Environment and Large Scale Pollutants

Lithosphere – solid ground – 100 km thick
Hydrosphere – ocean, rivers, lakes, ground water
Atmosphere – gases that surround us

Table 14.1 The 10 Most Abundant Elements of the Earth's Crust

Element	Average Percentage (by weight)
Oxygen	46
Silicon	28
Aluminum	8
Iron	6
Calcium	4
Sodium	3
Magnesium	2
Potassium	2
Titanium	0.6
Hydrogen	0.1

Table 14.2 The 10 Most Abundant Elements of the Earth's Oceans

Element	Average Percentage[a] (by weight)
Oxygen	86
Hydrogen	11
Chlorine	2
Sodium	1
Magnesium	0.1
Sulfur	0.09
Calcium	0.04
Potassium	0.04
Bromine	0.006
Carbon	0.003

[a] The total percentage is more than 100 because of the effects of rounding.

Table 14.3 The 10 Most Abundant Gases of the Earth's Atmosphere

Gas	Average Percentage (by volume in dry air)
N_2	78
O_2	21
Ar	0.9
CO_2	0.03
Ne	0.002
He	0.0005
CH_4	0.0002
Kr	0.0001
H_2	0.00005
N_2O	0.00005

The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Chemistry in the Atmosphere

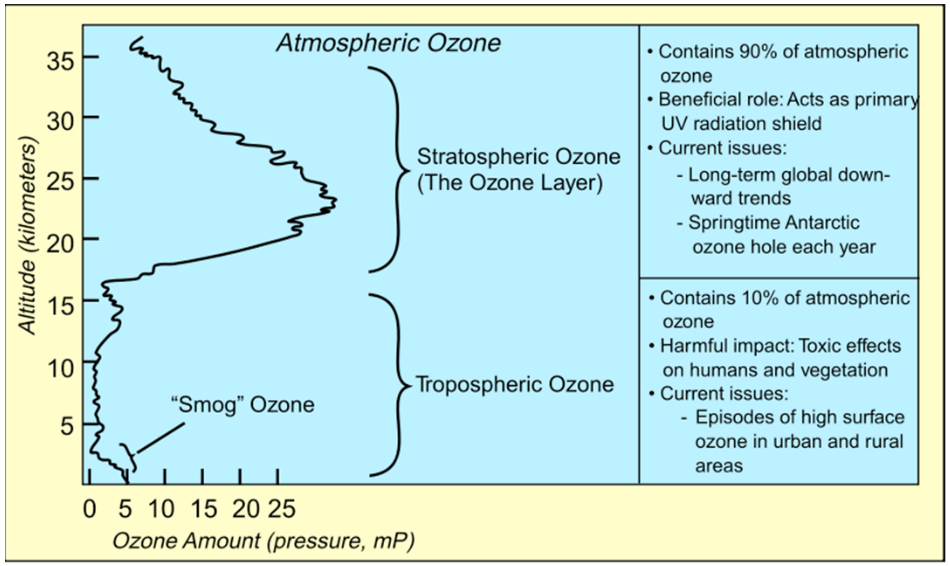
Smog

Los Angeles

Beijing

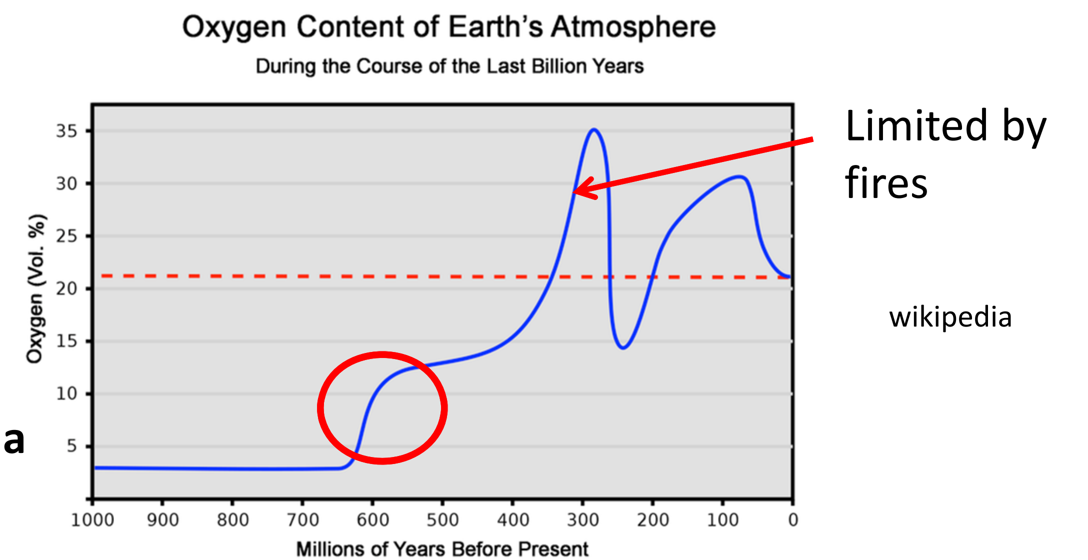
wikipedia

Atmosphere – not all gases are equally distributed



wikipedia

Concentrations are not stable over *long* time: initially zero but cyanobacteria photosynthesis eventually produced excess O_2 then photosynthetic plants caused a second rapid increase



wikipedia

Chemistry in Context 6th Edition, ACS, McGraw-Hill

Tropospheric Pollutants: Ozone in the troposphere fluctuates during the day

Ozone – *secondary pollutant* – formed with sun light

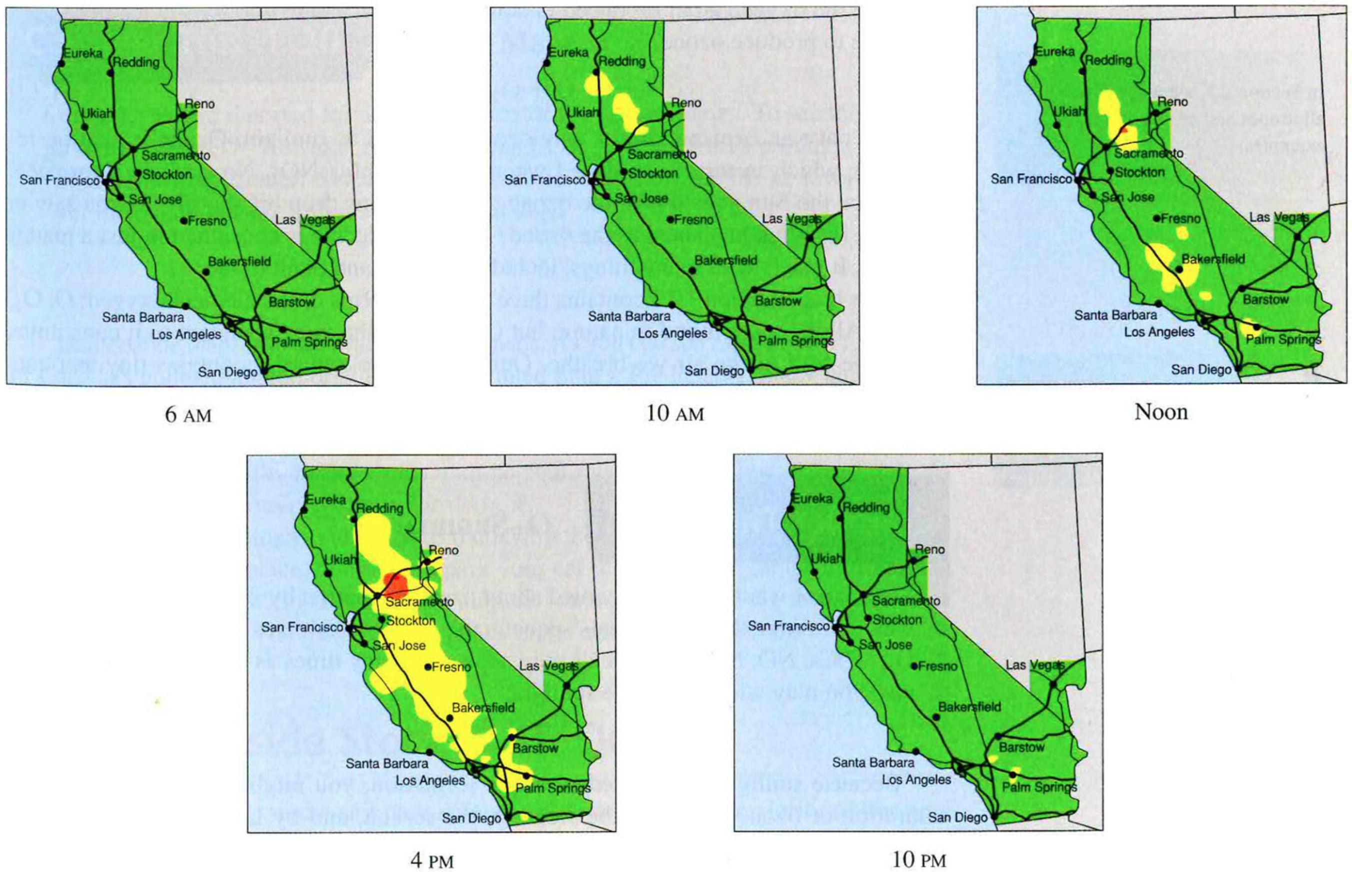


Figure 1.16
Ozone level maps for a summer day in California, July 2006.

The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Pollutants from Coal

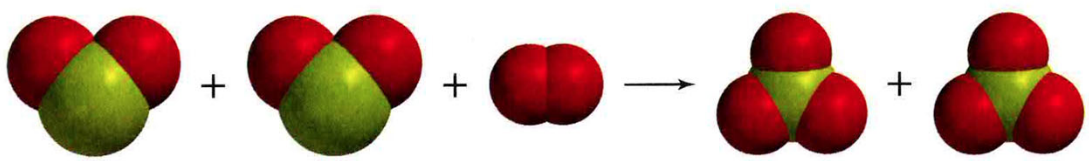
Oxides of sulfur or nitrogen

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

pyrite or iron pyrite; oxygen; iron oxide; sulfur dioxide

primary pollutants

$$2SO_2 + O_2 \longrightarrow 2SO_3 \qquad [1.8]$$



secondary pollutants

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

sulfur trioxide; water; sulfuric acid

'acid rain'

The Extraordinary Chemistry of Ordinary Things, 4th Ed.

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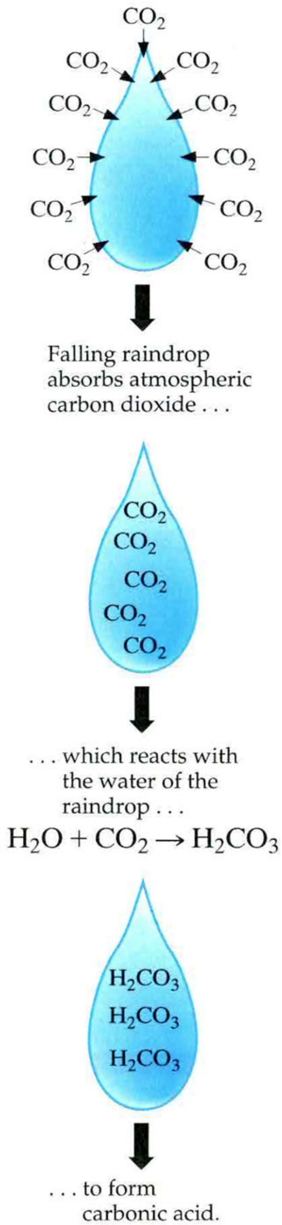

Acid rain

Sulfuric acid – $\mathbf{H_2SO_4}$

Nitric acid – $\mathbf{HNO_3}$

1920's

1990's

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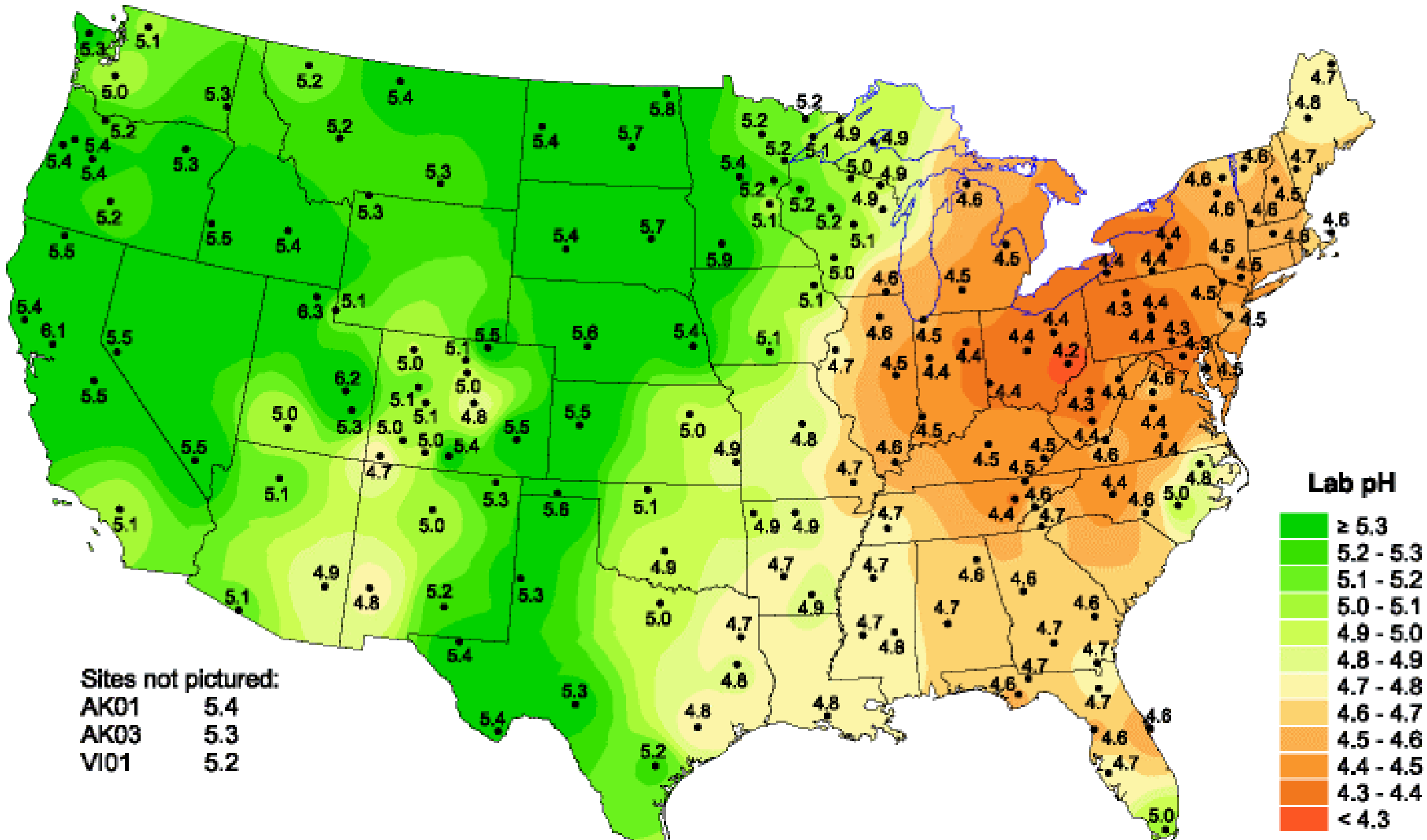
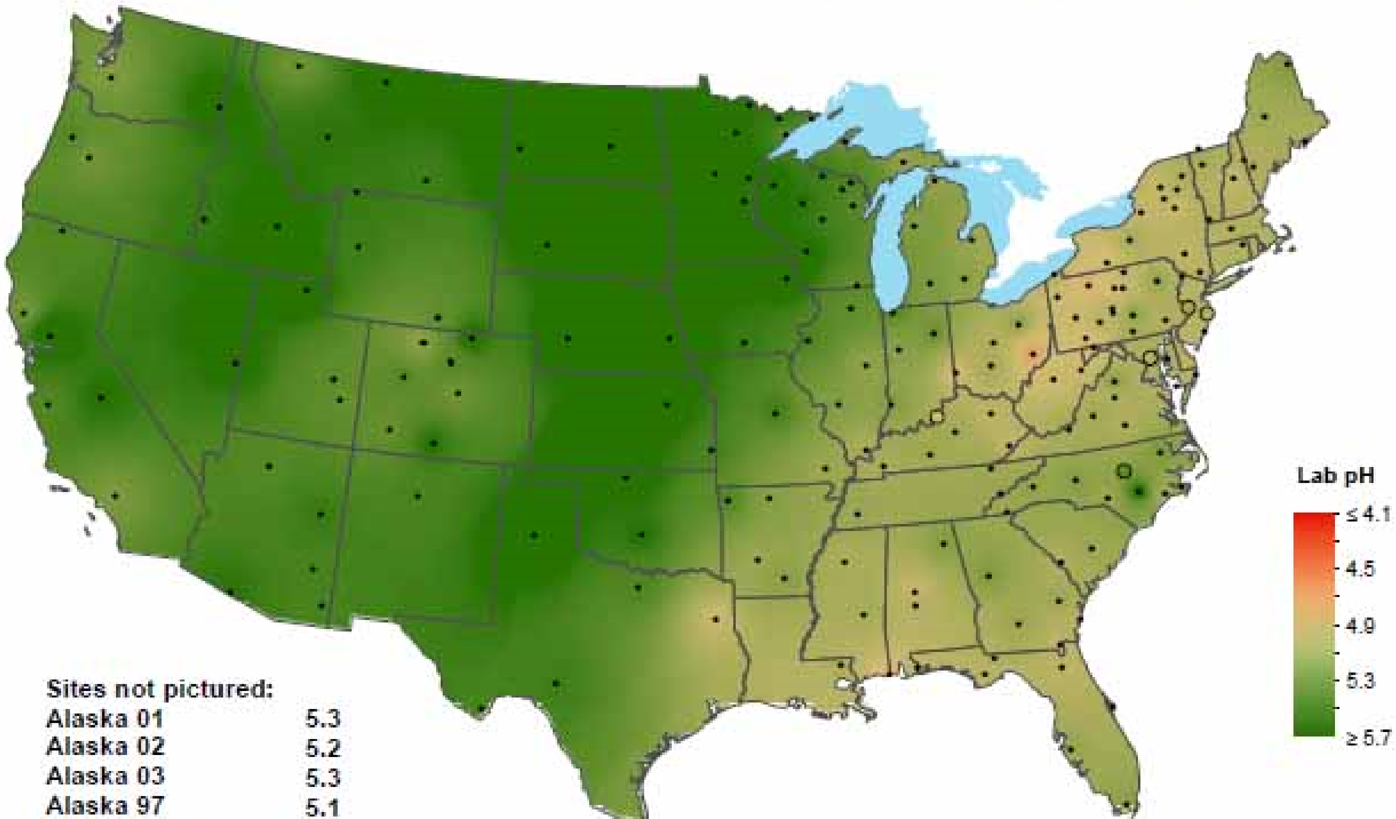
Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 1999



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2013



Sites not pictured:

Alaska 01	5.3
Alaska 02	5.2
Alaska 03	5.3
Alaska 97	5.1
Puerto Rico 20	5.2
British Columbia 22	4.4
Saskatchewan 21	5.5

National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

Air Pollution

Photochemical smog

$$\underset{\text{nitrogen}}{N_2} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{nitric oxide}}{2NO}$$

$$\underset{\text{nitric oxide}}{2NO} + \underset{\text{oxygen}}{O_2} \longrightarrow \underset{\text{nitrogen dioxide}}{2NO_2}$$

$$\underset{\text{nitrogen dioxide}}{NO_2} \xrightarrow{\text{sunlight}} \underset{\text{nitric oxide}}{NO} + \underset{\text{oxygen atom}}{O}$$

$$\underset{\text{oxygen atom}}{O} + \underset{\text{oxygen molecule}}{O_2} \longrightarrow \underset{\text{ozone}}{O_3}$$

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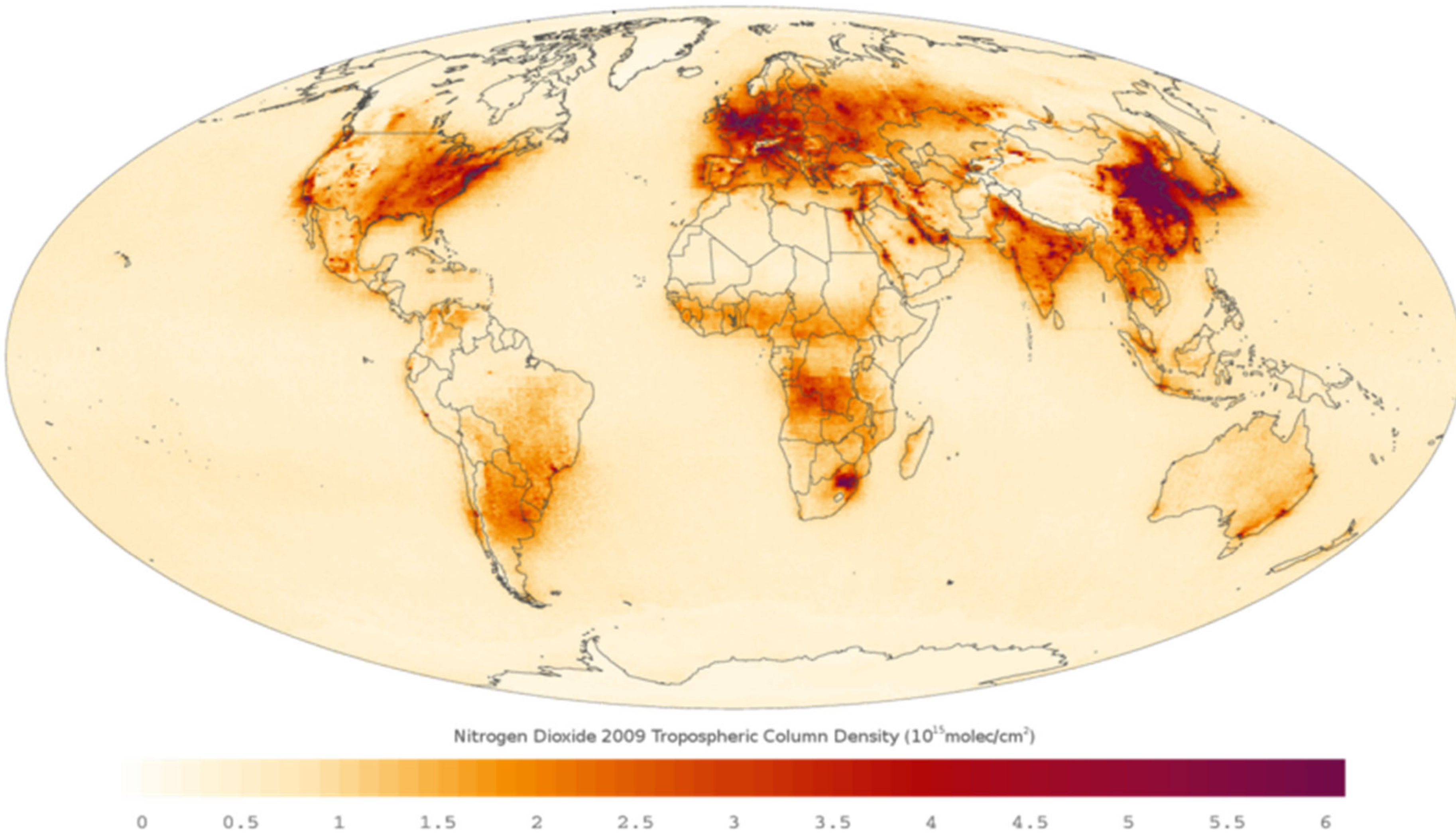
Thermal inversion

World NO_2 distribution: 2009



More pollutants

CO >>> odorless, tasteless and invisible

Volatile organic compounds and volatile organic solvents

Table 14.4 Major Sources of Air Pollution in the United States, 1998

	Millions of Tons				
	Carbon Monoxide	Nitrogen Oxides	Sulfur Dioxide	Volatile Organic Compounds	Total
Fuel combustion					
Highway vehicles	50.4	7.8	0.3	5.3	63.8
Electric utilities	0.4	6.1	13.2	0.1	19.8
All other nonvehicle sources	5.0	4.1	3.5	0.8	13.4
Industrial emissions (other than fuel combustion)	3.6	0.8	1.5	1.4	7.3
Waste disposal and recycling	1.2	0.1	0	0.4	1.7

SOURCE: *U.S. Statistical Abstracts, 2000,* Table 394.

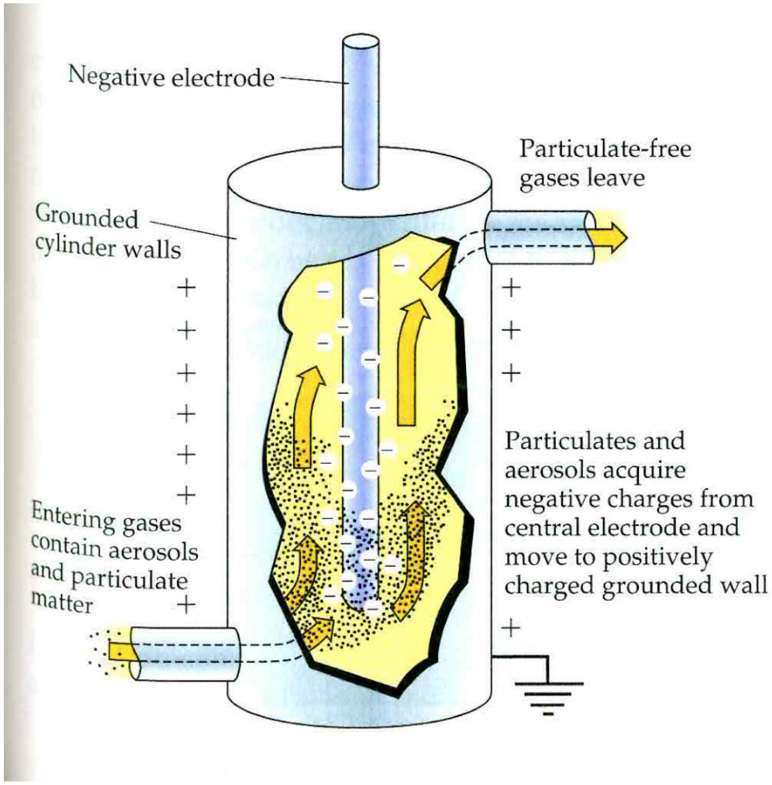
The Extraordinary Chemistry of Ordinary Things, 4th Ed.

See also: Real-time World Air Quality Index: https://waqi.info/

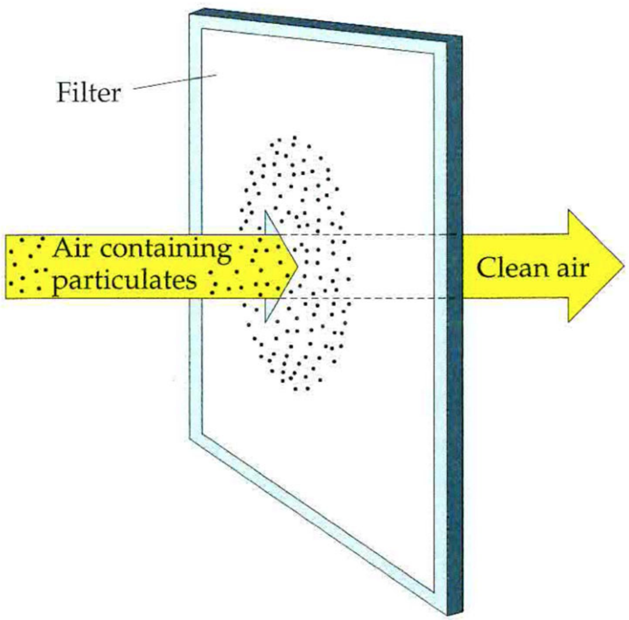
SO_X and NO_X

Byproduct of energy production: combustion of hydrocarbons containing N and S impurities

Electrostatic precipitator

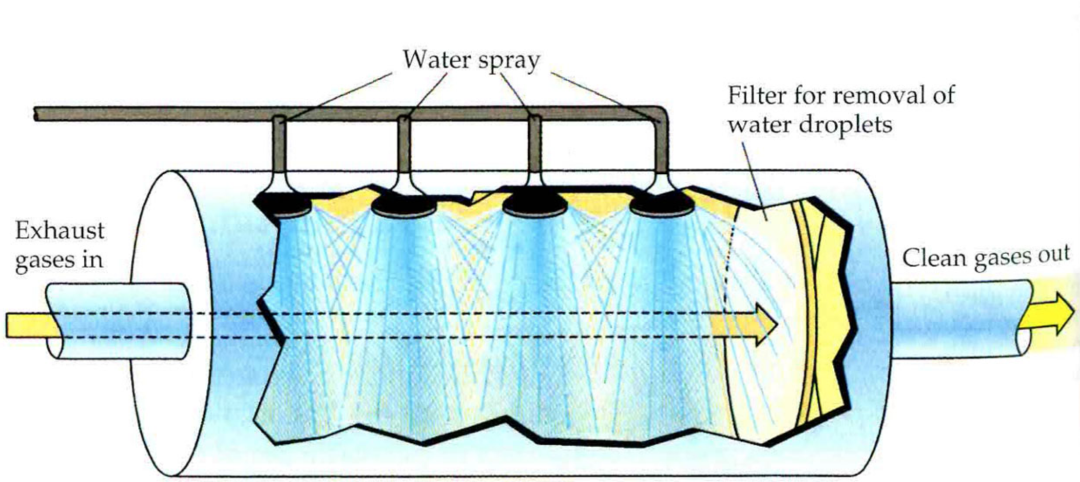


Filtration



The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Scrubbers



$$SO_2 + Mg(OH)_2 \longrightarrow MgSO_3 + H_2O$$

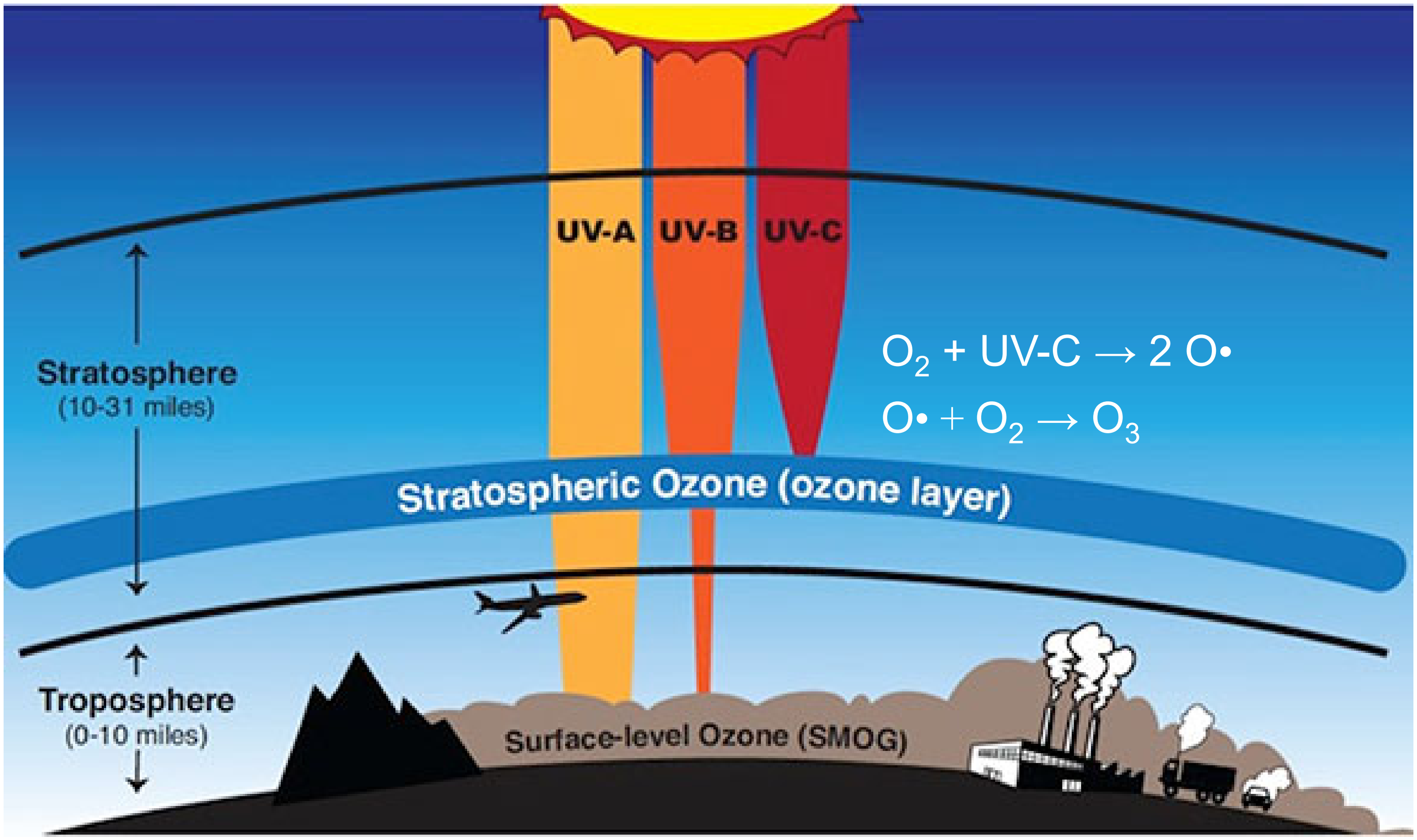
sulfur dioxide + magnesium hydroxide → magnesium sulfite + water

$$MgSO_3 \longrightarrow SO_2 + MgO$$

magnesium sulfite → sulfur dioxide + magnesium oxide

The Stratospheric Ozone Layer: Earth's Protective Blanket

UV A: 315-400 nm UV B: 280-315 nm UV C: 200-280 nm



$O_2 + \text{UV-C} \rightarrow 2\ O\bullet$

$O\bullet + O_2 \rightarrow O_3$

University Corporation for Atmospheric Research (UCAR): courtesy of NASA

Chlorofluorocarbons: unintended consequences and a success story

Ozone destruction in the stratosphere – CFCs, •OH, •NO

# of F

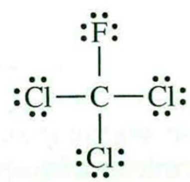
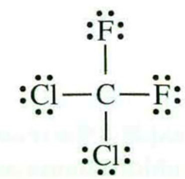
↓

Freon 12

↑

# of H + 1

Table 2.6 Two Important Chlorofluorocarbons

Freon 11 (CFC-11)	Freon 12 (CFC-12)
CCl_3F trichlorofluoromethane	CCl_2F_2 dichlorodifluoromethane
	

Uses of CFC:

- refrigerant
- aerosol for spray cans
- gas to expand plastic foam
- solvent for oil and grease
- sterilizer for surgical instruments

Halons contain bromine (Br) or fluorine (F) to replace some of the Cl

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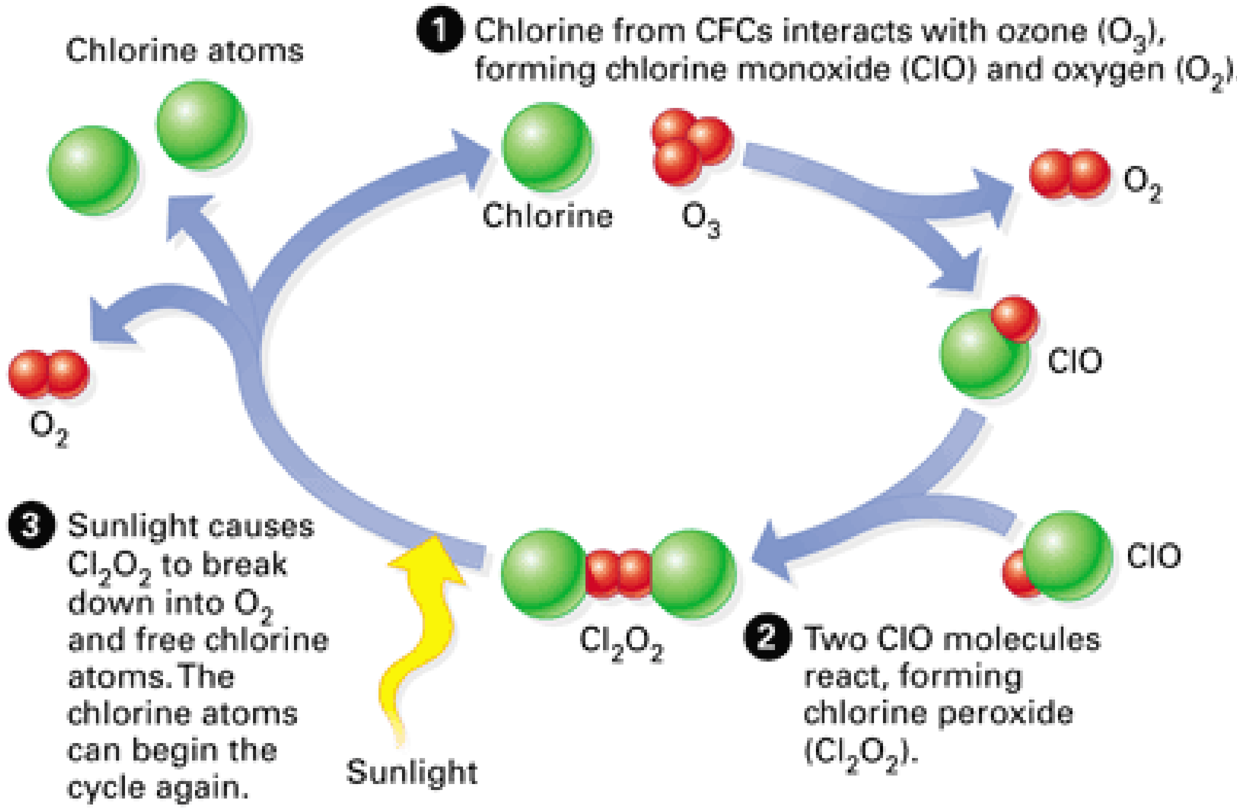
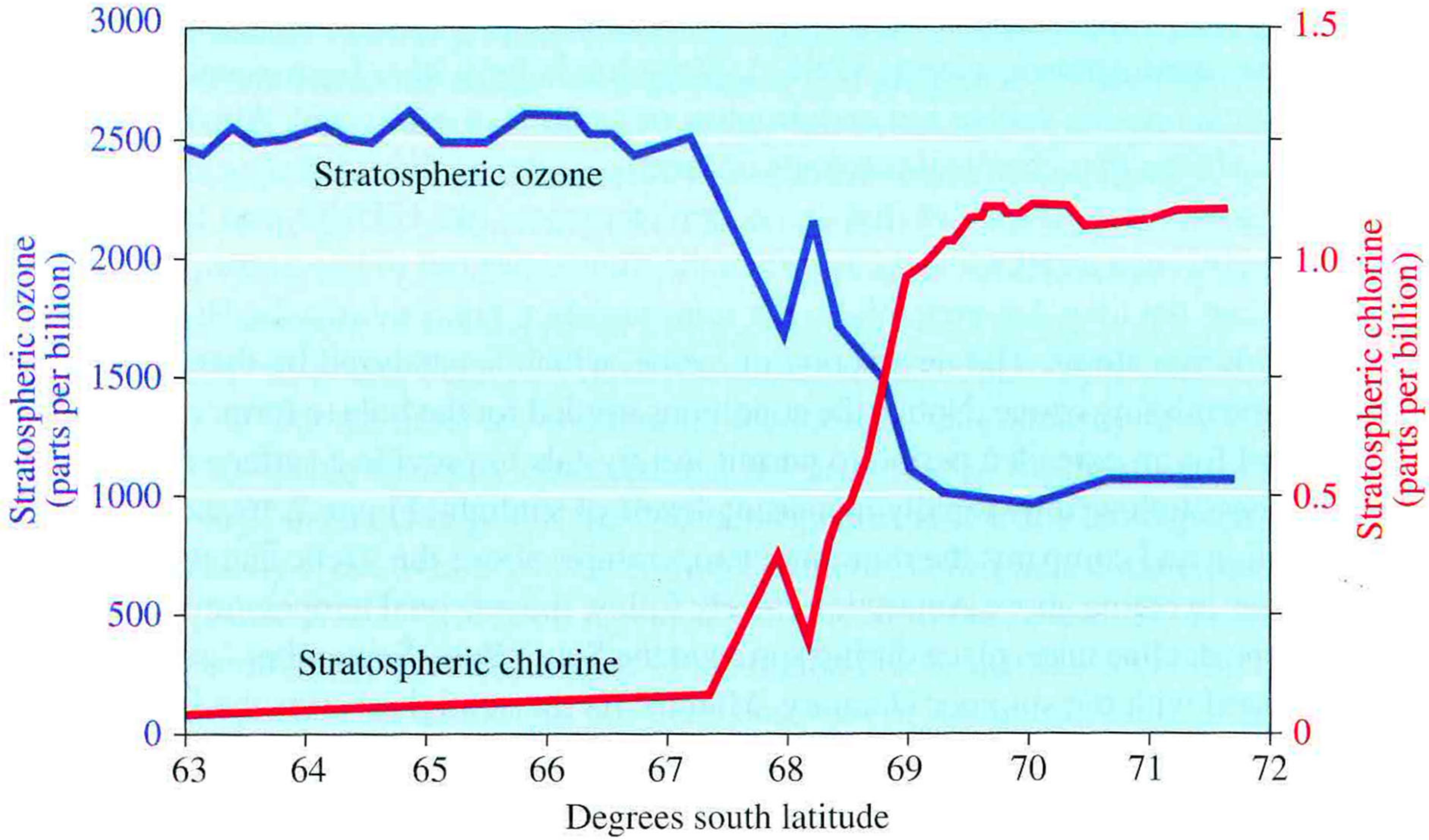
CFCs are destroyed by UV light at high altitudes

$$Cl_3CF + h\nu \longrightarrow Cl_2CF + Cl$$



From: On-line Textbook, http://biologytb.net23.net/text/index.html

At 20 -25 km Cl• forms HCl
Most O_3 destruction occurs at 40 km



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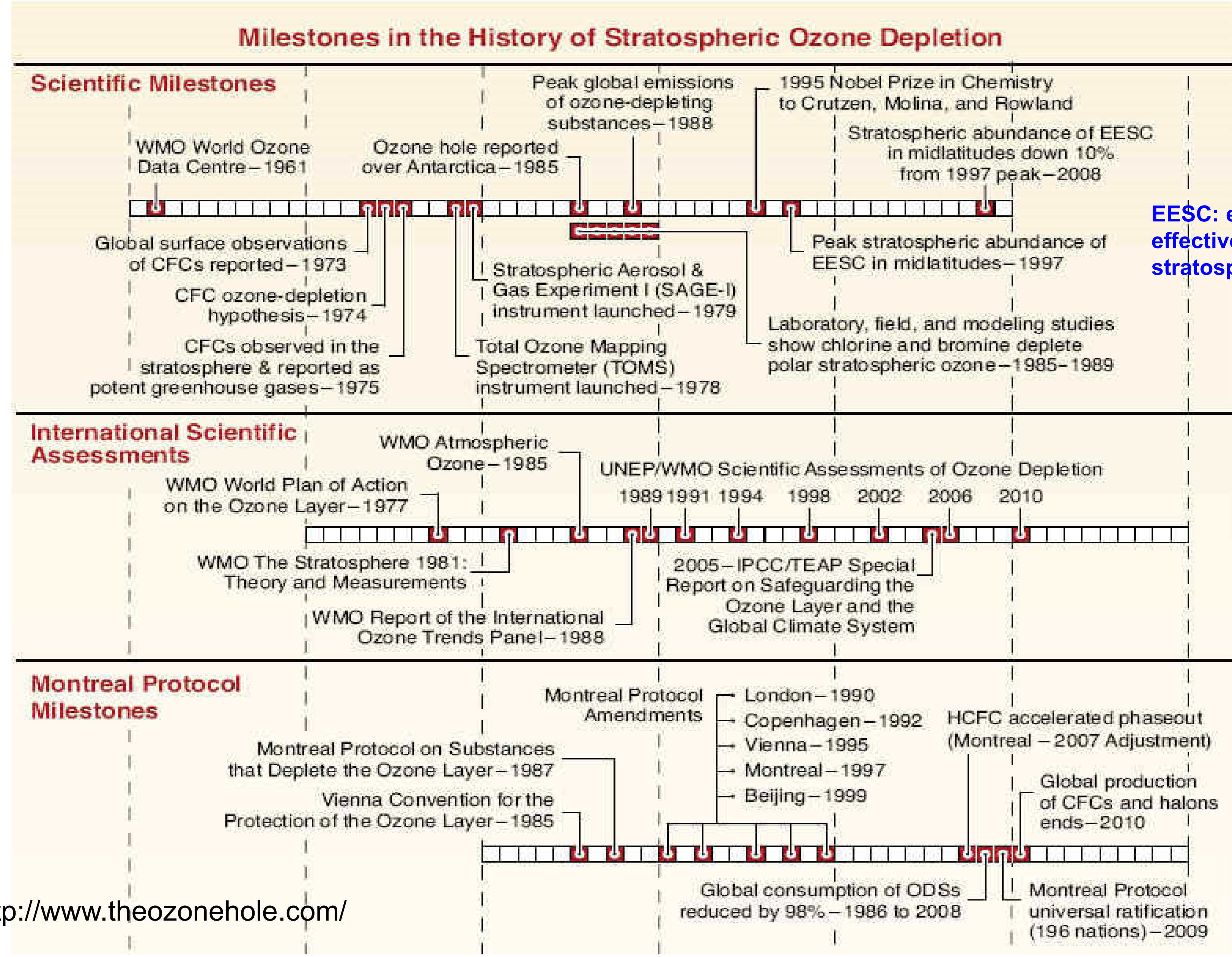
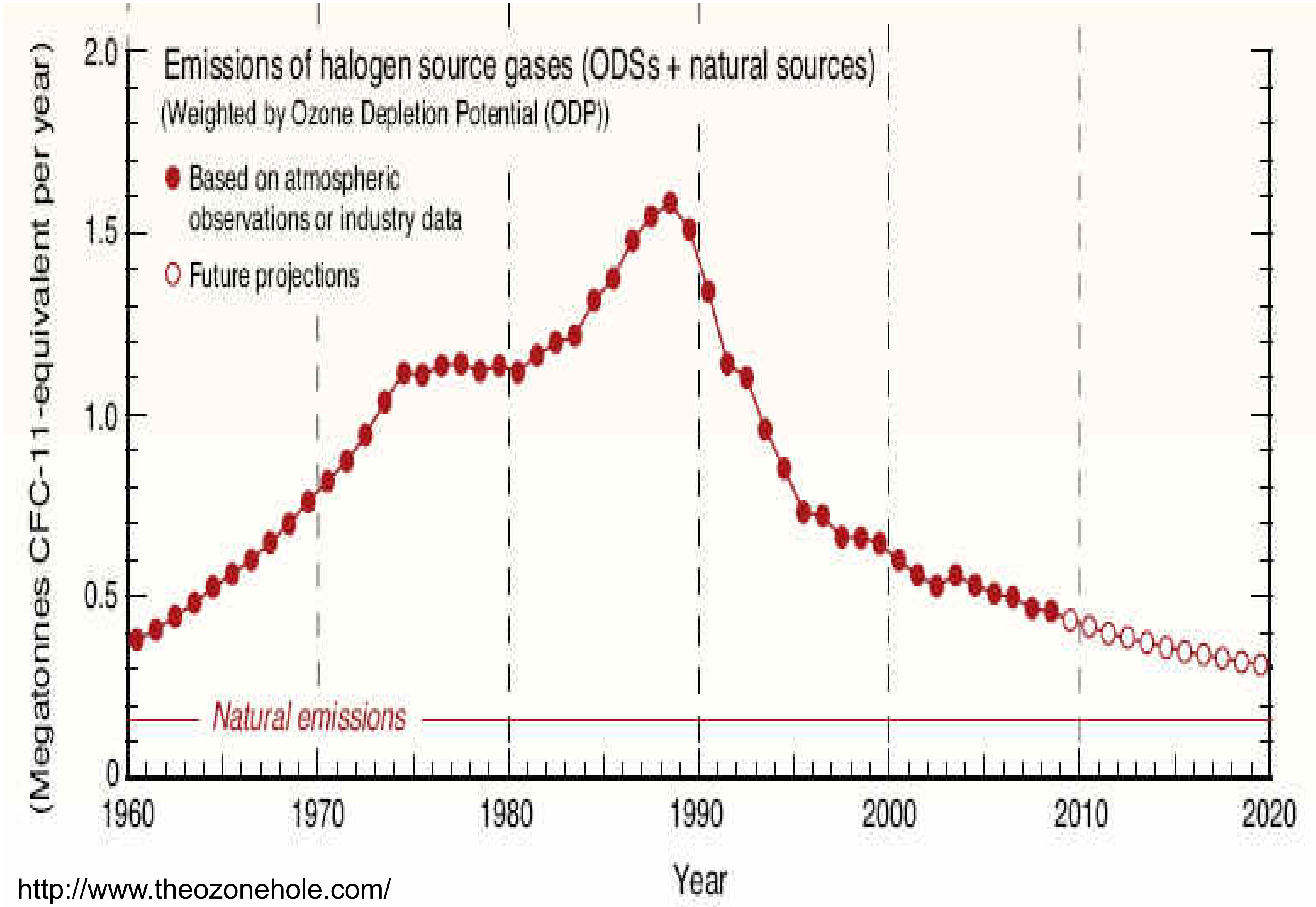


EESC: equiv. effective stratospheric Cl

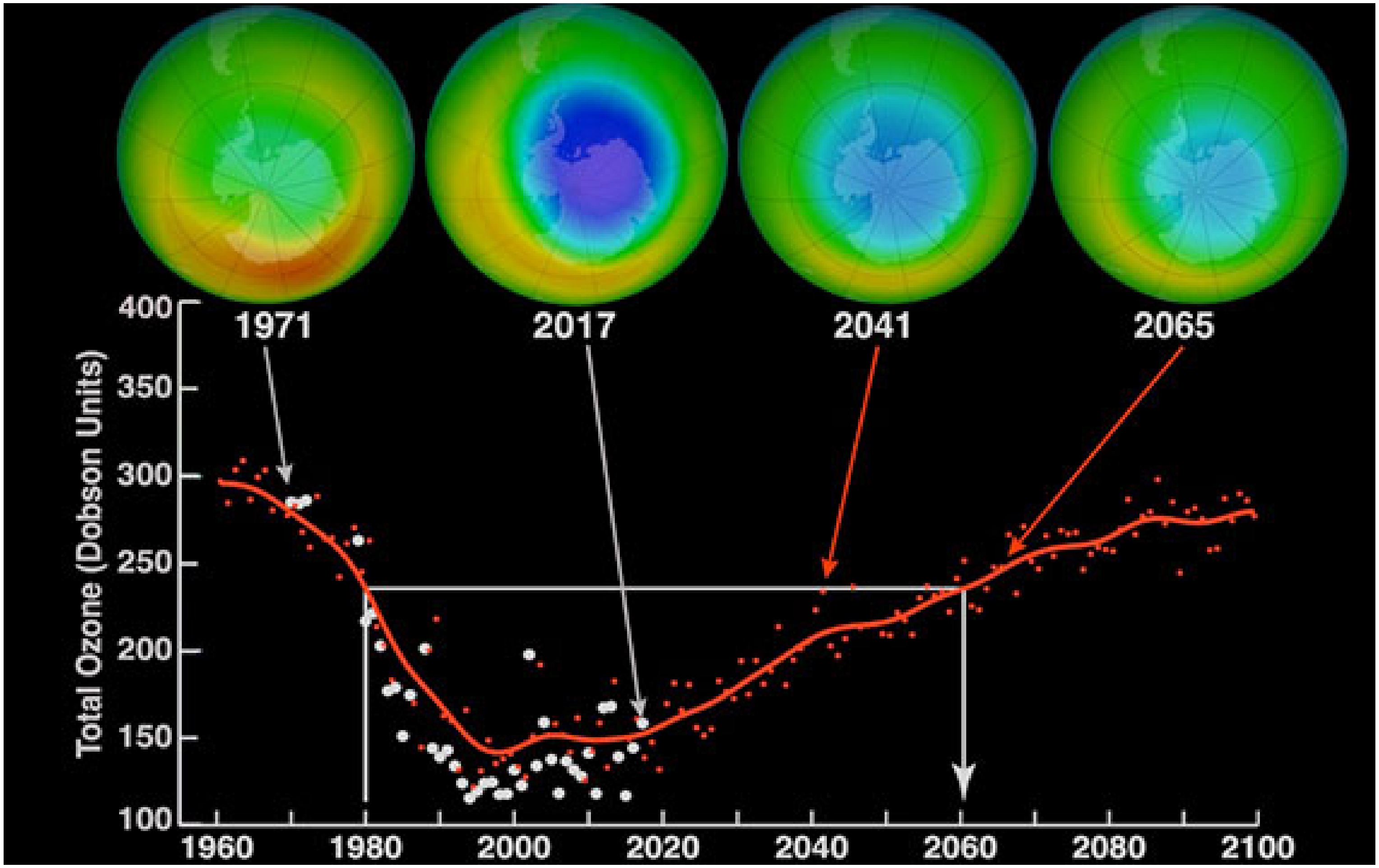
http://www.theozonehole.com/



http://www.theozonehole.com/

Banning OF CFC's: ***An Ozone Recovery Story ?***

2017 Antarctic ozone hole was the smallest since 1988



University Corporation for Atmospheric Research (UCAR): courtesy of NASA

Replacement CFCs

- Correct boiling point between -10 and -30 °C
- Not toxic
- Not too stable
- Not flammable

Chemistry in Context 6th Edition, ACS, McGraw-Hill

Table 2.7 Two Important Hydrochlorofluorocarbons

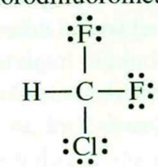
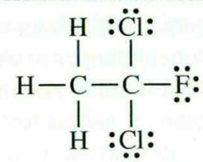
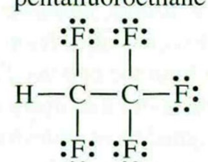
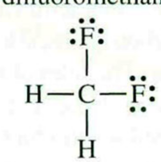
HCFC-22	HCFC-141b
$CHClF_2$	$C_2H_3Cl_2F$
chlorodifluoromethane	dichlorofluoroethane
	

Table 2.8 Two Important Hydrofluorocarbons

HFC-125	HFC-32
C_2HF_5	CH_2F_2
pentafluoroethane	difluoromethane
	

Greenhouse Gas Effects

Table 3.3 Global Warming Potential for Three Greenhouse Gases

Substance	Global Warming Potential (GWP)*	Tropospheric Abundance (ppm)	
CO_2	1	385	**385**
CH_4	23	1.8	**41**
N_2O	296	0.31	**92**

*GWP values are given for the estimated direct and indirect effects over a 100-year period and are relative to the assigned value of 1 for CO_2.

Net effect

Table 3.2 Greenhouse Gases–Concentration Changes and Lifetimes

	CO_2	CH_4	N_2O
Preindustrial concentration (1750)	278 ppm	0.700 ppm	0.270 ppm
2005 concentration	385 ppm	1.75 ppm	0.314 ppm
Average rate of concentration change, 1990–2005	1.5 ppm/year	0.007 ppm/year	0.0008 ppm/year
Global atmospheric lifetime	50–200 years*	12 years	114 years

*A single value for the atmospheric lifetime of CO_2 is not possible. Different removal mechanisms take place at different rates, leading to variation in atmospheric lifetime.

Nitrous oxide

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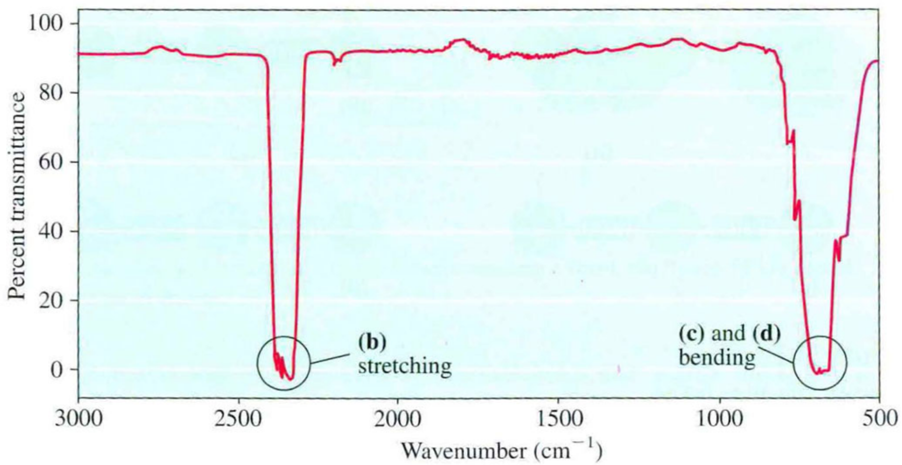

Figure 3.14
Infrared spectrum of carbon dioxide.
The letters (**b**), (**c**), and (**d**) refer to the molecular vibrations shown in Figure 3.13.

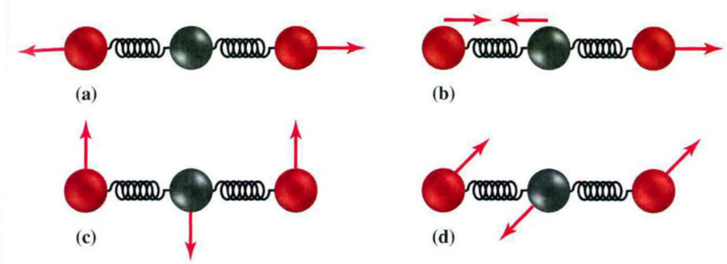

Figure 3.13
Molecular vibrations in CO_2.
Each spring represents a C-to-O double bond. Vibrations **a** and **b** are stretching vibrations; **c** and **d** are bending vibrations.

N_2 and O_2 have no effect: no dipole moment change on vibration

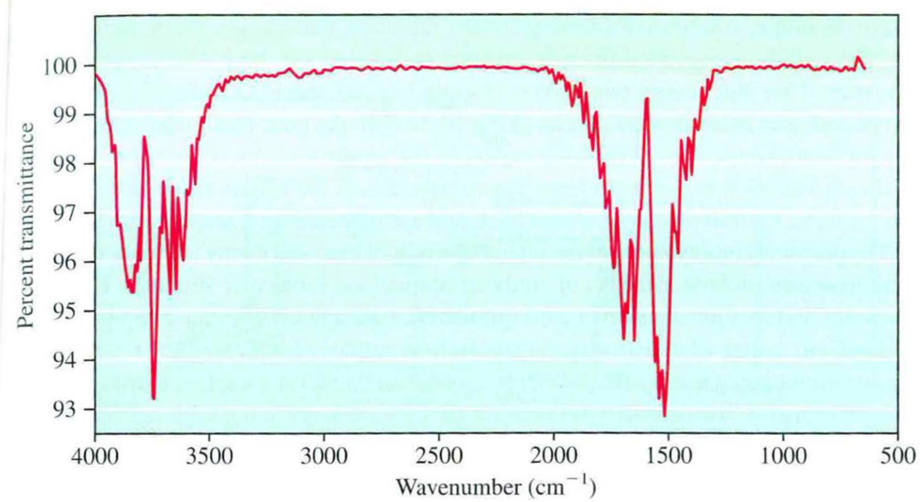

Figure 3.15
Infrared spectrum of water vapor.

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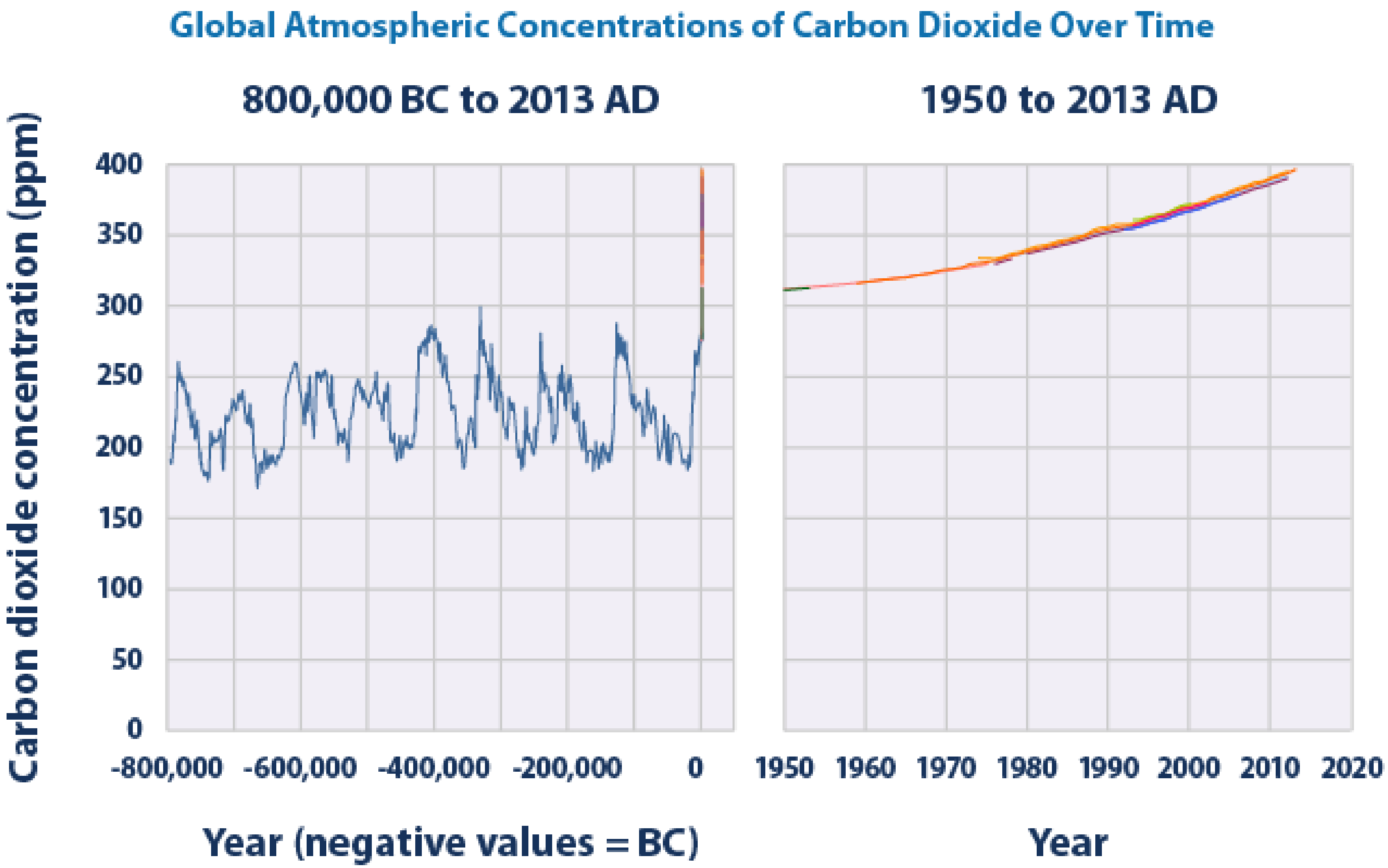
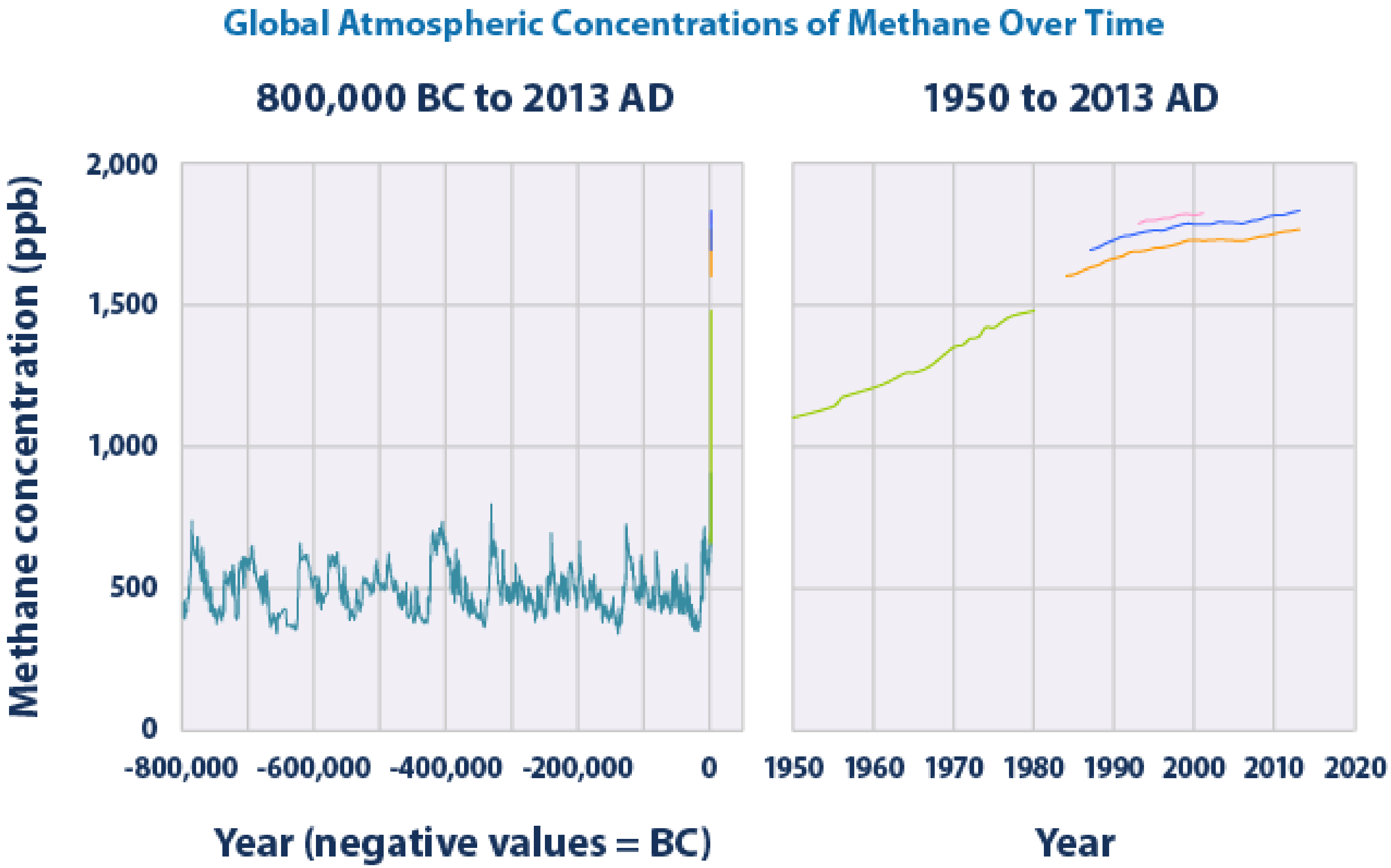


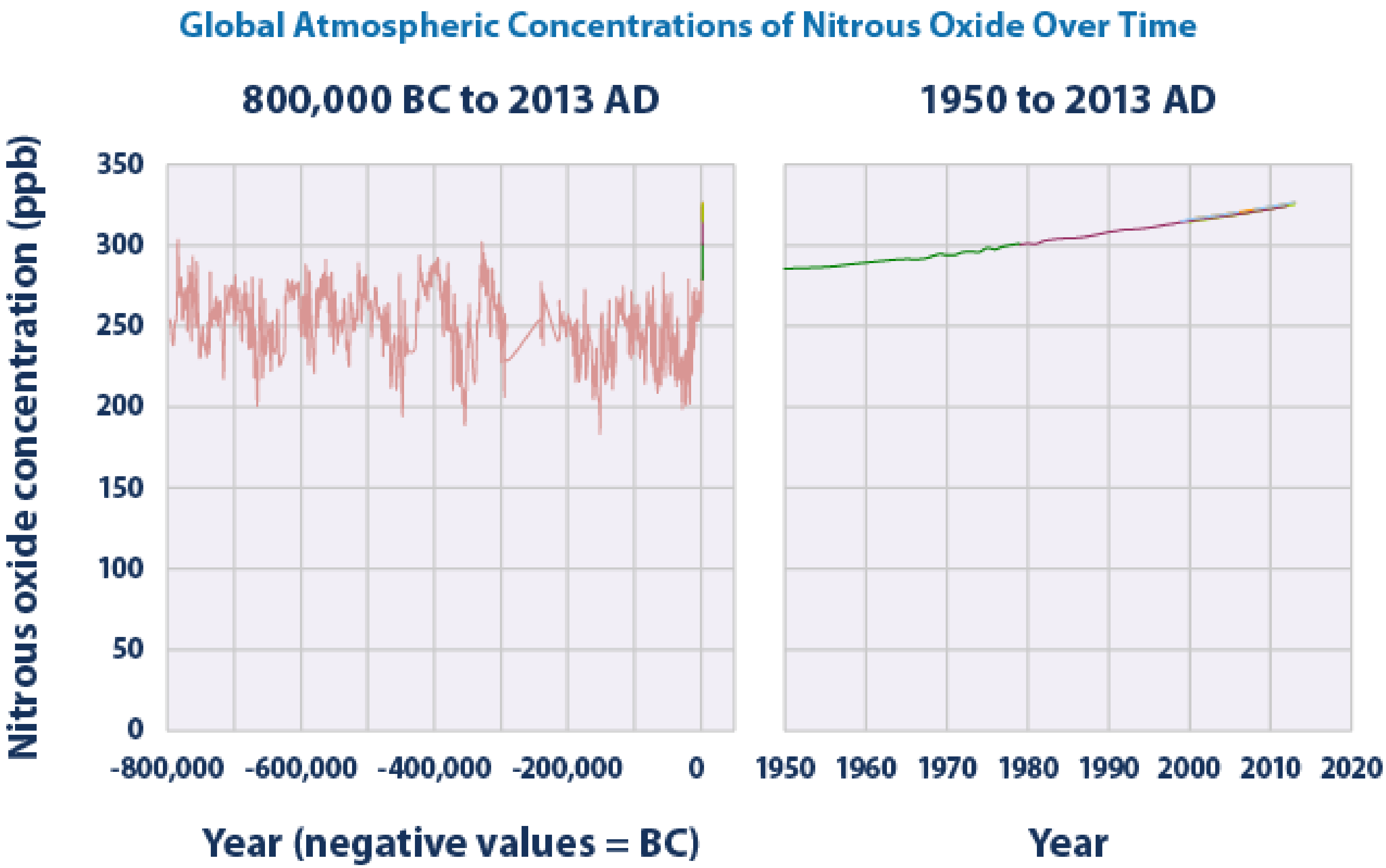
Data source: Compilation of 10 underlying datasets. See www.epa.gov/climatechange/indicators/ghg/ghg-concentrations.html for specific information.

For more information, visit U.S. EPA's "Climate Change Indicators in the United States" at www.epa.gov/climatechange/indicators.



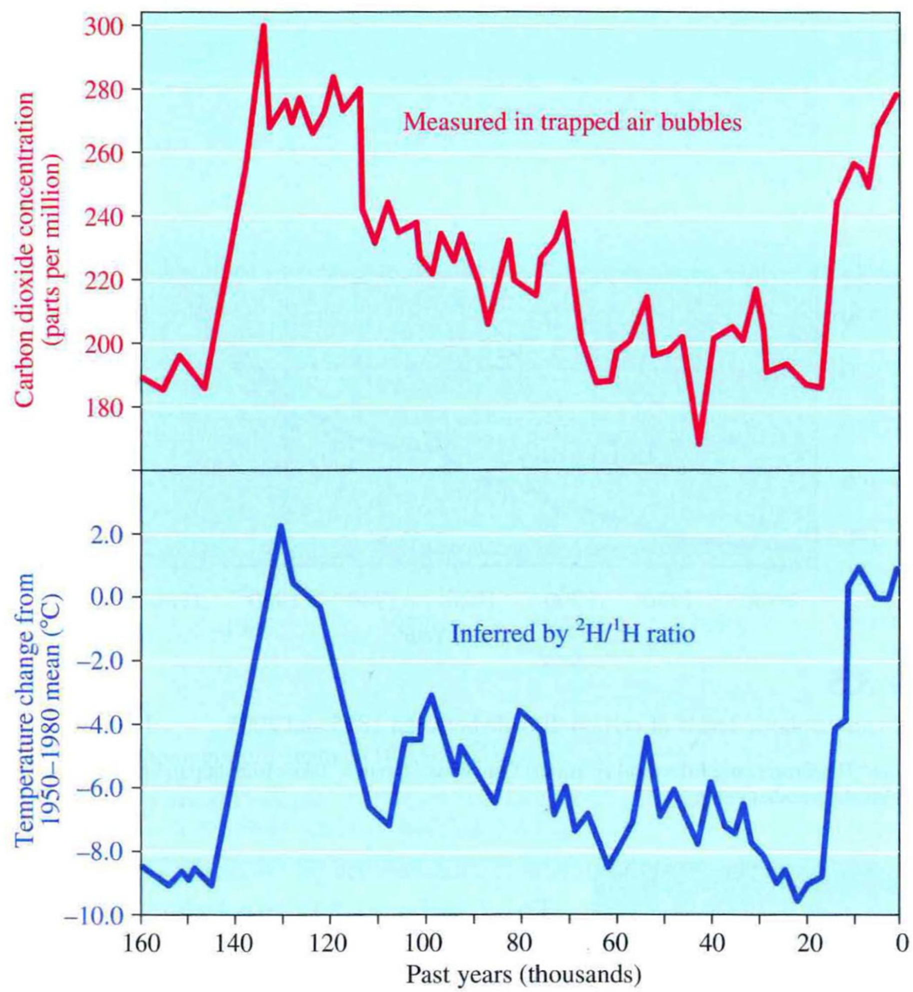
Data source: Compilation of five underlying datasets. See www.epa.gov/climatechange/indicators/ghg/ghg-concentrations.html for specific information.

For more information, visit U.S. EPA's "Climate Change Indicators in the United States" at www.epa.gov/climatechange/indicators.



Data source: Compilation of six underlying datasets. See www.epa.gov/climatechange/indicators/ghg/ghg-concentrations.html for specific information.

For more information, visit U.S. EPA's "Climate Change Indicators in the United States" at www.epa.gov/climatechange/indicators.



Global temperatures track CO_2 concentrations very closely

Figure 3.4

Atmospheric CO_2 concentration (red) and temperature change from the 1950–1980 mean (blue) over 160,000 years (ice core data).

Comparison to 1950-1980 mean values

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Intergovernmental Panel on Climate Change – 2007 Synthesis Report

http://www.ipcc.ch/publications_and_data/ar4/syr/en/contents.html

Summary of how to interpret language for policy makers!

Table 3.4 Judgmental Estimates of Confidence

Term	Probability That a Result Is True
Virtually certain	> 99%
Very likely	90–99%
Likely	66–90%
Medium likelihood	33–66%
Unlikely	10–33%
Very unlikely	1–10%

Source: *Summary for Policymakers, A Report of Working Group 1 of the Intergovernmental Panel on Climate Change*, Shanghai: IPCC, January 1, 2001.

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Observed changes in climate:

*“Warming of the climate system is **unequivocal**, as is now evident from observations of increases in global average air and ocean temperatures, widespread melting of snow and ice and rising global average sea level”*

Causes of change:

“Global GHG emissions due to human activities have grown since pre-industrial times, with an **increase of 70% between 1970 and 2004**

Global atmospheric concentrations of CO_2, methane (CH_4) and nitrous oxide (N_2O) have increased markedly as a result of human activities since 1750 and now **far exceed pre-industrial values** determined from ice cores spanning many thousands of years

Most of the observed increase in global average temperatures since the mid-20th century is **very likely** due to the observed increase in anthropogenic GHG concentrations. It is **likely** that there has been significant anthropogenic warming over the past 50 years averaged over each continent (except Antarctica)”

http://www.ipcc.ch/publications_and_data/ar4/syr/en/contents.html

Appendix: Naming of HCFC's and Halons

CFC	**C**hloro**F**luoro**C**arbons
0	Number of double bonds, omitted if zero
1	Number of carbon atoms minus 1, omitted if zero
2	Number of hydrogen atoms plus 1
3	Number of fluorine atoms
4	Number of chlorine atoms replaced by bromine, always used with prefix "b" (b1, b2), omitted if zero
a	Added to identify isomers, the isomer without suffix always has the smallest mass difference on each carbon atom. If there are more isomers the suffix is counting from a - z, omitted if only one isomer exists