Overview of Global Warming, Ozone Depletion, and Air Quality

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/fall2020
https://myelms.umd.edu/courses/1291919

https://www.videoblocks.com/video/earth-sunset-spacewalk-view-from-space-station-r7dydlcsgjd23vml0

Lecture 2

8 September 2020

Announcements

1) AOSC Weekly Seminar Sept 3: 3:30 pm (Thursday)

10

SEPTEMBER

https://aosc.umd.edu/seminars/department-seminar

AOSC Seminar by Dr. Bob Brammer, 09/10/2020

2020-09-10

3:30 p.m.

Zoom

AOSC Seminar

Dr. Bob Brammer

Brammer Technology, LLC

Title: An Introductory Survey of Corporate and Investment Climat

Finance and Implications for Atmospheric and Oceanic Science

Professionals and Students

Contact: Tim Canty

2) I have to sign off at 3:14 pm today due to UMD Senate meeting

3) However, Laura McBride will remain on the Zoom call and do her best to answer any questions. If you have further questions on today's material, please send me an email (with appropriate subject) and I will either try to answer via email or a personal Zoom meeting between now and Thursday

Overview of Global Warming, Ozone Depletion, and Air Quality

Course theme: effect of human activity on:

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

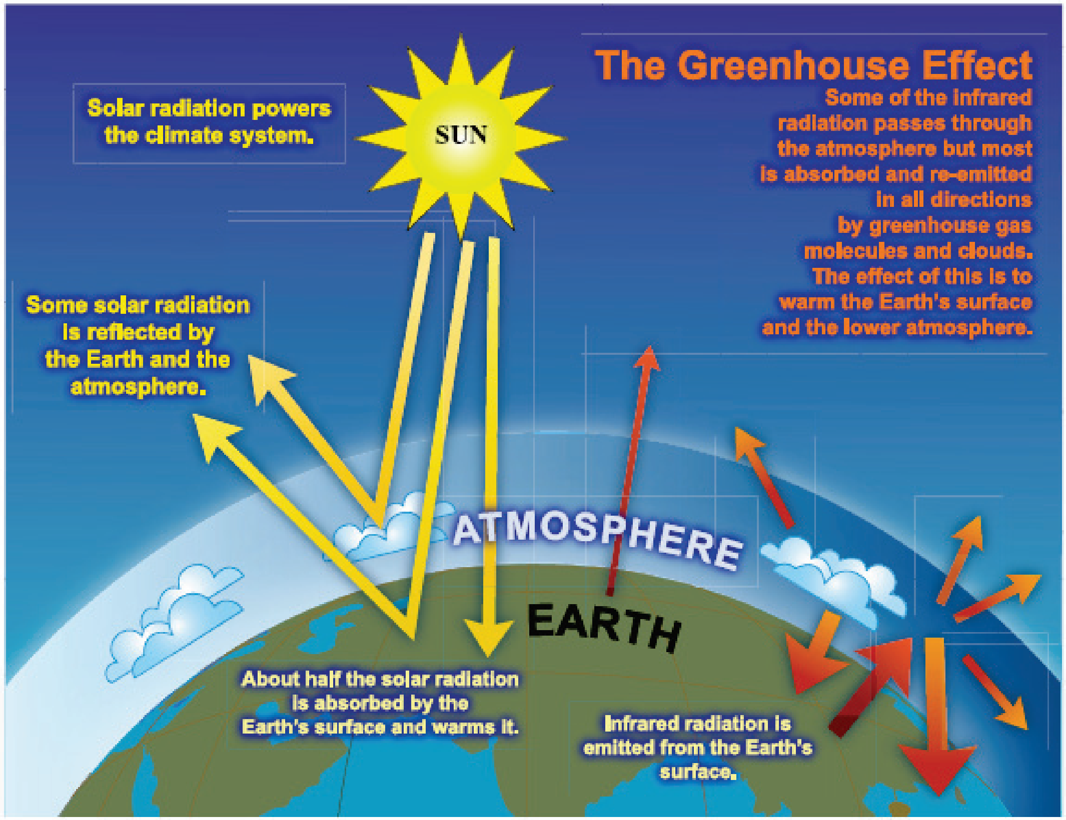
Today's goals:

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"**. Expect that when you review this lecture for the first and second exam, details will be understandable

3) Current events & linkages between topics, often thought of as "disparate" but connected in **profoundly important manners**

Greenhouse Effect

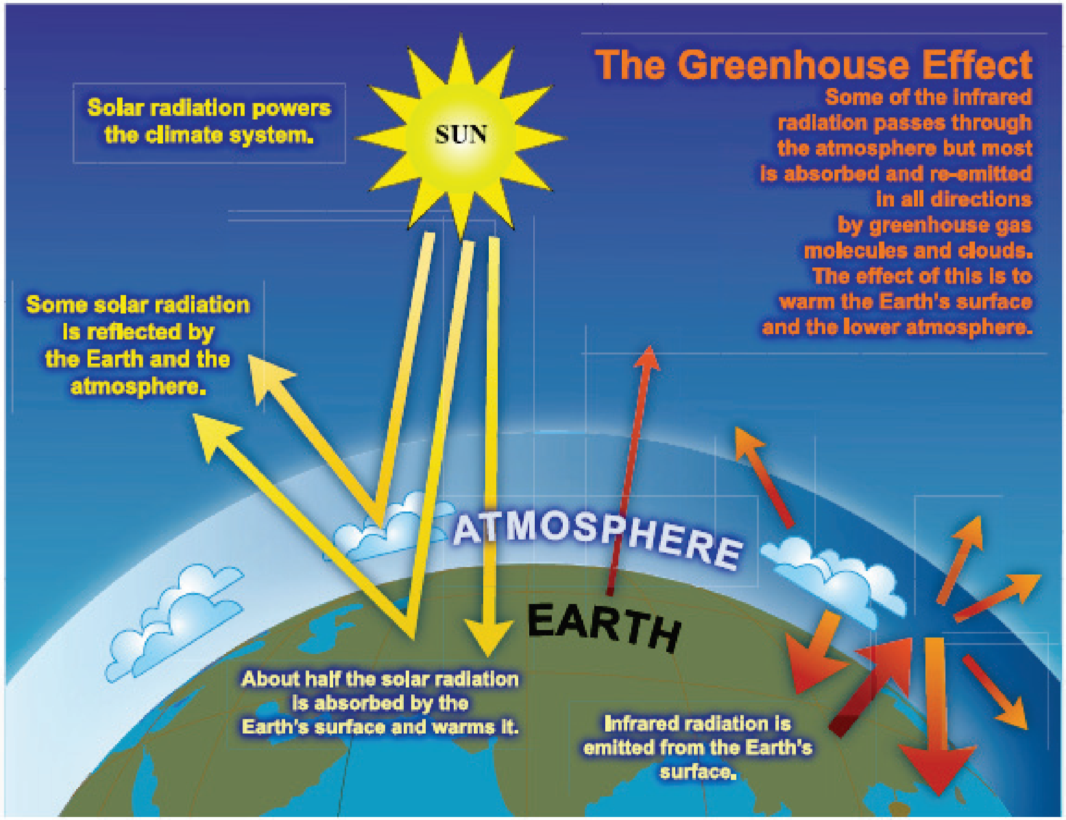


FAQ 1.3, Figure 1. *An idealised model of the natural greenhouse effect. See text for explanation.*

What is the most important greenhouse gas (GHG) ?

Question 1.3, IPCC, 2007

Greenhouse Effect

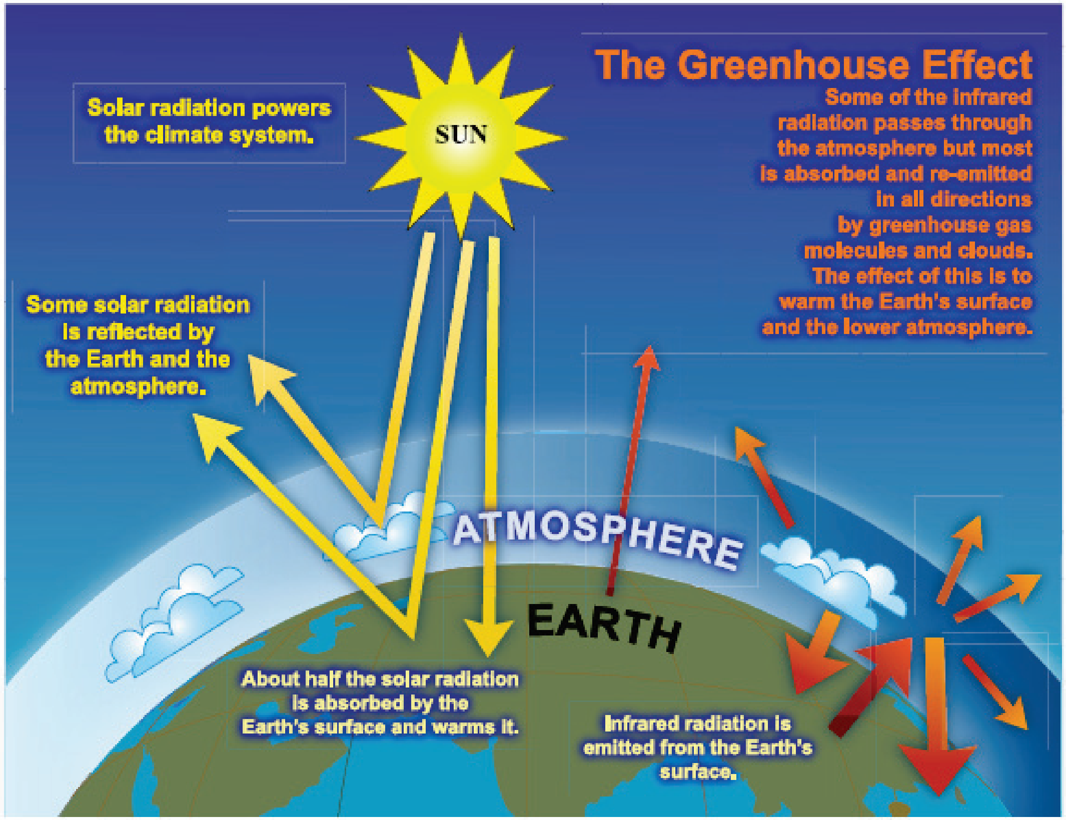


FAQ 1.3, Figure 1. *An idealised model of the natural greenhouse effect. See text for explanation.*

What is the most important *<u>anthropogenic</u>* greenhouse gas (GHG) ?

Question 1.3, IPCC, 2007

Greenhouse Effect



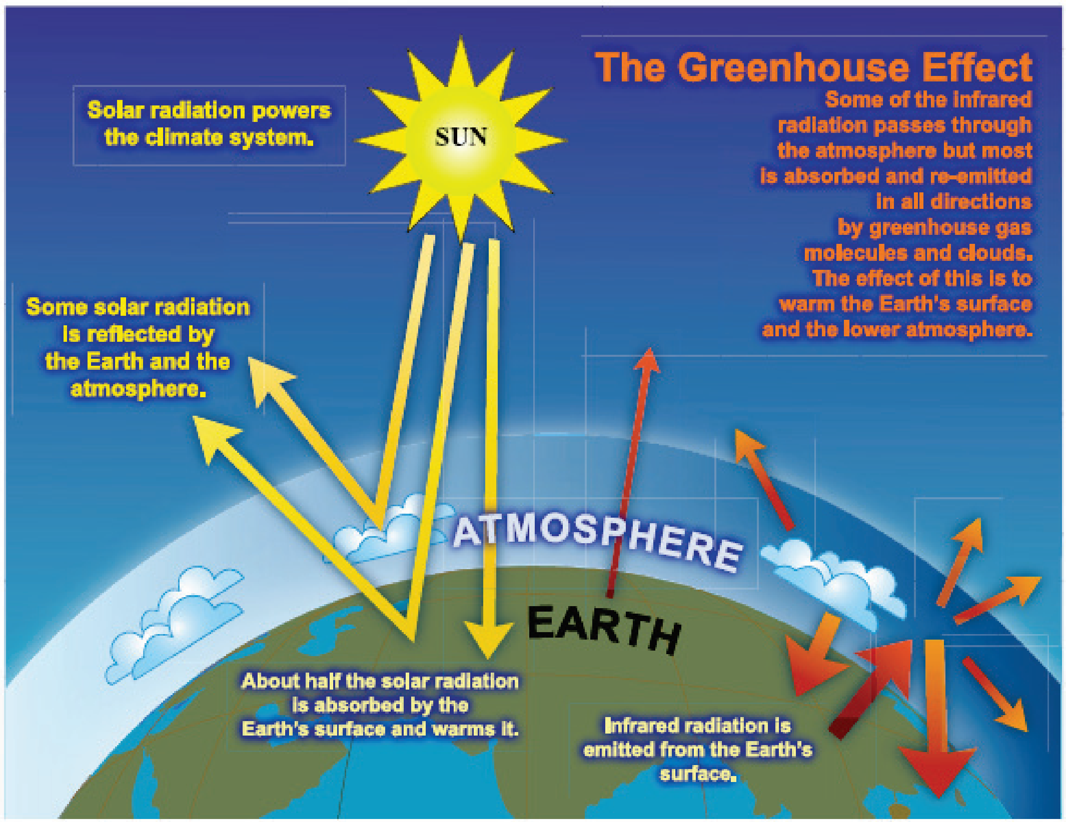
FAQ 1.3, Figure 1. *An idealised model of the natural greenhouse effect. See text for explanation.*

Question 1.3, IPCC, 2007

What is the most important *__anthropogenic__* greenhouse gas (GHG) ?

Second most important ?

Greenhouse Effect



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

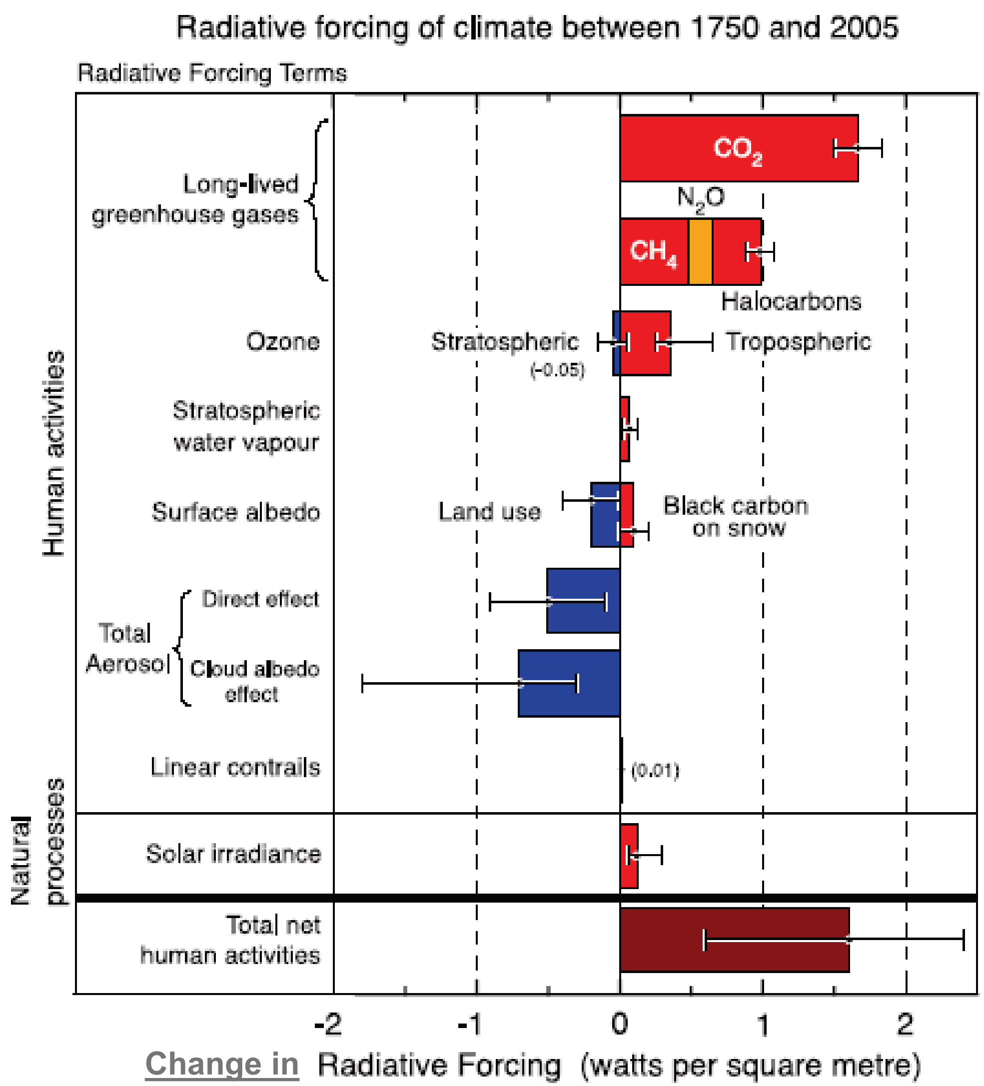
What is the most important *__anthropogenic__* greenhouse gas (GHG) ?

Second most important ?

Third ?

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

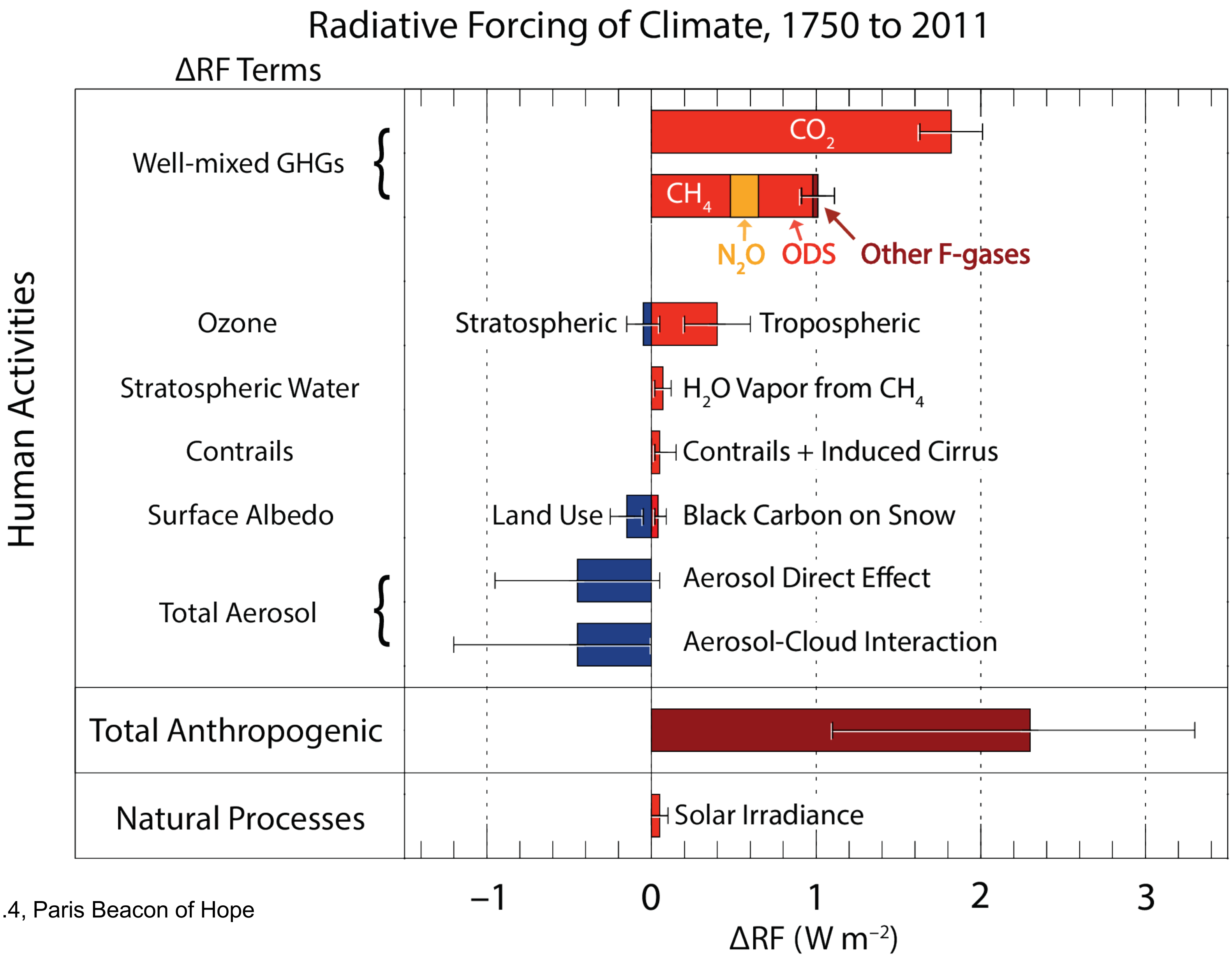
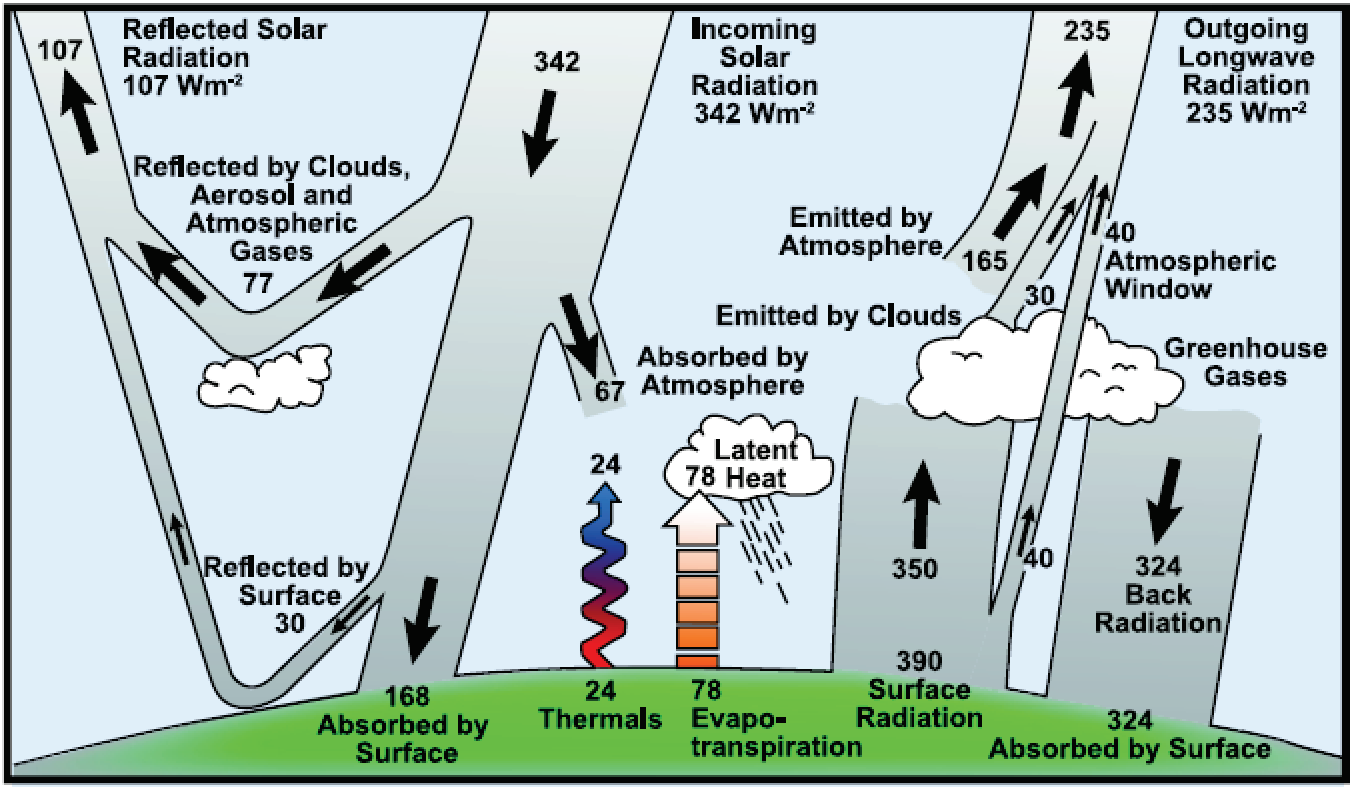


Figure 1.4, Paris Beacon of Hope

Radiative Forcing

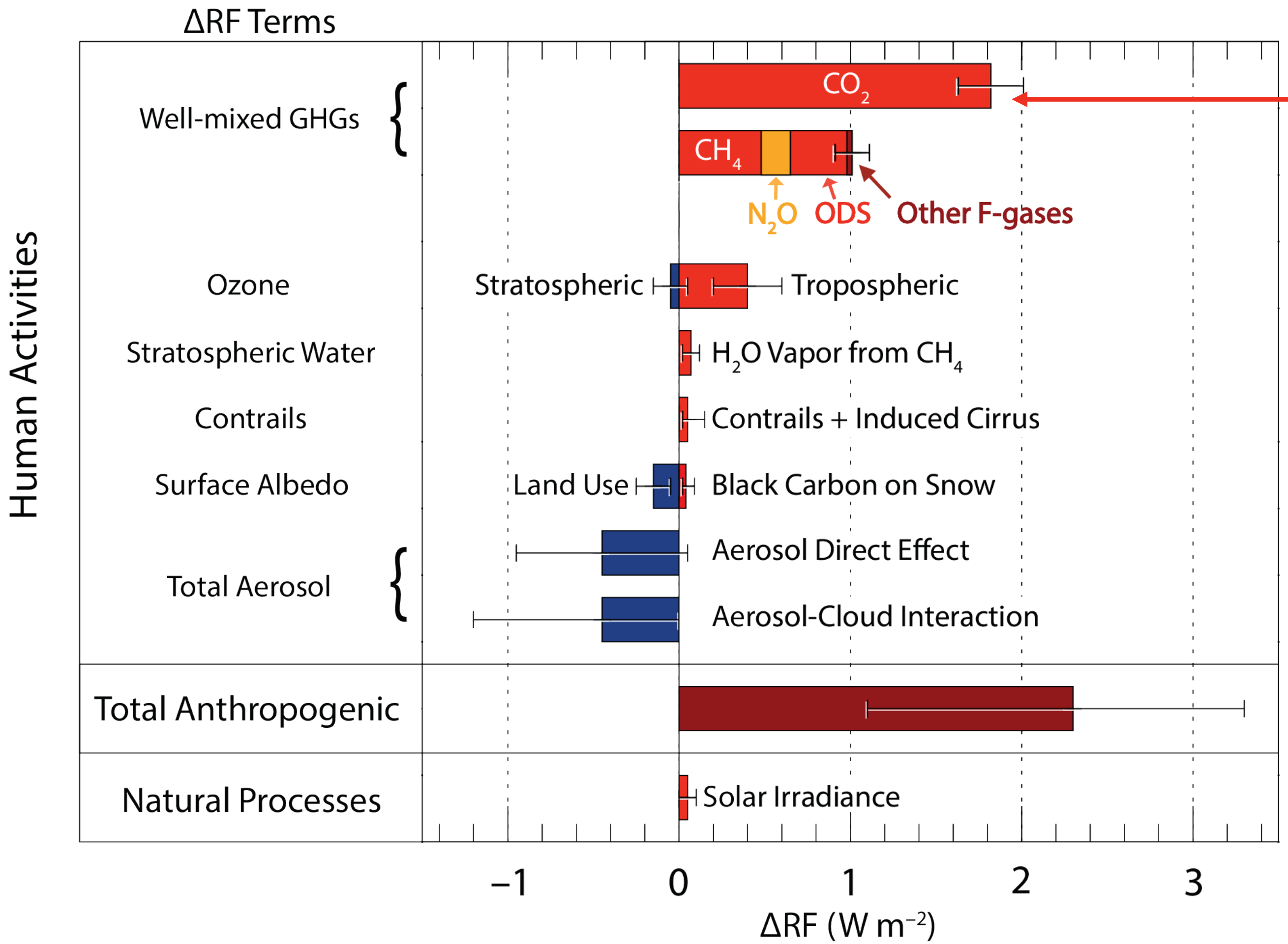


FAQ 1.1, Figure 1. *Estimate of the Earth's annual and global mean energy balance. Over the long term, the amount of incoming solar radiation absorbed by the Earth and atmosphere is balanced by the Earth and atmosphere releasing the same amount of outgoing longwave radiation. About half of the incoming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

Radiative Forcing of Climate, 1750 to 2011

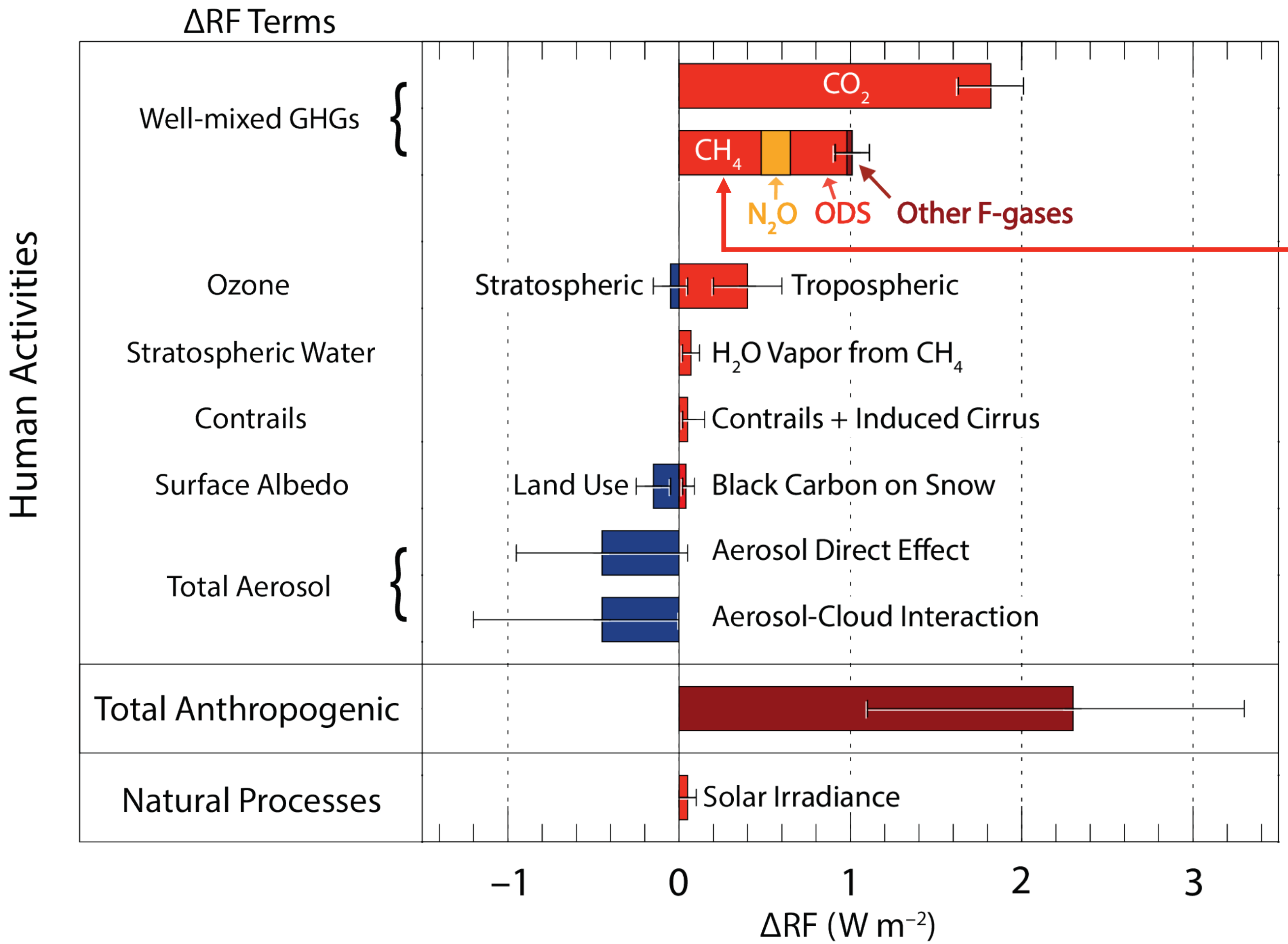


CO_2 is dominant anthropogenic (human) greenhouse gas (GHG). Once released, CO_2 persists in the atmosphere for hundreds of years.

Between 1750 and 2011, the rise in atmospheric CO_2 caused RF of climate to rise by 1.8 W m^{-2}

Figure 1.4, Paris Beacon of Hope

Radiative Forcing of Climate, 1750 to 2011



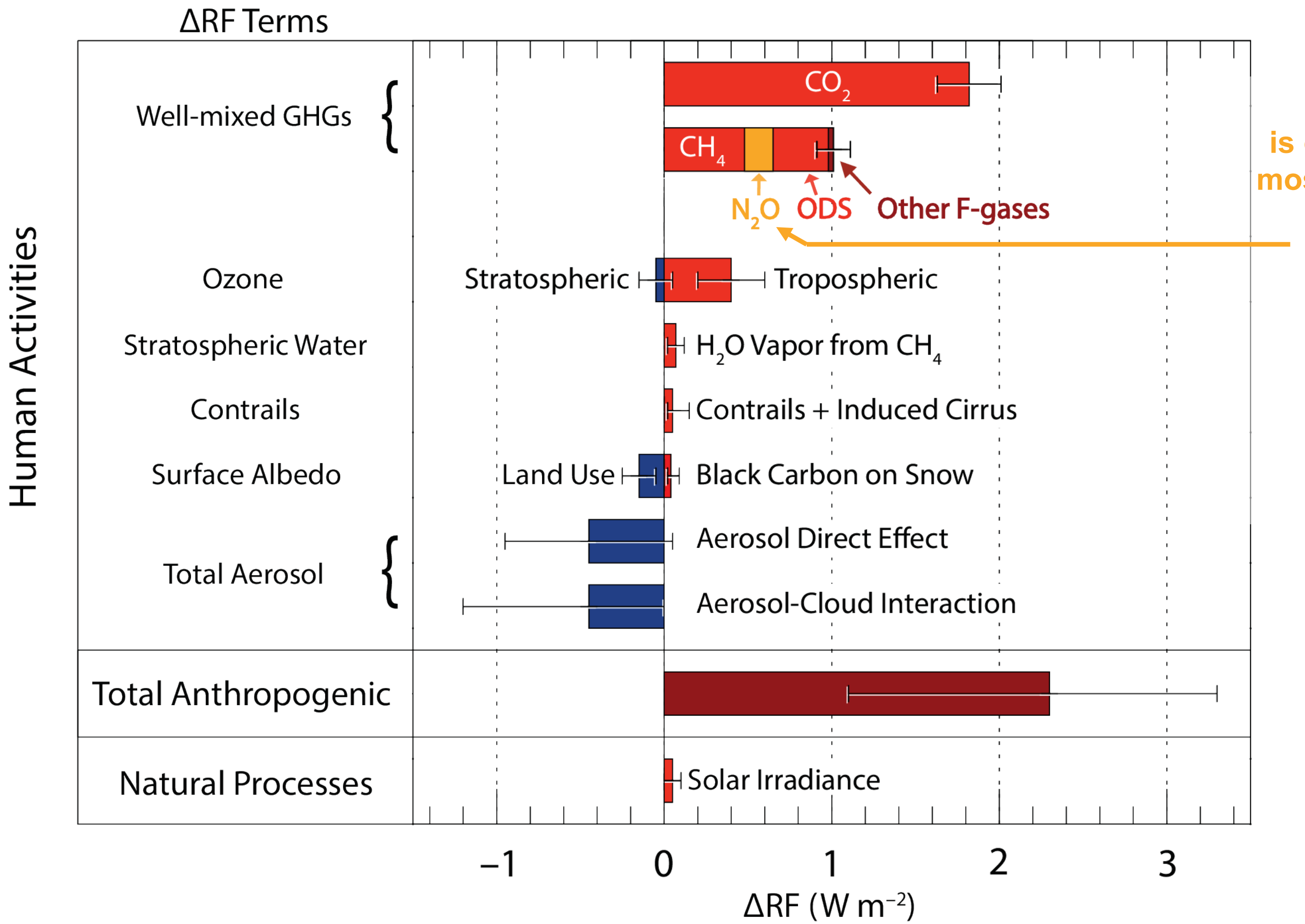
Methane (CH_4) is the 2nd most important human GHG. Once released, CH_4 persists in the atmosphere for about decade.

On a per molecule basis, CH_4 causes 30 times more warming than CO_2 over a 20-yr time horizon.

Between 1750 and 2011, the rise in atmospheric CH_4 caused RF of climate to rise by 0.48 W m^{-2}

Figure 1.4, Paris Beacon of Hope

Radiative Forcing of Climate, 1750 to 2011

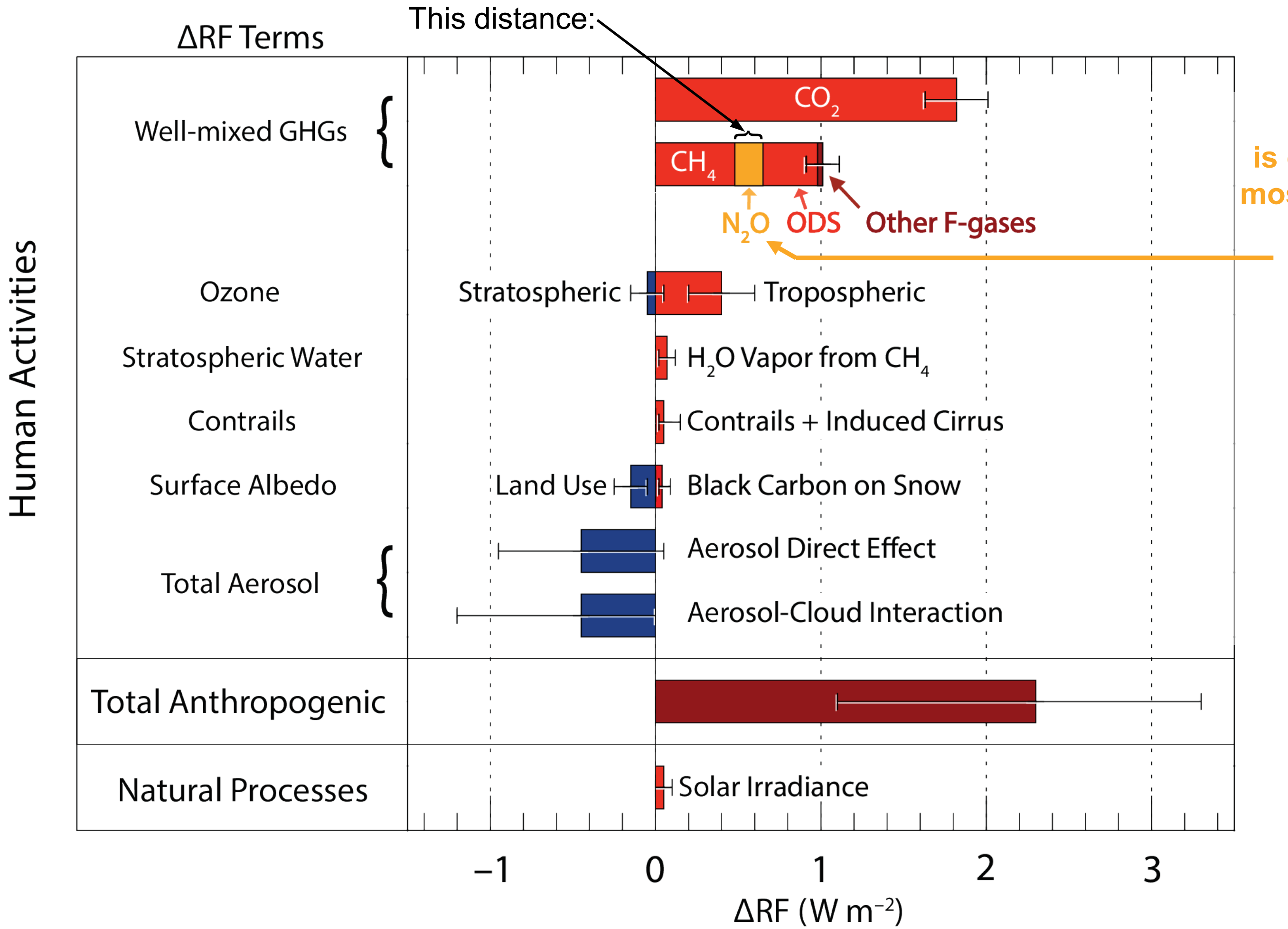


Nitrous oxide (N_2O) is commonly identified as the third most important anthropogenic GHG.

On either a per molecule or a per mass basis, N_2O causes 264 times more warming than CO_2 over a 20-yr time horizon.

Figure 1-4, Paris Beacon of Hope

Radiative Forcing of Climate, 1750 to 2011



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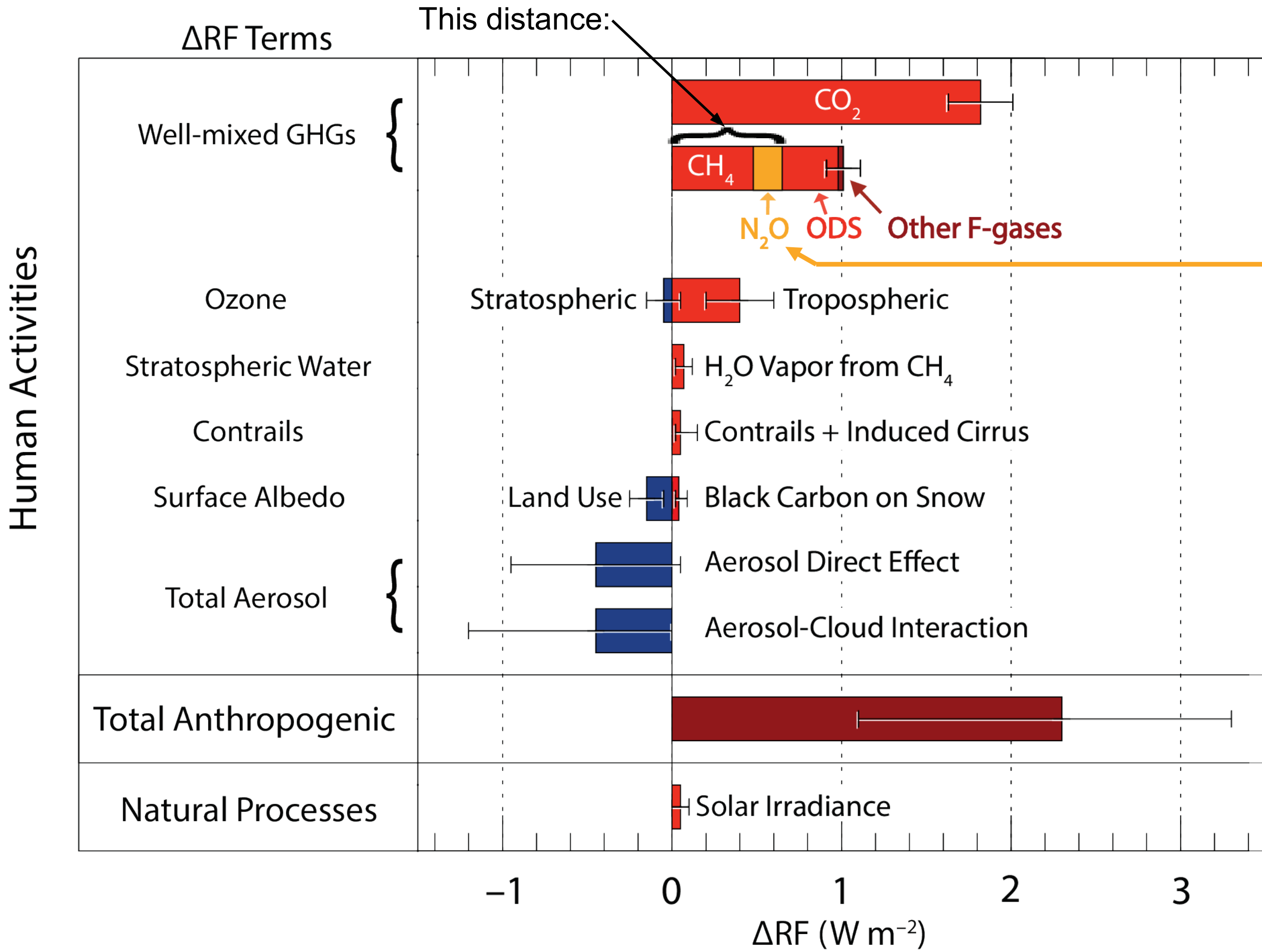
Between 1750 and 2011, the rise in atmospheric N_2O caused RF of climate to rise by 0.17 W m^{-2}

Figure 1-4, Paris Beacon of Hope

Radiative Forcing of Climate, 1750 to 2011



Nitrous oxide (N_2O) is commonly identified as the third most important anthropogenic GHG.

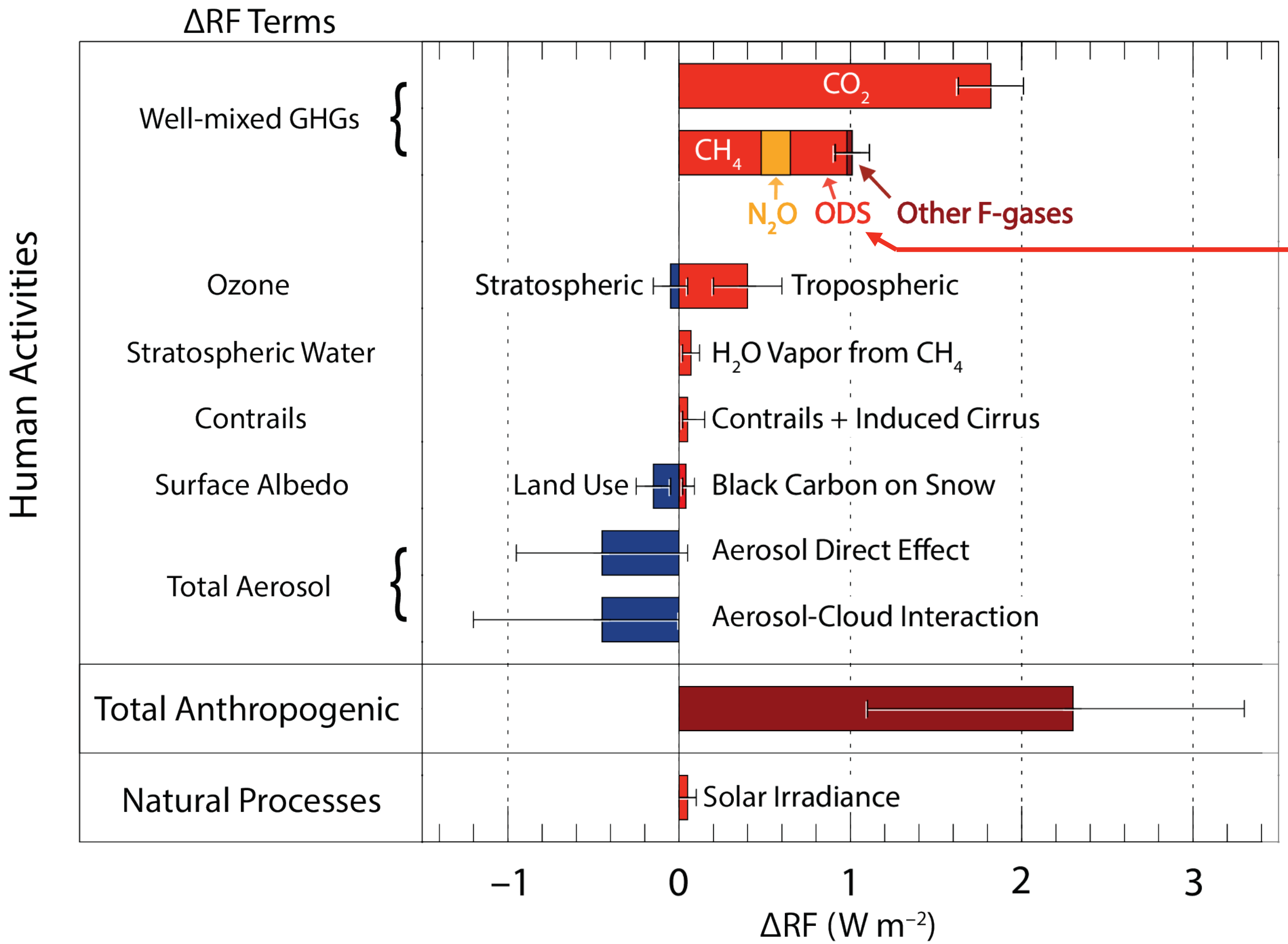
On either a per molecule or a per mass basis, N_2O causes 264 times more warming than CO_2 over a 20-yr time horizon.

Between 1750 and 2011, the rise in atmospheric N_2O caused RF of climate to rise by 0.17 W m^{-2}

The rise in RF of climate due to both CH_4 and N_2O was about 35% of the the rise in RF of climate due to CO_2

Figure 1-4, Paris Beacon of Hope

Radiative Forcing of Climate, 1750 to 2011



CFCs and other ozone depleting substances (ODS) also act as GHGs.

Between 1750 and 2011, the rise in ODS caused RF of climate to rise by 0.33 W m^{-2}

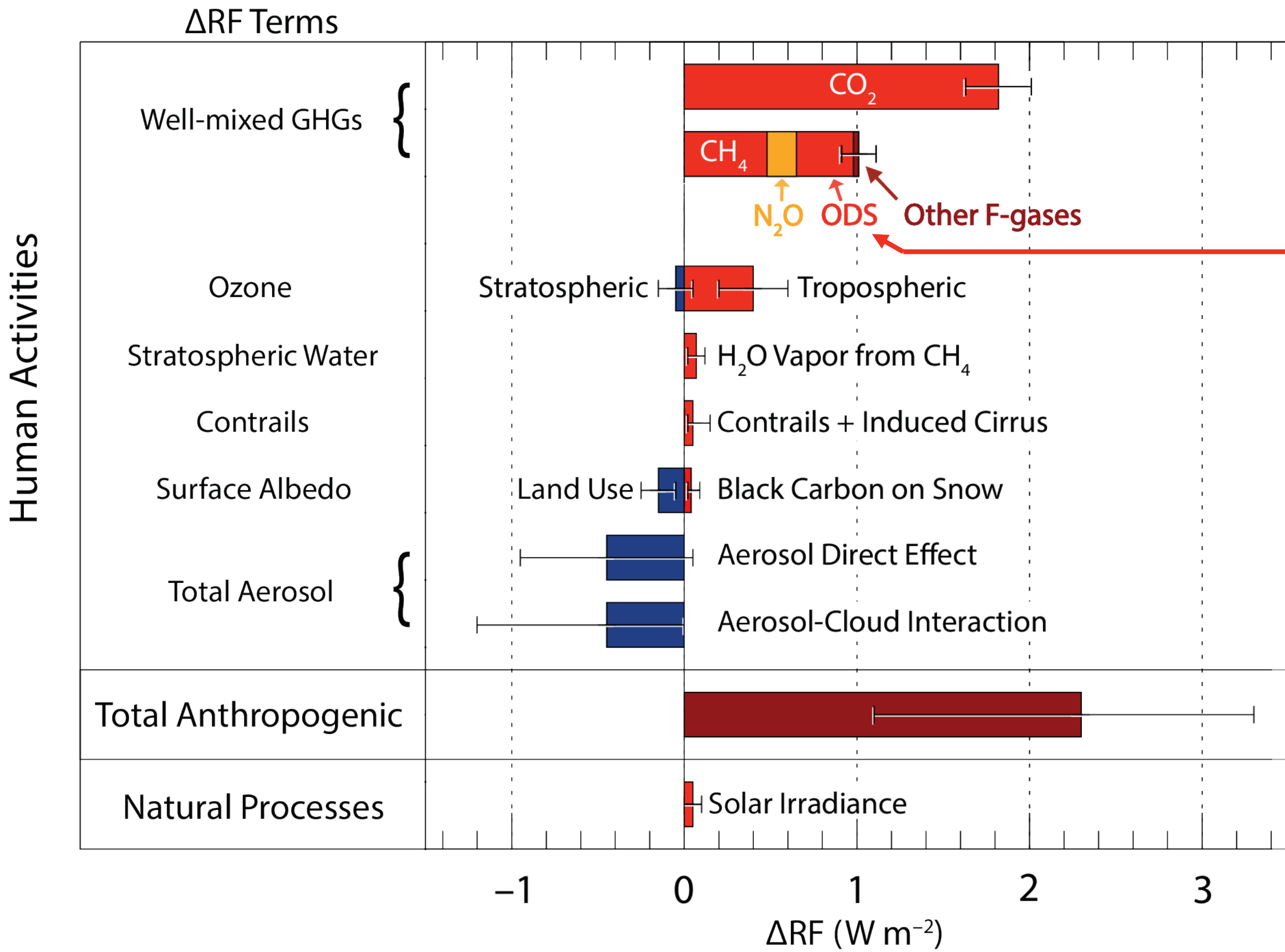
The rise in RF of climate due to CH_4, N_2O, and ODS was ***about half*** of the the rise in RF of climate due to CO_2

Industrial production of CFCs and other ODS was banned by the _______ _______

Atmospheric levels of CFCs have declined, although not quite as fast as had been expected.

Figure 1-4, Paris Beacon of Hope

Radiative Forcing of Climate, 1750 to 2011



CFCs and other ozone depleting substances (ODS) also act as GHGs.

Between 1750 and 2011, the rise in ODS caused RF of climate to rise by 0.33 W m^{-2}

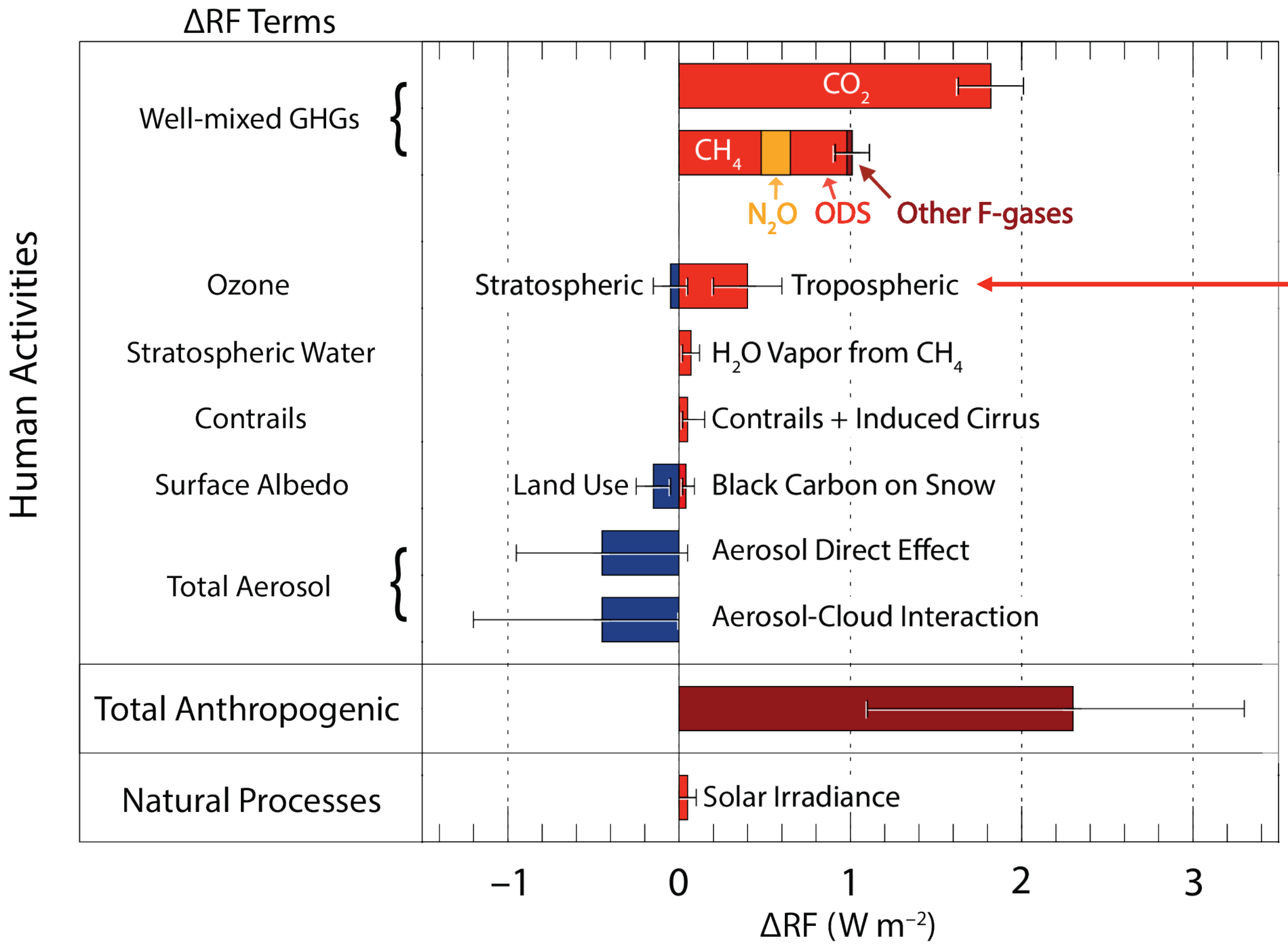
The rise in RF of climate due to CH_4, N_2O, and ODS was *about half* of the the rise in RF of climate due to CO_2

Industrial production of CFCs and other ODS was banned by the Montreal Protocol.

Atmospheric levels of CFCs have declined, although not quite as fast as had been expected.

Figure 1-4, Paris Beacon of Hope

Radiative Forcing of Climate, 1750 to 2011



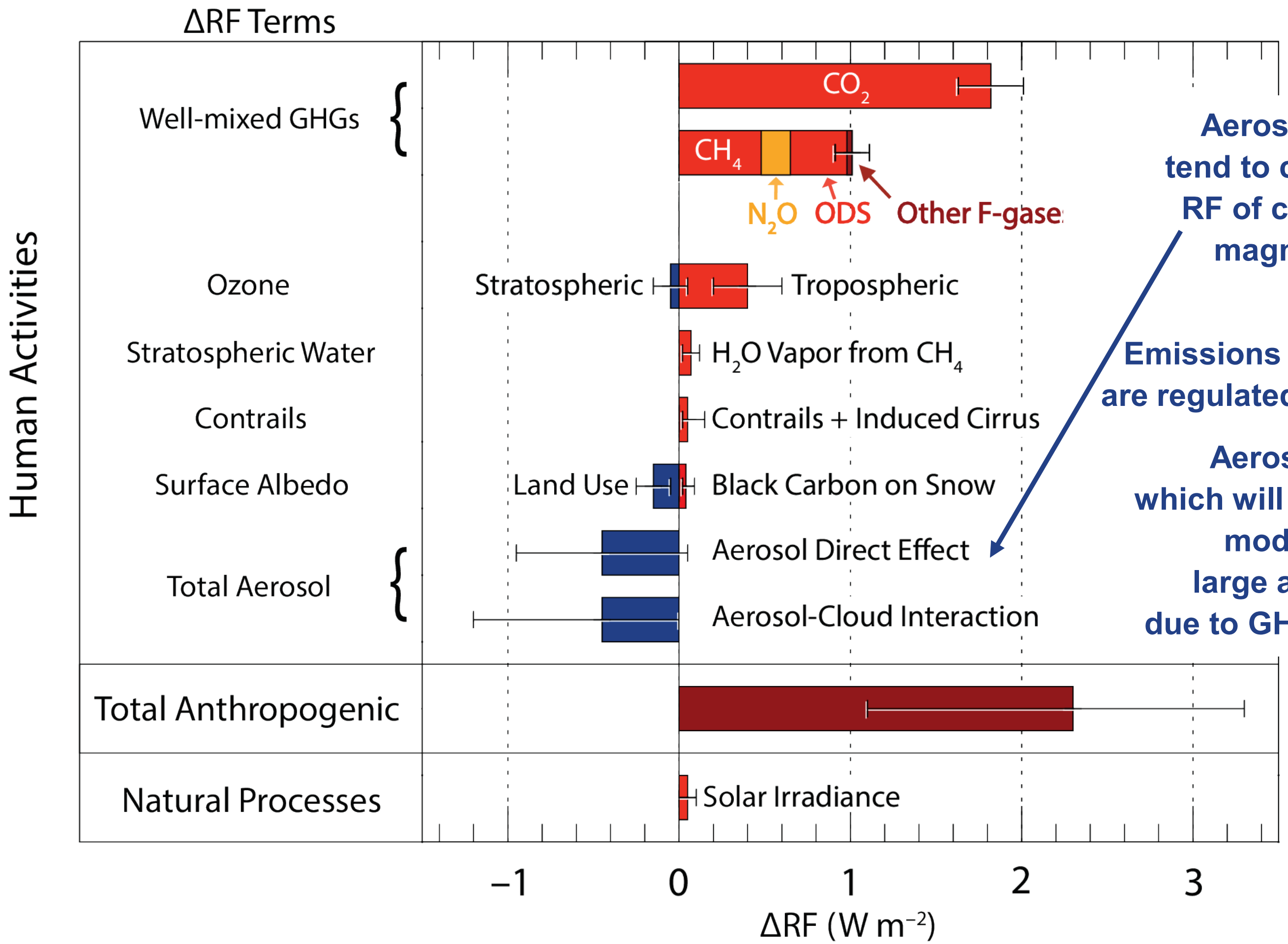
Ozone (O_3) acts as a GHG.

Between 1750 and 2011, the rise in tropospheric O_3 caused RF of climate to rise by 0.40 W m^{-2}

This rise is due to increasing levels of O_3 in Earth's troposphere, leading to poor public health. Efforts to combat the rise in tropospheric O_3 are led by air quality agencies.

Figure 1-4, Paris Beacon of Hope

Radiative Forcing of Climate, 1750 to 2011



Aerosols (small particulate matter) tend to cool climate, counter-acting the RF of climate due to GHGs. However, magnitude of this counter-action is not well known.

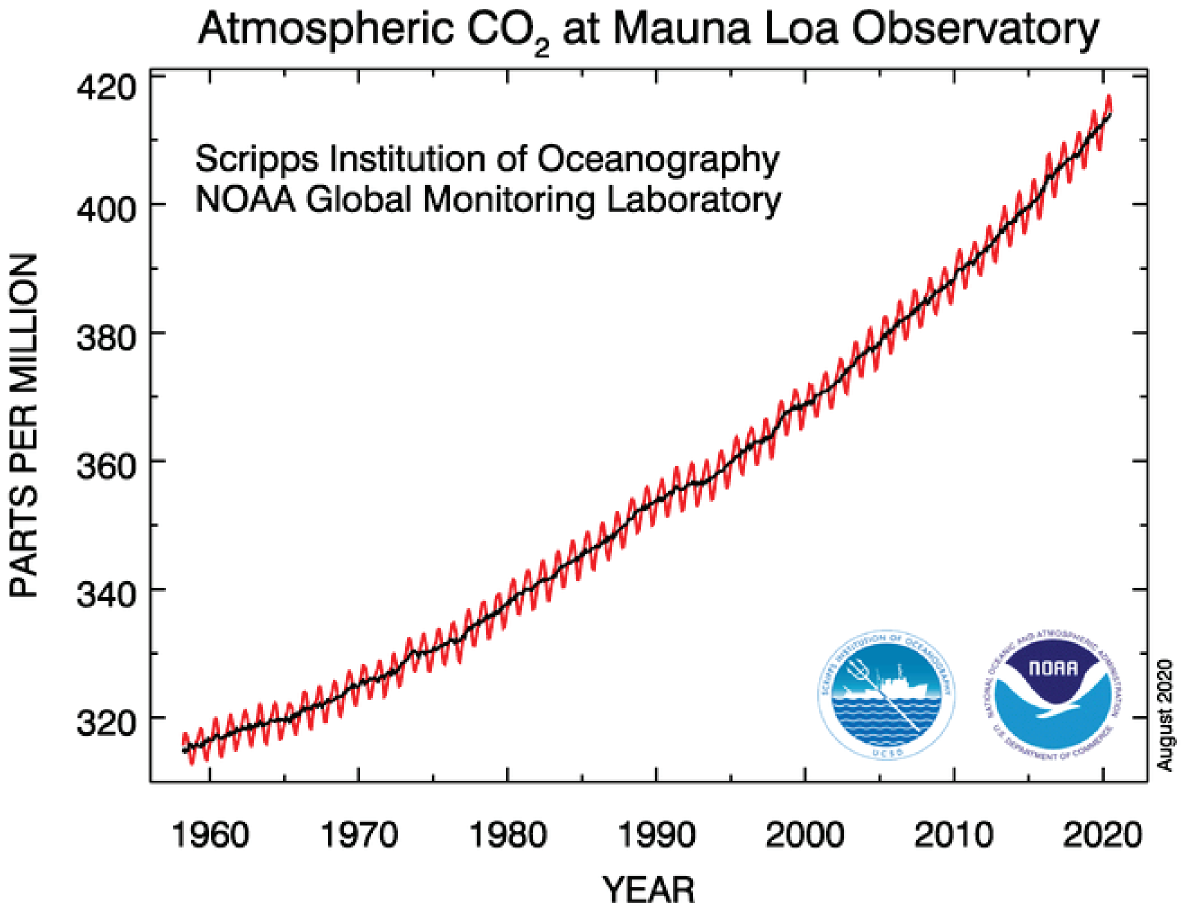
Emissions of pollutants that lead to aerosols are regulated worldwide by air quality agencies.

Aerosol levels are on the decline, which will either "unleash" a small amount, moderate amount, or perhaps a large amount of additional warming due to GHGs that are presently "masked".

Figure 1-4, Paris Beacon of Hope

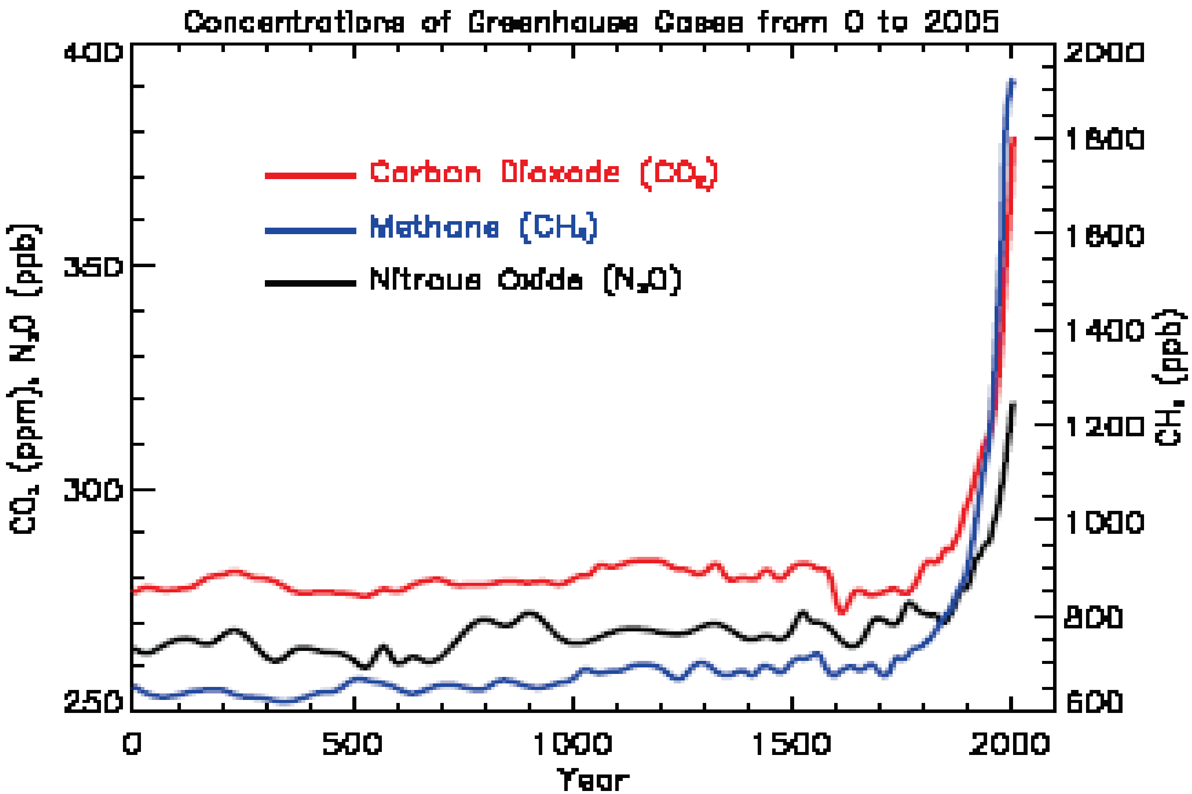
Modern CO_2 Record

CO_2 at MLO (Mauna Loa Observatory) on 6 Sept 2020: 411.9 parts per million (ppm)
6 Sept 2019: 408.5 parts per million (ppm)



Legacy of Charles Keeling, Scripps Institution of Oceanography, La Jolla, CA
https://www.esrl.noaa.gov/gmd/webdata/ccgg/trends/co2_data_mlo.png
See also https://www.co2.earth/daily-co2

GHG Record Over Last Several Millennia

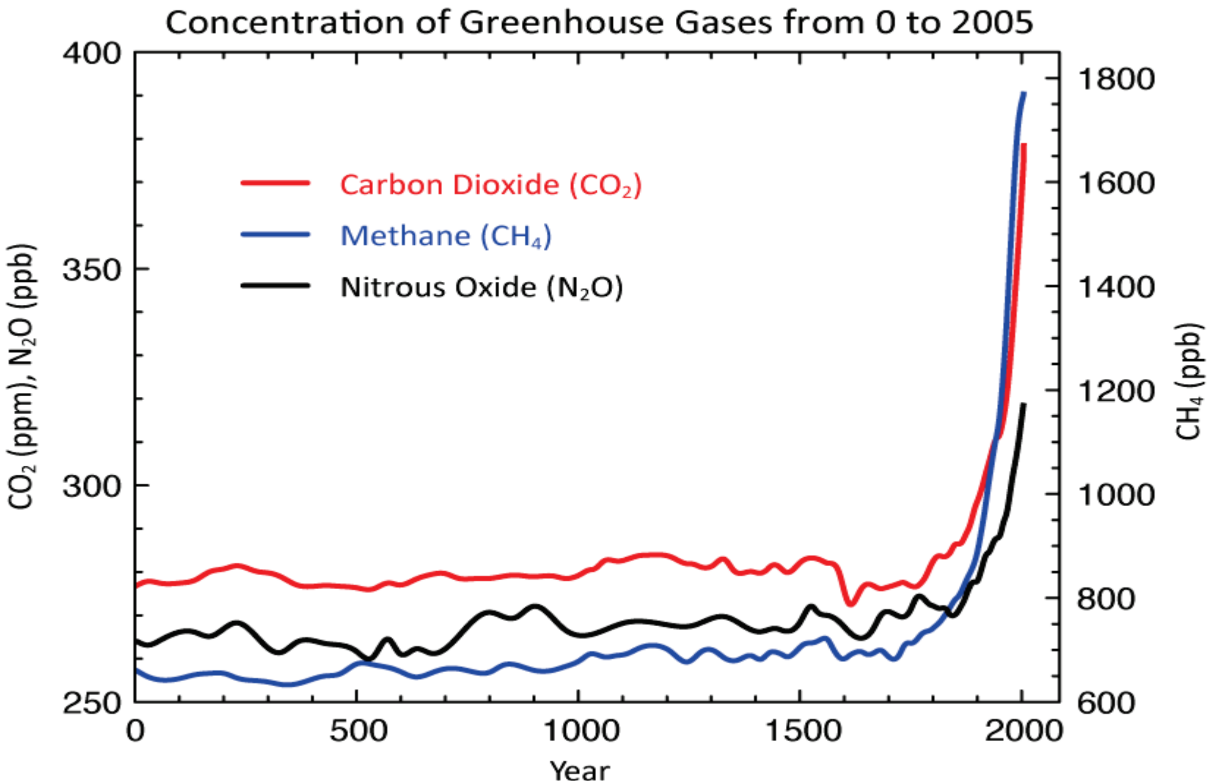


FAQ 2.1, Figure 1. *Atmospheric concentrations of important long-lived greenhouse gases over the last 2,000 years. Increases since about 1750 are attributed to human activities in the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb).*

Question 2.1, IPCC, 2007

Figure in the reading

GHG Record Over Last Several Millennia



FAQ 2.1, Figure 1 (Errata). *Revised figure showing atmospheric concentrations of important long-lived greenhouse gases over the last 2,000 years. Using the combined and simplified data from Chapters 6 and 2, the original figure displayed the CH_4 curve incorrectly. The revised figure shows the same data correctly plotted. For further details please refer to the original figure caption.*

Question 2.1, IPCC, 2007 … corrected
https://www.ipcc.ch/site/assets/uploads/2018/05/ar4-wg1-errata.pdf

Correction issued upon realization the line for CH_4 had been plotted incorrectly

GHG Record Over Last Several Millennia

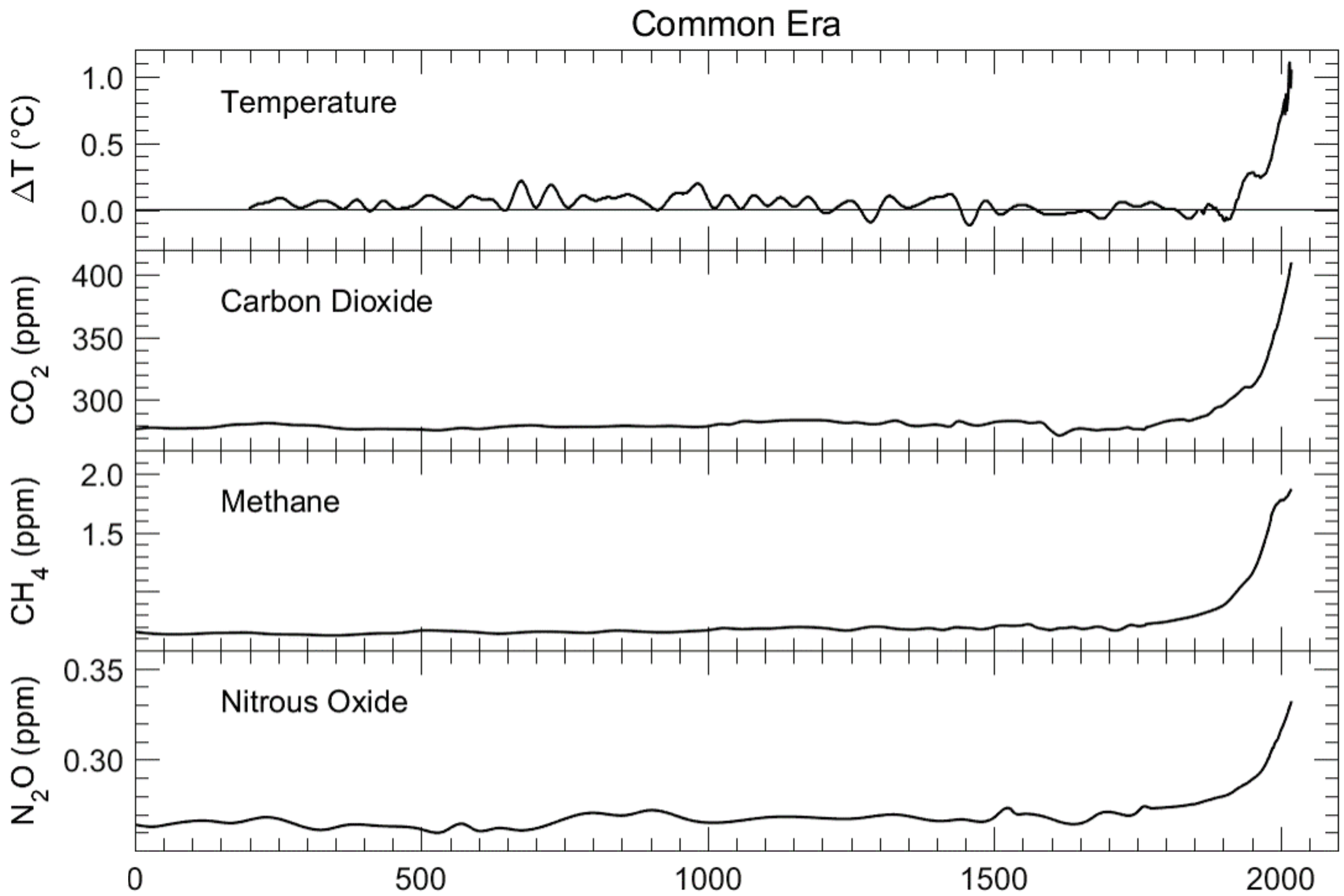


Figure 1.2, Paris Beacon of Hope (updated)

GHG Record Over Last Several Millennia

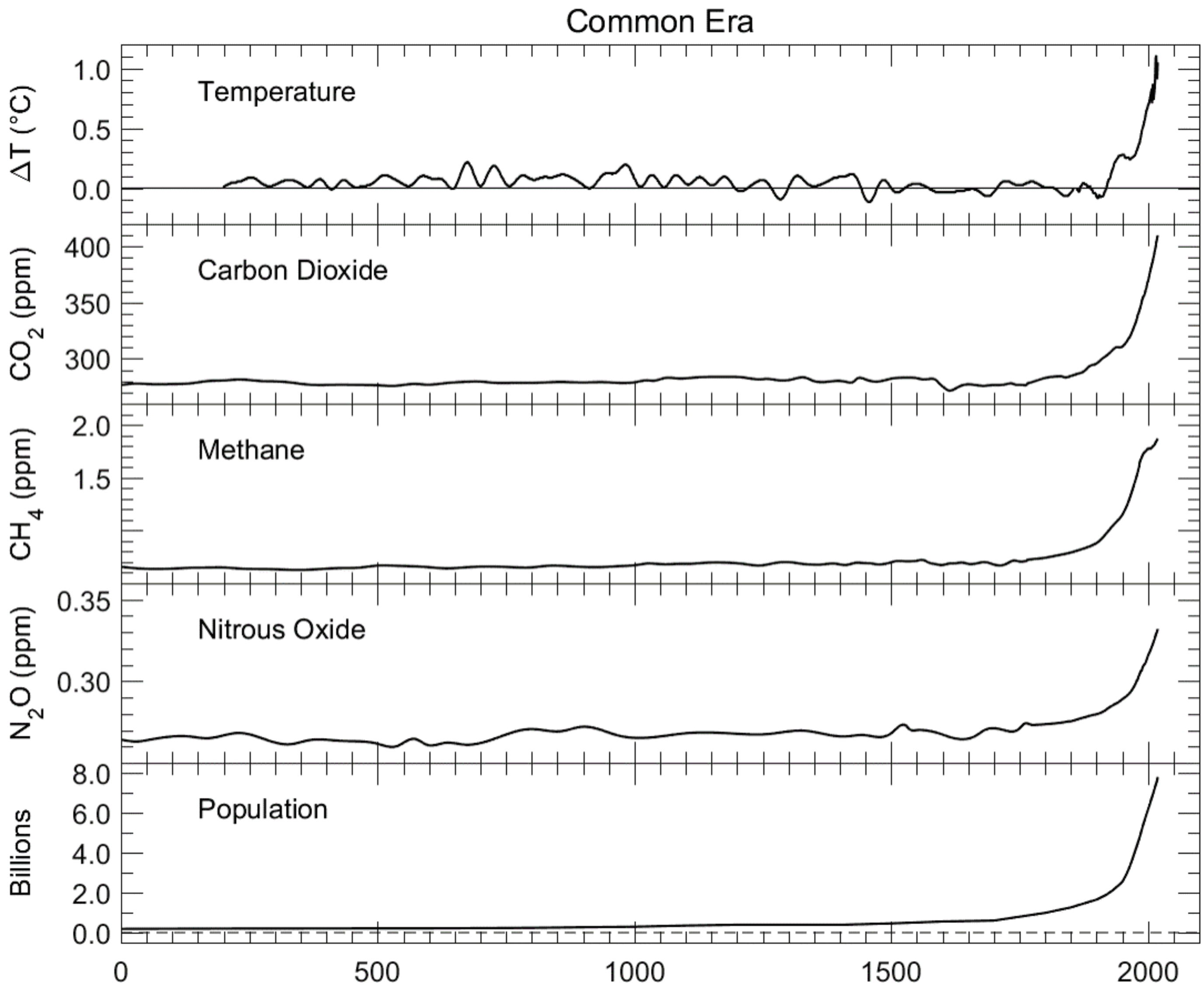
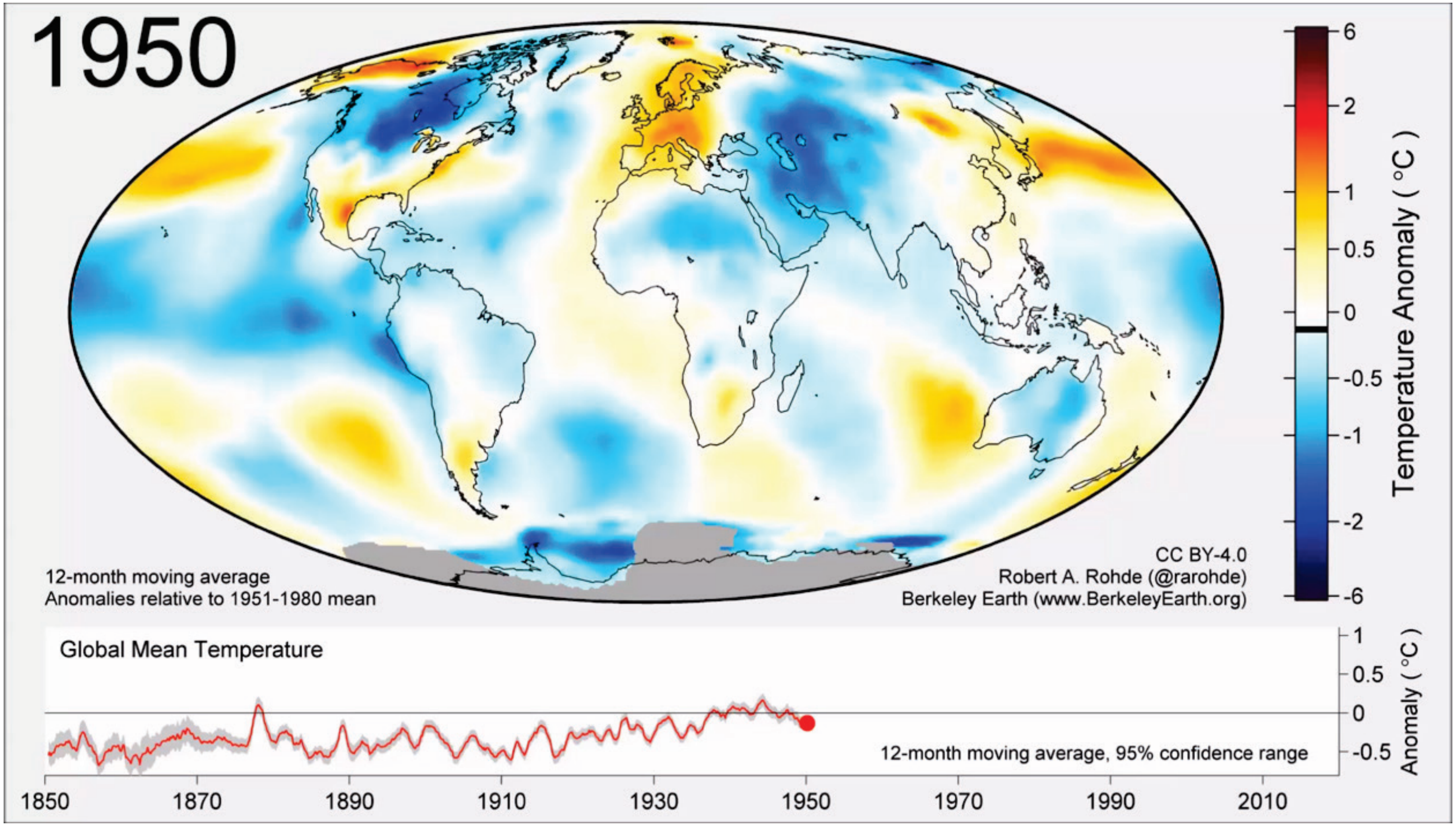


Figure 1.2, Paris Beacon of Hope (updated)

Berkeley Earth Animation of Global Warming

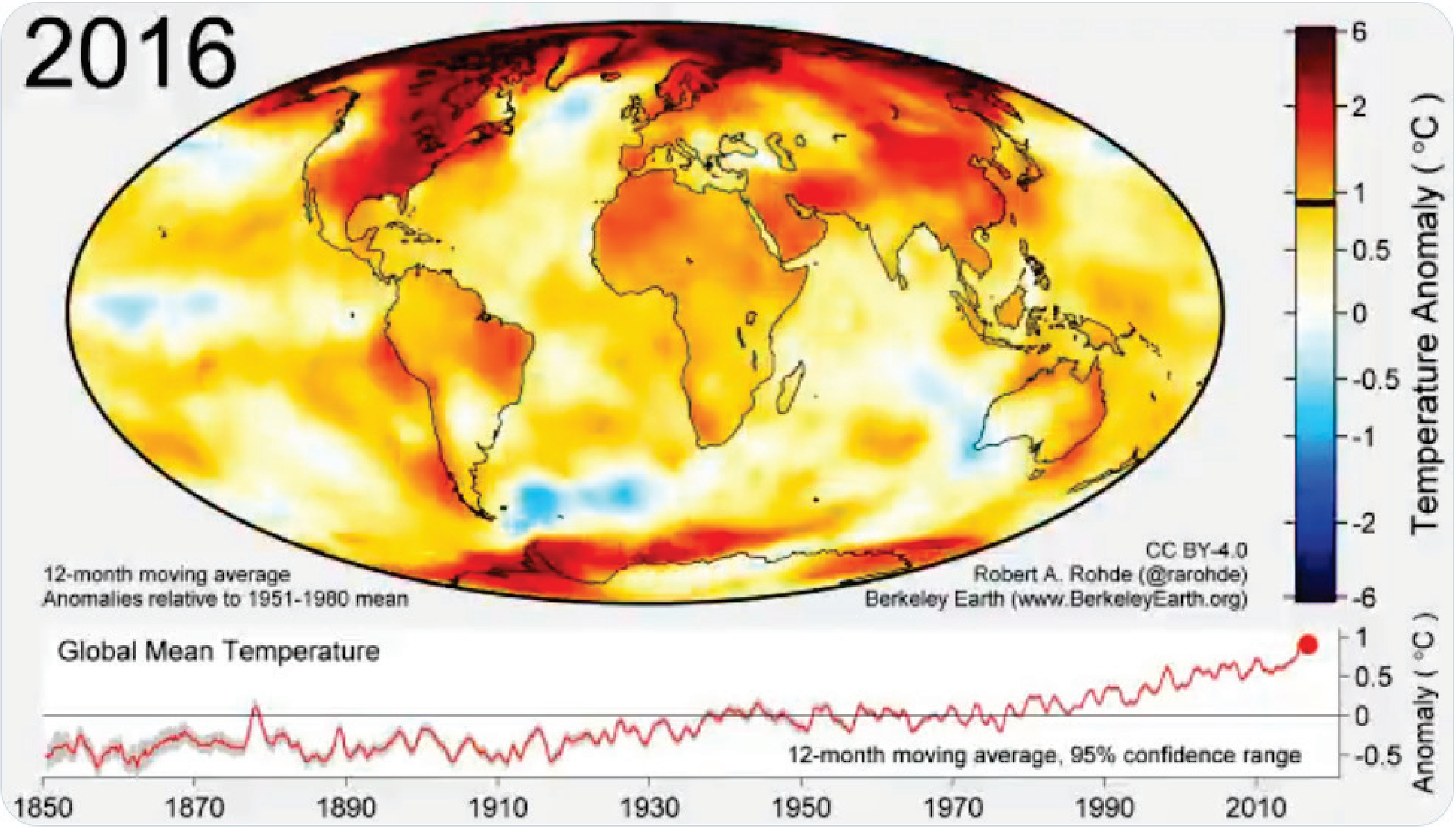


Note: movie file too large to include here. Can view at last link given below.

1°C (Celsius) warming is equivalent to 1.8°F (Fahrenheit) warming

Work of Robert Rohde and the Berkeley Earth Team
http://berkeleyearth.org
Animation at https://twitter.com/RARohde/status/1217496115429494786

Berkeley Earth Animation of Global Warming



2016 was the warmest year of the modern instrument record

Work of Robert Rohde and the Berkeley Earth Team
http://berkeleyearth.org
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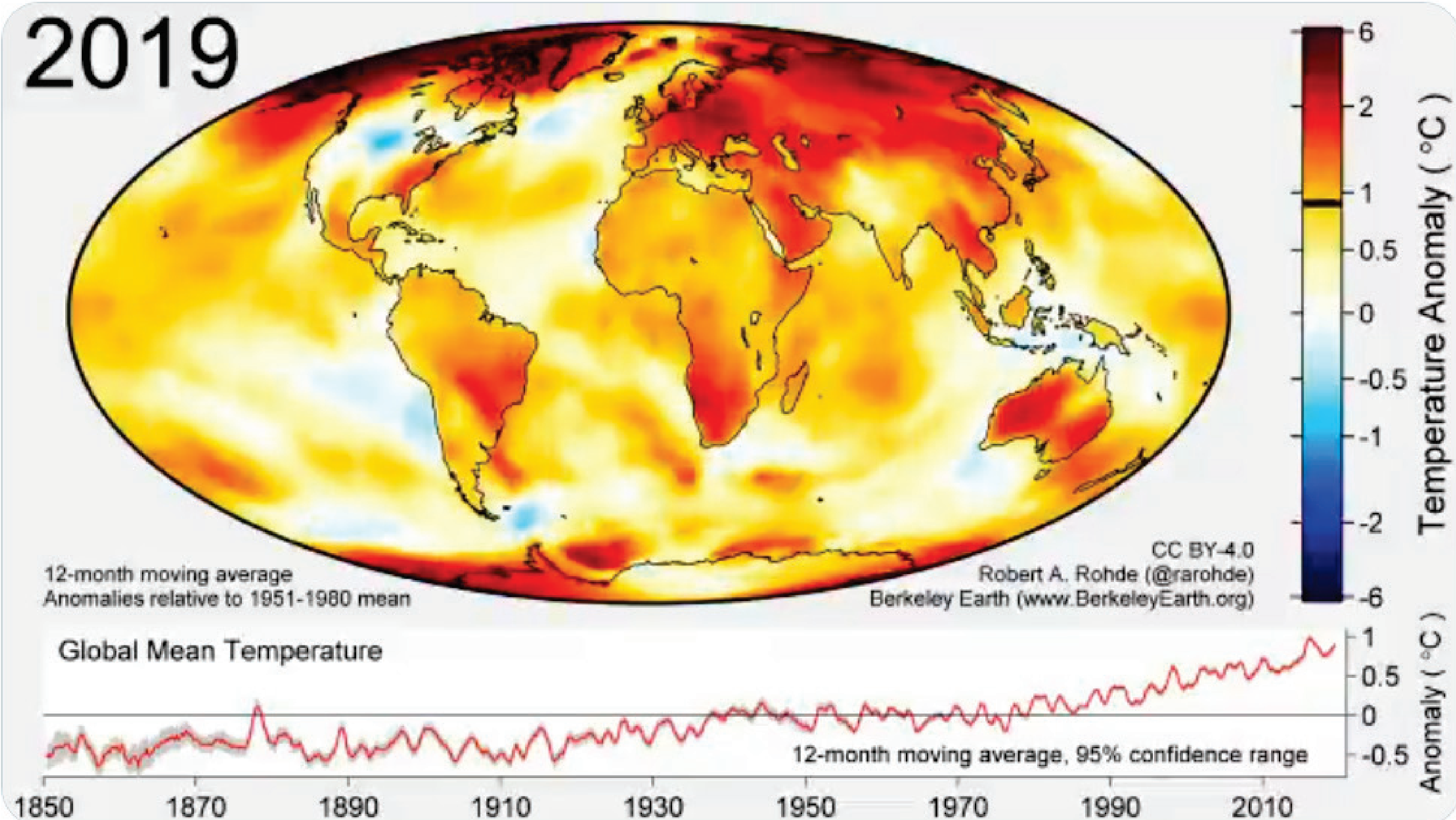
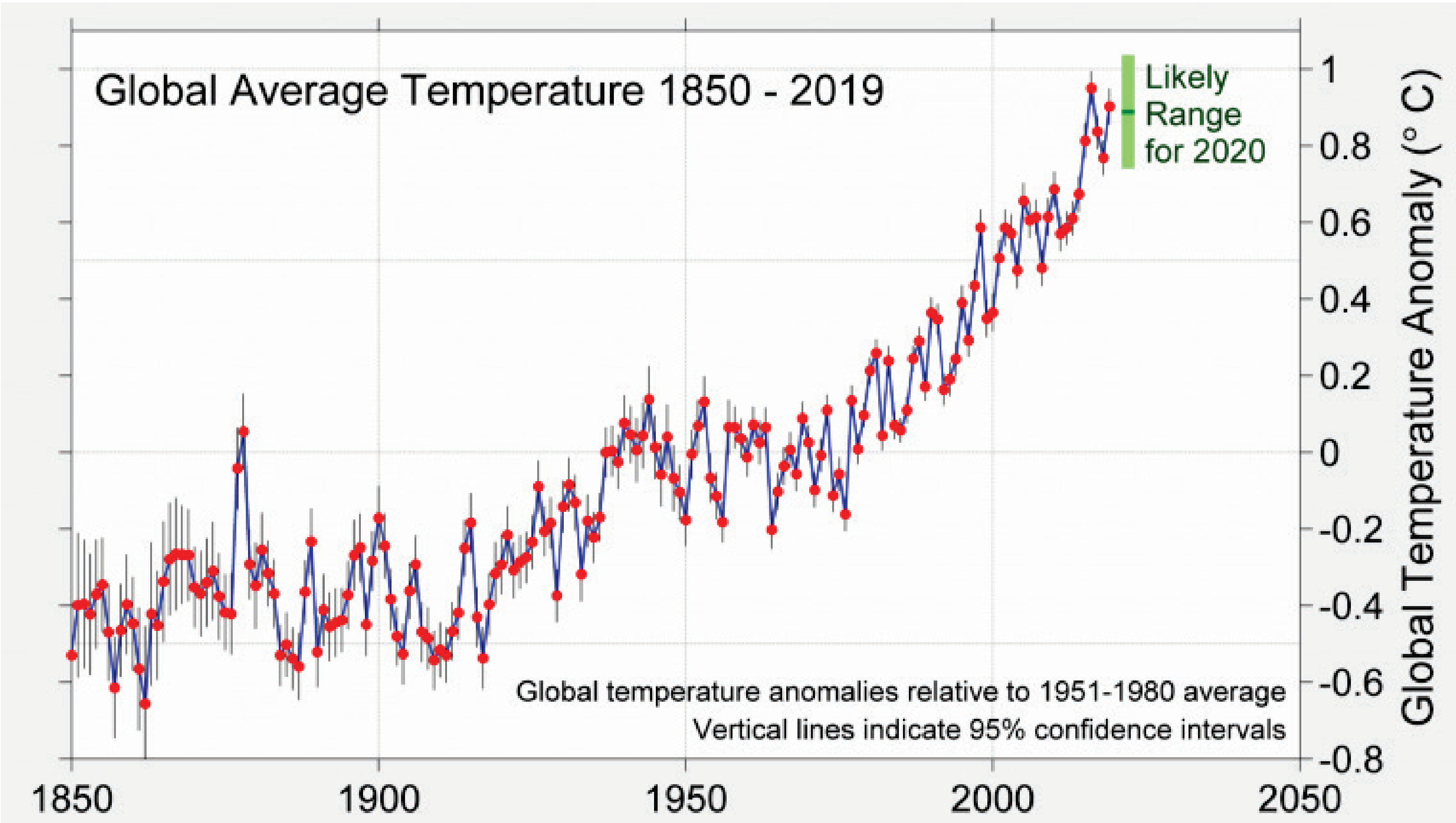
Berkeley Earth Animation of Global Warming



2019 was the second warmest year of the modern instrument record

Work of Robert Rohde and the Berkeley Earth Team
http://berkeleyearth.org
Animation at https://twitter.com/RARohde/status/1217496115429494786
http://berkeleyearth.org/2019-temperatures/

Berkeley Earth Animation of Global Warming



July 2020 is estimated to have been tied with July 2019 as the warmest July since records began in 1850, and 2020 will likely rival 2019 as second warmest year.

Work of Robert Rohde and the Berkeley Earth Team
http://berkeleyearth.org
https://berkeleyearth.org/july-2020-temperature-update

GWP – Global Warming Potential

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

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

$$\mathrm{GWP\ (N_2O)} = \frac{\int_{\text{time initial}}^{\text{time final}} a_{\mathrm{N2O}} \times [\mathrm{N_2O(t)}]\ \mathrm{dt}}{\int_{\text{time initial}}^{\text{time final}} a_{\mathrm{CO2}} \times [\mathrm{CO_2(t)\ dt}]}$$

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"

GHG	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)
100 Year Time Horizon				
CH_4	21	23	25	28, 34*
N_2O	310	296	298	265, 298*
20 Year Time Horizon				
CH_4	56	62	72	84, 86*
N_2O	280	275	289	264, 268*
*Allowing for carbon cycle feedback				

Table 1-1, Paris Beacon of Hope

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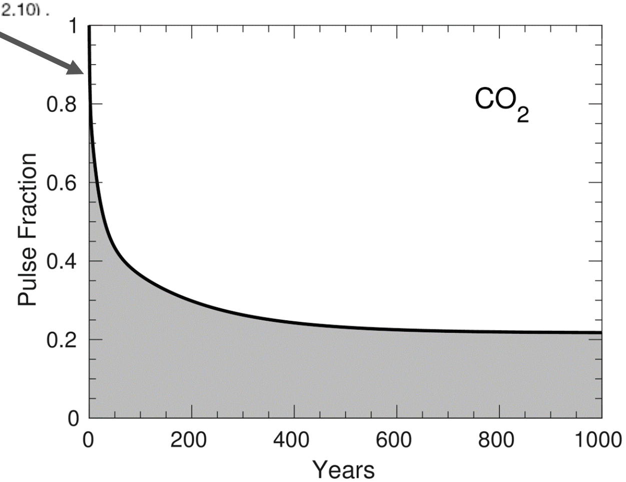
from IPCC 2007 “Physical Science Basis”



$$CO_2(t) = 0.217 + 0.186 \times CO_2(t{=}0)\, e^{-t/1.286} + 0.338 \times CO_2(t{=}0)\, e^{-t/18.59} + 0.249 \times CO_2(t{=}0)\, e^{-t/172.9}$$

where all times are given in units of year

GWP – Global Warming Potential

Table 1-1, Paris Beacon of Hope

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

$$\text{GWP}(N_2O) = \frac{\int_{\text{time initial}}^{\text{time final}} a_{N2O} \times [N_2O(t)]\,dt}{\int_{\text{time initial}}^{\text{time final}} a_{CO2} \times [CO_2(t)\,dt]}$$

GHG	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)
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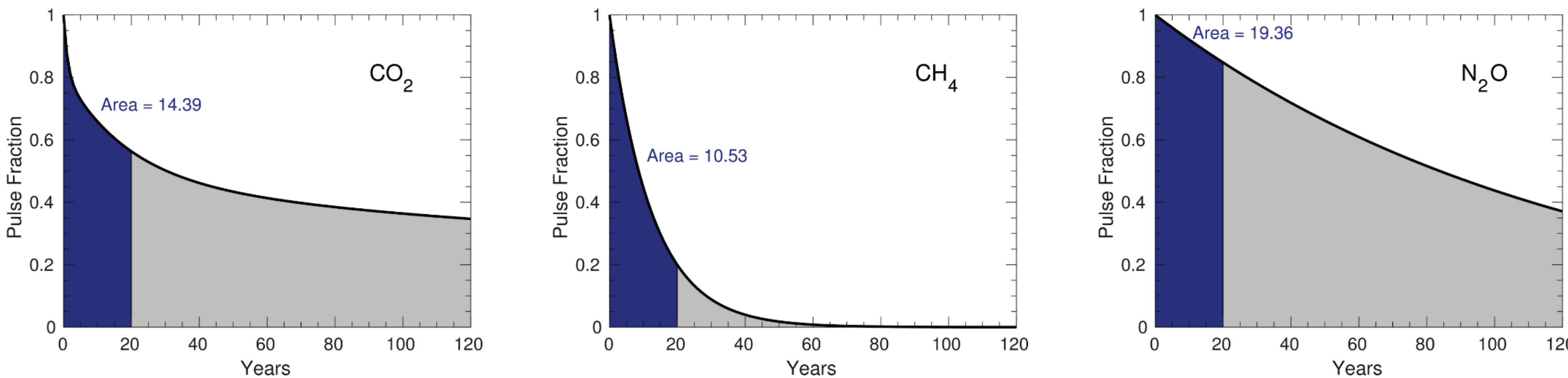
N_2O	310	296	298	265, 298*
20 Year Time Horizon				
CH_4	56	62	72	84, 86*
N_2O	280	275	289	264, 268*
*Allowing for carbon cycle feedback				



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$$CH_4(t) = CH_4(t{=}0)\, e^{-t/12.4}$$

$$N_2O(t) = N_2O(t{=}0)\, e^{-t/121.0}$$

where all times are given in units of year

GWP – Global Warming Potential

Table 1-1, Paris Beacon of Hope

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GHG	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)
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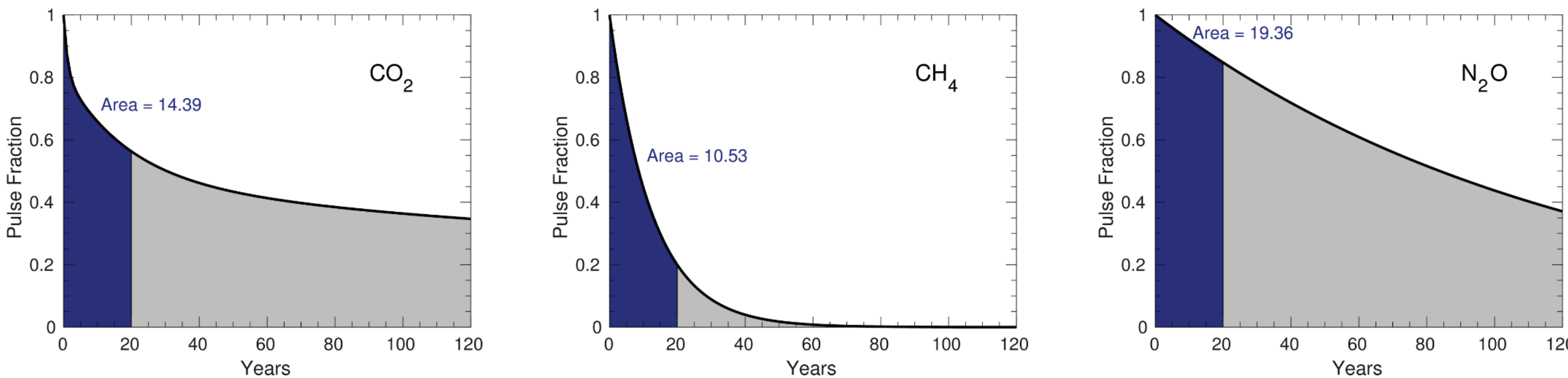
20 Year Time Horizon				
CH_4	56	62	72	84, 86*
N_2O	280	275	289	264, 268*
*Allowing for carbon cycle feedback				

20 Year Time Horizon means time final = 20 years in these integrals



$$CO_2(t) = 0.217 + 0.186 \times CO_2(t{=}0)\,e^{-t/1.286} + 0.338 \times CO_2(t{=}0)\,e^{-t/18.59} + 0.249 \times CO_2(t{=}0)\,e^{-t/172.9}$$

$$CH_4(t) = CH_4(t{=}0)\,e^{-t/12.4}$$

$$N_2O(t) = N_2O(t{=}0)\,e^{-t/121.0}$$

where all times are given in units of year

GWP – Global Warming Potential

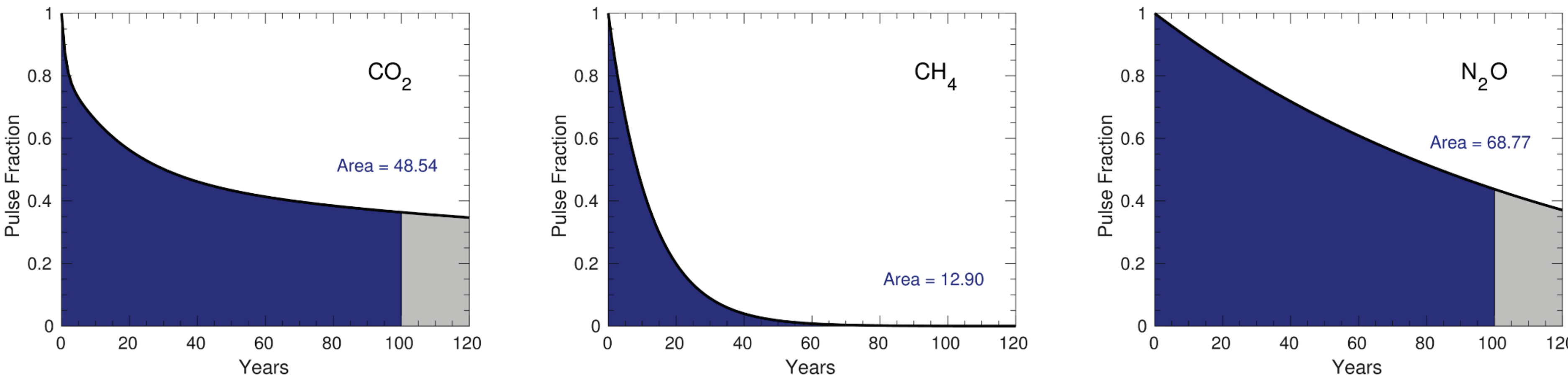
Table 1-1, Paris Beacon of Hope

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

$$GWP(N_2O) = \frac{\int_{\text{time initial}}^{\text{time final}} a_{N2O} \times [N_2O(t)]\, dt}{\int_{\text{time initial}}^{\text{time final}} a_{CO2} \times [CO_2(t)\, dt]}$$

GHG	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)
100 Year Time Horizon				
CH_4	21	23	25	28, 34*
N_2O	310	296	298	265, 298*
20 Year Time Horizon				
CH_4	56	62	72	84, 86*
N_2O	280	275	289	264, 268*
*Allowing for carbon cycle feedback				

100 Year Time Horizon means time final = 100 years in these integrals



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where all times are given in units of year

GWP – Global Warming Potential

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$$\mathrm{GWP}\,(N_2O) = \frac{\int_{\text{time initial}}^{\text{time final}} a_{N2O} \times [N_2O(t)]\,dt}{\int_{\text{time initial}}^{\text{time final}} a_{CO2} \times [CO_2(t)\,dt]}$$

GHG	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)
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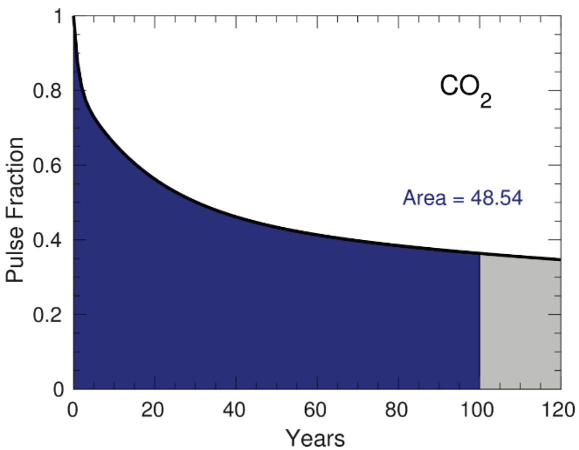
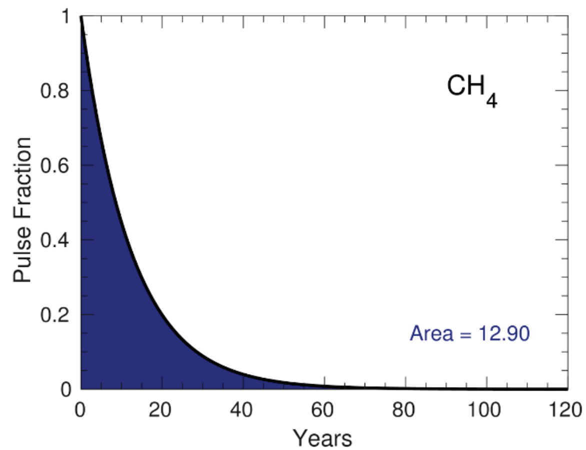
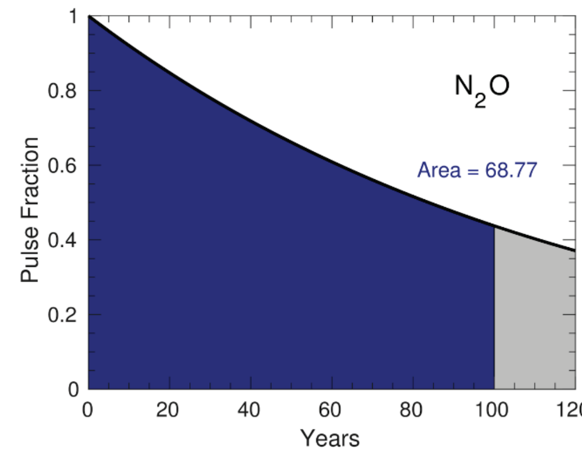
20 Year Time Horizon				
CH_4	56	62	72	84, 86*
N_2O	280	275	289	264, 268*
*Allowing for carbon cycle feedback				

These numbers (i.e., 1995, 2001, 2007, & 2013) are publication years







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$$\mathrm{GWP}\,(\mathrm{N_2O}) = \frac{\int_{\text{time initial}}^{\text{time final}} a_{\mathrm{N2O}} \times [\mathrm{N_2O(t)}]\ \mathrm{dt}}{\int_{\text{time initial}}^{\text{time final}} a_{\mathrm{CO2}} \times [\mathrm{CO_2(t)\ dt}]}$$

GHG	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)
100 Year Time Horizon				
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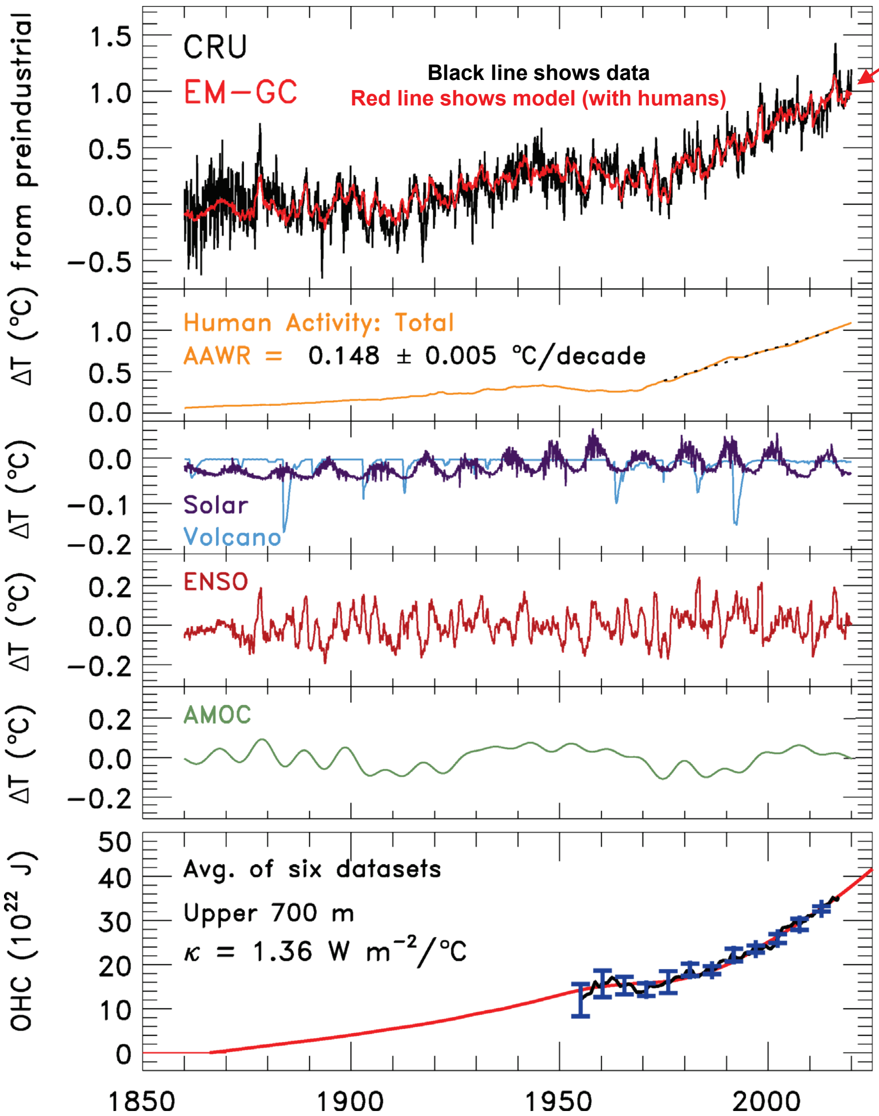
20 Year Time Horizon				
CH_4	56	62	72	84 86*
N_2O	280	275	289	264 268*
*Allowing for carbon cycle feedback				

CO_2 – equivalent emissions = Emissions of CO_2 +
Emissions of CH_4 × GWP of CH_4 +
Emissions of N_2O × GWP of N_2O +
etc.

Commonly, GWPs on 100 year time horizon are used, although ***many of us*** would prefer the 20 year time horizon

Are humans responsible?



$$\Delta T_{MDL\,i} = (1+\gamma)\left(\frac{GHG\ RF_i + LUC\ RF_i + Aerosol\ RF_i}{\lambda_p}\right) + C_0 + C_1 \times SOD_{i-6} + C_2 \times TSI_{i-1} + C_3 \times ENSO_{i-2} + C_4 \times AMOC_i - \left(\frac{Q_{OCEAN\,i}}{\lambda_p}\right)$$

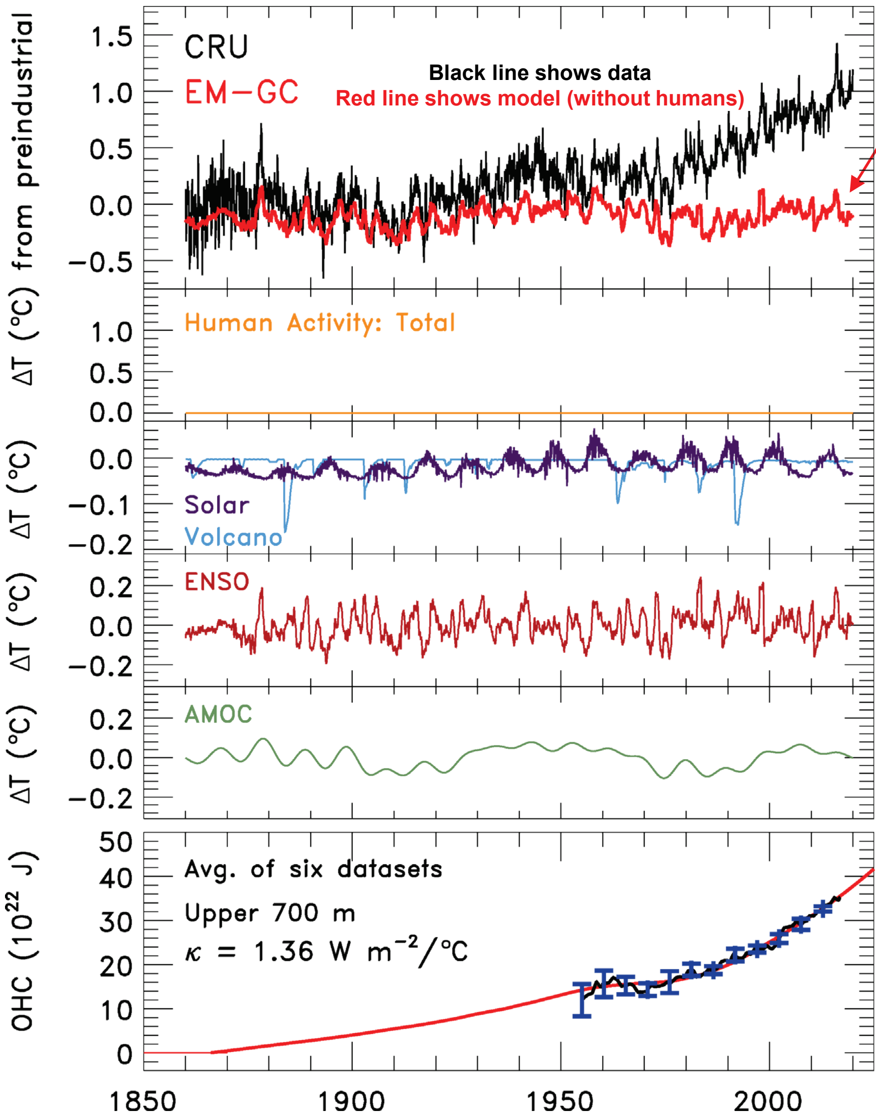
where:

- i denotes month
- $\lambda_p = 3.2\ \mathrm{W\,m^{-2}\,°C^{-1}}$
- $1+\gamma = \{1 - \lambda_\Sigma/\lambda_p\}^{-1}$
- GHG RF = RF due to all anthropogenic GHGs
- LUC RF = RF due to Land Use Change
- Aerosol RF = RF due to Tropospheric Aerosols
- SOD = Stratospheric Optical Depth
- TSI = Total Solar Irradiance
- ENSO = El Niño Southern Oscillation
- AMOC = Atlantic Meridional Overturning Circulation
- Q_{OCEAN} = Ocean heat export = $\kappa(1+\gamma)\{\Delta T_{MDL\,i} - \Delta T_{OCEAN\,SURFACE\,i}\}$

CRU: Climate Research Unit of East Anglia, United Kingdom
EM-GC: Empirical Model of Global Climate, Univ of Maryland

Canty *et al*., 2013 https://www.atmos-chem-phys.net/13/3997/2013/acp-13-3997-2013.html
Hope *et al*., 2017 https://link.springer.com/chapter/10.1007/978-3-319-46939-3_2
as well as Hope *et al*. (2020, submitted) & McBride *et al*. (2020, submitted). Figure provided by Laura McBride.

Are humans responsible?



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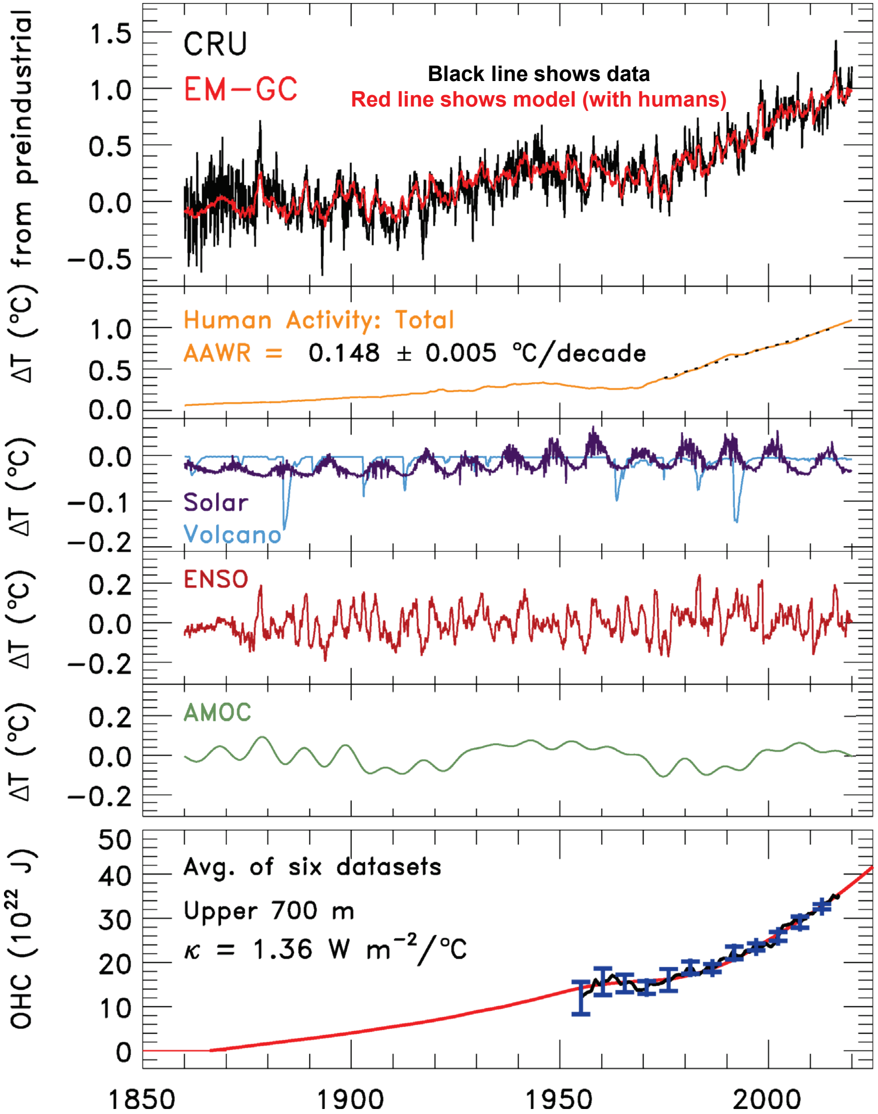

Global warming is caused by CO_2, the greatest waste product of modern society, as well as CH_4, N_2O, and other GHGs.

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

CRU: Climate Research Unit of East Anglia, United Kingdom
EM-GC: Empirical Model of Global Climate, Univ of Maryland

Canty *et al*., 2013 https://www.atmos-chem-phys.net/13/3997/2013/acp-13-3997-2013.html
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Are humans responsible?

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

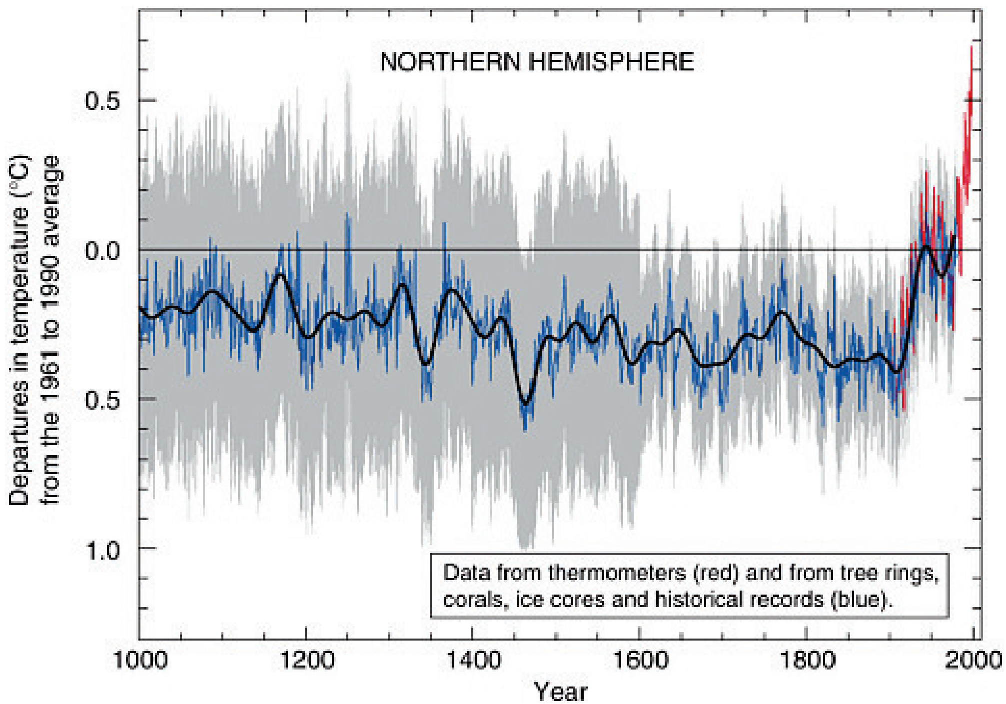
Volcanoes: no sustained forcing

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**



https://www.nap.edu/read/11676/chapter/3#14

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***IPCC Climate Change 2007* concludes:**

Very high confidence* the globally averaged net effect of human activities since 1750 has been one of warming

*** At least a 90% chance of being correct**

IPCC ⇒ Intergovernmental Panel on Climate Change

See Section 1.4 of https://www.ipcc.ch/site/assets/uploads/2017/09/WG1AR5_Chapter01_FINAL.pdf for definitions of high confidence, extremely likely, etc.

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***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 Section 1.4 of https://www.ipcc.ch/site/assets/uploads/2017/09/WG1AR5_Chapter01_FINAL.pdf for definitions of high confidence, extremely likely, etc.

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See Section 1.4 of https://www.ipcc.ch/site/assets/uploads/2017/09/WG1AR5_Chapter01_FINAL.pdf for definitions of high confidence, extremely likely, etc.

Caveat: it is much easier to *"understand the past"* than *"predict the future"*
we'll examine some of the uncertainties in projecting future climate change in later lectures

Ozone in the Atmosphere

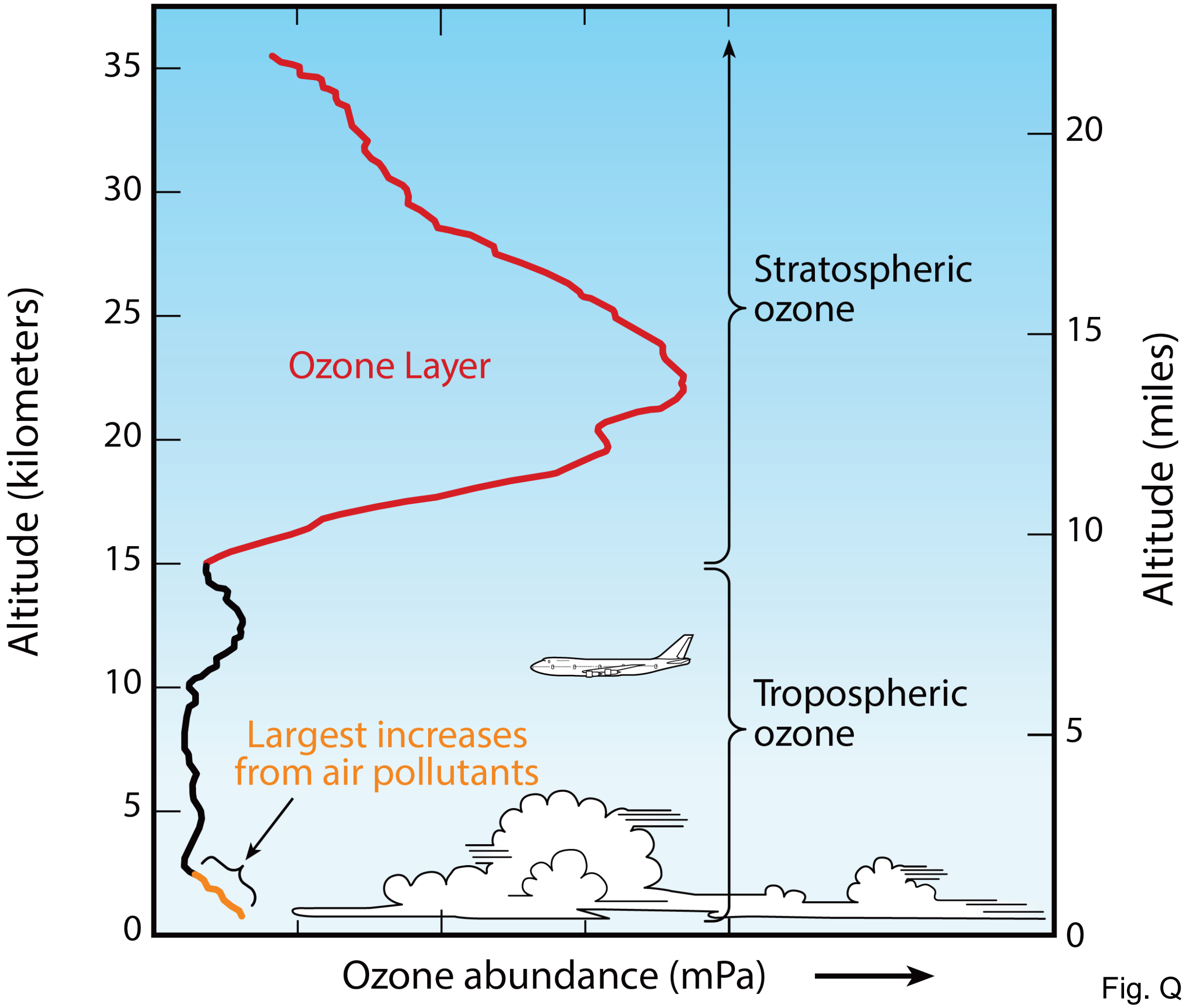
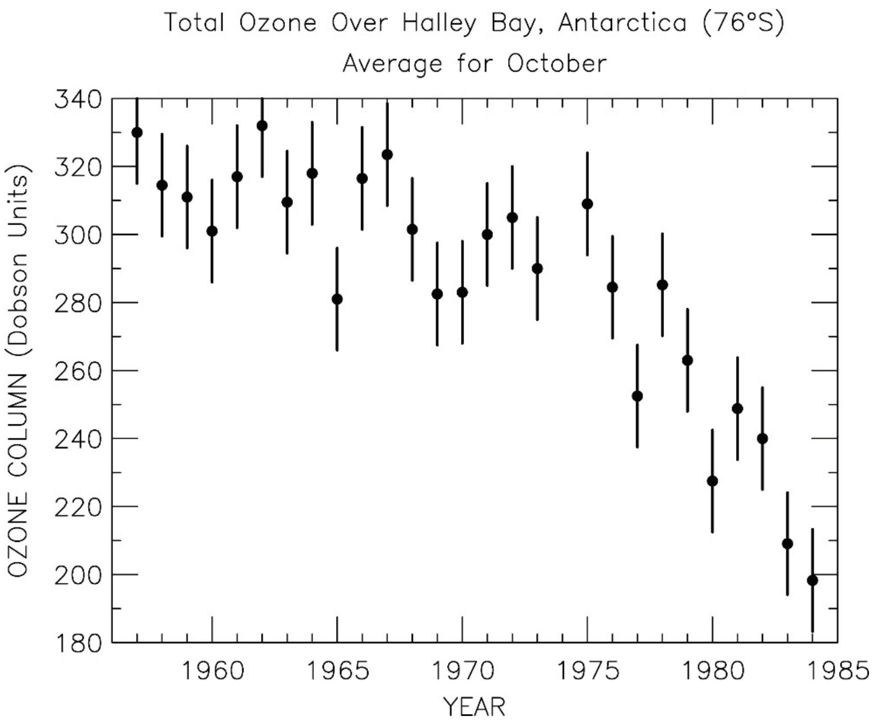


Fig. Q1-2
20 QAs about the Ozone Layer

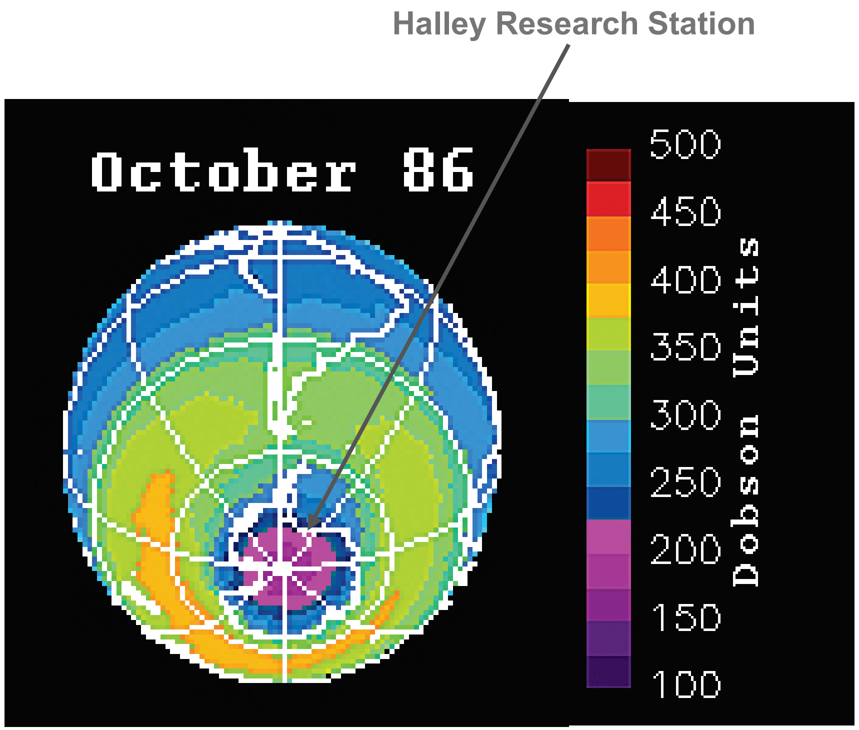
It is incredible that human activity both destroys stratospheric ozone (so-called good ozone) and produces tropospheric ozone (so-called bad ozone)

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.



Stolarski *et al*., Nature, 1986.

Earth's Atmosphere – Effect of Humans

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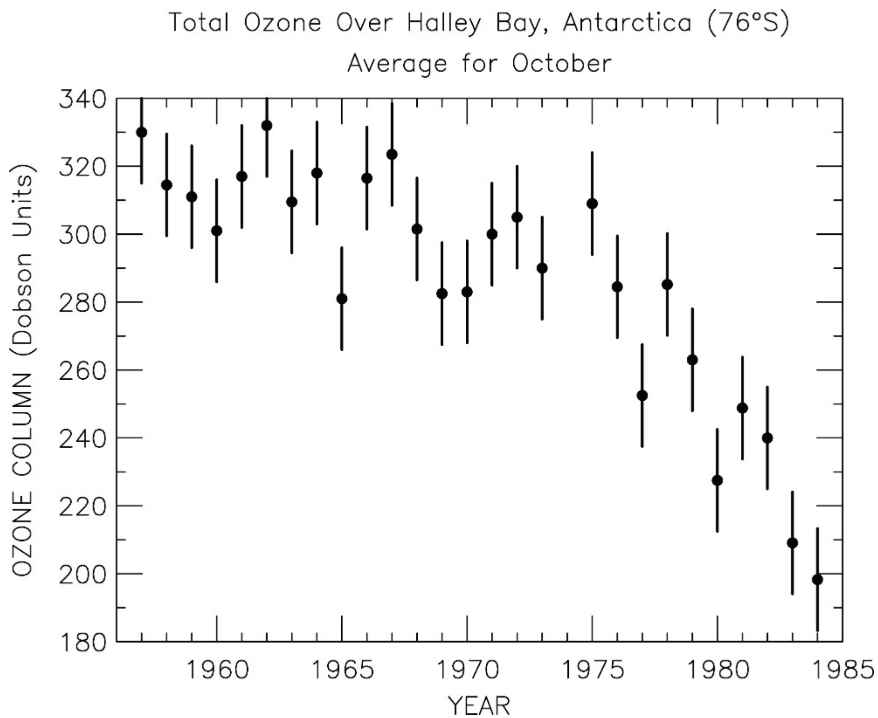
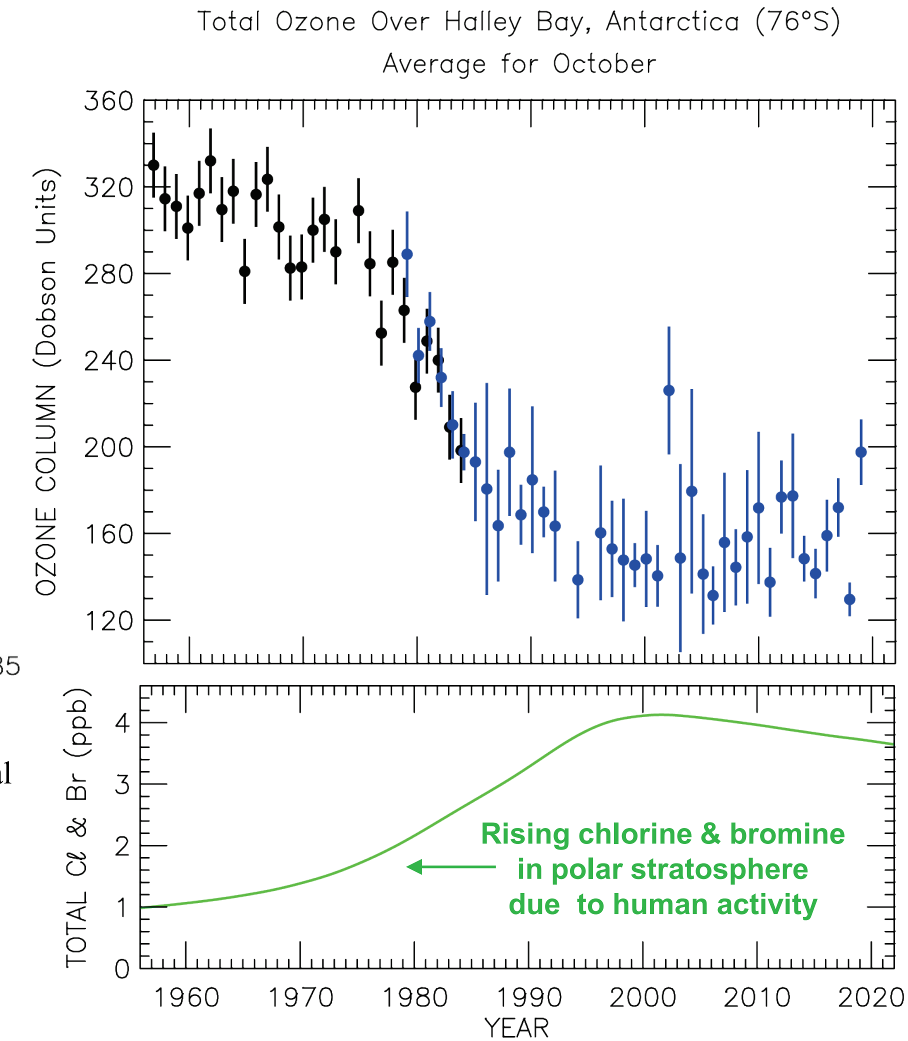
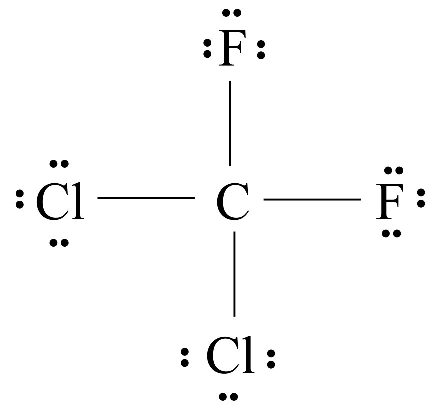


After Farman *et al*., Large losses of total ozone in Antarctica reveal Seasonal ClOx/NOx interaction, Nature, 315, 207, 1985.

Update



CFC-12



How is it eventually removed from the atmosphere ?

What does it produce upon its removal ?

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. However, we want non-chemists to at least have been exposed to this concept for tracking the position of electrons, central for understanding atmospheric chemical reactions.

Measurements of Reactive Chlorine From Space

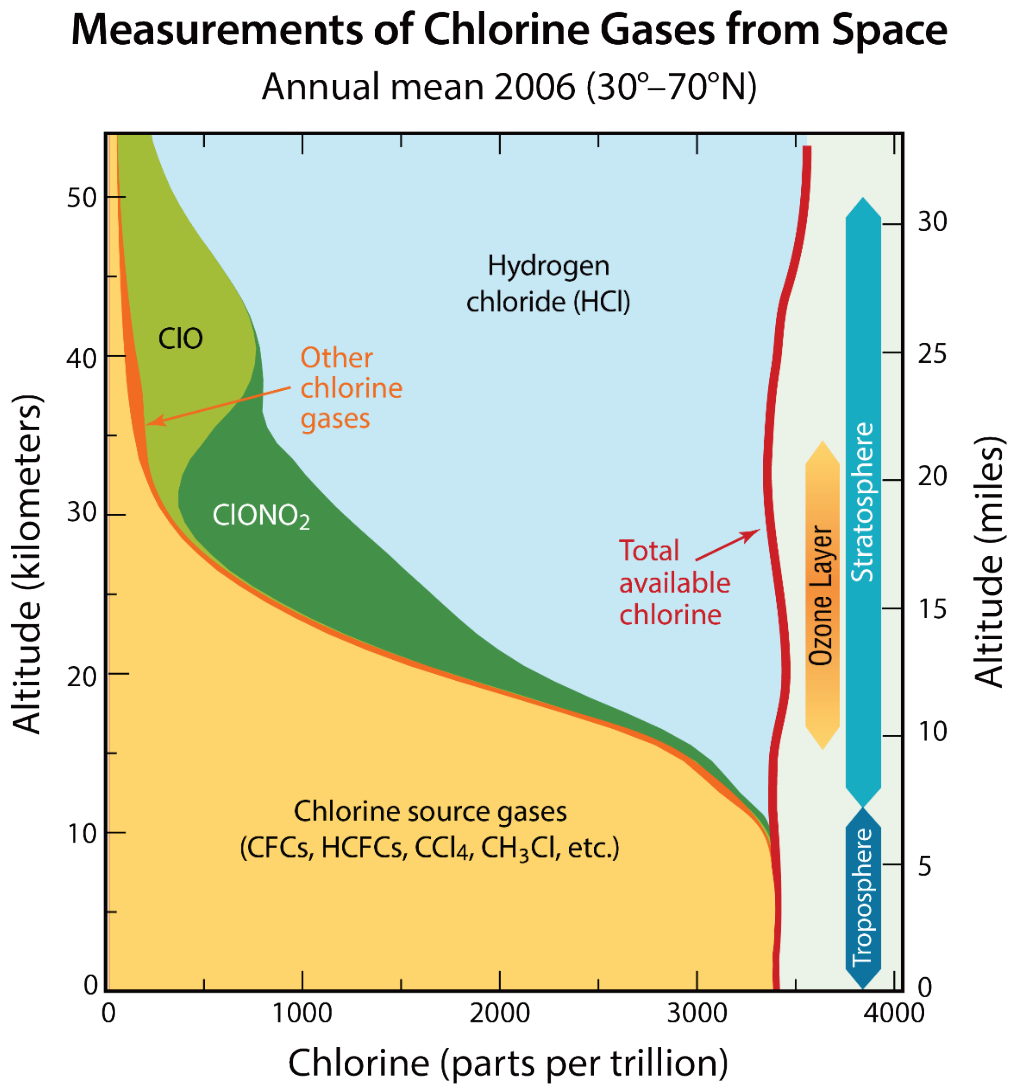
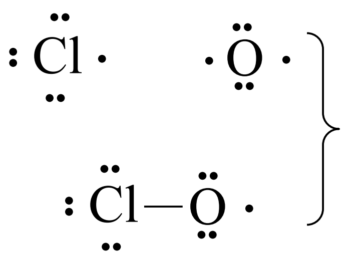


Fig. Q7-2, 20 QAs about the Ozone Layer

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



ClO : Chlorine monoxide

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

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Chlorine Radicals Lead to Ozone Loss

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

Chlorine Radicals Lead to Ozone Loss

$$ClO + ClO + M \rightarrow ClOOCl + M$$

$$Cl + \mathbf{O_3} \rightarrow ClO + \mathbf{O_2}$$

$$Cl + \mathbf{O_3} \rightarrow ClO + \mathbf{O_2}$$

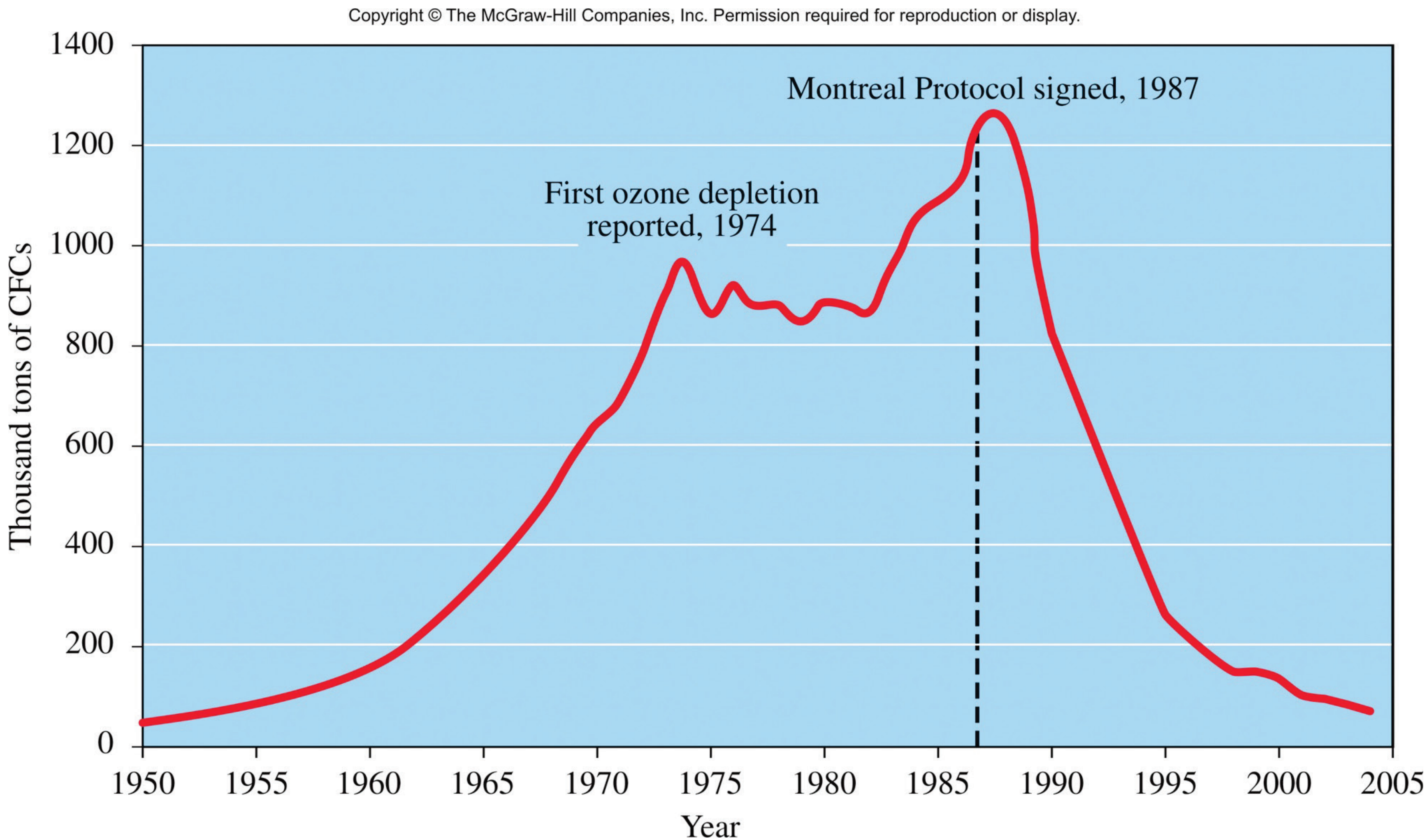
$$ClOOCl + h\nu \rightarrow ClOO + Cl$$

$$ClOO + \text{heat} \rightarrow Cl + \mathbf{O_2}$$

$$\text{Net:} \quad \mathbf{O_3 + O_3 \rightarrow 3\ O_2}$$

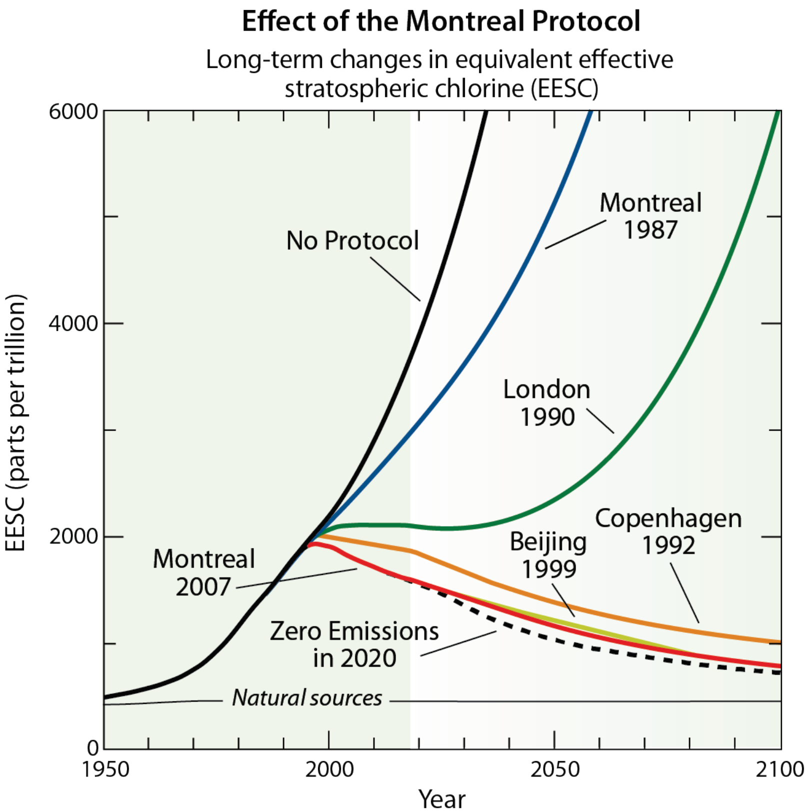
Catalytic loss of ozone: this chemistry causes the Antarctic ozone hole

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



CFCs: Chlorofluorocarbons

Contain some combination of chlorine, fluorine, and at least one carbon. Freons are a trade name for CFCs.

Bromocarbons:

Contain bromine, perhaps chlorine, and at least one carbon. Halons are a trade name for bromocarbons.

HCFCs: Hydro-chlorofluorocarbons

Same as CFCs, except one or more hydrogen has replaced a chlorine.

HFCs: Hydrofluorocarbons

Contain some combination of hydrogen, fluorine, and carbon. **These gases do not contain any bromine or chlorine, and hence pose no damage to the ozone layer.** Some HFCs are potent GHGs.

EESC: Equivalent, effective stratospheric chlorine. Reflects combined influence of chlorine and bromine on ozone, via a simple formula: [Chlorine] + 60 × [Bromine]

Figure Q14-1, 20 QAs about the Ozone Layer

CFC Usage Prior to the Montreal Protocol

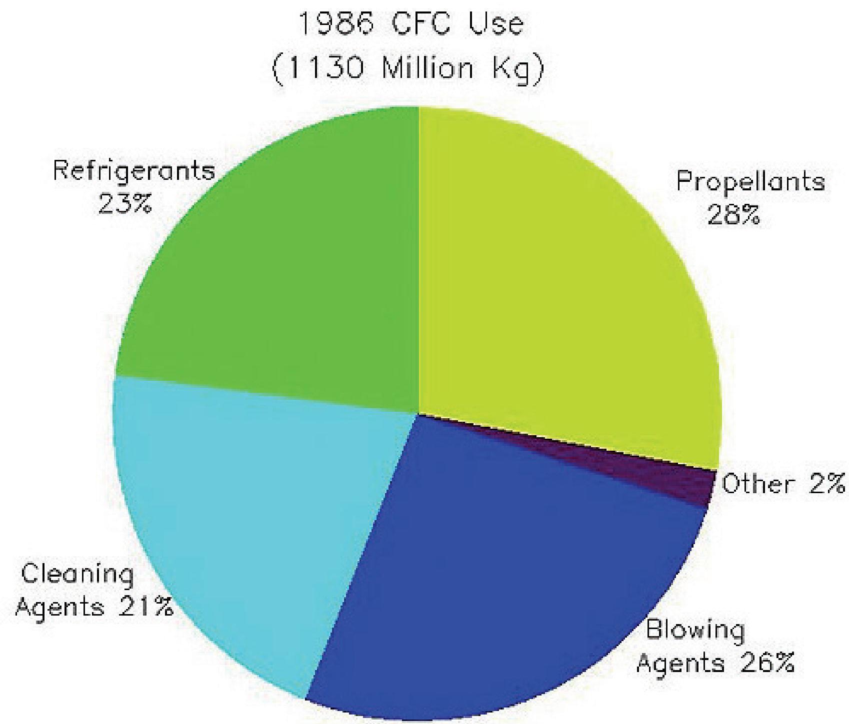
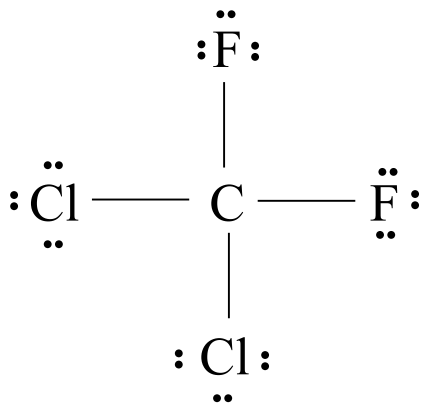


Figure 5b. Changing use patterns for CFCs (from Fisher and Midgley, 1994).

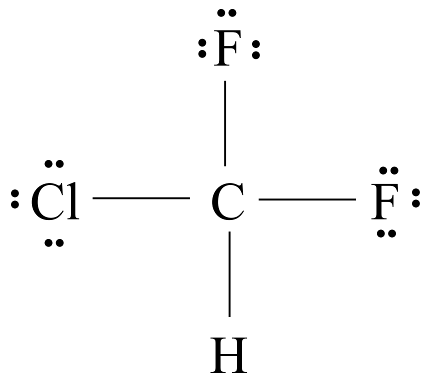
The uses of CFCs in various sectors before the 1987 Montreal Protocol, which required countries to phase out their production to protect the ozone layer.

From http://www.ccpo.odu.edu/SEES/ozone/class/Chap_10/index.htm
based upon https://agupubs.onlinelibrary.wiley.com/doi/epdf/10.1029/94JD00738

CFCs were replaced with HCFCs



CFC-12
or
Freon-12
or
R-12



HCFC-22
or
Freon-22
or
R-22

Phase out of CFCs and other Ozone Depleting Substances (ODSs)

CFCs & other ODSs	Phase 1 ⇨	HCFCs	Phase 2 ⇨	HFCs
CFC-11 CFC-12 CFC-113 CFC-114 CFC-115 CCl_4 CH_3CCl_3		HCFC-22 HCFC-141b HCFC-142b		HFC-23 HFC-143a HFC-125 HFC-134a etc.
Harmful to ozone layer		**Less harmful to ozone layer**		**Pose no risk to ozone layer, since no Cl or Br**

See http://www.atmos.umd.edu/~rjs/class/spr2020/supplemental_readings/Naming_Convention_for_CFCs_Halons.pdf
for a guide to CFC naming convention

Phase out of CFCs and other Ozone Depleting Substances (ODSs)

CFCs & other ODSs → (Phase 1) → HCFCs → (Phase 2) → HFCs

CFCs & other ODSs	HCFCs	HFCs
CFC-11	HCFC-22	HFC-23
CFC-12	HCFC-141b	HFC-143a
CFC-113	HCFC-142b	HFC-125
CFC-114		HFC-134a
CFC-115		etc.
CCl_4		
CH_3CCl_3		
Harmful to ozone layer	**Less harmful to ozone layer**	**But very harmful to Earth's climate**

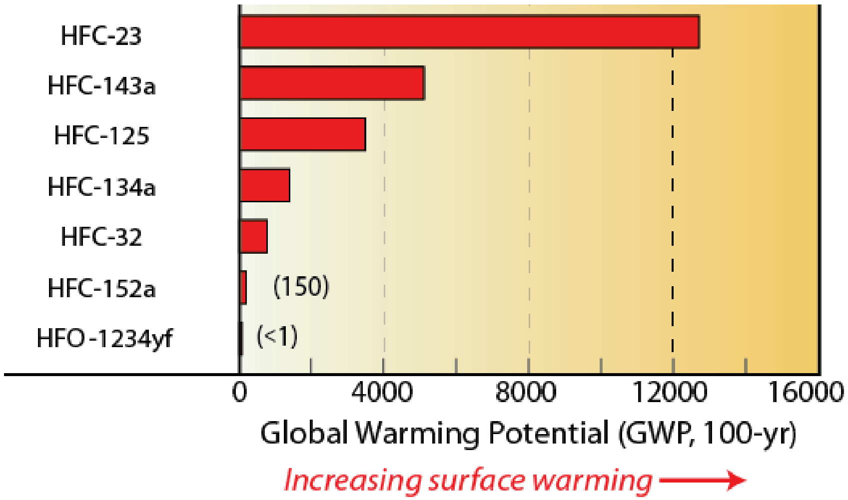


Figure Q17-3, 20 QAs about the Ozone Layer

Kigali Amendment

Tina Birmpili, Ozone Secretariat

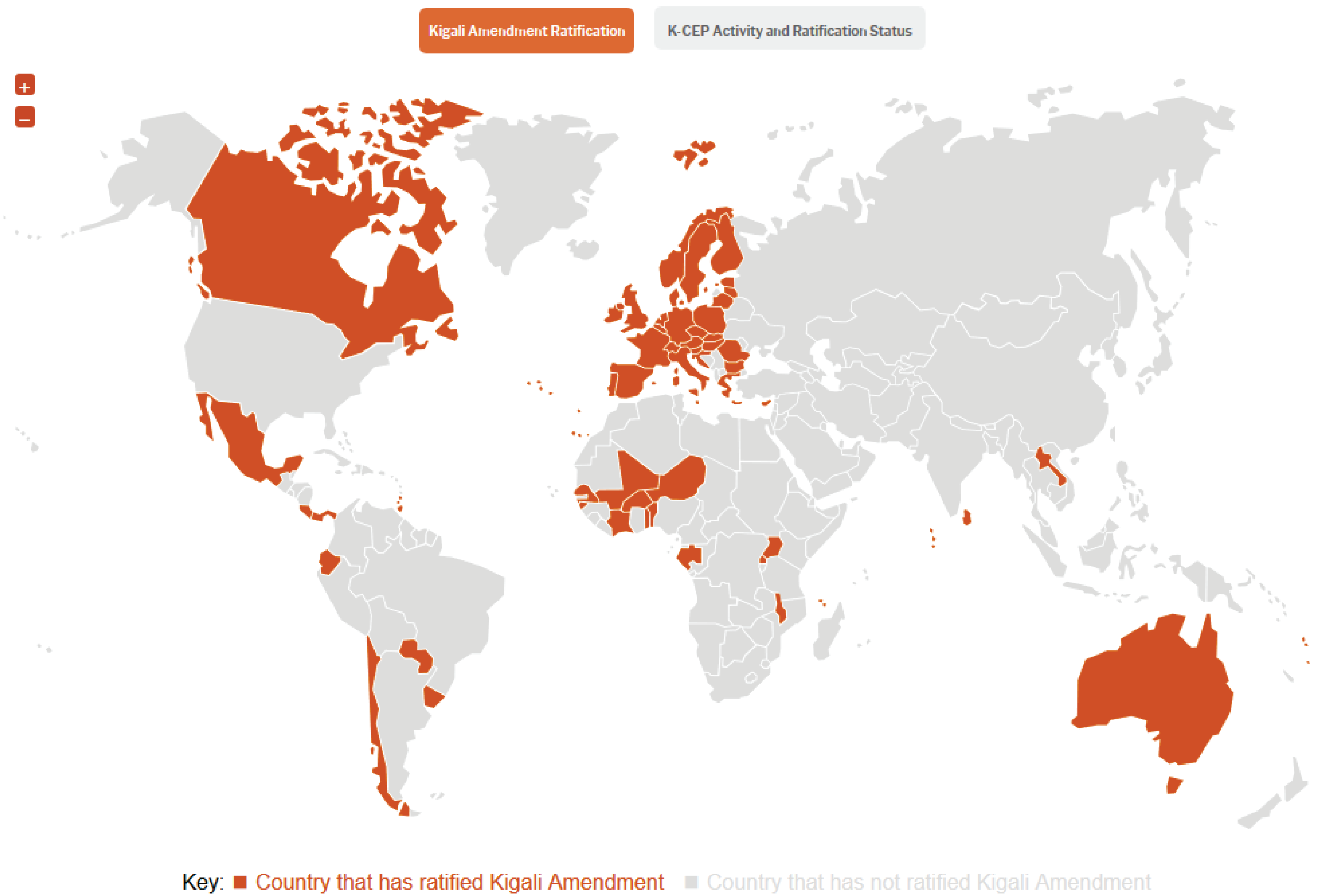
PhD in Environmental Management and Economics from *Imperial College of Science, Technology and Medicine*, London.

As of 1 January 2019, the future production of HFCs is controlled by the Montreal Protocol, based on amendment passed in Kigali, Rwanda in Fall 2017, hosted by Rwanda's Minister of Environment Vincent Biruta and Canada's Minister of Environment and Climate Change Catherine McKenna.

"Ozone Secretariat Executive Secretary Tina Birmpili added: "2017 marks the 30th anniversary of the Protocol's life and there is no better way to celebrate this anniversary than by seeking country support to ratify the Kigali Amendment and build on the next 30 years."

https://ozone.unep.org/unga-high-level-event-ratification-kigali-amendment

Ratification Status of the Kigali Amendment



Kigali Amendment went into force on 1 January 2019. To date, 65 countries have ratified.

https://www.k-cep.org/wp-content/themes/kigali/page-templates/map/MapRatification.html

Ratification Status of the Kigali Amendment

FAYE LEONE
Content Editor, SDGs and 2030 Agenda for Sustainable Development (US)

8 January 2019

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Kigali Amendment Enters into Force, Bringing Promise of Reduced Global Warming

The need for the Amendment emerged from the 1987 Montreal Protocol process, which controls ozone-depleting substances. With HFCs' use as an alternative to ozone-depleting substances in cooling equipment, their role in warming the atmosphere became a greater concern. In 2016, the Parties to the Montreal Protocol adopted the agreement on HFCs at the close of the 28th Meeting of the Parties (MOP 28) in Kigali, Rwanda. Governments agreed that it would enter into force on 1 January 2019, provided that at least 20 Parties to the Montreal Protocol had ratified it. On 17 November 2017, Sweden and Trinidad and Tobago deposited their instruments of ratification, bringing the number of Parties above the required threshold.

Kigali Amendment went into force on 1 January 2019. To date, 65 countries have ratified.

https://sdg.iisd.org/news/kigali-amendment-enters-into-force-bringing-promise-of-reduced-global-warming/

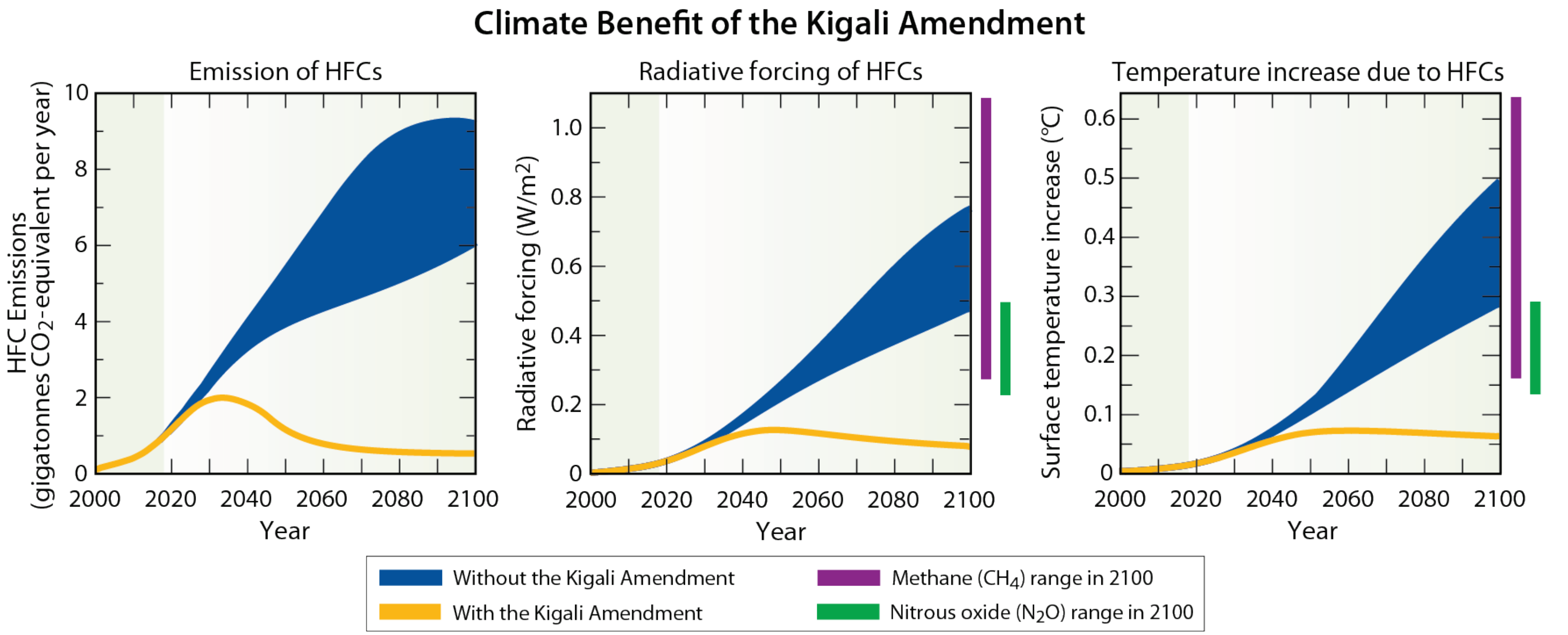
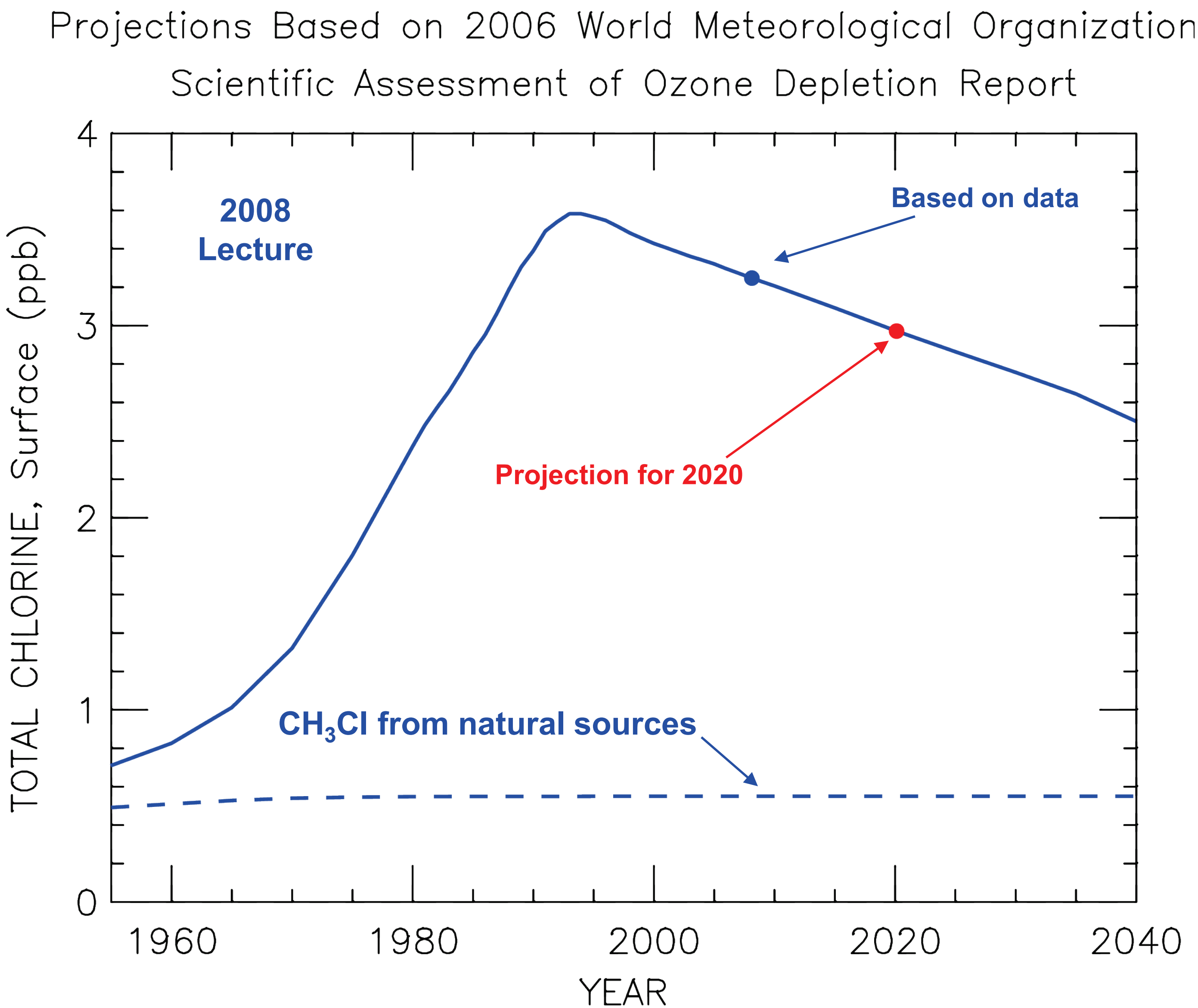
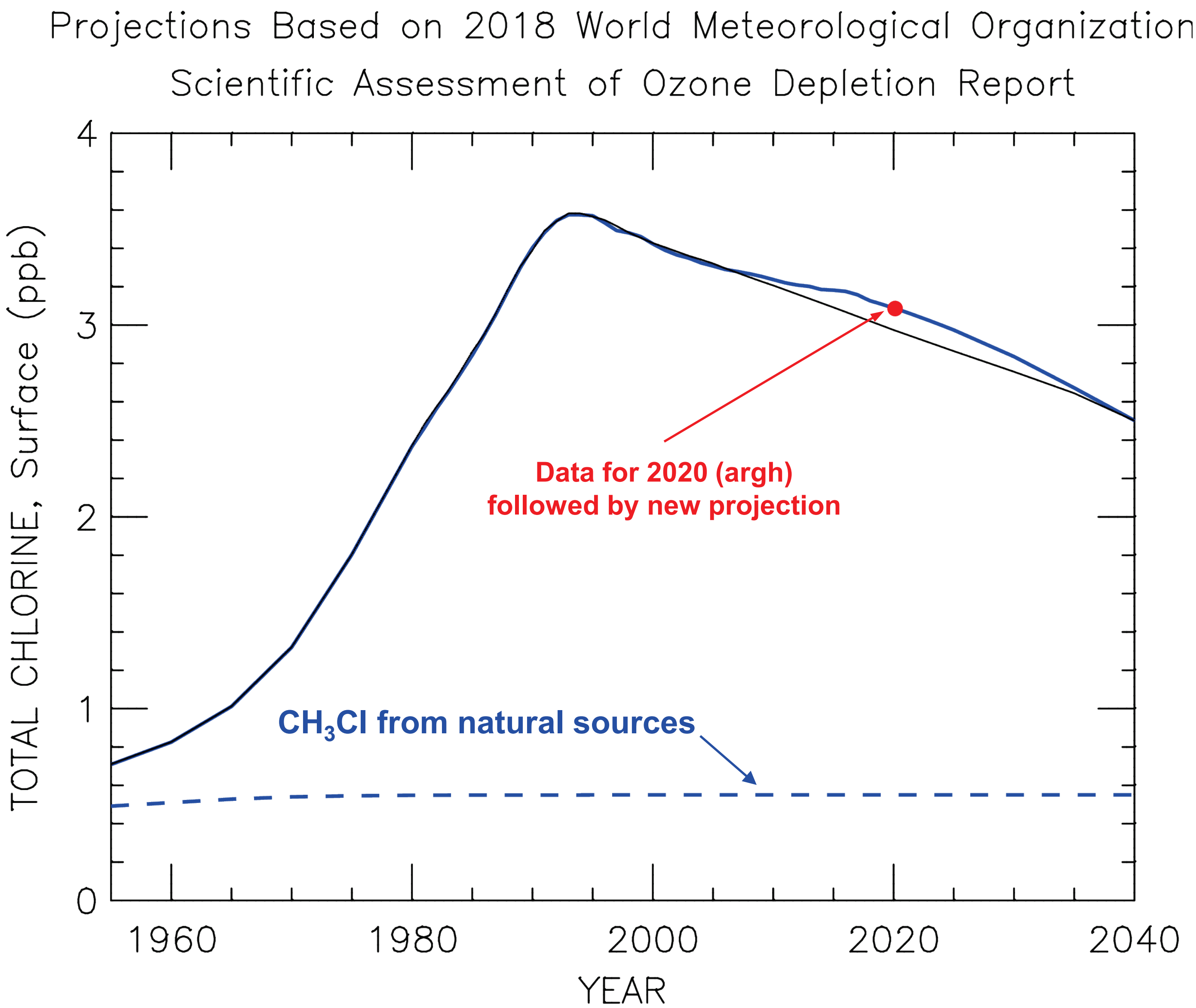


Figure Q19-2, 20 QAs about the Ozone Layer

Montreal Protocol Has Banned Industrial Production of CFCs & Other ODS



Montreal Protocol Has Banned Industrial Production of CFCs & Other ODS



Montreal Protocol Had Banned Most Industrial Production of CFCs & Other ODS

The New York Times

In a High-Stakes Environmental Whodunit, Many Clues Point to China

Interviews, documents and advertisements collected by The New York Times and independent investigators indicate that a major source — possibly the overwhelming one — is factories in China that have ignored a global ban and kept making or using the chemical, CFC-11, mostly to produce foam insulation for refrigerators and buildings.

"You had a choice: Choose the cheaper foam agent that's not so good for the environment, or the expensive one that's better for the environment," said Zhang Wenbo, owner of a refrigerator factory here in Xingfu, in Shandong Province, where he and many other small-scale manufacturers said that until recently, they had used CFC-11 widely to make foam insulation.

Billboards in Xingfu, China, promoting locally made refrigerators. The city has around 1,700 businesses involved in the production of cooking and refrigeration equipment. Gilles Sabrié for The New York Times

https://www.nytimes.com/2018/06/24/world/asia/china-ozone-cfc.html

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 ($\mu g/m^3$)
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
$PM_{2.5}$, 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 most of the U.S. is 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 Production

$$OH + \mathbf{CO} \rightarrow \mathbf{CO_2} + H$$

$$H + \mathbf{O_2} + M \rightarrow HO_2 + M$$

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

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

$$O + \mathbf{O_2} + M \rightarrow \mathbf{O_3} + M$$

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

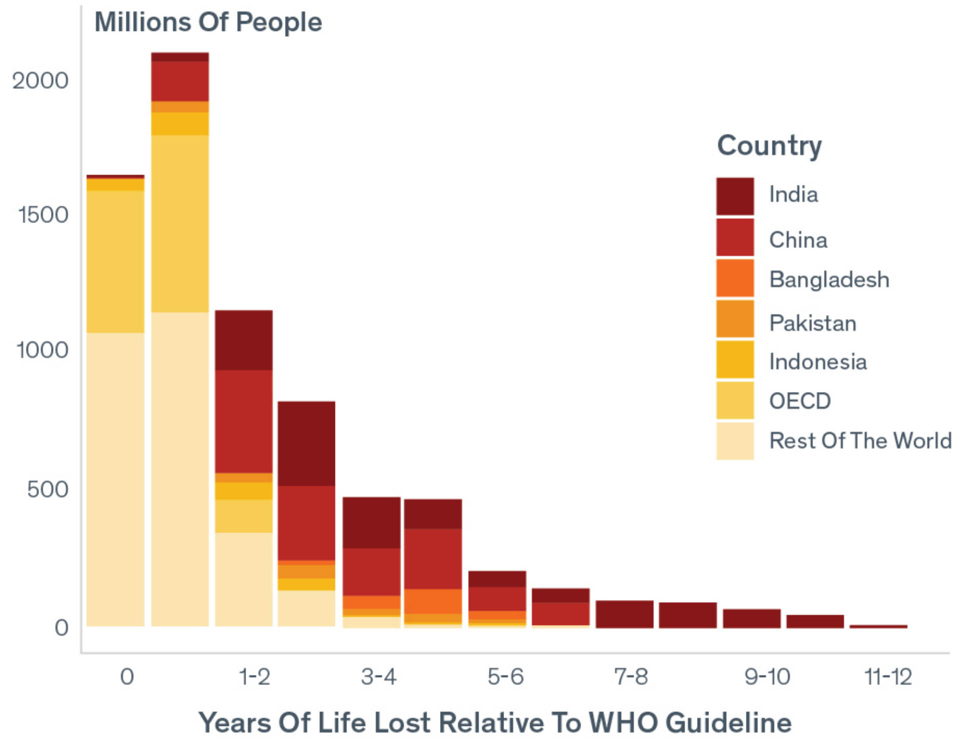
Oxidation of CO in the presence of elevated NO_x ($NO + NO_2$) leads to ***production*** of tropospheric ozone

Air Quality Standards and Why We Care

For more information, have a look at:

https://www.weforum.org/agenda/2018/11/deadly-air-pollution-shortens-lives-by-nearly-2-years-researchers

https://aqli.epic.uchicago.edu/pollution-facts

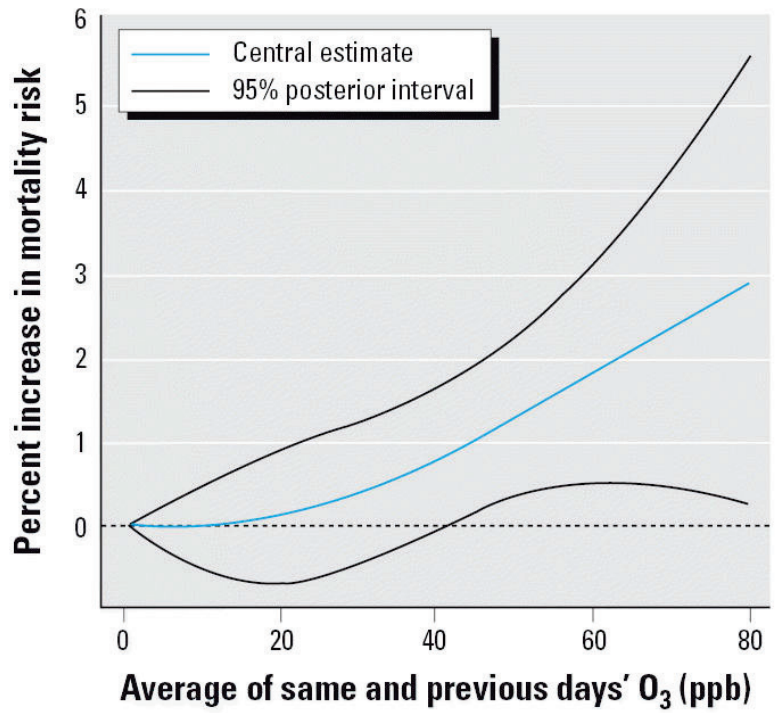


If all areas not in compliance with the WHO $PM_{2.5}$ guideline in 2016 were to permanently reduce their particulate pollution levels to meet the guideline, then, globally:

- 288 million people, all in northern India would live at least 7 years longer on average. These people represent 23 percent of India's current population.
- 347 million people in Asia would live 5-7 years longer on average. These include 35 percent of Nepal's population, 16 percent of Bangladeshis, 13 percent of Chinese, 10 percent of Pakistanis, 9 percent of Indians, and 1 percent of Indonesians.

https://aqli.epic.uchicago.edu/pollution-facts

Air Quality Standards and Why We Care

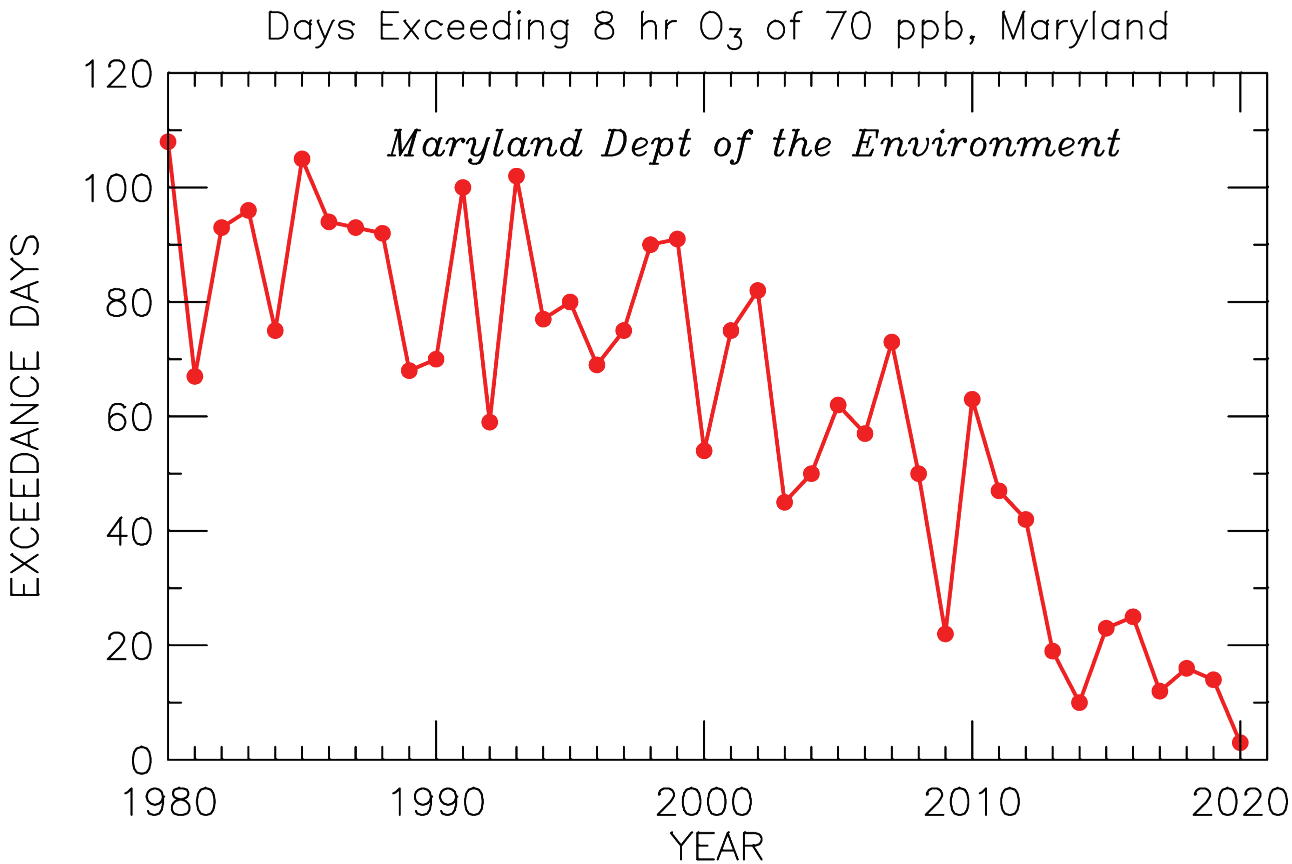


Increased risk of premature death (mortality) for all levels of surface O_3
Reductions in surface ozone will benefit public health, regardless of present conditions

Bell et al., 2006

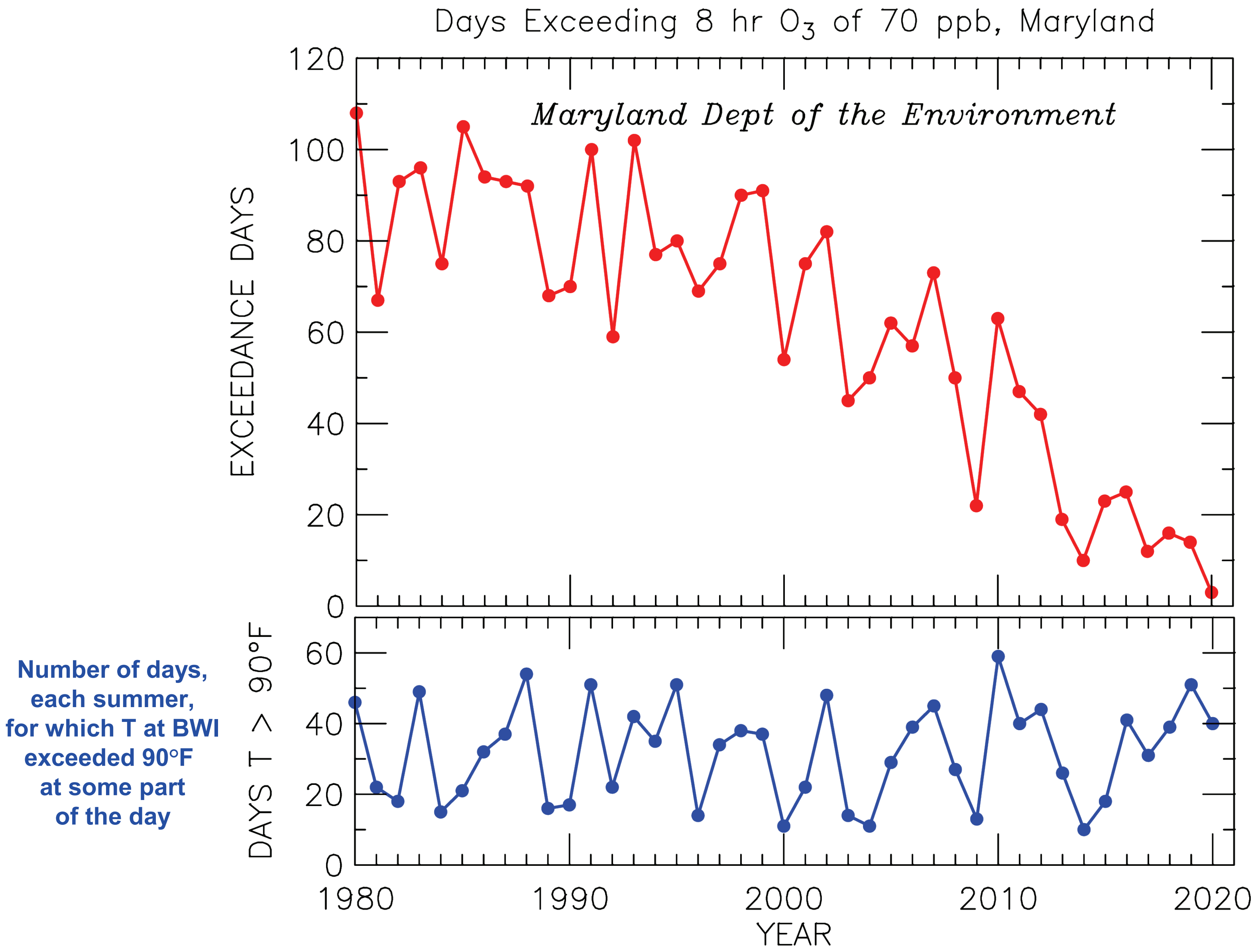
http://www.ncbi.nlm.nih.gov/sites/ppmc/articles/PMC1440776

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



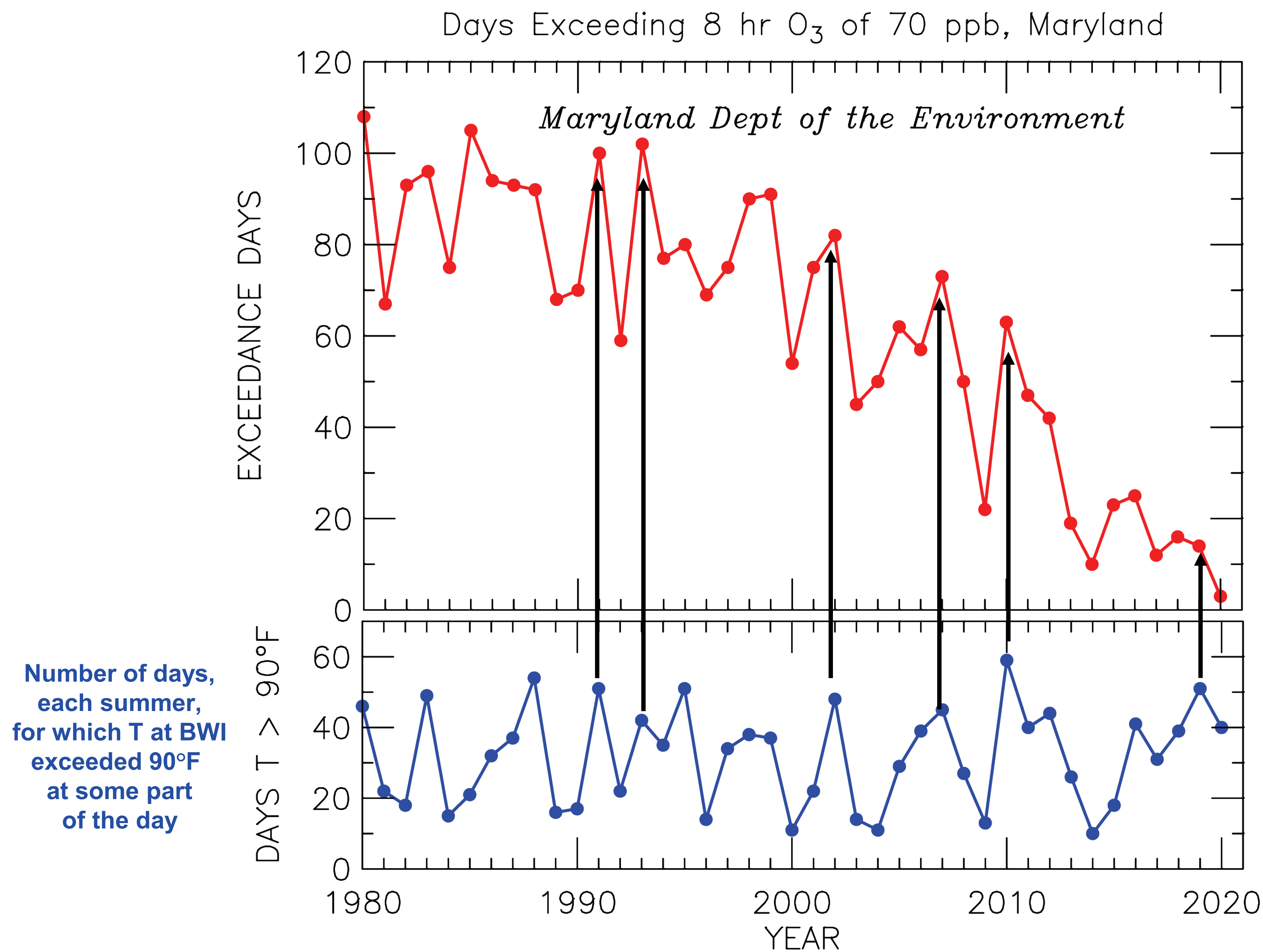
http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/SeasonalReports.aspx

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



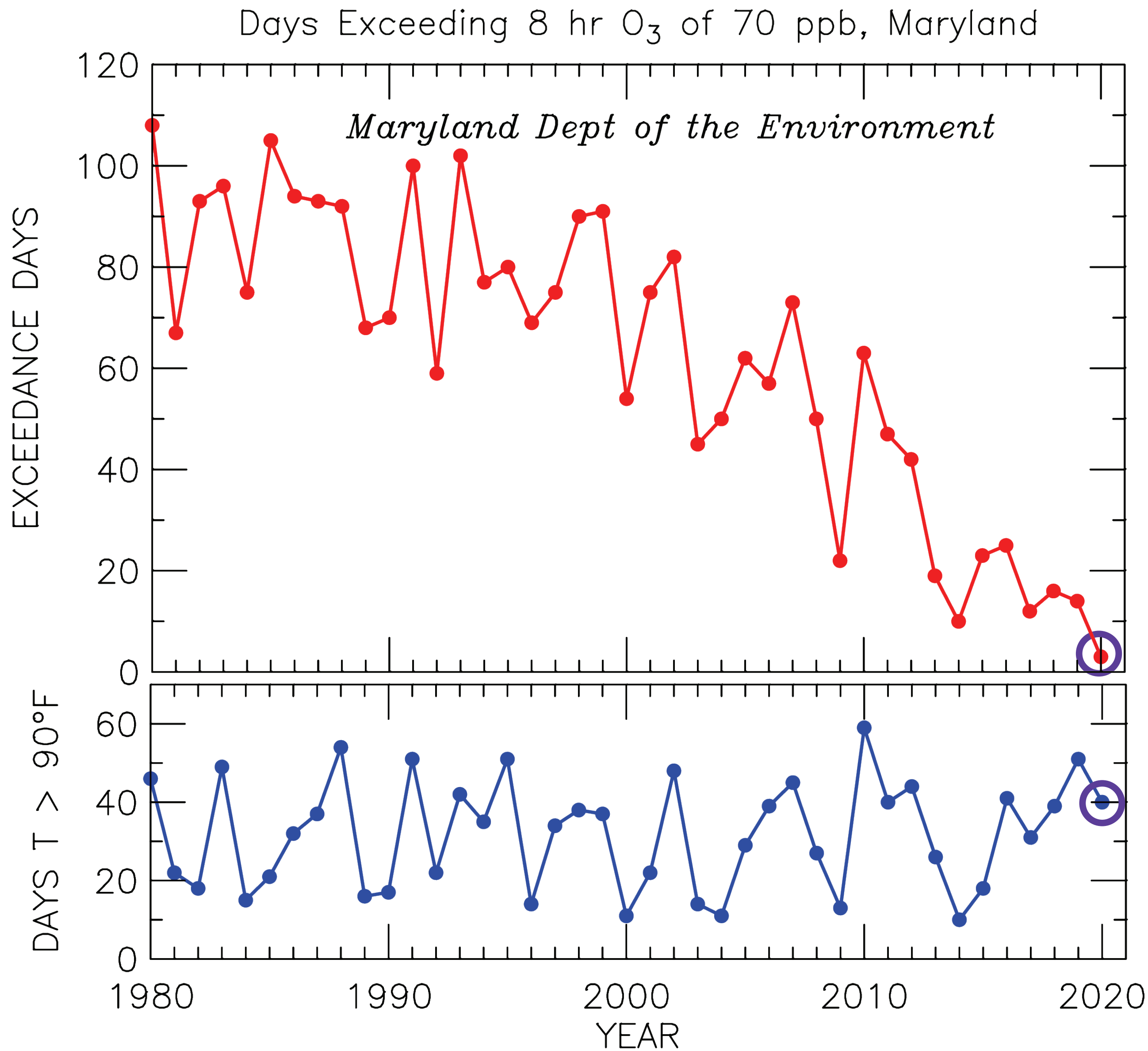
http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/SeasonalReports.aspx

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



3 surface ozone exceedances in Maryland during 2020. Would have expected many more (i.e., 12 to 16) given relation between Exceedance Days & Days T > 90°F from prior recent years.

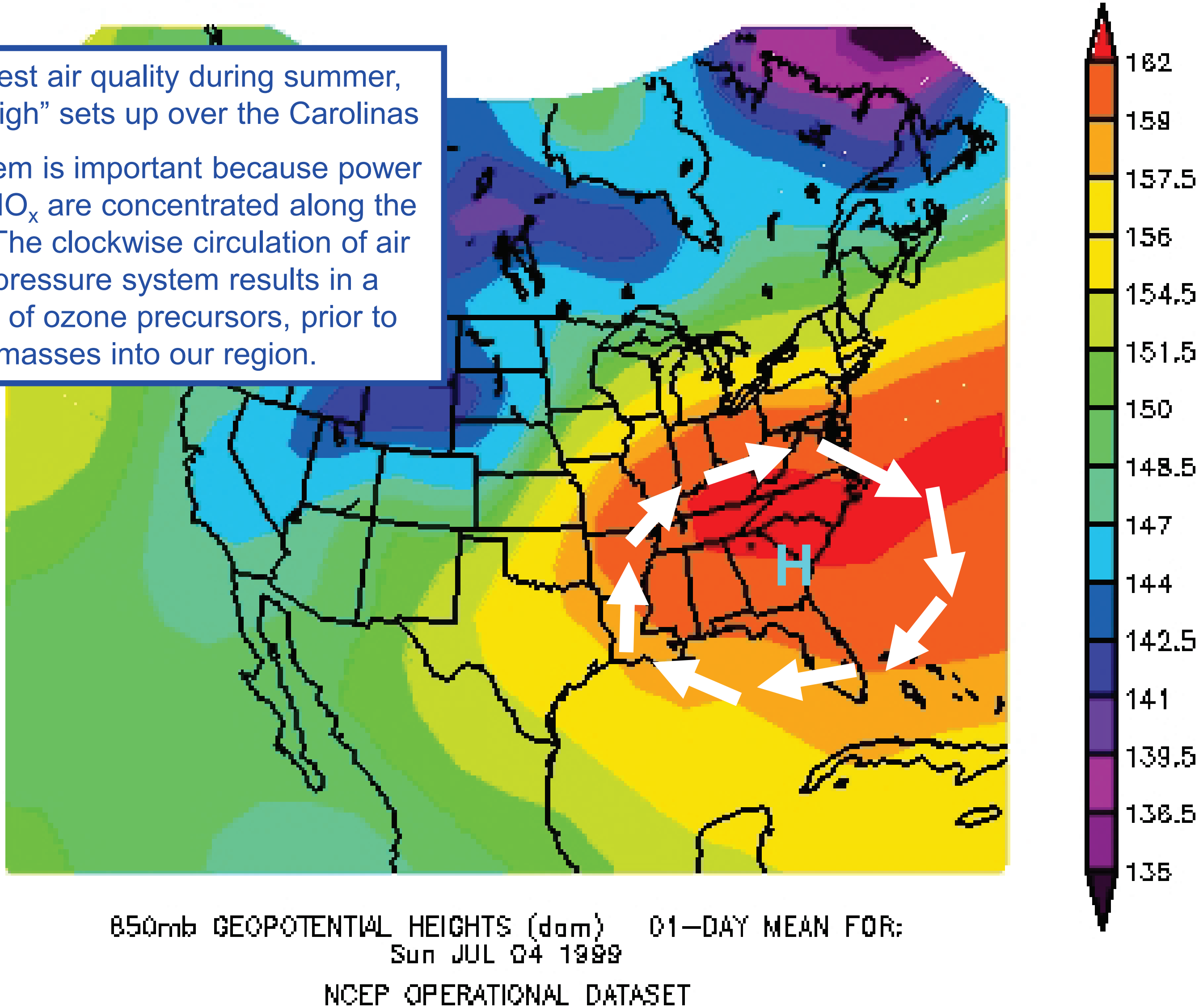
Number of days, each summer, for which T at BWI exceeded 90°F at some part of the day

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

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

Maryland has poorest air quality during summer, when a “Bermuda High” sets up over the Carolinas

This circulation system is important because power plant emissions of NO_x are concentrated along the Ohio River valley. The clockwise circulation of air around this high pressure system results in a significant build up of ozone precursors, prior to arrival of air masses into our region.



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

Temperature Inversions and Air Quality

Temperature inversion: increase in temperature with height

Inversions important for Air Quality because they inhibit vertical mixing of air

Air pollutants can accumulate in cities ringed by mountains, such as Los Angeles, Mexico City, Denver, etc.

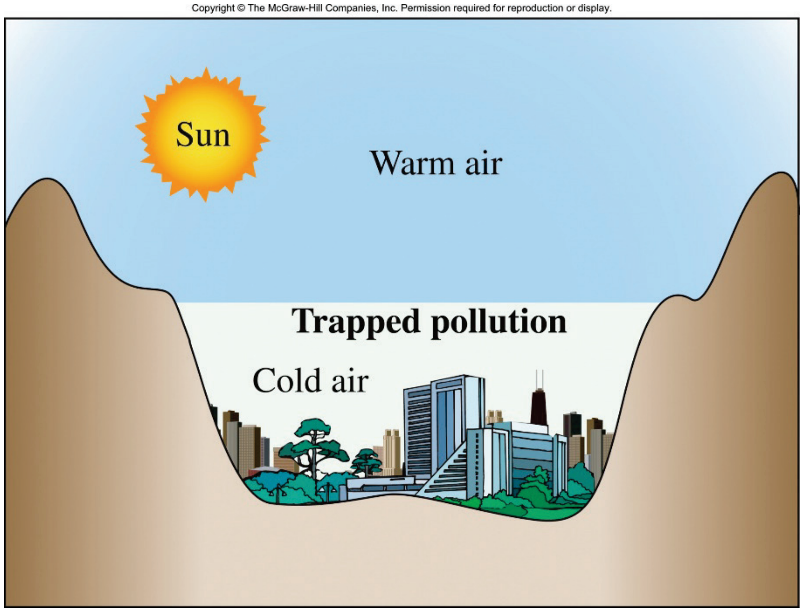
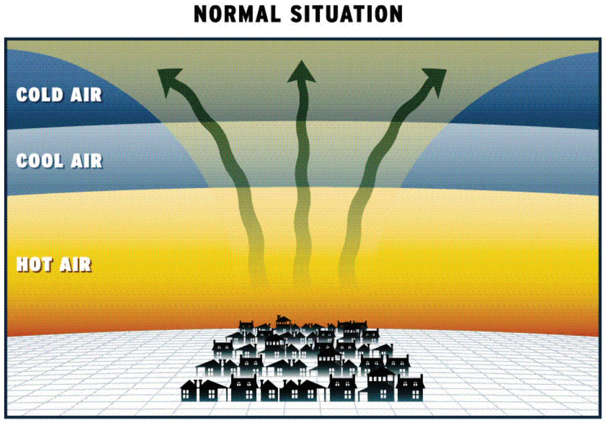
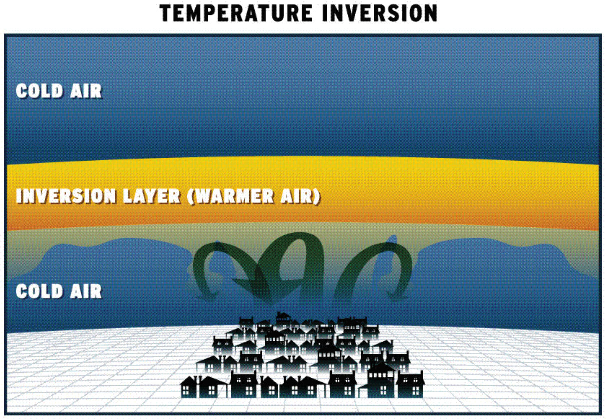


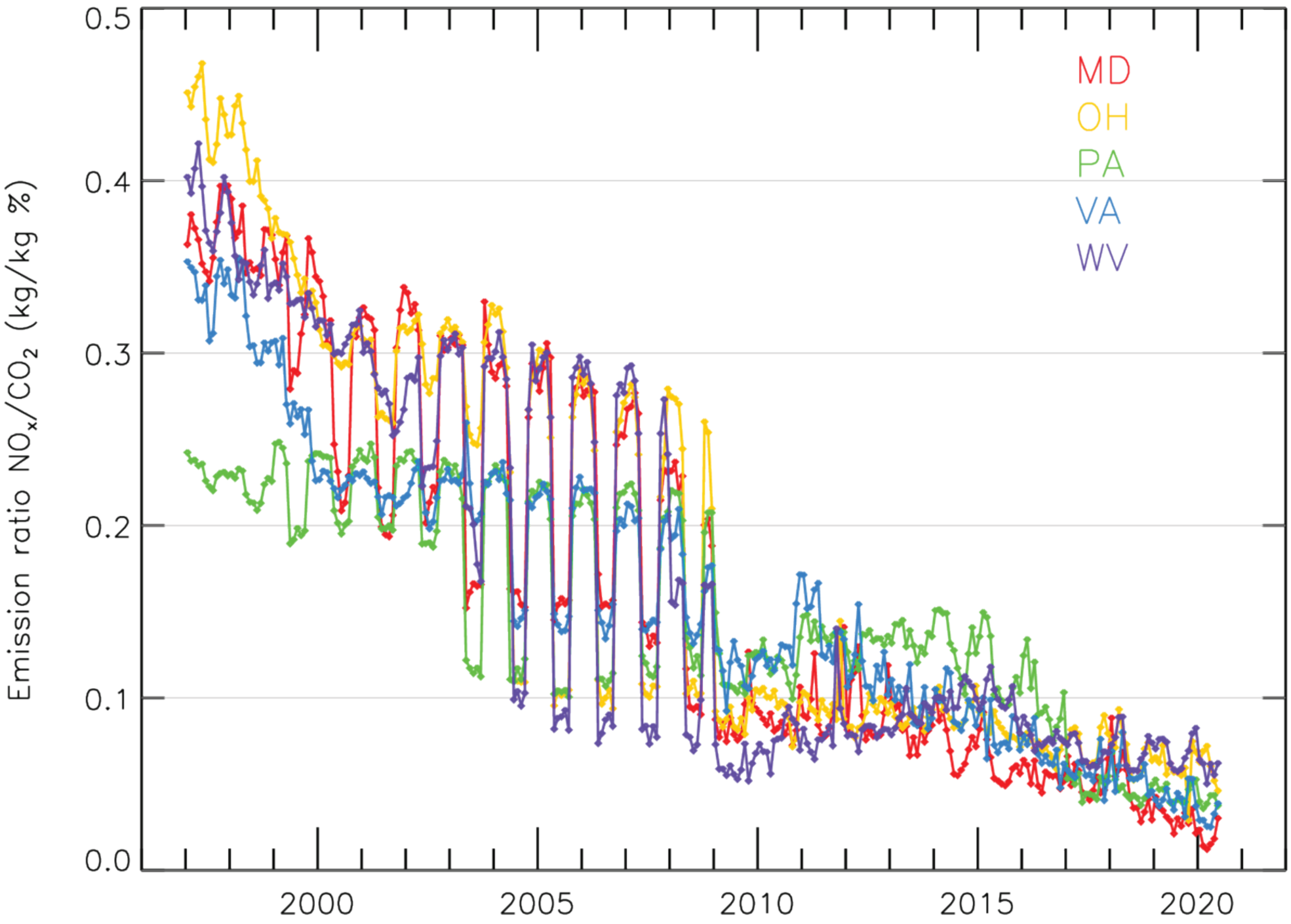
Figure 1.10, Chemistry in Context



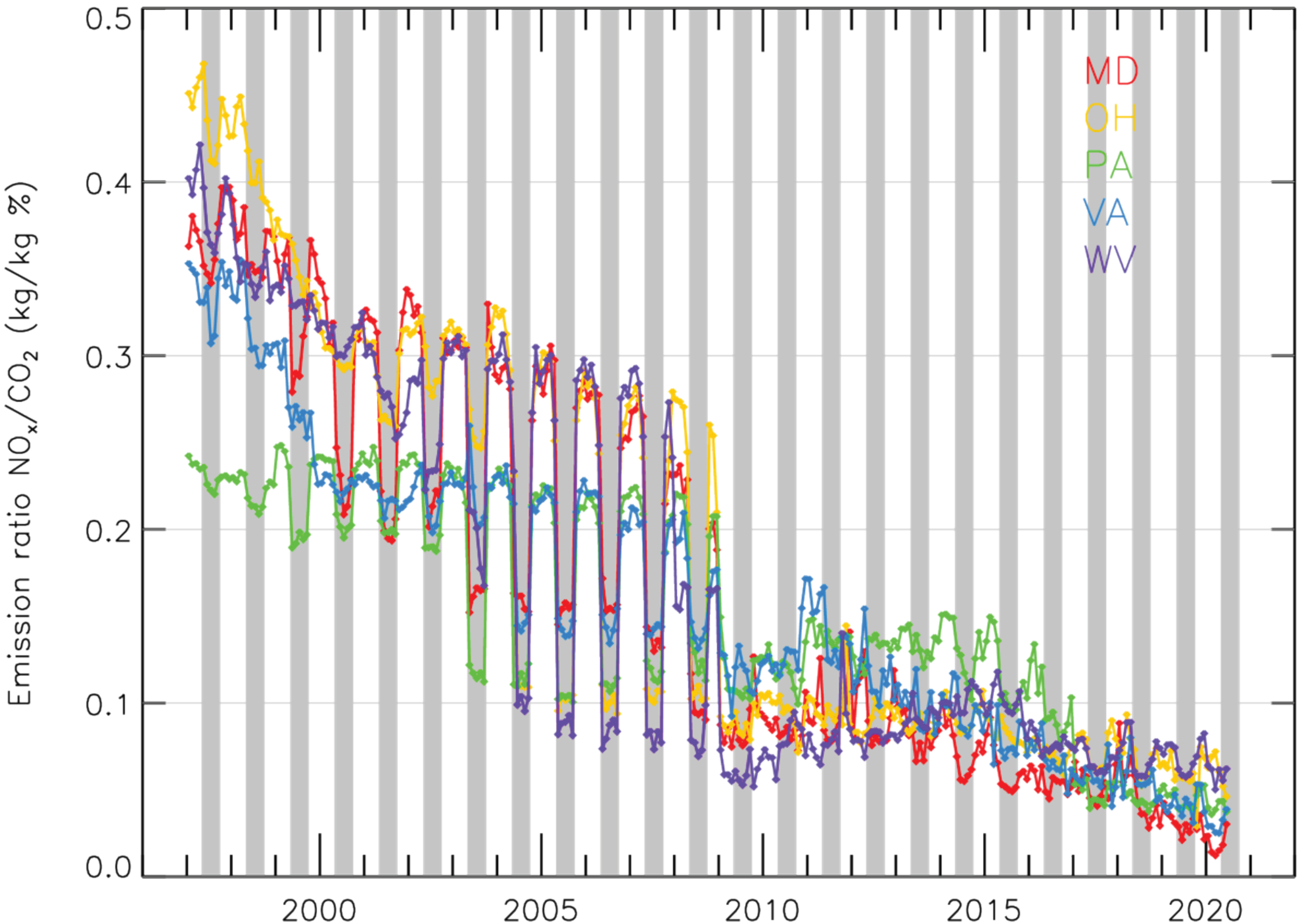


http://geographygems.blogspot.com/2011/09/smog.html

Trends in power plant emissions of NOx

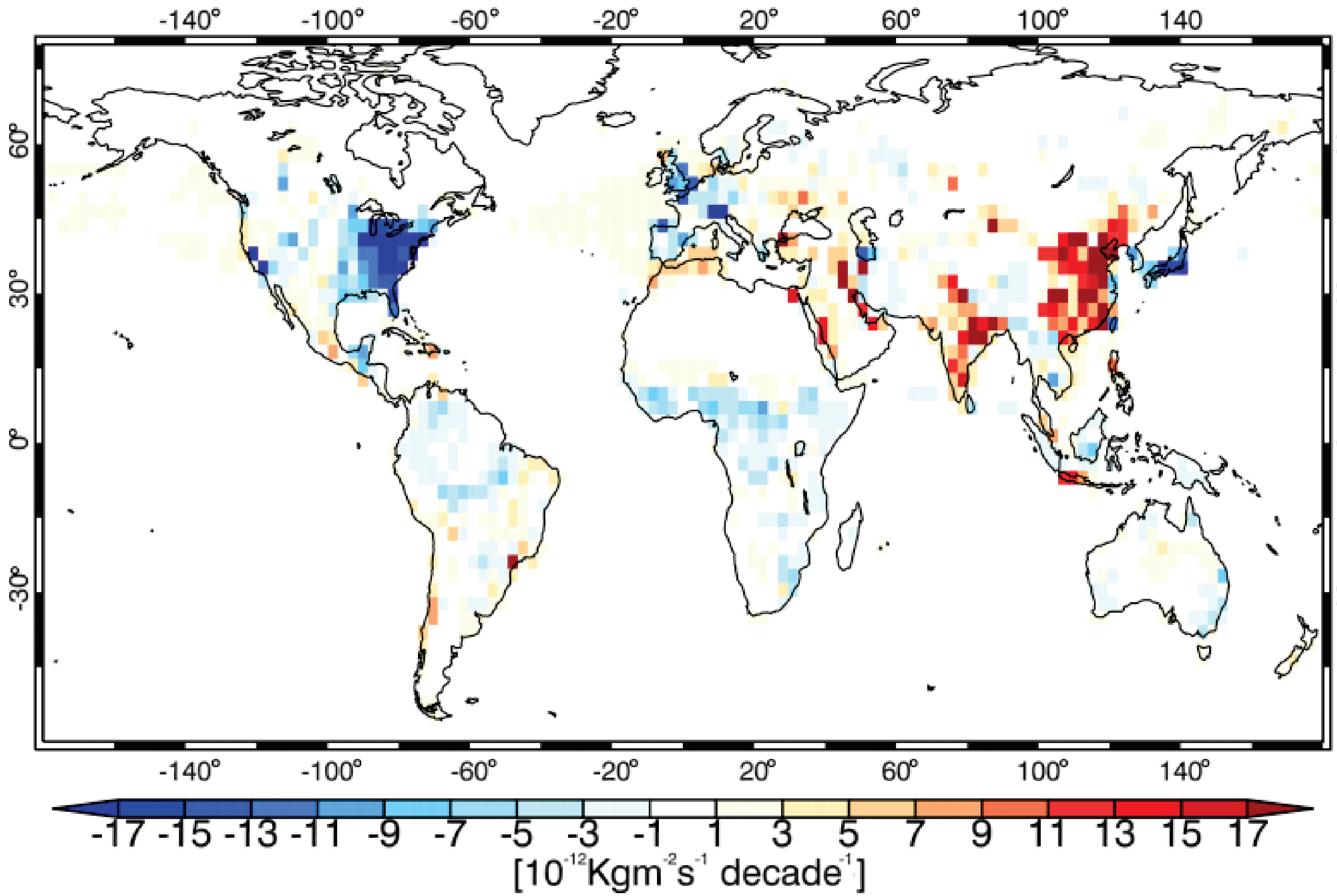


Trends in power plant emissions of NOx



Shading denotes "ozone season", April to Sept

NOx emission trend: 2005–2014



Global distribution of the trend in the surface emission of NO_x ($NO + NO_2$) in units of kg m^{-2} s^{-1} per decade, from the assimilation of multiple satellite data sets.

Miyazaki *et al.*, *ACP*, 2017
https://www.atmos-chem-phys.net/17/807/2017/

Wildfires are Raging in California and Colorado

Top: Creek fire in Sierra National Forest of Madera County near Fresno, California
https://kmph.com/news/local/gallery/creek-fire-fox26-viewers-capture-photos-and-video-of-aftermath
Bottom left: Bobcat Fire in Angeles National Forest near Los Angeles, California
https://www.facebook.com/WilsonObs/
Bottom right: Cameron Peak fire in Larimer County, Rocky Mountain National Park, near Boulder Colorado
https://www.denverpost.com/2020/09/06/cameron-peak-wildfire-evacuations-sunday/

As well as states of Utah, Oregon, and Washington

DailyMail.com

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At least one dead as wildfires trap hikers in California, decimate an entire town in Washington, burn in Utah and Colorado and lead to more than 100,000 losing power in Oregon during record heatwave

Military helicopters tried to rescue around 50 people trapped by wildfires in California on Monday night, but were beaten back by heavy smoke as wildfires spread across Western states in the midst of a record-breaking heatwave. The group of hikers and campers remain trapped by Lake Edison, 250 miles east of San Francisco in the Sierra National Forest. At least one person has died, said Fresno Fire Battalion Chief Tony Escobedo, and warned there may be multiple casualties. 'Rescue efforts were unsuccessful, military pilots tried valiantly to land but heavy smoke conditions prevented a safe approach,' the fire department tweeted. 'Another effort will be made shortly to evacuate the trapped people in Lake Edison and China Peak using night vision.' Monday's frantic rescue attempt came as wildfires blazed across swathes of the western United States on Monday night, destroying homes and devastating forests and grasslands, as record high temperatures and strong winds made the task of fire fighters even more challenging. In California, 14,100 fire fighters were battling 24 separate blazes, which have collectively destroyed 2 million acres.

Share 2.3k | 60 comments | 2 videos

https://www.dailymail.co.uk/news/article-8708045/Wildfires-rage-amid-record-breaking-temperatures.html

Wildfires are Raging in California and Colorado

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Tweet

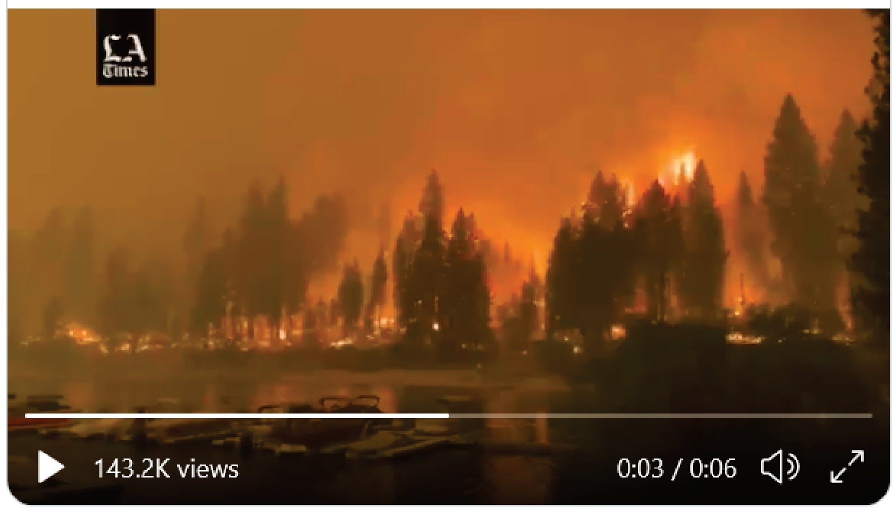
Robert Rohde
8,306 Tweets
Following

More Topics

Robert Rohde @RARohde · Sep 6
Wildfires surge when climate change makes local conditions hotter and drier than the existing local vegetation is able to tolerate.

At the start of the year Australia was burning, now it is California, and there will be more to come.

Kent K. Nishimura @kentnish · Sep 6
The #CreekFire has made its way to Shaver Lake. @latimes @latimesphotos
Show this thread



31 49

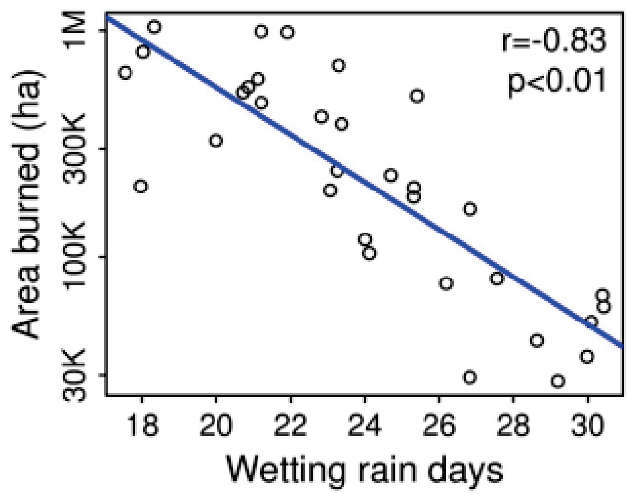
https://twitter.com/RARohde

July 2018 paper linking fires to climate change

Decreasing fire season precipitation increased recent western US forest wildfire activity

Zachary A. Holden[a,1], Alan Swanson[b], Charles H. Luce[c], W. Matt Jolly[d], Marco Maneta[e], Jared W. Oyler[f], Dyer A. Warren[b], Russell Parsons[d], and David Affleck[g]

[a]US Forest Service Region 1, Missoula, MT 59807; [b]School of Public and Community Health Sciences, University of Montana, Missoula, MT 59812; [c]US Forest Service Aquatic Science Laboratory, Rocky Mountain Research Station, Boise, ID 83702; [d]US Forest Service, Fire Sciences Laboratory, Rocky Mountain Research Station, Missoula, MT 59808; [e]Department of Geosciences, University of Montana, Missoula, MT 59812; [f]Earth and Environmental Systems Institute, Pennsylvania State University, University Park, PA 16802; and [g]Department of Forestry and Conservation, University of Montana, Missoula, MT 59812



Linear trends in logarithm of area burned versus wetting rain days, where wetting rain days is number of days with precipitation ≥2.54 mm (inch)

https://www.pnas.org/content/115/36/E8349.short

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PNAS

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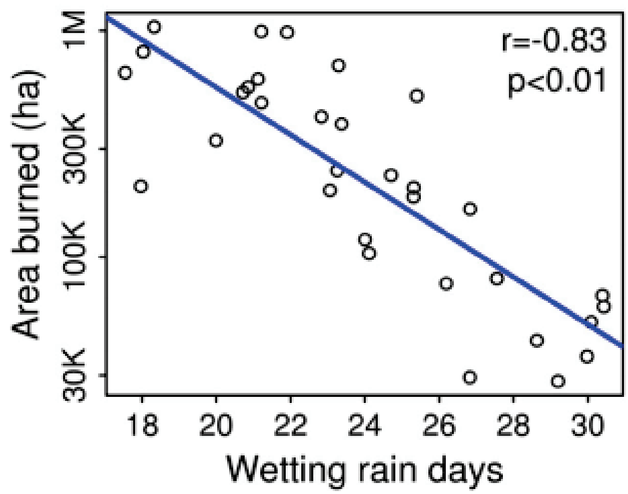

Linear trends in logarithm of area burned versus wetting rain days, where wetting rain days is number of days with precipitation ≥2.54 mm (0.1 inch)

https://www.pnas.org/content/115/36/E8349.short

Wildfires are Raging in California and Colorado

Paul Ottolenghi Wennberg
898 Tweets

Following

Paul Ottolenghi Wennberg @wennbergcaltech · Sep 6
Pasadena: 113F, 140 ppb ozone, <250 ppt NO and, now, a big fire in the Angeles forest. 2020 is really on a roll.

3 13 54

Paul Ottolenghi Wennberg @wennbergcaltech · Sep 6
now 200 ppb ozone. toxic.

4 3 18

Paul Ottolenghi Wennberg @wennbergcaltech · 8h
Data from Caltech air quality station set up for summer 'COVID' campaign. The airmass with very high ozone (and SO2 and CO) was observed between 2:15 and 2:45 PM yesterday. Other than that, ozone was 'only' between 100 and 150 ppb for most of the afternoon.

https://twitter.com/wennbergcaltech

Next Lecture: Fundamentals of Earth's Atmosphere

Great if you can complete Learning Outcome Quizzes 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) as well as 4 pages (433) or 7 pages (633) from *Atmospheric Environment* by Michael McElroy

Admission Ticket for Lecture 3 is posted on ELMS

Please have a calculator available for class on Thursday