Overview of Global Warming, Ozone Depletion, and Air Quality

AOSC / CHEM 433 & AOSC 633

Ross Salawitch & Walt Tribett



Lecture 2 5 February 2019

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Overview of Global Warming, Ozone Depletion, and Air Quality

Course theme: effect of human activity on:

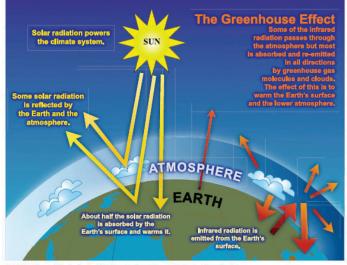
- climate change
- air quality
- stratospheric ozone depletion and recovery

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". Do expect, however, that when you review this lecture at the end of semester, details will be understandable
- 3) Current events & linkages between topics, often thought of as "disparate" but connected in **profoundly important manners**

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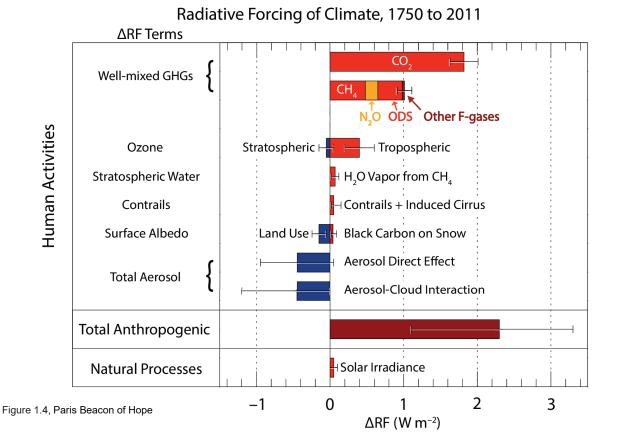
Greenhouse Effect



FAQ 1.3, Figure 1. An idealised model of the natural greenhouse effect. See text for explanation. Question 1.3, IPCC, 2007

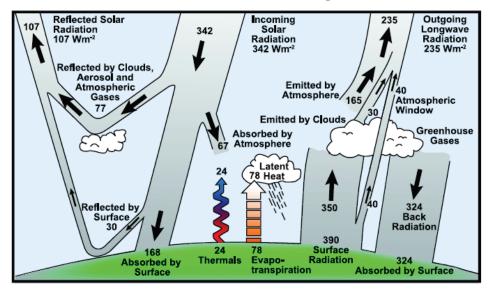
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Radiative Forcing



FAQ 1.1, Figure 1. Estimate of the Earth's annual and global mean energy balance. Over the long term, the amount of incoming solar radiation absorbed by the Earth and atmosphere 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 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 evaportanspiration and by longwave radiation that is absorbed by the Sabrate by douds and greenhouse gases. The atmosphere in turn radiates longwave energy back to Earth as well as out to space. Source: Kiehl and Tenberth (1997).

Question 1.1, IPCC, 2007

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

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Radiative Forcing of Climate, 1750 to 2011

CO₂ is dominant anthropogenic (human) greenhouse gas (GHG). Once released, CO₂ 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 Methane (CH₄) is the 2^{nd} most important human GHG. Once released, CH₄ persists in the atmosphere for <u>about decade</u>.

On a per molecule basis, CH₄ 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 Nitrous oxide (N_2O) is commonly identified as the third most important anthropogenic GHG.

> On either a per molecule or a per mass basis, N₂O causes 264 times more warming than CO₂ 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

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 <u>about half</u> 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.

Ozone (O₃) 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 O₃ in Earth's troposphere leading to poor public health. Efforts to combat the ruse in tropospheric O₃ are led by air quality agencies. 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".

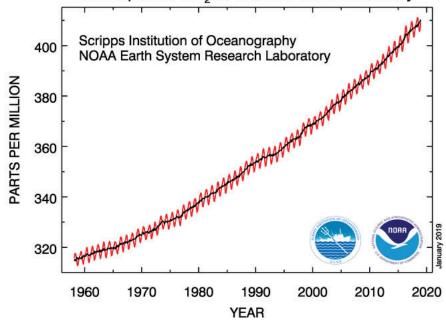
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Modern CO₂ Record

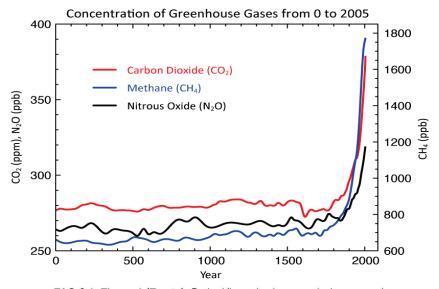
CO₂ at MLO on 20 Jan 2019: 412 parts per million (ppm) and rising !

Atmospheric CO₂ at Mauna Loa Observatory



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

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 line for CH₄ had been plotted incorrectly

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GHG Record Over Last Several Millennia

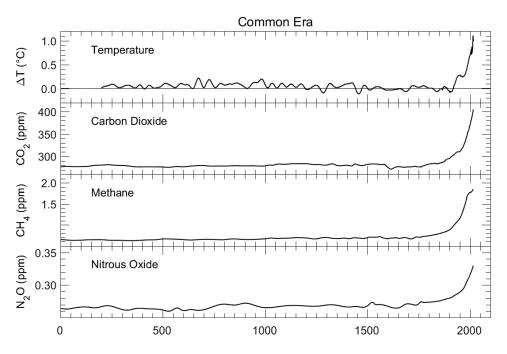
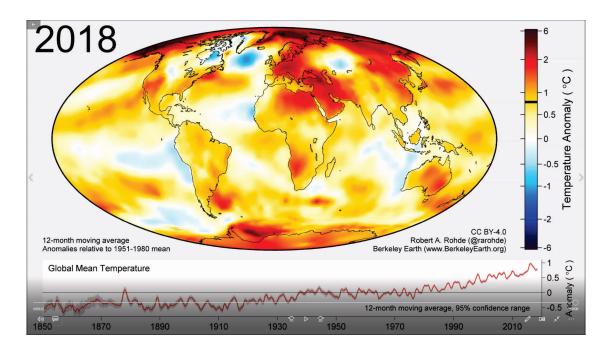


Figure 1.2, Paris Beacon of Hope

Berkeley Earth Animation of Global Warming



Work of Robert Rohde and the Berkeley Earth Team <u>http://berkeleyearth.org</u> <u>http://berkeleyearth.org/2018-temperatures/</u>

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GWP – Global Warming Potential

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

where:

 $a_{\rm CH4}$ = Radiative Efficiency (W m⁻² kg ⁻¹) due to an increase in CH₄

 $a_{\rm CO2}$ = Radiative Efficiency (W m⁻² kg⁻¹) due to an increase in CO₂

 $CH_4(t)$ = 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

$$\text{GWP}(N_2\text{O}) = \frac{\int_{\text{time initial}}^{\text{time final}} a_{\text{N2O}} \times [N_2\text{O}(t)] \text{ dt}}{\int_{\text{time initial}}^{\text{time final}} a_{\text{CO2}} \times [\text{CO}_2(t) \text{ dt}]}$$

GWP - Global Warming Potential

Table TS.2. Lifetimes, radiative efficiencies and direct (except for CH2) global warming potentials (GWP) relative to CO2. {Table 2.14}

Industrial Designation			Radiative	Global Warming Potential for Given Time Horizon			
or Common Name (years)	Chemical Formula	Lifetime (years)	Efficiency (W m ⁻² ppb ⁻¹⁾	SAR‡ (100-yr)	20-yr	100-yr	500-yr
Carbon dioxide	CO2	See below ^a	^b 1.4x10 ^{−5}	1	1	1	1
Methanec	CH ₄	12°	3.7x10-4	21	72	25	7.6
Nitrous oxide	N ₂ O	114	3.03x10-3	310	289	298	153

Notes:

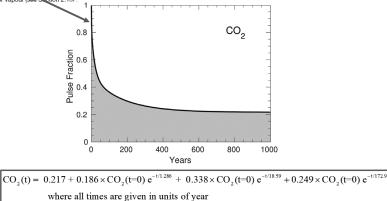
[‡] SAR refers to the IPCC Second Assessment Report (1995) used for reporting under the UNFCCC.

a The CO2 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 CO2 concentration value of 378 ppm. The decay of a pulse of CO2 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.

The radiative enclancy of CO₂ is calculated using the IPCC (1990) simplified expression as revised in the TAP, 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 CH₂ is 12 years as in the TAR (see also Se and stratospheric water vapour (see Section 2.10). ction 7.4). The GWP fo Indirect effects from enhancements of ozone



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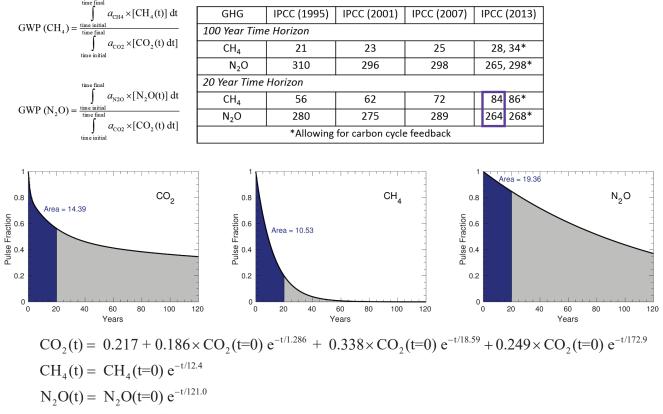
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GWP – Global Warming Potential

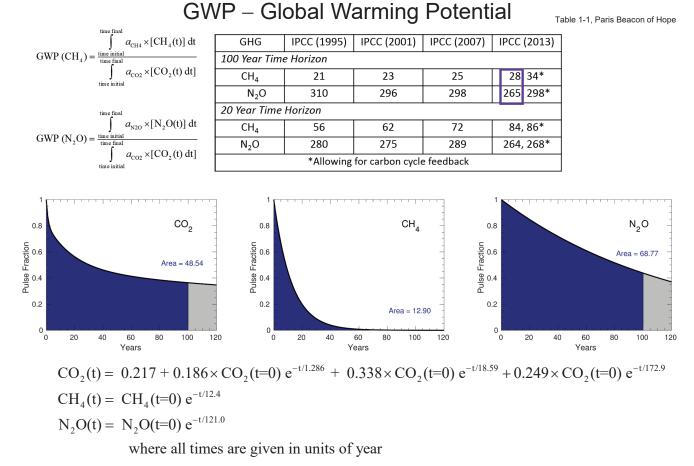
Table 1-1, Paris Beacon of Hope

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from IPCC 2007 "Physical Science Basis"



where all times are given in units of year



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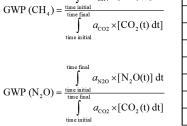
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GWP - Global Warming Potential

 GHG
 IPCC (1995)
 IPCC (2001)
 IPCC (2007)
 IPCC (2013)

 O'Year Time Horizon
 CH₄
 21
 23
 25
 28
 34*

 N.O
 310
 296
 298
 265
 298*



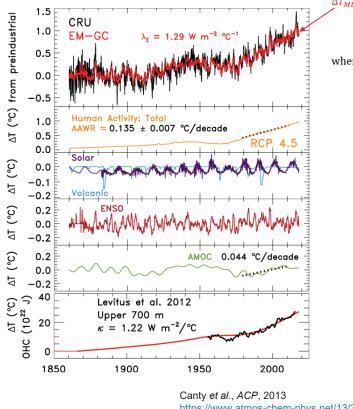
 $\int a_{\rm CH4} \times [\rm CH_4(t)] \, dt$

_	100 Year Time	e Horizon				
t]	CH ₄	21	23	25	28	34*
	N ₂ O	310	296	298	265	298*
	20 Year Time	Horizon				
lt	CH ₄	56	62	72	84	86*
t]	N ₂ O	280	275	289	264	268*
IJ		*Allowing	for carbon cycle	e feedback	_	

$$\begin{array}{l} \text{CO}_2 - \text{equivalent emissions} = \text{ Emissions of CO}_2 + \\ & \text{Emissions of CH}_4 \times \text{GWP of CH}_4 + \\ & \text{Emissions of N}_2\text{O} \times \text{GWP of N}_2\text{O} + \\ & \text{etc.} \end{array}$$

Commonly, GWPs on 100 year time horizon are used although entities such as the Sierra Club prefer the 20 year time horizon





GHG RF_i + LUC RF_i + Aerosol RF $\Delta T_{MDL i}$ λ_p $C_0 + C_1 \times SOD_{i-6} + C_2 \times TSI_{i-1} + C_3 \times ENSO_{i-2} + C_3 \times COD_{i-6} + C_2 \times TSI_{i-1} + C_3 \times COD_{i-6} + C_2 \times TSI_{i-1} + C_3 \times COD_{i-6} + C_2 \times TSI_{i-1} + C_3 \times COD_{i-6} + C_3$ $C_4 \times AMOC_i - \left(\frac{Q_{OCEAN_i}}{\lambda_n}\right)$

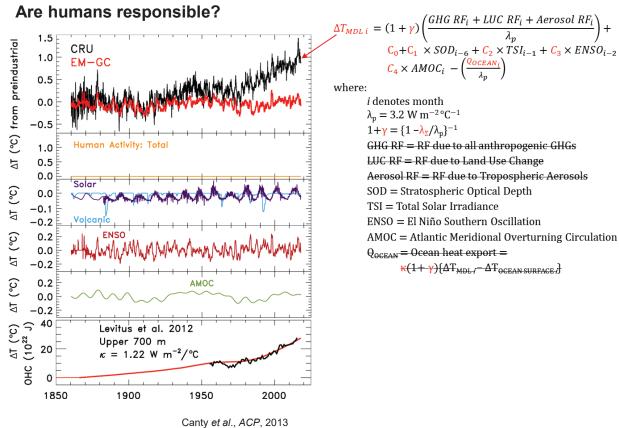
where:

i denotes month $\lambda_{\rm p} = 3.2 \text{ W m}^{-2} \,^{\circ}\text{C}^{-1}$ $1+\gamma = \{1 - \lambda_{\Sigma}/\lambda_n\}^{-1}$ GHG RF = RF due to all anthropogenic GHGsLUC 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 $Q_{OCEAN} = Ocean heat export =$ $\kappa (1 + \gamma) \{ \Delta T_{MDL i} - \Delta T_{OCEAN SURFACE i} \}$

https://www.atmos-chem-phys.net/13/3997/2013/acp-13-3997-2013.html updated by Austin Hope & Laura McBride

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Are humans responsible?

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

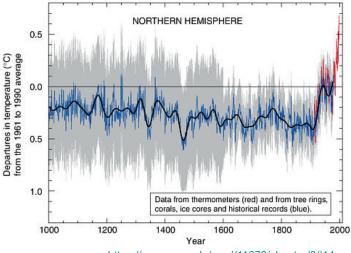
Volcanoes: no sustained forcing

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



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

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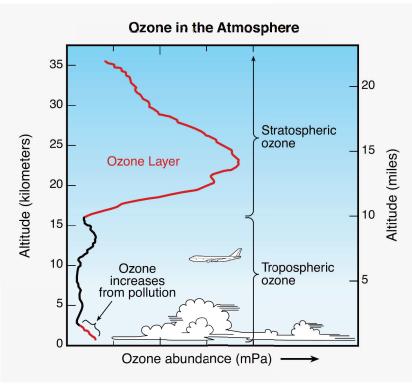
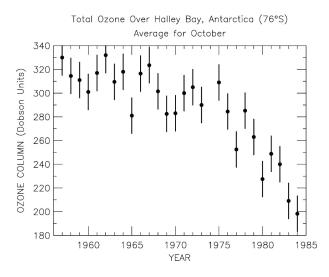


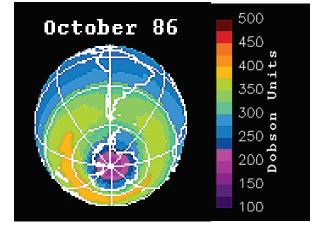
Fig. Q1-2, 20 QAs about O₃

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

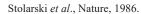
Earth's Atmosphere – Effect of Humans

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.

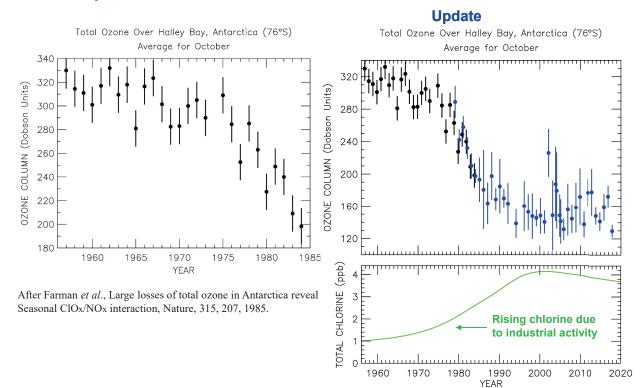


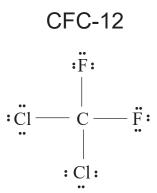
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Earth's Atmosphere – Effect of Humans

Stratospheric Ozone - shields surface from solar UV radiation





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

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Measurements of Reactive Chlorine From Space

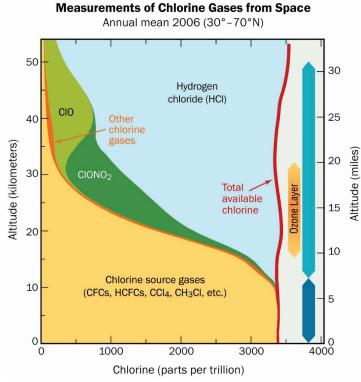
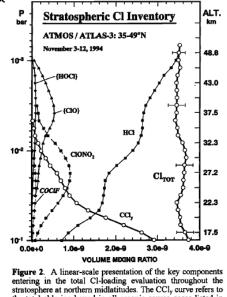


Fig. Q8-2, 20 QAs about O₃

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The 1994 northern midlatitude budget of stratospheric chlorine derived from ATMOS/ATLAS-3 observations

R. Zander,¹ E. Mahieu,¹ M. R. Gunson,² M. C. Abrams,³ A. Y. Chang,² M. Abbas,⁴ C. Aellig,⁵ A. Engel,⁶ A. Goldman,⁷ F. W. Irion,⁸ N. Kämpfer,⁹ H. A. Michelsen,¹⁰ M. J. Newchurch,¹¹ C. P. Rinsland,¹² R. J. Salawitch,² G. P. Stiller, 13 and G. C. Toc



Institute of Astrophysics, University of Liège, Belgium ²Jet Propulsion Laboratory, California Institute of Technology, CA ³Science Applications International Corporation, Hampton, VA ⁴NASA Marshall Space Flight-Center, AL ⁵Naval Research Laboratory, Washington, DC ⁶Forschungszentrum, Jülich, Germany ⁷University of Denver, Denver, CO ⁸California Institute of Technology, CA ⁹University of Bern, Switzerland ¹⁰Harvard University, Cambridge, MA 11 University of Alabama, Huntsville, AL

12NASA Langley Research Center, Hampton, VA 13IMK-Forschungszentrum Karlsruhe, Germany

the total chlorine bound in all organic source gases listed the text. Cl_{TOT} represents the summation over CCl_y, HCl, ClONO₂, ClO, HOCl and COClF.

Zander et al., GRL, 1996 https://agupubs.onlinelibrary.wiley.com/doi/epdf/10.1029/96GL01792

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CIO (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

$$: \ddot{Cl} \cdot \cdot \ddot{O} \cdot \\: \ddot{Cl} - \ddot{O} \cdot \end{cases}$$
 ClO : Chlorine monoxide

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

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

$$Cl + O_3 \rightarrow ClO + O_2$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClOOCl + hv \rightarrow ClOO + Cl$$

$$ClOO + heat \rightarrow Cl + O_2$$

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Chlorine Radicals Lead to Ozone Loss

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

$$Cl + O_3 \rightarrow ClO + O_2$$

$$Cl + O_3 \rightarrow ClO + O_2$$

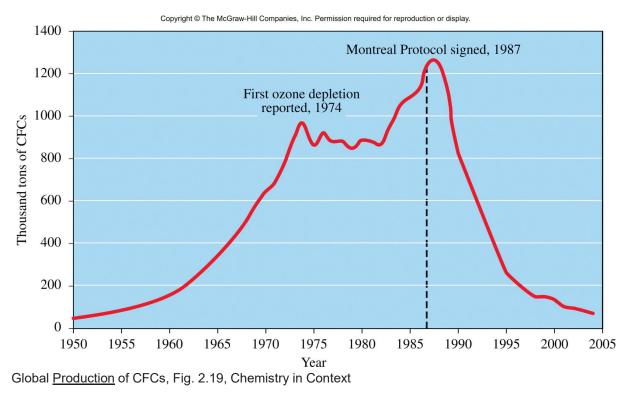
$$ClOOCl + hv \rightarrow ClOO + Cl$$

$$ClOOC + heat \rightarrow Cl + O_2$$

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

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

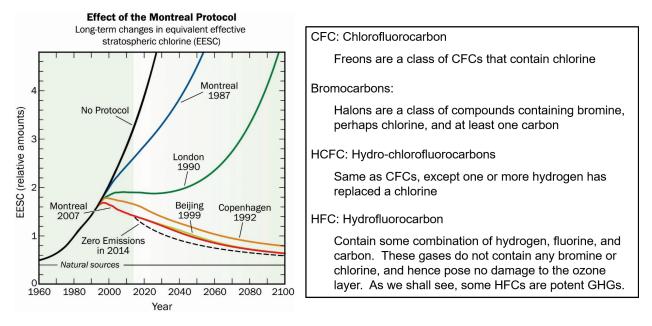
Montreal Protocol Has Banned Industrial Production of CFCs and Halons



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And Atmospheric Levels of these Pollutants are Declining



EESC: Equivalent, effective stratospheric chlorine. Reflects combined influence of chlorine and bromine on ozone. In this figure, the unit of the y-axis is "relative amount", which is an odd choice but c'est la vie.

Figure Q15-1, 20 QAs about O₃

CFC Usage Prior to the Montreal Protocol

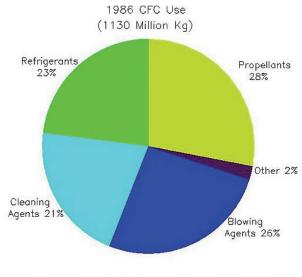


Figure 5b. Changing use patterns for CFCs (from Fisher and Midgley, 1994).

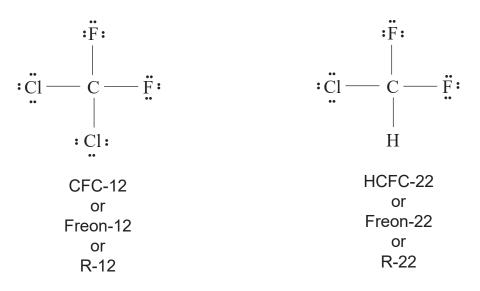
The uses of CFCs in various sectors before the 1987 Montreal Protocol, which required countries to phase out their production to protect the ozone layer.

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

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CFCs were replaced with HCFCs



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

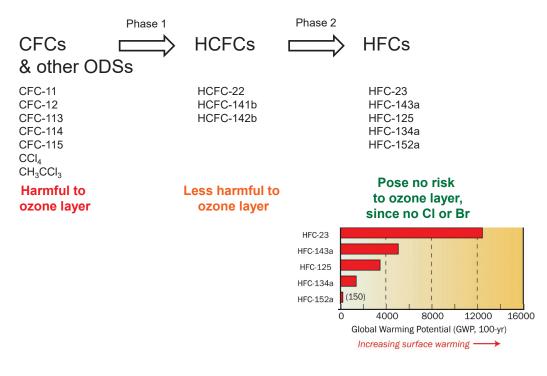


Figure Q18-3, 20 QAs about O₃

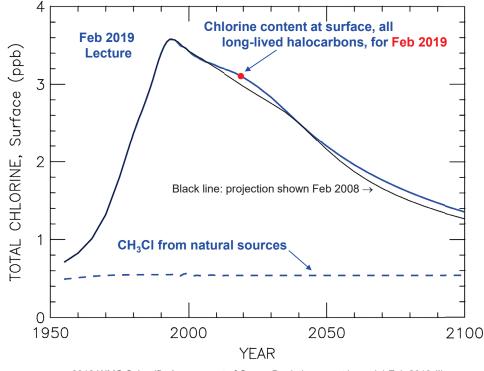
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Montreal Protocol Has Banned Industrial Production of CFCs & Other ODS

Projections Based on 2018 World Meteorological Organization

Scientific Assessment of Ozone Depletion Report



2018 WMO Scientific Assessment of Ozone Depletion report issued 4 Feb 2019 (!): https://www.esrl.noaa.gov/csd/assessments/ozone/2018

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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.



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

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Air Quality Index

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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 O₃, PM_{2.5}, and ultra-fine particles

Tropospheric Pollutants (The Air We Breathe)

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Table 1.2 U.S. Natio			
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			Note: A standard also e
Annual average	0.03	80	but lead does not
24-hr average	0.14	365	since most of the
3-hr average	0.50	1,300	

sts for lead, opear in this table S. is in compliance

 $^{*}\text{PM}_{10}$ refers to all airborne particles 10 μm in diameter or less. $\text{PM}_{2.5}$ 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.

Chapter 1 Source: U.S. Environmental Protection Agency. Standards also exist for lead, but are not included here.

Chemistry in Context

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

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Tropospheric Ozone Production

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

NO & NO₂: Emitted by fossil fuel combustion & biomass burning $N_2 + O_2 \xrightarrow{\text{High T}} 2 \text{ NO}$

CO: Emitted by fossil fuel combustion & biomass burning

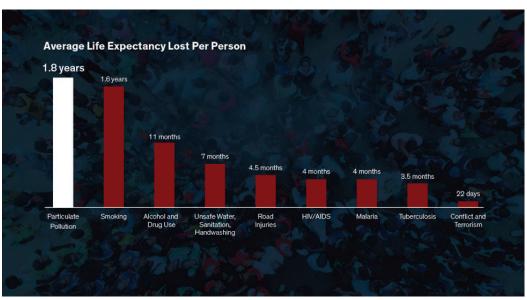
Tropospheric Ozone Production

$$OH + CO \rightarrow CO_2 + H$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
Net:
$$CO + 2O_2 \rightarrow CO_2 + O_3$$

Oxidation of CO in the presence of elevated NO_x (NO + NO₂) leads to **production** of tropospheric ozone

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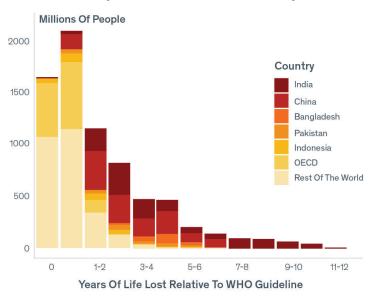


Air Quality Standards and Why We Care

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

Air Quality Standards and Why We Care



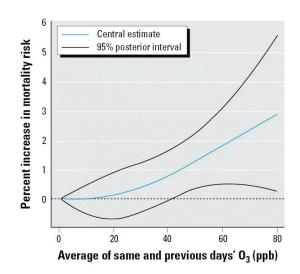
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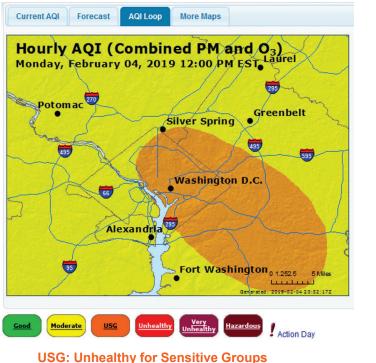
Air Quality Standards and Why We Care



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

Yesterday !!!!



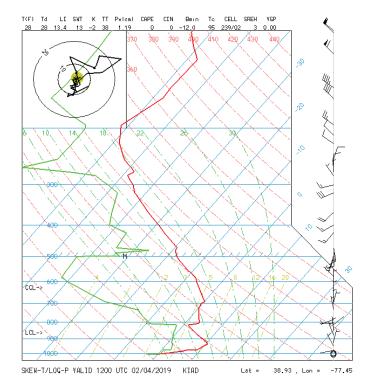
Air Quality Forecast Today Tomorrow Air Quality Index (AQI) Air Quality Index (AQI) Unhealthy for Sensitive Groups 107 76 Moderate Health Message: Unusually sensitive people should consider reducing prolonged or heavy exertion. Health Message: People with heart or lung disease, older adults, and children should reduce prolonged or heavy exertion. ACTION DAY AQI - Pollutant Details Unhealthy Particles (PM2.5) Particles ! for Sensitive 76 Moderate Gro

https://www.washingtonpost.com/weather/2019/02/04/theres-an-air-quality-alert-washington-sky-is-hazy-its-february-whats-going Anyone with asthma or other respiratory or cardiovascular conditions should sign up for AQI alerts at https://airnow.gov or http://www.enviroflash.info

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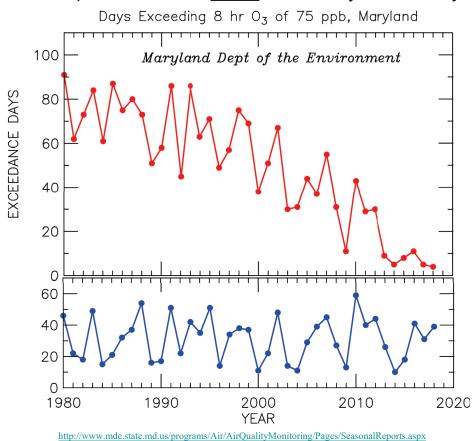
Air Quality Standards and Why We Care



Yesterday's Air Quality alert was driven by a temperature inversion as recorded at Dulles Airport <u>http://weather.rap.ucar.edu/upper/iad.gif</u> and explained in the Washington Post: <u>https://www.washingtonpost.com/weather/2019/02/04/theres-an-air-quality-alert-washington-sky-is-hazy-its-february-whats-going</u>

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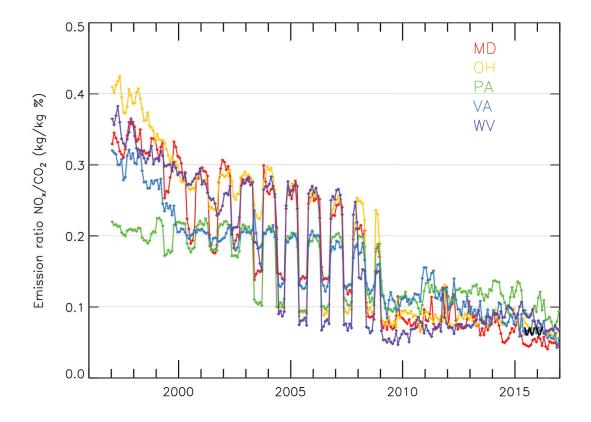




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Trends in power plant emissions of NOx



Copyright © 2019 University of Maryland. This material may not be reproduced or redistributed, in whole or in part, without written permission from Ross Salawitch. Nitrogen Dioxide (NO₂): Combustion product that leads to formation of tropospheric ozone

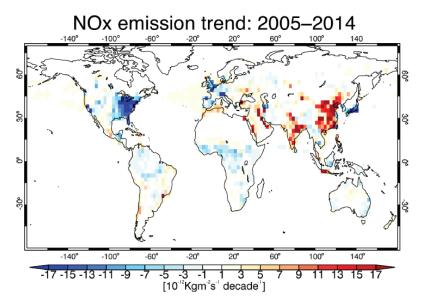


Figure 6. Global distribution of linear trend of the a posteriori surface NO_x emissions (in 10^{-12} kg m⁻² s⁻¹ per decade) for the period 2005–2014. The red (blue) colour indicates positive (negative) trends.

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

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

as well as 4 pages (433) or 7 pages (633) from *Atmospheric Environment* by Michael McElroy

Admission Ticket for Lecture 3 was posted on ELMS on Sat

Please bring a calculator to class on Thursday