

- **An entry for CHEM 433 has appeared on Testudo**
- **As far as I can tell, no one is actually registered for CHEM 433**
- **If it is important to anyone that they take CHEM 433 rather than AOSC 433, please see me after class**

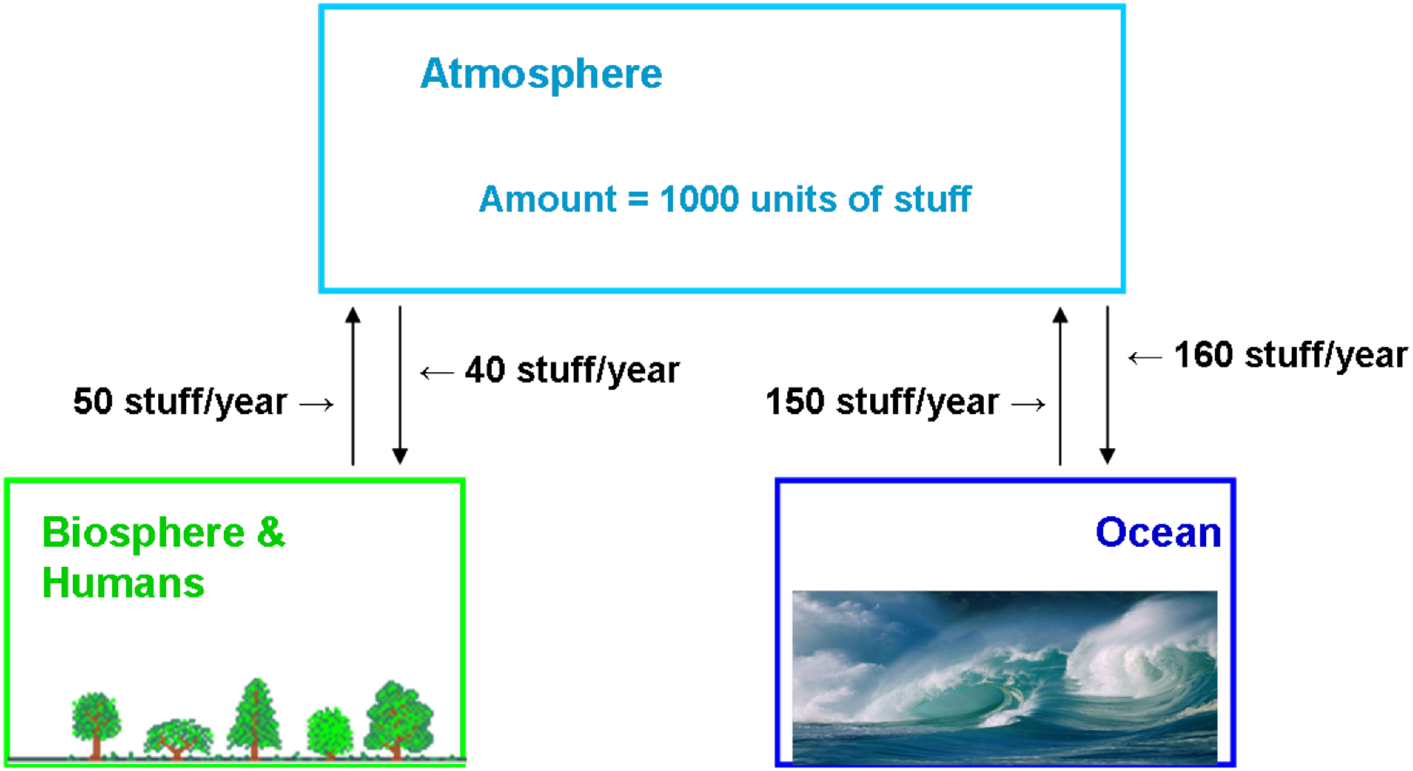
Lecture 2

31 January 2017

Learning Outcome Quiz, Question #4

The image below shows the amount of some material in the atmosphere in units of "stuff", as well as flux of this material into and out of the atmosphere in units of "stuff/year".

What is the lifetime of this material in the atmosphere?



Answer here:

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**

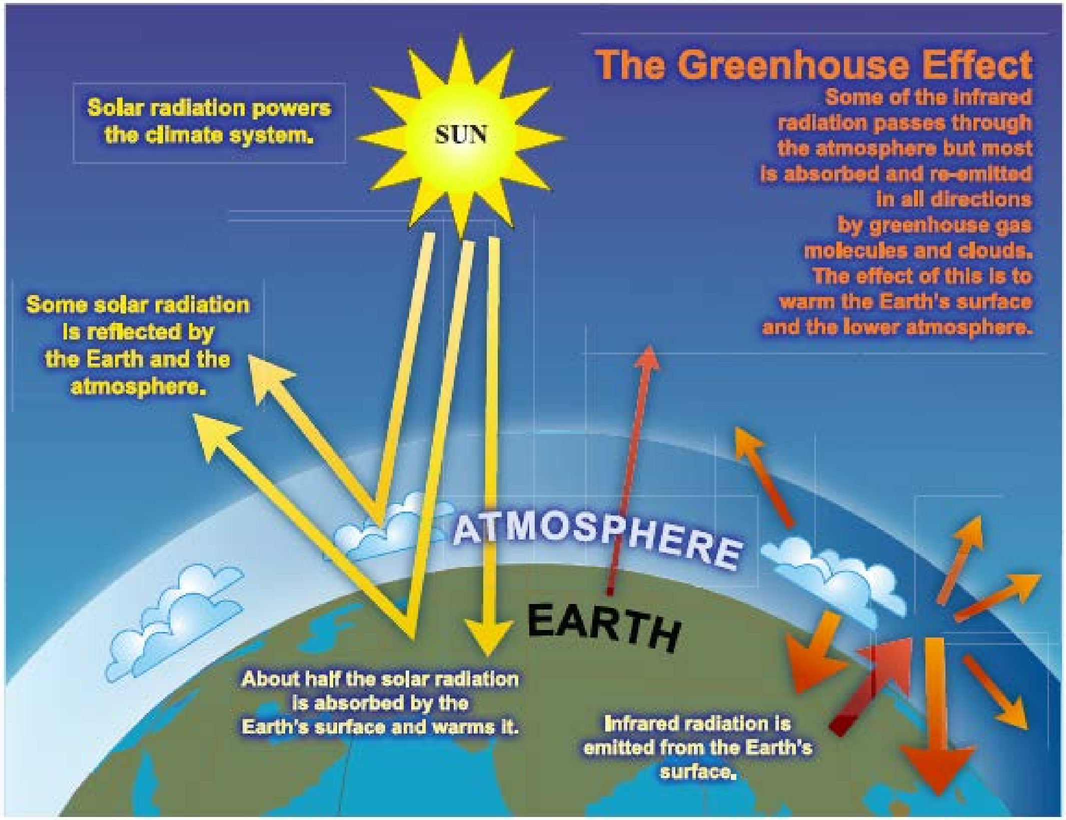
Today's goals:

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

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

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

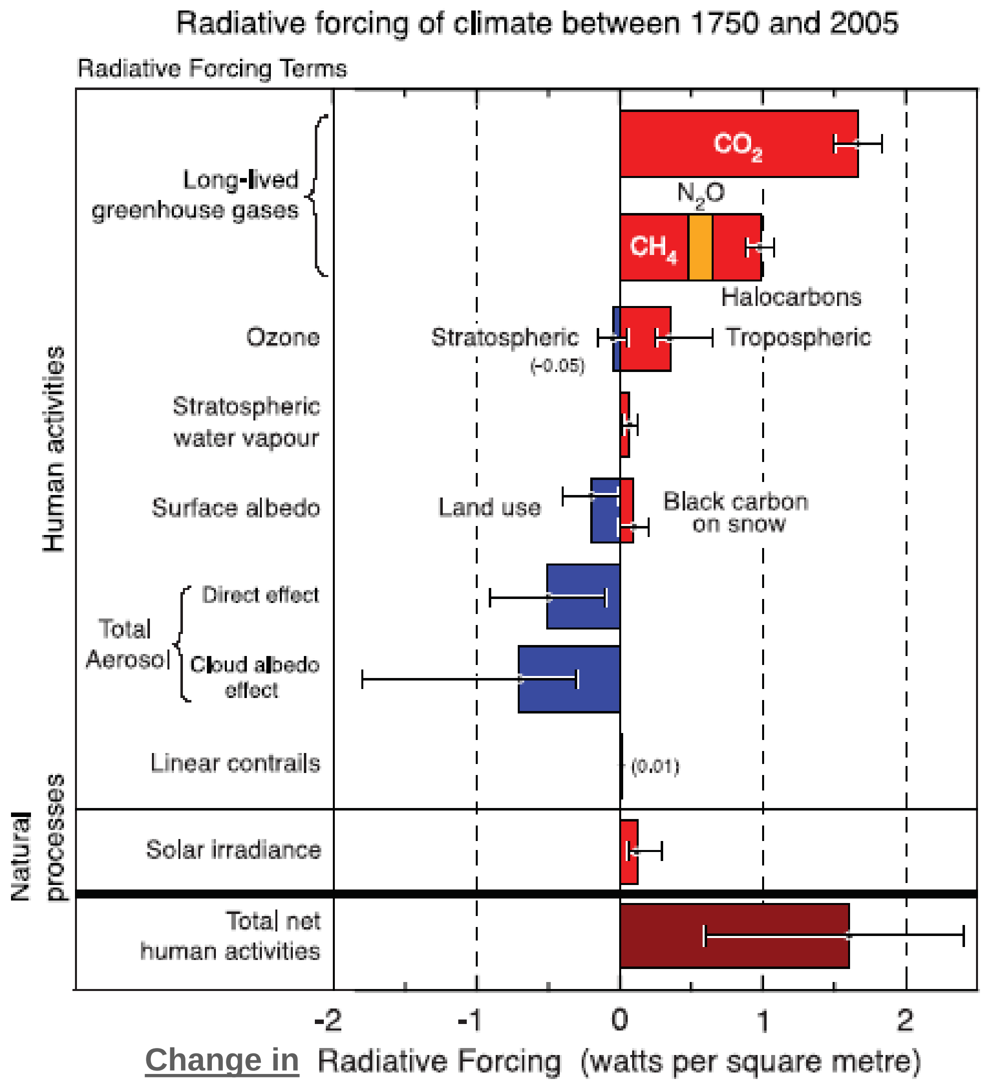
Greenhouse Effect



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

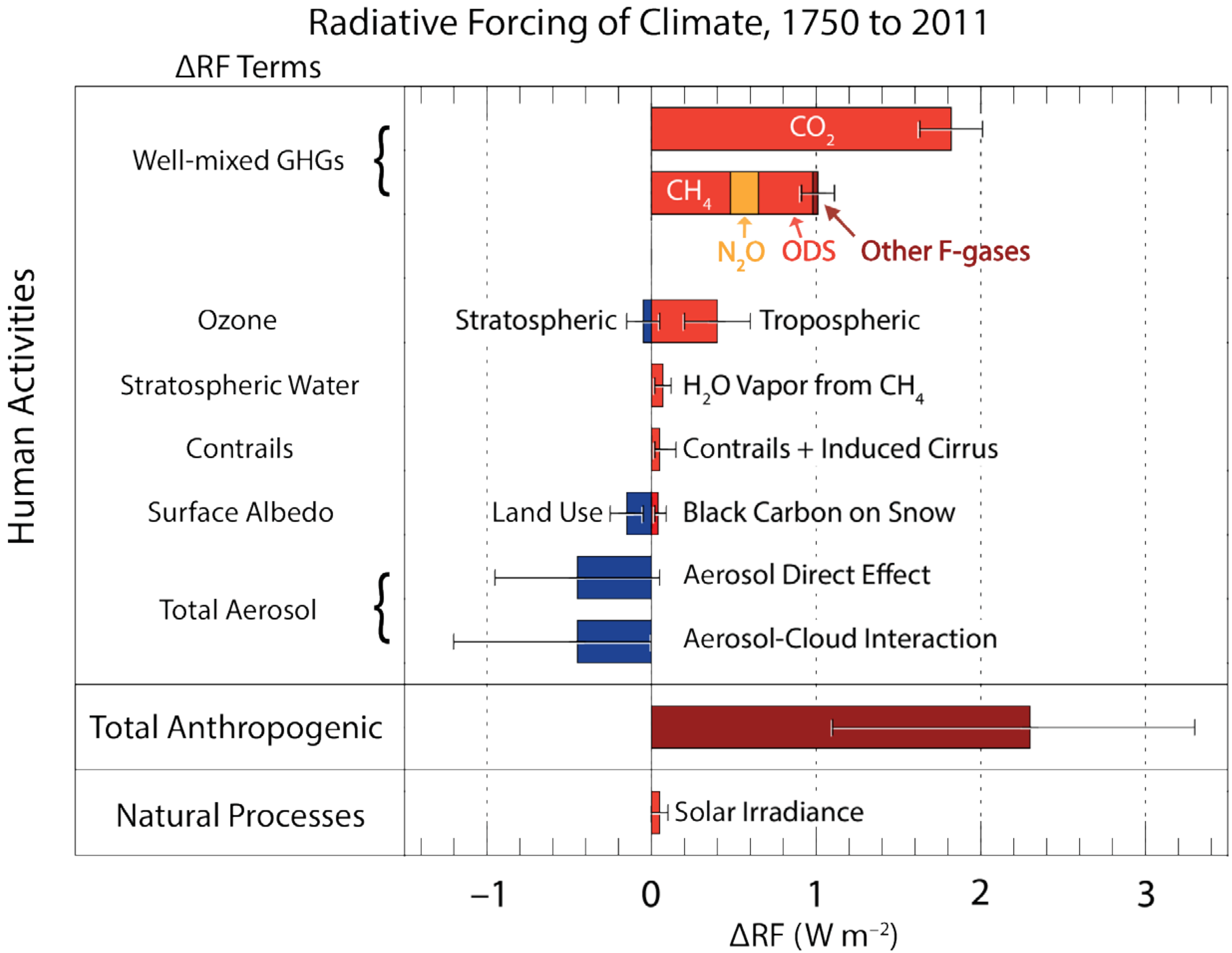
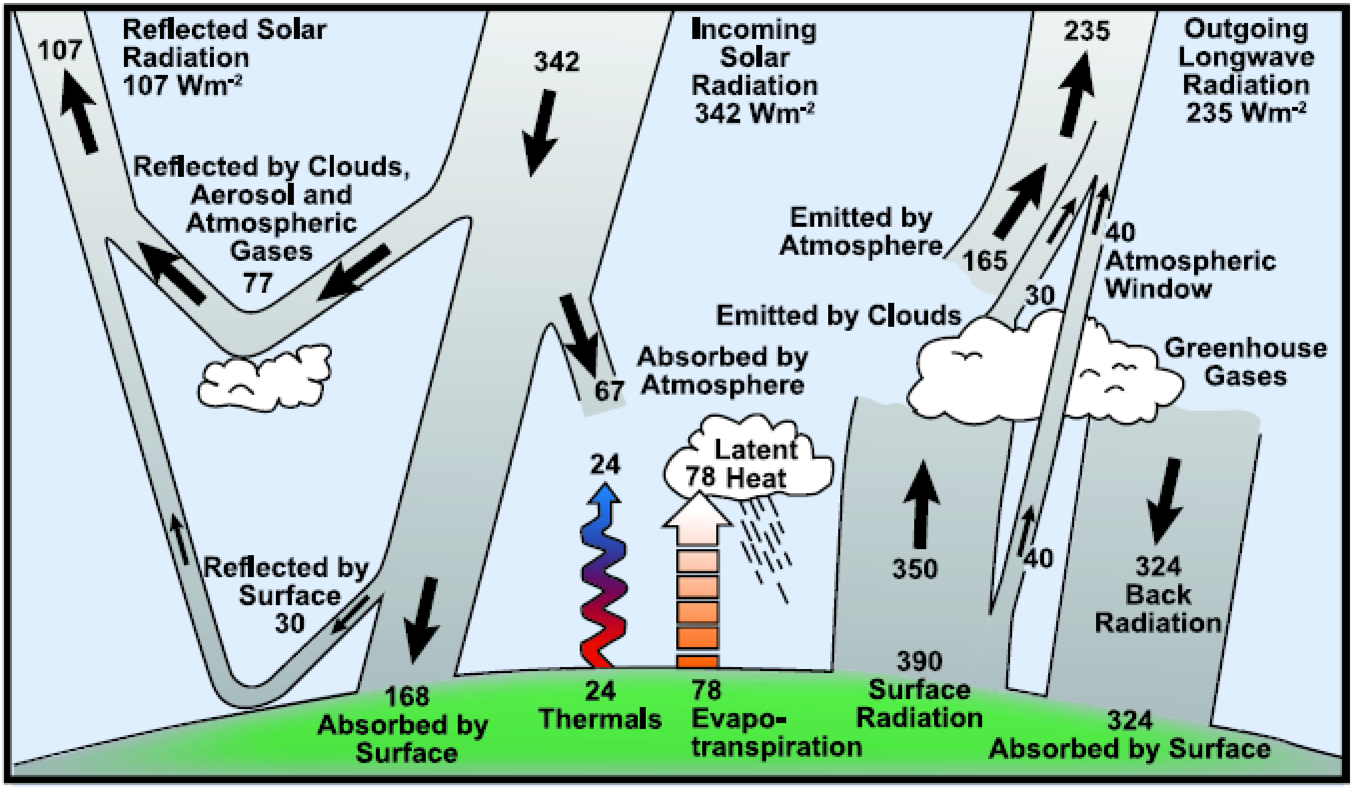


Figure 1-4, Paris Beacon of Hope

Radiative Forcing



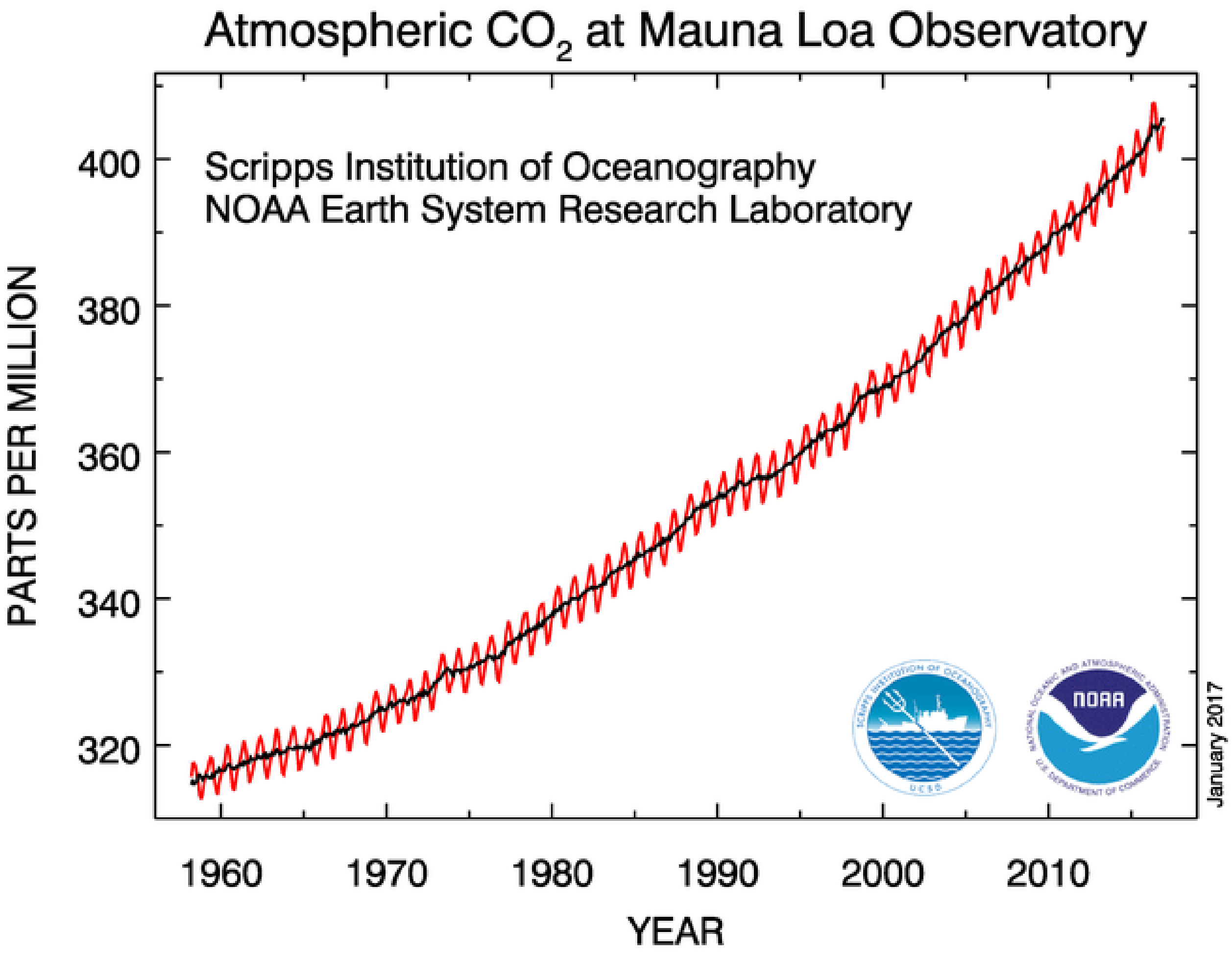
FAQ 1.1, Figure 1. *Estimate of the Earth's annual and global mean energy balance. Over the long term, the amount of incoming solar radiation absorbed by the Earth and atmosphere is balanced by the Earth and atmosphere releasing the same amount of outgoing longwave radiation. About half of the incoming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

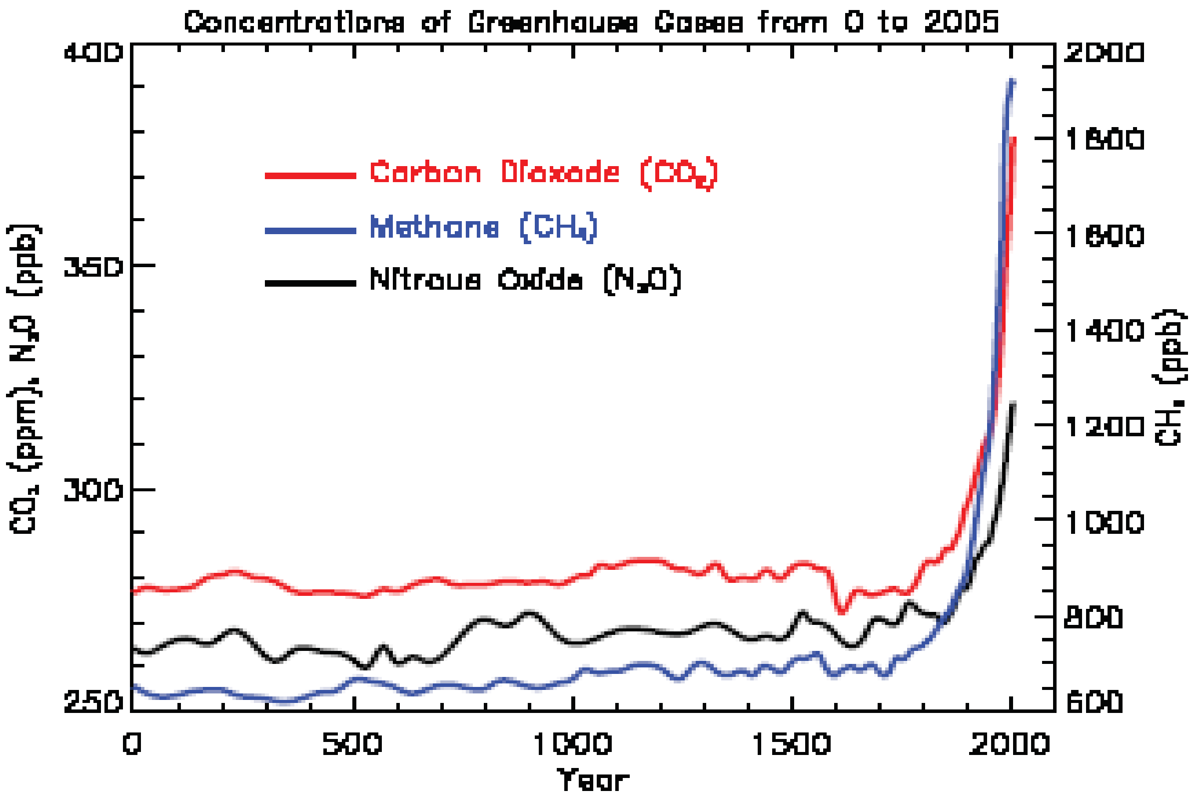
Modern CO_2 Record

CO_2 at MLO on 29 Jan 2017: 405.8 parts per million (ppm) and rising !



Legacy of Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
https://www.esrl.noaa.gov/gmd/ccgg/trends/full.html
See also https://www.co2.earth/daily-co2

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

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

where:

a_{CH4} = Radiative Efficiency (W m^{-2} 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.

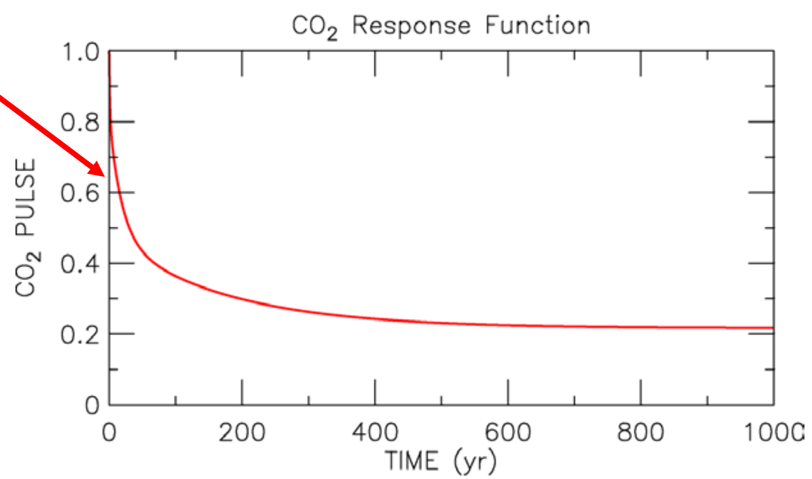
[a] The CO_2 response function used in this report is based on the revised version of the Bern Carbon cycle model used in Chapter 10 of this report (Bern2.5CC; Joos et al. 2001) using a background CO_2 concentration value of 378 ppm. The decay of a pulse of CO_2 with time t is given by

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

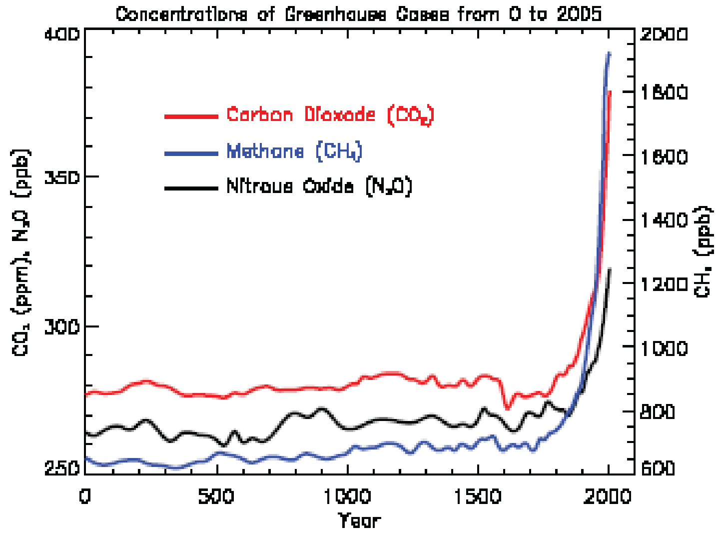
[b] The radiative efficiency of CO_2 is calculated using the IPCC (1990) simplified expression as revised in the TAR, with an updated background concentration value of 378 ppm and a perturbation of +1 ppm (see Section 2.10.2).

[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:

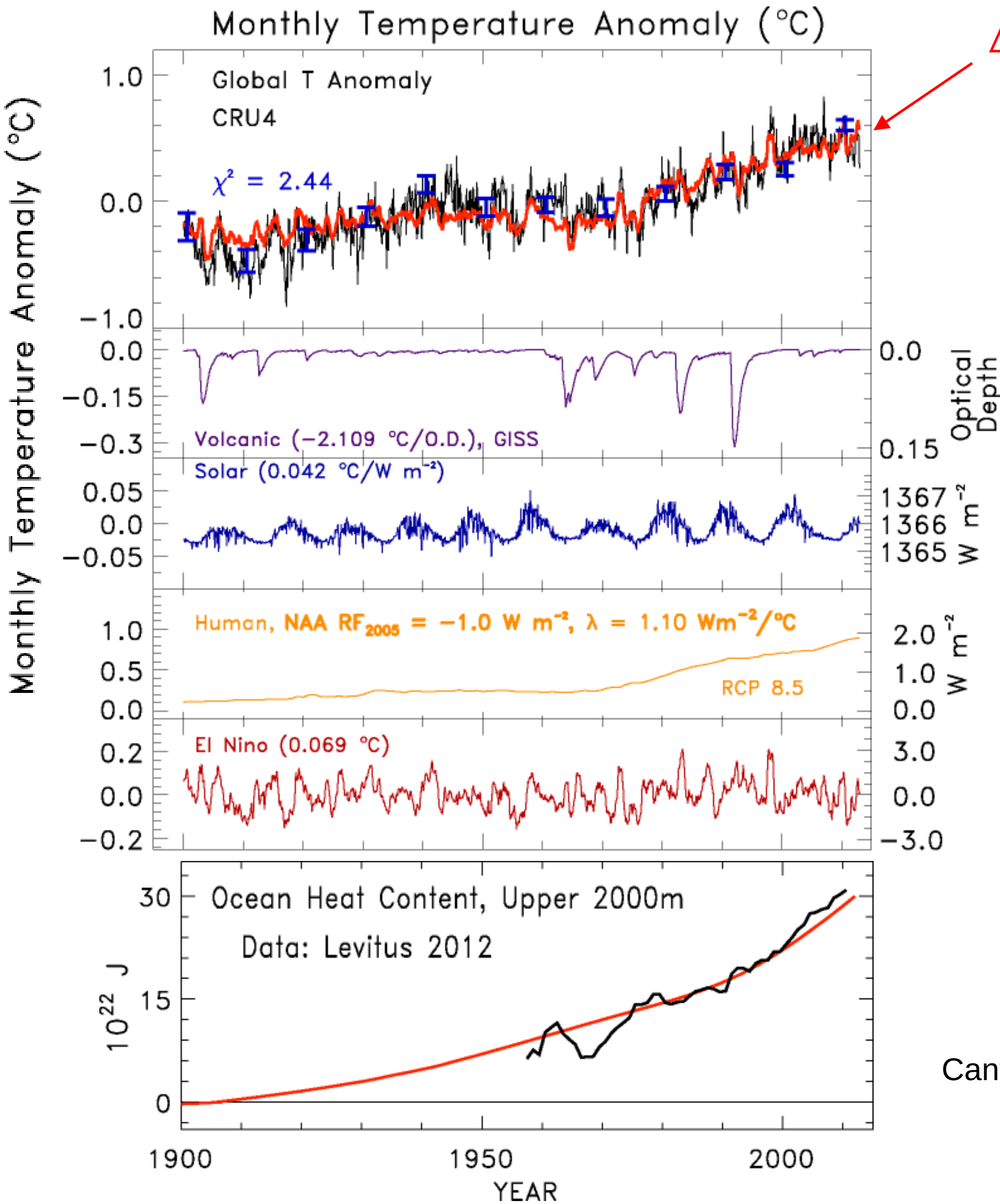
RF CH_4 relative to $CO_2 \approx 26.4 \times 1250$ ppb / 100 ppm = $26.4 \times 0.0125 = 0.33$

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?



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

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

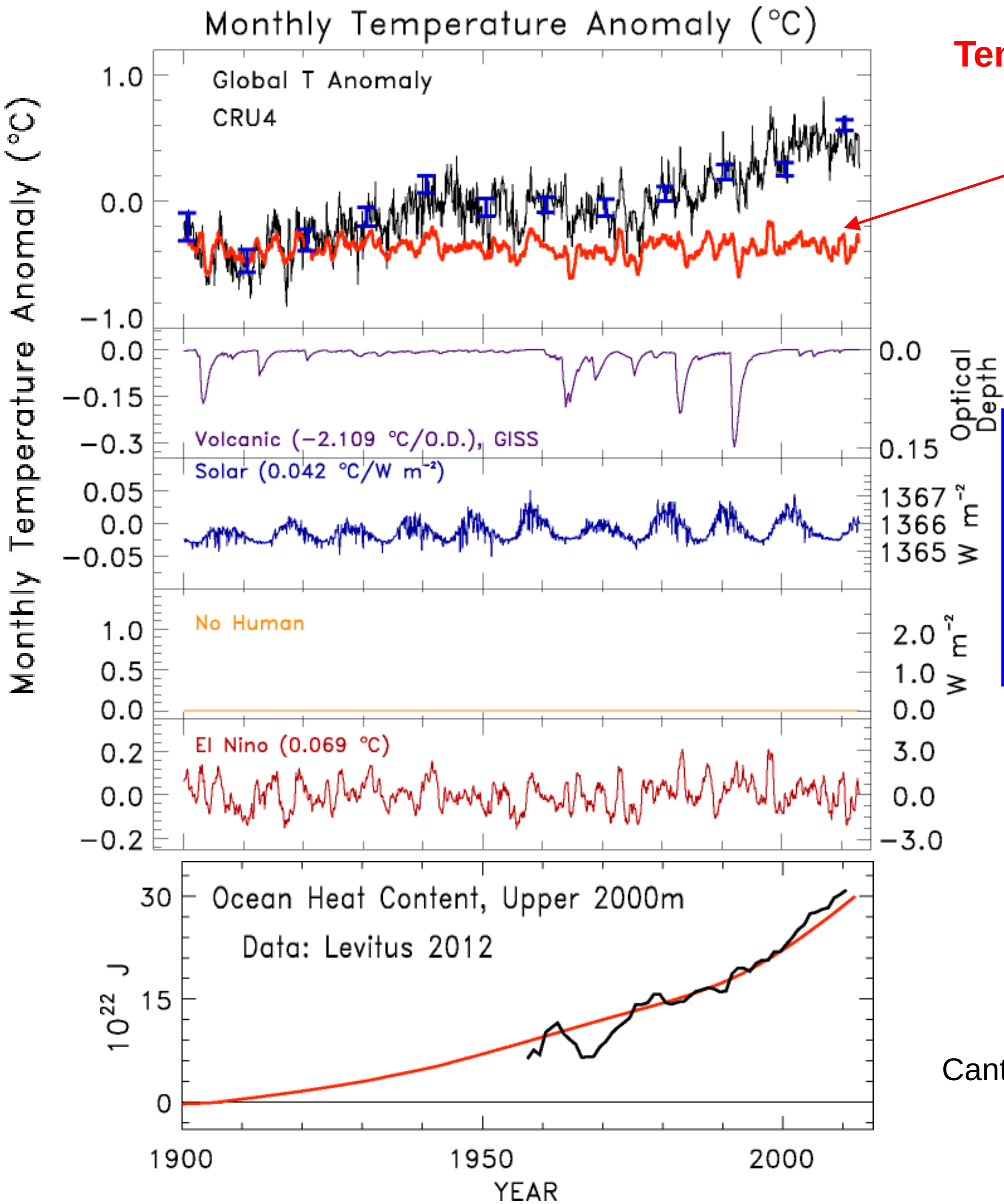
TSI = Total solar irradiance

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

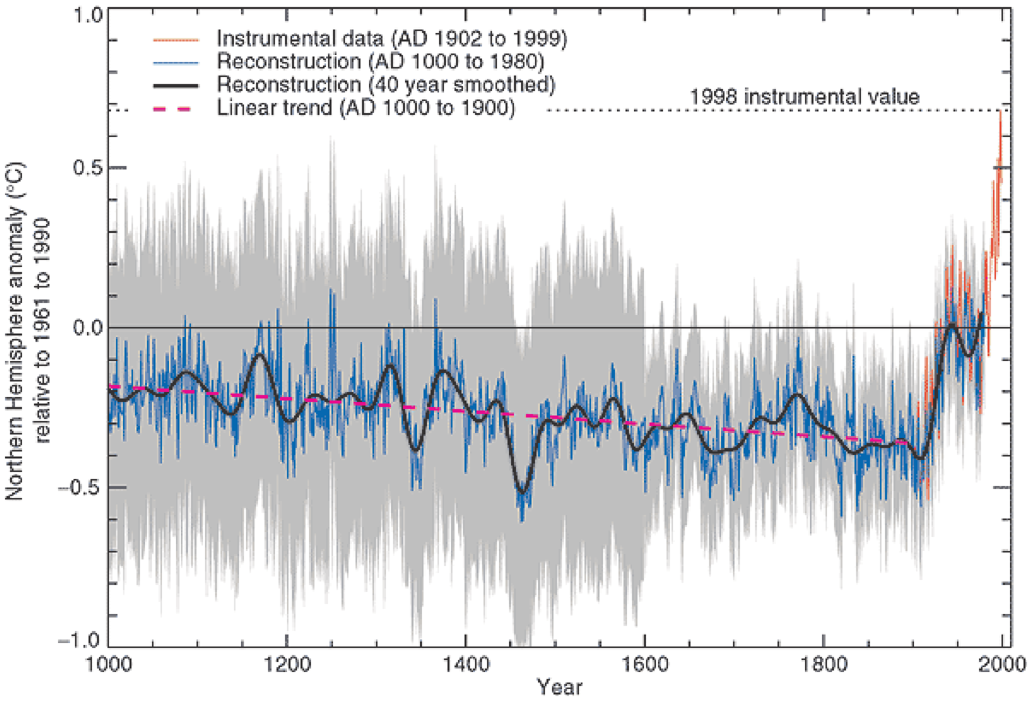
Volcanoes: no sustained forcing

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**



http://www.grida.no/publications/other/ipcc_tar/?src=/climate/ipcc_tar/wg1/069.htm

Are humans responsible?

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

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Solar variability:

Perhaps dominant forcing of Medieval Warming and Little Ice Age
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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.

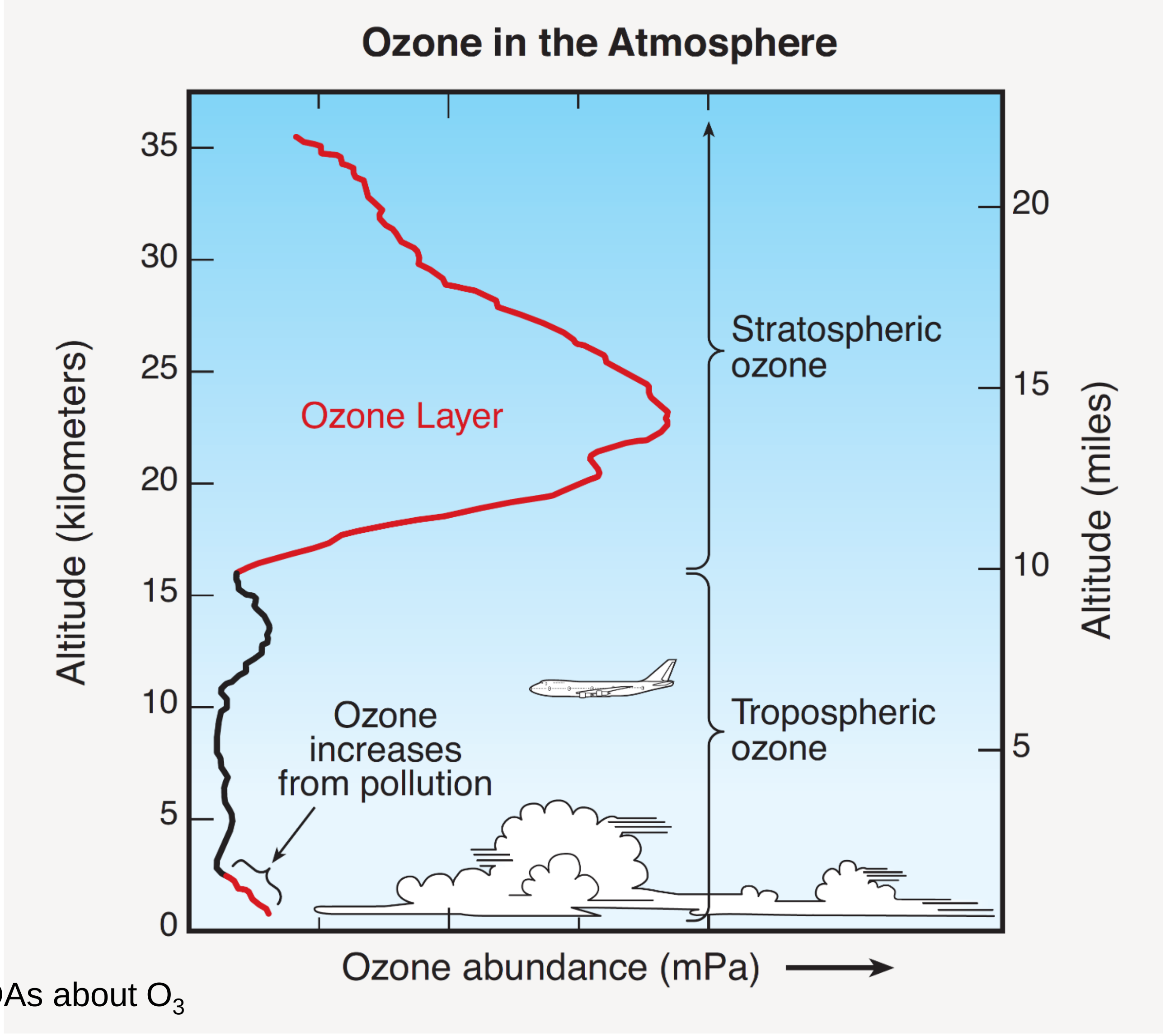
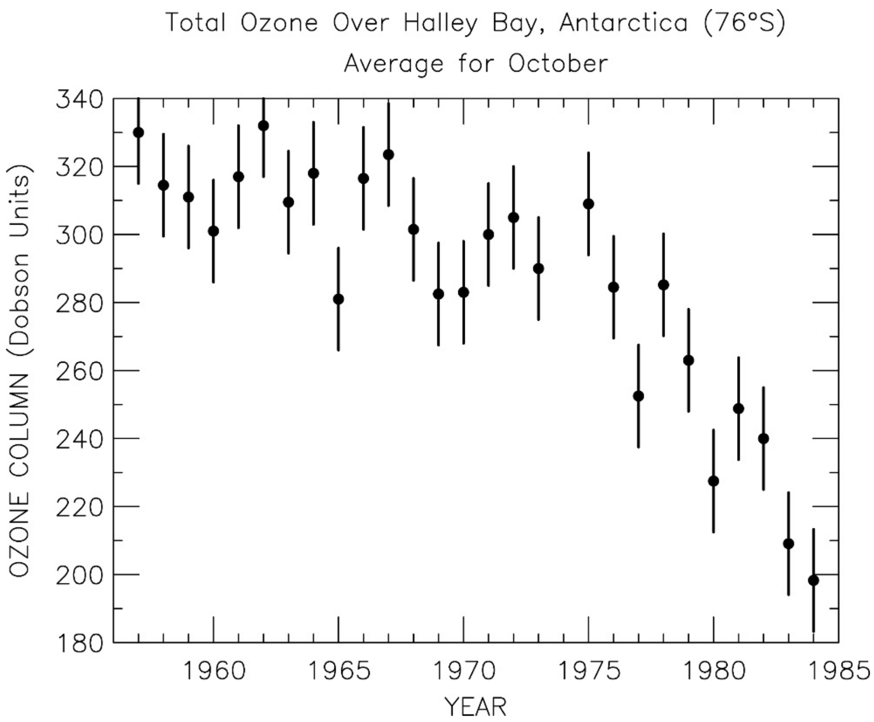


Fig. Q1-2, 20 QAs about O_3

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

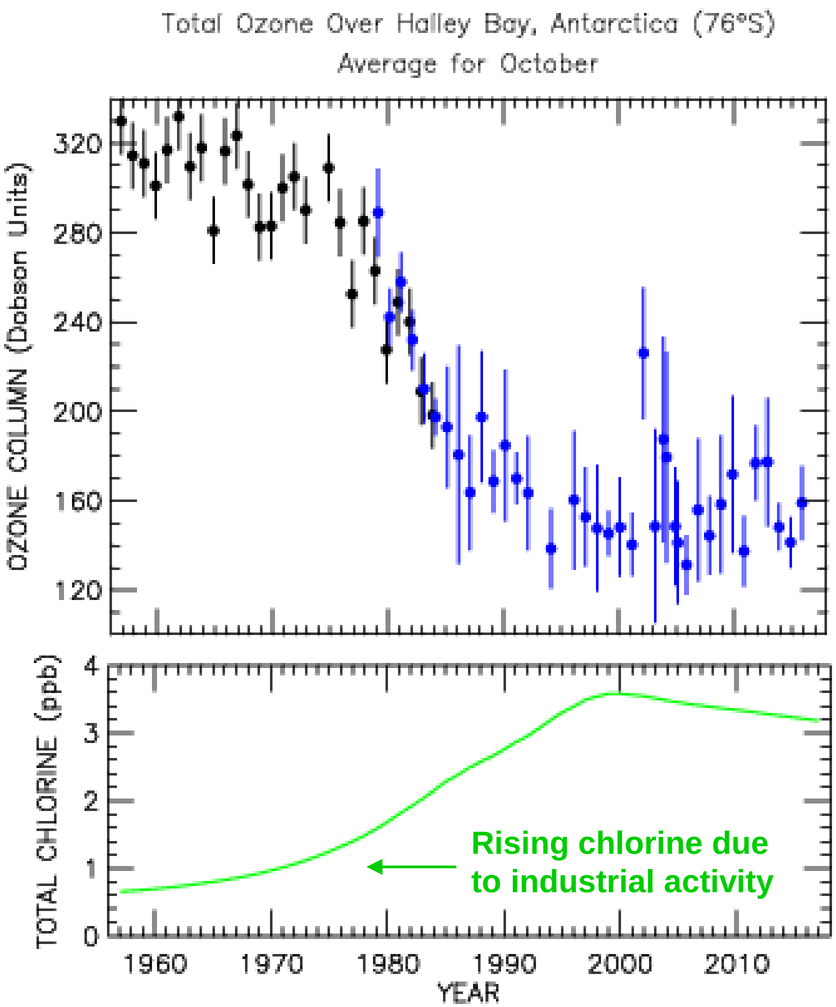
Earth's Atmosphere – Effect of Humans

Stratospheric Ozone – shields surface from solar UV radiation

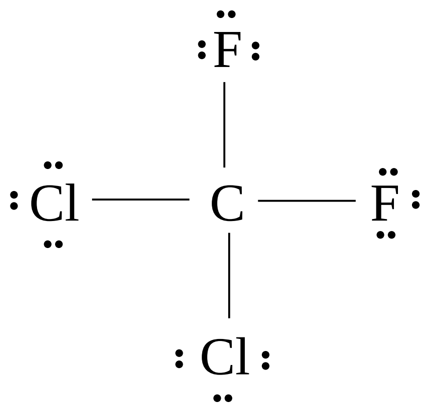


After Farman *et al*., Large losses of total ozone in Antarctica reveal Seasonal ClO_x/NO_x interaction, Nature, 315, 207, 1985.

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

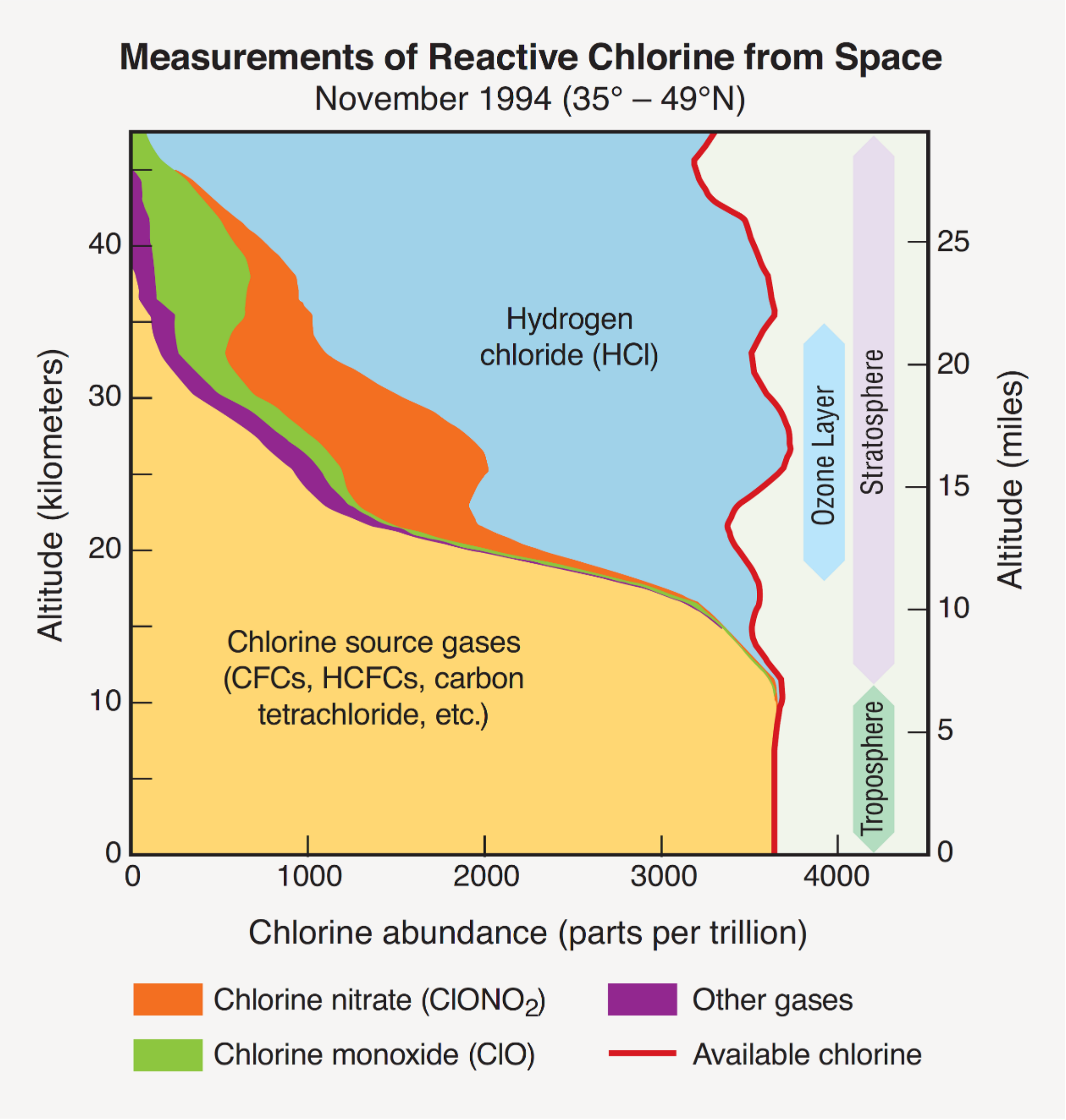
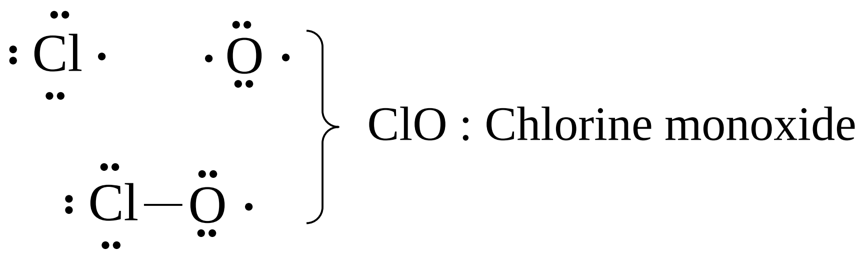


Fig. Q8-2, 20 QAs about O_3

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

Note: you will not be tested on Lewis Dot Structures. But ,we want the non-chemists to at least have been exposed to this concept for tracking the position of electrons, which is central for understanding atmospheric chemical reactions.

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 :

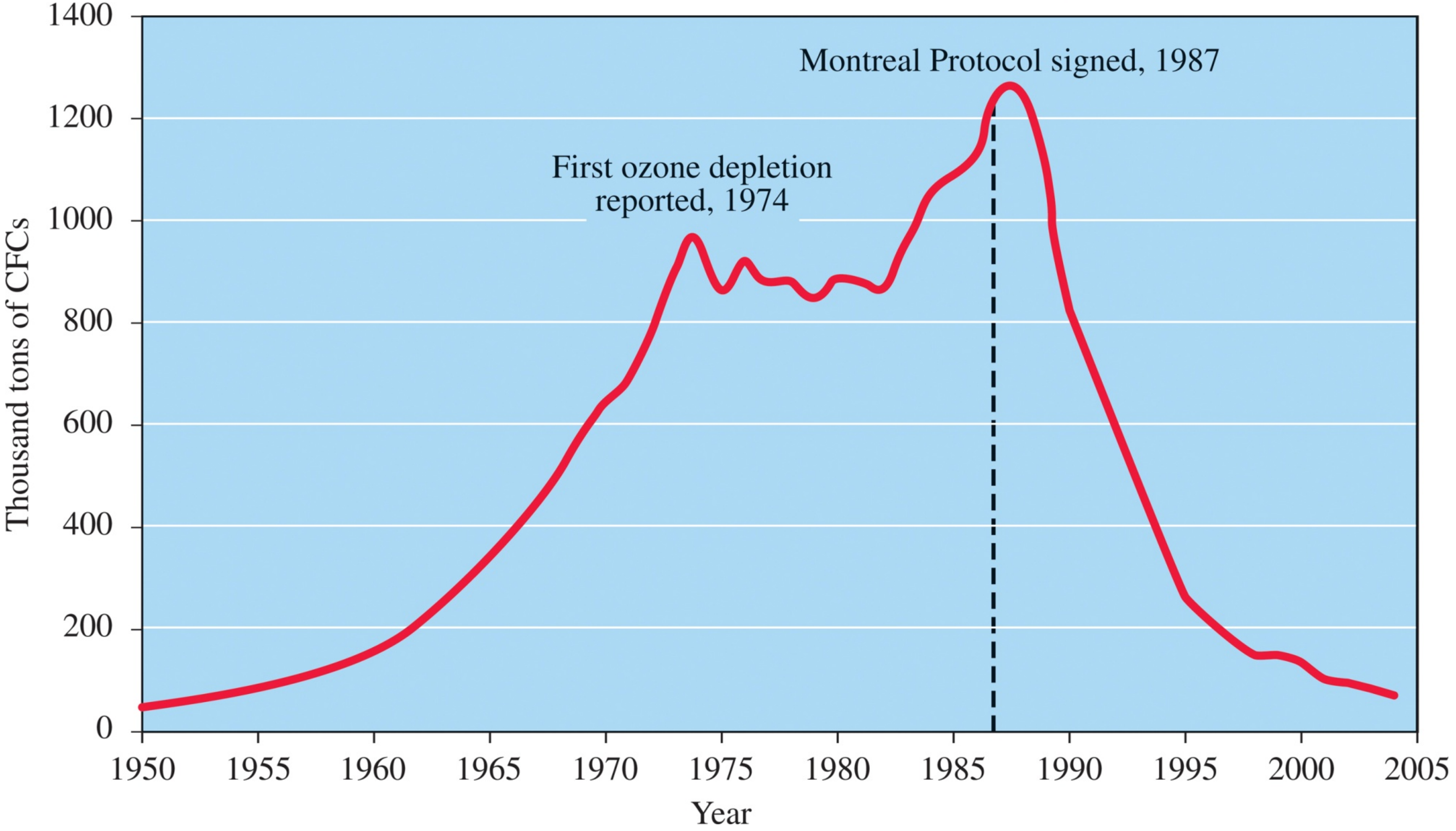
τ is the global atmospheric lifetime

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



Global Production of CFCs, Fig. 2.19, Chemistry in Context

And Atmospheric Levels of these Pollutants are Declining

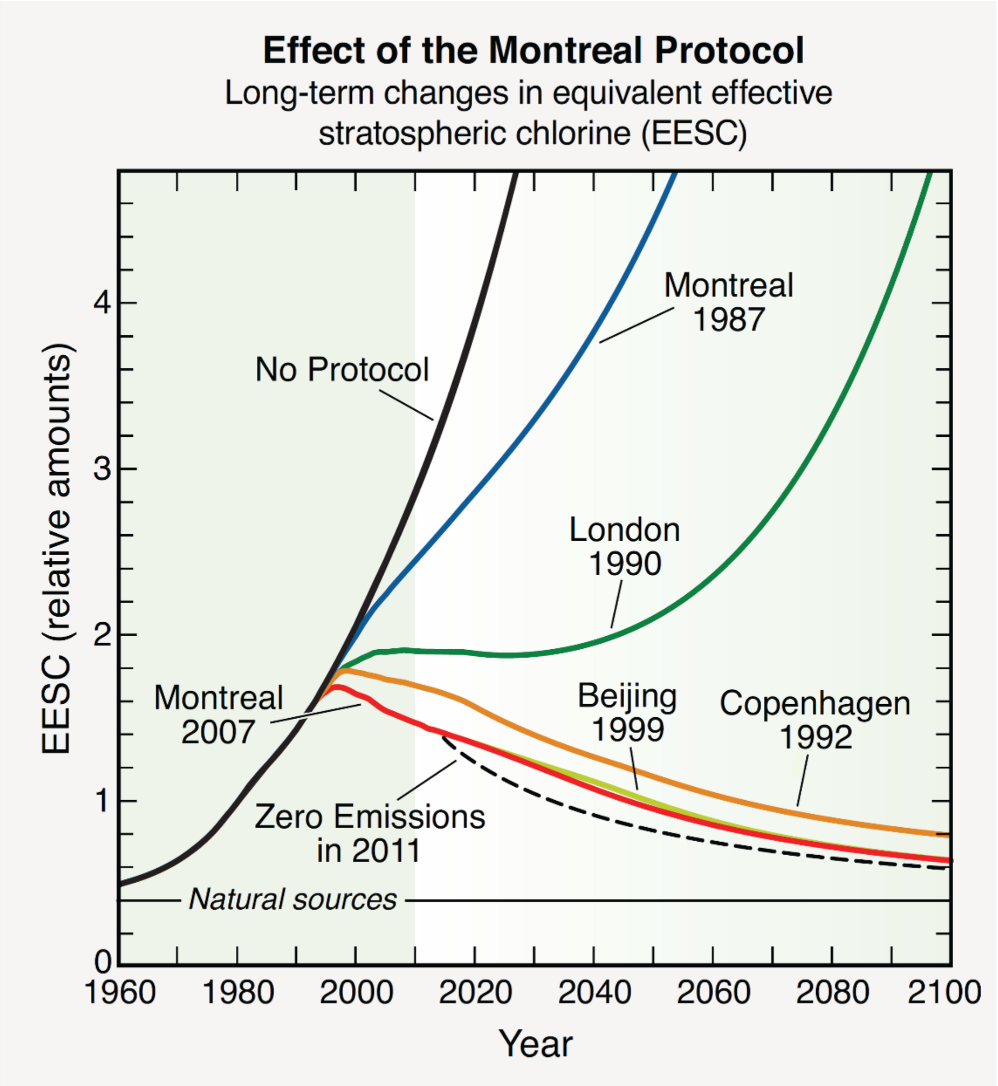
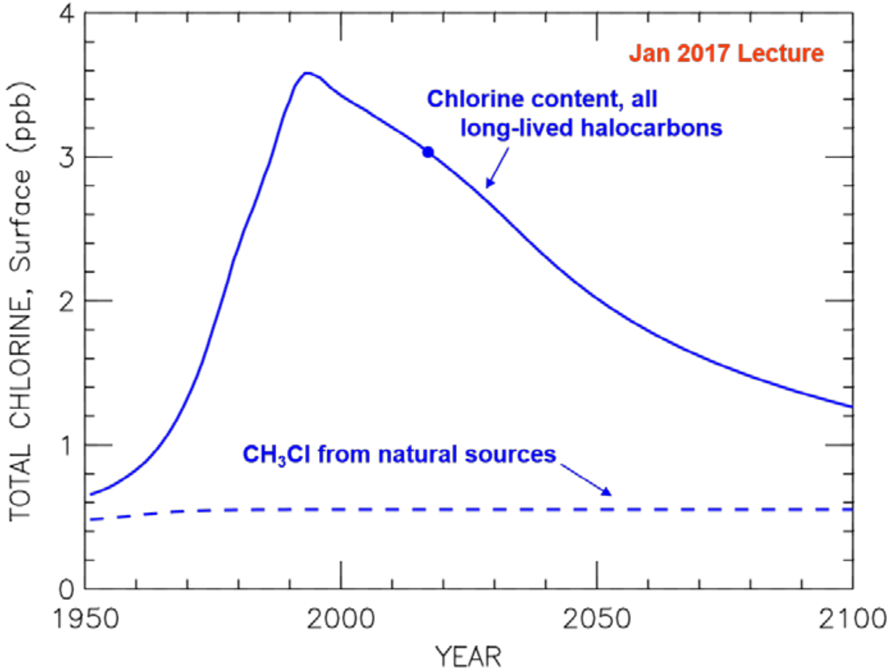
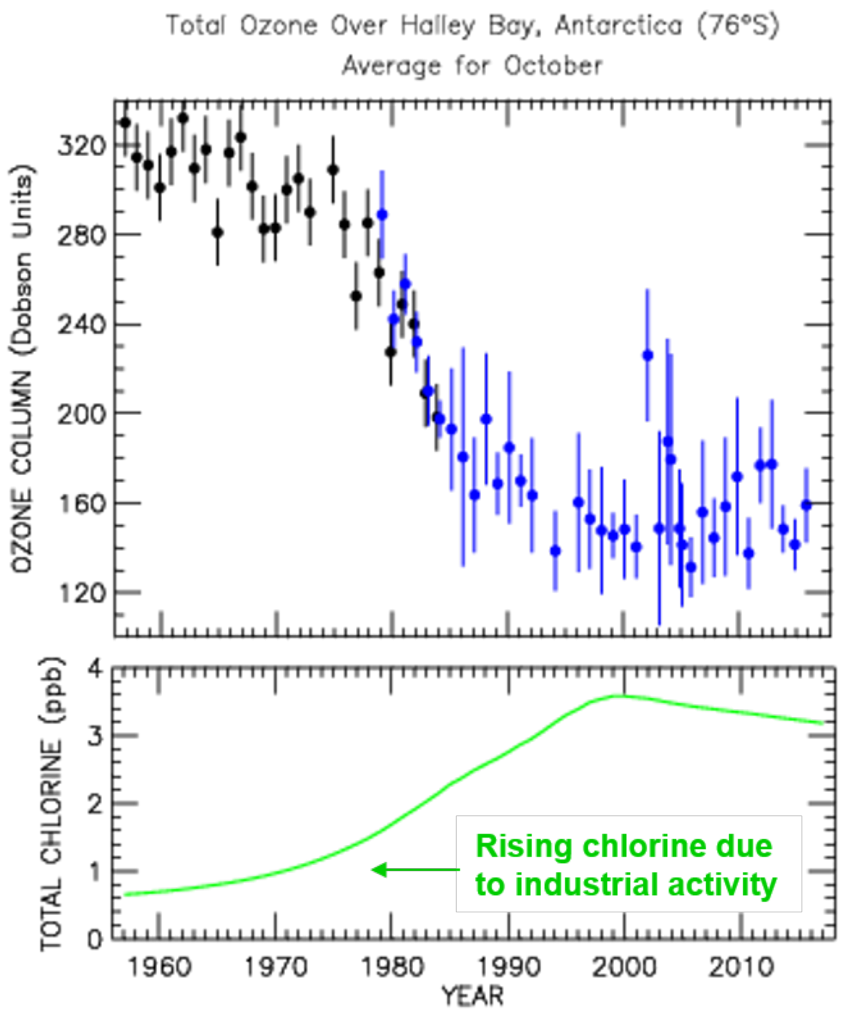


Figure Q15-1, 20 QAs about O_3

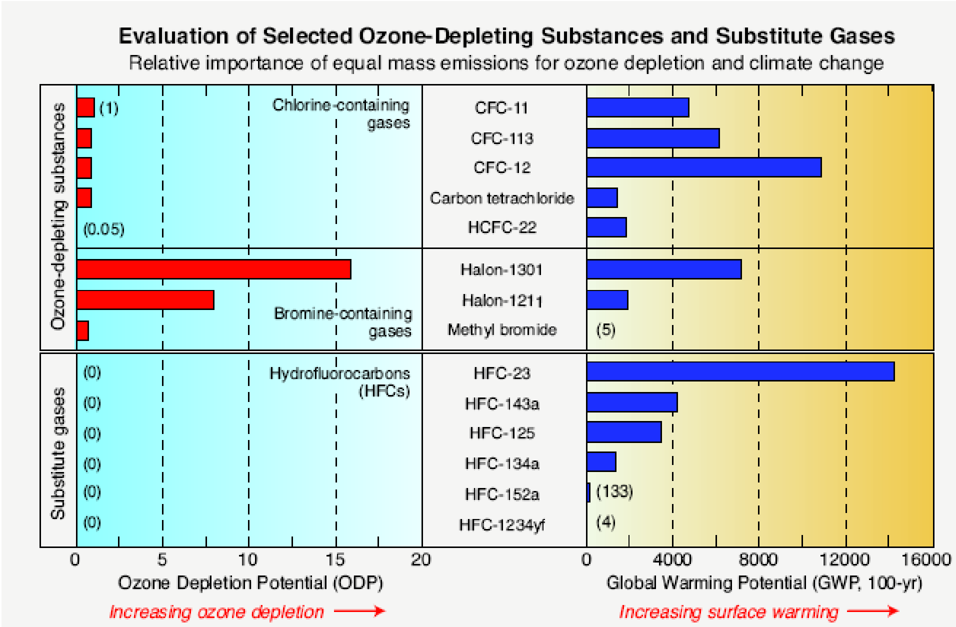
Montreal Protocol Has Banned Most Industrial Production of CFCs and Halons





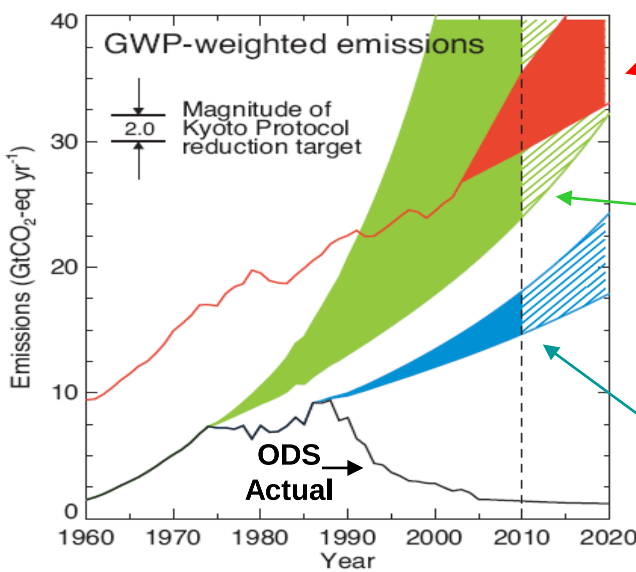
and the ozone layer is perhaps in *initial phase* of “recovery”

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)

Table 1.2 U.S. National Ambient Air Quality Standards

Pollutant	Standard (ppm)	Approximate Equivalent Concentration (μg/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
$PM_{2.5}$, 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)

Pollutant [links to historical tables of NAAQS reviews]		Primary/ Secondary	Averaging Time	Level	Form
Carbon Monoxide (CO)		primary	8 hours	9 ppm	Not to be exceeded more than once per year
			1 hour	35 ppm	
Lead (Pb)		primary and secondary	Rolling 3 month average	0.15 μg/m^3 [(1)]	Not to be exceeded
Nitrogen Dioxide (NO_2)		primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		primary and secondary	1 year	53 ppb [(2)]	Annual Mean
Ozone (O_3)		primary and secondary	8 hours	0.070 ppm [(3)]	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years
Particle Pollution (PM)	$PM_{2.5}$	primary	1 year	12.0 μg/m^3	annual mean, averaged over 3 years
		secondary	1 year	15.0 μg/m^3	annual mean, averaged over 3 years
		primary and secondary	24 hours	35 μg/m^3	98th percentile, averaged over 3 years
	PM_{10}	primary and secondary	24 hours	150 μg/m^3	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide (SO_2)		primary	1 hour	75 ppb [(4)]	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		secondary	3 hours	0.5 ppm	Not to be exceeded more than once per year

https://www.epa.gov/criteria-air-pollutants/naaqs-table as of 30 Jan 2017

Notes to table, prior page:

(1) In areas designated nonattainment for the Pb standards prior to the promulgation of the current (2008) standards, and for which implementation plans to attain or maintain the current (2008) standards have not been submitted and approved, the previous standards (1.5 µg/m3 as a calendar quarter average) also remain in effect.

(2) The level of the annual NO_2 standard is 0.053 ppm. It is shown here in terms of ppb for the purposes of clearer comparison to the 1-hour standard level.

(3) Final rule signed October 1, 2015, and effective December 28, 2015. The previous (2008) O_3 standards additionally remain in effect in some areas. Revocation of the previous (2008) O_3 standards and transitioning to the current (2015) standards will be addressed in the implementation rule for the current standards.

(4) The previous SO_2 standards (0.14 ppm 24-hour and 0.03 ppm annual) will additionally remain in effect in certain areas: (1) any area for which it is not yet 1 year since the effective date of designation under the current (2010) standards, and (2)any area for which an implementation plan providing for attainment of the current (2010) standard has not been submitted and approved and which is designated nonattainment under the previous SO_2 standards or is not meeting the requirements of a SIP call under the previous SO_2 standards (40 CFR 50.4(3)). A SIP call is an EPA action requiring a state to resubmit all or part of its State Implementation Plan to demonstrate attainment of the required NAAQS.

https://www.epa.gov/criteria-air-pollutants/naaqs-table as of 30 Jan 2017

Tropospheric Ozone Production

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

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

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

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

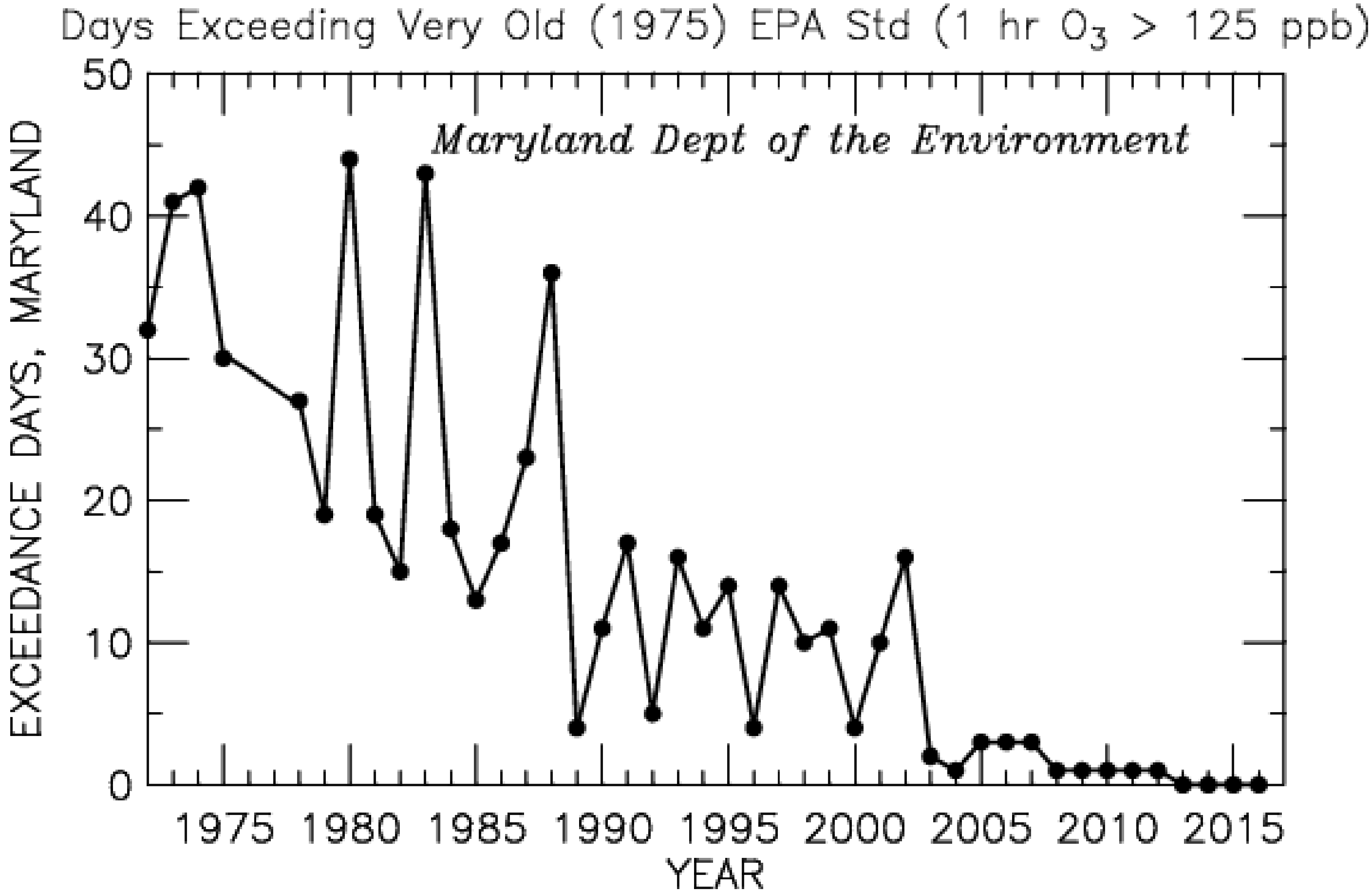
$$O + O_2 + M \rightarrow O_3 + M$$

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

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

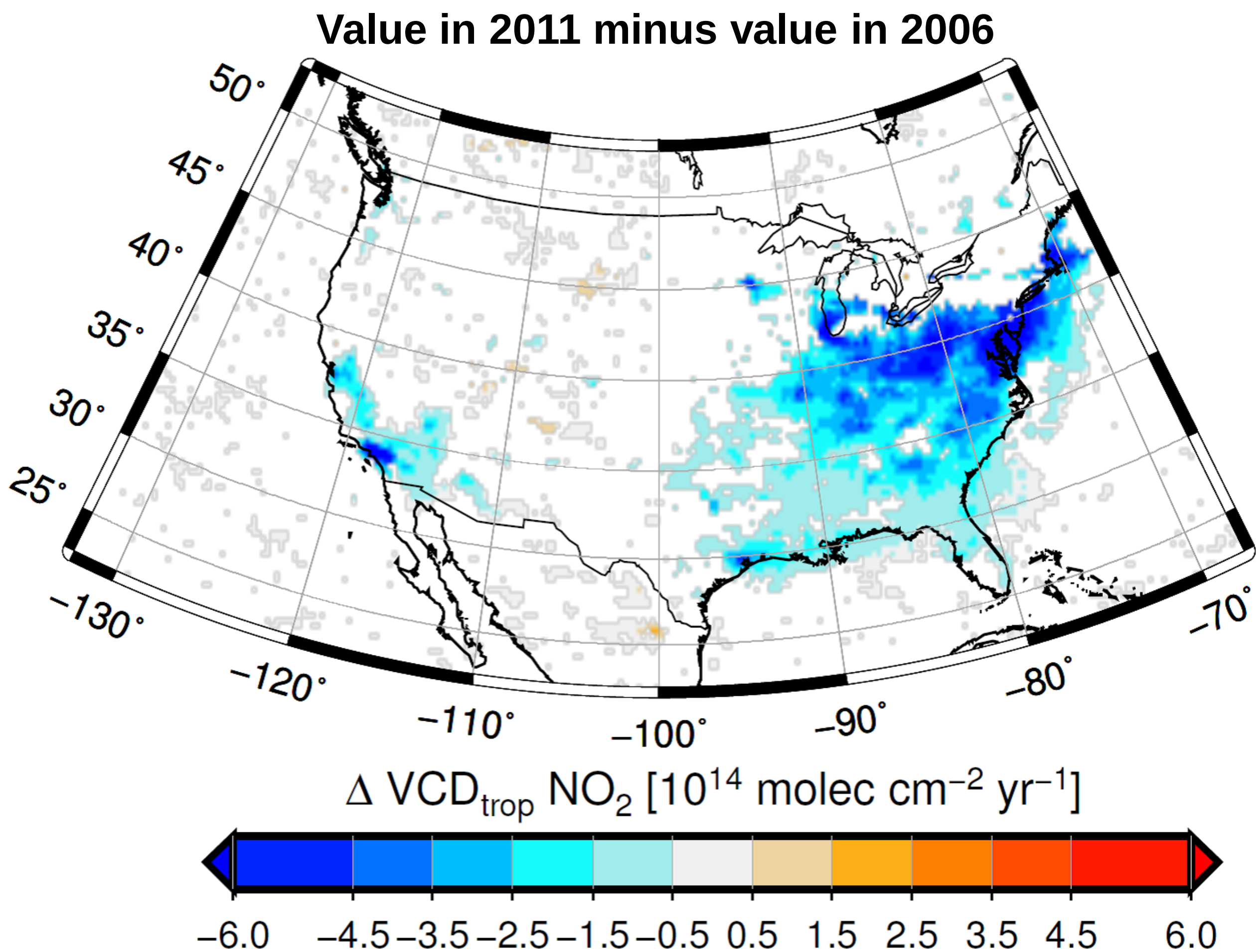
CO: Emitted by fossil fuel combustion & biomass burning

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



http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/SeasonalReports.aspx

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



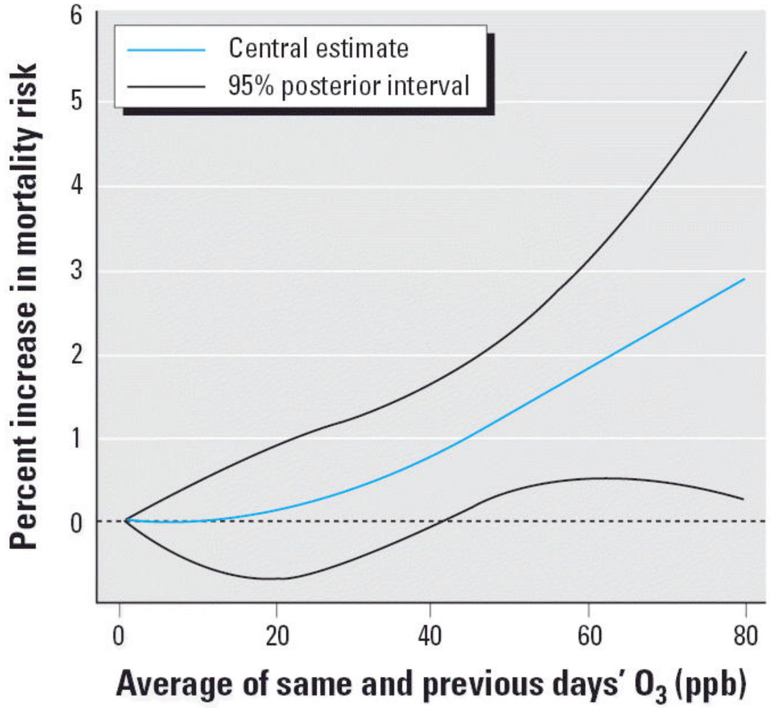
VCD_{trop} = Vertical Column Density in the Troposphere

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

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#	8 hr *	70 ppb

* 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 70 ppb

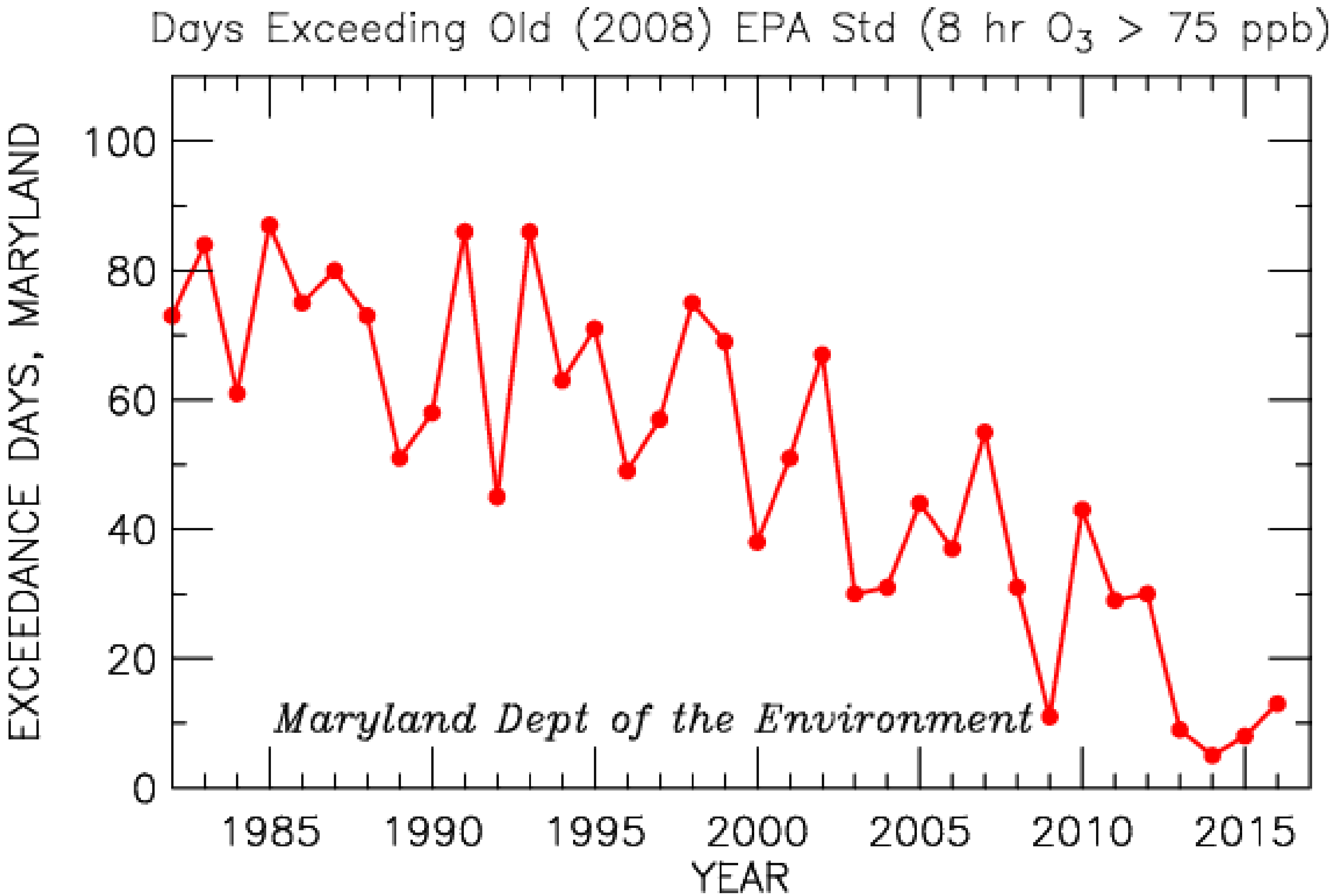


Increased risk of premature mortality for even low levels of surface O_3; further reductions will benefit public health

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

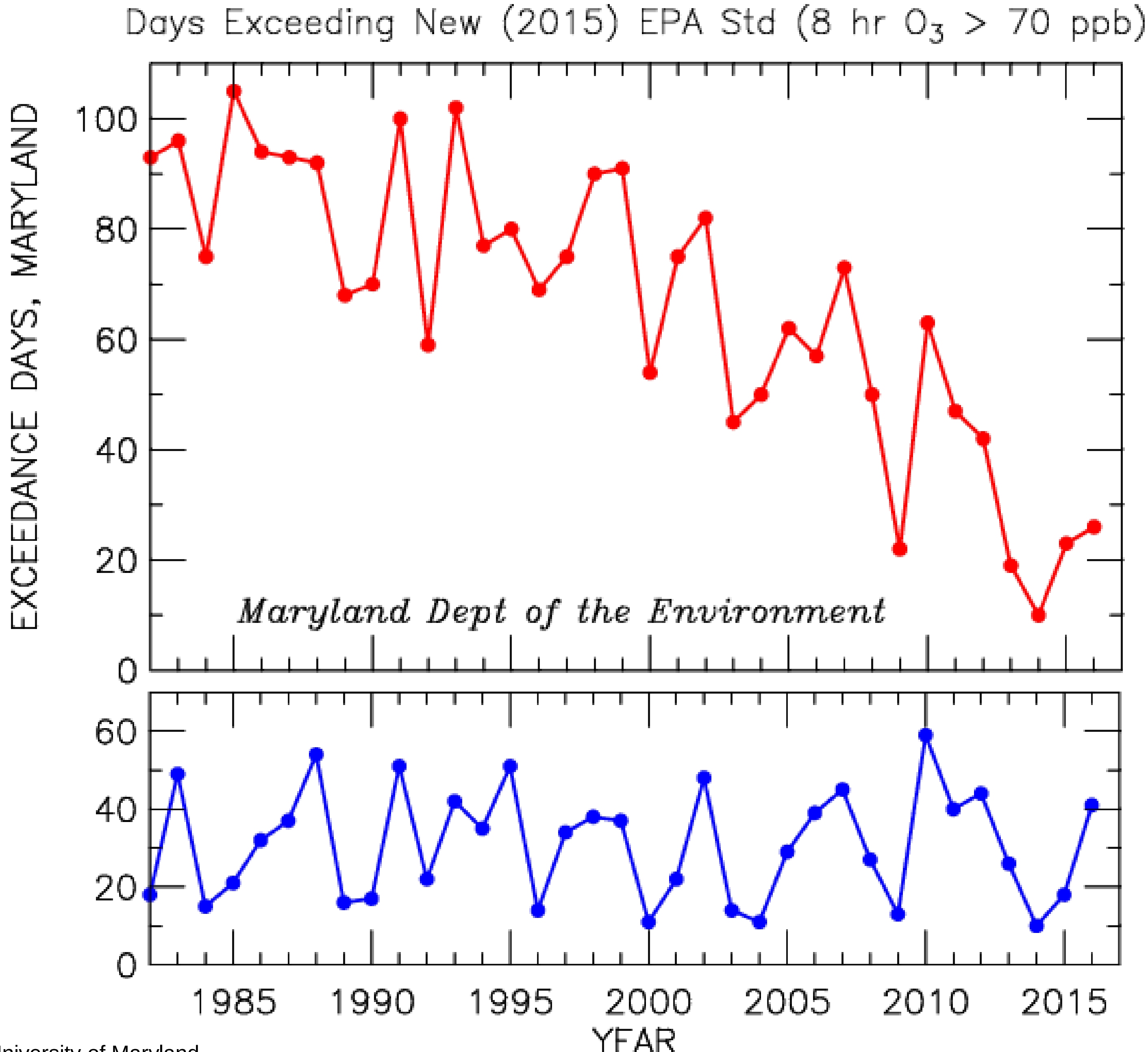
On October 1, 2015 the EPA lowered the NAAQS for ground-level ozone 70 ppb, based on extensive scientific evidence about the harmful effects of tropospheric ozone

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



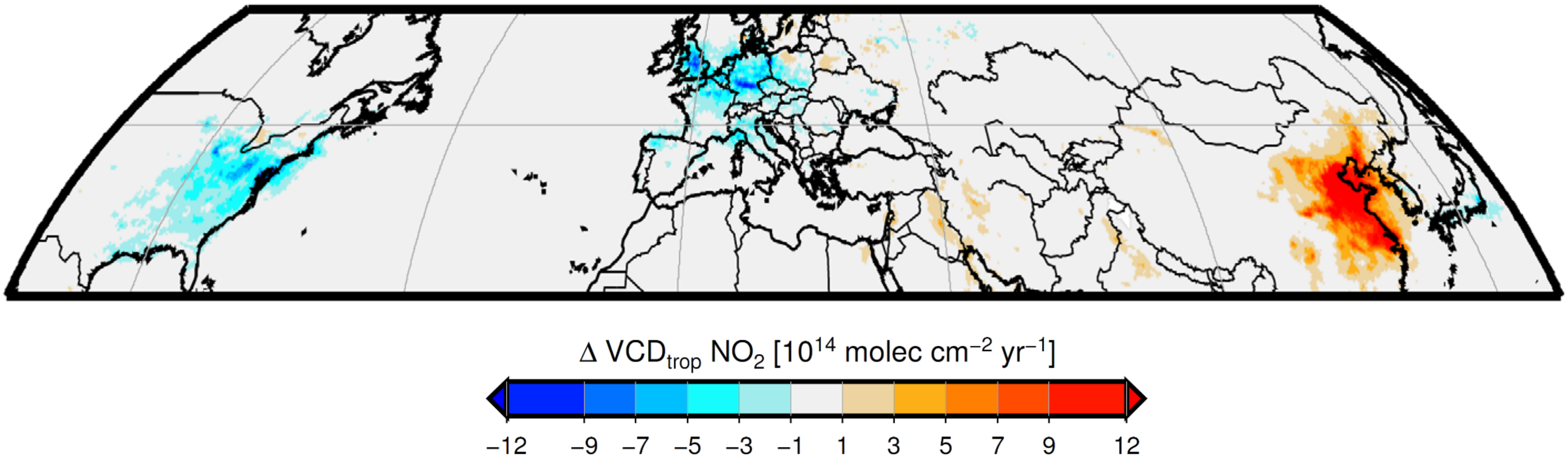
http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/SeasonalReports.aspx

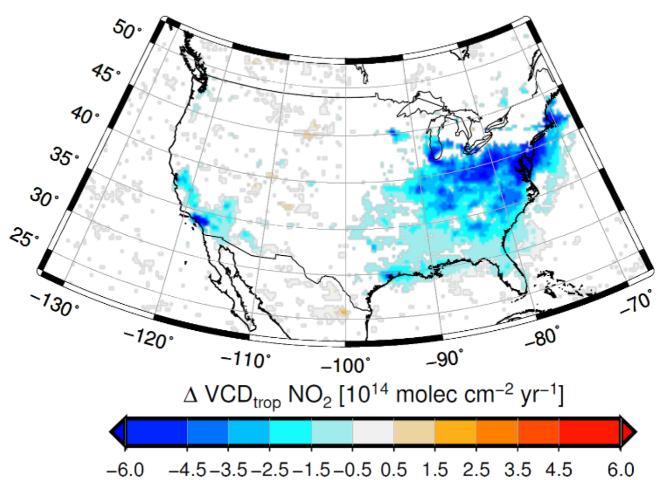
Significant Improvements in ***Local*** Air Quality since early 1980s



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

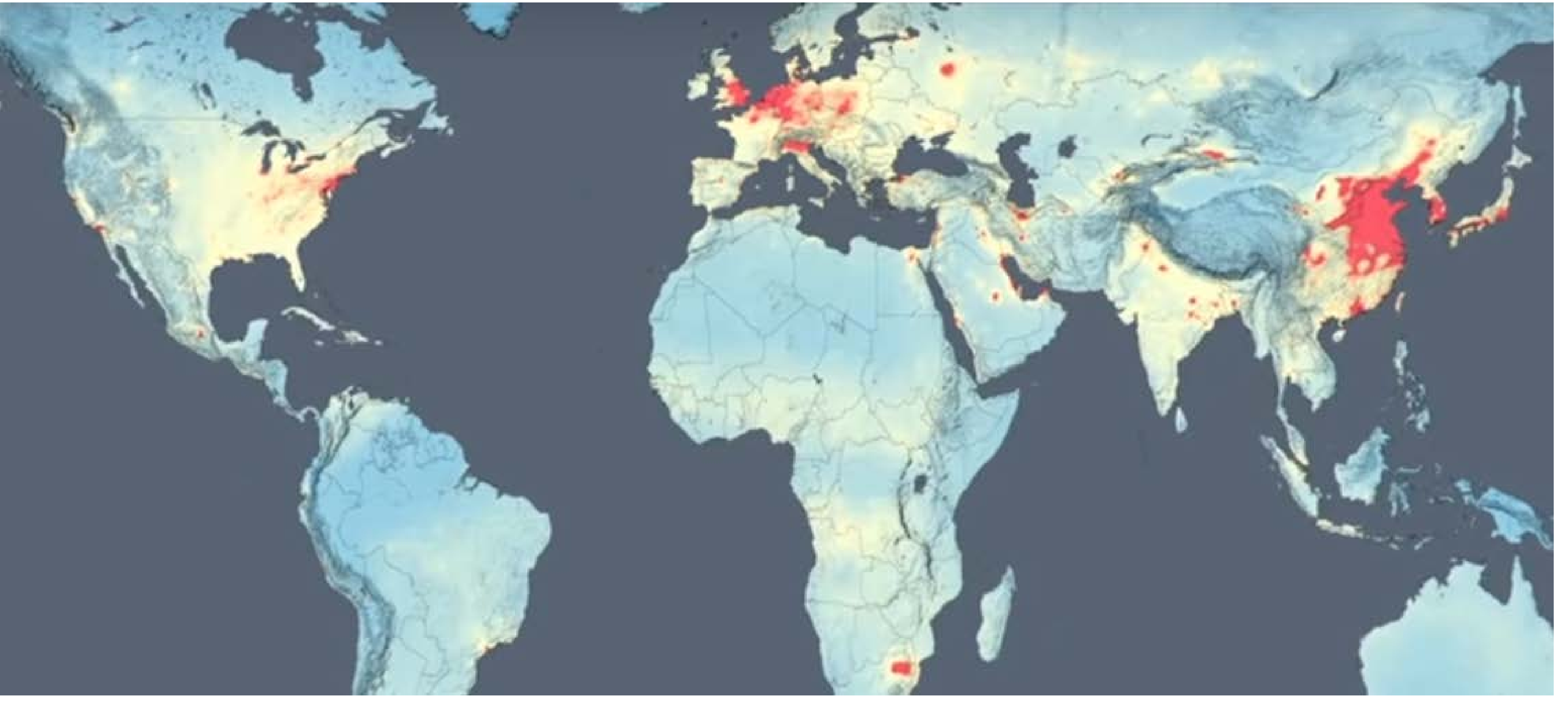
Value in 2011 minus value in 2006





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

Let's Go to Video



NO_2 column measurements: hot colors correspond to high values

https://www.youtube.com/watch?v=LKe5FdKInJs

Next Lecture: Fundamentals of Earth's Atmosphere

Please complete Learning Outcome Quizes following lecture to review salient "take away" messages

Next 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)
Copies available for those who do not yet have text

as well as 7 pages from *Atmospheric Environment* by McElroy

Also, you are responsible for reading all of Chapter 1, *Paris Beacon of Hope* (minus Methods) prior to the first exam, which is penciled in for 28 Feb

Admission Ticket for Lecture 3 is posted on ELMS

Please bring a calculator to class on Thursday