

Atmospheric Chemistry: Air Pollution and Global Warming
Summary of materials related to University of Washington course
Atm S 458 Air Pollution Chemistry
taught Autumn 2014 by Professor Joel Thornton
compiled by Michael C. McGoodwin (MCM). Content last updated 1/15/2015

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Introduction

Atmospheric chemistry is at the heart of some of the most important issues of our times, most particularly air pollution, environmental degradation, and global warming. I have compiled this summary to assist in learning some of the materials relevant to Atmospheric Chemistry—the subject of University of Washington course Atm S 458 “Air Pollution Chemistry”, as presented in fall 2014. This course was taught by Professor Joel A. Thornton (JAT). Some of the materials here are imported from an earlier summary I prepared in 2010 for courses taught by Robert A. Houze (RAH).

Sources: The materials in this summary represent selected course-related concepts assembled for the most part from various Web sources as well as the lecture notes, the textbooks, the assigned materials including articles, and other books. Note that blue links (URLs) shown in footnotes are “live” and can be followed in PDF documents such as this by clicking on them.

Textbooks: The main textbook used for this course is *Air Pollution and Global Warming: History, Science, and Solutions (2nd Edition)*, by Mark Z. Jacobson, Cambridge U Press, 2012. This is abbreviated below as *APGW*. A generous set of many of the figures from this book is available here¹ as multiple PowerPoint files. I found this to be an excellent textbook, well worth the cost, and I especially appreciated the many historical vignettes and etymological information which promote a better understanding of where the mysteries and issues of atmospheric chemistry have come from.

JAT also recommended the online textbook *Introduction to Atmospheric Chemistry*, by Daniel J. Jacob, Princeton University Press, 1999,² and I used this useful text extensively, hereafter referred to as *IAC*. I also make references to *Atmospheric Sciences: An Introductory Survey (2nd Edition)*, J. M. Wallace and P. V. Hobbs, Academic Press, 2006 (abbreviated *ASJ*).

I draw extensively on some of the components of the massive Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment Report (AR5), especially:

- The ~1500 page full report of the IPCC AR5 Working Group I [WGI] recently finalized, namely “*Climate Change 2013: The Physical Science Basis*”, hereafter called *IPCC_WGI_2013*,³ and
- the IPCC AR5 *Synthesis Report*, which synthesizes the reports of the 3 working groups, hereafter called *IPCC_SR_2014*.⁴

Acknowledgements, Copyrights, and Disclaimers: When I have taken material or diagrams from Wikipedia or other Web sources, I have always shown a URL citation. (URLs are of course expected to go out-of-date with time, and I will not attempt to keep these links current.) Where I have embedded editorial comments, clarifications, and questions of my own inside quoted material, I have enclosed these in [square brackets]. I have not tried to explore the medical effects of pollutants at a level appropriate for a physician, and instead have merely summarized comments made in the non-medical textbook. Similarly, I have mostly omitted discussion of the important but complex political and regulatory aspects.

This is a nonprofit project intended to promote personal and public scientific understanding regarding topics critical to the health and welfare of our fragile planet (or at least its biosphere). I have included some potentially copyrighted information, hopefully at an acceptable level. If you hold copyright on something I have used here and wish me to remove it, please advise and I will do so.

The Author: I am a retired physician and merely audited this class, thus I claim no expertise in this field. My personal goal has been to assimilate some of the important points at least qualitatively. This was a short one quarter course, so time to master the extensive material was quite limited.

¹ • <http://www.cambridge.org/us/academic/subjects/earth-and-environmental-science/atmospheric-science-and-meteorology/air-pollution-and-global-warming-history-science-and-solutions-2nd-edition> or

• <http://web.stanford.edu/group/efmh/jacobson/POLbook2/index.html> [Jacobson text]

² <http://acmg.seas.harvard.edu/people/faculty/djj/book/> [Jacob text]

³ Intergovernmental Panel on Climate Change (IPCC), Fifth Assessment Report [AR5], Working Group I [WGI] Report: *Climate Change 2013: The Physical Science Basis*. AR5’s WGI report was finalized in Sept. 2013.

AR5’s Full WGI Report downloaded at

http://www.ipcc.ch/pdf/assessment-report/ar5/wg1/WG1AR5_ALL_FINAL.pdf

(Page numbers that I show are those given at the bottom of the full report PDF pages.)

⁴ IPCC AR5’s *Synthesis Report* was approved October 2014: <http://www.ipcc.ch/report/ar5/syr/>

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<http://www.mcgoodwin.net/pages/atmscuw458.pdf>.

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MCM at McGoodwin period NET (please convert to standard format when using)

A Little Light Physics

Atmospheric chemistry includes numerous light-related reactions (such as photolytic cleavage of a molecule). The energy and therefore the wavelength and frequency of light photons are relevant. "Light" is taken to mean EM radiation of all wavelengths (or at least those relevant to this discussion).

Light is a wave-like electromagnetic radiation (EM radiation), having mutually perpendicular magnetic and electric fields, both of which oscillate perpendicular to the direction of propagation, and is also particle-like.

The relationship of light *wavelength* to *frequency* in vacuum is given in ASI-113 by

$$c^* = \lambda \tilde{\nu}$$

where c^* = speed of light in vacuum = $3 \times 10^8 \text{ m s}^{-1}$
 λ = wavelength (m are SI units, but usually expressed in μm or nm)
 $\tilde{\nu}$ = frequency (Hz or s^{-1})

Note the non-standard representation of frequency chosen by ASI, namely $\tilde{\nu}$. The quantity ν is used in ASI-113 to express the *wave number*, or number of waves per unit length in the direction of propagation = $1/\lambda$. However, frequency is more commonly represented as ν in traditional physics, and wavenumber can be represented by $\tilde{\nu}$.⁵ Hereafter, I will use the more conventional symbols (used also by RAH in his PDFs):

$$c^* = \lambda \nu$$

where c^* = speed of light in vacuum = $3 \times 10^8 \text{ m s}^{-1}$ (hereafter, this will be shown simply as c)
 λ = wavelength (m are SI units, but usually expressed in μm or nm)
 ν = frequency (Hz or s^{-1})

$$\nu = c/\lambda$$

Photons are the particles or wave packets that make up bulk light. The energy of one photon depends solely on the frequency:

$$E = h \nu$$

where E = energy (Joules)
 ν = frequency (Hz or s^{-1})
 h = Planck constant (or Planck's constant) = $6.626 \times 10^{-34} \text{ J s}$

Photons carry *momentum* with magnitude $|\vec{p}| = h/\lambda$ and hence exert pressure (expressed in N m^{-2} or Pa).

Blackbody Radiation

The mathematics of this topic is abstruse and my understanding imperfect. The idealized black body (blackbody) of physics absorbs all EM radiation falling on it without reflection or transmission through it—thus it appears black. It can be accurately approximated by a small opening on a closed cavity, where radiation is emitted. A blackbody emits EM radiation in a characteristic black body spectral radiance density distribution that is dependent only on its temperature.

Planck's Distribution Formula or Law

Black body radiation satisfies the Planck Formula,⁶ which is commonly expressed as

$$I(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{(e^{h\nu/kT} - 1)}$$

where $I(\nu, T)$ = emitted power per unit area of emitting surface in the normal direction,
per unit solid angle, per unit frequency ν
 ν = frequency s^{-1}

⁵ <http://en.wikipedia.org/wiki/Wavenumber>

⁶ • http://en.wikipedia.org/wiki/Planck%27s_law

• see also <http://scienceworld.wolfram.com/physics/PlanckLaw.html>

T = Temperature K
 h = Planck constant = 6.626069×10^{-34} J s
 k = Boltzmann constant = 1.38065×10^{-23} J K⁻¹
 c = speed of light = 299,792,458 m s⁻¹

The function $I(\nu, T)$ peaks at $h\nu = 2.82$ kT.

Trying to explain this initially empirical law caused a crisis for classical physics, and became one of the foundational issues for the new quantum theory.

The radiance is proportional to the cosine of the viewing angle. Therefore, the spectral radiance of a black body surface viewed from an arbitrary angle θ is $I(\nu, T) = I(\nu, T) \cos \theta$.

Alternate forms of this function are also used. It is given in the following form given in *ASI-117*,

$$B_{\lambda}(T) = \frac{2hc^2}{\lambda^5} \frac{1}{(e^{hc/\lambda kT} - 1)} = \frac{c_1 \lambda^{-5}}{\pi(e^{c_2/\lambda T} - 1)}$$

where $B_{\lambda}(T)$ = monochromatic intensity emitted by a blackbody

λ = wavelength m

$c_1 = 2hc^2\pi = 3.74 \times 10^{-16}$ W m²

(this constant includes a π to cancel out the π shown in the denominator of the RHS above)

$c_2 = hc/k = 1.45 \times 10^{-2}$ m K

$B_{\lambda}(T)$ has units of W m⁻² μ m⁻¹ sr⁻¹

The wavelength λ version of Planck's Law peaks in photon energy $E = h/\lambda \approx 4.98$ kT, whereas the frequency ν version peaks in photon energy $E = h\nu \approx 2.821$ kT (the mathematical explanation is subtle). Thus going from the former to the latter shifts the peak of the distribution to higher energies.

Wien's Displacement Law

Wilhelm Wien was German, so his last name is pronounced "Veen". There is an inverse relationship between the wavelength of the peak of the emission of a blackbody and its temperature when expressed as a function of wavelength, and this relationship is often called Wien's displacement law. The peak λ for a given temperature T is obtained⁷ by setting to zero the first derivative of $B_{\lambda}(T)$ with respect to T :

$$\lambda_{\max} = \frac{b}{T}$$

where

λ_{\max} = peak wavelength

T = absolute temperature K of the blackbody

$b = 2.89777 \times 10^{-3}$ m·K = 2,898 μ m·K (Wien's displacement constant)⁸

This is the relationship given in *ASI*. For example, for the Sun's photosphere where $T \approx 5780$ K, this formula yields a λ_{\max} of 0.501 μ m (501 nm, in the green part of the visible light spectrum), consistent with the predominance of solar EM radiation in the visible range and shortwave IR range. Similarly, for a color temperature given by $\lambda_{\max} = 0.475$, the corresponding $T = 6,100$ K.

Considering the spectrum of monochromatic absorptivity (*ASI-118*), the Earth's atmosphere is nearly transparent to and selectively passes visible light (the Sun's predominant radiation) plus a few windows in the IR, whereas it blocks UV and most IR wavelengths (the latter including most of the Earth's intrinsic emission).

In contrast to the Sun, the Earth behaves as a black body with $T = 255$ K (see below), so this yields $\lambda_{\max} = 11.4$ μ m (longwave "thermal" infrared emission).

Expressed using frequency ν , Wien's displacement law becomes

$$\nu_{\max} \approx 5.879 \times 10^{10} \text{ Hz K}^{-1} T$$

"Because the spectrum from Planck's law of black body radiation takes a different shape in the frequency

⁷ <http://physics.info/planck/>

⁸ <http://physics.nist.gov/cuu/Constants/codata.pdf>

domain from that of the wavelength domain, the frequency location of the peak emission does not correspond to the peak wavelength using the simple relationship between frequency, wavelength, and the speed of light.”⁹

Stefan-Boltzmann Law

This gives the total blackbody flux density F (the irradiance, or more precisely the exitance integrated over all wavelengths) obtained by integrating the Planck function over all wavelengths:

$$F = \epsilon\sigma T^4$$

where F = total blackbody flux density (irradiance, $\text{W}\cdot\text{m}^{-2}$)
 ϵ = Emissivity (0 to 1, dependent on wavelength)
 σ = Stefan-Boltzmann constant = $5.6704 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ (Ref.¹⁰)

One may use the Solar Constant F_S (above) as an alternate means of estimating the blackbody temperature of the Sun's photosphere. This yields an effective emission temperature $T_F = 5770 \text{ K}$. Like other real objects, the Sun does not exactly conform in emission spectrum to the emission of a black body, accounting for the discrepancy between the predicted T by Wien Displacement law color temperature versus the Stefan-Boltzmann predicted temperature.

This relationship is used to calculate the Equilibrium T of the Earth (see later).

Solar Spectrum and Earth Irradiance

Solar light wavelengths are often expressed as nm, μm (micrometers, $1 \mu\text{m} = 1000 \text{ nm}$), less commonly in Angstrom \AA (ångström, $1.0 \times 10^{-10} \text{ meters}$, 0.1 nm , $10^{-4} \mu\text{m}$).

(1) The first graph to follow shows solar spectral irradiance (sunlight flux in W of radiant energy per unit area normal to the direction of flow) at Earth's upper atmospheric boundary (extraterrestrial, in yellow), irradiance at sea level (after atmospheric absorption interactions varying with wavelength, in red), and superimposed black body curve for an idealized photosphere of temp of 5250 K (black curve). Despite the label, the ordinate value shown is actually $\text{W m}^{-2} \text{ nm}^{-1}$, i.e., additionally per wavelength interval nm. This is a linear-linear graph.¹¹ Sunlight with wavelength $< 300 \text{ nm}$ does not reach below 10-15 km in the troposphere.

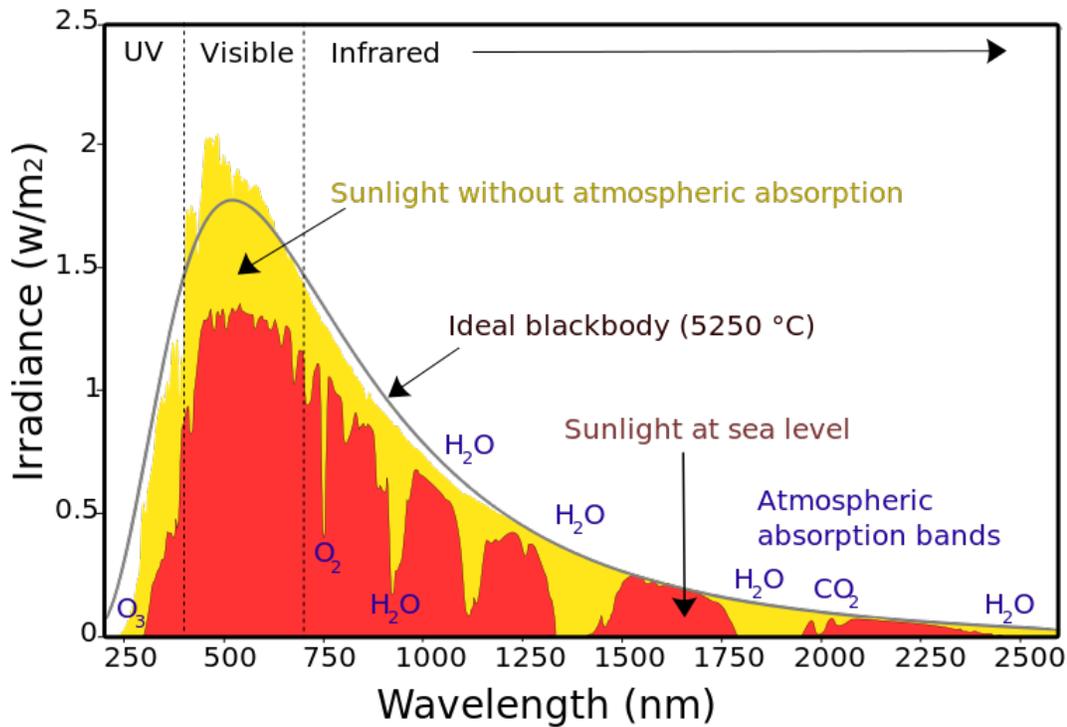
⁹ http://en.wikipedia.org/wiki/Planck%27s_law

¹⁰ <http://physics.nist.gov/cuu/Constants/codata.pdf>

¹¹ • <http://en.wikipedia.org/wiki/Sunlight>

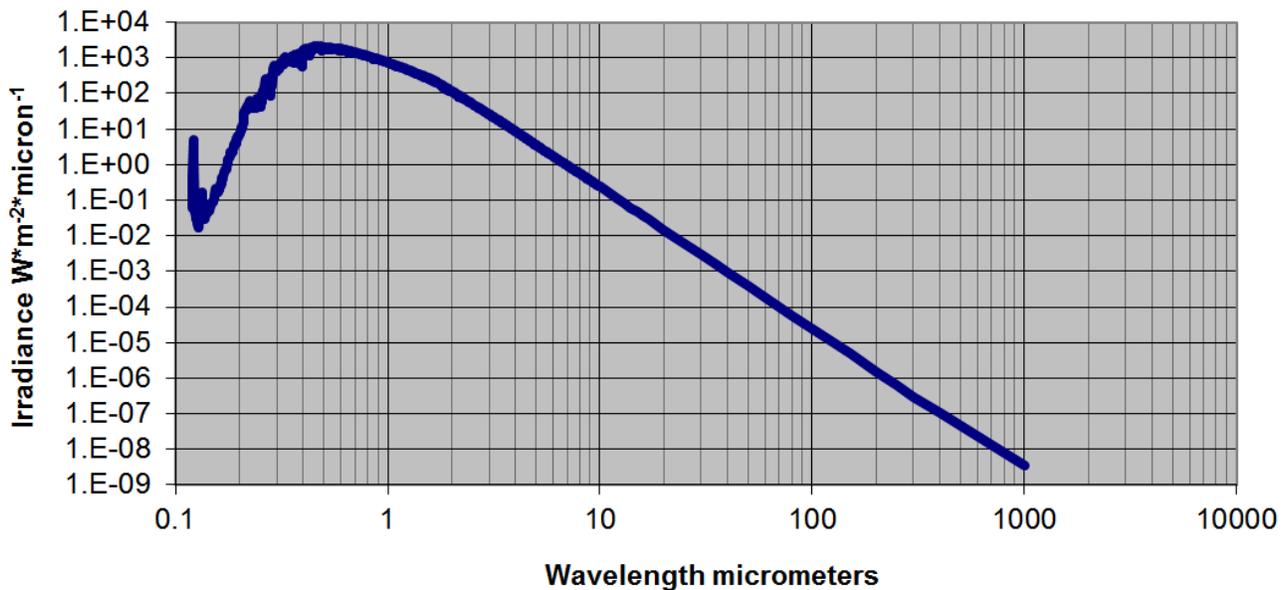
• see also <http://rredc.nrel.gov/solar/spectra/am1.5/>

Spectrum of Solar Radiation (Earth)



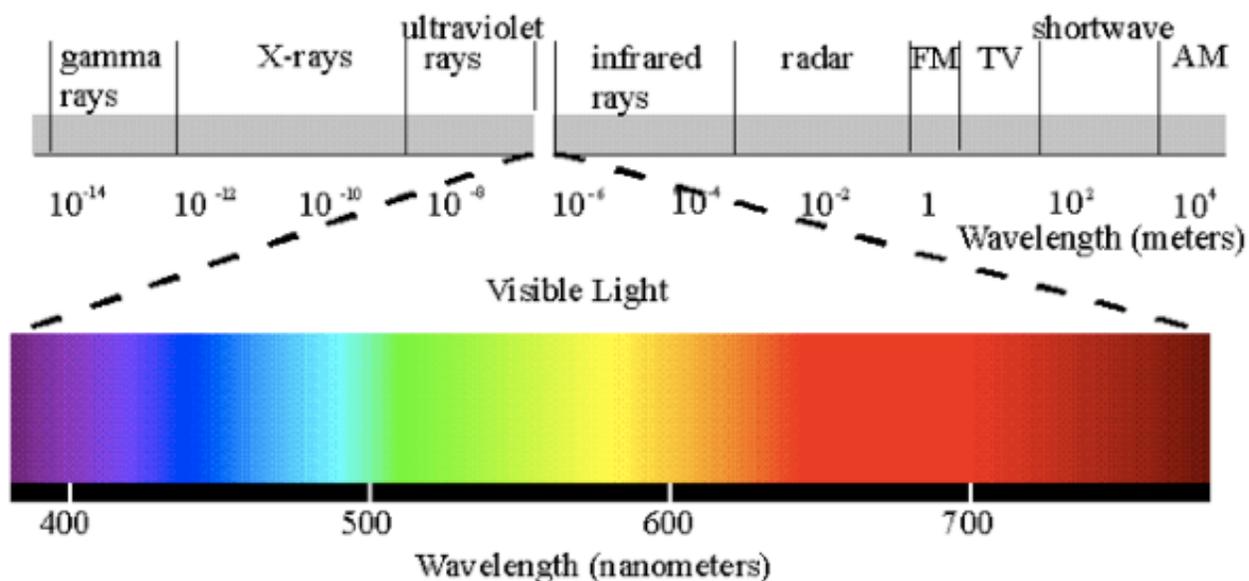
(2) The next graphs shows a Log-Log plot of extraterrestrial Irradiance against wavelength in micrometers. The data is the 2000 ASTM Standard Extraterrestrial Spectrum Reference E-490-00.¹²

Log-Log Plot of ASTM Standard Extraterrestrial Spectrum Reference E-490-00



¹² http://rredc.nrel.gov/solar/spectra/am0/E490_00a_AM0.xls , graph modified by MCM
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The following depicts the broader electromagnetic spectrum for reference:¹³



Divisions of Visible Light:

Visible light is usually taken to be 400 to 700 nm (though in ideal conditions for some persons, it extends from 380 to 800 nm).¹⁴ The names currently employed for color divisions (for which the defining range of wavelengths vary somewhat) are

- red 620-720 nm
- orange 590-620 nm
- yellow 570-590 nm
- green 495-570 nm
- blue 450-495
- violet 380-450 nm.

(Newton added *indigo* between blue and violet, thus the mnemonic ROYGBIV.)

Our current additive primary colors are RGB: red, green, and blue.¹⁵ The following summarizes basic facts about additive colors including how they are perceived,¹⁶

- Red + Green → Yellow (yellow is found in the spectrum between red and green, but humans perceive the same color from their combined red & green cones whether input is yellow or red + green light)
- Red + Blue → Magenta [magenta is not found on the visible spectrum of light]
- Green + Blue → Cyan (aqua; found in the spectrum between green and blue but humans perceive the same color with combined green and blue-violet cones, whether input is cyan or green + blue-violet light)

Pigments cause subtractive colors, not discussed here.

¹³ <http://nothingnerdy.wikispaces.com/THE+ELECTROMAGNETIC+SPECTRUM>

¹⁴ <http://en.wikipedia.org/wiki/Light>

¹⁵ http://en.wikipedia.org/wiki/Primary_color

¹⁶ <http://www.abelard.org/colour/col-hi.htm>

Divisions of Ultraviolet UV

The types of UV (as defined by the Second International Congress on Light in 1932 and incorporated into the ISO standard ISO-21348) are:¹⁷

Ultraviolet C (UVC), 100 to 280 nm. This is germicidal.

Ultraviolet B (UVB), 280 to 315 nm. It directly damages DNA and causes sunburn.

Ultraviolet A (UVA), 315 to 400 nm. UVA is now known to also cause significant damage to DNA via indirect routes (formation of free radicals and reactive oxygen species), and is able to cause cancer.

Per the WHO report, environmental and dermatological photobiologists commonly use these definitions:¹⁸

Ultraviolet C (UVC), 200 to 290 nm

Ultraviolet B (UVB), 290 to 320 nm

Ultraviolet A (UVA), 320 to 400 nm

Divisions of Infrared IR

The division of Infrared IR in the CIE scheme is¹⁹

Infrared-A, 700 nm to 1,400 nm

Infrared-B, 1,400 nm to 3,000 nm

Infrared-C, 3,000 nm to 1 mm

The division of Infrared IR in astronomy is

Near-Infrared, (0.7 - 1) to 5 μm

Mid-Infrared, 5 to (20 - 40) μm

Far-Infrared, (20 - 40) to (200 - 350) μm

Actinic flux (photons $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$) vary as a function of altitude and wavelength (see graph below).

The following table presents additional data about EM radiation:²⁰

Spectrum of Electromagnetic Radiation					
Region	Wavelength (Angstroms)	Wavelength (nanometers)	Wavelength (centimeters)	Frequency (Hz)	Energy (eV)
Radio	$> 10^9$	$> 10^8$	> 10	$< 3 \times 10^9$	$< 10^{-5}$
Microwave	$10^9 - 10^6$	$10^8 - 10^5$	$10 - 0.01$	$3 \times 10^9 - 3 \times 10^{12}$	$10^{-5} - 0.01$
Infrared	$10^6 - 7000$	$10^5 - 700$	$0.01 - 7 \times 10^{-5}$	$3 \times 10^{12} - 4.3 \times 10^{14}$	$0.01 - 2$
Visible	$7000 - 4000$	$700 - 400$	$7 \times 10^{-5} - 4 \times 10^{-5}$	$4.3 \times 10^{14} - 7.5 \times 10^{14}$	$2 - 3$
Ultraviolet	$4000 - 10$	$400 - 1$	$4 \times 10^{-5} - 10^{-7}$	$7.5 \times 10^{14} - 3 \times 10^{17}$	$3 - 10^3$
X-Rays	$10 - 0.1$	$1 - 0.01$	$10^{-7} - 10^{-9}$	$3 \times 10^{17} - 3 \times 10^{19}$	$10^3 - 10^5$
Gamma Rays	< 0.1	< 0.01	$< 10^{-9}$	$> 3 \times 10^{19}$	$> 10^5$

¹⁷ • <http://en.wikipedia.org/wiki/Sunlight> and

• http://www.spacewx.com/pdf/SET_21348_2004.pdf

The latter gives definitions of all Solar Irradiance Spectral Categories.

¹⁸ http://www.who.int/uv/health/solaruvradfull_180706.pdf

Solar Ultraviolet Radiation: Global burden of disease from solar ultraviolet radiation (WHO, 2006)

¹⁹ <http://en.wikipedia.org/wiki/Infrared>

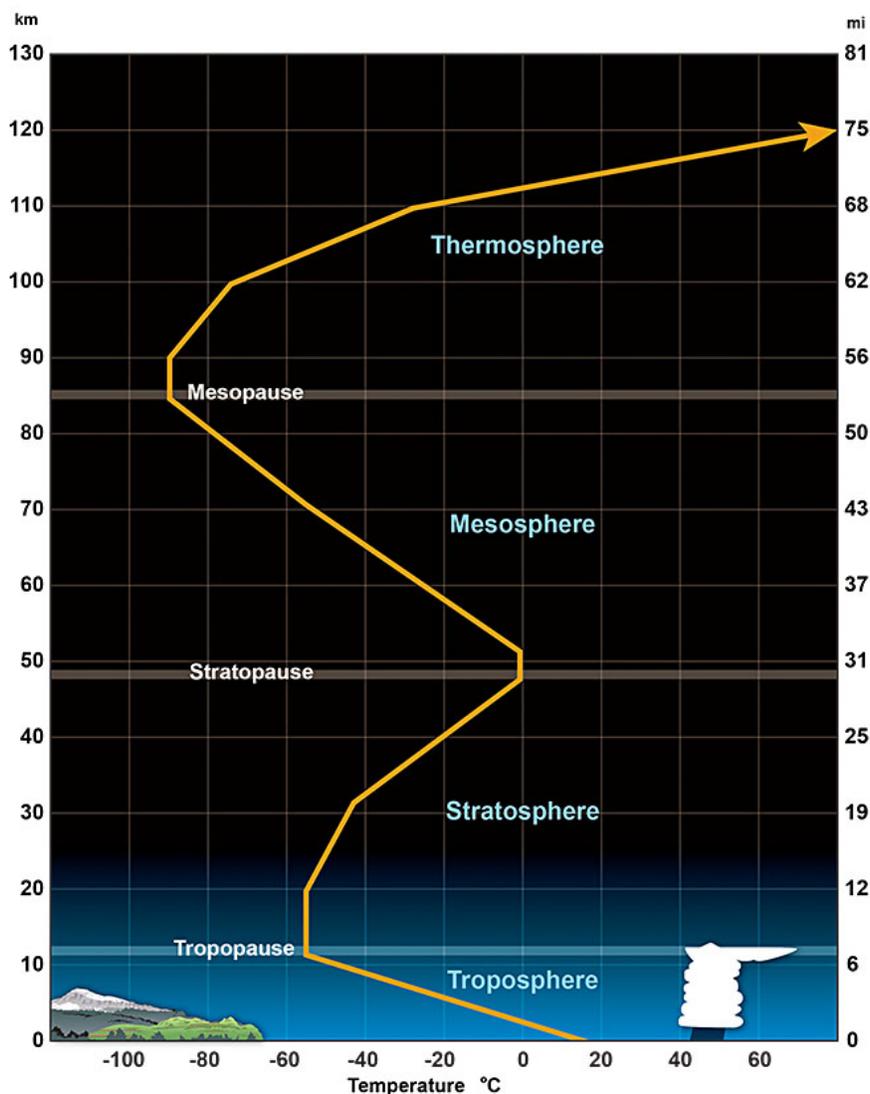
²⁰ <http://csep10.phys.utk.edu/astr162/lect/light/spectrum.html> modified by MCM

Selected Topics in General Atmospheric Science

Major Subdivisions of Atmospheric Sciences

- Atmospheric Physics
- Atmospheric Chemistry
- Atmospheric Dynamics
- Climatology
- Meteorology and Forecasting
- Extraterrestrial Planetary Atmospheric Science

Atmospheric Layers and Relation to Temperature (including the Boundary Layer)



Atmosphere Layers and Their Mean Temperatures:

“Standardized Temperature Profile: An average temperature profile through the lower layers of the atmosphere. Height (in miles and kilometers) is indicated along each side. Temperatures in the thermosphere continue to climb, reaching as high as (3,600°F) 2,000°C.”²¹ (per NOAA)

²¹ Atmospheric Structure (NOAA):

- <http://www.srh.noaa.gov/jetstream/atmos/atmprofile.htm> or
- <http://www.srh.noaa.gov/jetstream/atmos/images/atmprofile.jpg>

The model used in this graph is prob. the US Standard Atmosphere, 1976. The boundary layer (lower 10% of troposphere) is included but not explicitly shown. The vertical subdivisions of the atmosphere pertaining to clouds are termed Étages (low, middle, and high), are also not shown here.

Text (below) regarding these layers that follows is excerpted from NOAA²² and Wikipedia.²³ Layers are listed beginning with the lowest.

Troposphere (0 to 6–20 km)

The troposphere is divided into the bottom 10% or so, the boundary layer, and the free or background troposphere.

NOAA: “The troposphere begins at the Earth's surface and extends up to 4-12 miles (6-20 km) high. This is where we live. As the density of the gases in this layer decrease with height, the air becomes thinner. Therefore, the temperature in the troposphere also decreases with height. As you climb higher, the temperature drops from about 62°F (17°C) to -60°F (-51°C). Almost all weather occurs in this region... The height of the troposphere varies from the equator to the poles. At the equator it is around 11-12 miles (18-20 km) high, at 50°N and 50°S, 5½ miles [~9 km] and at the poles just under four miles [~6.5 km] high. The transition boundary between the troposphere and the [stratosphere] ... is called the tropopause. Together the tropopause and the troposphere are known as the lower atmosphere.”

Wikipedia: “The troposphere begins at the surface and extends to between 7 km (23,000 ft.) at the poles and 17 km (56,000 ft.) at the equator, with some variation due to weather. The troposphere is mostly heated by transfer of energy from the surface, so on average the lowest part of the troposphere is warmest and temperature decreases with altitude. This promotes vertical mixing (hence the origin of its name in the Greek word "τροπή", trope, meaning turn or overturn). The troposphere contains roughly 80% of the mass of the atmosphere.”

The Atmospheric Boundary Layer in the Troposphere and its Diurnal Variation

The atmospheric boundary layer [or planetary boundary layer PBL] is the “lowest part of the atmosphere and its behavior is directly influenced by its contact with a planetary surface. On Earth it usually responds to changes in surface radiative forcing in an hour or less. In this layer physical quantities such as flow velocity, temperature, moisture, etc., display rapid fluctuations (turbulence) and vertical mixing is strong. Above the PBL is the “free atmosphere” where the wind is approximately geostrophic (parallel to the isobars) while within the PBL the wind is affected by surface drag and turns across the isobars. The free atmosphere is usually non-turbulent, or only intermittently turbulent.”²⁴

According to *APGW* p. 50, the boundary layer is the bottom 50 to 3000 m of the troposphere, the location where most people live and where pollutants tend to concentrate (especially in the presence of an inversion). In the daytime, the boundary layer consists of

- (1) the surface layer (bottom 10% of troposphere) with a decreasing T with increasing altitude. Here there are strong changes in wind speed with height (wind shear).
- (2) Next is a convective mixed layer (where thermals provide good mixing of air and pollutants),
- (3) then an entrainment zone with a small inversion layer of increasing T with height at about 1-3 km which somewhat inhibits further rising of air. (In an inversion, the environmental lapse rate $\Gamma_e = -\Delta T/\Delta z$ is negative.) Above this is the boundary with the free troposphere beginning at about 500 to 3000 m.

At night, however the surface cools and

- (1) the surface layer forms a new inversion with rising T with increasing altitude (the environmental lapse rate $\Gamma_e = -\Delta T/\Delta z$ is negative). Buoyancy and thermals are diminished and pollutants emitted close to the surface during the night are trapped by this low-lying inversion.
- (2) Above this inversion is the stable nocturnal boundary layer, which exhibits a lower magnitude environmental lapse rate ($\Gamma_e = -\Delta T/\Delta z$) compared to daytime but still negative and thus still cooling with increasing altitude
- (3) Next is the residual layer (which is unchanged from daytime), and finally
- (4) the entrainment zone with a small inversion layer (also essentially unchanged).

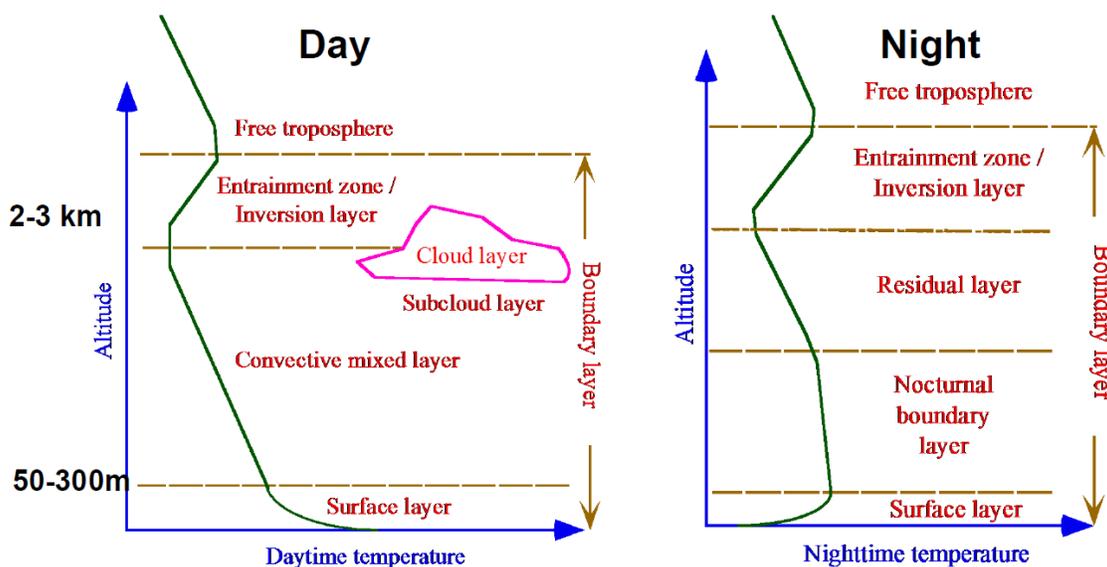
²² <http://www.srh.noaa.gov/srh/jetstream/atmos/layers.htm>

²³ Atmosphere layers: http://en.wikipedia.org/wiki/Atmosphere_of_Earth

²⁴ http://en.wikipedia.org/wiki/Planetary_boundary_layer

The following graphs depicting the day and night boundary layer are from APGW p. 50 fig. 3.4 per JAT notes.

Boundary layer = from surface to 500-3,000 m



Stratosphere (6–20 km to ~50–55 km)

NOAA: “The Stratosphere extends from the tropopause [6–20 km depending on latitude] up to 31 miles [50 km] above the Earth's surface. This layer holds 19 percent of the atmosphere's gases but very little water vapor... Temperature increases with height as [UV] radiation is increasingly absorbed by oxygen molecules leading to [photolysis and ultimately to] the formation of Ozone. The temperature rises from an average -76°F (-60°C) at the tropopause to a maximum of about 5°F (-15°C) at the stratopause due to this absorption of ultraviolet radiation. This increase in temperature with height means no convection occurs since there is no vertical movement of the gases [and thus minimal turbulence and mixing]... The transition boundary which separates the stratosphere from the mesosphere is called the stratopause [~50 km]. The regions of the stratosphere and the mesosphere, along with the stratopause and mesopause, are called the middle atmosphere by scientists.”

Wikipedia: “The stratosphere extends from the tropopause to about 51 km (32 mi). Temperature increases with height, which restricts turbulence and mixing. The stratopause, which is the boundary between the stratosphere and mesosphere, typically is at 50 to 55 km (31 to 34 mi). The pressure here is 1/1000th of sea level.”

Mesosphere (~50–55 km to 80–85 km)

NOAA: “The mesosphere extends from the stratopause [~50 km] to about 53 miles (85 km) above the earth. The gases, including the oxygen molecules, continue to become thinner and thinner with height. As such, the effect of the warming by ultraviolet radiation also becomes less and less leading to a decrease in temperature with height. On average, temperature decreases from about 5°F (-15°C) to as low as -184°F (-120°C) at the mesopause [the coldest place on Earth]. However, the gases in the mesosphere are still thick enough to slow down meteorites hurtling into the atmosphere, where they burn up, leaving fiery trails in the night sky.”

Wikipedia: “The mesosphere extends from the stratopause to 80–85 km (50–53 mi). It is the layer where most meteors burn up upon entering the atmosphere. Temperature decreases with height in the mesosphere. The mesopause [~80–85 km], the temperature minimum that marks the top of the mesosphere, is the coldest place on Earth and has an average temperature around -85 °C (-121 °F; 188.1 K). Just below the mesopause, the air is so cold that even the very scarce water vapor at this altitude can be [frozen] into polar-mesospheric noctilucent clouds. These are highest clouds in the atmosphere and may be visible to the naked eye if sunlight reflects off them about an hour or two after sunset or a similar length of time before sunrise.”

Lightning Sprites appear as luminous reddish-orange flashes. They often occur in clusters within the altitude range 50–90 km above the Earth's surface [thus is the mesosphere].”²⁵

Thermosphere (80–85 km to 690 km) and Ionosphere (60–300 km)

NOAA: “The Thermosphere extends from the mesopause to 430 miles (690 km) above the earth [the top margin is the thermopause or exobase]. This layer is known as the upper atmosphere... The gases of the thermosphere are increasingly thinner than in the mesosphere. As such, incoming high energy ultraviolet and x-ray radiation from the sun, absorbed by the molecules [primarily O₂ and N₂] in this layer, causes a large temperature increase... Because of this absorption, the temperature increases with height and can reach as high as 3,600°F (2,000°C) near the top of this layer; however, despite the high temperature, this layer of the atmosphere would still feel very cold to our skin because of the extremely thin air. The total amount of energy from the very few molecules in this layer is not enough to heat our skin.”

Wikipedia: “...The temperature of this layer can rise to 1,500 °C, though the gas molecules are so far apart that temperature in the usual sense is not well defined. The International Space Station orbits in this layer, between 320 and 380 km (200 and 240 mi). The top of the thermosphere is the bottom of the exosphere, called the exobase. Its height varies with solar activity and ranges from about 350–800 km.” ELVES are a dim, flattened, expanding red hued glow around 400 km in diameter and occur in the ionosphere ~100 km above the ground over thunderstorms.²⁶

NOAA: “Located [primarily] within the thermosphere, the **ionosphere** is made of electrically charged (ionized) gas particles. The ionosphere extends from 37 to 190 miles (60-300 km) above the earth's surface. It is divided into three regions or layers; the F-Region, E-Layer and D-layer. During the daytime the F-Layer splits into two layers then recombines at night.”²⁷ The ionosphere “includes the thermosphere and parts of the mesosphere and exosphere.”²⁸

Exosphere (690 km to 10,000 km)

NOAA: “The Exosphere is the outermost layer of the atmosphere. It extends from the thermopause [or exobase]—the transition boundary which separates the exosphere from the thermosphere below—to 6,200 miles (10,000 km) above the earth. In this layer, atoms and molecules escape into space and satellites orbit the earth.”

Wikipedia: “... extends from the exobase upward. Here the particles are so far apart that they can travel hundreds of kilometers without colliding with one another. Since the particles rarely collide, the atmosphere no longer behaves like a fluid. These free-moving particles follow ballistic trajectories and may migrate into and out of the magnetosphere or the solar wind. The exosphere is mainly composed of hydrogen and helium.”

Pressure, Flows, and Fronts

Pressure P is the force per unit area applied in a direction perpendicular to the surface of an object.²⁹ Gauge pressure is the pressure relative to [i.e., in excess of] the local atmospheric or ambient pressure... The SI unit for pressure is the pascal (Pa), equaling one newton per square meter (N m⁻² or kg·m⁻¹·s⁻²)... Non-SI measures such as pounds per square inch and bar are used in some parts of the world, primarily in the USA... Pressure is sometimes expressed in grams of force cm⁻², or as kg cm⁻² without properly identifying the force units. Using the names kilogram, gram, kilogram-force, or gram-force (or their symbols) as units of force is expressly forbidden in SI units.³⁰ Many meteorologists prefer units of hectopascals (hPa) for atmospheric air pressure, as hPa is equivalent to the widely used millibar (mbar or mb). In other fields, where the hecto-prefix is rarely used, pressures of similar magnitude are given in kilopascals (kPa). Inches or millimeters of mercury are also used in the United States. In medicine, blood pressure is commonly measured in millimeters of mercury, and lung-related pressures in centimeters of water.

²⁵ http://en.wikipedia.org/wiki/Sprite_%28lightning%29

²⁶ http://en.wikipedia.org/wiki/Upper-atmospheric_lightning

²⁷ http://www.srh.noaa.gov/srh/jetstream/atmos/ionosphere_max.htm

²⁸ <http://en.wikipedia.org/wiki/Ionosphere>

²⁹ <http://en.wikipedia.org/wiki/Pressure>

³⁰ <http://www.newworldencyclopedia.org/entry/Pressure>

Ideal Gas Law

The equation of state relating pressure P , volume V , and temp T is the simplified Ideal Gas Law:

$$p = \frac{nR^*T}{V} = \frac{nA}{V} \left(\frac{R^*}{A} \right) T = Nk_B T$$

Here (constant conversions may be needed)

p is pressure in hPa

n moles of gas molecules

R^* is the universal gas constant = 0.083145 m³ hPa mol⁻¹ K⁻¹

T is temp in K

V is volume in m³

N is the number density of molecules m⁻³ (= nA/V)

A is the Avogadro number (6.02252 x 10²³ molecules mol⁻¹)

k_B is the Boltzmann constant (1.3807 x 10⁻²⁵ m³ hPa K⁻¹ molec⁻¹)

The number density of gas molecules in air at 0 °C and 1 atm (known as the Loschmidt constant) is ~2.687×10²⁵ per cubic meter.³¹

Partial Pressure and Manometers

The partial pressure of a gas is the pressure it would exert in a given volume according to the ideal gas law if there were no other gases present. For CO₂ with mixing ratio 400 ppm, the partial pressure at 1 atm and 0 °C is 4×10⁻⁴ atm and the number of CO₂ molecules per m³ is about 1.075×10²² per cubic meter.

Evangelista Torricelli (not Toricelli) in 1643 first measured atmospheric pressure with a mercury barometer he invented. He pressure of 1000 hPa corresponds to a Hg column of 29.6 inches.³²

Because pressure is commonly measured by its ability to displace a column of liquid in a manometer, pressures are often expressed as a height of water or mercury (Hg) in the manometer column (e.g., centimeters of water, inches of water, inches of Hg, or millimeters of Hg). The pressure exerted by a column of liquid of height h and uniform density ρ is given by the hydrostatic pressure equation $p = \rho gh$. This assumes ρ and g are constant over the height of the column, but in fact fluid density and local gravity can vary with height and locale, so the height of a fluid column does not define pressure precisely. The units millimeters of mercury or inches of mercury are not based on a physical column of mercury—rather, they have been given precise definitions expressed in terms of SI units. Thus, one mm Hg (millimeter of mercury) is equal to one Torr = 1/760 std atm (see below). The water-based units still depend on the density of water, a measured rather than defined quantity.³³

Atmospheric Pressure Variation with Altitude (or Geopotential Height)

Standard Atmosphere of Pressure

The standard atmosphere (atm) is a defined constant: **One std atmosphere**³⁴ is an international reference pressure defined as 101,325 Pa or 1013.25 hPa, reflecting the true mean sea level pressure at the latitude of Paris, and is equal to

101325 Pa

101.325 kPa

1013.25 hPa (hPa are equivalent to millibars=mb=mbar)

1.01325 bar

760 Torr (mm Hg; by definition)

14.696 psi

At pressure = 1 atmosphere and temp = 15 °C, 1 m³ of air weighs 1.225 kg (the density is 1.225 kg/m³) according to the ISA (International Standard Atmosphere).³⁵

³¹ http://en.wikipedia.org/wiki/Loschmidt_constant

³² http://en.wikipedia.org/wiki/Evangelista_Torricelli

³³ <http://en.wikipedia.org/wiki/Pressure>

³⁴ http://en.wikipedia.org/wiki/Atmosphere_%28unit%29

³⁵ http://en.wikipedia.org/wiki/Density_of_air

Pressures at Varying Heights

While the average sea level atmospheric pressure is 1013.25 mb (29.92 mm Hg), the lowest recorded sea level pressure was 870 mb, and the highest recorded was 1084 mb (per RAH notes). According to ASI-7, the globally averaged surface pressure is 985 hPa (this of course encompasses latitudes other than that of Paris, and apparently includes land surfaces that are above sea level). (see also MT8-197)³⁶

At any given location on Earth, atmospheric pressure always decreases with height above sea level³⁷ in approximately exponential fashion, and is estimated (according to standard models) as follows:

Fraction of 1 Atm.	Pressure (mb or hPa)	Geopotential Height (m) and Approximate Layer US Std Atmosphere ³⁸	Geopotential Height (m) ICAO Std Atmosphere ³⁹
1 atm	1013.25 mb	0 m (sea level)	0 m (sea level)
	1000 mb	110 m	111 m
	850 mb	1,457 m	1,457 m
	700 mb	3,012 m	3,012 m
1/2 atm	506.625 mb	5,477 m (troposphere)	
	500 mb	5,574 m (troposphere)	5,574 m
	300 mb	9,177 m (near tropopause)	
1/4 atm	253.313 mb	10,278 m (upper troposphere or lower stratosphere)	
	250 mb	10,363 m (upper troposphere or lower stratosphere)	10,363 m
	200 mb	11,784 m	11,784 m
1/10 atm	101.325 mb	16,096 m (upper troposphere or lower stratosphere)	
	100 mb	16,180 m (upper troposphere or lower stratosphere)	16,180 m
1/100 atm	10.13 mb	30,967 m (stratosphere)	
1/1000 atm	1.01 mb	47,716 m (upper stratosphere)	

Thus more than 99.9% of the atmosphere lies below 50 km. It is also apparent that the 500 mb level is a good approximation to the 0.5 atm level, and the 250 mb level is a good approximation to the 0.25 atm level.

Here is a good calculator for Standard Atmosphere Properties according to the 1976 US Standard Atmosphere model.⁴⁰

Mathematical estimates of the mean atmospheric pressure (and other quantities such as mean free path) as a function of altitude are given by simple or quite complex models.⁴¹ It is extensively described in "U.S.

³⁶ MT8 = C. Donald Ahrens, *Meteorology today: an introduction to weather, climate, and the environment 8th Ed*, Belmont, California, Thomson/Brooks/Cole, 2007.

³⁷ http://en.wikipedia.org/wiki/Atmospheric_pressure#Altitude_atmospheric_pressure_variation

³⁸ U.S. Standard Atmosphere 1976: interpolated from Part 4 table I, see below.

³⁹ ICAO Std Atmosphere: <http://www.aviation.ch/tools-atmosphere.asp> and Skew T Log P diagram

⁴⁰ <http://www.luizmonteiro.com/StdAtm.aspx>

⁴¹ Modeling of the atmosphere pressure vs. altitude:

• http://www.engineeringtoolbox.com/air-altitude-pressure-d_462.html

• <http://www.regentsprep.org/Regents/math/algtrig/ATP8b/exponentialResource.htm>

Standard Atmosphere 1976⁴² of NASA/NOAA, which presents a model consisting of two submodels: one extending from 0 to 86 km and the second extending from 86 km to 1000 km. Part 4 Table I gives pressure, temperature T, and density ρ as a function of geometric and geopotential height up to 1000 km.

Estimating Typical Atmospheric Pressure versus Height or Altitude

These barometric formulas⁴³ apply to various height regimes below 86 km, according to the ISA (International Standard Atmosphere)⁴⁴

Equation 1 assumes T is not constant and has non-zero lapse rate:

$$P = P_b \cdot \left[\frac{T_b}{T_b + L_b \cdot (h - h_b)} \right]^{\frac{g_0 \cdot M}{R^* \cdot L_b}}$$

Equation 2, assumes T is constant:

$$P = P_b \cdot \exp \left[\frac{-g_0 \cdot M \cdot (h - h_b)}{R^* \cdot T_b} \right]$$

where

- P_b = static pressure (pascals)
- T_b = standard temperature (K)
- L_b = standard temperature lapse rate (K/m)
- h = geopotential height above mean sea level (meters).
- h_b = geopotential height above MSL at bottom of applicable layer b (meters; e.g., $h_1 = 11,000$ meters)
- R^* = universal gas constant for air: 8.31432 N·m / (mol·K) [i.e., J/(mol·K)]
- g_0 = gravitational acceleration (9.80665 m/s²), assumed to be constant or factored into h_b
- M = mean molecular mass of Earth's air (0.0289644 kg/mol = 28.9644 g/mol), assumed constant

Layer	Subscript b	Geopotential Height above MSL at bottom (m) h_b	Geometric Altitude above MSL (m) h_b	Static pressure (Pa) P_b	Standard temperature (K) T_b	Temperature lapse rate (K/m) L_b
Troposphere	0	0	0	101325.00	288.15	-0.0065
Tropopause	1	11,000	11,019	22632.10	216.65	0.0
Stratosphere	2	20,000	20,063	5474.89	216.65	0.001
Stratosphere	3	32,000	32,162	868.02	228.65	0.0028
Stratopause	4	47,000	47,350	110.91	270.65	0.0
Mesosphere	5	51,000	51,413	66.94	270.65	-0.0028
Mesosphere	6	71,000	71,802	3.96	214.65	-0.002

Subscript b defines 7 successive layers. MSL = mean sea level. The constants h_b , P_b , T_b , L_b are defined for the applicable layer in the table. According to the ISA, h and h_b are given in geopotential heights in m. However, altitude (m) may be used as a close approximation and the equivalent value is shown for reference.

⁴² U.S. Standard Atmosphere 1976 (see also Glossary):

- NASA/NOAA full description October 1976: <http://www.pdas.com/refs/us76.pdf>
- Hydrostatic equations (which I have not yet studied): <http://www.pdas.com/hydro.pdf>

⁴³ http://en.wikipedia.org/wiki/Barometric_formula

⁴⁴ http://en.wikipedia.org/wiki/International_Standard_Atmosphere

Constant Height/Altitude (Isobar) and Constant Pressure Height (Isohypse) Contour Plots

Weather maps showing isobars typically depict surface pressure isobars corrected to sea level. These are also called sea level pressure charts. Isobar charts may also be called constant height charts, especially when made for other heights such as 3000 m.) The correction for elevation may be done with the use of the hypsometric equation, which assumes a constant temperature:⁴⁵

$$Z_2 - Z_1 = \bar{H} \ln\left(\frac{p_1}{p_2}\right) = \frac{R_d \bar{T}_v}{g_0} \ln\left(\frac{p_1}{p_2}\right)$$

where Z_2 and Z_1 are the geopotential heights, \bar{T}_v is the mean virtual temperature [the temperature at which a theoretical dry air parcel would have a total pressure and density equal to the moist parcel air parcel], \bar{H} is the average scale height = $29.3T$, and p_1 and p_2 are the respective pressures. I have not shown a final calculation formula because the actual methods used seem to be complex and may vary depending on the amount of elevation above sea level and other factors.

Variations of pressure can also be mapped with constant pressure geopotential height (isohypse) contour line charts. Here, the height selected, usually a geopotential height, is chosen to create a virtual surface of constant pressure (such as 300 mb, 500 mb, or 850 mb). "...In the mountainous terrain of the western United States and Mexican Plateau, the 850 hPa pressure surface can be a more realistic depiction of the weather pattern than a standard surface analysis. [Presumably, mappers of isohypse contours for mountainous terrain such as in Colorado, already above the 850 hPa level, must interpolate fictitious values as best they can.] Using the 850 and 700 hPa pressure surfaces, one can determine when and where warm advection (horizontal flow coincident with upward vertical motion) and cold advection (coincident with downward vertical motion) is occurring within the lower portions of the troposphere. Areas with small dew point depressions and [that] are below freezing indicate the presence of icing conditions for aircraft. The 500 hPa pressure surface can be used as a rough guide for the motion of many tropical cyclones. Shallower tropical cyclones, which have experienced vertical wind shear, tend to be steered by winds at the 700 hPa level... Use of the 300 and 200 hPa constant pressure charts can indicate the strength of systems in the lower troposphere, as stronger systems near the Earth's surface are reflected as stronger features at these levels of the atmosphere... Minima in the wind pattern aloft are favorable for tropical cyclogenesis. Maxima in the wind pattern at various levels of the atmosphere show locations of jet streams."⁴⁶

It is misleading to refer to pressure height contour lines as isobars. The various contour lines shown graphically are indeed all at the same pressure, thus isobars in this sense, but what is plotted are contours of varying pressure geopotential heights, for which the pressure is the same across the entire graph. Such contour lines may be termed isoheights or isoheight contours (terms which are ambiguous), or better, isohypses or isohypse contours.⁴⁷ (The suffix -hypse derives from Greek hypsos = height.)⁴⁸ However, I note that some authors refer to constant pressure height surfaces as isobaric surfaces, and their isohypse maps as isobaric charts, an undesirable usage in my opinion. This terminology therefore appears to be a ready source of confusion for the uninitiated.

An aircraft flying into colder air and maintaining a constant pressure set by the altimeter is actually descending in geometric height and may fly into the terrain unless the altimeter is adjusted for the temperature—thus a preference for radio altimeters rather than pressure altimeters. (MT8-200)

Examples of 500 mb (500 hPa) Pressure Height Graphs (Isohypes)

In general, the atmosphere is colder and therefore denser in the polar than in the equatorial regions, and correspondingly, the 500 mb surface for polar regions lies at a lower height than for the equator. Pressure heights usually refer to Geopotential Height, an adjustment to geometric height (elevation above mean sea level) that reflects the variation of gravity with latitude and elevation.

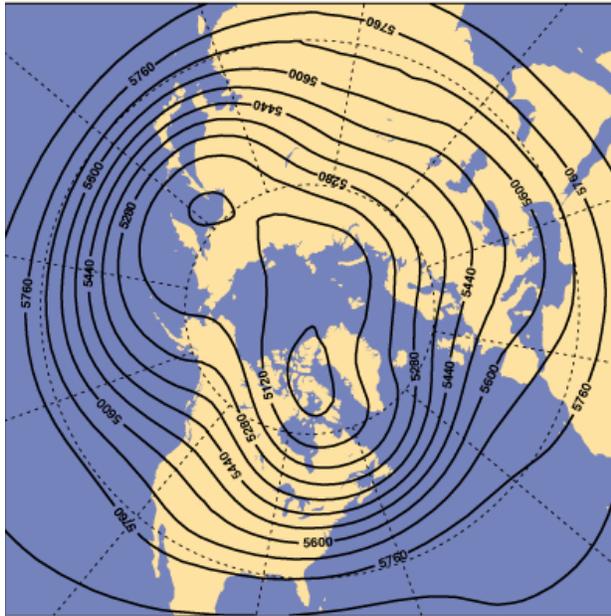
⁴⁵ ASI p. 70

⁴⁶ http://en.wikipedia.org/wiki/Weather_maps#Constant_pressure_charts

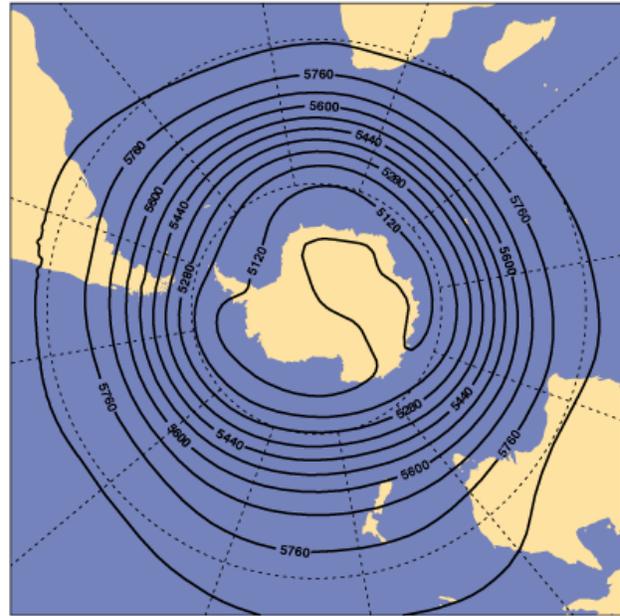
⁴⁷ http://en.wikipedia.org/wiki/Contour_line

⁴⁸ <http://www.yourdictionary.com/hypso-prefix>

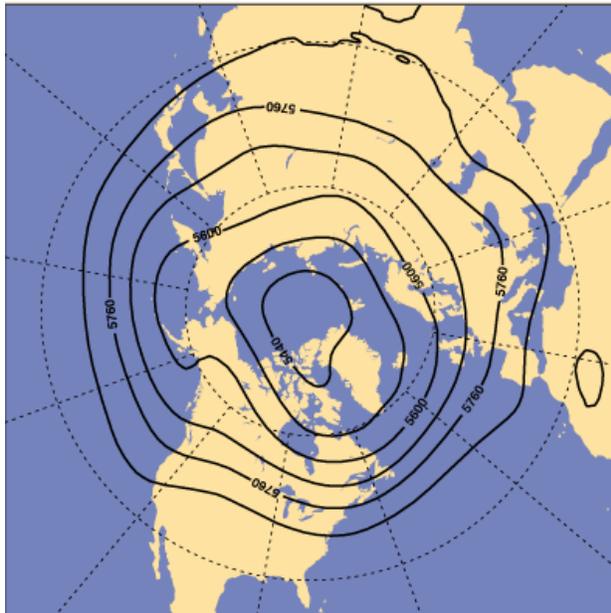
Geopotential height at 500 hPa



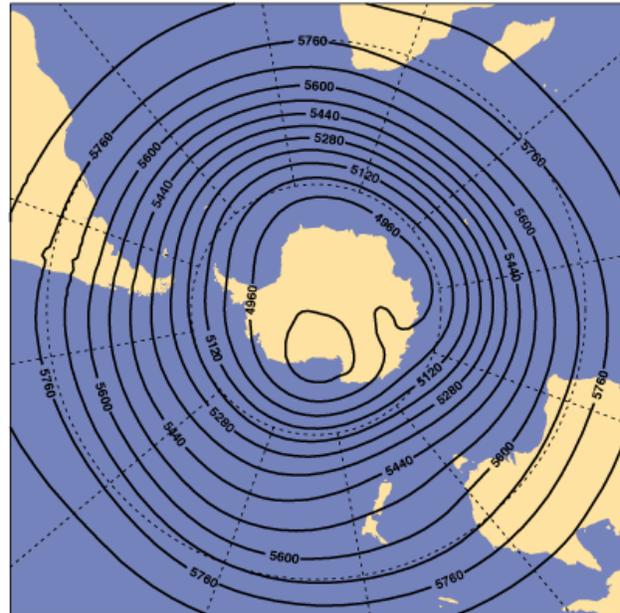
December-February



Geopotential height at 500 hPa



June-August



modified slightly from http://www.ecmwf.int/research/era/ERA-40_Atlas/images/full/D18_PS_JJA.gif
and http://www.ecmwf.int/research/era/ERA-40_Atlas/images/full/D18_PS_DJF.gif

Superimposed on this general trend of isohypse contours—and their associated geostrophic winds circling the poles (see below)—are long wavelength (LW) and shorter wavelength (SW) ridges and troughs of higher and lower pressure (corresponding to higher and lower heights of the 500 mb surface), the so-called planetary, baroclinic, or Rossby waves. These LW and SW waves are associated with significant weather systems, discussed under troughs and ridges.

Upper Level Atmospheric Pressures and Flows

Most of these topics are also addressed in Effects of Meteorology on Air Pollution.

Upper level flow parameters such as pressure are observed with probes such as the rawinsonde system launched from upper-level stations⁴⁹ and by other means. Upper level pressure is typically mapped using constant pressure surfaces, such as the 500 mb surface (or level—i.e., the virtual surface representing the

⁴⁹ <http://weather.uwyo.edu/upperair/>

height above sea level, often expressed in decameters, at which the atmospheric pressure has fallen to 500 mb). The discrete observational data obtained from these probes are interpolated to yield a Constant pressure geopotential height (isohypse) chart for various pressure levels such as 500 mb. (Further summary omitted here.)

Tropic to Polar variation: “In general constant pressure [geopotential height] surfaces (such as for 500 mb) slope downwards from the tropics to the poles.”⁵⁰ This means that the warmer temperatures of the tropics cause expansion of the air, thus causing a given pressure height surface to be at a higher altitude compared to the colder air in the polar regions, for which the contracted cold air attains the given pressure height surface at a lower altitude.

Convergence and Divergence: Convergence aloft (a net inflow of air molecules into a region of the atmosphere) is associated with increasing surface pressure, since the mass overhead per unit surface area, or weight of the column, will increase with time. In contrast, divergence aloft (a net outflow of air molecules from a region of the atmosphere) is always associated with decreasing surface pressure, since the mass per unit surface area, or weight of the column, will decrease with time. A high surface pressure develops under a region of maximum convergence aloft. A low surface pressure develops under a region of maximum divergence aloft. In general, rising air motion is associated with decreasing (Low) pressure (at least at the surface), adiabatic cooling, increasing relative humidity, condensation, clouds and precipitation. In contrast, sinking air motion is associated with increasing (High) pressure (at the surface), adiabatic warming, decreasing relative humidity, and relatively clear skies.⁵¹

Trough (Low), Ridge (High), Cyclone and Anticyclone, Blocking High: These are complex and sometimes frankly confusing topics. The large-scale (*synoptic*) pattern of the 500 mb surface apparent in views centered on the N Pole (see above and here⁵²), shows concentric pressure height contours. These contours correspond with jet streams aloft (predominantly westerlies) which encircle the pole (the geostrophic wind flow direction is along the pressure height contours in the absence of surface friction). Typically the pressure height isohypse contours are circumpolar contours which decrease in height value with increased latitude (see graph above).

Superimposed are large wave-like perturbations in the circularity of these pressure height contours. These planetary-scale waves (so-called *planetary waves*, aka *baroclinic and barotropic Rossby waves*)⁵³ are associated with *troughs* and *ridges*. These are most easily understood as phenomena defined on constant pressure height surfaces (such as 800, 750, 500, and 300 mb).

Troughs are elongated regions of relatively low or depressed pressure height surfaces, often associated with weather fronts. Ridges are elongated regions of relatively high or elevated pressure height surfaces, often associated with sinking air or a deep warm air mass. A trough is “an elongated area of relatively low atmospheric pressure, usually not associated with a closed circulation, and thus used to distinguish from a closed low. It is the opposite of ridge”⁵⁴. “Air will cool when it rises, thus a trough can be found where there is a lifting of air. A trough can also be found in a region dominated by a very cold air mass. This troughing will be most pronounced in the upper levels. A trough can bring in cloudy conditions and precipitation or they can bring in a cold air mass.”⁵⁵ In the NH, a trough on a constant pressure height map appears as a southward extension or meander of the pressure height contour lines, whereas a ridge appears as a poleward extension or meander of these lines. The axis of symmetry of the trough or ridge is often tilted, in the NH from SW to NE.

A strong meander can become detached and evolve to an enclosed cut-off rotating region (forming a *high pressure center* or *low pressure center*). The cut-off pressure height contour lines, which are often elliptical in shape, may be poleward of the westerly current and contain a closed high pressure region (H),⁵⁶ or they may be equatorward of the westerly current and enclose a low pressure region (L).⁵⁷

⁵⁰ former URL: http://atoc.colorado.edu/~cassano/atoc1050/Lecture_Notes/Chapter03/chapter3.pdf

⁵¹ Paraphrased partially from

http://atoc.colorado.edu/~cassano/atoc1050/Lecture_Notes/Chapter08/chapter8.pdf

⁵² http://www.atmos.washington.edu/~ovens/loops/wxloop.cgi?npole_h500+/-168/

⁵³ http://en.wikipedia.org/wiki/Rosby_wave

⁵⁴ <http://w1.weather.gov/glossary/index.php?word=trough>

⁵⁵ <http://www.theweatherprediction.com/habyhints2/457/>

⁵⁶ <http://amsglossary.allenpress.com/glossary/search?p=1&query=cut-off&submit=Search>

⁵⁷ <http://amsglossary.allenpress.com/glossary/search?id=cut-off-low1>

An *anticyclone*, per the US NWS⁵⁸, is “a large-scale circulation of winds around a central region of high atmospheric pressure, clockwise in the Northern Hemisphere, counterclockwise in the Southern Hemisphere”. A *cyclone* is “A large-scale circulation of winds around a central region of low atmospheric pressure, counterclockwise in the Northern Hemisphere, clockwise in the Southern Hemisphere”.⁵⁹ [Note that this usage of *cyclone* does not refer to a tornado.]

Effects of surface-based anticyclones include clearing skies as well as cooler, drier air. Fog can also form overnight within a region of higher pressure. Mid-tropospheric systems, such as the *subtropical ridge*, deflect tropical cyclones around their periphery and cause a temperature inversion (the environmental lapse rate $\Gamma_e = -\Delta T/\Delta z$ is negative), inhibiting free convection near their center, building up surface-based haze under their base. Anticyclones aloft can form within *warm core lows* such as tropical cyclones, due to descending cool air from the backside of upper troughs such as polar highs, or from large scale sinking such as the subtropical ridge. Such a cut-off high may act as a *blocking high* or blocking anticyclone, defined as “any high (or anticyclone) that remains nearly stationary or moves slowly compared to the west-to-east motion ‘upstream’ from its location, so that it effectively ‘blocks’ the movement of migratory cyclones across its latitudes. A blocking high may comprise a smaller-scale effect than that associated with large-scale blocking.”⁶⁰

See also Glossary on **Troughs and Ridges**

Wind Response to Pressure Gradients: Wind direction is not usually perpendicular to the isohypse (pressure height) contours. (This is contrary to what one might naively expect, assuming air flow were simply directed along the pressure gradient, but this is true only at the Equator where Coriolis effect is absent, or would also be true for a non-rotating Earth.) Rather, under the influence of the Coriolis Effect and a low Rossby number for large-scale flows, it is everywhere nearly parallel to isohypse (pressure height) contours. For example, the polar jet streams, which flow nearly parallel to pressure height contours for which pressure height and temp is decreasing toward the poles, are westerly winds in both hemispheres.

⁵⁸ <http://w1.weather.gov/glossary/index.php?word=ANTICYCLONE>

⁵⁹ <http://w1.weather.gov/glossary/index.php?word=cyclone>

⁶⁰ http://glossary.ametsoc.org/wiki/Blocking_high

Atmospheric Chemistry

This review touches only on some key chemical points of interest to me, and is not intended to be a general chemical review.

Review of QM Electron Orbitals and Configurations

The wavefunction Ψ of the non-relativistic Schrödinger wave equation reduces to three equations which when solved lead to the first three quantum numbers: n , ℓ , and m . The fourth quantum number, spin s , is given by the Dirac equation. "The Dirac equation (on a complex four-component spinor), ... is fully relativistic (with respect to special relativity) and predicts spin."⁶¹

Principle Quantum Number n

Principle quantum number n may take on the values 1, 2, 3, ..., ∞ .

Energy Levels of the Electron: These are determined to a first approximation (via the Bohr model) solely by the Principle Quantum Number n .⁶²

$$E = \frac{E_1}{n^2} = \frac{-13.6 \text{ eV}}{n^2}$$

where $n = 1, 2, 3$, etc.

The Principle Quantum Number n (1, 2, 3, ..., ∞) defines the main electron shells: $n = 1 \rightarrow$ K shell, $2 \rightarrow$ L shell, $3 \rightarrow$ M shell, $4 \rightarrow$ N, $5 \rightarrow$ O, $6 \rightarrow$ P, $7 \rightarrow$ Q. The ground state, for which $n = 1$, has the lowest energy (i.e., is the most negative and is most tightly bound).

The energy and wavelength of a photon emitted during a transition from a higher to a lower energy level for the Bohr hydrogen atom model are given by⁶³

$$E = h\nu = -13.6 \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right] \text{ eV}$$

$$\frac{1}{\lambda} = \frac{\nu}{c} = R \left[\frac{1}{n_i^2} - \frac{1}{n_f^2} \right]$$

where ν = frequency in s^{-1} , $h\nu$ is the photon energy in eV, n_i^2 is the initial value of n and n_f^2 is the final value, λ is the wavelength in m, and R is the Rydberg constant:

$$R = R_H = R_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^3 c} = 1.097\,373 \times 10^7 \text{ m}^{-1}$$

Here, m_e is the rest mass of the electron (9.109383×10^{-31} kg), e is the electrical charge of an electron ($1.6021767 \times 10^{-19}$ Coulombs), ϵ_0 is the permittivity of free space (8.854188×10^{-12} farads per meter), h is the Planck constant ($6.6260696 \times 10^{-34}$ J s), and c is the vacuum speed of light ($299,792,458$ m s^{-1}).

The final value of n determines whether the emitted photon is in the Lyman Series ($n = 1$), Balmer series ($n = 2$), Ritz-Paschen series ($n = 3$), etc.

This formula neglects effects of fine structure, Lamb shift, and hyperfine structure.⁶⁴

An analogous calculation applies to "hydrogenic" atoms or ions such as He II (singly ionized He), Li III (doubly ionized He), and C IV (triply ionized C).

Angular Momentum quantum numbers ℓ , m , and s

Quantum numbers ℓ and m pertain to orbital angular momentum, whereas s pertains to spin angular momentum.

⁶¹ http://en.wikipedia.org/wiki/Pauli_equation

⁶² http://en.wikipedia.org/wiki/Principal_quantum_number

⁶³ <http://hyperphysics.phy-astr.gsu.edu/hbase/hyde.html>

⁶⁴ http://en.wikipedia.org/wiki/Hydrogen_atom

The Orbital (or Azimuthal) Angular Momentum Quantum Number ℓ

The quantum number ℓ determines orbital angular momentum and the shape of the orbital, and has allowed values of:

$$\ell = 0, 1, 2, \dots, n-1$$

The values of ℓ define “subshells” of the main shell. Each subshell can hold $2(2\ell + 1)$ electrons, based on the allowed values of m and s (see below). The subshells are named with letters.⁶⁵

Value of ℓ	$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$	$\ell = 5$	6, (then 7, 8, 9, 10, 11)
Letter	s (sharp)	p (principal)	d (diffuse)	f (fundamental)	g	h	i, (then k, l, m, n, o)
Shape	sphere	3 dumbbells	4 dumbbells etc.	8 dumbbells etc.			
Max. Electrons in subshell: $2(2\ell + 1)$	2	6	10	14	18	22	26 ...

The term azimuthal refers to an angle in spherical coordinates: the anticlockwise angle ϕ between the positive x-axis and the projection of the vector onto the xy-plane. (In contrast, the polar angle θ is formed between the vector and the Z axis.)

The Magnetic Quantum Number m or m_ℓ :

m or m_ℓ has allowed values of:

$$m = -\ell, \dots, 0, \dots, \ell, \text{ thus there are } 2\ell+1 \text{ integral magnetic quantum number values allowed.}$$

This determines the energy shift of an atomic orbital due to an external magnetic field (as in Zeeman splitting of spectral line⁶⁶ in a static magnetic field), hence the name magnetic quantum number. In this sense, the magnetic quantum number denotes the energy levels available within a subshell.⁶⁷

The state it determines can be thought of loosely as the quantized projection of the angular momentum vector on the z-axis.⁶⁸

When $n = 0$ (ground state), ℓ and m are 0.

Spin Angular Momentum Quantum number s

Spin Quantum number s (or m_s) pertains to spin angular momentum, and is defined only as the component in one axis, such as the Z axis, for which s can take on values of

$$s = \pm 1/2.$$

As a result, the spin angular momentum S_z can be $\pm \hbar/2$, where $\hbar = h/(2\pi)$.

Spin was manifested in the hydrogen spectrum at very high resolution (for both protium and deuterium), in the form of closely spaced doublets about 0.016 nm apart (corresponding with $2P_{3/2}$ and $2P_{1/2}$ states), a phenomenon called fine structure. The 1922 Stern–Gerlach experiment, using silver atoms in an inhomogeneous magnetic field, showed splitting of the beam later deduced to be due to the 2 discrete states of $5s^1$ unpaired electron spin.

⁶⁵ http://en.wikipedia.org/wiki/Azimuthal_quantum_number

⁶⁶ http://en.wikipedia.org/wiki/Zeeaman_effect

⁶⁷ http://en.wikipedia.org/wiki/Magnetic_quantum_number

⁶⁸ http://wikipedia.org/wiki/Azimuthal_quantum_number

Overall Number of Electrons per Shell ($2n^2$)

Each spatial orbital defined by n , ℓ , and m can hold up to 2 electrons, which must have opposing spin $s = 1/2$ and $-1/2$. The Pauli exclusion principle requires that no two electrons have the same set of the 4 quantum numbers n , l , m , and s . For elements through $Z=118$,

The $n = 1$ K shell has only an s subshell with $\ell = 0$, allowing 2 electrons.

The $n = 2$ L shell has an s ($\ell = 0$) and p ($\ell = 1$) subshell, allowing $2 + 6 = 8$ electrons.

The $n = 3$ M shell has an s ($\ell = 0$), p ($\ell = 1$), and d ($\ell = 2$) subshell, allowing $2 + 6 + 10 = 18$ electrons.

The $n = 4$ N shell adds f ($\ell = 3$) and allows $2 + 6 + 10 + 14 = 32$ electrons.

The $n = 5$ O shell could add g ($\ell = 4$) and in theory would allow $2 + 6 + 10 + 14 + 18 = 50$ electrons

(but ground state EC's actually fill the O shell only to 32 total, with up to 14 in 5f, and none in 5g).

The $n = 6$ P shell could add h ($\ell = 5$) and in theory would allow $2 + 6 + 10 + 14 + 18 + 22 = 72$ electrons

(but ground state EC's actually fill the P shell only to 18 total, with up to 10 in 6d, and none in 6f)

The $n = 7$ Q shell could add i ($\ell = 6$)

(but ground state EC's actually fill the Q shell only to 8 total, with up to 6 in 7p, and no 7d, 7f, etc.)

Singlet versus Triplet States

(The following is excerpted from here⁶⁹ and is beyond my skill level): Consider electrons (or other particles) occurring in pairs and both with spin $\pm 1/2$. Each particle can be either spin up or spin down so the system has four basis states in all

$$\uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow$$

The total spin and its projection on a defined Z axis can be computed using the rules for adding angular momentum in quantum mechanics using the Clebsch–Gordan coefficients...

There are three possible states with total (combined) spin angular momentum $S = 1$:

$$\left. \begin{array}{l} |1, 1\rangle = \uparrow\uparrow \\ |1, 0\rangle = (\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2} \\ |1, -1\rangle = \downarrow\downarrow \end{array} \right\} s = 1 \quad (\text{triplet})$$

and a fourth possible state with total (combined) spin angular momentum $S = 0$

$$|0, 0\rangle = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2} \quad \left. \right\} s = 0 \quad (\text{singlet})$$

Thus a combination of two spin-1/2 particles can carry a total spin S of 1 or 0, depending on whether they occupy a triplet or singlet state.

The triplet designation appears in term symbols (see below) such as 3P_0 for the ground state of Carbon. Here, the total spin $S = 1$, and $2S + 1 = 3$ (thus it is a **triplet spin state** with $S = 1$).

Total spin angular momentum $S = 1/2$ yields multiplicity $2S + 1 = 2$, a **doublet** term.

Total spin angular momentum $S = 3/2$ yields multiplicity $2S + 1 = 4$, a **quartet** term.⁷⁰

The term **multiplet** applies when the initial and the final states of a transition both have multiple values of J .

“The effect of the spin-spin interaction is noted in Hund's rule #1 [see below]]. If you have two electrons, then the state in which their spins are parallel ($S=1$, triplet state) will be lower in energy than the state in which their spins are antiparallel ($S=0$, singlet state).”⁷¹

Electronic Configuration EC

The Electronic Configuration is the representation of the distribution of electrons of an atom or molecule in atomic or molecular orbitals. For example, the EC of the neon atom is $1s^2 2s^2 2p^6$, indicating there are 2 electrons in the $n=1$ or K shell, 2 in the $\ell = 0$ subshell of the $n = 2$ or L shell, and 6 in the $\ell = 1$ subshell of the

⁶⁹ http://en.wikipedia.org/wiki/Triplet_state

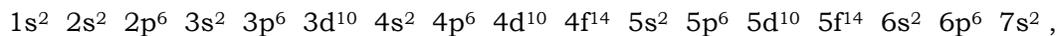
⁷⁰ <http://www.astro.sunysb.edu/fwalter/AST341/qn.html>

⁷¹ <http://hyperphysics.phy-astr.gsu.edu/hbase/atomic/atstruct.html#c3>

$n = 2$ shell (so 8 total in the $n=2$ or L shell). The superscript 1 is usually omitted, so we write $1s^2 2s^2 2p^6 3p^1$ rather than $1s^2 2s^2 2p^6 3p^1$.

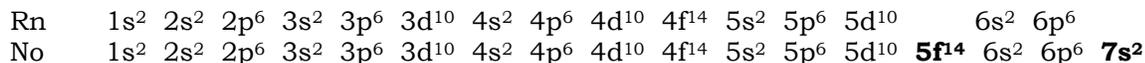
Because the 6 electrons in the p subshell consist of 3 pairs in different orbitals, they are sometimes represented arbitrarily as $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$ instead of $1s^2 2s^2 2p^6$. Thus C ($Z = 6$) may be represented as $1s^2 2s^2 2p_x^1 2p_y^1$.

The full EC for the highest Z atom for which the EC is well established is for Nobelium with $Z = 102$:⁷²



There are 2 electrons in K shell, 8 in L shell, 32 in M shell, 32 in N shell, 8 in O shell, and 2 in P shell.

This long EC may be abbreviated as $[\text{Rn}] 5f^{14} 7s^2$. This signifies that the EC includes all shells and subshell electrons found in the gas Radon $Z = 86$, plus 14 new electrons in the $n=5 \ell = 3$ subshell (none of which were found in Radon's 5f subshell) plus 2 new ones in the $n = 7 \ell = 0$ subshell. Note that Nobelium's EC compared to radon is



where new electrons are shown in bold face.

For all elements up to Uuo having $Z = 118$, the highest subshells with electrons are 7s and 7p, but no elements have electrons in subshell 6f.⁷³

EC's may depict the ground state (such as are usually shown in tables⁷⁴) or excited states. For example, "The ground state configuration of the sodium atom is $1s^2 2s^2 2p^6 3s^1$, as deduced from the Aufbau principle ... The first excited state is obtained by promoting a 3s electron to the 3p orbital, to obtain the $1s^2 2s^2 2p^6 3p^1$ configuration, abbreviated as the 3p level. Atoms can move from one configuration to another by absorbing or emitting energy. In a sodium-vapor lamp for example, sodium atoms are excited to the 3p level by an electrical discharge, and return to the ground state by emitting yellow light of wavelength 589 nm."⁷⁵

The Aufbau (meaning "building-up") rule and Madelung rule help determine the order in which electrons fill subshells:

1. Orbitals are filled in the order of increasing $n + l$;
2. Where two orbitals have the same value of $n + l$, they are filled in order of increasing n .

This rule gives the following order for filling the orbitals [truncated past 7p]:⁷⁶



The following elements are exceptions to the Aufbau principle: 24 Chromium, 29 Cu, 42 Mo, 44 Ruthenium, 45 Rhodium, 46 Palladium, 47 Silver, 57 Lanthanum, 58 Cerium, 64 Gadolinium, 78 Platinum, 79 Au, 89 Actinium, 90 Thorium, 91 Protactinium, 92 Uranium, 93 Neptunium, 96 Curium,

Valence, Octet Rule, Lewis Diagrams, Interatomic Bonds

The valence electrons are the electrons in the highest shell (largest n). The eight electrons of a closed shell have an $s^2 p^6$ electron configuration. All of the noble gases above helium have a $ns^2 np^6$ closed shell pattern, where $n = 2, 3, 4, 5$, and 6. For helium, $1s^2$ is a closed shell.

The octet rule is a rule of thumb that states that atoms of main-group elements tend to combine in such a way that each atom has eight electrons in its valence shell, giving it the same electronic configuration as a noble gas. A closed-shell configuration is one in which low-lying energy levels are full and higher energy levels are empty. For example the neon atom ground state has a full $n=2$ shell ($2s^2 2p^6$) and an empty $n=3$ shell. According to the octet rule, the atoms immediately before and after neon in the periodic table (i.e. C, N, O, F, Na, Mg and Al), tend to attain a similar closed shell configuration by gaining, losing, or sharing electrons. The argon atom has an analogous $3s^2 3p^6$ configuration. Although there is an empty 3d level for

⁷² http://en.wikipedia.org/wiki/Electron_configurations_of_the_elements_%28data_page%29

⁷³ http://www.periodni.com/electronic_configuration_of_the_elements.html

⁷⁴ • http://en.wikipedia.org/wiki/Electron_configurations_of_the_elements_%28data_page%29

• also http://www.periodni.com/electronic_configuration_of_the_elements.html

⁷⁵ http://en.wikipedia.org/wiki/Electron_configuration

⁷⁶ http://en.wikipedia.org/wiki/Electron_configuration

this shell, 3d is at considerably higher energy than 3s and 3p, so that $3s^2 3p^6$ is still considered a closed shell for chemical purposes.⁷⁷

The octet rule is especially useful for Main group elements:⁷⁸ [hydrogen], helium, lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, and other elements in columns 1 (alkali metals), 2 (Alkaline earth metals), and 13, 14, 15 (Pnictogens), 16 (Chalcogens), 17 (halogens), and 18 (noble gases) of the periodic table.⁷⁹

Halogens that are 1 electron short of a closed shell (e.g., Fluorine $1s^2 2s^2 2p^5$, also Cl, Br, I, and At) are highly reactive as they try to acquire an electron to close their shell (thereby becoming a negative ion or anion). Alkali metals having 1 electron in excess of a closed shell (e.g., Sodium, $1s^2 2s^2 2p^6 3s^1$, also Li, Na, K, Rb, Cs, and Fr) are highly reactive as they try to donate the electron to close their shell (thereby becoming a positive ion or cation). These elements tend to form ions and ionic bonds.

Bonds differ due to the difference in electronegativity X_{26} of the constituent elements. Covalent bonds share one or more pairs of electrons between 2 atoms, typically with similar electronegativities. A large difference in electronegativity leads to more polar (ionic) character of the bond, in which there is greater transfer of the electrons. Metallic bonds are characterized by delocalization of valence electrons. Secondary (van der Waals) bonds are weaker and include dipole to dipole bonds, H-bonds, and polar molecule-induced dipole bonds.

“The most commonly used method of calculation [of electronegativity] is that originally proposed by Linus Pauling. This gives a dimensionless quantity, commonly referred to as the Pauling scale, on a relative scale running from around 0.7 to 3.98 (hydrogen = 2.20).”⁸⁰ “A [bond with a] difference of electronegativity of over 1.7 is likely to be ionic, and [a bond with] a difference of less than 1.7 is likely to be covalent.”⁸¹

Lewis diagrams depict the valence electrons surrounding elements including those bonded in compounds. The electrons shared in 2-electron (single) covalent bonds, such as the 4 bonds in CH_4 , are each counted twice, once for each of the two bonded atoms. Double covalent bonds arise when 4 electrons are shared between 2 atoms. Triple covalent bonds arise when 6 electrons are shared between 2 atoms. The energy required to break covalent bonds are typically triple bond (like N_2) > double bond > single bond.

Bond configurations are often resonant structures that effectively spread electrons and bonds fractionally between more than one pair of atoms (such as the benzene ring and carbonate ion⁸²). As a result, the carbonate C-O bonds have a bond order of 1.33 (2/3 of the time single, 1/3 of the time double) and benzene intercarbon bonds have a bond order of 1.5. See below).

A dative covalent bond (aka coordinate bond or dipolar bond) is a kind of 2-center, 2-electron covalent bond in which the two electrons derive from the same atom.⁸³

[Note: some of the following is complex, subject to differing interpretations, and unclear to me. Needs work!]

Bonds with one or three electrons can be found in radical species, which by definition have an odd number of electrons.

One-electron bond: The simplest example of a one-electron bond is the dihydrogen cation, H_2^+ . One-electron bonds often have about half the bond energy of a 2-electron bond, and are therefore called half bonds. However, in the case of dilithium, the bond is actually stronger for the 1-electron Li_2^+ than for the 2-electron Li_2 .⁸⁴

Three-electron bond: Certain molecules with an odd number of total combined electrons (e.g. nitric oxide NO) attain octet configurations by means of a three-electron bond, which contributes one shared and one unshared electron to the octet of each bonded atom. Nitric oxide NO contains a 3-electron bond, in addition to two 2-electron bonds. The bond order is 2.5⁸⁵ (i.e., half-way between a double and a triple bond.) The third bond—the half bond—is variously depicted, as a dashed line above the double bond,⁸⁶ as a lone dot,⁸⁷ as 3

⁷⁷ http://en.wikipedia.org/wiki/Octet_rule quoted and paraphrased

⁷⁸ http://en.wikipedia.org/wiki/Main_group_element

⁷⁹ http://en.wikipedia.org/wiki/Periodic_table_%28large_version%29

⁸⁰ <http://en.wikipedia.org/wiki/Electronegativity>

⁸¹ http://en.wikipedia.org/wiki/Chemical_bond

⁸² <http://en.wikipedia.org/wiki/Carbonate>

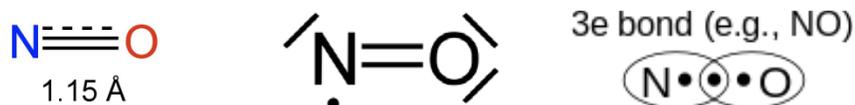
⁸³ http://en.wikipedia.org/wiki/Dipolar_bond

⁸⁴ http://en.wikipedia.org/wiki/Chemical_bond#One-_and_three-electron_bonds paraphrased

⁸⁵ <http://chemistry.tutorvista.com/organic-chemistry/bond-order.html>

⁸⁶ http://cnx.org/contents/39ed05df-dbef-4151-ae87-0e0646f82462@1/Oxides_of_Nitrogen

dots⁸⁸, or in the manner depicted further below⁸⁹ for O₂. The middle diagram immediately following and the 2 diagrams for O₂ depict all electrons involved.



Ground-state oxygen O₂, which is generally represented as obeying the octet rule, actually contains two three-electron bonds. The simplest example of three-electron bonding can be found in the helium dimer cation, He₂⁺. It is considered a "half bond" because it consists of only one shared electron (rather than two) in addition to one lone electron on each atom; in molecular orbital terms, the third electron is in an anti-bonding orbital which cancels out half of the bond formed by the other two electrons. The oxygen molecule O₂ can also be regarded as having two 3-electron bonds and one 2-electron bond, which accounts for its paramagnetism and its formal bond order of 2. The following diagrams seem to depict all 12 electrons involved:



Chlorine dioxide and its heavier analogues bromine dioxide and iodine dioxide also contain three-electron bonds. Molecules with odd-electron bonds are usually highly reactive. These types of bond are only stable between atoms with similar electronegativities.⁹⁰

Sigma and Pi Bonds: (This is a topic I need to explore more, my apologies for the rudimentary comments!) These terms refer to molecular bond orbital configurations:

Sigma bonds “are the strongest type of covalent chemical bond. They are formed by head-on overlapping between atomic orbitals... A σ -bond is symmetrical with respect to rotation about the bond axis. By this definition, common forms of sigma bonds are s+s, p_z+p_z, s+p_z and d_z²+d_z² (where z is defined as the axis of the bond). Quantum theory also indicates that molecular orbitals (MO) of identical symmetry actually mix or hybridize. As a practical consequence of this mixing of diatomic molecules, the wavefunctions s+s and p_z+p_z molecular orbitals become blended... The symbol σ is the Greek letter sigma. When viewed down the bond axis, a σ MO has a circular symmetry, hence resembling a similarly sounding "s" atomic orbital... Typically, a single bond is a sigma bond while a multiple bond is composed of one sigma bond together with pi or other bonds. A double bond has one sigma plus one pi bond, and a triple bond has one sigma plus two pi bonds.”⁹¹

Pi bonds: “In chemistry, pi bonds (π bonds) are covalent chemical bonds where two lobes of one involved atomic orbital overlap two lobes of the other involved atomic orbital. Each of these atomic orbitals is zero at a shared nodal plane, passing through the two bonded nuclei. The same plane is also a nodal plane for the molecular orbital of the pi bond. [diagrams help here—the nodal plane is so named because the wave function (or at least $|\psi|^2$) for the pi orbitals has a value of 0 on it.] The Greek letter π in their name refers to p orbitals, since the orbital symmetry of the pi bond is the same as that of the p orbital when seen down the bond axis. P orbitals often engage in this sort of bonding. D orbitals also engage in pi bonding, and form part of the basis for metal-metal multiple bonding. Pi bonds are usually weaker than sigma bonds. [A double bond is usually one sigma bond and one pi bond.] The C-C double bond has a bond energy less than twice the C-C single bond energy... A pi bond is weaker than a sigma bond, but the combination of pi and sigma bond is stronger than either bond by itself.”⁹²

⁸⁷ http://en.wikipedia.org/wiki/Nitric_oxide

⁸⁸ http://en.wikipedia.org/wiki/Chemical_bond

⁸⁹ Richard D. Harcourt, “The Pauling 3-Electron Bond”, *J. Chem. Educ.* Volume 62 Number 2 February 1985

⁹⁰ http://en.wikipedia.org/wiki/Chemical_bond#One-_and_three-electron_bonds paraphrased

⁹¹ http://en.wikipedia.org/wiki/Sigma_bond

⁹² http://en.wikipedia.org/wiki/Pi_bond

Term Symbols and Spectroscopic Notation

Atomic “levels” for each given electron configuration in multiple electron atoms are described with **Russell-Saunders Term Symbols**⁹³ in the form

$$2S+1L_J$$

where $p \propto \sigma^-$

S is the absolute value of the total electron spin

$2S + 1$ is the spin multiplicity (the number of possible orientations of spin angular momenta; it is the quantification of the amount of unpaired electron spin⁹⁴)

L is the total orbital angular momentum

(shown as $0 \rightarrow S, 1 \rightarrow P, 2 \rightarrow D, 3 \rightarrow F, 4 \rightarrow G, 5 \rightarrow H, 6 \rightarrow I, 7 \rightarrow K, 8 \rightarrow L, 9 \rightarrow M, N, O, Q, R, T, U, V, \text{etc.}$),

J is the total angular momentum (a number with values $L+S, L+S-1, \dots, \text{abs}(L-S)$).

Hund's rules⁹⁵ allow determination of the term symbol for the **ground state** of an atom or molecule. It is the state with maximum S and L. These rules assume that the repulsion between the outer electrons is much greater than the spin-orbit interaction, which is in turn stronger than any other remaining interactions. This is referred to as the LS coupling regime. Here are the rules:

1. For a given electron configuration, the term with maximum multiplicity $2S + 1$ has the lowest energy, thus also the term with maximum S. The orbitals of the subshell are each occupied singly with electrons of parallel spin before double occupation occurs. (This is occasionally called the "bus seat rule" since it is analogous to the behavior of bus passengers who tend to occupy all double seats singly before double occupation occurs. This arises because the electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus, so that such orbitals contract and electron-nucleus attraction energy becomes greater in magnitude (or decreases algebraically [to more negative values]).

2. For a given multiplicity, the term with the largest value of L has the lowest energy. This rule deals with reducing the repulsion between electrons. It can be understood from the classical picture that if all electrons are orbiting in the same direction (higher orbital angular momentum) they meet less often than if some of them orbit in opposite directions. In the latter case the repulsive force increases, which separates electrons. This adds potential energy to them, so their energy level is higher [less negative].

3. For a given term, in an atom with outermost subshell half-filled or less, the level with the lowest value of J lies lowest in energy. If the outermost shell is more than half-filled, the level with the highest value of J is lowest in energy. This rule considers the energy shifts due to spin-orbit coupling...

“Full shells and subshells do not contribute to the quantum numbers for total S (the total spin angular momentum) and for L (the total orbital angular momentum). It can be shown that for full orbitals and suborbitals both the residual electrostatic term (repulsion between electrons) and the spin-orbit interaction can only shift all the energy levels together. Thus when determining the ordering of energy levels in general only the outer valence electrons must be considered.”⁹⁶

Ground state term symbol

“It is relatively easy to calculate the term symbol for the ground state of an atom using Hund's rules. It corresponds with a state with maximum S and L.

1. Start with the most stable electron configuration. Full shells and subshells do not contribute to the overall angular momentum, so they are discarded.

If all shells and subshells are full then the term symbol is 1S_0 .

⁹³ • <http://hyperphysics.phy-astr.gsu.edu/hbase/atomic/term.html#c1> and

• http://en.wikipedia.org/wiki/Term_symbol

⁹⁴ http://en.wikipedia.org/wiki/Multiplicity_%28chemistry%29

⁹⁵ http://en.wikipedia.org/wiki/Hund%27s_rules (repeated quotes from this page are shown)

⁹⁶ http://en.wikipedia.org/wiki/Hund%27s_rules

2. Distribute the electrons in the available orbitals, following the Pauli exclusion principle. First, fill the orbitals with highest m_l value with one electron each, and assign a maximal m_s to them (i.e. $+\frac{1}{2}$). Once all orbitals in a subshell have one electron, add a second one (following the same order), assigning $m_s = -\frac{1}{2}$ to them.

3. The overall S is calculated by adding the m_s values for each electron. That is the same as multiplying $\frac{1}{2}$ times the number of unpaired electrons. The overall L is calculated by adding the m_l values for each electron (so if there are two electrons in the same orbital, add twice that orbital's m_l).

4. Calculate J as

if less than half of the subshell is occupied, take the minimum value $J = |L - S|$

if more than half-filled, take the maximum value $J = L + S$

if the subshell is half-filled, then L will be 0, so $J = S$.

Example 1: Fluorine with electronic configuration $1s^2 2s^2 2p^5$

1. Discard the full subshells and keep the $2p^5$ part. Thus there are five electrons to place in subshell p ($l = 1$)

2. There are three orbitals ($m_l = 1, 0, -1$) that can hold up to $2(2l + 1) = 6$ electrons. The first three electrons can take $m_s = \frac{1}{2}$ (\uparrow) but the Pauli exclusion principle forces the next two to have $m_s = -\frac{1}{2}$ (\downarrow) because they go to already occupied orbitals.

3a. $S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} - \frac{1}{2} = \frac{1}{2}$

3b. $L = 1 + 0 - 1 + 1 + 0 = 1$ [here we have summed the m_l 's], which is "P" in spectroscopic notation.

4. As the fluorine $2p$ subshell is more than half filled, $J = L + S = 3/2$.

Its ground state term symbol is then $^{2S+1}L_J = {}^2P_{3/2}$. [MCM: is this a doublet state?]

Example 2: The ground state of Carbon C is 3P_0 , signifying that the total spin $S = 1$, $2S + 1 = 3$ (a **triplet spin state** as $S = 1$), total ang. momentum is $1 \rightarrow P$, and the grand total angular momentum $J = 0$.

A different carbon state is given by 3P_2 , signifying that the total spin $S = 1$, $2S + 1 = 3$ (a triplet spin state), total ang. momentum is $1 \rightarrow P$, and the grand total angular momentum $J = 2$.

Excited States: Hund's rules also work fairly well (with exceptions) for excited states. Thus, in the helium atom, Hund's first rule correctly predicts that the $1s2s$ triplet state (3S) is lower than the $1s2s$ singlet (1S). Similarly for organic molecules, the same rule predicts that the first triplet state (denoted by T_1 in photochemistry) is lower than the first excited singlet state (S_1), which is generally correct.

Molecule Term Symbols: These have the general form:

$$^{2S+1}\Lambda_{\Omega, (g \text{ or } u)}^{(+ \text{ or } -)}$$

where

S is the total spin quantum number

Λ is the projection of the orbital angular momentum along the internuclear axis

Ω is the projection of the total angular momentum along the internuclear axis

u/g is the parity (ungerade=odd and gerade=even)

$+/-$ is the reflection symmetry along an arbitrary plane containing the internuclear axis

Organic Compounds

Organic compounds contain C and H. Representative examples of some of the simpler organic compounds include (all quotes and paraphrases from Wikipedia; not all listed are important in atmospheric chemistry):

Alkane: a saturated acyclic hydrocarbon consisting only of hydrogen and carbon atoms and all bonds are single bonds, linear or branched, chemical formula C_nH_{2n+2} . Examples: methane (CH_4), ethane (C_2H_6), propane, butane and isobutane, pentane, isopentane, neopentane, hexane, heptane, octane, trimethylpentane (isooctane), etc.

Alkene (olefin): an unsaturated hydrocarbon containing at least one carbon-carbon double bond. The simplest acyclic alkenes, with only one double bond and no other functional groups, known as mono-enes,

form a homologous series of hydrocarbons with the general formula C_nH_{2n} . They have two hydrogen atoms less than the corresponding alkane (with the same number of carbon atoms). The simplest is ethylene (ethene, C_2H_4), others are hex-1-ene, and 2-propyl-1-pentene.

Alkyne: an unsaturated hydrocarbon containing at least one carbon—carbon triple bond between two carbon atoms. Examples are acetylene (C_2H_2), propyne.

Cycloalkane: hydrocarbon compounds that have one or more rings of carbon atoms in the chemical structure of their molecules. Cycloalkanes consist of only carbon (C) and hydrogen (H) atoms and are saturated because there are no multiple C-C bonds. Example: cyclopropane (C_3H_6), cyclobutane, cyclopentane, cyclohexane, etc.

Cycloalkene (cycloolefin): a type of alkene hydrocarbon which contains a closed ring of carbon atoms, but has no aromatic character. (Thus, there is at least one double bond.) Examples: Cyclopentene (C_5H_8), cyclopropene

Isoprene: 2-methyl-1,3-butadiene (C_5H_8 or $CH_2=C(CH_3)CH=CH_2$)

Aromatic compounds: These have one or more rings exhibiting aromaticity, an unusually stable nature of some flat rings, a manifestation of cyclic delocalization and of resonance. Examples: Benzene (C_6H_6) and other aromatic hydrocarbons (only C and H having alternating double and single bonds between carbon atoms forming rings); heterocyclic aromatics (in which one or more of the atoms in the aromatic ring is an element other than carbon), aromatic rings with other functional groups attached (toluene $C_6H_5CH_3$, TNT, ASA, nucleotides), etc.

Alcohols: any organic compound in which a hydroxyl functional group (-OH) is bound to a saturated carbon atom. Examples: Methanol (CH_3OH), ethanol (CH_3CH_2OH), 1-propanol, isopropyl alcohol, butyl alcohol, Ethane-1,2-diol (Ethylene glycol), Propane-1,2-diol (Propylene Glycol), Propane-1,2,3-triol (glycerol), Hexane-1,2,3,4,5,6-hexol (mannitol), sorbitol, etc.

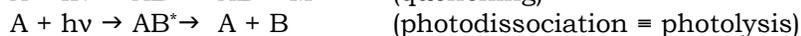
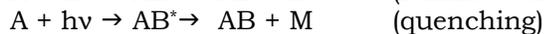
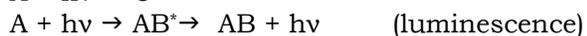
Aldehyde: an organic compound containing a formyl group. The formyl group is a functional group with the structure R-CHO, consisting of a carbonyl center (a carbon double bonded to oxygen) bonded to hydrogen and an R group, which is any generic alkyl or side chain. The group without R is called the aldehyde group or formyl group. Aldehydes differ from ketones in that the carbonyl is placed at the end of a carbon skeleton. Examples: formaldehyde (CH_2O or HCHO), acetaldehyde (CH_3CHO), butyraldehyde.

Ketone: an organic compound with the structure $RC(=O)R'$, where R and R' can be a variety of carbon-containing substituents. Ketones and Aldehydes are simple compounds that contain a carbonyl group (a carbon-oxygen double bond). They are considered "simple" because they don't have reactive groups like -OH or -Cl attached directly to the carbon atom in the carbonyl group, as in carboxylic acids containing -COOH. Examples: acetone ($(CH_3)_2CO$ or Propan-2-one), acetylacetone, methylethyl ketone, cyclohexanone, benzophenone, diacetyl, etc.

Types and Rates of Chemical Reactions

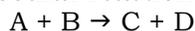
Chemical reactions may be

Unimolecular: involves a single molecule reactant



Examples include photolysis of NO_2 radical induced by photons of $\lambda < 420$ nm.

Bimolecular reactions involve two reactants such as

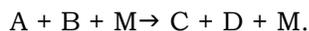


One reactant may be unspecified and unchanged (often representing air molecules mostly O_2 or N_2 and designated M) but serving to provide kinetic energy, such as in thermal decomposition (thermolysis), isomerization, and collision reactions.

Isomerization Reaction:

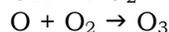
For example, excited Criegee biradical + M \rightarrow Excited formic acid

Termolecular: reactions are of 3 reactants,. The third is often unspecified and unchanged (often representing air molecules mostly O_2 or N_2 and designated M), but serves to impart or absorb kinetic energy. General example



Termolecular reactions are also termed pressure-sensitive or pressure-dependent reactions, because the concentration of M (as well of A and B) depends on pressure, and reaction rate constant rises with P.

Examples include



Molecular species that are lost at a rate proportional to the reactant's concentration are said to have a characteristic lifetime or e-folding lifetime. For reactions in which a reactant is lost at a rate proportional to the concentration, this is defined as the time τ_A required for the concentration of a substance to decrease to $1/e = 36.79\%$ of the initial amount. It is therefore a little longer than the half-life ($t_{1/2} = \tau_A \ln 2 = 0.69 \tau_A$). If the initial concentration is $[A_0]$, and the reaction proceeds proportional to the concentration with a rate coefficient given by J (units s^{-1}), then

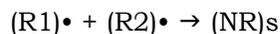
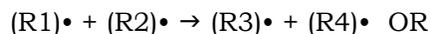
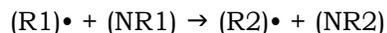
$$\frac{d[A]}{dt} = J[A] \Rightarrow \frac{[A]}{[A_0]} = e^{-J\tau_A} \Rightarrow \tau_A = 1/J$$

Many species in the atmosphere are long lived: O_2 , N_2 , and CO_2 . Others are much shorter lived: OH, NO, NO_2 , and O_3 .

For many bimolecular reactions $A + B \rightarrow C$, an intermediate short-lived excited product AB^* is generated when available kinetic energy is sufficient to overcome an energy barrier. Increasing T increases kinetic energy in collisions, in some cases increasing the reaction rate. The excited product AB^* then collides with surrounding gas molecules, O_2 or N_2 primarily but designated M and of density [M], and yielding the final product C. If AB^* is short lived, the rate of formation of C may be derived to be

$\frac{dC}{dt} = \frac{(k_3 k_1)[A][B]}{k_2 + k_2[M]} [M]$ where the k's are rate constants (though they may be T dependent inasmuch as T affects available energy; details omitted from this extensive subject).⁹⁷

Radical reactions often follow these patterns ($R\bullet$ = radical, NR = nonradical), in which radicals are generally "conserved":



Photolysis: For photochemical processes such as photolysis, the reaction may proceed at a rate proportional to reactant [AB], with the rate "constant" obtained from the integral over wavelengths of the product of⁹⁸
the absorption cross section ($cm^2 \text{ molec}^{-1}$), a probability of absorption
the photodissociation quantum yield (molec quanta^{-1}), the prob. of bond breaking after absorption
the solar spectral actinic flux ($\text{quanta } cm^{-2} s^{-1} nm^{-1}$, dependent on sun position, absorption, etc.

Actinic flux ($\text{photons } cm^{-2} s^{-1} nm^{-1}$) varies with altitude and wavelength, a relationship which is shown in the following graph for various altitudes 0 km to 50 km under typical atmospheric conditions and a solar zenith angle of 30 degrees:⁹⁹

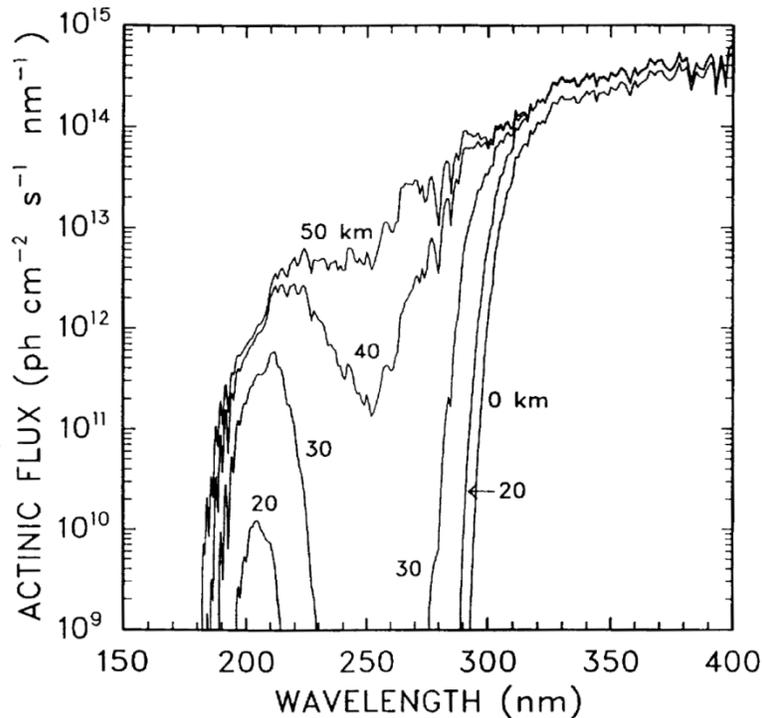
It is apparent from the graph which follows for instance that the rate of O_2 photolysis, which requires $\lambda < 243$ nm, will vary substantially with altitude, though in a possibly complex manner. Specifically, there are essentially no photons of 240 nm at 30 km and lower altitudes. However, photons of 200 nm will be present even as low as 20 km.

⁹⁷ • http://en.wikipedia.org/wiki/Reaction_rate_constant and

• <http://www.csus.edu/indiv/m/mackj/chem142/kinetics.pdf>

⁹⁸ http://ruc.noaa.gov/wrf/WG11/wrf_tutorial_2011/Photolysis.pdf

⁹⁹ Image from DeMore, W. B. et al, "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling (January 15, 1997), nasa_techdoc_19970037557.



Next are depicted photolysis (dissociation) rate coefficients J as a function of altitude for O_2 , O_3 , and NO_2 :¹⁰⁰

Photolysis Rates for O_2 , NO_2 , and O_3

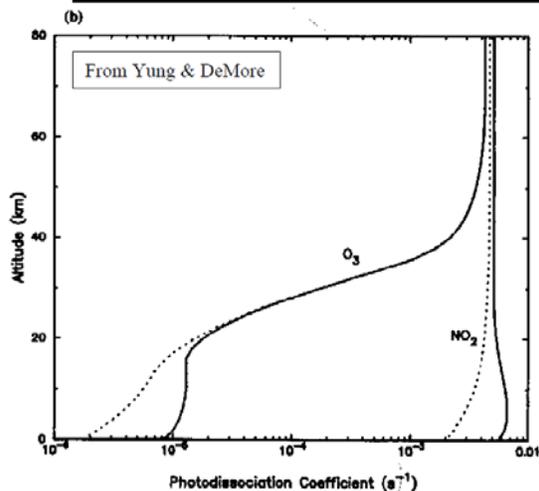
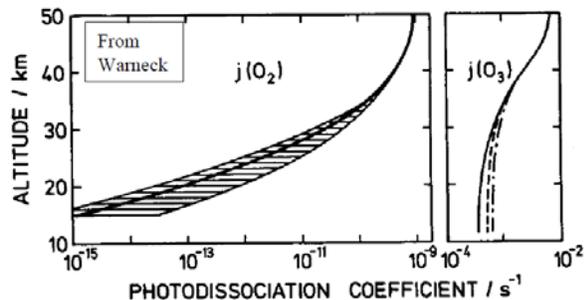


Figure 2.26 (b) Photodissociation coefficient for O_3 [$O_3 + h\nu \rightarrow O_2 + O(^1D)$] and NO_2 [$NO_2 + h\nu \rightarrow NO + O$] in Earth's atmosphere. The dotted line gives the contribution of the direct attenuated solar flux; the solid line gives the sum of the direct and diffuse fluxes. The calculations are diurnally averaged for a midlatitude atmosphere in spring with surface reflectivity of 0.25 and without aerosols. The total ozone column in the model is 341 DU (Dobson units). From the authors' Caltech/Jet Propulsion Lab model of Earth's atmosphere. See, for example, Michelangeli, D. V., Allen, M., and Yung, Y. L., 1989, "El Chichon Volcanic Aerosols: Impact of Radiative, Thermal and Chemical Perturbations." *J. Geophys. Res.* **94**, 18429.

Typical values for photodissociation coefficients, J , for O_3 , O_2 , & NO_2 as a function of altitude. Photolysis rate for O_2 is strongly altitude dependent because the lower you go the less UV radiation capable of breaking O_2 is available (self-shielding). Photolysis rate for O_3 becomes altitude dependent below 40 km for similar self-shielding reasons. On the contrary, visible NO_2 photolysis occurs with about the same rate throughout the atmosphere because there is not enough of it for self-shielding.



¹⁰⁰ modified from http://cires.colorado.edu/jjimenez/AtmChem/CHEM-5151_S05_L7.pdf

Here are some of the important atmospheric photolytic reactions, including altitudes at which they occur, wavelength requirement, and the approximate rate coefficient:¹⁰¹

<i>Process</i>	<i>Altitude</i>	<i>Wave-length (nm)</i>	<i>Approx. Rate</i>
$O_2 + h\nu \rightarrow O(^1D) + O(^3P)$	>50 km	< 174	10^{-12} s^{-1}
$O_2 + h\nu \rightarrow O(^3P) + O(^3P)$	stratosphere and above	< 246	10^{-10} s^{-1}
$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta)$	all	< 310	10^{-5} s^{-1} at 10 km 10^{-3} s^{-1} at 40 km
$NO_2 + h\nu \rightarrow NO + O(^3P)$	all	250-400	$8 \times 10^{-3} \text{ s}^{-1}$ at surface 10^{-2} s^{-1} in stratosphere
$NO_3 + h\nu \rightarrow NO_2 + O(^3P)$	all	400-625	0.2 s^{-1} at surface 0.25 s^{-1} in stratosphere
$NO_3 + h\nu \rightarrow NO + O_2$	all	585-625	$\sim 0.02 \text{ s}^{-1}$ independent of altitude
$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$	lower stratosphere	<220	10^{-8} s^{-1} at 30 km 10^{-6} s^{-1} at 50 km
$N_2O_5 + h\nu \rightarrow NO_3 + NO_2$	stratosphere	<320	$2 \times 10^{-5} \text{ s}^{-1}$ at 30 km
$ClONO_2 + h\nu \rightarrow \text{products}$	stratosphere	<320	$6 \times 10^{-5} \text{ s}^{-1}$
$CH_2O + h\nu \rightarrow HCO + H$	all	<350	$3 \times 10^{-5} \text{ s}^{-1}$
$\quad \quad \quad \rightarrow H_2 + CO$			$4 \times 10^{-5} \text{ s}^{-1}$

Here O(¹D) is the excited higher energy singlet state of atomic O, whereas O(³D) is the unexcited lower energy triplet state of atomic O. Thus the latter can arise from O₂ photolysis at longer wavelengths.

Chemical Composition of Earth's Atmosphere: Overview

These topics are discussed in APGW chapters 2 and 3.

Chemical Evolution of Earth's Atmosphere and the Organisms Influencing This

Earth formed c. 4.6 bya.

Earth's *first atmosphere* likely contained mostly H and He (APGW p. 35), but some of this was lost with enhanced solar wind (solar T-Tauri stage) and gravitational escape.

The *second atmosphere* evolved from outgassing from the mantle through volcanos, fumaroles, steam well, and geysers. OH bound to crustal materials became detached and reacted with reduced gases H₂, CH₄, NH₃, N₂ and H₂S forming oxidized gases including H₂O, CO, CO₂, NO and NO₂, and SO₂. Free elemental oxygen was absent in the early prebiotic atmosphere. (APGW p. 36) It was dominated by CO₂ and H₂. Water vapor condensed to form the oceans.

Abiotic synthesis of compounds such as amino acids and nucleic acids began about 3.5 bya...

After the first prokaryotic cells (lacking nuclei but with nucleoid linear DNA in the cytoplasm) developed in c. 3.5 b.y.a, there evolved fermenting bacteria producing CO₂ (and ethanol, from glucose).

Sulfur cyanobacteria (purple and green sulfur bacteria) were limited to specialized environments (hot springs) but did anoxygenic photosynthesis (PS) beginning c. 3.5 b.y.a. Purple sulfur bacteria oxidized H₂S by combining CO₂ and H₂S with hv to form CH₂O (carbohydrate), H₂O, and 2S (atomic sulfur) and H₂SO₄. Green

¹⁰¹ modified from JAT lecture notes, source unknown

sulfur bacteria also do anoxygenic photosynthesis. “They use sulfide ions, hydrogen or ferrous iron as an electron donor... Elemental sulfur deposited outside the cell may be further oxidized.”¹⁰² They also¹⁰³ produce elemental S and H₂SO₄. Stromatolites formed c. 3.5 bya, residua of cyanobacteria and (per APGW) sulfur bacteria.

Denitrifying bacteria produce N₂ and arose c. 3.2 b.y.a., in a 2 stage process. Organic compounds reacted with NO₃⁻ producing CO₂ and NO₂⁻. Organic compounds then reacted with NO₂⁻ producing CO₂ and N₂. This process for making N₂ came to dominate over photolytic production of N₂ from NH₃.

Methanogenic bacteria produced CH₄ by c. 2.9 b.y.a. . They reacted 4H₂ and CO₂ yielding CH₄ and 2H₂O.

Oxygenic photosynthesis began in prokaryotic cyanobacteria between c. 3.5 and 2.8 b.y.a. (APGW p. 39) “Photosynthesis in cyanobacteria uses water as an electron donor and produces oxygen as a by-product, though some may also use hydrogen sulfide, a process which occurs among other photosynthetic bacteria such as the purple sulfur bacteria. Carbon dioxide is reduced to form carbohydrates via the Calvin cycle... The large amounts of oxygen in the atmosphere are considered to have been first created by the activities of ancient cyanobacteria.”¹⁰⁴

The “first eukaryotic bacteria” according to APGW p. 37 arose c. 2.1 to 1.85 b.y.a., but all bacteria are prokaryotic. Perhaps the author means the first eukaryotic unicellular organisms such as protozoa.

Nitrifying bacteria converted NH₃ to NO₃⁻ beginning c. 1.8 b.y.a. in an aerobic process requiring O₂.

N₂ reached a peak in the atmosphere about 800 m.y.a. and has declined somewhat since. (APGW fig. 2.11)

Nitrogen fixing organisms, which are not the same as nitrifying bacteria, include free living cyanobacteria, and symbiotic bacteria and other prokaryotes. This aerobic process began 1.5 b.y.a. (APGW p. 37).

Eukaryotic cells began c. 2.1 to 1.85 bya. They of course have a defined cell nucleus and organelles.

The first (eukaryotic) shelled marine invertebrates arose 0.57 b.y.a.. Green plants and land plants arose 0.395 to 0.43 b.y.a., approximately the time when green-plant eukaryotic PS began (opinions differ). Flowering plants (angiosperms) arise c. 140 b.y.a. In green plants (which use chloroplasts derived from endosymbiotic cyanobacteria), oxygenic PS combines 6CO₂ and 6H₂O with hv to form C₆H₁₂O₆ (glucose) and 6O₂. In cellular respiration, eukaryotes reverse this process, combining glucose C₆H₁₂O₆ and 6O₂ to form 6CO₂ and 6H₂O, and in the process producing energy efficiently.

Cyanobacteria that did oxygenic PS arose c. 3.5 to 2.8 b.y.a., producing initially small amounts of O₂ but this was initially all taken up by iron in rocks, leading to banded-iron formation and red beds (due to of Fe₂O₃). The Great Oxygenation Event [GOE] occurred gradually beginning 2.45 b.y.a., when the oceans and seabed rock could no longer fully absorb the O₂. “Cyanobacteria, which appeared about 200 million years before the GOE, began producing oxygen by photosynthesis. Before the GOE, any free oxygen they produced was chemically captured by dissolved iron or organic matter. The GOE was the point when these oxygen sinks became saturated and could not capture all of the oxygen that was produced by cyanobacterial photosynthesis. After the GOE, the excess free oxygen started to accumulate in the atmosphere.”¹⁰⁵ Although the GOE began on a small scale in c. 2.45 b.y.a, atmospheric accumulation of O₂ accelerated when O₂ land sinks became saturated, starting c. 0.85 b.y.a.

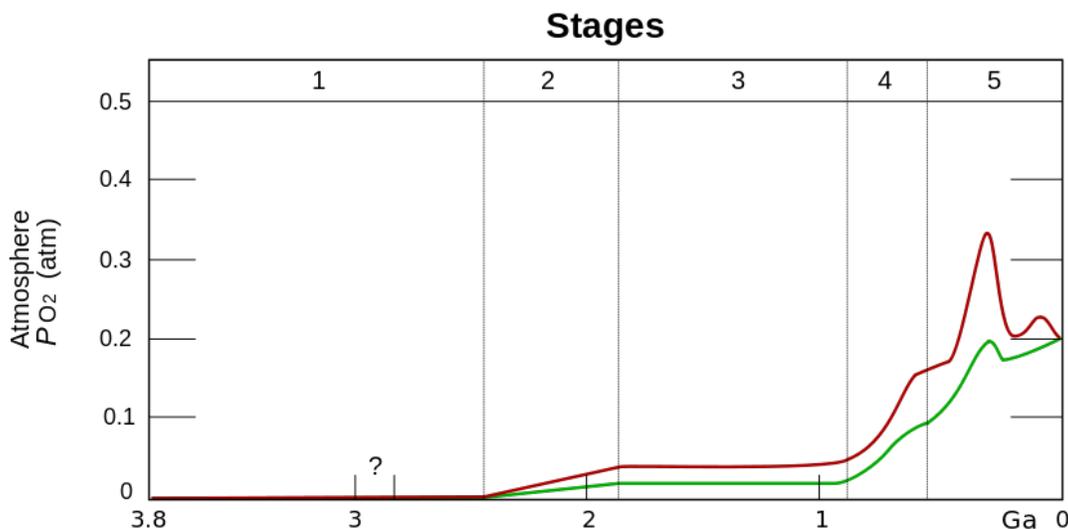
¹⁰² http://en.wikipedia.org/wiki/Green_sulfur_bacteria

¹⁰³ Robert G. Wetzel, *Limnology: Lake and River Ecosystems*, 2001, p. 317

¹⁰⁴ <http://en.wikipedia.org/wiki/Cyanobacteria>

¹⁰⁵ http://en.wikipedia.org/wiki/Great_Oxygenation_Event

In the following graph, O₂ build-up in the Earth's atmosphere from the Archaean to the present is depicted. Red and green lines represent the range of the estimates while time is measured in billions of years ago (Ga).¹⁰⁶



Composition of the Modern Atmosphere (Selected)

Tables here are derived from Wikipedia,¹⁰⁷ from RAH, and APGW p. 55-6

Fixed Well-Mixed Gases (Dry Air) in Modern Atmosphere (APGW table 3.2)

Gas	Concentration by Volume	
Nitrogen (N ₂)	780,800 ppmv	78.08%
Oxygen (O ₂)	209,500 ppmv	20.95%
Argon (Ar)	9,300 ppmv	0.93%
Neon (Ne)	15 ppmv	0.0015%
Helium (He)	5 ppmv	0.0005%
Krypton (Kr)	1 ppmv	0.0001%
Hydrogen (H ₂)	0.55 ppmv	0.000055%
Xenon (Xe)	0.05 ppmv	5 × 10 ⁻⁶ %

Variable Components (Clean air numbers) in Modern Atmosphere

Gas or Other Component	Concentration by Volume	
Water vapor (H ₂ O)	0.40% over full atmosphere, typically 1%–4% at surface	
Carbon dioxide (CO ₂)	390 ppmv ¹⁰⁸	0.039%
	higher in CO ₂ domes	
Methane (CH ₄)	1.79 ppmv	0.000179%

¹⁰⁶ ibid

¹⁰⁷ http://en.wikipedia.org/wiki/Atmosphere_of_Earth

¹⁰⁸ Keeling Curve: http://en.wikipedia.org/wiki/Carbon_dioxide_in_Earth%27s_atmosphere

Nitrous oxide (N ₂ O)	0.3 ppmv	0.00003%
Carbon monoxide (CO)	0.1 ppmv	0.00001%
Particulates: dust, pollen and spores, sea spray and salt, volcanic ash	0.01 - 0.15 ppmv	
Ozone (O ₃)	0.0 to 0.07 ppmv	0 to 7 × 10 ⁻⁶ %
Nitrogen dioxide (NO ₂)	0.02 ppmv	2 × 10 ⁻⁶ %
Iodine (I)	0.01 ppmv	1 × 10 ⁻⁶ %
Chlorofluorocarbons (CFCs).	0.0002 ppmv	
	variable	

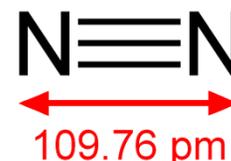
Specific Elements and Compounds in the Atmosphere

The following listing is in approximate order by mixing ratios of the principle element or molecule.

Nitrogen and the Nitrogen Cycle

See further below for Nitrogen Oxides NO_x.

Nitrogen is a nonmetal, with an electronegativity of 3.04. It has five valence electrons in its outer shell and is, therefore, trivalent in most compounds. The triple bond needed to satisfy the octet rule in molecular nitrogen (N₂) is one of the strongest and tightest bonds (high enthalpy of atomization = +945.5 kJ mol⁻¹).¹⁰⁹

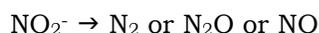


Nitric Oxide (nitrogen monoxide) bond structure and representation is discussed above. Its behavior is discussed below.

In the atmosphere,



Molecular N (N₂) arises currently primarily from **denitrification** of nitrite by denitrifying bacteria:



Nitrogen N₂ is **fixed** to ammonia or ammonium ion in an aerobic process by certain legume-associated and also free-living prokaryote bacteria:



Once fixation has occurred, fixed N can be incorporated into amino acids and other biological compounds.

NH₃, NH₄⁺ are also produced by **ammonification** of certain N containing organic compounds.

Nitrite ion NO₂⁻ is produced from NH₃ or NH₄⁺ by **Nitrification** (aerobic).

Nitrate ion NO₃⁻ arises from NO₂⁻.

Nitrite ion NO₂⁻ is also produced from NO₃⁻

Nitric acid HNO₃ is produced by reaction of NO₂ with H₂O:



or



HNO₃ exists as a gas or in aqueous solution.

¹⁰⁹ • <http://en.wikipedia.org/wiki/Nitrogen> and

• http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Descriptive_Chemistry/p-Block_Elements/Group_15%3A_The_Nitrogen_Family/Chemistry_of_Nitrogen

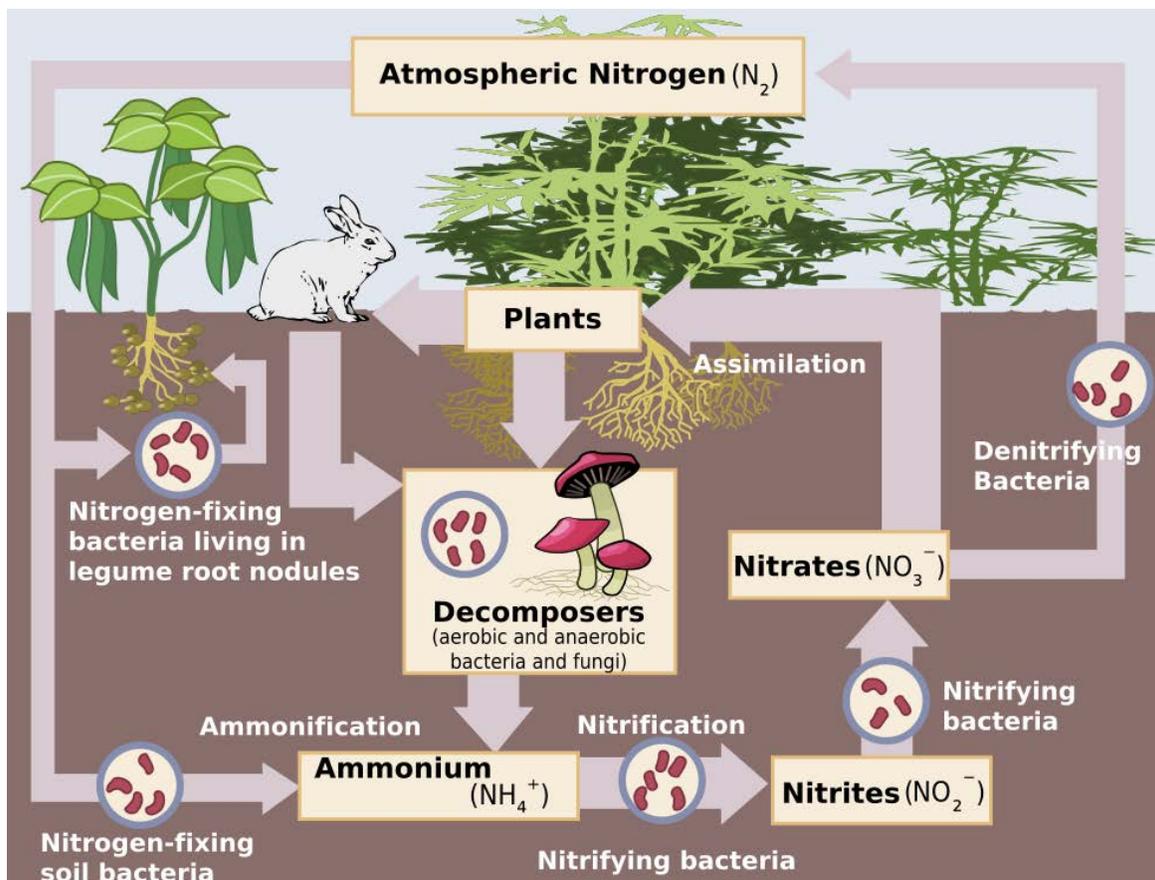
Much more about chemistry of N and its products (NO_x , NO_y , HNO_3 , etc.) follows in discussions about urban pollution, acid deposition, etc.

For a review of inorganic N, see here¹¹⁰—this discussion includes definitions for NO_x and “ NO_y ”¹¹¹:

$\text{NO}_y = \text{NO}_x + \text{all of N reservoir species}$

$\text{NO}_y = (\text{NO} + \text{NO}_2) + \text{HNO}_3 + \text{PAN} + \text{HONO} + \text{NO}_3 + 2\text{N}_2\text{O}_5 + \text{organic nitrates (RNO}_3) + \text{particulate nitrate (pNO}_3^-) + \text{other reservoir species produced from the oxidation of NO}_x$.

A simplified Nitrogen Cycle in the biosphere is colorfully summarized as follows:¹¹²



The diagram omits N_2 from volcanos, sources and sinks of NO_x (such as combustion and lightning), and nitrates from anthropogenic fertilizers and weathering, etc.

A quantitative box model of the Nitrogen Cycle, including oceans and lithosphere, is given in Jacob:¹¹³

¹¹⁰ • http://cires.colorado.edu/jimenez/AtmChem/CHEM-5151_S05_Nitrogen.pdf from 2005

• see also 2013 course material: <http://cires.colorado.edu/jimenez-group/wiki/index.php/AtmChem-5151>

¹¹¹ <http://en.wikipedia.org/wiki/NOx>

¹¹² <http://www.macroevolution.net/nitrogen-cycle-diagram.html>

¹¹³ <http://acmg.seas.harvard.edu/publications/jacobbook/bookchap6.pdf>

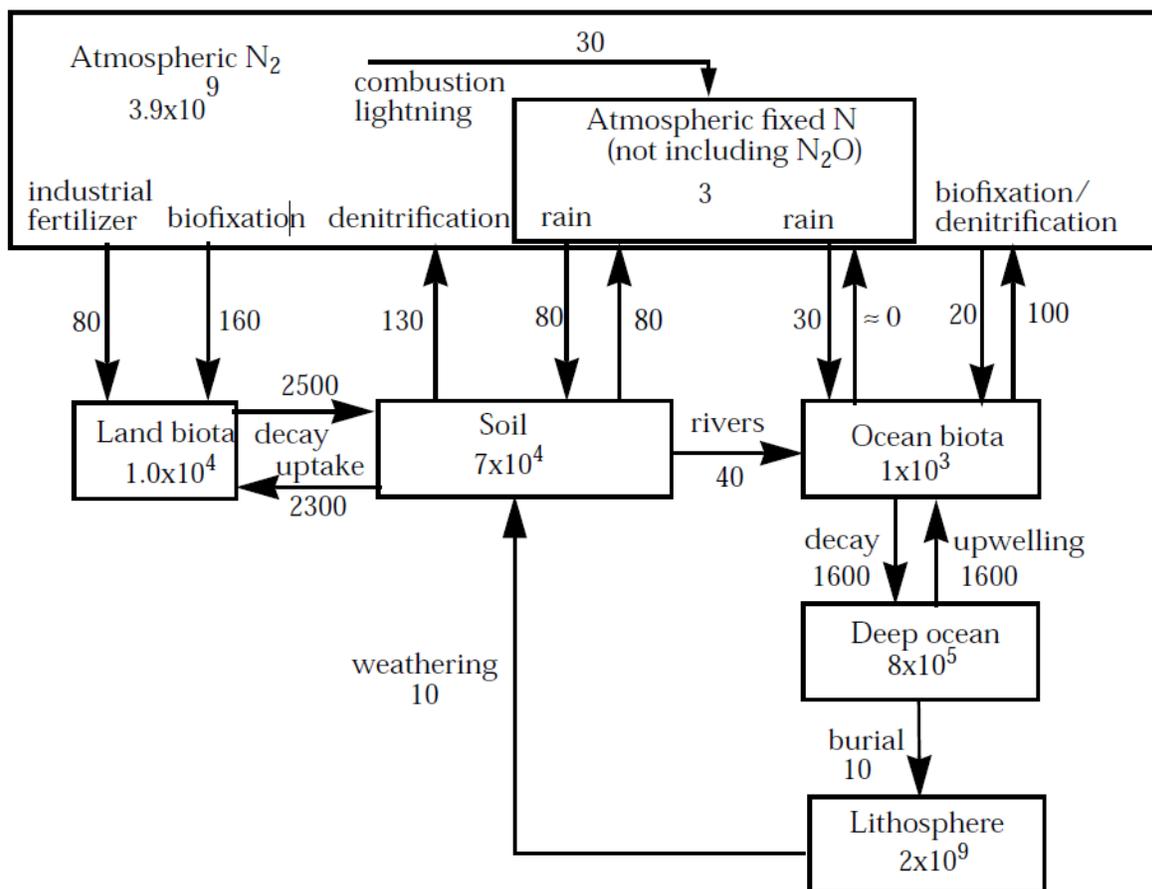


Figure 6-3 Box model of the nitrogen cycle. Inventories are in Tg N and flows are in Tg N yr⁻¹. A teragram (Tg) is 1×10^{12} g.

Oxygen: Allotropes O₂ and Ozone O₃, Ions, and Radicals; Sources and Sinks of O₂

Oxygen is produced primarily by green plants and cyanobacteria, but also by atmospheric chemical reactions. The main atmospheric sinks are aerobic respiration, photolysis, dissolution in ocean, chemical reactions on soils and rock surfaces, and burning of fuels and biomass. (APGW p. 41) It was originally termed “dephlogisticated air” in an erroneous theory proposed by Johann Becher and refined by George Stahl. The generation of oxygen by green plants was discovered by Joseph Priestley in 1772.

Atomic Oxygen

O has EC = (He) (2s)²(2p)⁴ with Term Symbol ³P₂. In the ground state it has 2 unpaired electrons and is thus a bi-radical for which ³P₂ is the lower energy and thus the ground state. Here, S = 1, Multiplicity = 3, L = 1, J = 2. The 2p orbitals are filled as follows: ↑↓ ↑ ↑, showing the 2 unpaired electrons (bi-radical). This state is also shown as O(³P).

The first excited state for atomic oxygen is the singlet ¹D state, which is higher in energy. It is also shown as O(¹D). The 2p orbitals are filled as follows: ↑↓ ↑↓. Here, S = 0, Multiplicity = 1, L = ?2, J = ?. [MCM: I am unsure why it is called D, is it because L = 2?] It is highly reactive: the one 2p empty orbital is more electrophilic and more prone to undergo bond-forming addition reactions than the triplet ground state.¹¹⁴

The second (higher) excitation state of atomic oxygen has 2p orbitals ↑↓ ↑ ↓ and is termed O(¹S) [MCM: Is this because L = 0? Are these Term Symbols.] It is extremely reactive and shorter lived.

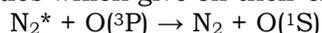
¹¹⁴ <http://three.usra.edu/articles/RadChemO2Sidebar.pdf>

Auroral Light Emissions

Auroras occur in the extremely rarefied near-vacuum atmosphere of the thermosphere.¹¹⁵ Although a little off-topic for this summary, it is informative to learn more about the exotic photochemistry of auroral emissions, which involves primarily oxygen and nitrogen.

RED O(¹D) > 150 km: Transitions from the first excited state O(¹D) to ground state O(³P) emit photons of 630 or 636.4 nm, thus a **red/orange** doublet, which is the dominant color in the aurora borealis/australis at very high altitudes > 150 km (the upper thermosphere). This color “fades below 150 km, as the excited oxygen atoms in the O(¹D)-state are de-excited by collisions with nitrogen molecules much faster than by radiation [emission]”.¹¹⁶ The radiative lifetime of O(¹D) is long, about 110 second,¹¹⁷ thus the necessity for low N₂.

GREEN O(¹S) 100 to 150 km: Transitions from the second excited state O(¹S) to the first excited state O(¹D) give off a sharp 557.7 **green** photon. “The green colour of the aurora below 150 km height [c. 100 miles] stems from the 558 nm line of Oxygen [i.e., arising from transition from O(¹S) to O(¹D)]. It is not seen at [greater altitudes] since the O(¹S)-state is not reached from the O(³P) ground state in [photon] collisions with electrons or protons. It is assumed that this O(¹S) state is produced in collisions of O(³P) with excited nitrogen molecules which give off their energy and take over angular momentum:



This line vanishes at high altitudes [> 150 km] where the concentration of N₂ is too low.”¹¹⁸ The radiative lifetime of O(¹S) is shorter than for O(¹D), but still rather long at 0.74 second, thus the necessity for relatively infrequent collisions. (JAT notes and here¹¹⁹)

RED-VIOLET N₂* < 100 km & PURPLE-BLUE N₂* ions: “The other major thermosphere constituent, molecular nitrogen N₂, is exceptionally stable and there are not many nitrogen atoms below 400 km to make aurorae. The few nitrogen atoms emit a faint green masked by that of oxygen. In very intense displays there is a deep red violet or pink-red border beneath the usual green curtains [from O(¹S)]. This is emission from excited molecular nitrogen [N₂*]. Nitrogen molecular ions [N₂⁺] produce purple blue aurorae at very high altitudes.”¹²⁰

Molecular Oxygen O₂ (Dioxygen)

O₂ is bonded with a bond length of 121 pm, bond order of 2 and with enthalpy 498.36 kJ mol⁻¹. It occupies 3 states with molecular term symbols: ³Σ_g⁺, ¹Δ_g, ¹Σ_g⁻ of which the first is the ground state, a “triplet” bi-radical [diradical] analogous to monoatomic O(³P) and that is paramagnetic (attracted to the poles of a magnet). “The two oxygen atoms are chemically bonded to each other with a spin triplet electron configuration with bond order of two, often simplified in description as a double bond, or as a combination of one two-electron bond and two three-electron bonds.”¹²¹ Bond structure and representation is discussed above.

The oxygen cycle in the biosphere (photosynthesis and respiration/decay) is presented in the following simplified box model by Jacob:¹²² (The diagram omits incorporation of O into other compounds, sedimentation such as Fe₂O₃, reduction of compounds on the ocean floor, and the large reservoir of O in the lithosphere.)

¹¹⁵ MCM: The references I have found can be unclear or contradictory as to whether auroras arise from atomic rather than diatomic oxygen, but I believe that it is atomic O. This topic warrants further exploration. See for example, <http://www.colorado.edu/chemistry/chem5151/kalina.pdf>

¹¹⁶ <https://www.itp.uni-hannover.de/~zawischa/ITP/atoms.html>

¹¹⁷ <http://www.atoptics.co.uk/highsky/auror3.htm>

¹¹⁸ <https://www.itp.uni-hannover.de/~zawischa/ITP/atoms.html>

¹¹⁹ <http://www.atoptics.co.uk/highsky/auror3.htm>

¹²⁰ *ibid.*

¹²¹ <http://en.wikipedia.org/wiki/Oxygen>

¹²² <http://acmg.seas.harvard.edu/publications/jacobbook/bookchap6.pdf>

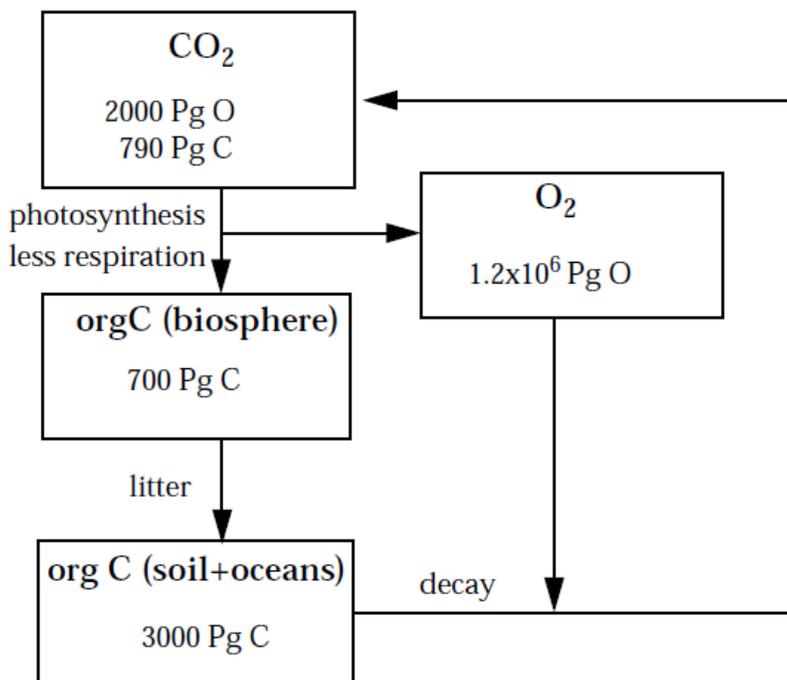


Figure 6-4 Cycling of O₂ with the biosphere; orgC is organic carbon. A petagram (Pg) is 1x10¹⁵ g.

Other Radicals and/or Highly Reactive Forms

Superoxide anion •O₂⁻ is a radical with minus 1 charge. The addition of an electron fills one of its two degenerate molecular orbitals, leaving a charged ionic species with a single unpaired electron remaining and a net negative charge of -1. Both dioxygen and superoxide ion are free radicals that exhibit paramagnetism.¹²³

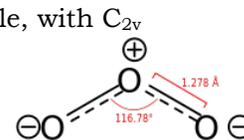
Peroxide anion [O-O]²⁻ is a reactive ion with a minus 2 charge. The 2 O's are linked by a single bond with bond order one. Each O has oxidation state of -1. The anion is very reactive, and easily cleaved into reactive radicals. The peroxide ion can be compared with other molecular oxygen ions superoxide O₂⁻ and ozonide O₃⁻, but contrary to them, the peroxide is not a radical and not paramagnetic.¹²⁴

The related **peroxy** or **peroxide group** has the form R—O—O—R, where the O's are in oxidation state -1.

Ozone O₃

Ozone was discovered in 1839 by Christian Friedrich Schönbein, 1799-1868.

According to experimental evidence from microwave spectroscopy, ozone is a bent molecule, with C_{2v} symmetry (similar to the water molecule). The O—O distances are 127 pm... The O—O—O angle is 116.78°... Ozone is a polar molecule... The bonding can be expressed as a resonance hybrid with a single bond on one side and double bond on the other producing an overall bond order of 1.5 for each side... Ozone is a powerful oxidizing agent, far stronger than O₂.¹²⁵ Ozone is diamagnetic, which means that its electrons are all paired and it is repelled by the poles of a magnet.



It has a noticeable odor: when > 0.001 for hypersensitive people, when > 0.003 (50% confidence level), when > 0.02 ppmv (90% confidence level).¹²⁶ It is slightly purple. It is one of the named criteria air pollutants established as US National Ambient Air Quality Standards (NAAQS) by the EPA under the 1970 US Clean Air Act Amendments (CAAA70). Average troposphere O₃ away from polluted areas is 20 to 40 ppbv at sea level

¹²³ <http://en.wikipedia.org/wiki/Superoxide>

¹²⁴ <http://en.wikipedia.org/wiki/Peroxide>

¹²⁵ <http://en.wikipedia.org/wiki/Ozone> including structure image

¹²⁶ <http://www.ozoneservices.com/articles/007.htm>

and 30 to 70 ppbv at higher altitudes. In urban polluted air, it typically rises to 70 to 150 ppbv but can rise to as high as 550 ppbv or more, peaking during the afternoon of a sunny day.

In the stratosphere, peak value of mixing ratio is 10 ppmv, the peak occurring at about 25 - 32 km,¹²⁷ with a peak number density of 3 to 4 x 10¹² molecules cm⁻³.¹²⁸ Stratospheric ozone, which in ppmv is much higher than in ground smog, is “good” because it absorbs UV photons, heating up the stratosphere while protecting life on Earth.

Sources: are primarily atmospheric chemical reaction of O with O₂, discussed further below. (Ozone is not directly emitted by autos or other sources of pollution and smog precursors.) Sinks: are photolysis, atmospheric reaction in gas phase and on surface, dissolution in surface water, and deposition to sea ice, snow, soil, vegetation, and structures.

There are significant health effects:

Increased susceptibility to bacterial infection at > 100 ppbv

Headache at >150 ppbv.

Chest pain at > 250 ppbv

Shortness of breath cough and dyspnea at >300 ppbv

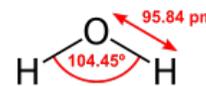
Chronic exposure causes lung tissue injury and respiratory disease, exacerbating pre-existing chronic asthma or COPD.

Ozone also affects rubber, textiles, dyes, fibers, paints, and some plants and trees. (APGW p. 65-6)

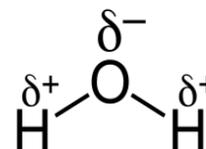
See more details about O₃ under Photochemical Smog and Stratospheric Ozone Depletion.

Water Vapor H₂O

Water vapor is measured with a hygrometer. The water molecule forms an angle, with hydrogen atoms at the tips and oxygen at the vertex. This angle formed is 104.48°... Because oxygen has a higher electronegativity than hydrogen, the side of the molecule with the oxygen atom has a partial negative charge.¹²⁹



We are fortunate to live on Earth where Ice, liquid water, and water vapor can coexist. The triple point of water, the single combination of pressure and temperature at which liquid water, solid ice, and water vapor can coexist in a stable equilibrium, occurs at exactly 273.16 K (0.01 °C, by definition) and a partial vapor pressure of 611.73 pascals (ca. 6.1173 millibars, 0.0060373 atm). At that point, it is possible to change all of the substance to ice, water, or steam by making arbitrarily small changes in pressure and temperature. In contrast, on Venus temperatures and pressures are such that water is always in the vapor phase.



The following is a simplified phase diagram for water showing the principle 3 states and the triple point (where liquid water, ice I_h, and water vapor are in equilibrium), as well as how the Kelvin and Celsius scales are defined, etc.¹³⁰ (In more complete diagrams, there are as many as 16 known crystalline and amorphous solid phases of water, and there are other triple points where 3 phases are in equilibrium.)¹³¹

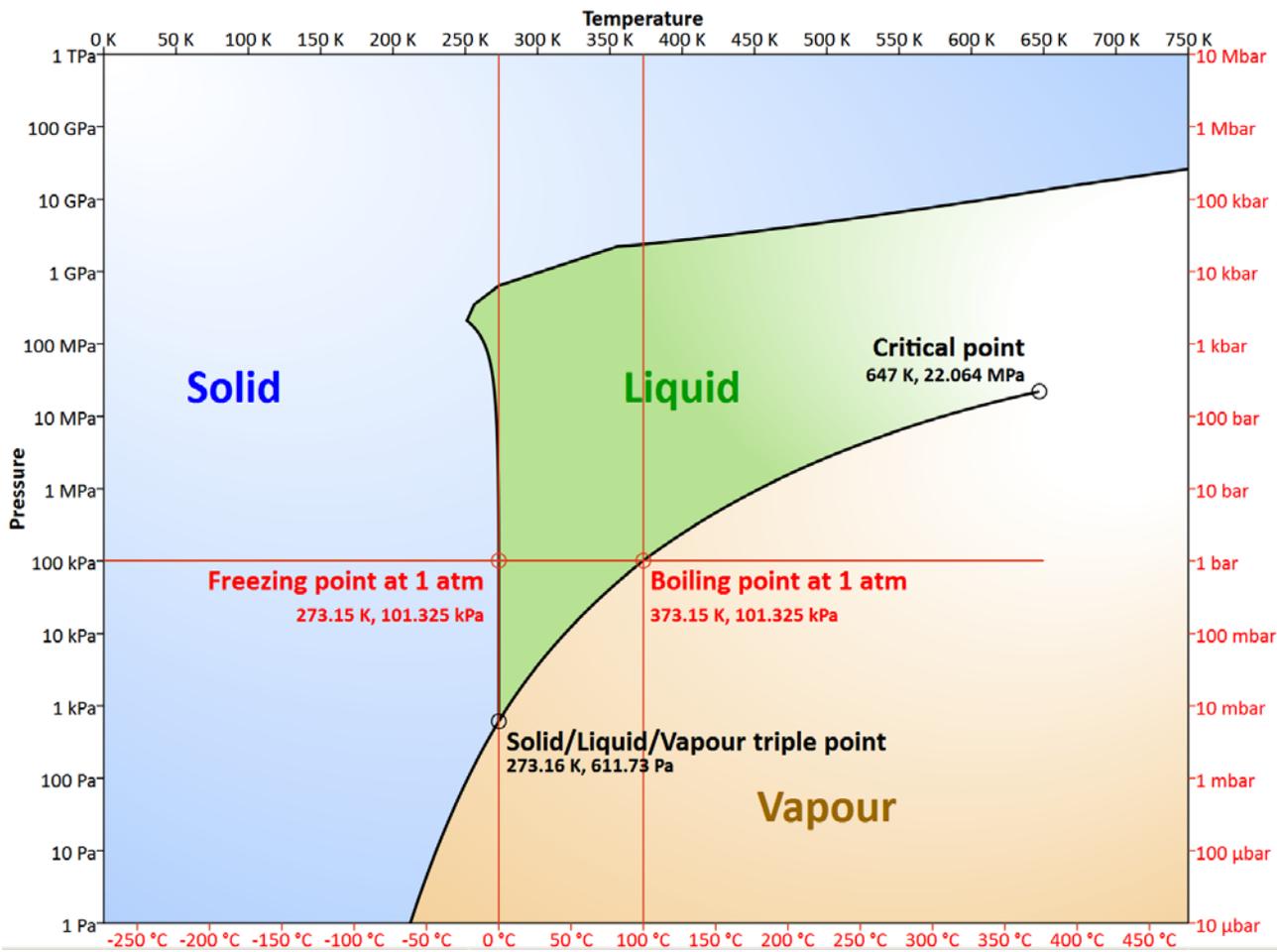
¹²⁷ per APGW figure 11.7 p. 239 and graph later included, “Vertical profiles of UV, O₃, and O₂)

¹²⁸ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/index.htm> Chapter 10 diagram.

¹²⁹ http://en.wikipedia.org/wiki/Properties_of_water (images)

¹³⁰ http://en.wikipedia.org/wiki/Properties_of_water#Triple_point

¹³¹ <http://en.wikipedia.org/wiki/Ice>



Sources are

- Evaporation from oceans, lakes, rivers, and soil
- Sublimation from sea ice and snow
- Transpiration from plant leaves
- Atmospheric chemical reaction
- Evaporation during power plant industrial water cooling
- Evaporation during irrigation
- Fossil fuel, biofuel, and biomass burning combustion

Sinks are

- Condensation to liquid water in clouds
- Vapor deposition to ice crystals in clouds
- Deposition to oceans, sea ice, snow, and soils
- Atmospheric chemical reaction.

Water vapor is found with mixing ratio up to 4 to 5 %.

Carbon Dioxide CO₂

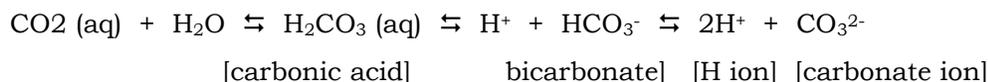
The gas was discovered by Joseph Black (1728-1799).

A compound O=C=O composed of 2 oxygen atoms each covalently double bonded to a single carbon atom in a linear centrosymmetric arrangement.

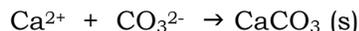
It exists in Earth's atmosphere as a trace gas at a concentration of about 0.04 per cent (400 ppm) by volume, as of 2014. The pre-industrial value (in the mid-1700s) was about 275 ppmv, so the difference may be inferred to be the anthropogenic component. (CO₂ levels were much higher in the early Earth atmosphere, up to 80% of the total mole fraction, APGW Fig. 2.11.)

The atmospheric composition of carbon dioxide (CO₂) is steadily rising (as shown in the following “Keeling Curve” of Charles David Keeling),¹³² an indisputable fact central to the politically charged debate on global warming.

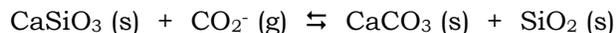
In water, dissolved CO₂ forms carbonic acid, bicarbonate, and carbonate.



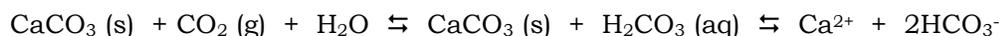
At ocean alkaline pH 8.1, organisms can synthesize calcium carbonate (calcite) for shells which precipitate, removing CO₂.



CO₂ can also be removed from the atmosphere by chemical weathering at the atomic level of various calcium silicate rocks and minerals, which creates calcium carbonate and silicon dioxide.



The following reversible reaction can consume or release CO₂, depending on the concentration of the gas. It proceeds to the right when CO₂ is high, as in soils:



Quantitation of CO₂

The amount of CO₂ expressed as carbon in the global atmosphere is estimated at 2,184.83 Tg-C/ppmv CO₂.

Current emission rate (2010) from fossil fuels and permanent deforestation is estimated at 10,200 Tg-C yr⁻¹ = 10.2 Gt C (Gigatonnes C) (APGW p. 61) Another estimate, for 2013, for Fossil fuels, cement production, land-use change is 9.9 billion metric tonnes (9.9 Gt C).¹³³

At 393 ppmv CO₂, the total atmosphere C (gaseous and particulate) is 859 gigatonnes C (859 Gt), almost all as CO₂. (APGW p. 62)

Sources of CO₂:

Bacterial fermentation, bacterial anaerobic respiration, aerobic respiration (plants, animals, fungus, protozoa etc.), evaporation from oceans, atmospheric chemical reactions, volcano outgassing, biomass burning, fossil fuel combustion, cement production, etc. (See later graph)

Sinks of CO₂:

Oxygenic photosynthesis PS, sulfur-producing PS, dissolution, deposition in snow, ice, soil, vegetation, chemical weathering, photolysis in upper atmosphere, etc.

The estimated calculated rates of production and consumption can be used to produce the data-constrained e-folding lifetime of CO₂, which is estimated at about is 30 to 50 years. This lifetime appears to be slowly rising, probably because of rising ocean temperatures (reducing solubility in oceans) and permanent deforestation (reducing uptake by PS). (APGW p. 58, see also fig 3.12 here¹³⁴)

¹³² http://en.wikipedia.org/wiki/Carbon_dioxide_in_Earth's_atmosphere

¹³³ <http://co2now.org/Current-CO2/CO2-Now/global-carbon-emissions.html>

¹³⁴ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/APGWCh3Figs.pptx>

Storage Reservoirs of Carbon:

Reservoirs in Earth's atmosphere, oceans, sediments, and land in 2011 (APGW p. 62) are listed as follows:

Region	Component	Gigatonnes C (GT-C)
Atmosphere	gas and particulates	859 Gt
Surface Oceans		
	Live organic C	5 Gt
	Dead organic C	30 Gt
	Bicarbonate ion	500 Gt
Deep Oceans		
	Dead organic C	3,000 Gt
	Bicarbonate ion	40,000 Gt
Ocean Sediments		
	Dead organic C	10,000,000
Land/ocean sediments		
	Carbonate rock	60,000,000
Land		
	Live organic C	800
	Dead organic C	2,000

Health Effects of CO₂ excess:

CO₂ is not generally toxic except in high concentrations:

Mixing ratios of 1.5% affect respiration.

Mixing ratios of 3.0% cause headaches, dizziness, and nausea.

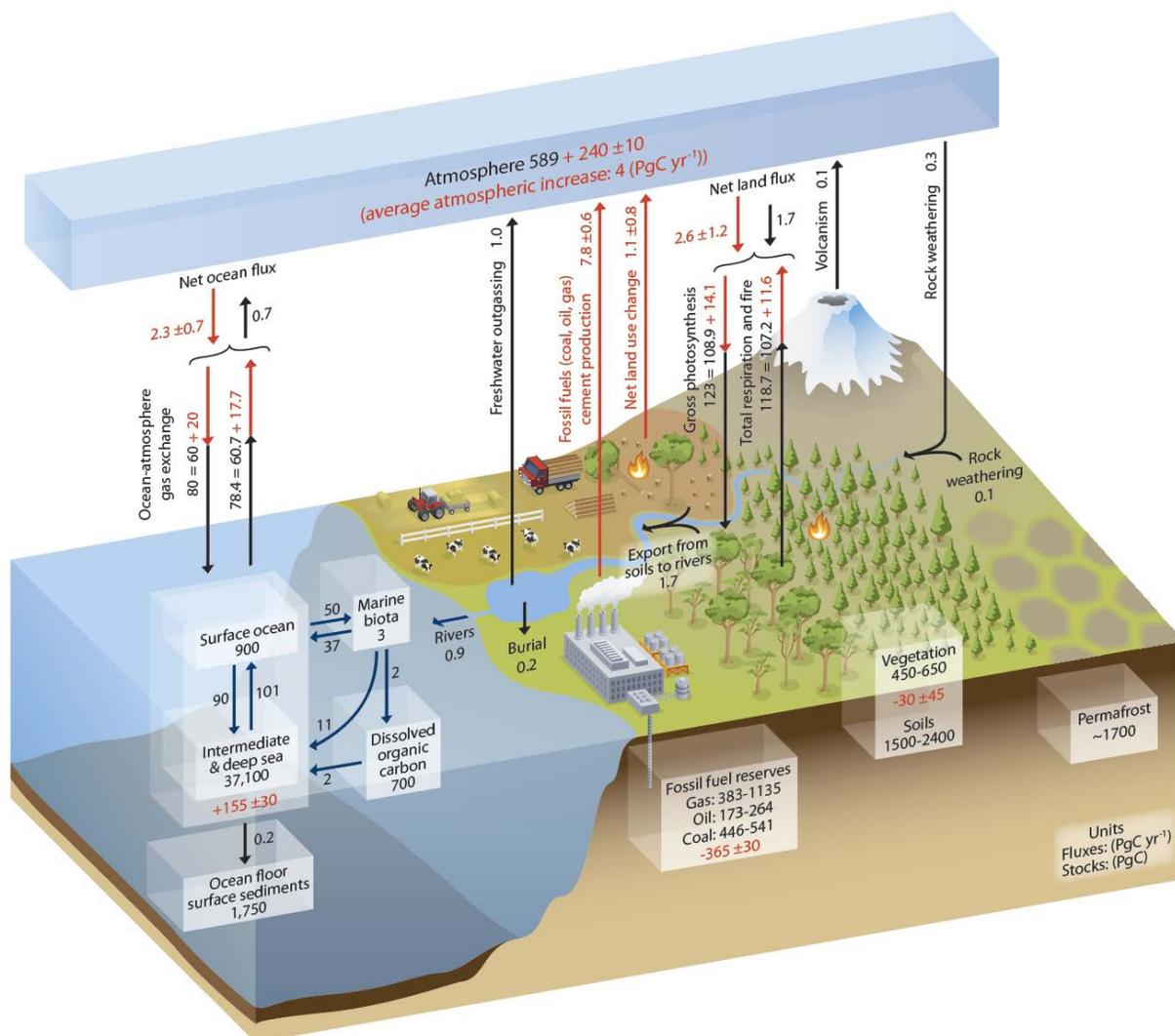
High concentrations (such as were emitted by Lake Nyos, Cameroon August 21, 1986) can cause fatal asphyxiation.

CO₂ is a greenhouse gas on the rise. For Global Distribution of CO₂ and Timeline (Keeling Curve), see Global Warming

Dissolved CO₂ in the oceans has caused falling ocean pH (acidification), from ~8.25 in 1750 to ~8.13 in 2000. (APGW p. 297)

(Other atmospheric constituents, such as the stratospheric ozone, are also changing due to anthropogenic effects.)

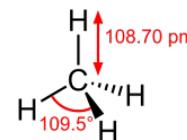
The carbon cycle is summarized in the IPCC 2013 report as follows:¹³⁵



Here, the carbon stocks/stores/reserves C masses are shown as PgC (1 petagram C = 10^{15} gC) and exchange fluxes of C are shown as PgC/yr C). Numbers in black are estimated preindustrial levels, <~1750. Red arrows are estimated anthropogenic flux perturbations from the 1750 value to the average value over the 2000–2009 time period. Red reservoir numbers are cumulative changes in the stores/reservoirs from ~1750 to 2011. Positive red reservoir or flux values means an increase in that reservoir or flux. Uncertainties are shown as 90% conf. levels.

Methane CH₄

Methane is a chemical compound with the chemical formula CH₄. It is a tetrahedral molecule with four equivalent C-H single bonds.¹³⁶ It is the most reduced form of C, the simplest alkane and most abundant hydrocarbon, the main component of natural gas. It is a greenhouse gas, and can absorb thermal IR 25 times more efficiently (on a per mole basis) than CO₂. Its e-folding lifetime against chemical breakdown in the atmosphere is quite



¹³⁵ IPCC_WGI_2013, fig. 6.1, PDF page 487.

¹³⁶ <http://en.wikipedia.org/wiki/Methane> (image)

long, 8 to 12 years. It is an important contributor to tropospheric ozone. Current mixing ratio is c. 1.85 ppmv and are relatively constant in the troposphere. There are no direct harmful effects at current levels, but it contributes to global warming.

Sources are methanogenic bacteria (in rice paddies, cattle, termites, lakes, wetlands and peat bogs, and landfills); natural gas leaking during mining, transport, burning, and oil production; deep ocean release (including methane clathrates); thawing of permafrost; burning of fossil fuel, biomass, and biofuel, and atmospheric chemical reaction. 80% of methane in the atmosphere is biogenic.

Sinks include atmospheric chemical reaction, dissolution in surface water, deposition to sea ice, snow and ice caps, soil, vegetation, and structures; and methanotrophic bacteria. (APGW p. 64)

Methane, included in Total Organic Gases, is often excluded from "Reactive Organic Gases" because of its stability and long lifespan.

Higher order alkanes are found in trace quantities: ethane, butane, propane.

Methane is a greenhouse gas on the rise.

Carbon Monoxide CO

Carbon monoxide is a linear molecule consisting of one carbon atom and one oxygen atom, connected by a triple bond that consists of two covalent bonds as well as one dative covalent bond.¹³⁷ It is a minor greenhouse gas because it absorbs thermal-IR radiation. It is one of the named criteria air pollutants established as US National Ambient Air Quality Standards (NAAQS) by the EPA under the 1970 US Clean Air Act Amendments (CAAA70). In the free troposphere, mixing ratios are in the range of 50 to 150 ppbv.

Sources are

Fossil fuel and biofuel combustion (especially incomplete combustion)

Biomass burning (including wildfires)

Atmospheric chemical reaction

Plants and biological activity in oceans

Sinks are

Atmospheric chemical reaction to CO₂

Dissolution in surface water (low)

Deposition to sea ice, snow, soil, vegetation, and structures

Emissions in the US in 2008 were 70 million tonnes of CO from anthropogenic sources. US emissions of CO declined between 1970 to 2008 by about 62%. (APGW p. 63)

Health Effects of CO excess:

100 ppmv for 2-3 hours causes slight headache.

200 ppmv for 2-3 hours causes headache, loss of judgement

400 ppmv for 1-2 hour causes frontal headache.

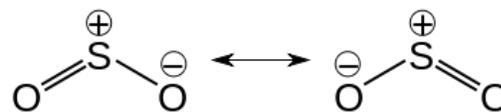
800 ppmv for 45 min causes dizziness, nausea, and convulsions; insensible in 2 hours.

1600 ppmv for 20 min causes HA, ↑HR, dizziness, and nausea within 20 min; death < 2 hours.¹³⁸

Sulfur Dioxide SO₂

SO₂ is a bent molecule in which a S=O double bond resonates between the two arms, so that each bond has a bond order of 1.5.¹³⁹

Sulfur dioxide has a strong odor when > 0.5 ppmv. It is a precursor to sulfurous and sulfuric acid. (APGW p. 66) It is one of the named criteria air pollutants established as US National Ambient Air Quality Standards (NAAQS) by the EPA under the 1970 US Clean Air Act Amendments (CAAA70). In the free troposphere, mixing ratios are about 10 pptv to 1 ppbv.



Sources are: oxidation of dimethylsulfide DMS (H₃C-S-CH₃, the most abundant biological sulfur compound emitted to the atmosphere, arising from marine phytoplankton), volcanic emission (of SO₂, H₂S, or elemental

¹³⁷ http://en.wikipedia.org/wiki/Carbon_monoxide

¹³⁸ http://en.wikipedia.org/wiki/Carbon_monoxide_poisoning

¹³⁹ http://en.wikipedia.org/wiki/Sulfur_dioxide (diagram)

S = brimstone¹⁴⁰), fossil fuel combustion, mineral ore processing such as roasting ores, and chemical manufacturing. Sinks are atmospheric chemical reaction to produce sulfuric acid; dissolution in cloud drops and surface water; deposition to sea ice, snow, soil, vegetation, and structures. (APGW p. 66)

Anthropogenic emissions have fallen in the US and are thought to have slowly fallen globally, attaining about 8 Tg in the US and Canada in 2011, and about 101 Tg globally in 2011.¹⁴¹

Health effects:

1-30 ppbv: typical for polluted air

> 300 ppbv: taste

> 500 ppbv: odor

1500 ppbv: bronchial restriction

40,000 ppbv: death

SO₂ ultimately combines with OH, H₂O, and O₂ etc. in differing gas and water phase pathways, ultimately forming H₂SO₄ (sulfuric acid) This pollutant is more extensively discussed in the section on Acid Deposition.

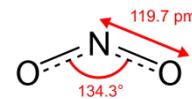
Nitric Oxide NO, Nitrogen Dioxide NO₂, and Combined Nitrogen Oxides NO_x

Nitric Oxide NO bond structure and representation is discussed above. It is a colorless gas, a free radical, a precursor to O₃, HNO₃, and nitrate NO₃⁻. NO is not regulated

Sources of NO are: **Denitrification** in soils and plants; Lightning; Fossil fuel and biofuel combustion; Biomass burning; Photolysis and kinetic chemical reaction. Sinks are atmospheric chemical reaction; Dissolution in surface water; Deposition to sea ice, snow, soil, vegetation, and structures.

In the sea level background troposphere, mixing ratios are about 5 pptv. In the upper free troposphere, NO mixing ratios are 20 to 60 pptv. Levels in urban polluted environments rise to 0.1 ppmv in the early morning. NO does not have directly harmful effects, but its byproducts do. (APGW p. 67).

Nitrogen Dioxide NO₂ is a reddish brown gas (it absorbs short blue and green leaving some green and red) that is heavier than air and has a strong odor. Nitrogen dioxide (bond structure diagram to right) is a paramagnetic, bent molecule with C_{2v} point group symmetry,¹⁴² and the two bonds have a bond order of 1.5. It is an intermediary between NO emission and O₃ formation, and a precursor to nitric acid, a component of acid deposition. It is one of the named criteria air pollutants established as US National Ambient Air Quality Standards (NAAQS) by the EPA under the 1970 US Clean Air Act Amendments (CAAA70). It reduces O₃ in the upper stratosphere.



Sources of NO₂ are: Atmospheric chemical reaction; Fossil fuel and biofuel combustion; Biomass burning. NO₂ emission from combustion is about 10 to 15% of the total emission of NO_x from combustion. Sinks are: Atmospheric chemical reaction; Dissolution in surface water; Deposition to sea ice, snow, soil, vegetation, and structures.

In the sea level background troposphere, mixing ratios are about 10 to 50 pptv. In the upper free troposphere, NO₂ mixing ratios are 30 to 70 pptv. Levels in urban polluted environments rise to 150 to 250 ppbv, peaking in midmorning because sunlight breaks down most NO₂ later. Indoor levels rise to 20 to 50 ppbv in homes with gas cooking, sometimes peaking as high as 400 to 1000 ppbv (and these levels can reduce lung capacity). NO₂ lung injury mostly affects children and asthmatics. Levels > 80 ppbv cause sore throat and increased resp. infections and absences from school. Much higher levels can cause bronchitis (25-100 ppmv) and death (> 150 ppmv). (APGW p. 67).

NO_x: NO and NO₂ are grouped in air pollution science as Nitrogen Oxides **NO_x**, representing [NO] + [NO₂], pronounced like “nocks”. This term does not include other oxides of N, such as N₂O, N₂O₄, N₂O₅, and N₄O, which are apparently not directly important for air pollution (though N₂O₅ is a reservoir species for NO_x, and N₂O is important for Global Warming).

¹⁴⁰ <http://www.photovolcanica.com/VolcanoInfo/Kawah%20Ijen/Kawah%20Ijen.html>

¹⁴¹ Z Klimont et al, “The last decade of global anthropogenic sulfur dioxide: 2000–2011 emissions”, 2013 Environ. Res. Lett. 8 014003 doi:10.1088/1748-9326/8/1/014003, corrected version as of 1 March 2013.

¹⁴² http://en.wikipedia.org/wiki/Molecular_symmetry

Production rates quoted in 1997 of NO_x in Tg N per yr are:¹⁴³

Fossil Fuel (mobile and stationary)	22.0
Tropical Biomass burning	7.9
Lightning	5 (non-anthropogenic, in upper troposphere)
Soil microbial	7 (i.e., non-anthropogenic plus fertilizers)
NH ₃ oxidation	0.9
Stratosphere decomposition of N ₂ O	0.64
Aircraft	0.85
TOTAL	44

NO_x has a lifetime of < 1 day.¹⁴⁴

Nitric acid as a pollutant that is more extensively discussed in the section on Acid Deposition.

Lead Pb as an Environmental Pollutant

Lead Pb (from L. plumbum), as of 1976, is one of the named criteria air pollutants established as US National Ambient Air Quality Standards (NAAQS) by the EPA under the 1970 US Clean Air Act Amendments (CAAA70), and levels were regulated as of 1977-8. It becomes an atmospheric pollutant in the form of an aerosol component. Ingested or inhaled, it can lead to toxic levels and lead poisoning, especially in children.

Seneca recognized the noxious effects of lead in ancient Roman times, 61 CE, and Marcus Vitruvius Pollio advised in the first century BCE against using it for water pipes. Silver and lead mining and smelting released lead that increased lead levels by 4x over natural lead levels in Greenland ice cores from 500 BCE to 300 CE. Other metals such as Cu and Fe were also found.¹⁴⁵

Sources are: leaded fuel combustion in vehicles, lead acid battery manufacturing, lead ore crushing and smelting, dust from soils contaminated with lead based paint; solid waste disposal; and crustal physical weathering. Sinks are: deposition to oceans, sea ice and ice caps, snow, soil, and vegetation; Inhalation.

Lead was added to gasoline to boost octane, in the form of tetraethyl lead. The mixture, called "ethyl", was invented by Thomas Midgley, Jr. (1889-1944) in 1921 and first marketed in 1923. It eventually caused numerous cases of lead poisoning in lab and refinery workers, as well as in Midgley. By the 1930s, 90% of gasoline was leaded, despite warning signs and alarms. It was regulated in air and gasoline only beginning in 1977. The invention c. 1973 and introduction of the catalytic converter in the mid-1970s led to the phase-out of lead in gasoline (beginning in 1975, nearly complete in the US by 1986, banned completely in the US as of 1/1/1996),¹⁴⁶ in part because it poisoned the converters. (Catalytic Converters contained platinum, palladium and/or rhodium, and were intended to convert CO and incompletely burned HC to CO₂ and H₂O. They also attempted to reduce NO via $2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$.)

Lead health effects include mental retardation, learning deficits and reduced IQ, behavior disorders including even an association with violent crime,¹⁴⁷ neurologic impairment, abdominal pains, blindness, deafness, coma, and death. (APGW p. 68-70)

Hazardous Organic Compounds

The 1990 Clean Air Act Amendments (CAAA90) established emission standards for 189 hazardous (toxic) air pollutants thought to pose a risk for cancer, birth defects, or environmental/ecological damage. Some of these also affect photochemical smog formation (as Reactive Organic Gases or Volatile Organic Compounds). Some of these included (APGW p. 70):

Benzene: Gasoline combustion, solvents, tobacco smoke

Styrene: Plastic and resin mfr, clothing, building materials

¹⁴³ D. S. Lee, et al "Estimations of Global NO_x Emissions and their uncertainties", *Atmospheric Environment*, Volume 31, Issue 12, June 1997, table on p. 1740

¹⁴⁴ JAT slide.

¹⁴⁵ Hong S et al, "Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilizations.", *Science*. 1994 Sep 23;265(5180):1841-3.

¹⁴⁶ <http://yosemite.epa.gov/R10/airpage.nsf/webpage/Leaded+Gas+Phaseout>

¹⁴⁷ "The Crimes Of Lead", *C&EN*, Volume 92 Issue 5 | pp. 27-29, February 3, 2014

Toluene (toluol): Gasoline combustion, fuel and biomass burning; petroleum refining; detergents; painting; building materials

Xylene: Gasoline combustion, lacquers, glues

1,3-Butadiene (not the same as isoprene, 2-methyl-1,3-Butadiene): Mfr. of rubber, combustion of fossil fuels; tobacco smoke

Acetone: Nail polish; Paint remover; cleaning solvent

Methylethylketone MEK: Solvent in paints, adhesives, cosmetics

Methylene chloride: Solvent, paint stripper, degreaser

Vinyl chloride: PVC, plastics, building materials

Other organic compounds found in trace quantities include ethane.

Overview of Urban Air Pollution

This topic is initially presented in *APGW* Chap. 4, excluding particulates/aerosols, and further developed in chapters pertaining to specific topics such as acid deposition, etc.

Population growth is a major contributor. Global Population has increased exponentially from 300 million in 0 CE, 1 billion in 1800, 2 billion in 1927, 3 billion in 1960, 4 billion in 1974, 5 billion in 1987, 6 billion in 1999, 7 billion in 2012, and 9 billion in 2050.

In 1763 to 1775,¹⁴⁸) James Watt developed an improved coal-fired steam engine, patenting one in 1769, initiating the industrial revolution (c. 1760 to c. 1840 or 1880). Metal foundries in West Germany 1876 with mining of silver and lead in Germany, Austria, and Hungary. Coal consumption in US, for steel manufacturing, iron manufacturing, railway transportation, manufacture of soda ash (sodium carbonate Na_2CO_3), etc., causing much pollution by 1900. Efforts in early U.K. to regulate locomotive steam engine smoke 1845 and furnace smoke 1853. US regulations by 1869. MA had first state regulation 1910. Federal involvement by 1910.

The cleaner background troposphere (above the boundary layer) contains inorganic gases (partly anthropogenic), long lived light organic gases (partly anthropogenic), and a few naturally emitted short-lived heavy organic gases (particularly the hemiterpene isoprene).

Polluted air, which is mostly in the boundary layer, contains inorganic gases and short-lived light and heavy organic gases. The heavy MW organic gases, including aromatic species such as toluene and xylene, break down rapidly in polluted urban air and generally do not reach the background troposphere. Higher mixing ratios of NO_x are found, as well as higher reactive organic gases (ROG, i.e., total organic gases typically excluding methane).

Types of Air Pollution by Atmospheric or Geographic Region

(per *APGW* p. 57)

Indoor air pollution

Gases: NO_2 , CO, HCHO, SO_2 , organic gases, radon

Particles: Black carbon, organic matter, sulfate, nitrate, ammonium, allergens, asbestos, fungal spores, pollen, tobacco smoke

Outdoor urban air pollution

Gases: O_3 , NO, NO_2 , CO, ethene, toluene, xylene, PAN

Particles: Black carbon, organic matter, sulfate, nitrate, ammonium, soil dust, sea spray, tire particles, lead

¹⁴⁸ http://en.wikipedia.org/wiki/Watt_steam_engine

Acid deposition

Gases: SO₂, H₂SO₄, NO₂, HNO₃, HCl, CO₂

Particles: Sulfate, nitrate, chloride

Stratospheric ozone reduction

Gases: O₃, NO, HNO₃, HCl, ClONO₂, chlorofluorocarbons

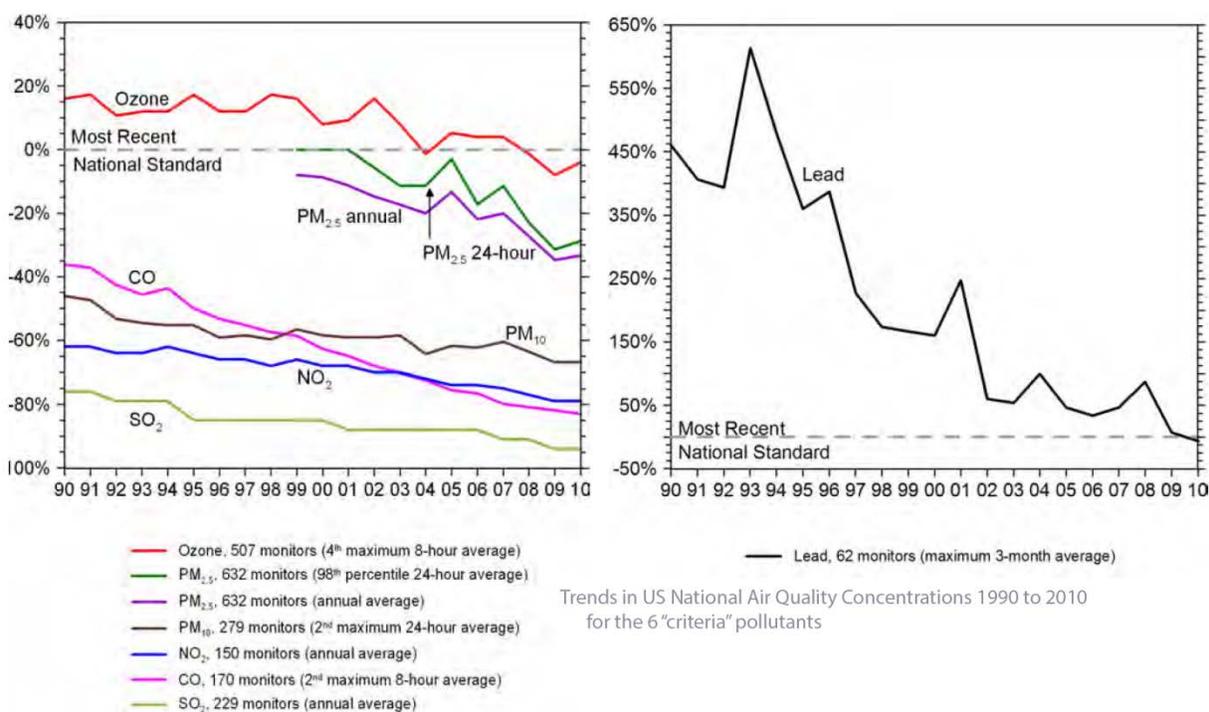
Particles: chloride, sulfate, nitrate

Global climate change

Gases: H₂O, CO₂, CH₄, N₂O, O₃, chlorofluorocarbons

Particles: black carbon, organic matter, sulfate, nitrate, ammonium, soil dust, sea spray

Trends in US Air Quality 1990 to 2010



The 2 graphs above from the EPA show that air quality for the 6 "criteria pollutants" (O₃, CO, NO₂, SO₂, PM, and Pb) has improved, but least of all for ozone. (The reduction of averaged national ozone levels is primarily due to CA sites—other areas such as the Boston area have not decreased in ozone.¹⁴⁹) The dotted line for the left graph (the 0% level) represents the "national air quality standards for specific pollutants to safeguard human health and the environment. These standards define the levels of air quality that EPA determines are necessary to protect against the adverse impacts of air pollution based on scientific evidence."¹⁵⁰ The left graph show that NO_x emission have declined somewhat.

¹⁴⁹ <http://www.epa.gov/airtrends/ozone.html>

¹⁵⁰ <http://www.epa.gov/air/airtrends/2011/report/sixcommon.pdf>

ROG emissions (named VOC here), shown in the following graph, have declined 1970 to 2003 substantially despite a substantial rise in GDP.¹⁵¹

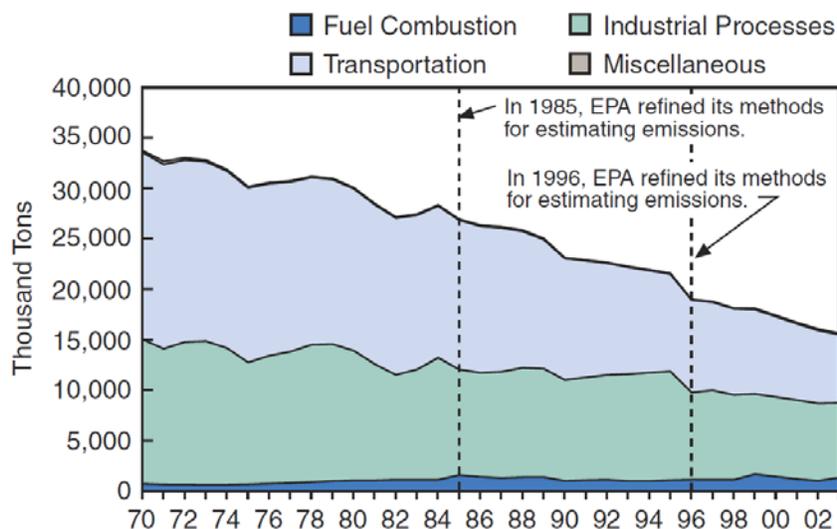


Figure 13. National Trends in VOC Emissions, 1970–2003.

US power plant emissions of NO_x decreased from 1,924 ktons in 1990 to 481 ktons in 2008 (per slide of JAT lecture notes). Alternatively, “In 2008, power plant SO₂ emissions were 52 percent lower and NO_x emissions were 54 percent lower than they were in 1990.”¹⁵²

London-type Smog

Smog was coined from smoke + fog by Dr. Henry Antoine Des Voeux in 1905. London type smog is caused by coal and chemical combustion in the presence of low lying temp inversion and fog, was prominent (as “pea-soup fog”) by 1900. However, bad air from burning cheap sea coal (soft dirty high sulfur bituminous coal) had led to annoyance at least back to 1272, when King Edward I banned the burning of sea-coal. A four-day fog in 1952 killed roughly 4,000 Londoners.¹⁵³ Similar severe London style smogs occurred in Belgium 1930, Reading, Donora, and Pittsburgh Pennsylvania 1948. London type smog is worsened by low-lying temperature inversion (for which the environmental lapse rate $\Gamma_e = -\Delta T/\Delta z$ is negative), worse in the winter, the same conditions promoting fog.

“London-type smog is mainly a product of burning large amounts of high sulfur coal. Clean air laws passed in 1956 have greatly reduced smog formation in the United Kingdom; however, in other parts of the world London-type smog is still very prevalent. The main constituent of London-type smog is soot; however, these smogs also contain large quantities of fly ash, sulfur dioxide, sodium chloride and calcium sulfate particles. If concentrations are high enough, sulfur dioxide can react with atmospheric hydroxide to produce sulfuric acid, which will precipitate as acid rain.”¹⁵⁴

Fly ash (flue ash) includes silicon dioxide (SiO₂) (both amorphous and crystalline) and calcium oxide (CaO). Severe and similar London-type smog occurred in coal areas of Pennsylvania like Donora...

¹⁵¹ <http://www.epa.gov/airtrends/aqtrnd04/pdfs/2003ozonereport.pdf> “The Ozone Report: Measuring Progress through 2003”

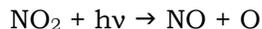
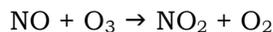
¹⁵² <http://www.nrdc.org/air/pollution/benchmarking/2008/benchmark2008.pdf> “Benchmarking Air Emissions”, June 2012

¹⁵³ <http://www2.epa.gov/aboutepa/londons-historic-pea-soupers>

¹⁵⁴ http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Case_Studies%3A_Kinetics/Smog

Photostationary-State Ozone, Night vs. Day in the Background Troposphere, and PAN

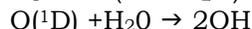
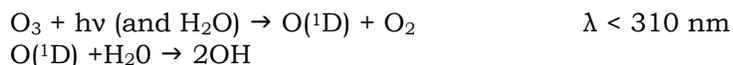
In the background troposphere, the O₃ mixing ratio is primarily controlled by 3 reactions involving itself and NO_x: (APGW p. 85)



Under these conditions, where O₃ is in much higher concentration more abundant than NO_x, the volume mixing ratio of O₃ is roughly proportional to the mixing ratio of NO₂ divided by the mixing ratio of NO. (In polluted air, this ratio is higher due to increased peroxy radicals, leading to greater O₃ production. APGW p. 89)

During the day, NO₂ is slowly removed by reaction with OH to form nitric acid, which serves as a sink for NO_x.

The OH radical primarily derives from ozone (APGW p. 86), and will be depend on H₂O and O₃ concentrations:



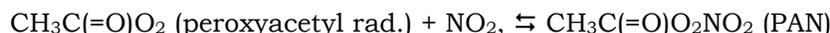
At night, absence of photolysis prevents formation of NO and O, and O₃ production ceases. Emitted NO will destroy O₃ at night. NO₂ becomes available to make N₂O₅ (short lived dinitrogen pentoxide) and, in hydrometeor droplets, HNO₃.

Daytime Ozone production: During the day, ozone production occurs in the background troposphere by a variety of processes (APGW p. 86-88):

Subject Reactant	Other reactants involved in producing O ₃ including, including intermediate products and/or precursors to O ₃ mentioned for other Subject Reactant (shown in bold face)	e-folding lifespan for this reaction in backgnd trop.
CO	OH, H, CO ₂ , H, O ₂ , HO ₂ (hydroperoxy rad), NO, NO ₂ , O hν < 420 nm	28-110 d
Methane CH ₄	OH, H, CH ₃ , H ₂ O, O ₂ , CH ₃ O ₂ (methyl peroxy rad), NO, NO ₂ , O, CH ₃ O (methoxy rad.) hν < 420 nm	8-12 yr
Formaldehyde HCHO	CH ₃ O, O ₂ , HCHO, HO₂ , HCO (formyl rad.), H, CO , H ₂ , OH, H ₂ O, CO hν < 334 or < 370 nm	very short
Ethane C ₂ H ₆ (or Propane C ₃ H ₈)	OH, C ₂ H ₅ (ethyl rad.), H ₂ O, O ₂ , C ₂ H ₅ O ₂ (ethylperoxy rad.), NO, NO ₂ , C ₂ H ₅ O [ethoxy rad.], O hν < 420 nm	ethane: 23-93 d propane: 5-21 d
Acetaldehyde (CH ₃ CH=O)	C₂H₅O [ethoxy rad.], O ₂ , CH ₃ CH=O, HO₂	
PAN peroxyacetyl nitrate	CH ₃ CH=O, OH, CH ₃ C=O (acetyl rad.), H ₂ O, O ₂ , CH ₃ C(=O)O ₂ (peroxyacetyl rad.), NO ₂ , CH ₃ C(=O)O ₂ NO ₂ (PAN, peroxyacetyl nitrate)	300 K: 25 min 280 K: 13 hr c

PAN (peroxyacetyl nitrate):

PAN (peroxyacetyl nitrate) forms from acetaldehyde in a reaction that is reversible:



The reverse reaction takes place by thermal decomposition. At 300K, the e-folding lifespan is only 25 min, at 280K it is 13 hr, but at cooler temps such as in the upper troposphere, it can last for months. Thus PAN can serve as a long-lived reservoir of NO_x which allows NO_x pollution to spread widely from its urban source until

it encounters warmer temps and decomposes back to NO₂. PAN is an eye irritant, but is said to not have other health effects.

Photochemical Smog (PC Smog)

PC Smog is mostly found in the boundary layer, close to the ground. It arose with the automobile in LA CA and worsened between 1910 and 1940, at times reducing visibility to 3 blocks or worse. Open-air incineration was banned in LA in 1957. Also severe in Pittsburgh (APGW mult. pages). Arie Haagen-Smit in 1952 worked out the chemical reactions of PC smog, particularly the mechanism of ozone formation from nitrogen oxides and ROGs in the presence of sunlight.

PC smog contains emitted primary pollutants (NO_x, ROG¹⁵⁵, CO, SO₂), secondary pollutants and reaction intermediaries (such as O₃), and particulate matter PM (aerosols). The main contributors to PC smog are NO_x and ROG. CO₂ and Methane are not primary pollutants with respect to smog and O₃ formation, but CO₂ domes and methane domes can form over cities and raise local temperatures and thus accelerate O₃ formation.

Ozone is an important secondary pollutant that is not emitted by automobiles, but is synthesized in the atmosphere in a complex series of reactions, in the presence of NO_x and ROGs (both of which are emitted), and sunlight.

Health effects of PC smog include damage to the lungs (PM etc.). Hospital admissions and respiratory deaths often increase during periods when ozone levels are high, especially in the young, elderly, patients with asthma, COPD, CF, and other respiratory conditions: The EPA lists these effects of smog in a lay 2004 publication:

Pollutant	Effects
Nitrogen oxides NO _x	<ul style="list-style-type: none">• can contribute to problems with heart and lungs• links to decreased resistance to infection
Volatile organic compounds (VOCs) or ROG	<ul style="list-style-type: none">• eye irritation• respiratory problems• some are carcinogens
Ozone O ₃	<ul style="list-style-type: none">• coughing and wheezing• eye irritation• respiratory problems
Peroxyacetyl nitrate (PAN)	<ul style="list-style-type: none">• eye irritation• respiratory problems

The same EPA article also says, “Chemicals such as nitrogen oxides, ozone and peroxyacetyl nitrate (PAN) can have harmful effects on plants. These substances can reduce or even stop growth in plants by reducing photosynthesis. Ozone, even in small quantities, can achieve this, but PAN is even more toxic to plants than ozone.”¹⁵⁶

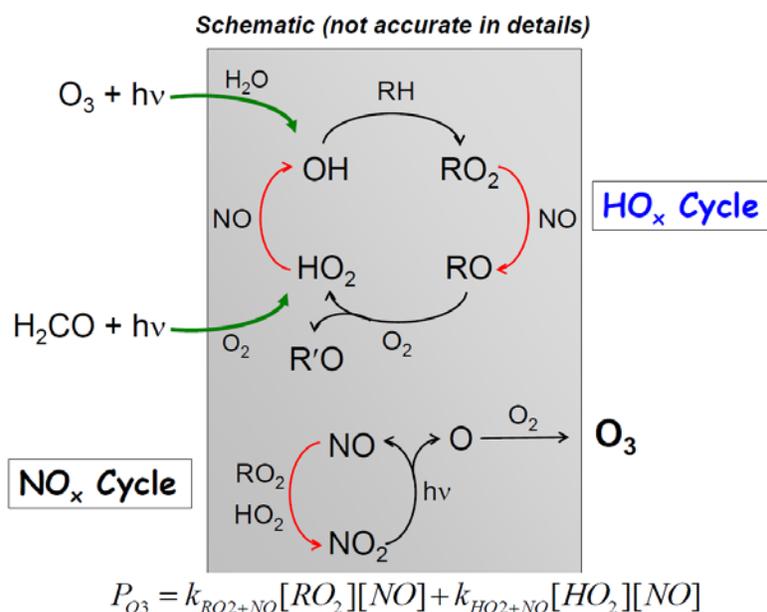
The following diagram of HO_x and NO_x cycles and the equations that follow summarize the coupled (interlocking) cycles that lead to catalytic photochemical ozone formation in PC smog.¹⁵⁷ As these are schematic, they are not depicted stoichiometrically.

¹⁵⁵ The terms VOC (volatile organic compounds that have a high vapor pressure at ordinary room temperature) and ROG are not entirely identical (ROG omits methane). We are concerned with ROGs with respect to their reactivity in PC smog, but the terms appear to be used interchangeably by many.

¹⁵⁶ http://www.epa.sa.gov.au/xstd_files/Air/Information%20sheet/info_photosmog.pdf

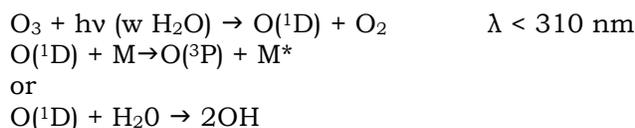
¹⁵⁷ JAT lecture notes, source unknown.

Photochemical O₃ Production



Initiation of PC O₃ Production

The key to catalyzed production of ozone is the generation of OH radical in the initiation phase (here O(¹D) is the excited state "O singlet D"):



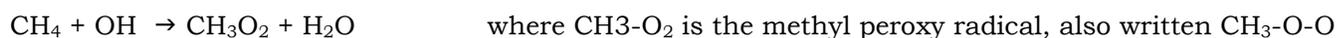
The generation of OH in the final reaction depends on the presence of H₂O and is less productive in the dryer winter or in dry urban areas like Phoenix.

APGW p. 91 also states that OH is generated in the early morning urban air by reaction of HONO (nitrous acid) with hv

Propagation of PC O₃ Production

Once OH is formed, coupled rapid cycles begin that create more O₃. The highly reactive OH can react with reactive organic gases such as methane or other organic gases (including various hydrocarbons, represented here generically by RH):

The HO_x Cycle: (pronounced "hocks")



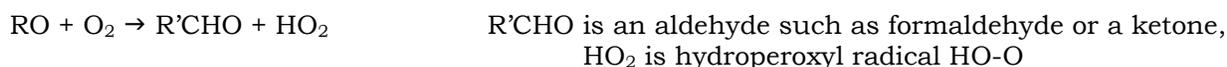
or



then NO from the NO_x cycle joins in:



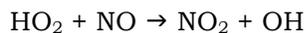
then



The HO₂ is also produced by this reaction:



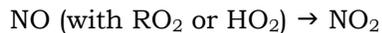
then



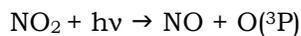
again using NO, the OH is regenerated, thus it is a catalyst

The NO_x Cycle

The RO₂ generated in the HO_x cycle also reacts in the NO_x cycle with NO to generate NO₂



then



O is highly reactive atomic O radical. NO is regenerated catalyst



Finally,



New Ozone O₃ has been synthesized

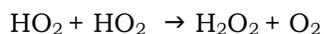
The ozone is synthesized from only a small fraction of the HO_x and NO_x cycles completed.

Termination of PC O₃ Production

The reactions in propagation forming O₃ are terminated when conditions are no longer favorable for them to continue—light and HC emissions have diminished, and available rate-limiting reactants (see rate formula for P_{O3} in diagram) RO₂, NO, and/or HO₂ are declining.

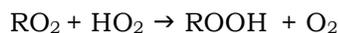
Low NO_x

Reactions consume HO₂ or RO₂ without using NO_x, preventing further generation of OH.



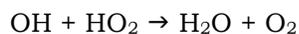
Self-reaction of hydroperoxyl forms Hydrogen peroxide H-O-O-H

or



organic peroxy + hydroperoxyl form Organic peroxide R-O-O-H

then

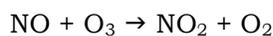


OH is consumed

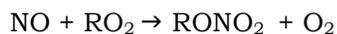
The peroxide is relatively stable and eventually is cleansed by precipitation. Nitric acid is not produced here.

High NO_x

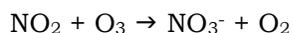
The OH and NO₂ are consumed to make nitric acid, so that NO is no longer regenerated.



NO consumed as before, forming NO₂



Alkyl nitrate (nitrate ester) formed, further consuming NO



NO₂ consumed as before, forming nitrate ion

The following continuation reactions generate HNO₃. The latter 2 reactions take place at night per IAC,¹⁵⁸ because NO₃⁻ radicals are rapidly photolyzed during the day.



Nitric acid (g) (per JAT), further consuming NO₂



Dinitrogen pentoxide (nocturnal, otherwise would photolyze NO₃⁻)

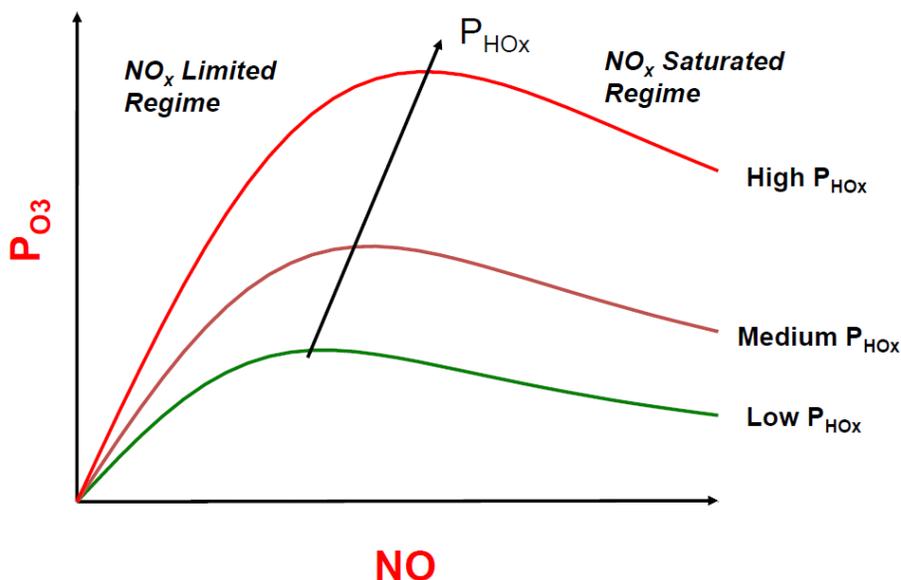


Nitric acid

The HNO₃ eventually falls out as acid deposition.

¹⁵⁸ <http://acmg.seas.harvard.edu/people/faculty/djj/book/bookhkw11.html#81848>

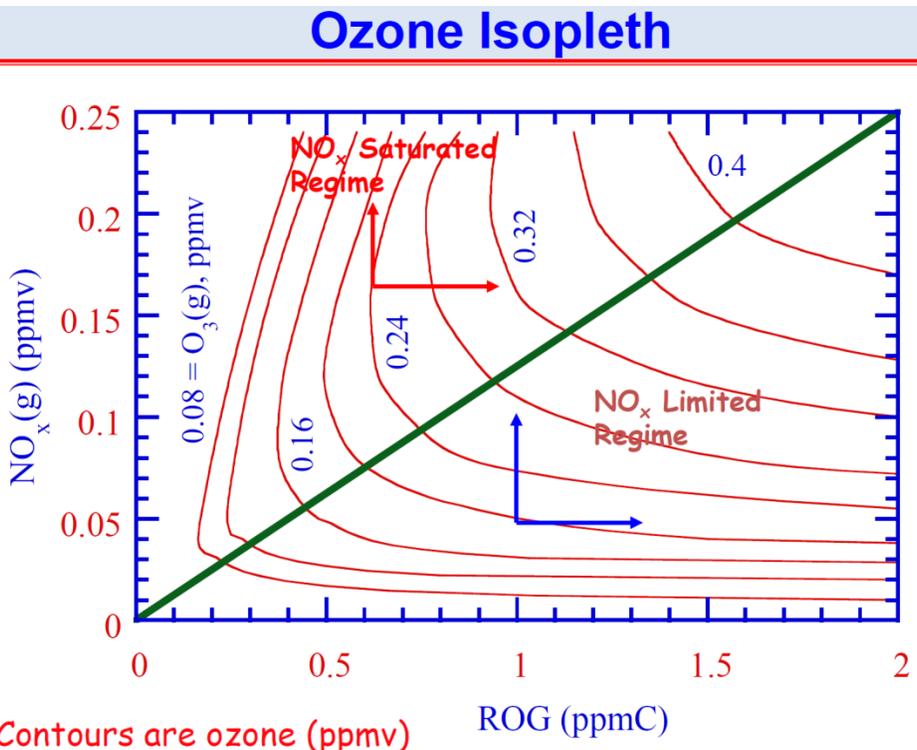
P_{O₃} Dependence on P_{HO_x} and NO



Ozone production efficiency increases as the rate of NO₂ production increases, and decreases as the rate of conversion of NO₂ to HNO₃ increases. The

Ozone Isopleth and P_{O₃}

This diagram¹⁵⁹ shows the relationship between ROG, NO_x, and O₃.



An isopleth is a curve along which a function of two variables has a constant value.

¹⁵⁹ APGW p. 89 and JAT lecture notes.
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In the lower right portion, the NO_x Limited Regime, changing ROG makes little difference to O₃ whereas increasing NO_x does change P_{O₃} (the production rate of O₃).

In the upper left, the NO_x Saturated Regime, changing ROG strongly affects O₃ whereas increasing NO_x has little effect on O₃.

These relationships depict why it is complex to manage O₃ as a pollutant by controlling primary pollutants. For example, reducing NO_x when ROG is low can increase O₃! Other factors such as meteorology also complicate matters.

The P_{O₃} also depends on HO_x mixing ratio. Increasing HO_x increases P_{O₃}, especially in the NO_x saturated regime.

An upwind region (such as LA) may serve as a source region for primary pollutants such as NO_x whereas a downwind site like San Bernardino may serve as a receptor region and exhibit greater secondary pollutants, including O₃ and PAN.

The Most Important Ozone-Related ROGs Found in a 1987 Southern CA study

(Ozone Generating capacity, order is with weighting of both Ozone Reactivity and Abundance):¹⁶⁰

- m- and p-Xylene
- Ethene
- Acetaldehyde
- Toluene
- Formaldehyde
- i-Pentane [isopentane]
- Propene
- o-Xylene
- Butane
- Methylcyclopentane

Alkenes and aromatic ROGs are important ozone precursors. Methane is the least reactive VOC (so that it is not included in ROG).

Ethene reacts as shown above and leads to formaldehyde and glycol aldehyde, both of which contribute to O₃ production. Ethene can react with O₃, forming formaldehyde...

Aromatics such as xylene and toluene form ozone (APGW p. 94), going through peroxy radicals (like benzylperoxy rad.) and benzylaldehyde intermediaries.

Isoprene and Terpenes

These produce O₃, even though they are mainly biogenic emissions (from plants, trees, algae, bacteria, and animals). They react with OH to form peroxy radicals, which again convert NO to NO₂. The lifetime with respect to reaction with OH is shorter for isoprene and other terpenes (1 to 3 hours) compared to anthropogenic ROG emissions like n-Octane (3 days) and n-Butane (9 days).¹⁶¹ In cities with nearby forests such as Atlanta, terpenes can account for up to 40% of O₃ formation above background levels (measured in the troposphere away from forests). This led Ronald Reagan to say in 1981, "trees cause more pollution than automobiles do", but this is misleading as anthropogenic NO_x is required to make PC smog out of ROGs including natural terpenes. Isoprene emissions are maximal across the SE US: E TX, N LA, AR, MS, AL, GA, TN, NC, SC.

US emissions of terpenes are greater than the sum of US anthropogenic HC emissions: "Methane [80% of which is biogenic] and isoprene each comprise about a third of the annual global VOC emission from all natural and anthropogenic sources." "Tropical broadleaf trees contribute almost half of the estimated global annual isoprene emission due to their relatively high emission factors and because they are often exposed to conditions that are conducive for isoprene emission. The remaining flux is primarily from shrubs which have

¹⁶⁰ W. P. L. Carter, "Development of Ozone Reactivity Scales for Volatile Organic Compounds", EPA-600/3-91/050, August 1991, etc.

¹⁶¹ <http://anrcatalog.ucdavis.edu/pdf/8484.pdf> "Urban Trees and Ozone Formation..."

a widespread distribution. The annual global isoprene emission estimated with MEGAN ranges from about 500 to 750 Tg isoprene (440 to 660 Tg carbon).¹⁶²

Ozone from Alcohols Including Oxygenated Fuels

Internal combustion engines generate CO, NO_x, and unburned hydrocarbons (ROG) such as acetaldehyde (from ethanol) or formaldehyde (from methanol). Some of these ROGs are carcinogenic. This is a complex topic but relevant to the use of “oxygenated” gasoline incorporating ethanol, other alcohols, and ethers. APGW p. 97 cites studies that evaluate the effects on emissions from switching to high ethanol fuel (E85) compared to gasoline. The effects vary with temperature, see table:

Substance	22 °C	-7 °C
NO _x	-38%, better	-21%, better
CO	+1%, sl. worse	+94%, worse
Non-methane HC (ROG)	+14%, sl. worse	+133%, worse
Benzene [carcinogen]	-65%, better	-15%, sl. better
1,3 Butadiene [carcinogen]	-66%, better	-0.3%, unchanged
Acetaldehyde [carcinogen]	+4,500%, much worse	+8,200%, much worse
Formaldehyde [carcinogen]	+125%, worse	+204%, worse

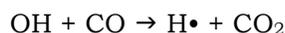
Negative percents represent improvement with E85 compared to gasoline. All 4 carcinogens moved in the unfavorable direction with colder temperatures compared to 22 °C.

APGW p. 98 includes a simulation that shows the extent in 2020 of changes that would occur if E85 were universally adopted: ozone deaths in LA increase by a mean of 9%. The author, Mark Jacobsen, summarizes, “E85 may increase ozone-related mortality, hospitalization, and asthma by about 9% in Los Angeles and 4% in the United States as a whole relative to 100% gasoline... E85 also increased peroxyacetyl nitrate (PAN) in the U.S. but was estimated to cause little change in cancer risk. Due to its ozone effects, future E85 may be a greater overall public health risk than gasoline. However, because of the uncertainty in future emission regulations, it can be concluded with confidence only that E85 is unlikely to improve air quality over future gasoline vehicles. Unburned ethanol emissions from E85 may result in a global-scale source of acetaldehyde [a carcinogen] larger than that of direct emissions.”¹⁶³

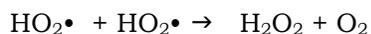
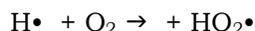
As the EPA rationale for oxygenated fuels was ostensibly to reduce CO (and ROG) during the cold months, these findings appear discouraging, is there any upside?¹⁶⁴

Photochemical Oxidation of CO

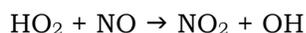
The highly reactive OH radical also cleanses the air of CO:



CO is oxidized to CO₂



stable hydrogen peroxide, which eventually precipitates
(or HO₂• may react with NO in the NO_x cycle to make O₃)



OH is regenerated as a catalyst;
NO is also a catalyst because regenerated

¹⁶² A. Guenther et al.: “MEGAN estimates of global isoprene”, *Atmos. Chem. Phys.*, 6, 3181–3210, 2006

¹⁶³ “Effects of Ethanol (E85) versus Gasoline Vehicles on Cancer and Mortality in the United States”, Mark Z Jacobson, Department of Civil and Environmental, Engineering, *Environ. Sci. Technol.* 2007, 41, 4150-4157

¹⁶⁴ • <http://www.epa.gov/otaq/fuels/gasolinefuels/winterprograms/index.htm>

• also, <http://www.epa.gov/otaq/fuels/basicinfo.htm>

Aerosol Particles in the Global and Polluted Atmosphere

This important topic is presented in *APGW* Chap. 5 and in *IAC* Chapter 8. We did not study this chapter and the following is somewhat limited.

Aerosols affect health, affect visibility by scattering light, and affect Earth's climate. This chapter does not review their effects on visibility and climate.

An aerosol is defined by Jacobson (*APGW* p. 2) as, "an ensemble of solid, liquid, or mixed-phase particles suspended in air." An aerosol particle is a single solid, liquid, or mixed-phase particle among such an ensemble. The surrounding gas is an integral part of the aerosol.

In contrast, a hydrometeor is an ensemble of liquid, solid, or mixed-phase water particles suspended in or falling through air. The distinction with aerosols is only that hydrometeors contain much more water, and they can also get larger: namely, hail up to 115 mm.

The concept of *suspended* is relative: particles are characterized by their rate of descent under gravity (sedimentation)¹⁶⁵ as represented in the ideal by Stokes Law, which yields a terminal velocity of a sphere falling in a fluid.¹⁶⁶ Obviously, gravel thrown into the air would not be regarded as an aerosol because it falls out very rapidly and does not seem suspended, but there is a continuum from very high to very low rates of descent. The following derives from *APGW* p. 106:

Particle Diameter (μm)	Time to Fall 1 km in near-surface conditions
0.02 μm (20 nm)	228 year
0.1 μm (100 nm)	36 year
1.0 μm (1,000 nm)	328 day
10 μm	3.6 day
100 μm	1.1 hr
1,000 μm	4 min
5,000 μm	1.8 min

Particle Sizes Defined

The size of aerosol particles range from 1 nm to 10 μm and are defined as:

nanoparticles (aka EPA ultrafine particles) < 100 nm (< 0.1 μm)
fine particles 100 nm to 2,500 nm (0.1 μm -2.5 μm)
coarse particles > 2,500 nm (2.5 μm)

Especially for medical, environmental, and regulatory purposes, particles are grouped by size ranges also as follows [note: an RBC = 7 μm in average size]:

PM₁ All particles < 1 μm (1,000 nm), also called submicron particles as 1 μm = 1 micron
PM_{2.5} All particles < 2.5 μm (2,500 nm)
PM₁₀ All particles < 10 μm (10,000 nm)

Particles exceeding 1 μm are supermicron particles.

¹⁶⁵ <http://en.wikipedia.org/wiki/Sedimentation>

¹⁶⁶ http://en.wikipedia.org/wiki/Stokes%27_law

Typical Number, Area, and Mass Concentrations (per *APGW* p. 102, at sea level) are as follows

	Diameter (μm)	Number density or concentration of molecules or particles (#/cm ³)	Mass Concentration (μg m ⁻³)
Gas molecules	0.0005 μm (0.5 nm)	2.45x10 ¹⁹	1.2 x 10 ⁹
Aerosol particles			
Small PM₁	< 0.1 μm (100 nm)	10 ³ -10 ⁶	<1
Medium	0.1-2.5 μm	1-10 ⁴	<250
Large	2.5-8,000	<1 - 10	<500
Hydrometeor particles			
Fog drops	5-20 μm	1-500	10 ⁴ - 10 ⁶
Cloud drops	10-200 μm	1-1,000	10 ⁴ - 10 ⁷
Drizzle	200-1,000	0.01-1	10 ⁵ - 10 ⁷
Raindrops	1,000-8,000 μm	0.001-0.01	10 ⁵ - 10 ⁷
Hail	5,000-115,000	0.0001-0.001	10 ⁵ - 10 ⁷

Clearly, aerosols and even hydrometeors normally occupy a small component of the number density and mass concentration compared to air molecules.

Empiric Modes of Aerosol Distribution

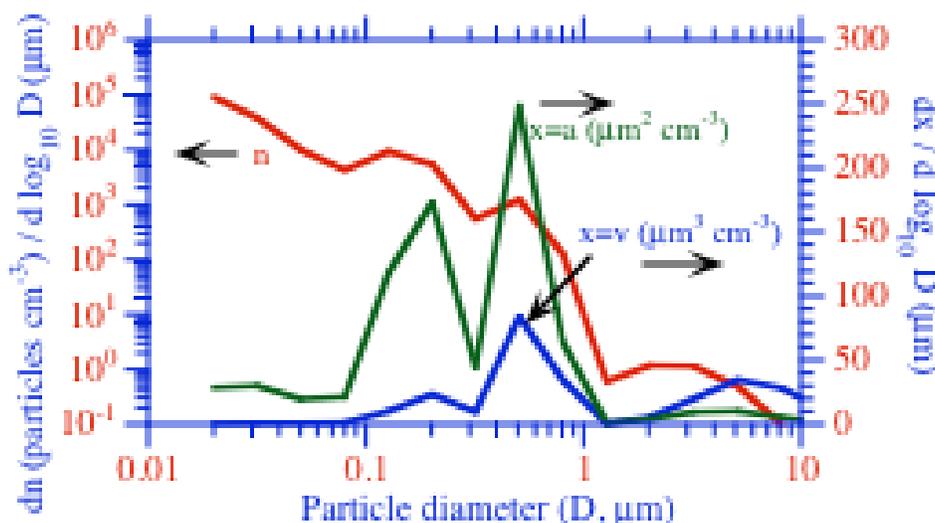
Size distributions can be broken into modes based on statistical measurements, of which a representative example is (*APGW* p. 102):

Mode	Diameter Range (nm)	Comments including vehicle emissions
Nucleation	< 100 nm (0.1 μm)	Fine particles, often emitted and thus primary particles, or newly nucleated particles (formed directly from gas phase). Newly nucleated particles often contain sulfate ion and water, sometimes ammonium cation CH ₄ ⁺ . Growth to accumulation size is by coagulation (coalescence) and condensation.
Submode 1	<10 nm (0.01 μm)	Often contain sulfate and water. For vehicle exhaust, this mode has lubricating oil and unburned fuel oil and sulfuric acid.
Submode 2	10-100 nm	For vehicle exhaust, this mode has black carbon spherules (soot) coated with lubricating oil, unburned fuel oil, and sulfuric acid.

Accumulation	100 – 2,500 nm (0.1 - 2 μm)	Fine particles, fall only slowly so that sedimentation is minimal, but they may be removed by rain (rainout and washout, discussed below). These are in a size range likely to affect health due to deep alveolar penetration. They are similar in size to the λ of visible light, so can affect visibility. Metals from industrial emissions re-condense on accumulation mode soot particles (and coarse fly ash), with Fe in greatest abundance. Sulfuric acid condenses most commonly to this mode with maximal areal density. Ammonium cation NH_4^+ often balances the sulfate ions. HNO_3 is inhibited from entering particles already containing H_2SO_4 .
Submode 1	~ 200 mean	Newer. These are often produced by burning biomass, biofuel, and fossil fuel.
Submode 2	~ 500-700 mean	Aged—i.e., what were once smaller grow by coagulation and gas-to-particle conversion.
Coarse	> 2,500 nm (2.5 μm)	These arise as sea spray, wind-blown soil and dust, volcano emissions, plant debris, fossil fuel combustion emissions, tire erosion, etc. Some have grown by coagulation from accumulation mode. Metals from industrial emissions re-condense on accumulation mode soot particles (and coarse fly ash), with Fe in greatest abundance. These particles sediment out in hours to days.

Particulate distribution plots are often log-normal or log-log (in which a mode may appear as a peak, called in the text “bell-shaped”).

The following log-log diagram is from *APGW* p. 103, and shows the multiple modes of particulates in a sample of polluted air in California:



Here as is typical, number density (red) is greatest for the smallest (nucleation mode) particles plus a smaller accumulation mode peak, surface areal density ($\mu\text{m}^2 \text{cm}^{-3}$) peaks in the 2 subaccumulation modes (0.1 – 2.5 μm), and the mass or volume density $\mu\text{m}^3 \text{cm}^{-3}$ peaks in the coarse mode.

Number concentrations of particles in clean marine air are about 100 cm^{-3} .

Sources and Compositions

Emission sources include Sea spray, Soil dust, Volcanos, Biomass and biofuel burning, Fossil-fuel combustion (internal combustion, etc.), Industrial activity, and Miscellaneous sources. Globally, > 50% of aerosols are anthropogenic. Some aerosols form from homogeneous nucleation.

Sea spray (bursting air bubbles and spume drops)

These inject coarse sea water particles into the air. Sea water mass percent includes water 96.78%, Cl 1.88%, Na 1.05%, Mg 0.125%, S 0.088%, Ca 0.04%, K 0.04%, and C 0.003%. Sea water molar concentration (mol/kg, rounded) includes water 53.6, Cl 0.55, Na 0.47, Mg 0.05, SO₄⁻ 0.03, Ca 0.01, and K 0.01.¹⁶⁷ The mass concentration ratio of Cl to Na is 1.8:1. Sea spray acidification occurs when Cl evaporates as HCl gas upon entry of H₂SO₄ or HNO₃ into drops. Dehydration of droplets cause them to have more concentrated solutes and shrink in size. Sea spray also contains organic matter.

Soil dust and fugitive dust emissions¹⁶⁸

Soil contains inorganic materials (rocks and minerals) and organic materials (plant litter and animal remains) as well as water. Important rocks and minerals include sedimentary rocks such as limestone and chalk (containing calcite CaCO₃ and dolomite, etc.), sulfates, chlorides, shell fragments, igneous rocks such as granite, metamorphic rocks such as marble, gypsum, quartz, potassium and plagioclase feldspars, hematite, clays (kaolinite, illite, smectite, vermiculite, chlorite), marble, and other compounds containing Si, Al, and Fe, etc. Particles are formed by physical and chemical weathering, etc., and enter the air as wind-blown dusts (mostly in coarse mode). Sedimentation rates are shown above, and clearly particles of 1 to 10 μm can potentially travel long distances if injected high and accompanied by strong winds.

Volcanos

These emit magma containing 1 to 4 percent gas by mass. Of gases, water vapor makes up 50-80 percent of gas mass. Some other gaseous constituents include: CO₂(g), SO₂(g), OCS(g) [carbonyl sulfide], N₂(g), CO(g), H₂(g), S₂(g), HCl(g), Cl₂(g), and F₂(g). Others include HF, He, and H₂S. The most hazardous are SO₂, CO₂, and HF.¹⁶⁹

Volcanoes also emit particles. The most abundant are silicate minerals, and they range in size from <0.1 to 100 μm. Particles also have BC [black carbon], OM [organic matter], Na, and many other elements. Particles of < 4 μm injected into the stratosphere by large eruptions can stay aloft for many months, whereas larger particles fall out faster, mostly by rain mechanisms rather than sedimentation. SO₂ and OCS injected volcanically into the stratosphere contribute to the Junge layer (stratospheric aerosol layer) of aerosol particles ~0.14 μm diameter and containing sulfuric acid and water. (This layer is also discussed under stratospheric ozone depletion.)

Biomass burning

This is defined as (open) burning of forests, woodlands, grassland, and agricultural land, either to clear land, stimulate grass growth, manage forest growth, or satisfy rituals, etc. (but not burning for fuel or heating). Jacobson includes natural fires as well as anthropogenic burning in this category. Gases emitted include CO(g), CO₂(g), CH₄(g) NO_x(g), ROG, and SO₂(g). Particle constituents include ash [inorganic solid or liquid residue of burning, sometimes including unburned primary organic compounds POM], plant fibers, soil dust, organic matter, and soot (black carbon BC spherules coated by POM). Soot formed at higher temperatures has a higher ratio of BC to OM (rendering the smoke blacker), whereas smoldering biomass produces less BC and lighter smoke. Soot POM [Primary Organic Matter] coatings include aliphatic HCs and polycyclic aromatic hydrocarbons PAHs [mutagens known to be carcinogenic]. Burned vegetation emits metals (Ti, Mn, Zn, Pb, Cd, Cu, Co, Sb, As, Ni, and Cr, as well as K⁺, Ca²⁺, Mg²⁺, Na⁺, NH₄⁺, Cl⁻, NO₃⁻, and SO₄²⁻), and sulfuric acid, which condense on soot or ash. Young smoke particles are found in the upper nucleation and lower accumulation modes. "Soot, particularly diesel exhaust pollution, accounts for over one quarter of the total

¹⁶⁷ <http://en.wikipedia.org/wiki/Seawater>

¹⁶⁸ Fugitive dust emission definitions: It "is PM suspended in the air by wind action and human activities. It has not come out of a vent or a stack, and is usually not a by-product of burning. Fugitive dust particles are composed mainly of soil minerals (e.g. oxides of silicon, aluminum, calcium, and iron), but can also contain sea salt, pollen, spores, tire particles, etc." [http://www.arb.ca.gov/pm/fugitivedust_large.pdf]

"Fugitive Dust is not discharged to the atmosphere in a confined flow stream. Common sources of fugitive dust include unpaved roads, agricultural tilling operations, aggregate storage piles, and heavy construction operations." [<http://www.epa.gov/ttnchie1/ap42/ch13/final/c13s02.pdf>]

¹⁶⁹ <http://volcanoes.usgs.gov/hazards/gas/>

hazardous pollution in the air. Long-term exposure to urban air pollution containing soot increases the risk of coronary heart disease.”¹⁷⁰

Biofuel burning

A biofuel is a burnable fuel that contains energy arising from geologically recent carbon fixation, such as from plants. Although the term is often used to refer to newer biodiesel and ethanol fuels, etc., it can also include burning for fuel purposes of wood, peat, dung, etc. (but not of fossil fuels). According to APGW p. 104, it produces particulate emissions similar to Biomass burning.

Fossil fuel combustion

This is usually by internal combustion and is almost always anthropogenic. Fuels consist of coal (which derives from the metamorphic sequence: peat < peat coal < lignite coal < bituminous soft coal < anthracite hard coal, etc.), oil (petroleum), natural gas (containing methane, ethane, and other HC gases), gasoline (a complex soup which includes C4 to C12 hydrocarbons), kerosene (which includes C6 to C16 HCs), and diesel fuels (which include C8 to C21 HCs). Gases emitted include NO_x, ROG, CO, CO₂, CH₄, and SO₂. Particles emitted include soot (BC + OM), OM alone, SO₄²⁺, metals, and fly ash (which contains O, Si, Al, Fe, Ca, and Mg).¹⁷¹ Diesel combustion emits more soot and ammonium, and 10x-100x as much aerosol particle mass compared to gasoline combustion—this excess is only somewhat improved by after-treatment. Diesel exhaust particles include,

for < 15 nm: unburned fuel, unburned lubricating oil, and sulfate;

for 15 to 200 nm, BC aggregates coated by PAHs, unburned fuel and oil, etc.

Diesel exhaust particles contain LMW HC (< C₂₄) which readily evaporate.

Industrial sources

These can emit (as with coal above) soot, sulfate, fly ash, and metals (often Fe₂O₃, Fe₃O₄, Al₂O₃, SiO₂, and inorganic carbonaceous compounds of various degrees of oxidation. Fly ash is usually in the coarse mode, thus > 2.5 μm. Metals are especially emitted in high temperature processes, such as waste incineration, smelting, steel mill furnaces, cement kilning,¹⁷² and power plant combustion. Lead Pb is an important particulate pollutant arising from lead ore crushing and smelting, other ore smelting, metals processing, leaded aviation fuels (and formerly leaded auto gasoline), lead acid battery manufacturing, lead ore crushing and smelting, and solid waste disposal. (APGW p. 111 and here¹⁷³)

Miscellaneous emission sources of atmospheric particles

These include tire rubber particles (usually > 2.5 μm), pollen, spores, bacteria, plant debris, and meteoric debris. The latter makes a small contribution of Fe, Ti, and Al etc. to the stratosphere. (It is estimated that 15,000 tonnes [15,000,000 kg] of meteoroids, micrometeoroids and different forms of space dust enter Earth's atmosphere each year.¹⁷⁴) The plant-derived particles can serve as nucleation sites for ice crystals and cloud drops. Plant isoprene and monoterpenes become oxidized and nucleate to evolve to aerosols (Dr. Cassandra Gaston).

¹⁷⁰ <http://en.wikipedia.org/wiki/Soot>

¹⁷¹ Fly ash: “Also known as flue-ash, is one of the residues generated in combustion, and comprises the fine particles that rise with the flue gases... In an industrial context, fly ash usually refers to ash produced during combustion of coal.” Depending on the industrial origin, it can include any of: O, Si, Al, Fe, Ca, Mg, SiO₂, CaO, gypsum, quartz, hematite, and clays, and also As, Be, Bo, Cd, Cr, hexavalent Cr, Co, Pb, Mn, Hg, Mo, Ni, Se, Sr, Tl, and V, dioxins, and PAHs. [http://en.wikipedia.org/wiki/Fly_ash and APGW p. 111]

¹⁷² Cement kilning: calcium carbonate and clay and/or shale are heated, and react with silica-bearing minerals to form a mixture of calcium silicates, particularly alite (Ca₃O·SiO₄), the principle ingredient in Portland cement. In the process, CO₂ is evolved. [http://en.wikipedia.org/wiki/Cement_kiln]

¹⁷³ <http://www.epa.gov/air/lead/basic.html>

¹⁷⁴ <http://en.wikipedia.org/wiki/Meteoroid>

Another estimate: 100-300 metric tons of cosmic dust enter the atmosphere each day = 36,500,000 to 109,500,000 kg /yr

[<http://www.universetoday.com/94392/getting-a-handle-on-how-much-cosmic-dust-hits-earth/>]

Homogeneous nucleation

Unlike emissions and meteoric debris, this is the only way new particles can form in the atmosphere in situ. Condensable gas molecules aggregate to form liquid or solid clusters. If they reach a critical size (15-20 molecules), they can become stable and grow. No nucleus is required that would present a nucleation surface. (In the process of heterogeneous nucleation, an existing particle serves as the nucleation surface for cluster formation, but this is not a new particle. Heterogeneous nucleation is common when there are particles available.) Once nucleation has occurred, condensation of a condensable gas or vapor deposition (gas to solid) may be able to progress. Nucleation may be homomolecular, binary, or ternary (if 3 different species nucleate). Homomolecular nucleation occurs with oxidation products of toluene, xylene, terpenes, and NH_4Cl , the latter forming a solid. Water nucleation requires a cloud condensation nucleus CCN. Homomolecular water nucleation typically does not arise homogeneously, almost always heterogeneously. Water and sulfuric acid undergo binary homogeneous nucleation commonly, beginning at a size of 1 to 3 nm. These can form in great numbers over the ocean, with DMS(g) as input. Water, sulfuric acid, and ammonia gas (when present) readily undergo ternary homogeneous nucleation.

Processes Affecting Particle Size and Evolution

In addition to emission and homogeneous nucleation, methods of particle growth include (in brief):

Coagulation

The general name for two particles colliding and sticking together or coalescing. These processes may be driven or influenced by Brownian motion (especially very small particles), gravitational collection (in which the larger particle is falling faster and runs into the slower falling smaller particle), turbulent inertial motion, turbulent shear, diffusio-phoresis, thermophoresis, electric charge, Van der Waals forces,¹⁷⁵ and fractal geometry effects (involving microbial and inorganic aggregates).¹⁷⁶ Coagulation affects the number density of particles, but presumably does not change the mass of material involved in coagulation, and does not involve gases

Other Growth Processes

The following involve gases, and include:

Condensation/Evaporation

In condensation, after nucleation, a gas of a certain species condenses as a liquid on a liquid surface, usually of the same species. (Vapor deposition to a solid surface is discussed below.) In evaporation, a liquid on the surface evaporates to a gas. The saturation vapor pressure SVP for the species along with the nearby partial pressure of the species vapor determines whether vapor will condense or liquid will evaporate:

If ambient (nearby) $P_g > \text{SVP}$, condensation occurs.

If ambient $P_g < \text{SVP}$, evaporation occurs.

The lower the SVP, the more likely condensation is to occur. For water and other gases, the SVP increases superlinearly with T, so that gases are more likely to evaporate and condensation is less likely to occur at higher temperatures, and gases are more likely to condense and evaporation is less likely to occur at lower temperatures.

When condensation occurs, latent heat of evaporation is released, warming the surface of the particle, increasing SVP, slowing the vapor transfer to the surface. Also, the depletion in local ambient vapor partial pressure reduces further drop growth temporarily.

¹⁷⁵ Van Der Waals Forces: These are relatively weak intermolecular attractions, which may arise from: (1) molecules that have permanent electric dipoles and align so as to attract, (2) molecules that are permanent dipoles temporarily distorts the electron charge in other nearby polar or nonpolar molecules, thereby inducing further polarization and attraction. (3) molecules that have no permanent dipoles, but can develop instantaneous fluctuating dipole moments which can induce an opposite attractive dipole in an adjacent molecule. Paraphrased from:

<http://hyperphysics.phy-astr.gsu.edu/hbase/chemical/waal.html>

<http://www.britannica.com/EBchecked/topic/622645/van-der-Waals-forces>

<http://www.chemguide.co.uk/atoms/bonding/vdw.html>

¹⁷⁶ http://www.engr.psu.edu/ce/enve/logan/web_presentations/Fractals.pdf

Inspecting the formula for condensation (APGW p. 115), the rate of droplet growth is increased by an increase in any of the following:

- radius r of the drop
- the diffusion coefficient D [per APGW, though it appears in both numerator and denominator]
- the gradient (difference) between the ambient pressure and the SVP
- the thermal conductivity

Condensation rate is slowed by an increase in:

- latent heat

The effect of T is difficult to determine by inspection of the formula, although we know that condensation is more likely at lower temperature.

Condensing gases occur primarily in accumulation mode, which presents the largest surface area for surface processes.

Sulfuric acid condensing onto accumulation mode affects visibility. Sulfuric acid has a low SVP so that once condensed it does not readily evaporate.

High MW organic gases condense primarily onto accumulation mode. Condensable gases include toluene, xylene, alkylbenzene, alkane, alkene, etc.

Water condenses on accumulation and coarse-mode particles (cloud condensing nuclei CCN) to form cloud and rain particles. Relative humidity is partial pressure of H_2O (p_w) divided by SVP (p_s), expressed as a %. If $p_w > p_s$, water vapor condenses on CCN, but if $p_w < p_s$, water vapor evaporates from the aerosol particle surface.

Water can remain liquid below its freezing point (the supercooled state) if there are no CCNs.

Vapor Deposition / Sublimation

Vapor deposition is deposition of a gas on an aerosol particle surface as a solid. (If deposition is to a liquid, this is called condensation, discussed above.) The opposite of vapor deposition, change from a solid to a gas, is sublimation.

Water vapor depositing to ice is common when $T <$ freezing point of water and $p_w > p_s$. Vapor deposition also occurs with NH_4Cl .

Dissolution, Dissociation, and Hydration

Dissolution is the process in which a gas, suspended over an aerosol particle, diffuses to and dissolves in a liquid on the surface. (This differs from mere condensation. Note that this usage is an accepted and precise chemical definition.) The aerosol particle's surface liquid is the solvent, and the gas that is dissolved is the solute, and the solvent plus one or more solutes is the solution. This process depends on the solubility of the gas in the liquid. Ionization or dissociation, anions, cations, electrolytes (that dissociate partly or completely), and acid/base chemistry can play a role in the dissolution process. Dissolution of an acid raises pH.

Hydration involves the bonding of liquid water to a solute in a solution. It can swell particles to produce a haze even when relative humidity is $< 100\%$. (Details omitted, but Kohler theory of droplet formation is discussed here¹⁷⁷)

Important processes involving dissolving gases (especially HCl , HNO_3 , NH_3 , and SO_2) include:

$HCl(g)$ dissolves in water particles and ionizes to H^+ and Cl^- . Cl^- may be depleted along coastal regions in aerosol droplets due to sea spray acidification, due to presence in the droplets of excess NO_3^- and SO_4^{2-} . The HCl is released from the droplets as a gas which can presumably cause acid effects in coastal areas.

A similar process called soil dust acidification results from the effect of HNO_3 on soils with $CaCO_3$, in which the carbonate evaporates as CO_2 ...

Sulfuric acid in the gas phase condenses and does not then evaporate. Water vapor hydrates it, yielding a solution of sulfuric acid and water, which dissociates producing bisulfate HSO_4^- (also a strong acid) and subsequently SO_4^{2-} .

Ammonia gas NH_3 arises from soil emissions, manure use and management, savannah and agricultural burning, forest fires, chemical production, and other sources. When dissolved in water it forms NH_4^+ , which

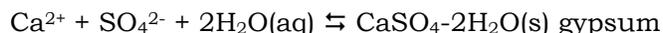
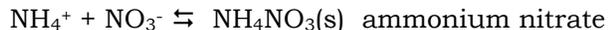
¹⁷⁷ <http://www.mcgoodwin.net/pages/atmscuw301.pdf>

joins with particles with an abundance of acidic anions such as sulfate, nitrate, or chloride, but not particles with abundant cations. NH_4^+ is commonly present with sulfate in accumulation mode.

Solid Precipitation

When the relative humidity decreases or the ion concentration has risen, ions in solutions may combine (crystallize) to form solids (solid precipitation). Solids may also form by chemical reaction on the surface of particles.

Common solid formation reactions



Removal Processes

Aerosol particles are removed by rainout, washout, sedimentation, and dry deposition:

The 2 most important methods are (especially for small particles over long periods of time)

(1) Rainout, which “occurs when an aerosol particle CCN activates to form a liquid cloud drop or ice crystal, and the drop or crystal coagulates with other cloud drops or crystals to become rain or graupel, which falls to the surface.” This occurs only in the troposphere, and can remove volcanic particles from it. (APGW p. 120)

(2) Washout, which “occurs when growing or falling precipitation particles coagulate with aerosol particles that are either interstitially between cloud drops or in the clear sky below clouds that the rain passes through. When the precipitation falls to the surface, it brings the aerosol particles with it.” (APGW p. 120)

The following are important for large particles over short periods and small particles over long periods of time:

Sedimentation is the sinking of particles to lower altitudes under the force of gravity and against the drag forces imposed by air. As mentioned before, the rate of descent is approximately governed by Stokes Law and is size dependent. Recall that $0.1 \mu\text{m}$ particles take 36 years to fall 1 km. Despite the differing densities, the sedimentation rate of gases is negligible. Jacob states, “turbulent mixing ... maintains a homogeneous lower atmosphere. Only above 100 km does significant gravitational separation of gases begin to take place, with lighter gases being enriched at higher altitudes.”¹⁷⁸

Dry deposition is a process by which gases and aerosol particles are carried by molecular diffusion, turbulent diffusion, or winds to the surface (of various types) and then rest on and bond to the surface. It can remove small particles near the ground more effectively than it can remove gases.

Particle Morphology and Shape

Aerosol particles as they grow acquire more layers and attachments. Some become fibrous or grow crystals. Soot particles are irregular, and become built up with numerous randomly oriented graphitic spherules. Soot is hydrophobic but some of its organics can condense water. Fossil fuel soot BC is mostly $< 100 \text{ nm}$ initially (nucleation mode), but accumulation mode often eventually exceeds emissions mode. Soot grows probably by coagulation and growth. Biomass burning smoke particles initially are 100 to 130 nm , but the mass increases by up to 40% during early aging. Soot is often coated with nitrate or sulfate (the latter common in North America), often ammonium sulfate. Soot becomes more spherical and internally mixed with other components.

Health Effects of Aerosol Particles

This is a capsule review. There are a number of hazardous substances, especially compounds such as benzene, polychlorinated biphenyls PCBs, PAHs, metals, and S. PM_{10} have been correlated with asthma, COPD, and increased mortality, etc., for which there may be no lower threshold for toxic effects. $\text{PM}_{2.5}$ is considered more hazardous, causing more resp. illness and premature death—long term exposure may reduce life by 2 years. A $\text{PM}_{2.5} > 25 \mu\text{g}/\text{m}^3$ is considered unhealthy (per Dr. Cassandra Gaston). Most damage may be from ultrafine particles, $< 100 \text{ nm}$. High aerosol particles and SO_x exhibit a link with cardiopulmonary

¹⁷⁸ <http://acmg.seas.harvard.edu/people/faculty/djj/book/bookchap2.html>

disease, asthma, hospitalization, decreased lung function, and mortality. PM_{2.5} result in more illness and premature death than do large particles. The specific chemical causes have not yet been isolated. Black carbon looks very bad, however. Lungs of nonsmokers in polluted areas can resemble those of smokers. A 2004 study in the journal *Circulation* gives the following results:¹⁷⁹

TABLE 4. Adjusted RRs and 95% CIs for a 10 µg/m³ Increase in PM_{2.5} (Average) and for Former and Current Smoker (vs Never Smoker) for Various Cause-of-Death Categories

Cause of Death	PM _{2.5}	Former Smoker	Current Smoker
All cardiovascular diseases plus diabetes	1.12 (1.08–1.15)	1.26 (1.23–1.28)	1.94 (1.90–1.99)
Ischemic heart disease	1.18 (1.14–1.23)	1.33 (1.29–1.37)	2.03 (1.96–2.10)
Dysrhythmias, heart failure, cardiac arrest	1.13 (1.05–1.21)	1.18 (1.12–1.24)	1.72 (1.62–1.83)
Hypertensive disease	1.07 (0.90–1.26)	1.21 (1.07–1.37)	2.13 (1.86–2.44)
Other atherosclerosis and aortic aneurysms	1.04 (0.89–1.21)	1.63 (1.45–1.84)	4.21 (3.71–4.78)
Cerebrovascular disease	1.02 (0.95–1.10)	1.12 (1.06–1.18)	1.78 (1.67–1.89)
Diabetes	0.99 (0.86–1.14)	1.05 (0.94–1.16)	1.35 (1.20–1.53)
All other cardiovascular diseases	0.84 (0.71–0.99)	1.22 (1.09–1.38)	1.78 (1.56–2.04)
Diseases of the respiratory system	0.92 (0.86–0.98)	2.16 (2.04–2.28)	3.88 (3.66–4.11)
COPD and allied conditions	0.84 (0.77–0.93)	4.93 (4.48–5.42)	9.85 (8.95–10.84)
Pneumonia and influenza	1.07 (0.95–1.20)	1.23 (1.13–1.34)	1.89 (1.70–2.09)
All other respiratory diseases	0.86 (0.73–1.02)	1.54 (1.36–1.74)	1.83 (1.57–2.12)

Here, the increase in relative mortality risk (RR) for various cardiac and pulmonary conditions for persons who smoked, and for persons exposed to long-term PM_{2.5} at 10 µg m⁻³ are compared to persons who never smoked (and whose risk is taken to be 1.0). The article states, “Statistically robust associations between PM_{2.5} and overall cardiovascular disease mortality were observed. Predominant PM mortality associations were with ischemic heart disease, but statistically significant associations were also observed with the combined category of dysrhythmias, heart failure, and cardiac arrest.” These disorders were made worse by smoking.

An earlier (2002) study also authored by Pope et al (*APGW* p. 124), showed “Fine particulate and sulfur oxide-related pollution were associated with all-cause, lung cancer, and cardiopulmonary mortality. Each 10 µg m⁻³ elevation in fine particulate air pollution [i.e., long-term exposure to PM_{2.5}] was associated with approximately a 4%, 6%, and 8% increase in all-cause, cardiopulmonary, and lung cancer mortality, respectively.”¹⁸⁰

The American Lung Association webpage on Particle Pollution provides a good summary¹⁸¹ of the EPA’s 2009 *Integrated Science Assessment on Particulate Matter* (a 2,200+ page report!), stating:

EPA Concludes Fine Particle Pollution Poses Serious Health Threats:

- Causes early death ([from] both short-term and long-term exposure)
- Causes cardiovascular harm (e.g. heart attacks, strokes, heart disease, congestive heart failure)
- Likely to cause respiratory harm (e.g. worsened asthma, worsened COPD, inflammation)
- May cause cancer [note that causality is not yet proven]
- May cause reproductive and developmental harm

¹⁷⁹ C. Arden Pope III, et al, “Cardiovascular Mortality and Long-Term Exposure to Particulate Air Pollution: Epidemiological Evidence of General Pathophysiological Pathways of Disease”, *Circulation*. 2004; 109: 71-77, doi: 10.1161/01.CIR.0000108927.80044.7F

¹⁸⁰ C. Arden Pope III, et al, “Lung Cancer, Cardiopulmonary Mortality, and Long-term Exposure to Fine Particulate Air Pollution”, *JAMA* 287:1132, 6 Mar 2002.

¹⁸¹ <http://www.stateoftheair.org/2013/health-risks/health-risks-particle.html>, quoting U.S. Environmental Protection Agency, *Integrated Science Assessment for Particulate Matter*, December 2009. EPA 600/R-08/139F <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=216546>

Effects of Meteorology on Air Pollution

This topic is presented in *APGW* Chap. 6, , a chapter we did not read in our class. I have also summarized general atmospheric circulation and winds in a separate document.¹⁸²

Forces Influencing Horizontal Winds

Horizontal winds respond to four forces:

Pressure Gradient Force PGF

This force is proportional to the pressure difference divided by the distance between two locations (i.e., $\Delta p/\Delta x$). The force is directed from high to low pressure. PGF per unit mass is given by $(1/\rho)(\Delta p/\Delta x)$, where ρ is density.

Friction Force FF

This is in the opposite direction from the wind when near the surface, with magnitude proportional to the wind speed.

Apparent Coriolis Force ACoF (Coriolis Effect)

This is a virtual force appearing as a force to an observer on a rotating body. For Earth's atmosphere, it is zero at the equator, maximal at the poles, proportional to the wind speed, zero for air at rest, and acts at a 90° angle to the direction of air flow (to the right in the NH, to the left in the SH). The Coriolis force is given by

$$ACoF = 2\Omega V \sin \varphi$$

where Ω = angular rotation rate of Earth = 7.29×10^{-5} radians/s

V is the current speed m/s

φ is latitude in degrees

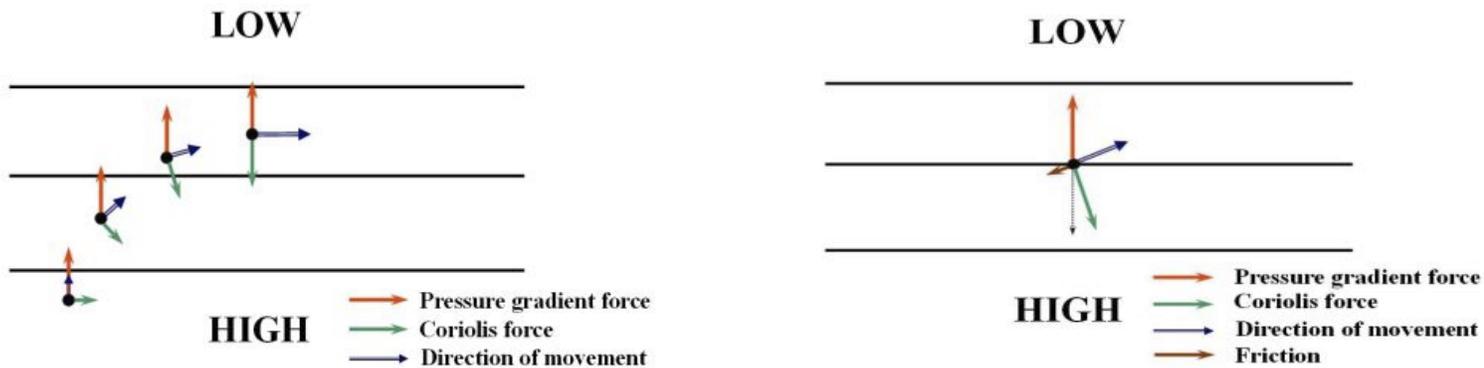
Apparent Centrifugal Force ACfF

This is a virtual force appearing as an outward force to an observer who is rotating with the air rotating about an axis. The force is directed outward from the axis of rotation.

¹⁸² <http://www.mcgoodwin.net/pages/atmscuw301.pdf>

Horizontal Winds

Winds include the following:



Geostrophic Wind and Boundary Layer Winds

This term applies to the theoretical model of straight isobars and no surface friction. Only 2 forces are involved. The diagram¹⁸³ on the left (above) shows how air parcels accelerate to form geostrophic winds aloft: “An air mass moving from high pressure to low pressure under the pressure gradient force in the northern hemisphere [with no friction from proximity to the surface]. As the air mass starts to move, it is deflected to the right by the Coriolis force. The deflection increases until the Coriolis force is balanced by the pressure gradient force. At this point, the wind will be blowing parallel to the isobars. When this happens, the wind is referred to as the ‘geostrophic wind’ [and there is ‘geostrophic balance’].”

The geostrophic wind speed V may be estimated using above formulas for PGF and Coriolis force, namely that

$$V = \frac{1}{\rho 2\Omega \sin\phi} \frac{\Delta p}{\Delta x}$$

E.g., for latitude 30° , isobars aloft of 570 mb and 566 mb separated by 150 km, V is calculated to be 50 m/s.¹⁸⁴

When friction exists for wind near the surface, a 3rd force (FF) is applied (right diagram above), and the equilibrium wind direction shifts toward the lower pressure isobar. This is because the friction slows the flow, lessening the Coriolis force without changing the strength of the PGF from high to low pressure.¹⁸⁵ Such winds are not geostrophic by definition, and may be termed **boundary layer winds**.

Gradient Winds

These are analogous to geostrophic winds except that the isobars are curving. Surface friction may be absent or present in gradient winds, resulting in 3 or 4 forces to consider.

A pressure gradient is also present and causative for geostrophic winds, despite the definition assigned to ‘gradient winds’.

NH

(See diagrams to follow.)

For air aloft near a low/high pressure center, the forces of PGF, ACoF, and the added centrifugal force ACfF cause cyclonic/anticyclonic (counterclockwise/clockwise) ‘Gradient Winds’ to curve or rotate about the center.

For air near the surface and a low/high pressure center, the friction force FF is added to the other 3, and cyclonic/anticyclonic (counterclockwise/clockwise) ‘Gradient Winds’ curve or rotate about the center with a component of convergence/divergence toward/away from the center.

¹⁸³ http://www.hko.gov.hk/education/edu01met/wxphe/ele_geostrophicwind_e.htm

¹⁸⁴ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/APGWCh6Figs.pptx>

¹⁸⁵ http://en.wikipedia.org/wiki/Geostrophic_wind

SH

For air aloft near a low/high pressure center, the forces of PGF, ACoF, and the added centrifugal force ACfF cause cyclonic/anticyclonic (clockwise/counterclockwise) 'Gradient Winds' to curve or rotate about the center.

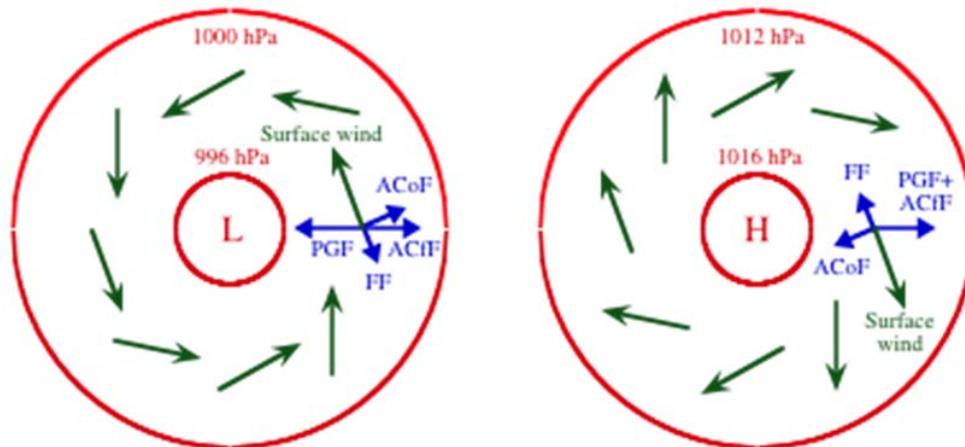
For air near the surface and a low/high pressure center, the friction force FF is added to the other 3, and cyclonic/anticyclonic (clockwise/counterclockwise) 'Gradient Winds' curve or rotate about the center with a component of convergence/divergence toward/away from the center.

Wind Speeds

Gradient winds about low/high pressure centers are slower/faster than geostrophic winds with the same pressure differential.¹⁸⁶ However, Jacobson also states, "Pressure gradients are weaker and winds are slower around a center of high [pressure] than around a center of low."¹⁸⁷

Diagram of Surface Winds With Convergence and Divergence

The following diagram is for the NH and is taken from APGW p. 130:



The resultant arrows of wind direction explain why cyclonic flow about a surface low pressure center is convergent at the center. Air at the surface converging toward a surface low pressure center must rise and cool, often causing clouds and stormy weather.

Diverging air at a surface high pressure center pulls air aloft downward, which becomes compressed and warms, thus is often associated with warm weather and fair skies.

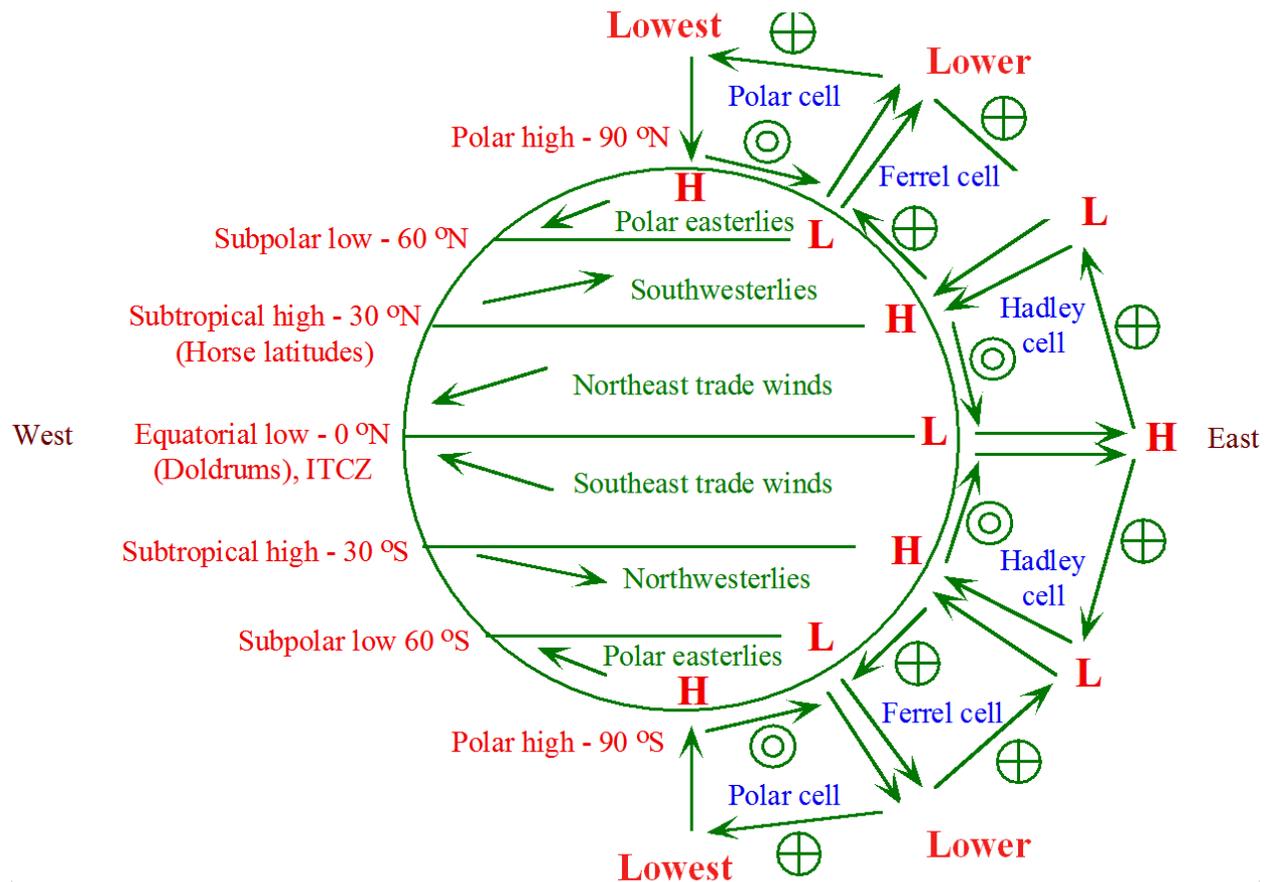
¹⁸⁶ <http://ww2010.atmos.uiuc.edu/%28Gh%29/guides/mtr/fw/grad.rxml>

¹⁸⁷ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/APGWCh6Figs.pptx>

Patterns of Global Air Circulation

Global patterns of horizontal and vertical air movements are relevant in the distribution of pollutants.

The following 3-cell model diagram originated by Ferrel after Hadley, taken from Jacobson,¹⁸⁸ shows global winds patterns averaged zonally and over long time periods:



Comparisons of NH and SH behavior are shown with a slash (e.g., SW/NW). The 3 cells in each hemisphere are the Hadley cell, the Ferrel cell, and the Polar cell.

Hadley Cell (ITCZ near equator to 30° N/S)

The intensely heated moist air at the surface that converges in the equatorial zone (or more precisely, at the **Intertropical Convergence Zone ITCZ**, which varies in latitude) rises and diverges aloft. This causes a surface low pressure **L** (i.e., the **equatorial low-pressure belt L**), much clouds and rain, and an apparently unnamed high pressure **H** aloft. (That is, the height of a given pressure surface such as 500 mb, or the pressure measured at a given altitude such as 5 km, is relatively high compared to that at other latitudes.)

The diverging air at the H aloft in the adjoining Hadley cells moves North/South and in a westerly direction (toward the NE/SE, shown as the back end of a feathered arrow entering the page).

At about 30° N/S (the **Horse Latitudes**), the Hadley air aloft converges with Ferrel cell air at a low pressure region **L** aloft (relatively low pressure or pressure heights). This L aloft is called the **subtropical front**, where there are sharp temperature contrasts, and strong westerly (eastward) winds at the tropopause, called the **subtropical jet stream**. This jet stream, located at about 30° N/S, does not meander much and is weaker than the polar front jet stream (see below).¹⁸⁹

¹⁸⁸ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/APGWCh6Figs.pptx>

¹⁸⁹ The tropics are between the Equator and ~23° (the tropics of Cancer and Capricorn). The subtropical zone is between ~23° and ~38°. <http://en.wikipedia.org/wiki/Subtropics>

Air at the **subtropical front L** converges, descends and warms, and arrives at a surface high pressure zone (i.e., **the subtropical high-pressure belts H**). At the surface subtropical high H, it diverges N/S and S/N in part flowing back toward the equator, while also flowing to the adjacent Ferrel cell. On the surface, the Hadley air returning toward the Equator turns by ACoF to a northeasterly/southeasterly direction (toward the SW/NW), shown as the front tip of an arrow rising out of the page. These consistent surface winds are called the **NE/SE trade winds** (named from their apparent source, not the destination), and converge at the ITCZ, completing the Hadley cycle.

Ferrel Cell (~30° N/S to ~60° N/S)

Air diverging poleward from the subtropical high pressure belt H, as surface Ferrel cell air, turns toward the east. This is therefore westerly flow (moving toward the NE/SE), and these winds are called **Southwesterlies / Northwesterlies**. In the higher latitude regions of the Ferrel cells, apparently due to greater surface friction and lower ACoF turning, the Ferrel westerlies appear to be oriented more toward the poles, compared to the more SW/NW equatorward flow of the easterly Hadley cell trade winds.¹⁹⁰

At ~60° N/S, the poleward moving surface air encounters the surface **Subpolar low-pressure belts L** where surface polar air from the Polar cell is converging with Ferrel air at the **Polar Front**. Here, temperatures vary sharply, converging air rises to an unnamed L aloft, cooling and causing storms. Pressure gradients and winds at the polar front tend to be stronger than at the subtropical front. At the tropopause, the strong **polar front jet streams** form, where wind speeds can be greater than 160 km/hr. These are predominantly westerly (west to east) winds aloft, but are subject to much meandering (causing Arctic Cold Fronts etc.).

The air aloft in the Ferrel cell tends not to flow equatorward, as one might guess, but rather poleward at mid-latitudes and therefore, by the effect of the ACoF, become generally westerly (moving toward the East, thus depicted aloft as entering the page). This is apparently related to the declining heights of constant pressure surface (or declining pressure for a given height) as one moves poleward toward colder more compressed air. Pressures for a given height aloft are lower as one moves toward the pole, thus the pressure gradient favors poleward and therefore westerly movement aloft.

Westerly Ferrel cell winds aloft also are favored by the distribution of surface H pressure centers (at ~30°) and L pressure centers (at ~60°). For example, in the NH, wind curve CCW about a L (e.g., the Aleutian Low), and then CW about an adjacent H at lower latitude (e.g., the Pacific High), yielding an overall westerly (eastward) flow. (APGW p. 134)

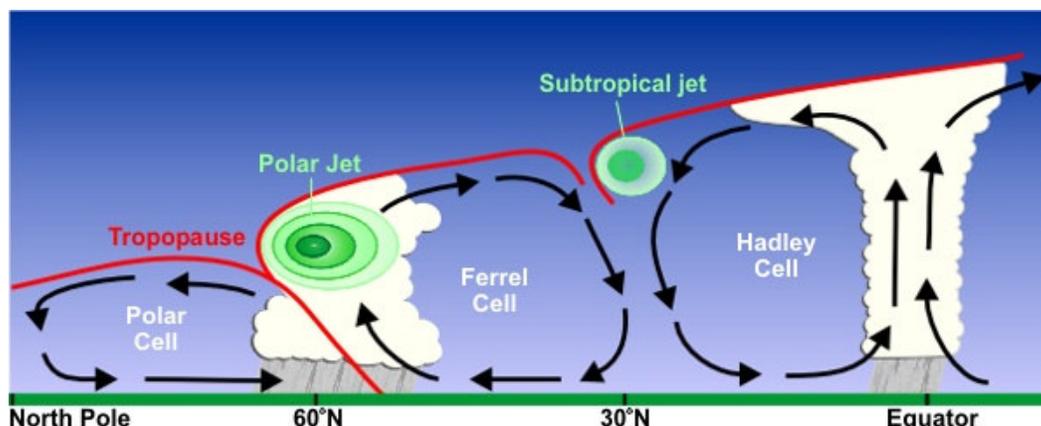
Polar Cell (~60° N/S to the N/S Pole)

Air moving poleward aloft in the polar cell turns eastward by the ACoF, so that polar cell air aloft is westerly (eastward). At the poles, the pressure aloft is at the lowest (i.e., a given pressure surface is found at the lowest height, or pressure for a given height is lowest). The increasingly frigid air descends at the pole, increasing surface pressure at the **Polar High H**. This air diverges to return to the Subpolar Low at 60° N/S, and this flowing surface air is turned by ACoF toward the west (**polar easterlies**) in both hemispheres.

¹⁹⁰ APGW p. 133 and http://en.wikipedia.org/wiki/Prevailing_winds [These sources are somewhat unclear.]

Jet Streams

The 3 cells and their jet streams are diagrammed in cross section here:¹⁹¹



Semi-permanent Pressure Systems

Low: The **subpolar low-pressure belt L** dominates in the SH. In the NH, the semi-permanent L centers around ~45-65°N include the **Aleutian Low** and the **Icelandic Low** (both of which move N in summer and S in winter). (APGW p. 134) These tend to have strong pressure gradients, fast converging cyclonic winds, upward vertical air movements, cloudy and sometimes stormy conditions, low penetration of solar radiation (reducing photochemical reactions), some of which tend to reduce near-surface air pollution.¹⁹²

High: The subtropical high-pressure belts H include **semi-permanent H centers** often over the ocean and centered around ~25-45°N. These include in the NH the **Pacific High** and the **Bermuda-Azores High** (both of which move N in summer and S in winter). In the SH, they include centers in the S Pacific, S Atlantic, and Indian Oceans. These tend to have weak pressure gradients, slow diverging anti-cyclonic winds, downward vertical air movements, clear sunny fair conditions (promoting photochemical reactions), some of which tend to increase air pollution.

Thermal Pressure Systems

These form seasonally over land and result from surface heating and cooling.

Low: Differences in albedo, heat absorption, specific heats (water has higher specific heat than soil), and infrared radiation lead to warmer land than ocean in the daytime or summer, and cooler land than ocean at night or winter. The specific heat of sand is especially low. Relatively warm air rises (possibly producing clouds and rain) and diverges aloft, lowering surface pressure, thus causing a surface **thermal low pressure system L**. These form typically at 25-45°N including over deserts such as the Mojave Desert, N India, and Iranian plateau, especially in the summer. Descending air in the semi-permanent highs at the same latitudes warms and helps to clear the skies of clouds, adding to surface heating. Converging and rising moist replacement air at a surface L in summer may create monsoon conditions such as over India. Thermal low pressure systems tend to have variable pressure gradients, variable speed converging cyclonic winds, upward vertical air movements, variable clouds and sometimes stormy conditions, some of which tend to reduce near-surface air pollution.

High: During the winter, land cooling causes increasing air density, convergence aloft and descent of negatively buoyant air (or stagnation) with formation of a surface **thermal high pressure system H**. These form at ~45-65°N and include the **Siberian High** and **Canadian High**. These tend to have variable pressure gradients, variable speed diverging anti-cyclonic winds, downward vertical air movements, cloudless fair conditions (promoting photochemical reactions), some of which tend to increase air pollution.¹⁹³

¹⁹¹ http://en.wikipedia.org/wiki/Jet_stream

¹⁹² <http://web.stanford.edu/group/efmh/jacobson/POLbook2/APGWCh6Figs.pptx> and APGW p. 136

¹⁹³ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/APGWCh6Figs.pptx> and APGW p. 136

Effects of Large-Scale Pressure Systems on Air Pollution

This is presented beginning at APGW p. 135 and only briefly summarized here, see this¹⁹⁴ for details.

Vertical Pollutant Transport

Mechanisms of vertical transport and mixing are discussed, involving adiabatic dry/unsaturated lapse rate Γ_d , wet/saturated lapse rates Γ_w , and environmental lapse rate $\Gamma_e = -\Delta T/\Delta z$. These allow assessment of the stability of air with respect to rising or sinking.

When $\Gamma_e < \Gamma_w$, the air is absolutely stable and a near-surface air parcel containing pollutants does not rise and is trapped.

When $\Gamma_e = \Gamma_w$, the air is “wet neutral”, there is no rising or falling, and pollutants dilute out more slowly than with unstable air.

In the regime where $\Gamma_d > \Gamma_e > \Gamma_w$, the air is “conditionally unstable”, see cited sources for details.

When $\Gamma_e = \Gamma_d$, the air is “dry neutral”, there is no rising or falling, and pollutants dilute out more slowly than with unstable air.

When $\Gamma_e > \Gamma_d$, the air is absolutely unstable, and a near-surface air parcel containing pollutants continues to rise and be diluted.

Temperature Inversion

The presence of a temperature inversion (a layer with negative $\Gamma_e = -\Delta T/\Delta z$, from whatever cause) makes air stable with respect to vertical rising, trapping pollutants. (However, stable profiles which can also trap pollutants are not always associated with temperature inversion.)

The parts of an inversion are named as follows: Going up from the surface, an inversion begins at its **base** (located at the **inversion base height** in km, also called the **mixing depth**, which is related to where pollutants mix, either below the base or in actuality within the inversion layer as well). The height of the inversion layer from base to **top** is the **inversion thickness** in km. The **inversion strength** is the temperature difference °C from base to top.

There are several types of inversions, described as follows:

Radiation Inversion (Nocturnal, Infrared)

As previously discussed, these form at night over land when land cools by unbalanced IR emission to space in the absence of much incoming solar radiation. (Oceans do not cool at night sufficiently for these to form, apparently due primarily to their high heat capacity and thermal inertia.) The adjacent near-surface air is cooled by the cool land, the coolest temperature being immediately next to the surface. The strength of the inversion is maximized by a long cloudless night when air is relatively dry and calm, so that mixing is minimized. Radiation inversions can sometimes form in the daytime if incoming sunlight is blocked by mountains, or is coming in at a low angle in deep winter, etc.

A rising air parcel moving along its dry adiabat will stop rising if it encounters the same temperature in the inversion air around it (though it oscillates about its final altitude initially). If a rising warmed parcel starts out hot enough, it may be able to penetrate the inversion layer (called “popping” or escaping the inversion), because its dry adiabat does not intersect the inversion portion of the environmental profile—i.e., it is always warmer than air in the inversion layer.

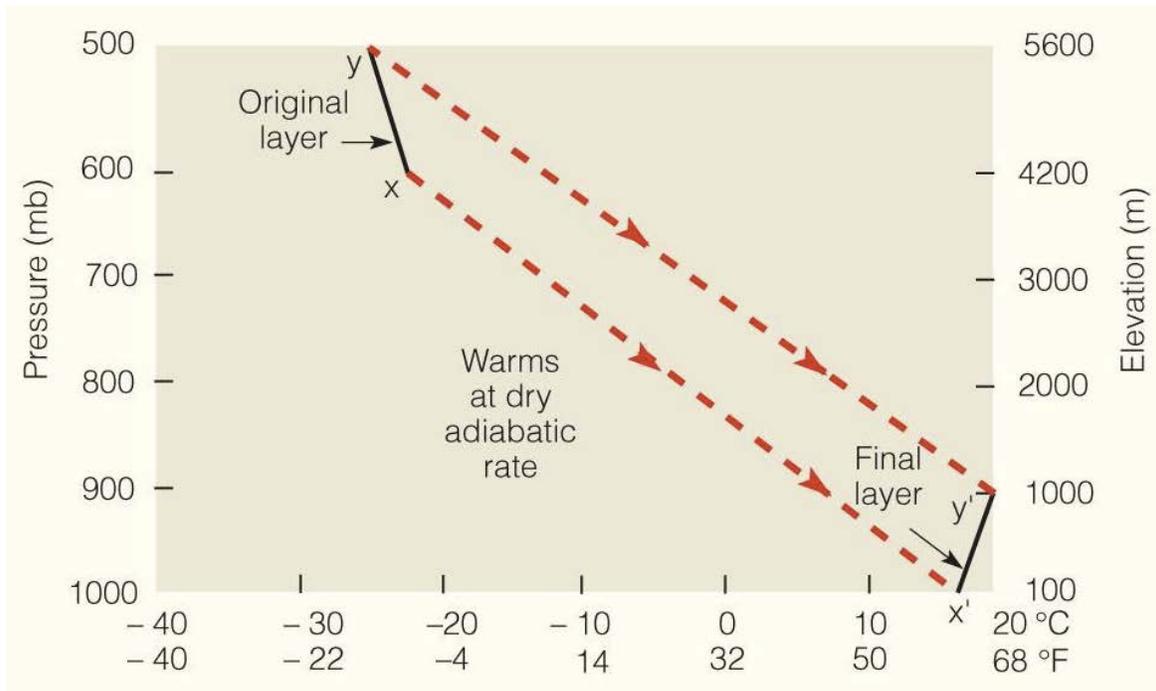
Marine Inversion

These form over coastal areas. Warming air over land rises, pulling in cooler air overlying the adjacent ocean—the wind resulting is an **onshore sea breeze**. The cooler denser marine air wedges under the warm air, which is further displaced upward. This creates cool air below warmer air, thus a **marine inversion**, a process which also contributes to the air pollution in Los Angeles.

¹⁹⁴ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/APGWCh6Figs.pptx> and APGW p. 138

Large-scale Subsidence Inversions

These occur in conjunction with surface high pressure systems with divergence, leading to air descent and compression with adiabatic warming, producing stabilization of the surface layer, sometimes leading to formation of an inversion ($\Gamma_e = -\Delta T/\Delta z$ is negative). As a result the air stagnates and near-surface pollutants build up.

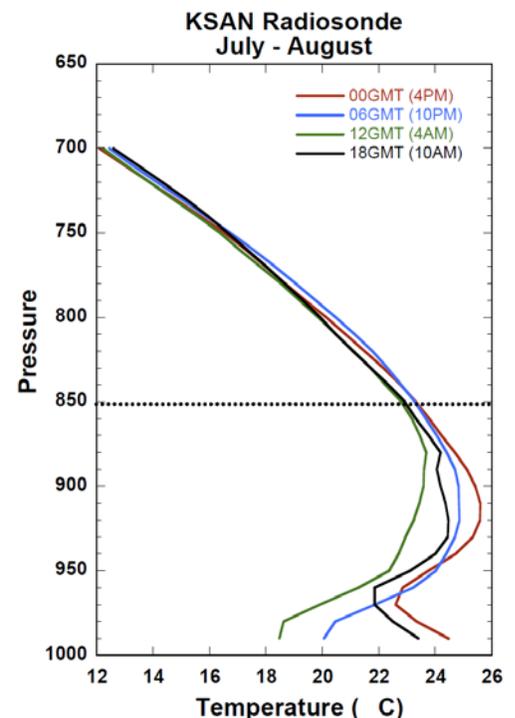


In the example shown above,¹⁹⁵ the original layer before its descent has a positive Γ_e , thus no inversion. However, when it descends (in response to a surface high pressure systems with divergence) and warms adiabatically, the layer is compressed to a smaller height thickness. The temperature profile is altered to a more stable profile— y has descended along its dry adiabat to y' further vertically than x has descended to x' along its dry adiabat—and in this case an actual inversion with negative Γ_e has resulted.

A subsidence inversion may be aloft and not reach the surface (whereas a radiation inversion usually does).

The (North) Pacific High is a common site of large scale subsidence inversions. Inversions are often maximal (having lowest base height and greatest inversion thickness) in the summer, and in the morning and early afternoon. Such inversions occur commonly over Los Angeles and contribute to its severe air pollution.

It is possible to have a combined radiation and large-scale subsidence inversion. In the example shown at the right,¹⁹⁶ the inversion over San Diego has greatest strength at 4 AM (12 GMT, green) and lowest strength at 4 PM (00 GMT, red). Although the source does not so state, this is quite likely a combined inversion.



Mean temperature profile at San Diego as a function of time of day.

¹⁹⁵ http://apollo.lsc.vsc.edu/classes/met130/notes/chapter6/subs_inv_formation.html

see also *APGW* p. 140.

¹⁹⁶ http://meteora.ucsd.edu/~jnorris/sio209.f09/inversions_sio209.pdf See also *APGW* fig. 6.12 p. 140

Small-scale Subsidence Inversion

When cool air descends a mountain slope, it is compressed and warms adiabatically. This warmer air, lying above somewhat trapped cooler marine air below, constitutes a **small-scale subsidence inversion**. This process occurs in the LA basin when warm air flows east to west from the San Bernardino Mountains.

Frontal Inversion

Cold fronts arise around low pressure centers, especially the cyclones found at 60°N. A cold front is the leading edge of a cold air mass that intrudes below and uplifts a less dense warmer air mass. The warm air over colder air constitutes a **frontal inversion**. These are not usually important for pollution buildup due to the strong winds and uplift present.

Horizontal Pollutant Transport

Various winds contribute to move pollution horizontally.

Wind Speeds

These are strongest usually about surface low pressure systems, due to stronger pressure gradients. These clear out pollutants but also suspend dust and particulates to a greater degree, especially if bare soil is exposed.

Wind Direction

Circulation about low and high pressure centers has been discussed. Winds in the NH from a L to the west tend to be southerly or southwesterly (due to CCW rotation), whereas winds from a H to the west tend to be northerly or northwesterly (due to CW rotation). Jacobson states that when the summer Pacific High is NW of the San Francisco Bay area, the CW rotation passes through the Sacramento Valley, bringing hot polluted air into the San Francisco Bay Area. (APGW p. 143)

Santa Ana winds

In fall and winter, the **Canadian high pressure** (aka North American High, a thermal H system) forms over the **Great Basin** (a cool elevated plateau covering much of Nevada, Oregon and Utah). CW circulation brings cold air down from the Rocky Mountains, compressing and warming it adiabatically. This passes over the Mojave Desert into S. California as an easterly warm dry dusty air. Descending from the San Bernardino Mtns., they bring dusty katabatic (downflowing) winds to the LA basin that if strong enough displace the cooler marine air, clearing air pollution (while the dry warm air also fuels seasonal wildfires). If weaker, however, their easterly flow is opposed by the westerly marine air, sometimes leading to stagnation and severe air pollution. These winds are strongest October to December.

Long-Range Transport of Air Pollutants

Chimneys and stacks exacerbate down-wind pollution. Pollutants can be carried long distances, including trans-boundary, for instance from Asia to N America, from N America to Europe, or smoke from Indonesia to other Asian countries, acid deposition from China to Japan,

This is especially true for SO₂, which can travel thousands of kilometers. The 380 m Inco Superstack, a nickel smelting stack in Sudbury Ontario, has reduced local pollution but has dispersed sulfur dioxide and nitrogen dioxide gases over a large area including the US. It produces substantial arsenic, nickel and lead emissions, the latter contaminating the region to a level harmful to children.¹⁹⁷ The components and/or reservoirs of PC smog, such as O₃, HC, and PAN, can undergo long-range transport. Dust blown from the Gobi desert is worst in March and April, and it can reach all the way to the West coast of N America, where it has caused an increase in PM₁₀ from 20 to 50 µg m⁻³. (APGW p. 144) At a wind speed of 50 m/s, polluted wind (e.g., at 5 km height) could theoretically encircle the globe at 30°N in only 8 days.

¹⁹⁷ http://en.wikipedia.org/wiki/Inco_Superstack

Cloud Cover

Clouds reduce UV radiation penetration, thus reducing photolysis below. In addition, rainout and washout help remove pollutants from the air (though the removal may be only temporary if the pollutants re-evaporate). PC smog concentrations tend to be lower in the boundary layer of low pressure systems than that of high-pressure systems.

Effects of Local Meteorology on Air Pollution

Again only briefly summarized here. See APGW p. 144. Topics include

Ground Temperatures

Warm ground produces high inversion base heights, which reduce pollution mixing ratios, whereas cold ground produces low inversion base heights, increasing near-surface pollution mixing ratios.

Warm ground surfaces enhance convection, increasing surface winds increasing dispersion and decreasing mixing ratios (while also increasing dusts and aerosol particles). Cooler ground surfaces reduce winds and enhance buildup of pollutants.

Warmer temperatures increase biogenic emissions from trees (apparently including terpenes, though I am unsure of this and Jacobson is vague),¹⁹⁸ CO from vehicles, and O₃ production rates, etc..

Soil Liquid Water Content

Cooling of ground from increased soil water (through evaporation and increased specific heat of wetter soil) reduces convection, reducing mixing heights and slowing winds, thereby enhancing near-surface buildup of ozone, etc. Drying of soil has the opposite effect. Thus rainfall, irrigation, and climate change may play a role in pollution concentrations.

Urban Heat Island Effect

Urban heating occurs from altered albedo of asphalt roads and roofs, etc.; reduced evapotranspiration from missing vegetation; altered emissivities and heat capacities (water >> land); increased heat generation, etc. Higher temps foster increased mixing depths and faster winds but higher temps increase ozone and other pollution generation, as well as possibly thunderstorms.

Local Winds

These carry pollutants, and include:

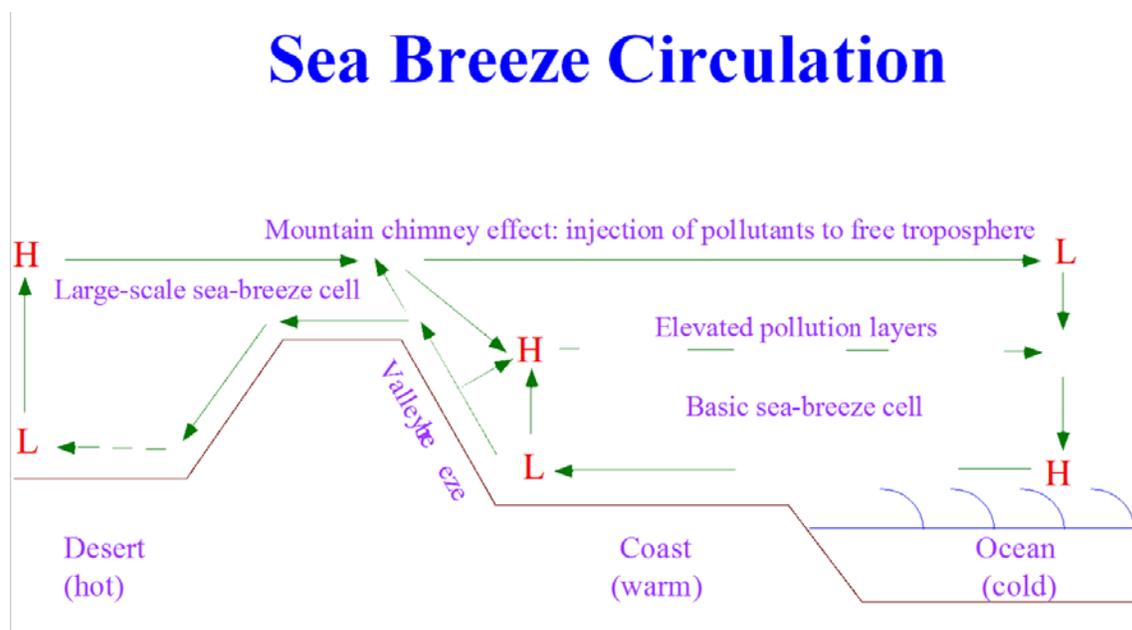
Sea, Lake, and Bay Breezes

Valley and Mountain Breezes

Chimney Effect and Elevated Pollution Layers

¹⁹⁸ See for example <http://biology.unm.edu/litvak/pubs/constable99.pdf>

Some of these effects combine together, and are illustrated in the diagram¹⁹⁹ below, which depicts the daytime situation of both local breezes and a large-scale sea breeze cell.



Due to daytime heating of land > water, rising air (convection) over land is associated with a local surface low-pressure L over land. The rising air diverges at a H aloft, setting up a shallow low-pressure thermal system. The air aloft returning toward the ocean converges over water at an L aloft and descends to a H over water. At night, these flows reverse, so that a (weaker) surface land (offshore) breeze forms.

Sea breezes can move pollutants from the sources on the W side of LA to become secondary pollutants on the E side of LA.

The greater heating over the inland desert (e.g., the Mojave Desert) creates greater convection, a stronger surface L, and a probably a greater H aloft. This draws a large-scale sea breeze toward the desert L. Sea breezes are maximal in the summer when land heating is greatest.

The **valley breeze** blows up a mountain from a sea breeze in a valley. Heating of the mountainside can also cause a **mountain chimney effect**, in which rising air carries and injects pollutants to higher altitude in **elevated pollution layers** in the background troposphere, where the pollutants build up (in some cases to higher than ground levels). The return flow from the sea breeze circulation may be an elevated pollution layer.

The elevated pollution layer is often an inversion layer, and in some cases the pollutants spread horizontally in that inversion layer. Smokestacks and large fire plumes can inject pollutants higher, into an inversion layer, again forcing horizontal spread. Elevated O₃ pollution layers in the boundary layer may form by the destruction of surface ozone arising from the effect of NO emissions during the night. The surface O₃ is replenished during the day... (APGW p. 149)

Plume Dispersion from Smokestacks

The pattern of vertical and horizontal dispersion from smokestacks is affected by the atmospheric stability profile and environmental lapse rate Γ_e , etc. Variations in stability conditions cause a variety of dispersion patterns including fanning (spreading horizontally), looping (oscillating vertically up and down), lofting (vertically rising), fumigating (downwashing vertically to the surface), and coning (slow spreading vertically both up and down).

¹⁹⁹ fig. 6.19 from Jacobson APGW p. 146

Effects of Air Pollution on Visibility, UV Radiation, and Colors

This topic is presented in *APGW* Chap. 7, a chapter we did not read in our class.

Light, such as a beam of sunlight, is reduced in intensity along the initial direct path by absorption or scattering, caused by gases or by aerosols and hydrometeor particles.

Absorption of Light by Gases

In this process, light entering a substance is partly removed from the incident beam and converted to internal energy causing a focal change of T, and some of this added energy is re-emitted as thermal-IR, heating the surrounding air.

Gas absorption of UV is discussed elsewhere (“Effect of Ozone (and N₂ and O₂) in Absorbing UV”, also *APGW* p. 154 and 240). Far-UV is absorbed mainly by O₂ and N₂ (but also by H₂O vapor, and CO₂). For Near-UV, UV-C and part of UV-B are absorbed by O₃, whereas UV-A is mainly absorbed by pollution-borne NO₂. Visible light is absorbed weakly by O₃ and by Nitrate radical (when present, usually greatest at night and early morning), but only NO₂ (if present) generally affects visibility. IR is absorbed by a variety of gases in wavelength-dependent distinctive patterns, see *APGW* p. 269 and discussion with global warming.

Ozone absorbs in the historically named Chappuis (0.45 to 0.75 μm), Huggins (0.31 to 0.35 μm), and Hartley (<0.31 μm) bands (*APGW* p. 154). Its absorption in the stratosphere causes stratospheric heating with T inversion.

The reduction to beam intensity I, due to absorption in a beam starting with intensity I₀, is given by

$$I = I_0 e^{-\sigma_{a,g,q}(x-x_0)}$$

where $\sigma_{a,g,q}$ is the **gas absorption extinction coefficient**, which varies with the matter phase (liquid or gas etc.), type of gas, and wavelength
(x-x₀) is the path length traveled to drop from I₀ to I beam intensity

The gas absorption extinction coefficient σ is given by the **absorption cross section b** (an effective cross section expressed in area units) multiplied by the number density N of the species (molecules per unit volume). It has qualifying coefficients (here, process=absorption a, phase=gas g, and gas species q) and is expressed in units of inverse distance. The total absorption extinction coefficient sums the effects of the extinction coefficients of all the individual gases. NO₂ has a higher gas absorption extinction coefficient for blue and green than for red (*APGW* p. 155), so that light passing through smog containing NO₂ is tinged red or reddish brown.

Absorption of Light by Aerosols and Hydrometeor Particles

Absorption to a high and nearly uniform degree occurs across the spectrum of UV, visible light, and Solar-IR from **black carbon BC** particles (which are nearly pure elemental C). BC is found in soot from diesel engines and combustion of biofuels, biomass, and coal. **Brown carbon BrC**, which has BC plus more organic carbon **OC**, appears brown, yellow, or gray. It is found primarily in soot from biofuel and biomass burning, but also coal combustion and apparently also diesel. BrC has strong short UV absorption but lesser long UV and short visible light absorption. The BrC organics with strongest absorption in visible and long UV include nitrated aromatics, aromatic HCs, PAHs, phenols, etc. The organics are often in **tar balls**, which are spherical but despite the name are only 30 to 500 nm in size, are often quite abundant, and cause considerable absorption. Soil dusts, which contain hematite, aluminum oxide, silicon dioxide, and other minerals, absorb various wavelengths of UV and visible light (*APGW* p. 159).

The reduction to beam intensity I, due to absorption by an aerosol particle, for a beam with starting intensity I₀, is given by

$$I = I_0 e^{-4\pi\kappa(x-x_0)/\lambda}$$

where κ is the **imaginary index of refraction** of a presumed spherical particle
(x-x₀) is the path length traveled to drop from I₀ to I beam intensity

Note the use of *refraction* although the process is presumably one of absorption, not scattering. Even though λ appears explicitly in the equation, the term κ is said to be wavelength dependent (*APGW* p. 160). Increased κ is associated with increased absorption and decreased transmission. Increased wavelength is associated with decreased absorption and increased transmission. BC has the highest κ across the spectrum. The imaginary index of refraction may differ greatly from the real index of refraction of the substance.

Absorption by BrC and BC particles contributes to the reduction of UV reaching the ground in polluted air (along with gas absorption, Rayleigh scattering, and aerosol particle scattering). This reduction of UV, according to modeling, causes decreased photolysis, and decreased near-surface O₃ in some circumstances, but increased ozone in other, and in any event, pollution particles have disproportionate harmful effects ... (complex details omitted). (APGW p. 161)

Scattering of Light by Gases and Aerosol Particles

In scattering, light entering or encountering a differing substance is redirected without loss or transfer of energy. Scattering processes include one or more of: **reflection**, **refraction**, **dispersion** (a type of refraction), and **diffraction**. Scattering by particles can occur, by **Rayleigh scattering** when Diameter/λ < 0.03. Scattering by larger particles is said to occur in the **Mie regime** (for 0.03 ≤ Diameter/λ < 32) or the **geometric regime** (for Diameter/λ ≥ 32).

Rayleigh scattering (mostly by gas molecules)

Rayleigh scattering RS occurs when light scatters, primarily from gas molecules (but may also be from tiny aerosol particles). The scattering molecules or particles must be much smaller than the wavelength λ (specifically, 2πr/λ ≫ 1, or as APGW p. 165 states, Diameter/λ < 0.03), and the index of refraction must be near 1. RS causes no (or only minimal)²⁰⁰ change in photon energy or wavelength. For blue light of λ = 450 nm, the particle size should be < 13 nm (therefore only the very smallest of PM₁ particles might qualify). It arises from electric polarizability of the particles, and the scattered light is polarized. The probability distribution for RS has equal amplitude forward and backward, but lower probability at 90 degree angles. RS cross section is proportional to 1/(λ⁴).²⁰¹ This means that short wavelength blue light is far more likely to be scattered than longer wavelength red light, explaining why the noon sun overhead is the most white (minimal scattering), the mid-afternoon sun is yellowish (absorption by RS of all blue and some green), and sunsets are orange-red (absorption of all blue and green by RS). The sky is blue due to RS and this blue light is polarized. (APGW p. 156-7) Tiny **smoke** particles and aerosols over the **Blue Ridge Mountains** scatter the firelight or ambient light in the blue λ preferentially and therefore appear blue (this is caused by RS or Mie regime scattering). After sunset, sunlight from below the ocean horizon is refracted due to the change of index of refraction, is scattered by aerosols prevalent in near-surface ocean air, and after differential scattering again reaches the distant observer as red light from much of the western horizon. Light originating from below the horizon and scattering in the upper atmosphere between sunset and **dusk** or between **dawn** and sunrise is called **twilight**, an illumination of the sky when there would be darkness if there were no atmosphere. The sky may be purple in twilight when green and some red light is absorbed by stratospheric ozone following a volcanic eruption causing SO₂ aerosol injection into the stratosphere. (APGW p. 172). The sun can appear red when sunlight passes through and is scattered by particulate pollution.

Reflection

Reflection occurs when light bounces off an object at an angle (with respect to the normal) equal to the incident angle. (The normal is a line perpendicular to the surface at the point of beam contact.) Preferential reflection of some wavelengths (versus absorption of others) confers characteristic colors observed for objects.

Refraction

Refraction occurs when light passes from one medium M₁, having an index of refraction (refractive index) n₁, into a different medium M₂, having an index of refraction n₂. The angle relationship (with respect to the normal) are given by Snell's Law:

$$\sin \theta_2 = \left(\frac{n_1}{n_2} \right) \sin \theta_1$$

where θ₂ is the angle in medium M₂ of the beam with respect to the normal, etc.

The index of refraction for a medium is defined as c/v, where c is the speed of light in vacuum, and v is the **phase velocity** of light in the medium. It is apparent that when light passes into a medium with greater

²⁰⁰ Minimal change in energy may occur from a small fraction of scattered photons that undergo inelastic Raman scattering, which is usually included in Rayleigh scattering

http://en.wikipedia.org/wiki/Raman_scattering

²⁰¹ http://en.wikipedia.org/wiki/Rayleigh_scattering

index of refraction n (slower v), it is bent closer to the normal, whereas when light passes into a medium with lesser index of refraction n (faster v closer to c), it is bent further from the normal. The index of refraction depends on wavelength and is usually ≥ 1 (but may be a little < 1 for specific conditions, because the phase velocity rather than the group velocity is being used).²⁰²

Refracted light in a medium can be absorbed (not a scattering process), transmitted, refracted out, internally reflected, etc.

Dispersion (Dispersive Refraction or Chromatic Dispersion)

As polychromatic light (having multiple wavelengths) passes into a new medium (such as a thicker atmosphere with higher index of refraction), the angle of refraction of the light varies with the wavelength. This causes the beam to split (disperse) into its constituent colors, with blue light (which is slower in phase velocity than red) refracted (bent) to a greater extent than red light. (In optical glass, a typical index of refraction is 1.5293 for blue, greater than the 1.5204 for red light.)²⁰³ Fluctuating atmospheric refraction causes small point sources such as stars to twinkle.

Diffraction

In diffraction, light changes direction when encountering an obstacle but retains the same frequency. It behaves according to **Huygen's principle**, which states that each point of an advancing light wavefront can be considered to be the source of a new series of concentric secondary spherical waves (which sum by constructive and destructive interference). This causes light to appear to bend around an obstruction. The obstruction may be a particle, cloud drop, or raindrop. Diffraction is observed with single slit or circular apertures that are small relative to wavelength. The minimal resolvable detail is expressed with the Rayleigh Criterion, which allows the generalization that the limit of resolution of an imaging process is on the order of the wavelength used.²⁰⁴

Combined and Predominant Forms of Scattering

Particle scattering can be by any of these mechanisms, often a combination, but aerosol particle scattering is most affected by diffraction and double refraction. The net effect can be forward scattering (which dominates), backscattering, or sidescattering.

Optical Effects of Scattering

Rainbow and Fogbow

The **primary rainbow** is seen when rain is forward (above the anti-solar point, which is located below the horizon) and the low morning or afternoon sun is behind the observer. It arises from double refraction with an intervening internal reflection in a **rainbow cone** of water droplets, with the cone's axis parallel to the incoming rays that will be seen and directed to the anti-solar point. (Drops inside the cone, thus inside the primary rainbow, brighten the sky inside the cone, but do not impart colors.) Red and violet light refract through differing angles. Red light is seen at the outer part of the rainbow cone (furthest in angle from the cone's axis)—the angle formed between incoming red light and the returning ray that reaches the eye is 42.5° . The violet light entering the eye is on a cone which forms an angle with its incoming sun ray of 40° , and it is perceived to be closer in toward the cone's axis than the red light.²⁰⁵ Other spectral colors take up intermediate positions according to the mnemonic ROYGBIV. Relative color intensities vary with droplet size: blue is minimal if droplets are large > 1 mm; red weakens if droplets are small. A white **fogbow** appears with

²⁰² http://en.wikipedia.org/wiki/Refractive_index

²⁰³ <http://hyperphysics.phy-astr.gsu.edu/hbase/geoopt/dispersion.html>

²⁰⁴ <http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/raylei.html#c1>

²⁰⁵ The **angle of minimal deviation** or **rainbow angle** is 137.5° , defined as the minimal total deviation of the sun ray that can reach the eye. This minimally deviated ray arises for deep red light. The angle formed between the incident and returning ray path is given by $180^\circ - 137.5^\circ = 42.5^\circ$. The center of a rainbow is on the cone's axis located opposite the sun at the anti-solar point (below the horizon). This and much more information are available at the excellent and very extensive website on Atmospheric Optics:

<http://www.atoptics.co.uk/>

very fine fog droplets < 0.05 mm (Mie scattering is involved,²⁰⁶ and diffraction smears out the colors).²⁰⁷ Similar bows may also be seen arising in clouds as **cloudbows**. **Supernumerary arcs** may be seen just inside the violet or blue side of the primary rainbow, usually near the top, and arise from uniformly sized small droplets in cones inside the primary rainbow, due to complex processes (they can also arise near secondary rainbows). A rainbow segment seen near the ground may be predominantly red, due to the usual scattering effects of long atmosphere paths. Spoke-like **rainbow spokes** may be seen, centered on the anti-solar point and extending up to the primary rainbow, but having white or dark neutral color. Sea spray can form a *Sea Water Bow*, with angular size smaller than standard rainbow due to higher refraction of seawater. **Reflection rainbows** can form from reflection of rainbow light off sand, water, etc., and may be seen above or below the primary rainbow. Moonlight at night can also form **lunar rainbows** or **moonbows**. The **secondary rainbow**, if present, also arises on a cone with axis centered at the anti-solar point, is further out by 9° with respect to the primary. Its inner color violet is positioned at an angle of 51° . The secondary bow has its color sequence reversed, with violet on the outer part and red on the inner, and is more widely spaced out.²⁰⁸ Higher order rainbows are possible. In between primary and secondary is a darker band. There are many other interesting rainbow-related or iridescent effects in the atmosphere, some of which require more complex explanations than geometric optics can provide.

Ice Crystal Halos and Other Ice Effects

These form as white foci of brighter light around the sun or moon, and include upper and lower **tangent arcs** and **sun pillars**. Lateral foci at 22° and greater are called **parhelia** or **sundogs** (and arise from flat plate crystals falling with hexagonal faces almost horizontally).²⁰⁹ Other phenomena include diamond dust, circumzenithal arc, 22° halo, and parhelic circle.

Particle Scattering and Absorption Quantitation

These measures are given in *APGW* p. 165, and I will minimally summarize this complex body of information. Scattering by particles occurs in Rayleigh, Mie, or Geometric regimes. The quantification starts with single-particle scattering efficiency and single-particle absorption efficiency. The Mie regime presents the strongest absorption Q_a and total scatter Q_s for BC particles affecting visible light (wavelength of $0.5 \mu\text{m}$). This diagram is from *APGW* p. 165:

Soot Absorption/Scattering Efficiencies

Single soot particle absorption/scattering efficiencies and forward scattering efficiencies at a wavelength of 0.50 micron

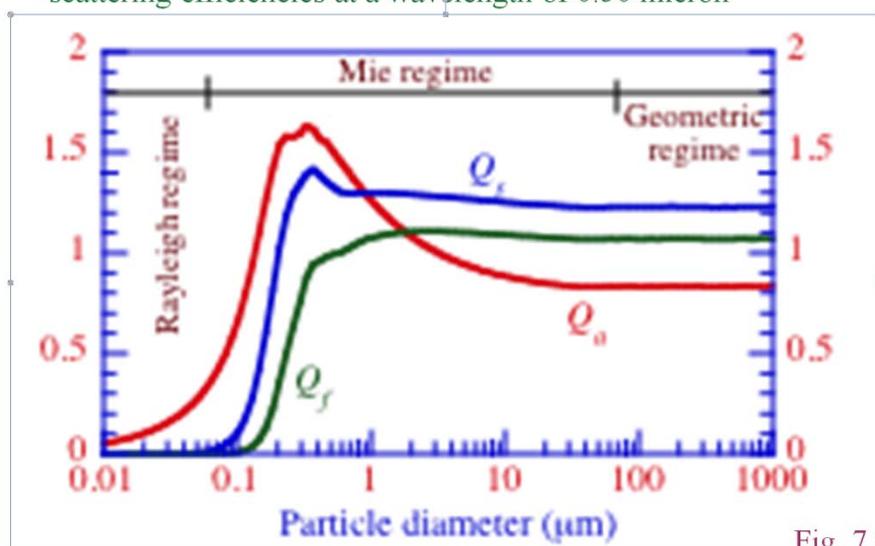


Fig. 7.20

²⁰⁶ <http://www.atoptics.co.uk/droplets/fogbow.htm>

²⁰⁷ <http://hyperphysics.phy-astr.gsu.edu/hbase/atmos/rbowpri.html>

²⁰⁸ <http://www.physicsclassroom.com/class/refrn/Lesson-4/Rainbow-Formation>

²⁰⁹ <http://www.atoptics.co.uk/halo/parhelia.htm>

Specifically, the absorption and scatter are greatest for BC particles of 0.2 to 0.4 μm (in Mie regime and in particle accumulation mode). Water particles show total scattering (forward plus backward) of visible light maximally 0.3 to 2 μm . The accumulation mode of particles is therefore the region of highest light reduction. Much of the accumulation mode in urban areas contains sulfate particles, a strong contributor to light reduction, mostly by scattering. Absorption of visible light, as opposed to scatter, only becomes comparable when droplets are the size of rain, > 1000 μm . Light scattering from rain clouds causes their bottoms to appear dark or gray.

Measures of Atmospheric Horizontal Visibility

The has been expressed for horizontal distances as

- (1) **Visual Range:** The actual distance at which an ideal dark object can be seen
- (2) **Prevailing Visibility:** The greatest range at which a person can see defined landmarks at over 50% of the horizon (but not necessarily at the remainder of the horizon). Usually made at airports.
- (3) **Meteorological Range MR:** This is now the preferred standard for visibility. A perfectly absorbing black test object against a white background, which thus where black has emission light intensity $I = 0$, is viewed at increasing distance until scattered light causes the **contrast ratio CR** to fall to 0.02. This number is the liminal or threshold contrast ratio for human perception, which is subject to individual variation, but 0.02 is considered to be a reasonably representative standard. The contrast ratio $CR = (I_B - I)/I_B$. Here, I_B is the **background intensity** of light when viewing near the object, and I is the intensity along the path to the test object. If $CR = 1$ the black test object is perfectly seen against the background intensity. If $CR = 0$, the black test object cannot be discerned against the background light intensity. The MR is derived from the **total extinction coefficients σ_t** , which are the sum of extinction [i.e., attenuation] coefficients for absorption plus scattering in to and out from the path, by gases as well as by particles (presumably by Rayleigh as well as Mie regime scattering). The differential equation resulting gives a solution:

$$CR = \frac{I_B - I}{I_B} = e^{-\sigma_t x}$$

where x is the distance from target to viewer

total extinction coefficients σ_t is expressed in appropriate distance units km^{-1} or m^{-1}

For $\lambda = 0.55 \mu\text{m}$ (green light), this give the **Koschmieder equation for MR:**

$$x = \frac{3.912}{\sigma_t}$$

where x = Meteorological Range MR

Considering Rayleigh scattering by normal atmospheric gases (the ultimate limiting factor), clean air has a maximal MR of about 350 km at 0.55 μm . Polluted air with NO_2 at 0.25 ppmv has MR_{NO_2} from NO_2 absorption alone [Rayleigh scattering ignored] reduced to 64 km. ($\text{MR}_{\text{NO}_2} = 1590 \text{ km}$ for 0.01 ppmv, but this also ignores Rayleigh scattering) For Denver's brown cloud in conditions of maximal pollution, NO_2 at high mixing ratios caused 37% of visibility reduction (from absorption), and particles caused the other 63% (from scattering and absorption). (APGW p. 167-8) Aerosol particle pollutants in PC smog (such as in LA) are the most significant causes of reduced visibility: scattering by aerosol particles causes 60 to 95% of visibility reduction, and absorption by aerosol particles causes 5 to 40%, with NO_2 less important.

Prevailing Visibility is estimated by $V \approx 1.9/\sigma_t$ in km. The geographic distribution of reductions of Prevailing Visibility (which is correlated with high total extinction coefficients σ_t) varies from winter to summer, and depends on winter inversions, high vs. low relative humidity, degree of particle loading, smog, power plant emissions, and particles emitted from vegetation. (APGW p. 169-170)

Colors Imparted to the Atmosphere

White hazes occur in high humidity <100% when aerosol particles absorb water but have not yet or cannot form fog or rain (details are complex and here omitted). They become visibly prominent in the Mie regime (in the range 0.3 to 2 μm), where they scatter all visible light and create white haze. These commonly occur over polluted urban areas even in sunny conditions. They often contain sulfates and varying amounts of water. The term *white haze* presumably does not apply to overtly dirty hazes (from dust, ash, sand, BC, BrC, etc.) Hazes may be dry or wet depending on how hygroscopic they are, the relative humidity, and their resultant water content—dry hazes have little water. Clouds form from wet haze when $\text{RH} = 100\%$ and the particles are

“activated” to grow without limit. Clouds and fog are similar to white hazes, in that they also scatter all visible wavelengths, and may be hard to tell apart.

NO₂ imparts a brown, yellow, or reddish-green color to PC smog. Nitrated aromatics, PAHs, and tar balls impart reddish or brown to smog. Soil dust contributes reddish or brown color. BC contributes black.

Smog can cause red sunset or sunrise skies, even in the afternoon in severe conditions.

Volcanic eruptions can add sulfate aerosols to the stratosphere, which scatter visible light through the ozone layer, which weakly absorbs green and some red, leaving blue and red = purple skies. (This explanation unclear to me.)

International Regulation of Urban Smog

This topic is presented in *APGW* Chapter 8, a chapter we did not read in our class and which I am omitting.

Indoor Air Pollution

This topic is presented in *APGW* Chapter 9, a chapter we did not read in our class and which I am omitting.

Acid Deposition

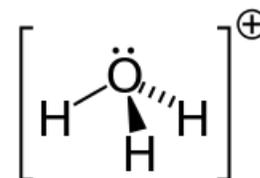
This topic is presented in *APGW* Chap. 10 and *IAC* Chap 13. The name acid deposition is used in preference to acid rain because it reflects the fact that atmospheric acids can be deposited in several phase combinations: as gas to liquid, gas to solid, liquid to liquid, or liquid to solid.

The Basics of Acids and pH

An acid for the purposes of this summary is any chemical compound that, when dissolved in water, gives a solution with a pH less than 7.0. Acids as commonly conceived are defined only in aqueous solutions. However, compounds that can form acids in water can also exist as dry gases, including H₂SO₄, HNO₃, and HCl, as pure liquids (such as liquid H₂SO₄), or as solids, such as tartaric or citric acid.

Definitions and Types of Acids: An acid is commonly defined as an aqueous solution with pH < 7 (and is a “proton donor”), a base has pH > 7 (and is a “proton acceptor”). One unit of pH decrease represent a 10x increase in hydronium ion concentration. “Aqueous solutions of acids have a pH of less than 7. A lower pH means a higher acidity, and thus a higher concentration of positive hydrogen ions in the solution. ..

- The Arrhenius definition defines acids as substances which increase the concentration of hydrogen ions (H⁺), or more accurately, hydronium ions (H₃O⁺) [see diagram, also called oxonium or hydroxonium], when dissolved in water.
- The Brønsted-Lowry definition is an expansion: an acid is a substance which can act as a proton donor. By this definition, any compound which can easily be deprotonated can be considered an acid. Examples include alcohols and amines which contain O-H or N-H fragments.”²¹⁰
- A Lewis acid is defined by a third definition. It reacts with a Lewis base to form a Lewis adduct.”²¹¹ (Any species that donates a pair of electrons to a Lewis acid to form a Lewis adduct is a Lewis base. “A molecular entity (and the corresponding chemical species) that is an electron-pair acceptor and therefore able to react with a Lewis base to form a Lewis adduct, by sharing the electron pair furnished by the Lewis base.”²¹²)
Example: BF₃ + F → BF₄, for which F is the Lewis base and BF₃ is the Lewis acid (because the B is electron deficient and has an empty orbital and can receive an electron pair). With H⁺ + OH⁻ → H₂O, H⁺ (ignoring its heavy solvation/binding with the solvent H₂O, see below) is a strong Lewis acid, OH⁻ is the base, and H₂O is the adduct. “In many cases, the interaction between the Lewis base and Lewis acid in a complex is indicated



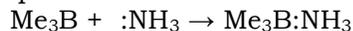
²¹⁰ <http://en.wikipedia.org/wiki/Acid>

²¹¹ http://en.wikipedia.org/wiki/Lewis_acids_and_bases

²¹² • <http://goldbook.iupac.org/L03508.html>

• see also <http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch11/lewis.php>

by an arrow indicating the Lewis base donating electrons toward the Lewis acid using the notation of a dative bond—for example, $\text{Me}_3\text{B} \leftarrow \text{NH}_3$. [Me_3B is trimethylborane] Some sources indicate the Lewis base with a pair of dots (the explicit electrons being donated), which allows consistent representation of from the base itself to the complex with the acid:



A center dot may also be used: $\text{Me}_3\text{B} \cdot \text{NH}_3$, similar to the notation for hydrate coordination in various crystals. In general, however, the donor–acceptor bond is viewed as simply somewhere along a continuum between idealized covalent bonding and ionic bonding.”

Conjugate Acid and Base: Per the Brønsted–Lowry acid–base theory, a conjugate acid of a base is formed by the reception by the base of a proton (H^+), thus it is the base with a hydrogen ion added to it. A conjugate base is formed by the removal of a proton from its conjugate acid: the conjugate base of an acid is that acid with a hydrogen ion removed.²¹³

Hydronium Ion: In aqueous solution, hydrogen ions (protons) rapidly protonate water to form the hydronium ion (positive, thus a cation). A proton sometime actually binds to more than one water molecule to form such species as H_5O_2^+ , H_7O_3^+ , etc.

pH: The pH of a solution is the base 10 (i.e., decimal) logarithm of the reciprocal of the hydrogen ion activity, a_{H^+} , a quantity which expresses the effective concentration of a species in a mixture.²¹⁴ However, pH is often taken to be simply

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = \log_{10} (1/[\text{H}_3\text{O}^+])$$

where concentrations are expressed in molarity M, meaning moles/(L of resultant solution).

Note that $1 \text{ L} = 10^{-3} \text{ m}^3 = (10 \text{ cm})^3 = 1000 \text{ cm}^3$. pH can range from extreme acidity (< 0 , i.e., negative pH values) to strongly alkalinity or basicity (> 14).

The abbreviation pH may mean power of hydrogen.

As noted, water reacts with itself to form hydronium and hydroxide ions:



The pH expresses the relative activity of hydronium versus hydroxide (OH^-) ions.²¹⁵ At equilibrium with pure water, the ions are in equal concentration and with equilibrium ionization constant $\sim 1 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$, so $[\text{H}_3\text{O}^+] \sim 1 \times 10^{-7}$ and $\text{pH} \approx 7$.

More precisely, the $[\text{H}_3\text{O}^+]$ of pure water is $\sim 1.0 \times 10^{-7}$ mole/L at IUPAC “standard ambient temp and pressure” ($T = 298.15 \text{ K}$ or $25 \text{ }^\circ\text{C}$ and $P = 1000 \text{ hPa}$), so the pH of pure water is close to 7 at SATP.

Representative pH values for aqueous solutions or foods include 7 for water, tomatoes 4.5, vinegar 5% 2.4 - 2.8, lemon juice 2.0 to 2.6, lime juice 2.0 to 2.35, blood 7.4, household ammonia 11 to 12, $\text{Ca}(\text{OH})_2$ (slaked lime) 12.4, NaOH (lye) 13 to 14.

pK and pKa: the prefix p is also used more generally to signify decimal cologarithm of , as in the term pK_a , used for acid dissociation constants. The general quantity pK was later defined as $-\log_{10} K$.

The meaning of the equilibrium dissociation/ionization constant is given as the following dimensionless quantity (assuming ions are sufficiently dilute that water activity = 1):

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \cong 1 \times 10^{-14}$$

The $\text{pK}_{\text{water}} = -\log_{10} K_{\text{water}} = 14$ at SATP. The pK_{water} exhibits substantial variation with T and P, as shown here.²¹⁶

The strength of an acid is expressed by the pK_a , where

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{where } [\text{HA}] = \text{concentration of the undissociated acid.}$$

(K_a is dimensionless because of the implied $[\text{H}_2\text{O}]$ in the denominator.)

$$\text{pK}_a = -\log_{10} K_a. \quad \text{pK}_a \text{ is also dimensionless.}$$

²¹³ http://en.wikipedia.org/wiki/Conjugate_acid

²¹⁴ http://en.wikipedia.org/wiki/Thermodynamic_activity

²¹⁵ <http://en.wikipedia.org/wiki/Hydronium>

²¹⁶ http://en.wikipedia.org/wiki/Self-ionization_of_water

A weak acid has $pK_a = -2$ to 12 , strong acids have $pK_a < -2$.²¹⁷ H_2SO_4 is virtually completely dissociated in aqueous solution or is said to have $pK_a \approx -3$, HCl has $pK_a \approx -9$, HNO_3 -1.4 . (For interest, the strongest acids also include trifluoromethanesulfonic acid with $pK_a \approx -12$ and Perchloric acid $HClO_4$ with $pK_a \approx -10$.)

Types of Acid Deposition

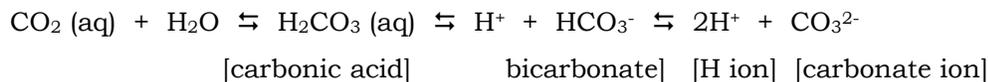
This can be wet (acid forming in and depositing from rain, fog, or haze) or dry (direct deposition of gaseous acid or acids in solid dust, smoke, or other essentially dry particles to soil or other surfaces). The acids of greatest concern in air pollution are H_2SO_4 , HCl , and HNO_3 . Acid deposition first arose from SO_2 and NO_x in coal burning. Acid fog, with pH as low as 2 to 4, can be more acidic than acid rain (pH 4.0 - 4.3), presumably because fog develops in stagnant air and the volume of water in which the acidity dissolves is much smaller.

Alkali industry: This manufactured soda ash (Na_2CO_3) and potash (K_2CO_3), originally made from wood ashes, potash, Spanish barilla ashes, and kelp. They were used in making soap, bleaches, paper, etc., but the feedstocks became scarcer and more expensive. The Leblanc process for conversion of $NaCl$ to Na_2CO_3 was developed in 1789, but it led to substantial release of gaseous CO_2 , HCl , H_2SO_4 and NO_x , as well as of soot and CaS (which formed gypsum). This dirty process was gradually replaced by the cleaner Solvay process in the 1880s to 1920s.

The concept of acid rain from burning of high sulfate coal was first described by Robert Smith in 1872. Active international interest arose in the 1950s and 1960s because Scandinavian lakes were being acidified by emissions from continental Europe.

Carbonic Acid H_2CO_3

As previously mentioned, in water dissolved CO_2 from the atmosphere forms carbonic acid, bicarbonate, and carbonate.



Only the first dissociation reaction to HCO_3^- occurs in rain water.

Rainwater is always at least mildly acidic, with pH no greater than 5.6, due to dissolved CO_2 (at a 2011 mixing ratio of 383 PPMV), which forms carbonic acid H_2CO_3 . Other acids may lower pH considerably more.

Sulfuric Acid H_2SO_4

H_2SO_4 is produced ultimately from SO_2 , and requires a change of S oxidation state from S(IV) to the fully oxidized state S(VI). The S(IV) family includes SO_2 , H_2SO_3 , HSO_3^- , and SO_3^{2-} . The S(VI) family includes H_2SO_4 , HSO_4^- , and SO_4^{2-} .

Formation in gas phase:

In the gas phase, when humidity is $< 70\%$, sulfur dioxide reacts (rather slowly) with water vapor to form the bisulfite ion HSO_3^-



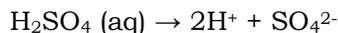
which is then oxidized to SO_3



This reacts with water vapor



Eventually, the $H_2SO_4(g)$ condenses with variable amounts of water to form $H_2SO_4(l$ or $aq)$ droplets usually containing some degree of water. $H_2SO_4(aq)$ dissociates almost completely to SO_4^{2-} at $pH > 2$.

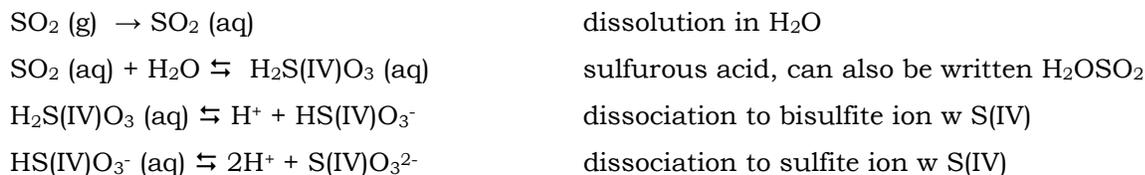


²¹⁷ http://en.wikipedia.org/wiki/Acid_dissociation_constant

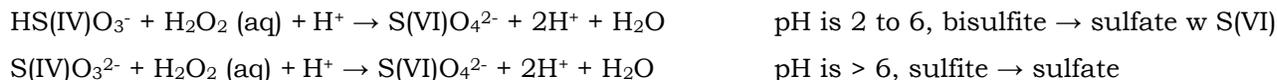
²¹⁸ <http://acmg.seas.harvard.edu/people/faculty/djj/book/bookchap13.html#pgfid=105767> (Jacob)

Formation in aqueous phase (cloud droplets and rain drops):

The following reaction sequence is 60% complete in 20 minutes, thus much faster than gaseous phase.



The final oxidation of S(IV) to S(VI) takes place by one of two reactions, depending on pH, both of which utilize H_2O_2 and are acid (H^+) catalyzed:



The last reaction is extremely fast and is now thought to provide the dominant atmospheric pathway for completion of oxidation of SO_2 to H_2SO_4 .^{219, 220}

The more basic reactions take place when droplets contain alkaline substances such as NH_4^+OH or CaCO_3 .

The sulfurous acid H_2SO_3 molecule is transient in the gas phase but is not found in aqueous solution.²²¹

Clouds are efficient producers of acid deposition. They can convert SO_2 to $\text{H}_2\text{SO}_4 (\text{aq})$ that deposits in nearby regions within about 1 or 2 days.²²²

The global atmospheric sulfur input, which is converted to SO_2 and SO_4^{2-} is summarized as follows (expressed as Tg S yr⁻¹):²²³

DMS from phytoplankton	22
Volcanoes	10
Combustion and Smelters	64
TOTAL	96

Global emissions of SO_2 have declined in recent years, especially in the US power generating sector, but China is going up rapidly.

Tall smokestacks, such as the 420 m stack in Kazakhstan, move the acid deposition further downwind, which may or may not have a net beneficial effect.

Nitric Acid HNO_3

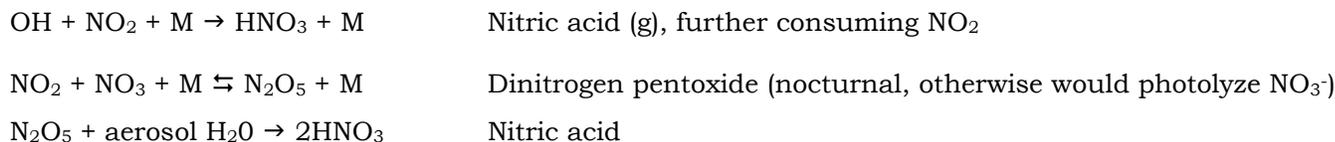
HNO_3 as previously mentioned, this primarily arises from hydroxyl and NO_2 .



and is also shown as



As before, the following continuation reactions generate HNO_3 . The latter 2 reactions take place at night.



²¹⁹ <http://acmg.seas.harvard.edu/people/faculty/djj/book/bookchap13.html#pgfld=105767>

²²⁰ Chandler AS et al, "Measurements of H_2O_2 and SO_2 in clouds and estimates of their reaction rate", *Nature* 336, 562 - 565 (08 December 1988); doi:10.1038/336562a0

²²¹ http://en.wikipedia.org/wiki/Sulfurous_acid

²²² JAT lecture

²²³ JAT lecture notes

The HNO_3 eventually leaves the atmosphere as acid deposition: wet or gas phase (in which HNO_3 can react directly with the soil and structures).

Hydrochloric Acid HCl

In water, this is a strong acid which dissociates to H^+ and Cl^- . It is abundant in gas phase over oceans, arising from sea spray and sea water evaporation (APGW p. 117). It is produced by coal burning and thus found in London-style smogs. It formerly was released by the alkali industry in the production of K_2CO_3 and Na_2CO_3 (used in the manufacture of soap, see above). It arises naturally from volcanos and anthropogenically from metallurgical processing, ClO_2 synthesis, hydrogen production, metal etching, masonry cleaning, etc. It occurs in acid deposition, though currently in the US, Cl^- is in considerably lower concentration in acid rain than SO_4^{2-} and NO_3^- .²²⁴ It also arises from chlorinated compounds and serves as a reservoir for Cl in the catalytic destruction of O_3 in the stratosphere (see section on stratospheric ozone and APGW p. 250-1, 256).

Effects of Acid Deposition

The effects are widespread and well described by the EPA: it affects lakes, streams, fish and other aquatic animals, ecosystems, trees and plants, soils, human health, materials and coatings, statues (of marble or limestone), and visibility.²²⁵ Jacob in IAC summarizes, "In areas where the biosphere is sensitive to acid rain, there has been ample evidence of the negative effects of acid rain on freshwater ecosystems. Elevated acidity in a lake or river is directly harmful to fish because it corrodes the organic gill material and attacks the calcium carbonate skeleton. In addition, the acidity dissolves toxic metals such as aluminum from the sediments. There is also ample evidence that acid rain is harmful to terrestrial vegetation, mostly because it leaches nutrients such as potassium and allows them to exit the ecosystem by runoff."²²⁶ Acid accumulated in snow can lead to highly acidic snow runoff in spring. Soil changes include removal of important trace nutrients (Ca, Mg, K, Na, etc.) and release into solution of toxic Al^{3+} and Fe^{3+} , which can be toxic to roots (APGW p. 228)

Some areas have natural or anthropogenic alkali compounds and minerals which help to buffer the effects of acidity—these include NH_4OH , NaOH (manufactured called caustic soda or lye), $\text{Ca}(\text{OH})_2$ (manufactured called slaked or hydrated lime), and CaCO_3 (calcium carbonate as calcite or aragonite). Calcium compounds reacting with H_2SO_4 tend to form $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), contributing to buildup of deposits in soils such as gypcrust and gypsum-containing caliche. In Sweden, efforts are being made to reduce lake acidity with application of slaked lime $\text{Ca}(\text{OH})_2$ or other alkali. NH_4OH in the atmosphere can neutralize acid and cause otherwise acidic rain to have a pH of 6 or greater. Beijing has rain that is less acidic than expected, because of blowing soil and dust—from deforested and desert areas—that lift dusts with neutralizing CaCO_3 into the air.

Regulation of Acid Deposition

This is an important topic, involving

- Emission trading system for SO_2

- Switching to lower S coal (from Wyoming and other western US states) rather than the NE US coal.

- Lower S gasoline and diesel

- Flue gas scrubbers for power plants, smelters, and other large coal burning installations

I'll not try to list the many relevant laws and regulatory policies. However, these measures have produced a measurable and apparently significant reduction of acid deposition throughout the US, with particular need for and resultant improvement in the NE US. The reduction appears more impressive for SO_4^{2-} and total H^+ than for NO_3^- . Animated maps from National Atmospheric Deposition Program NADP, prepared for each year from ~1985 to 2012, nicely depict the reduction trends mentioned.²²⁷

²²⁴ Slide per JAT for NY and MN sites, source and date not stated.

²²⁵ <http://www.epa.gov/acidrain/effects/>

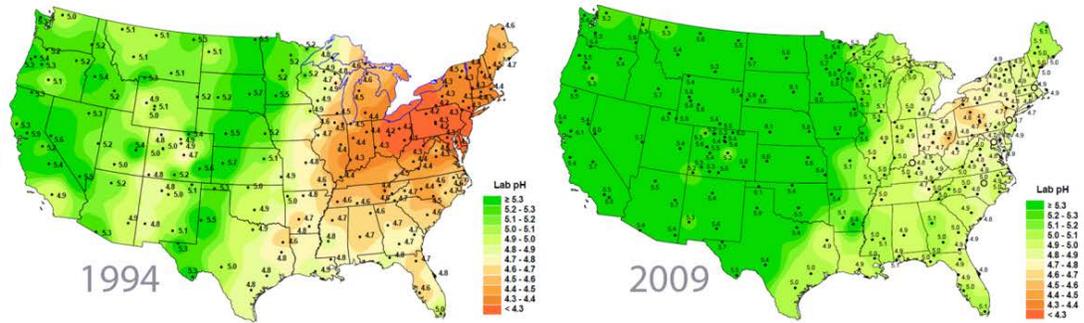
²²⁶ <http://acmg.seas.harvard.edu/people/faculty/djj/book/bookchap13.html#pgfid=106628>

²²⁷ <http://nadp.sws.uiuc.edu/data/animaps.aspx>

Select Deposition Animations and Concentration PDFs for SO_4 , H^+ ion, etc.

The following graph of rainwater pH is modified from the APGW textbook website,²²⁸ which draws upon National Trends Network NTN maps of the NADP.²²⁹

U.S. Rainwater pH



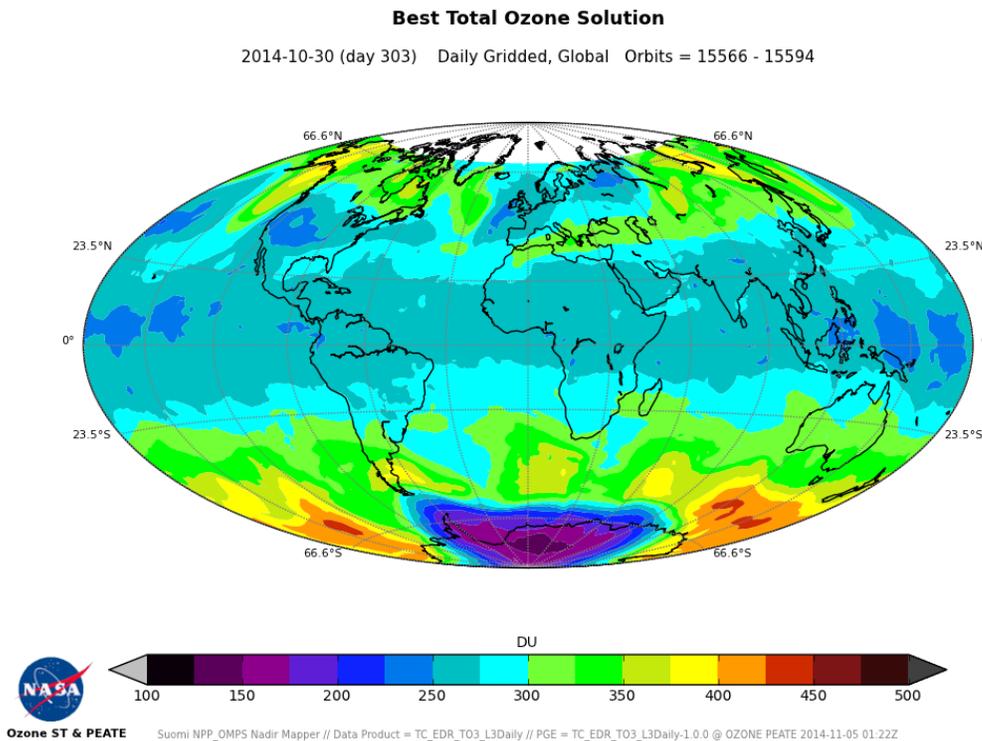
U.S. National Atmospheric Deposition Program/National Trends Network

The Clean Air Interstate Rule (CAIR, 2005) regulates interstate transport of pollutants, specifically SO₂ and NO_x, that contribute to acid deposition.

Stratospheric Ozone Depletion and the Antarctic Ozone Hole

This topic is covered in APGW Chap. 11 and IAC Chapter 10.

The global distribution of total ozone column on 10/30/2014 is shown in the following satellite based image. A prominent Antarctic hole is apparent: Data is lacking in the N polar region.²³⁰

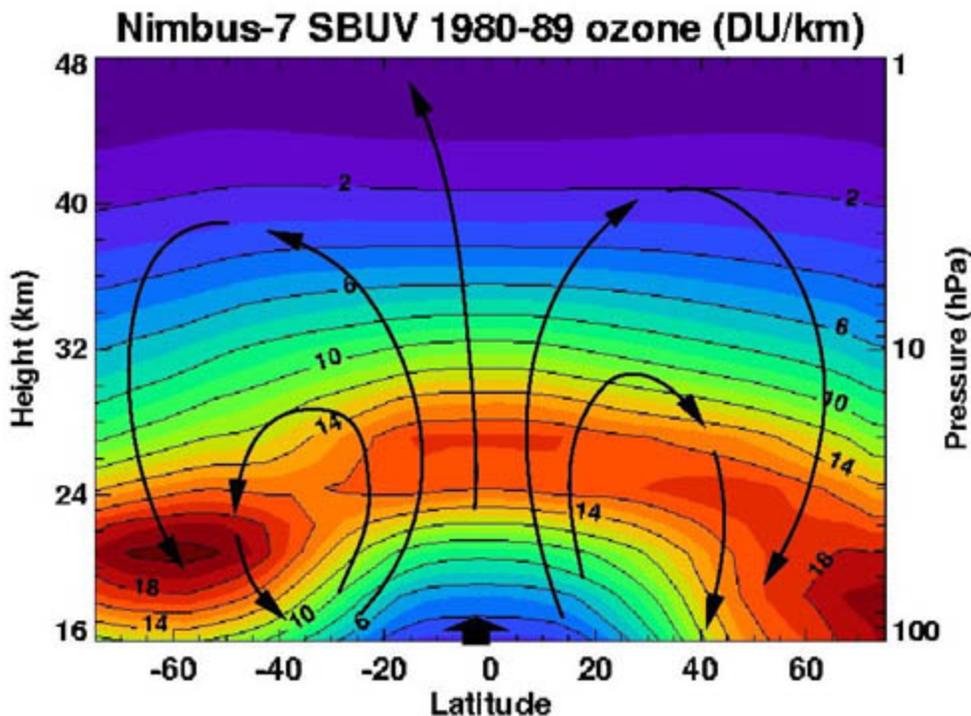


²²⁸ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/index.html> Jacobson Chapter 10

²²⁹ <http://nadp.sws.uiuc.edu/NTN/annualmapsByYear.aspx#1997>

²³⁰ <http://ozoneaq.gsfc.nasa.gov/> This is from NASA's Ozone Mapping Profiler Suite onboard the Suomi NPP spacecraft, using back-scattered Ultraviolet (BUV) radiation sensors.

The meridional and vertical transport of trace gases from the tropics to the poles in the atmosphere is represented by the Brewer-Dobson circulation model.²³¹ It is a residual circulation, “since the general air flow remains zonal and planetary waves in the extratropics disturb this flow and cause a slow meridional drift.”²³² Here the contours represent measured local ozone density expressed as DU per km altitude [as determined by the Nimbus-7 satellite’s solar backscatter UV and total ozone mapping spectrometer (SBUV/TOMS) instrument].



Most ozone in the atmosphere is present in the stratosphere (90%), the remainder in the troposphere (10%). The “ozone layer” is a region of greatest number density and mixing ratios, which is said to be at about 15-30 km (in the lower stratosphere). The peak mixing ratio of stratospheric O₃, 3000 – 5000 ppbv (JAT slide) or nearly 10 ppmv (APGW p. 239), compares to 40 – 100 ppb at the surface.²³³ The number density (shown on Fig. 11.4 of Jacobson) peaks at about 25 km at about 6 molecules cm⁻³ x 10⁻¹², whereas the mixing ratio peaks higher, at about 30 km. UV absorption is primarily a factor of number density, how many molecules of O₃ are interposed in the light beam before reaching the detector.

Effect of Ozone (and N₂ and O₂) in Absorbing UV

Atmospheric ozone (O₃) is essential for absorption of potentially harmful ultraviolet light. Essentially all UV-C (defined as 100 < λ < 280 nm) is blocked either by dioxygen [O₂] (100 < λ < 200 nm) or else by ozone (200 < λ < 280 nm) in the atmosphere. The ozone layer in the stratosphere and troposphere also blocks most, but not quite all, of the sunburn-producing UV-B band (280 < λ < 315 nm) ... The band of UV closest to visible light, UV-A (315 < λ < 400 nm), is hardly affected by ozone (though some is absorbed in the polluted troposphere by NO₂ and particles), and most of it reaches the ground.²³⁴ Far-UV is strongly absorbed in the mesosphere and thermosphere by N₂ in a range (10 < λ < 100 nm). In the higher stratosphere, mesosphere, and thermosphere, O₂ also absorbs far UV in a range (10 < λ < 250 nm).²³⁵ The resulting effects of atmospheric absorption of UV on ground level intensities is depicted in the earlier graph, “Spectrum of Solar Radiation (Earth)”.

²³¹ http://en.wikipedia.org/wiki/Brewer-Dobson_circulation

²³² M Weber et al, “The Brewer-Dobson circulation and total ozone from seasonal to decadal time scales”, *Atmos. Chem. Phys.*, 11, 11221–11235, 2011 www.atmos-chem-phys.net/11/11221/2011/, doi:10.5194/acp-11-11221-2011

²³³ JAT slide, source unknown.

²³⁴ http://en.wikipedia.org/wiki/Ozone_layer

²³⁵ APGW p. 240

The Earth's ozone layer blocks 97-99% of solar UV.²³⁶ "98.7% of the ultraviolet radiation that reaches the Earth's surface is UV-A."²³⁷ Of the photon energy arriving at sea level, about 5% is UV-A/B and 95% is visible light and IR.²³⁸

Measurement of Ozone (Dobson Units)

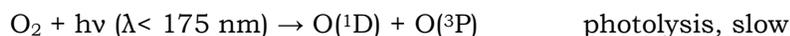
The amount of ozone in the air column from ground level to the top of the atmosphere is expressed in Dobson units, where 1 D. U. = 2.7×10^{16} molecules of ozone per cm^2 of ground area. At 273 K and 1 atm, 293 Dobson units of pure O_3 would occupy a column only 2.93 mm high. (It is remarkable how such a thin layer could play such an important role in world health!)

Chapman Cycle (1930)

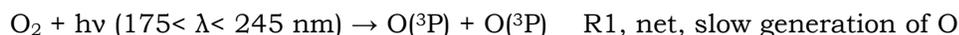
An initial understanding of the reactions creating and destroying atmospheric ozone were worked out by Sydney Chapman in 1930. The peak rate of O_3 production occurs in the stratosphere at an altitude low enough to have adequate number density of O_2 and high enough that adequate high energy UV photons are present.

Creation of O_3

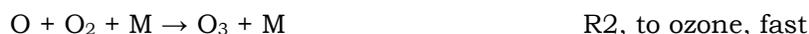
O_3 is produced in the stratosphere by the photochemical reactions beginning with photolysis of O_2 :²³⁹



or in the following reaction (the bond energy of O_2 is 498 kJ mol^{-1} , corresponding to the energy of a 240 nm UV photon, present only at high altitude):²⁴⁰



Subsequently,



(where M is a third body such as N_2). The more photons that are available, the more ozone is produced. (In the troposphere, the requisite O originates from NO_2 photolysis rather than from O_2 photolysis.)²⁴¹ The stratospheric O_3 mixing ratio of about 10 ppmv is much higher than that of polluted troposphere air (0.2 - 0.35 ppmv) or free troposphere air (0.020 - 0.040 ppbv). (APGW p. 239) Most ozone is produced in the tropics, but the stratosphere is stable to convection, inhibiting vertical mixing, and normally allows horizontal transport (migration) between the equator to the poles.

Destruction of O_3

The absorption of UV photons by ozone can split it into diatomic oxygen (O_2) and monoatomic oxygen (O) and eventually produces all O_2 .²⁴²



²³⁶ <http://www.physlink.com/education/askexperts/ae300.cfm>

²³⁷ <http://en.wikipedia.org/wiki/Ultraviolet>

²³⁸ APGW p. 240

²³⁹ • <http://en.wikipedia.org/wiki/Ozone>

• also http://disc.sci.gsfc.nasa.gov/ozone/additional/science-focus/about-ozone/ozone_cycle.shtml

²⁴⁰ <http://acmg.seas.harvard.edu/people/faculty/djj/book/> Jacob Chapter 10 p. 162, including rate discussion (rapid vs. slow) and quantitation

²⁴¹ APGW p. 240

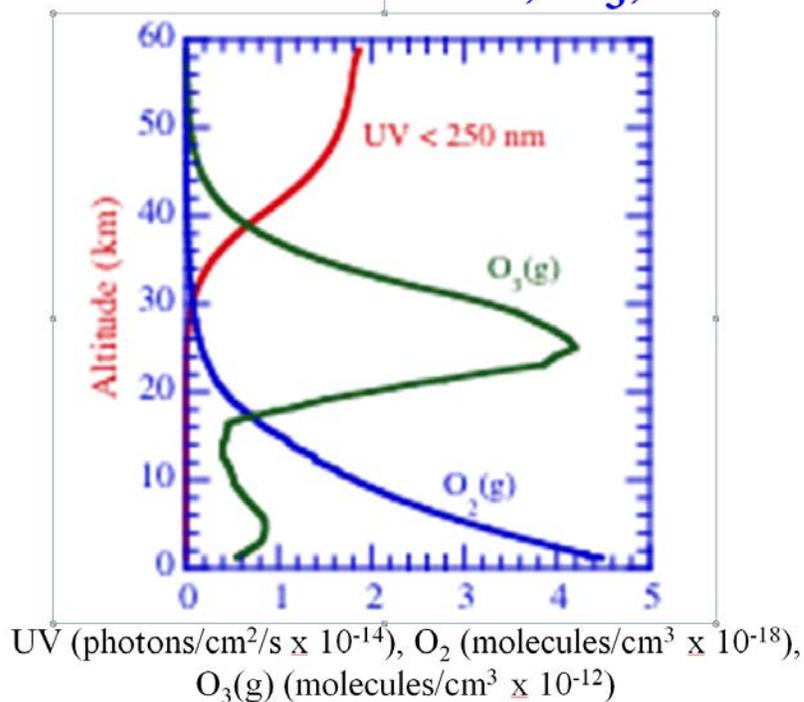
²⁴² http://disc.sci.gsfc.nasa.gov/ozone/additional/science-focus/about-ozone/ozone_cycle.shtml

Note that O and O₃ cycle in an odd-oxygen O_x family cycle. The ratio [O] / [O₃] is ≪ 1 throughout the stratosphere, and O₃ is the main component of O_x. The above pathways of O₃ synthesis and dissociation are called Chapman Cycle reactions (APGW p. 241). Despite their successes, they are not adequate to explain the excess of stratospheric ozone depletion. The Chapman mechanism “overestimates the observed O₃ concentrations by a factor of 2 or more.”²⁴³ There must therefore be additional sinks of O₃.

Peak Synthesis of O₃

In the following graph (from the APGW website and fig. 11.7), the peak of O₃ number density extends from about 15 km to 40 km peaking at about 26 km. This peak forms in the ozone layer at a balance point where UV < 250 nm persists somewhat and O₂ number density remains adequate.

Vertical Profiles of UV, O₃, and O₂



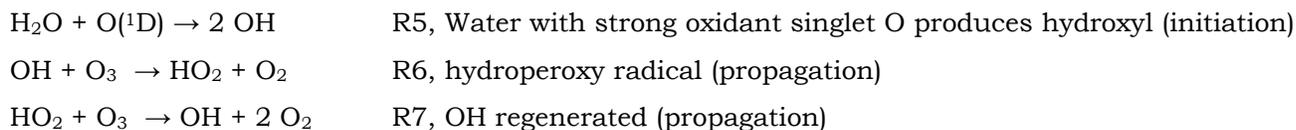
Catalytic Loss Cycles for Ozone: HO_x, NO_x, and ClO_x

The additional sinks for ozone in the stratosphere include hydrogen oxide radicals (HO_x), Nitrogen oxide radicals (NO_x), Chlorine [and bromine] radicals (ClO_x).²⁴⁴

HO_x Family Catalytic Loss of Ozone

As deduced in the 1950s, these occur from oxidation of water vapor, which has been transported to the stratosphere or generated by oxidation of CH₄. The HO_x family = OH and HO₂.

In the stratosphere, OH forms with the help of a high energy single O:



(OH can also form in the stratosphere from reaction of O(¹D) with methane CH₄ or H₂, APGW p. 243.)

²⁴³ <http://acmg.seas.harvard.edu/people/faculty/djj/book/> Jacob Chapter 10, e.g., fig. 10.5

²⁴⁴ Paul Crutzen, “My Life With O₃, NO_x and Other YZO_xs”, Nobel Lecture, December 8, 1995

The next effect is 2 O₃ consumed, 3 O₂ generated:



Thus HO_x chain reaction sequence is terminated when HO_x has been lost:



These reactions are a significant sink for O₃, particularly in the lower stratosphere where it is dominant, but are insufficient to explain all stratospheric O₃ loss.²⁴⁵

NO_x Family Catalytic Loss of Ozone

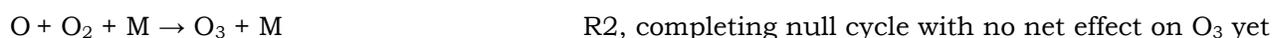
Recall that NO_x family = NO and NO₂

The primary source of NO_x in the stratosphere is N₂O, as determined in the 1970s. N₂O, which is also a greenhouse gas, is generated during nitrification and/or denitrification processes²⁴⁶ by anaerobic bacteria in suboxic regions of oceans, estuaries, and soils,²⁴⁷ especially when enriched with N-containing fertilizer. It also comes from biomass burning, the chemical industry, and livestock.²⁴⁸ N₂O is stable, has no sinks in the troposphere, and reaches the stratosphere gradually. N₂O as measured in ice cores has been increasing presumably from cultivation and use of fertilizers etc., from 285 ppbv in the 18C to 310 ppbv today, thus growing 0.3% per year.

In the stratosphere, it generates NO (analogous to H₂O + O(¹D) → 2 OH):



(Only 5% of N₂O undergoes this reaction, the remaining N₂O reacts to form N₂.) NO in the stratosphere is a concern that arose in the 1960s regarding the planned SST aircraft, which was intended to fly in the middle stratosphere, because of the persistence of NO_x in the stratosphere and its effects on ozone O₃:



The null cycle generates NO₂ from NO, thus NO_x. A few of the NO₂ from R9 however react with O:

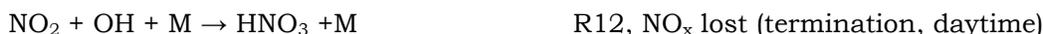


The net reaction is



When R11 occurs, 2 O₃ has been lost in a catalytic cycle (chain length ~10⁵) that does not consume the NO_x.

NO_x loss via OH terminates the reactions in daytime by:



At night, O(¹O) and therefore OH are absent and photolysis of NO₃ is not taking place, and termination occurs by



N₂O₅ and HNO₃ are relatively long-lived temporary reservoirs, hours-days and weeks, resp.) They eventually are converted back to NO_x:



²⁴⁵ <http://acmg.seas.harvard.edu/people/faculty/djj/book/> Jacob Chapter 10, p. 170

²⁴⁶ Skiba U, et al, "Nitrification and denitrification as sources of nitric oxide and nitrous oxide in a sandy loam soil", *Soil Biology and Biochemistry*, November 1993 DOI: 10.1016/0038-0717(93)90007-X

²⁴⁷ APGW p. 42

²⁴⁸ <http://acmg.seas.harvard.edu/people/faculty/djj/book/> Jacob Chapter 10, table 10-1



The group NO_y refers to NO_x + reservoirs HNO_3 and N_2O_5 . The disposal of NO_y ultimately require mixing of HNO_3 in the troposphere and raining out. The compound HO_2NO_2 (peroxynitric acid) also serves as a reservoir that slowly decomposes back to the reactants that formed it, HO_2 and NO_2 .²⁴⁹ CO and CH_4 contribute to stratospheric O_3 synthesis primarily when NO_x is present as from aircraft exhaust, and this injects water vapor, a potentially important anthropogenic source (APGW p. 243).

These NO_x reactions largely explain the missing O_3 consumption in the Chapman mechanism, and are the dominant catalytic loss cycle for ozone in the stratosphere, at least well removed from the poles.

The following summary diagram for NO_x and NO_y is taken from IAC.²⁵⁰

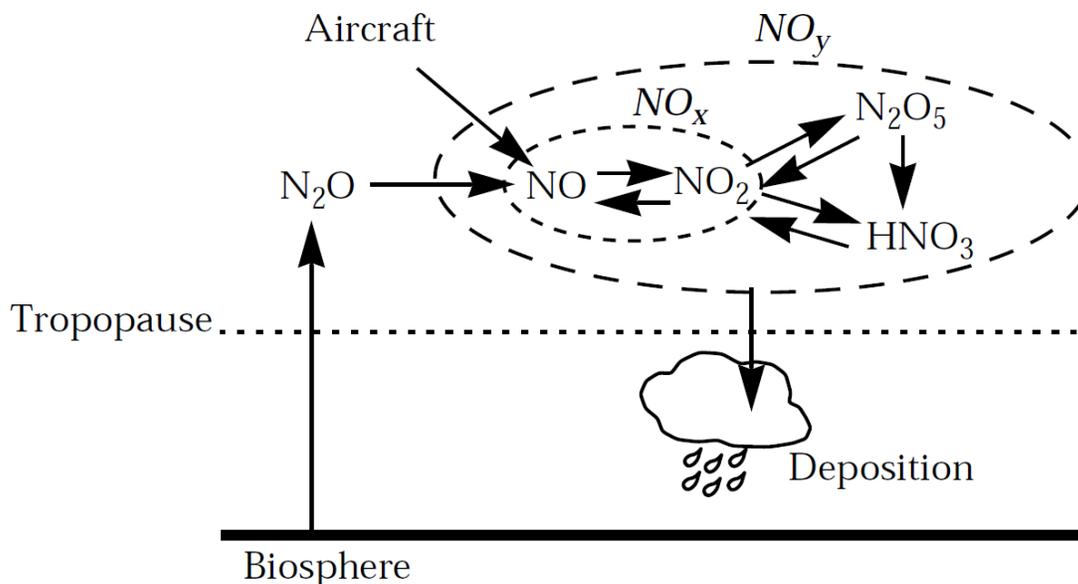


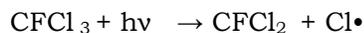
Figure 10-6 Sources and sinks of stratospheric NO_x and NO_y .

ClO_x Family Catalytic Loss of Ozone

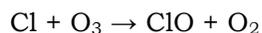
Some halogenated hydrocarbons are found in nature: CH_3Cl is the most abundant organohalogen of all,²⁵¹ CH_3Br is produced by marine organisms and a few Brassicaceae, and HCl has large natural sources. However, the compounds of interest for O_3 depletion are almost entirely anthropogenic. 82% of stratospheric Cl is anthropogenic—the rest comes from volcanoes, sea spray, and biogenic sources such as salt marshes of CH_3Cl , etc. (APGW p. 250).

In 1974, Mario Molina and Sherwood Rowland, noting the rise by 2-4% /yr, warned of the potential growing impact of anthropogenic chlorofluorocarbons (CFCs) on the stratospheric ozone.²⁵²

The cycle begins with photolytic generation of Cl radical from a halocarbon, such as CFC-11 or CFC-12:



R20, photolysis of CFC-11 to a radical, initiation
 $\lambda < 250 \text{ nm}$ for CFC-11
 $\lambda < 230 \text{ nm}$ for CFC-12



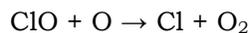
R21, to chlorine monoxide radical, propagation

²⁴⁹ APGW p. 242

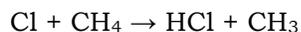
²⁵⁰ <http://acmg.seas.harvard.edu/people/faculty/djj/book/> Jacob Chapter 10, fig. 10-6

²⁵¹ <http://en.wikipedia.org/wiki/Chloromethane>

²⁵² Molina, M.J., and F.S. Rowland. 1974. "Stratospheric sink for chlorofluoromethane: Chlorine atom-catalyzed destruction of ozone." *Nature* 249:810-812. doi:10.1038/249810a0



R22, propagation, rate limiting

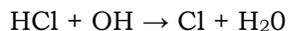


R23, termination to methyl radical

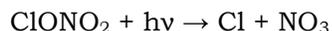


R24, to Chlorine nitrate = $\text{ClONO}_2 = \text{ClONO}_2$, termination

The non-radical HCl and ClONO_2 serve as temporary reservoirs, but eventually return to ClO_x :



R25



R26

The ClO_x family is Cl and ClO. (Some authors also include Cl_2O_2 = chlorine peroxide = ClO dimer, which plays a role in the ozone hole).

The family Cl_y , analogous with NO_y etc., is defined as $\text{ClO}_x + \text{reservoirs} = \text{ClO}_x + \text{HCl} + \text{ClONO}_2$

The following diagram summarizes the stratospheric halocarbon Cl interrelationships:²⁵³

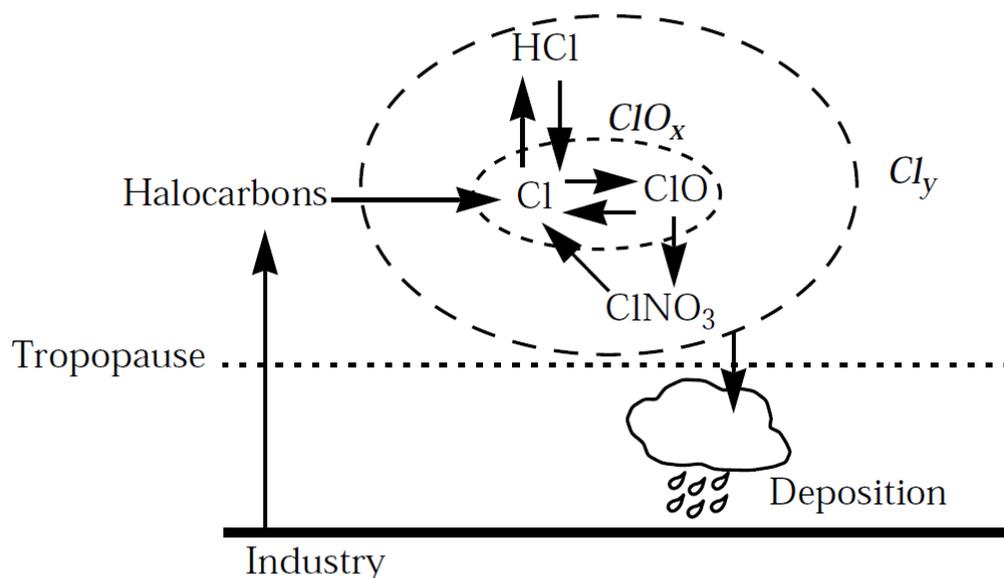


Figure 10-8 Sources and sinks of stratospheric ClO_x and Cl_y

The increasing use of huge quantities in the 1960s and 1970s of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), including Dupont's dichlorodifluoromethane ($\text{CF}_2\text{Cl}_2 = \text{R-12}^\circledR = \text{Freon-12}^\circledR$) led to accumulation of these highly stable products in the upper atmosphere.²⁵⁴ CFC-12 was first presented to the ACS in 1930. These compounds became widely used as refrigerants, propellants in aerosol applications, blowing agents in foams, and solvents. Chlorofluoromethanes (Freon 31[®], R-31[®], HCFC-31[®]), and related compounds such as Halon[®], 1,1,1-trifluoroethane (halothane[®]), carbon tetrachloride CCl_4 , and trichloroethane (methyl chloroform) were also involved.²⁵⁵

The relevant halocarbons for ozone depletion include CFCs, HCFCs, other chlorocarbons (including CCl_4 , CH_3CCl_3 , and CH_3Cl), bromocarbons (including halons and CH_3Br), fluorocarbons and fluorine compounds (including hydrofluorocarbons HFCs, perfluorocarbons PFCs, and SF_6). The numbering scheme of halocarbons is explained here.²⁵⁶ For instance, CFC-12 encodes $12+90=102$ CHF (1 C, 0 H, and 2 F).

²⁵³ <http://acmg.seas.harvard.edu/people/faculty/djj/book/> Jacob Chapter 10, fig. 10-8

²⁵⁴ <http://en.wikipedia.org/wiki/Chlorofluorocarbon>

²⁵⁵ http://en.wikipedia.org/wiki/Ozone_depletion

²⁵⁶ <http://www.epa.gov/ozone/geninfo/numbers.html>

The ODP (ozone depletion potential) is the ratio of global loss of ozone due to given substance over the global loss of ozone due to CFC-11 of the same mass.²⁵⁷

The GWP (global warming potential) expresses the global atmospheric heating potential resulting from a compound compared to the same mass of CO₂ over 100 years, where CO₂ is assigned a GWP = 1.

The halocarbon compounds differ substantially in lifetime, mixing ratios, ozone depletion potential ODP, and global warming potential GWP. I will not attempt to summarize this extensive information—see for example, APGW p. 246, the EPA data,²⁵⁸ or the massive UNEP Ozone Secretariat documents for 2011.²⁵⁹

However, here are some general observations. CFCs take about a year to reach the tropopause, and are not broken down in the troposphere (because photolysis takes far-UV of 100 to 250 nm, occurring at 12 to 20 km (APGW p. 249). HCFCs are more readily broken down by OH in the troposphere than CFCs, so less proportionately reach the stratosphere. They in general have shorter lifetimes, significantly lower ODP, but still rather high GWP (see EPA tables and APGW p. 248). Br is more efficient than Cl for breaking down ozone. HFCs and PFCs strongly absorb thermal-IR and have high GWPs. (APGW p. 248).

It has been estimated that it would take only about a year to replenish stratospheric ozone if the compounds with high ODPs were removed (APGW p. 252).

Recent Generalized (“Global”) and Mid-Latitude Ozone Depletion in the Stratosphere

Since the late 1970s (per APGW p. 243), a net decline of ~5% total in the total global volume of ozone in Earth’s stratosphere has been observed (presumably including the polar regions). This trend is seen from land based Dobson Spectrophotometers (figure on left, here for stations at US continental latitudes).²⁶⁰ The last 10 years or so may show some degree of stabilization.

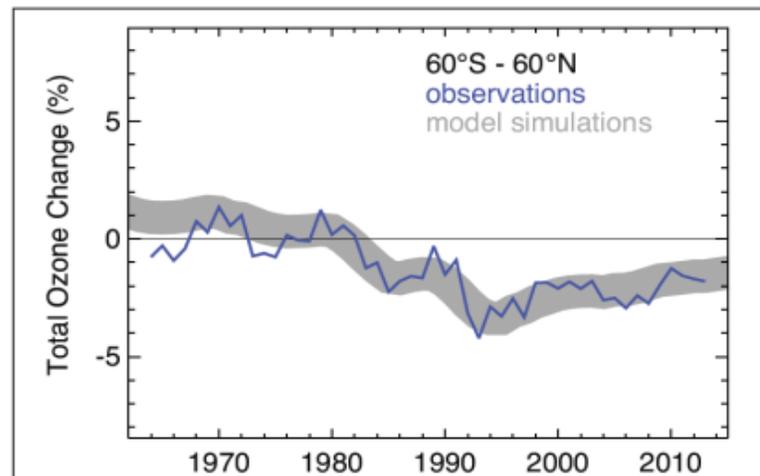
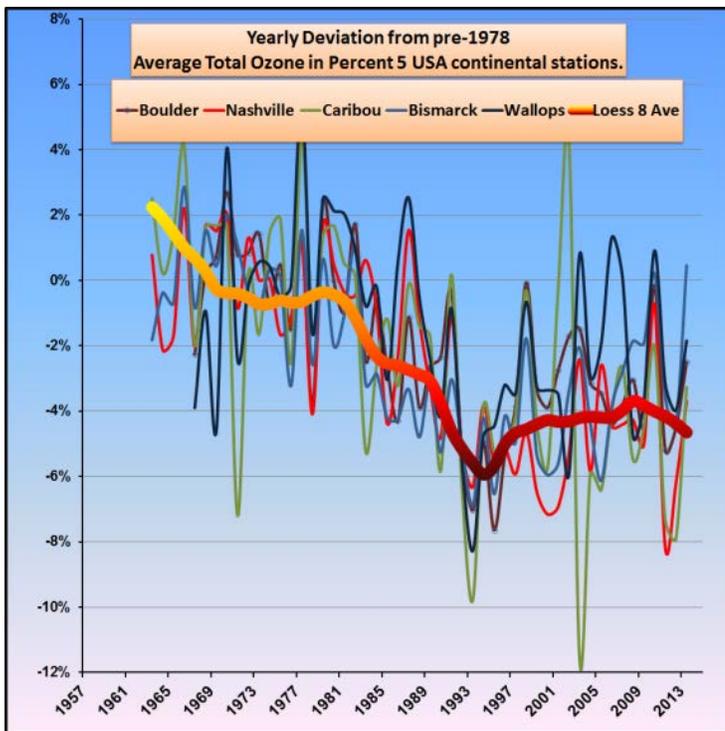


Figure ADM 3-1. Annual-mean changes in total column ozone averaged over 60°S–60°N from observations (blue) and from CCMVal-2 coupled chemistry-climate model simulations (gray shading, representing multi-model mean plus observed range of interannual variability (± 2 standard deviations, estimated over 1998–2008). The observed changes are with respect to the 1964–1980 average; the model values are referenced to the observations over 1998–2008. Adapted from Figure 2-2 of Chapter 2.

²⁵⁷ http://en.wikipedia.org/wiki/Ozone_depletion_potential

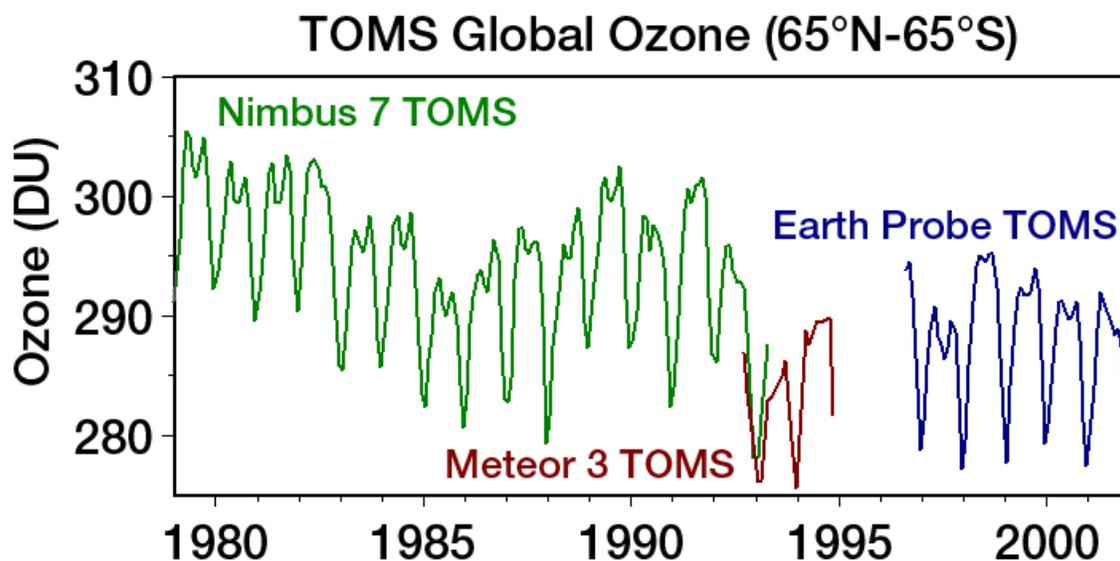
²⁵⁸ <http://www.epa.gov/ozone/science/ods/index.html>

²⁵⁹ http://ozone.unep.org/new_site/en/scientific_assessment_2010.php “The 2010 Assessment of the Scientific Assessment Panel”

²⁶⁰ <http://www.esrl.noaa.gov/gmd/about/ozone.html>

The figure on the right above is averaged data from the *Scientific Assessment of Ozone Depletion 2014*, again excluding polar latitudes (source of this data in Chapter 2 of the main report not yet available).²⁶¹

The decline is also apparent in global monthly average total ozone amount determinations by satellite from 65 N to 65 S latitudes by the Total Ozone Mapping Spectrometer (TOMS), deployed on the Nimbus-7 (Nov. 1978 - May 1993), Meteor-3 (Aug. 1991 - Dec. 1994), Earth Probe (July 1996 - current), and ADEOS (Sep. 1996 - June 1997) satellites.²⁶²



Note that all 3 graphs above exclude the polar zones, but the 5% figure for decline quoted is truly global (90 S to 90 N). Accelerated depletion was observed to coincide with the massive injection of aerosols from the 1982 El Chichón and 1991 Mount Pinatubo volcanic eruptions (from Cl reactions taking place on particle surfaces), but ozone dips partly recovered. The TOMS curves show annual fluctuations that are maximal around September and minimal around January.²⁶³

The WMO/UNEP summarizes in 2014, “Total column ozone averaged over 60°S–60°N and between 2008 and 2012 is lower by about 2% than it was during 1964–1980; this is slightly less than the value of about 2.5% for 2004–2008 reported in the last Assessment [in 2010]... Corresponding values for midlatitudes of the Northern and Southern Hemispheres (35°N–60°N and 35°S–60°S) are decreases of 3.5% and 6%, respectively, the same as reported in the last Assessment [report of 2010] ... for the 2004–2008 period. The larger depletion in the Southern Hemisphere compared to the Northern Hemisphere is linked to the Antarctic ozone hole. Tropical column ozone levels are almost unchanged since 1964–1980.”²⁶⁴

The reporting of ozone levels is complex and I have not fully explored this subject.

Recent Polar Region Ozone Depletion in the Stratosphere: Holes and Dents

Observing and Quantitating Antarctic Ozone Holes

Before 1950 and 1980, no Antarctic instruments showed ozone levels < 220 Dobson units (the threshold subsequently defining Antarctic O₃ depletion “hole”). A disproportionate decline in springtime stratospheric O₃ was first observed with ground-based Dobson instruments at Halley Bay, Antarctica (75°35'S) in 1985

²⁶¹ *Scientific Assessment of Ozone Depletion 2014: Assessment for Decision-Makers*, World Meteorological Organization WMO/United Nations Environment Programme UNEP. (Full report to be available in 2015.) Figure modified from figure on p. 19. Hereafter termed SAOD:ADM2014

http://www.esrl.noaa.gov/csd/assessments/ozone/2014/assessment_for_decision-makers.pdf

²⁶² • <http://disc.sci.gsfc.nasa.gov/acdisc/TOMS>

• http://en.wikipedia.org/wiki/Ozone_depletion

²⁶³ M Shiotani, “Annual, quasi-biennial, and El Niño-Southern Oscillation (ENSO) time-scale variations in equatorial total ozone”, *Journal of Geophysical Research: Atmospheres* Volume 97, Issue D7, 20 May 1992

²⁶⁴ SAOD:ADM2014 p. 19

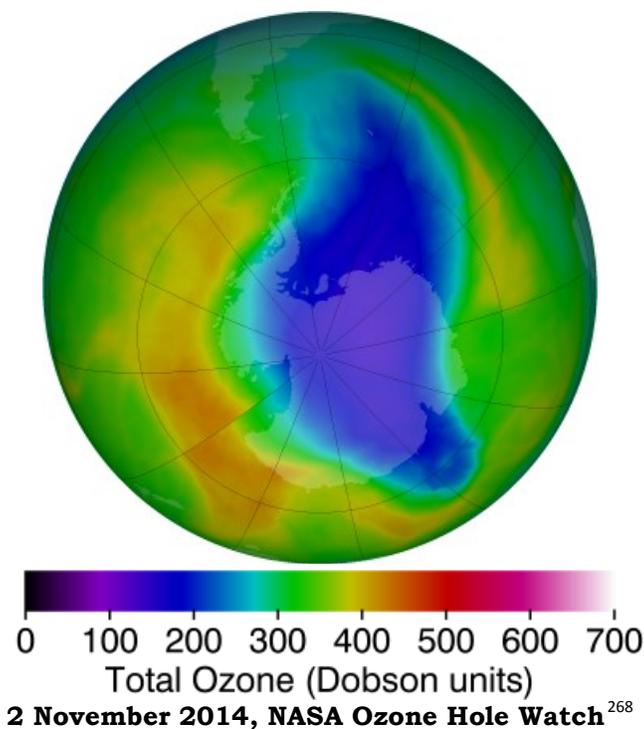
(part of the British Antarctic Survey). Satellite imaging eventually confirmed the extent of the Antarctic ozone hole.²⁶⁵

“Reductions of up to 70% in the ozone column observed in the austral (southern hemispheric) spring over Antarctica and first reported in 1985 ... are continuing. Through the 1990s, total column ozone in September and October [over Antarctica] have continued to be 40–50% lower than pre-ozone-hole values.”²⁶⁶

The Antarctic Holes are confined to SH Spring—September to November—and not seen at other seasons. They are found almost entirely at polar latitudes > 60 S.

The WMO/UNEP summarizes in 2014, “The Antarctic ozone hole continues to occur each spring, as expected for the current ODS abundances [i.e., ozone-depleting substances]. The Arctic stratosphere in winter/spring 2011 was particularly cold, which led to large ozone depletion as expected under these conditions.”²⁶⁷

A recent satellite image of the SH/Antarctica ozone hole was made in Nov. 2014:



NASA provides further detailed quantitative information about the atmospheric “ozone hole” over Antarctica. In the paired graphs that follow, data averaged over about a month’s period each year is given, showing the maximal averaged size each year of the spring ozone hole (in km²) attained, and the lowest averaged DU attained. The worst ozone hole, based on lowest DU, occurred in 1994, when a DU of 73 was measured, presumably a single reading. (The graph indicates a higher DU minimum of 92 in 1994, but this is averaged for a ~1 month period.) The largest ozone hole by area was found in 2006, namely 29.3x10⁶ km² (which is larger than the 50 USA states that cover ≈ 9.9 x10⁶ km², and is again presumably from a single reading. (The graph indicates an maximal area of 27x10⁶ km² in 2006, but this is averaged for a ~1 month period.) The NASA webpage also includes several useful animations. For 2014, the largest hole was 24 km² on 9/11/2014 and the lowest ozone was 114 DU on 9/20/2014.²⁶⁹

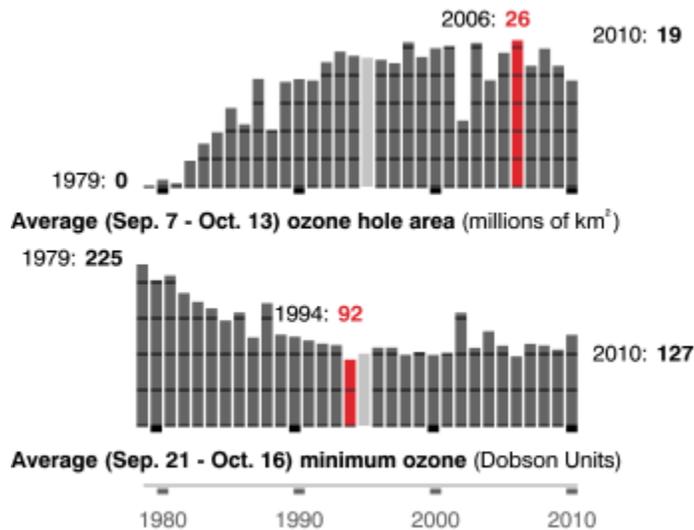
²⁶⁵ <http://ozonewatch.gsfc.nasa.gov/>

²⁶⁶ http://en.wikipedia.org/wiki/Ozone_depletion

²⁶⁷ SAOD:ADM2014 p. ES-1

²⁶⁸ <http://ozonewatch.gsfc.nasa.gov/>

²⁶⁹ <http://ozonewatch.gsfc.nasa.gov/>



Note: No data were acquired during the 1995 season
<http://ozonewatch.gsfc.nasa.gov/> and
http://ozonewatch.gsfc.nasa.gov/meteorology/annual_data.html

The following is again from the *Scientific Assessment of Ozone Depletion 2014*,²⁷⁰ and as noted presents values averaged over 1 week periods from multiple years and a range of longitudes. The ozone abundance at a particular altitude is expressed as partial pressure of O₃ in millipascals, whereas the atmospheric pressure is expressed as hPa (100 Pascal) units. The ratio of these units is therefore 10⁻⁵. (An actual set of measurements made during a single year is shown later below.)

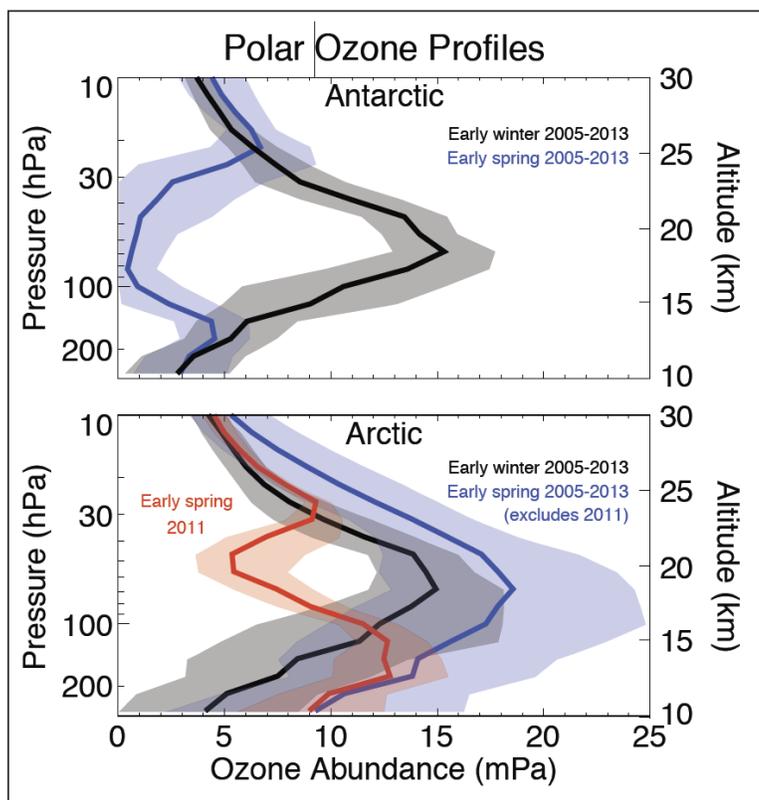
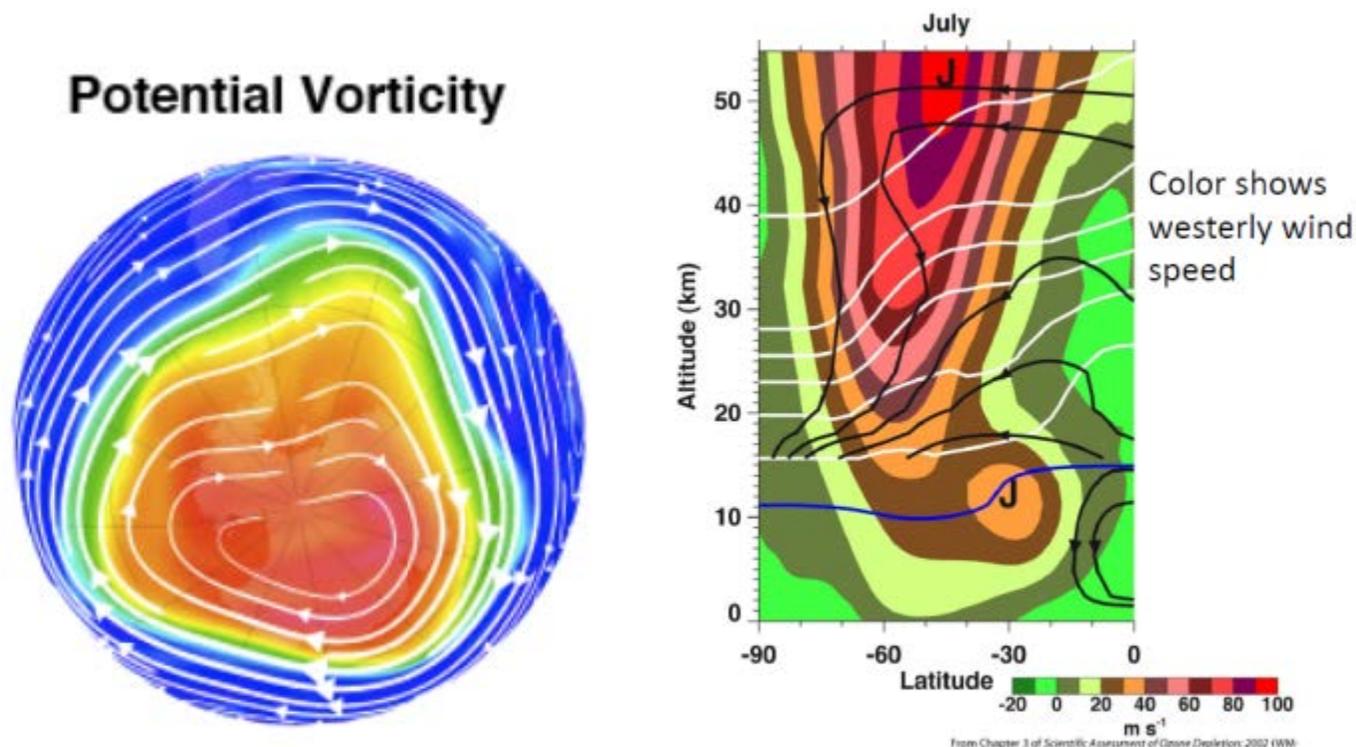


Figure ADM 4-2. Polar ozone profiles for the Antarctic (top) and Arctic (bottom) from the Aura Microwave Limb Sounder satellite remote measurements of the lower stratosphere (~10 to 30 km) between 2005 and 2013. The figure shows the range of ozone changes between early winter (in the first week of January/July for Arctic/Antarctic) and early spring (using here a late March or early October week for Arctic/Antarctic). The Antarctic panel illustrates the recurring deep ozone depletion in the ozone hole region for the 9 years from 2005 through 2013; a region deep inside the vortex (south of 77°S and for longitudes between 4°E and 20°E) was used for this illustration. Polar Arctic profiles (using here a similar latitude/longitude region in the Northern Hemisphere) exhibit more variability as a result of larger dynamical activity. The deep Arctic ozone loss in 2011 (with red range shown here), while quite unprecedented, did not reach the depth and vertical extent of loss observed in the typical Antarctic ozone hole. The shaded ranges shown encompass more than 90% of the ozone values in the chosen regions. Average values are shown as thick colored lines for each of the shaded cases.

Mechanism of Hole Formation

The explanation for Antarctic hole formation is surprisingly complex, with many moving parts. For our class, we read a paper summarizing the experimental evidence for the role of CFCs and ClO in the formation of the Antarctic ozone hole.²⁷¹

The Polar Vortex and Meridional Stratospheric Advection



The polar vortex is a persistent, large synoptic scale cyclone that circles the planet's geographical poles, clockwise in the SH. The polar vortex is stronger in the winter (beginning in about May, because of greater descent of very cold air over the poles). In the Antarctic winter and spring, the persistent polar vortex acts as a barrier, trapping cold polar air and preventing normal meridional stratospheric advection and mixing in of new O₃ from the warmer tropics and mid-latitudes, and allowing a buildup of Cl• etc. The left diagram shows the polar vortex generally westerly wind direction and suggests the speed (vorticity).²⁷²

Polar Vortex cuts off warm, ozone/NO_x rich mid-latitude air

The right diagram again in SH winter is a meridional cross section which showing westerly wind speeds as a function of altitude and latitude for the Antarctic polar vortex (zonal, apparently averaged across longitude).²⁷³ Winter wind speeds are highest in the stratosphere, from about 30 to 50 km.

²⁷¹ J. G. Anderson, et al, "Free Radicals Within the Antarctic Vortex: The Role of CFCs in Antarctic Ozone Loss", *Science*, Vol. 251 4 January 1991

²⁷² Note that westerly flows about the S pole appear clockwise in direction, whereas a similar view of the N pole would show counterclockwise flow. Vorticity increases from blue to green, yellow, orange, and red.

http://ozonewatch.gsfc.nasa.gov/facts/vortex_NH.html

²⁷³ JAT lecture, but taken from the following article

The preceding graph was derived from the following version,²⁷⁴ which shows the variation from winter to summer in the polar vortex:

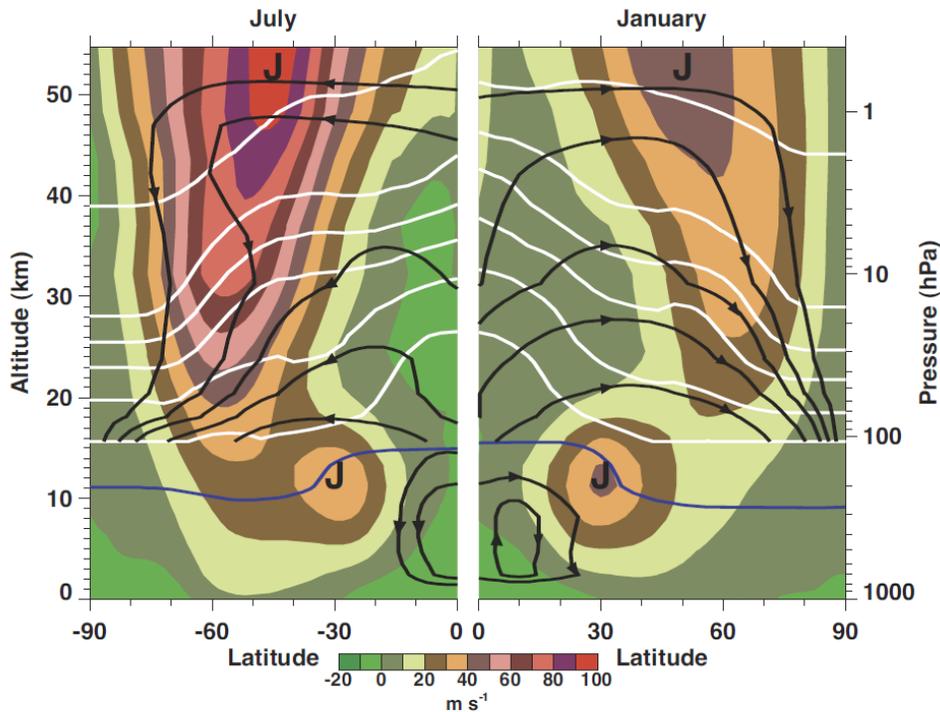


Figure 3-11. Zonal-mean sections of zonal velocity (shaded), the mean meridional streamfunction (black lines), and an atmospheric trace gas (white contours) for midwinter (July in the Southern Hemisphere and January in the Northern Hemisphere). The data were obtained from multiannual climatologies. The figure illustrates the stronger polar night jet in the Southern Hemisphere, the stronger subtropical jet in the northern winter, along with consistent differences in the strength and structure of the mean meridional circulation and trace gas distributions.

In the caption for this graph, reference is made to the mean meridional streamfunction in black—this quantity is defined elsewhere as “the vertically integrated northward mass flux at latitude ϕ from pressure level p to the top of the atmosphere”.²⁷⁵ I have not worked out the reference to trace gas.

Stratospheric Aerosol Layer (SAL)

There is normally an aerosol layer in the stratosphere at 15-30 km, which provides particles, mostly of $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$, that are ~ 700 nm in size and with number density of $\sim 10 \text{ cm}^{-3}$. The Stratospheric Aerosol Layer is also called the Junge Layer (after Christian Junge, who discovered it in 1960).

“The stratospheric aerosol layer is sustained by natural emissions of carbonyl sulfide (OCS) through biogenic processes [it is emitted from oceans, volcanoes and deep sea vents]. Carbonyl sulfide is relatively stable [and] can mix into the stratosphere where it is photochemically broken down resulting in the formation of microscopic droplets of sulfuric acid.

Another sulfur-containing gas, sulfur dioxide (SO_2), is normally too reactive to reach the stratosphere, instead it is rained out (as acid rain downwind of its sources). Volcanic eruptions, however, can inject SO_2 directly into the stratosphere where it too undergoes transformation into sulfuric acid... Only a small number of eruptions in this century have had a significant impact on the Junge Layer. The most recent example is the June 1991 eruptions of Mt. Pinatubo... The eruptions had near-global effects on weather and climate via the introduction of sulfur dioxide and aerosols into the atmosphere. Satellite observations showed that the stratospheric aerosol layer was significantly enhanced for over three years. Many parts of the world

²⁷⁴ “CHAPTER 3 Polar Stratospheric Ozone: Past and Future” from *Scientific Assessment of Ozone Depletion: 2002 NOAA Earth System Research Laboratory Chemical Sciences Division*

²⁷⁵ [ftp://www.iges.org/pub/straus/CLIM_753/GC_Unit2.pdf](http://www.iges.org/pub/straus/CLIM_753/GC_Unit2.pdf)

experienced a drop in average temperature of approximately 1 degree Fahrenheit in 1992 compared to the 30-year average.”²⁷⁶

Polar Stratospheric Clouds (PSCs)



This image above is described as follows: “Polar Stratospheric Cloud, seen from the NASA DC-8 on 14 January 2003 (photograph by Paul Newman, GSFC)... The clouds have a colorful appearance because they contain similar sized, small particles each of which diffracts sunlight in a similar manner. This image is notable for illustrating the high altitude (approximately 70,000 ft. [21 km]) of the polar stratospheric clouds, well above the cirrus cloud deck that lies below the DC-8 airplane...”²⁷⁷

The cold winter polar air allows condensation of particles with the SAL particles as nuclei to form optically thin Polar Stratospheric Clouds (PSCs, aka nacreous clouds). When temps are about 195 K [-109° F], nitric acid and H₂O grow on the seed H₂SO₄ + H₂O particles in multiple phases, including gases, supercooled liquid particles (ternary solutions of H₂SO₄, HNO₃, and H₂O, which form Type Ib PSC), water ice, and ice-like crystals of HNO₃•3H₂O (nitric acid trihydrate), HNO₃•2H₂O (nitric acid dihydrate), and HNO₃•H₂O (nitric acid monohydrate).²⁷⁸ The latter ice-like crystals form Type Ia PSCs—the particles have sizes of 1 μm (0.01 μm to 3 μm) and number concentrations of ≤ 1 cm⁻³.

When temperatures are colder than about 187 K [-123° F], water vapor deposits on the aerosols creating typical ice crystals. These are Type II PSCs, and consist almost entirely of water. The particles have sizes of 20 μm (1 μm to 100 μm) and number concentrations of ≤ 0.1 cm⁻³. It is thought that these fall out from the stratosphere faster.²⁷⁹

²⁷⁶ <http://www.albany.edu/faculty/rgk/atm101/junge.htm>

²⁷⁷ <http://remus.jpl.nasa.gov/kiruna/a015.htm> Polar Stratospheric Cloud, seen from the NASA DC-8 on 14 January 2003 (photograph by Paul Newman, GSFC)

²⁷⁸ <http://acmg.seas.harvard.edu/people/faculty/djj/book/> Jacob Chapter 10, p. 183

²⁷⁹ http://en.wikipedia.org/wiki/Polar_stratospheric_cloud and *APGW* p. 253-4

Heterogeneous Reactions Activate Chlorine in the Winter

A complex soup of reactions are facilitated by interaction on the surfaces of the aerosol particles in solid, liquid, gas, and mixed phases. A gas such as chlorine nitrate ClONO_2 (g) adsorbs to a particle and reacts with water, forming HOCl, etc. Reactions ensue (not detailed here), generating gaseous Cl_2 , HOCl, and ClNO_2 (chlorine nitrite)—all of which are relatively active forms of Cl—from relatively inactive (reservoir) forms of Cl (HCl and ClONO_2). This is called chlorine activation, and occurs in the winter months when temps are low and there is little or no sun to photolyze anything. (APGW p. 254)

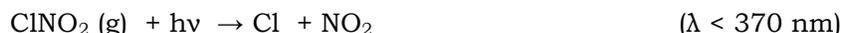
Stratospheric Denitrification by Winter Sedimentation

HNO_3 can adsorb to Type II PSC particles, which may then sediment out to lower regions of the stratosphere, resulting in stratospheric denitrification. This effects removes HNO_3 , reducing the tying-up of active Cl as inactive ClONO_2 . (APGW p. 255) This is shown by IAC to occur in July to September. The reactions that would otherwise take place if HNO_3 were still in good supply (and which would suppress O_3 loss), are:²⁸⁰

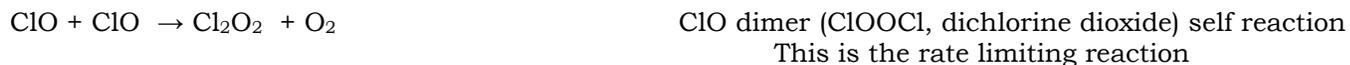


Release of Cl, Destruction of O_3 Begins, Buildup of ClO* (in the Spring)

When the sun finally comes up in the SH spring, accumulated Cl-containing gases such as Cl_2 begin to photolyze, releasing atomic Cl, and a catalytic cycle that destroys O_3 begins:



The chlorine radical immediately reacts with O_3 .



This sequence is the dimer mechanism, important in the spring (causing 70% of ozone loss), at which time ClO concentrations can build up so that the sequence proceeds rapidly. (APGW p. 255) It requires low NO_x .

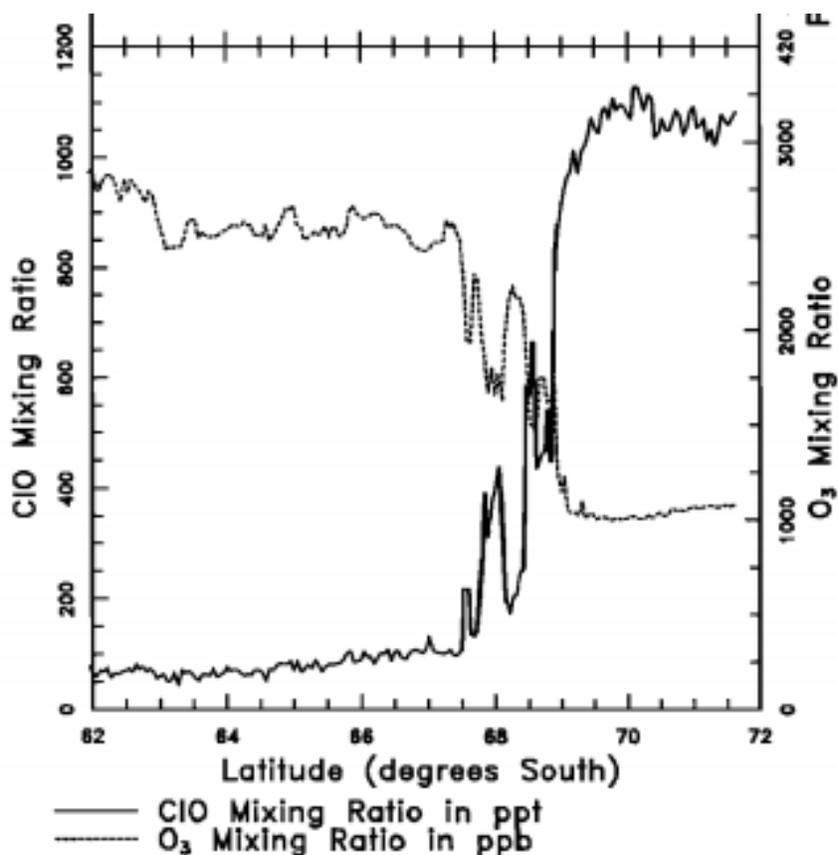
An alternate catalytic path of O_3 destruction (which accounts for about 30% of ozone loss)²⁸¹ reacts Cl and/or Br with O_3 and forms ClO and BrO, but does not include the ClO-dimer intermediate (details omitted).

The buildup of ClO anticorrelates with O_3 (when one rises, the other falls). This is documented by aircraft measurements (while flying at constant potential-temperature), which show an abrupt rise in ClO when crossing from outside to inside the polar vortex. (Here, the ClO is said to have attained a threshold value at which point dimerization accelerates.) O_3 falls with rising ClO.

²⁸⁰ <http://acmg.seas.harvard.edu/people/faculty/djj/book/> Jacob Chapter 10, p. 184-5

²⁸¹ <http://acmg.seas.harvard.edu/people/faculty/djj/book/> Jacob Chapter 10, p. 181, and APGW p. 255

The following is a representative summary from a flight 9/16/1987, starting at latitude 62° S on the left. By 70° S, after having crossed over the polar vortex, the ClO in pptv has sharply risen (upper curve on right) whereas O₃ in ppbv has correspondingly sharply dropped (lower curve on right):²⁸²



Ozone Depletion in the Spring

The Antarctic ozone hole is found in the SH spring, in September to November. Depletion is found to be near-total during October in what was earlier the layer of peak ozone over Antarctica, in the lower stratosphere from about 15 to 25 km (or 12 to 25 km per JAT).

²⁸² J. G. Anderson, et al, "Ozone destruction by chlorine radicals within the Antarctic vortex: The spatial and temporal evolution of ClO-O₃ anticorrelation based on in situ ER-2 data", *Journal of Geophysical Research: Atmospheres* (1984–2012) Volume 94, Issue D9, first publ. 20 August 1989.

The following diagram (similar to this²⁸³), shows the decline of stratospheric O₃ from a peak 8/21/1992 (date shown in DD/MM format as “21/8”) of 259 DU to a nadir 10/11/1992 (shown as “11/10”) of 105 DU:²⁸⁴

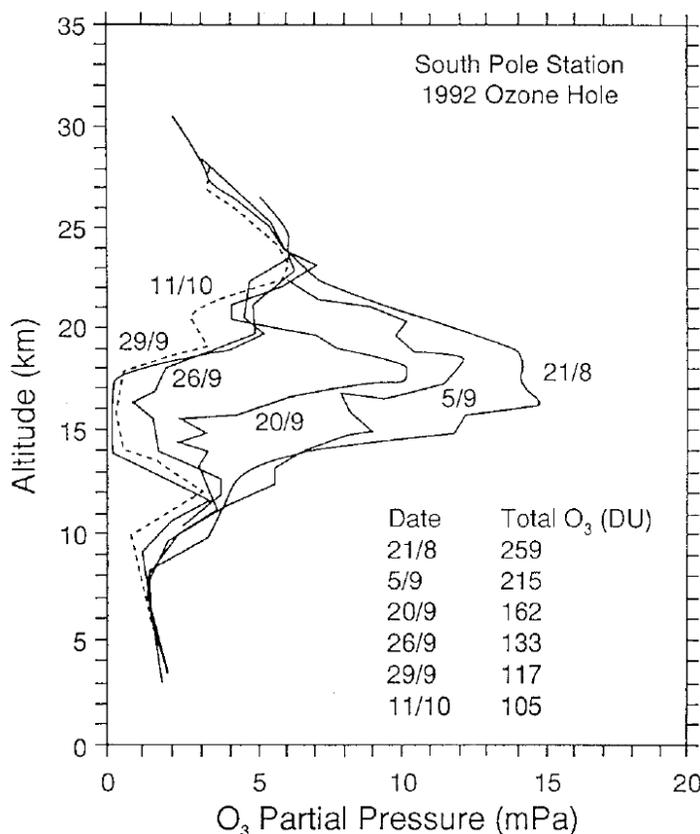


Figure 23. Ozone profiles measured above the South Pole in spring 1992 [Hofmann and Oltmans, 1993].

Resolution of the Ozone Hole in Late Spring (November)

In November, warming causes the polar vortex to break down, and the PSCs disappear. Ozone can then advect into the polar regions again and is regenerated as well, and the Antarctic hole dissipates.

Arctic Dents

The Arctic tends to be warmer than the Antarctic, because its surface is a thin layer of ice over a warmer liquid ocean rather than an icy high mountainous continent. This causes more thermal-IR to radiate back to the stratosphere, warming it. In addition, the polar vortex is weaker in the Arctic, so there is less reduction of meridional stratospheric mixing of O₃.

In the Arctic (NH) spring, the amount of ozone depletion is more variable year-to-year than in the Antarctic. The greatest Arctic O₃ declines, up to 30% [to values of 240-260 DU] are in the winter and spring, when the stratosphere is colder.²⁸⁵ The Arctic reduction, which does not drop below the hole-defining level of 220 DU, has been referred to as the Arctic ozone dent rather than a hole. In years for which the Arctic dent does not appear, it is thought that this is due to warmer conditions with a lack of PSC ice particle formation (which are

²⁸³ <http://acmg.seas.harvard.edu/people/faculty/djj/book/> Jacob Chapter 10 , fig 10-10

²⁸⁴ http://www.cee.mtu.edu/~reh/papers/pubs/non_Honrath/Staehelin01_1999RG000059.pdf, J. Staehelin, N. R. P. Harris et al, Ozone Trends: A Review, *Reviews of Geophysics*, 39, 2 / May 2001

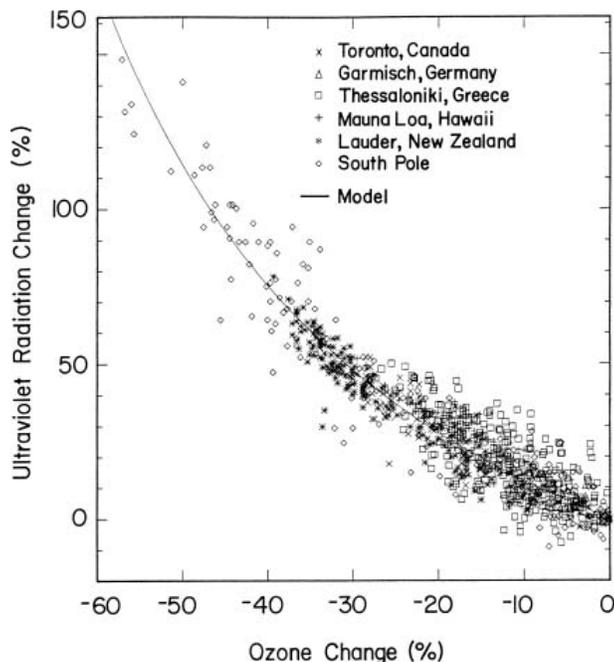
²⁸⁵ http://en.wikipedia.org/wiki/Ozone_depletion

needed for the surface reactions with chlorine and bromine).²⁸⁶ Ozone may actually be maximal near the pole in the spring (March to May) due to northward transport, descent, and accumulation (APGW p. 238).

Potential Health Effects

“The ozone hole over Antarctica has in some instances grown so large as to reach southern parts of Australia, New Zealand, Chile, Argentina, and South Africa...”,²⁸⁷ thus putting human populations at increased risk from UV exposure.

The decrease of UV absorption resulting from a decline in total ozone, with a resultant rise in injurious UV-B reaching the surface, is expressed by this graph (the data points have apparently been obtained over a number of years after 1980 and prior to 1998):



Increases in Erythematous (Sunburning) Ultraviolet Radiation [UV-B] Due to Ozone Decreases²⁸⁸

Comparing the 1970s to 1998, the increase in UV-B in 1998 was about 7% in the NH winter and spring mid-latitudes, 4% in the NH summer and fall mid-latitudes, 6% in the SH full year mid-latitudes, and 130% in the Antarctic spring. (APGW p. 245)

Surface UV in the SH improved slightly in 1999 to 2006. Reduction of atmospheric particulate air pollution in about the same period also caused a rise in surface UV in the NH. (APGW p. 245) However, the WHO states, “Estimating the resultant changes in actual ground-level ultraviolet radiation remains technically complex. However, exposures at northern mid-latitudes, for example, are likely to peak around 2020, with an estimated 10% increase in effective ultraviolet radiation relative to 1980s levels.”²⁸⁹

²⁸⁶ APGW p. 244

²⁸⁷ *ibid.*

²⁸⁸ <http://www.esrl.noaa.gov/csd/assessments/ozone/1998/faq8.html>

²⁸⁹ <http://www.who.int/globalchange/summary/en/index7.html>

The most recent²⁹⁰ available *Scientific Assessment of Ozone Depletion: 2010* report provided the following answer to their question 17, “Does depletion of the ozone layer increase ground-level ultraviolet radiation?”²⁹¹

In the first figure to follow, the effects of ozone changes are combined with effects on clouds and aerosols. The increases in erythemal UV radiation from 1979 to 2008 are seen to be greatest in mid and higher latitudes (the graphs do not extend poleward of about $\pm 55^\circ$). The maximum increase of about 6% is found at a SH latitude of about -55° :

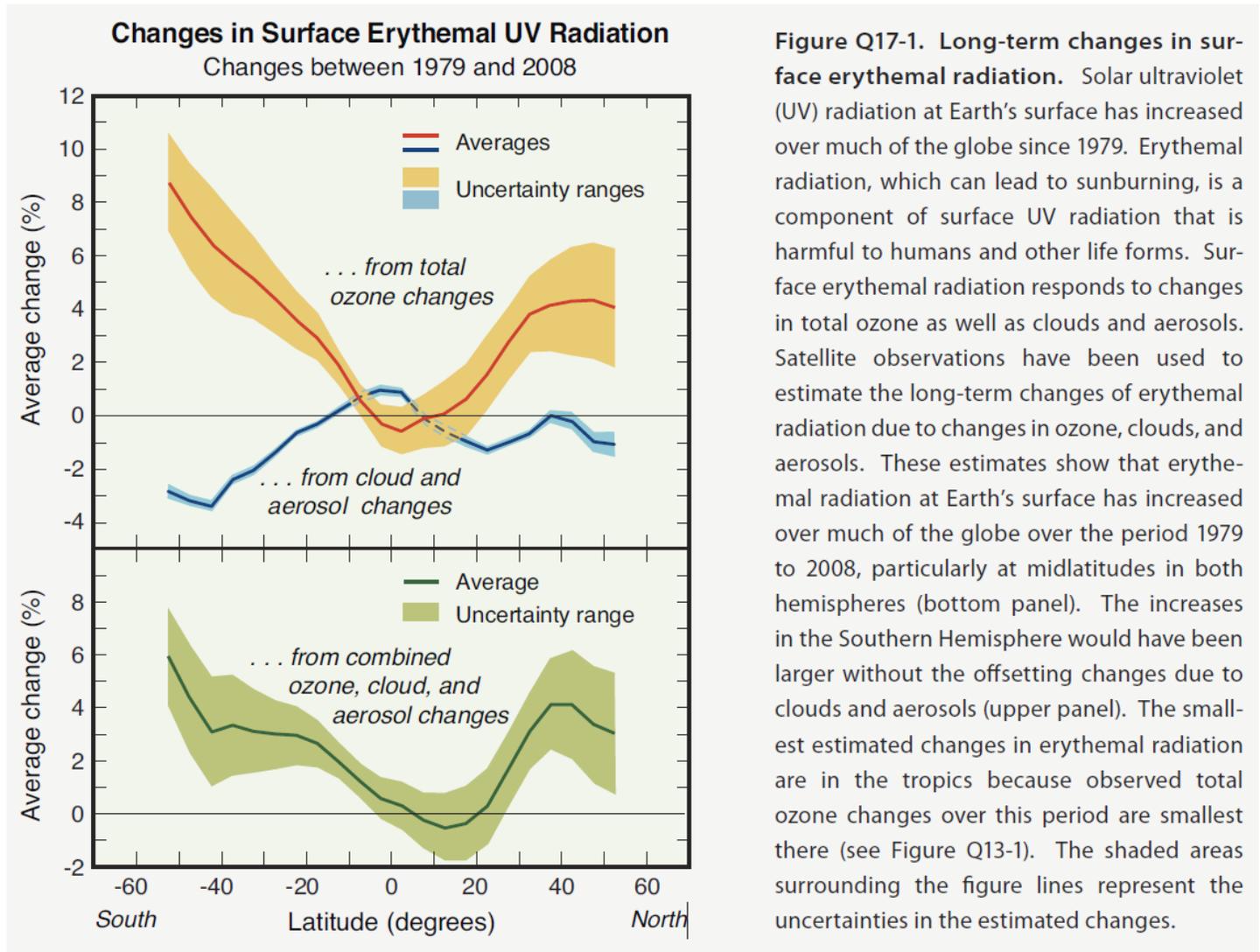


Figure Q17-1. Long-term changes in surface erythemal radiation. Solar ultraviolet (UV) radiation at Earth’s surface has increased over much of the globe since 1979. Erythemal radiation, which can lead to sunburning, is a component of surface UV radiation that is harmful to humans and other life forms. Surface erythemal radiation responds to changes in total ozone as well as clouds and aerosols. Satellite observations have been used to estimate the long-term changes of erythemal radiation due to changes in ozone, clouds, and aerosols. These estimates show that erythemal radiation at Earth’s surface has increased over much of the globe over the period 1979 to 2008, particularly at midlatitudes in both hemispheres (bottom panel). The increases in the Southern Hemisphere would have been larger without the offsetting changes due to clouds and aerosols (upper panel). The smallest estimated changes in erythemal radiation are in the tropics because observed total ozone changes over this period are smallest there (see Figure Q13-1). The shaded areas surrounding the figure lines represent the uncertainties in the estimated changes.

²⁹⁰ The 2014 full report is not yet available.

²⁹¹ <http://www.esrl.noaa.gov/csd/assessments/ozone/2010/twentyquestions/Q17.pdf>

In the following figure, a dramatic rise in UV index due to ozone depletion is apparent at Palmer Antarctica. There, spring UV index rose from formerly low levels to levels frequently higher than what are found in spring and summer in San Diego. (Values of UV Index in the mid-teens represent very strong UV light.)²⁹²

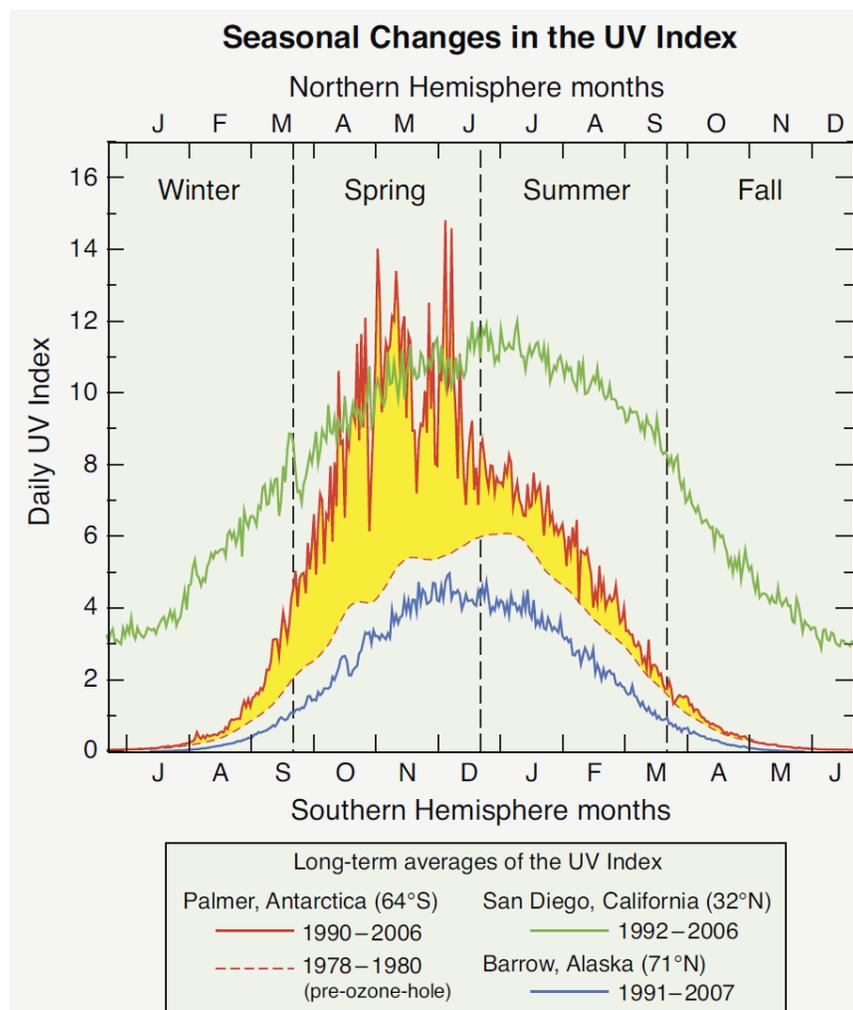


Figure Q17-2. Long-term changes in the UV Index. The UV Index is a measure of the erythemal radiation that reaches the surface at a particular location and time. Sunburning in humans is caused by erythemal radiation. The UV Index varies with total ozone above a location, as well as the Sun’s midday position in the local sky, which depends on latitude and season. The highest values of the UV Index occur in the tropics, where the midday Sun is highest throughout the year and where total ozone values are low. The lowest average UV Index values occur at high latitudes. The figure shows daily maximum UV Index values at several locations. Values are higher throughout the year in San Diego, a low-latitude location, than in Barrow, a high-latitude location. UV Index values are zero at high latitudes in winter when darkness is continuous. Measurements at Palmer, Antarctica, demonstrate the effect of Antarctic ozone depletion. Normal values estimated for Palmer are shown for 1978–1980, a period before the appearance of the “ozone hole” (see red dashed line). In the period 1990–2006, Antarctic ozone depletion increased the UV Index at Palmer throughout spring and into summer (see yellow shaded region). Springtime values at Palmer now routinely equal or exceed those measured in spring and summer in San Diego, which is located at much lower latitude.

the UV Index at Palmer throughout spring and into summer (see yellow shaded region). Springtime values at Palmer now routinely equal or exceed those measured in spring and summer in San Diego, which is located at much lower latitude.

²⁹² <http://www2.epa.gov/sunwise/calculating-uv-index>

The Greenhouse Effect, Global Warming, and Ocean Acidification

This topic is presented in *APGW* Chap. 12, published in 2012. *APGW* p. 287 asserts a warming rate of +1.3 °C per 100 years, during the period 1955 to 2010, as determined by land and ship measurements.

This summary also draws on the massive IPCC 2013-4 WG1 report which I have cited earlier and abbreviate as *IPCC_WGI_2013*. Global warming is indeed taking place. IPCC5 states, “The globally averaged combined land and ocean surface temperature data as calculated by a linear trend, show a warming of 0.85 [0.65 to 1.06] °C over the period 1880 to 2012, for which multiple independently produced datasets exist. The total increase between the average of the 1850–1900 period and the 2003–2012 period is 0.78 [0.72 to 0.85] °C, based on the single longest dataset available. For the longest period when calculation of regional trends is sufficiently complete (1901 to 2012), almost the entire globe has experienced surface warming”:²⁹³

1.1 Observed changes in the climate system

Warming of the climate system is unequivocal, and since the 1950s, many of the observed changes are unprecedented over decades to millennia. The atmosphere and ocean have warmed, the amounts of snow and ice have diminished, and sea level has risen.

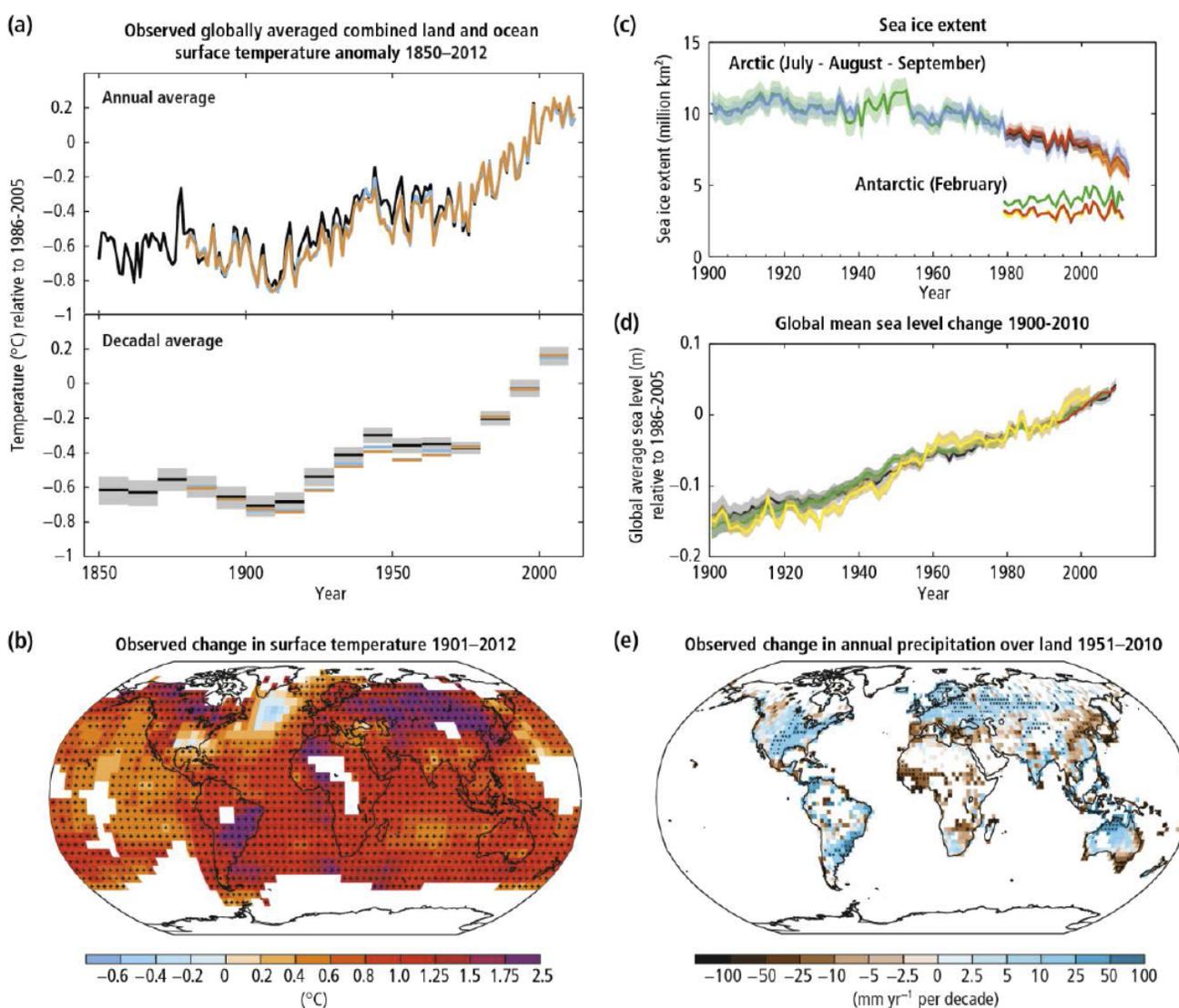


Figure (a) shows global warming. T is globally averaged over land and ocean and graphed with annual and with decadal averaging.

²⁹³ *IPCC_SR_2014* p. 37-38, including the figure above.

Figure (b) shows a “map of the observed surface temperature change, from 1901 to 2012, derived from temperature trends ... Grid boxes where the trend is significant, at the 10% level, are indicated by a + sign.” There is a preponderance of positive change in higher and polar latitudes, especially in the NH.

Figure (c) shows declining Arctic sea ice areal extent. “Over the last two decades, the Greenland and Antarctic ice sheets have been losing mass (high confidence). Glaciers have continued to shrink almost worldwide (high confidence). Northern Hemisphere spring snow cover has continued to decrease in extent (high confidence). There is high confidence that there are strong regional differences in the trend in Antarctic sea ice extent [area], with a very likely increase in total [areal] extent.” [The possible increase may be due to a miscalculation.²⁹⁴]

Figure (d) shows rising sea level of about 0.2 m since 1900. “Over the period 1901–2010, global mean sea level rose by 0.19 m [0.17 to 0.21] ... The rate of sea-level rise since the mid-19th century has been larger than the mean rate during the previous two millennia.”²⁹⁵

Overview of the Causes of the Greenhouse Effect and Global Warming

The **greenhouse effect** results from the effect of infrared-absorbing constituents in the atmosphere. Greenhouse gases, like greenhouse glass, allow passage of incoming (mostly visible) light with little absorption. Some of this light is absorbed at or near the surface causing warming. When the surface and near-surface atmosphere emit outgoing photons as thermal IR (a range defined as 4 to 1,000 μm), the greenhouse gases absorb some of the outgoing radiation in the troposphere, causing a **radiative forcing** that raises the temperatures of the surface and troposphere until a new radiative balance is achieved. (*IPCC_WGI_2013* p. 1455 and *APGW* p. 264)

Global Warming GW is the increase in Earth’s temperature (specifically the surface and troposphere) beyond the degree which is attributable to the natural greenhouse effect, and due to the presence of anthropogenic effects, including greenhouse gases and aerosols. GW of the surface and troposphere is accompanied by stratospheric cooling (see later figure). A GW component also arises at the surface and troposphere from certain anthropogenic aerosols and deposited **warming particles** (namely **black carbon BC** and **brown carbon BrC**). These absorb solar radiation and lead to further net warming, though not by greenhouse effect. Some BC and BrC occur naturally rather than anthropogenic ally (modified from *APGW* p. 263). The **urban heat island effect** also contributes minimally (≤ 0.1 °C) to global warming. (*APGW* p. 271, 288) Other aerosols are called **cooling particles** because they offset some of the overall warming effects.

Changes in internal variability are on the order of ± 0.3 °C maximally. (*APGW* p. 288)

Feedbacks and Indirect Effects

A variety of feedbacks and indirect effects potentially affecting climate are discussed in *APGW* (p. 289-294) but details are omitted here. These must be analyzed by computer modeling. Topics include:

Positive Feedbacks of Gases to Climate (*APGW* p. 289)

- Water-vapor-temperature-rise feedback
- Snow-albedo feedback
- Water-vapor-high-cloud feedback
- Solubility-carbon dioxide feedback
- Saturation-vapor-pressure-water-vapor feedback
- Bacteria-carbon-dioxide feedback
- Permafrost-methane feedback

Negative Feedbacks of Gases to Climate

- Water-vapor-low-cloud feedback
- Plant-carbon-dioxide feedback

Effects of Aerosol Particles on Climate (*APGW* p. 290)

²⁹⁴ <http://news.sciencemag.org/climate/2014/07/has-expansion-antarctic-sea-ice-accelerated>

²⁹⁵ *IPCC_SR_2014* p. 40

- Daytime stability effect (heated air is more stable)
- Smudge-pot effect (aerosol traps thermal IR)
- Indirect effects on clouds
- Semi-direct Effect (reduced cloud cover increases surface warming)
- Cloud absorption effect (aerosol between versus within liquid water-droplets)
- Effect of airborne absorbing particles on surface albedo
- Snow darkening effect
- Self-feedback effect
- Photochemistry effect (aerosols intercept UV, altering photolysis)
- Particle effect through large-scale meteorology
- Rainout effect

Main drivers of global warming

The main drivers of global warming and balance of incoming shortwave sunlight (SWR, $\lambda < 4 \mu\text{m}$, mostly visible) and outgoing longwave radiation (LWR, $\lambda > 4 \mu\text{m}$, mostly thermal IR) are depicted qualitatively as follows (IPCC_WGI_2013 p. 126):

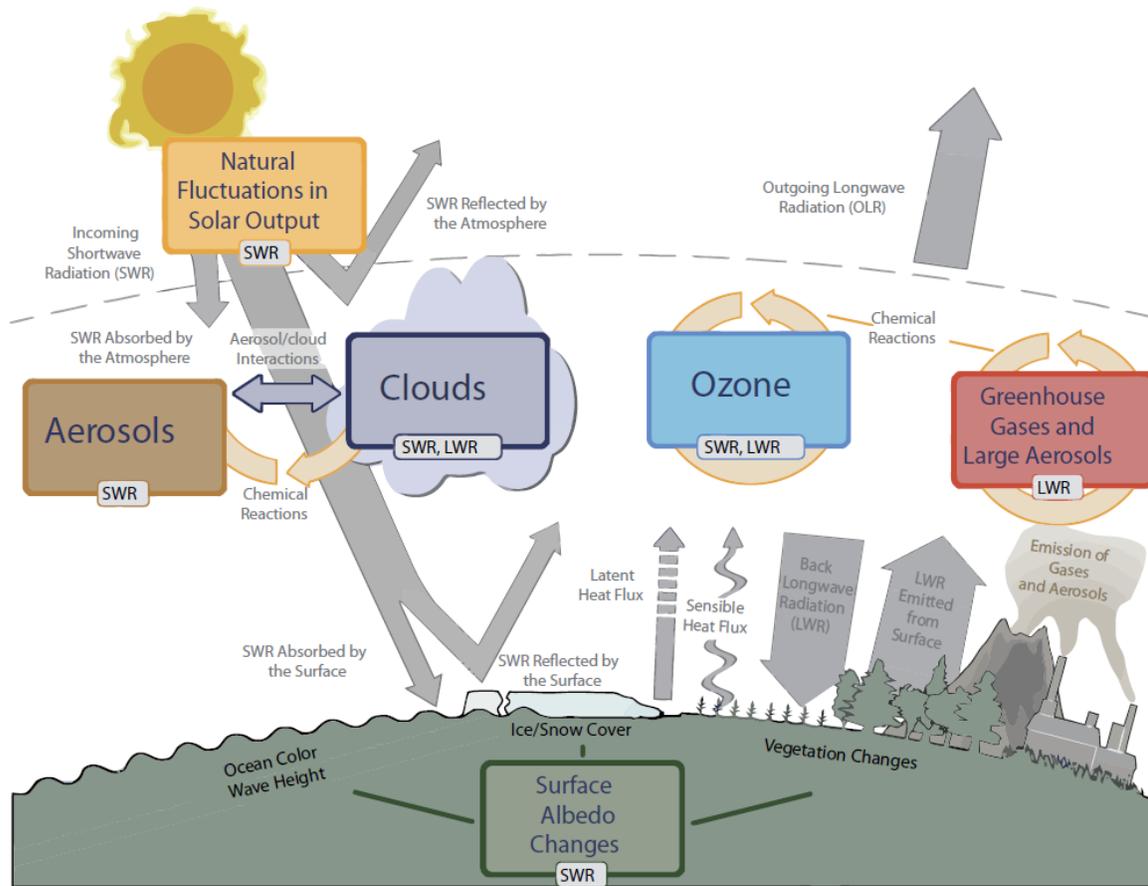


Figure 1.1 | Main drivers of climate change. The radiative balance between incoming solar shortwave radiation (SWR) and outgoing longwave radiation (OLR) is influenced by global climate 'drivers'. Natural fluctuations in solar output (solar cycles) can cause changes in the energy balance (through fluctuations in the amount of incoming SWR) (Section 2.3). Human activity changes the emissions of gases and aerosols, which are involved in atmospheric chemical reactions, resulting in modified O_3 and aerosol amounts (Section 2.2). O_3 and aerosol particles absorb, scatter and reflect SWR, changing the energy balance. Some aerosols act as cloud condensation nuclei modifying the properties of cloud droplets and possibly affecting precipitation (Section 7.4). Because cloud interactions with SWR and LWR are large, small changes in the properties of clouds have important implications for the radiative budget (Section 7.4). Anthropogenic changes in GHGs (e.g., CO_2 , CH_4 , N_2O , O_3 , CFCs) and large aerosols ($>2.5 \mu\text{m}$ in size) modify the amount of outgoing LWR by absorbing outgoing LWR and re-emitting less energy at a lower temperature (Section 2.2). Surface albedo is changed by changes in vegetation or land surface properties, snow or ice cover and ocean colour (Section 2.3). These changes are driven by natural seasonal and diurnal changes (e.g., snow cover), as well as human influence (e.g., changes in vegetation types) (Forster et al., 2007).

The quantitative energy flows and balance in W m^{-2} are estimated in the following diagram (*IPCC_WGI_2013* p. 181):

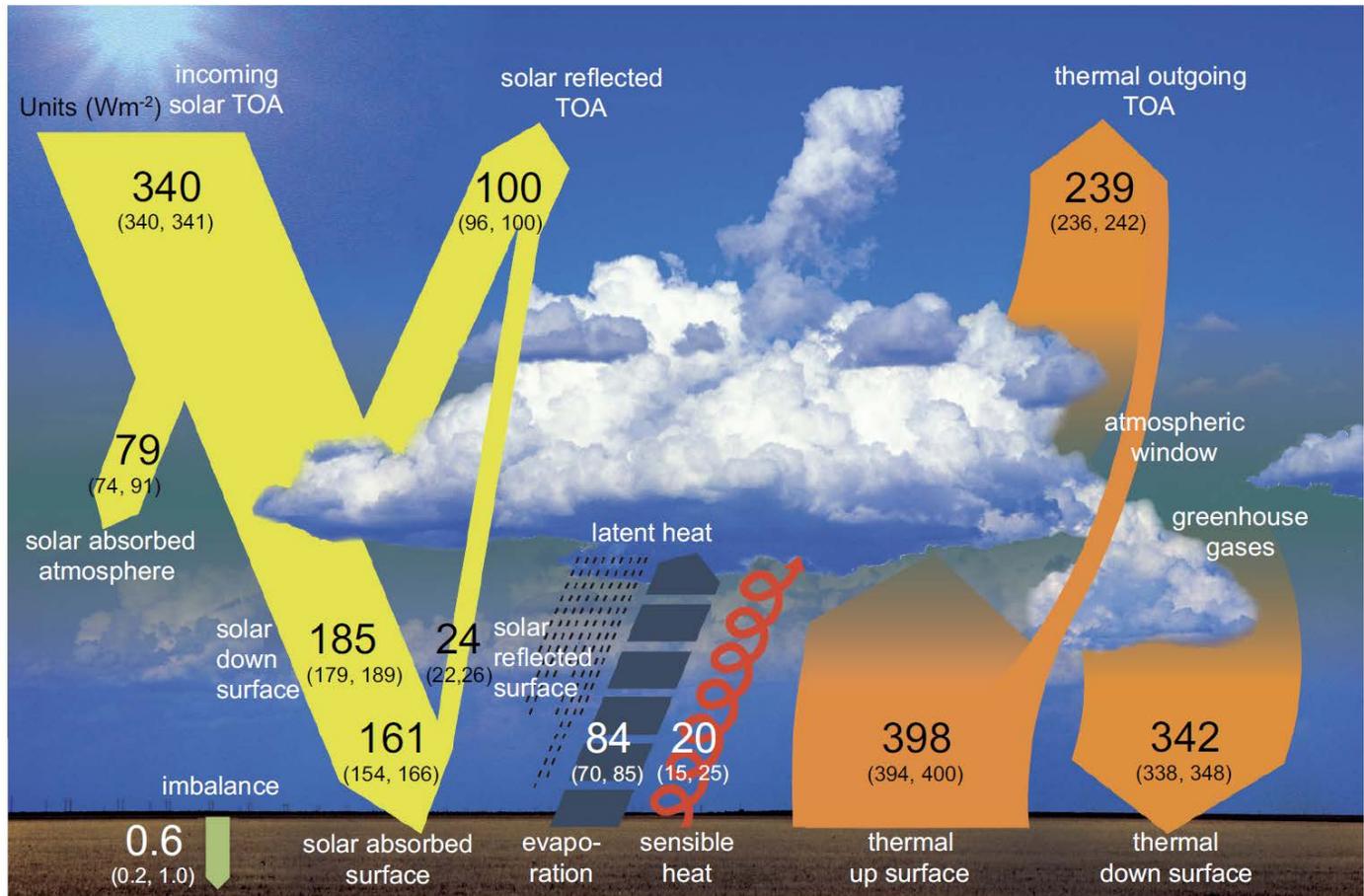


Figure 2.11: | Global mean energy budget under present-day climate conditions. Numbers state magnitudes of the individual energy fluxes in W m^{-2} , adjusted within their uncertainty ranges to close the energy budgets. Numbers in parentheses attached to the energy fluxes cover the range of values in line with observational constraints. (Adapted from Wild et al., 2013.)

Here, *TOA* is the top of the atmosphere (beyond any effect of the atmosphere). *Sensible heat* was termed *thermals* in 2007. *Latent heat* is released when water vapor condenses, as in clouds. *Evaporation* is actually evapotranspiration, and includes water evaporated in transpiration by plants. *Thermal up surface* is thermal IR [LWR] radiated upward from the surface. This diagram shows that incoming light energy [SWR], allowing for reflection still as SWR, is about 240 W m^{-2} , and outgoing thermal energy LWR is 239 W m^{-2} , thus they are nearly in balance within the error limits.

Radiative forcing RF is defined by IPCC5 as “the change in the net, downward minus upward [thus positive downward], radiative flux (expressed in W m^{-2}) at the tropopause or top of atmosphere due to a change in an external driver of climate change, such as, for example, a change in the concentration of carbon dioxide or the output of the Sun. Sometimes internal drivers are still treated as forcings even though they result from the alteration in climate, for example aerosol or greenhouse gas changes in paleoclimates. The traditional radiative forcing is computed with all [surface and] tropospheric properties held fixed at their unperturbed values, and after allowing for stratospheric temperatures, if perturbed, to readjust to radiative-dynamical equilibrium. Radiative forcing is called instantaneous if no change in stratospheric temperature is accounted for. The radiative forcing once rapid adjustments are accounted for is termed the **effective radiative forcing [ERF]**. For the purposes of this report, radiative forcing is further defined as the change relative to the year 1750 and, unless otherwise noted, refers to a global and annual average value...” (*IPCC_WGI_2013* p. 1460)

Radiative Forcing is further described (*IPCC_WGI_2013* p.13), “In the traditional RF concept employed in previous IPCC reports all surface and tropospheric conditions are kept fixed. In calculations of RF for well-mixed greenhouse gases and aerosols in this [IPCC5] report, physical variables, except for the ocean and sea ice, are allowed to respond to perturbations with rapid adjustments. The resulting forcing is called **Effective Radiative Forcing (ERF)** in the underlying report. This change reflects the scientific progress from previous

assessments and results in a better indication of the eventual temperature response for these drivers. For all drivers other than well-mixed greenhouse gases and aerosols, rapid adjustments are less well characterized and assumed to be small, and thus the traditional RF is used.” The ERF is estimated (in the figure²⁹⁶ below) for years 1950, 1980, and 2011, all compared to year 1750.

The positive RF of BC, the effect of which is emphasized in *APGW*, is shown in the upcoming figure SPM.5 to be offset by negative RF of other aerosol components. NMVOC = non-methane volatile organic compounds. Land use is primarily permanent deforestation.

Quantitation of the *drivers* leading to GW are enumerated in this graphic for the leading emissions and drivers (*IPCC_WGI_2013* p. 14):

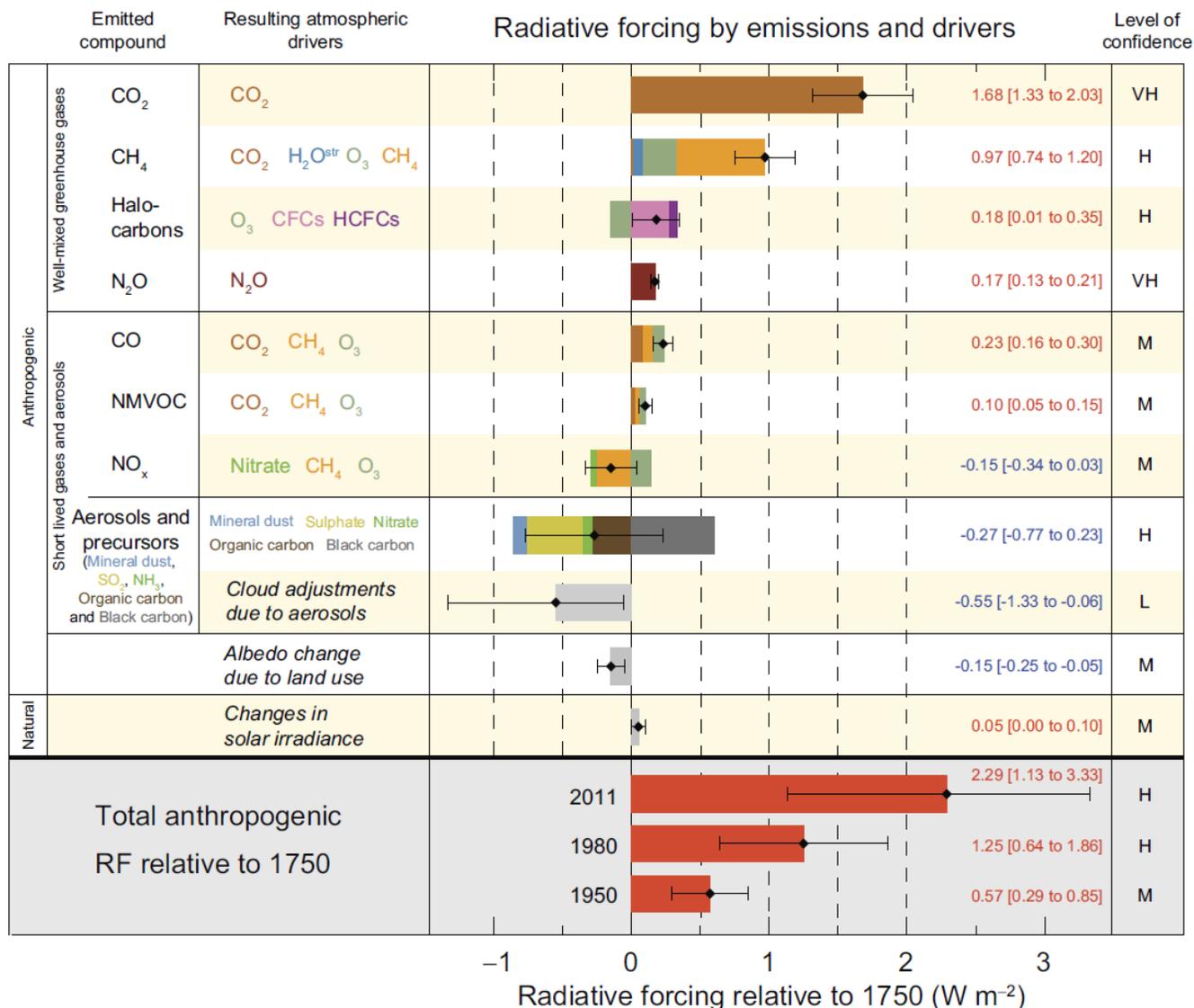


Figure SPM.5 | Radiative forcing estimates in 2011 relative to 1750 and aggregated uncertainties for the main drivers of climate change. Values are global average radiative forcing (RF¹⁴), partitioned according to the emitted compounds or processes that result in a combination of drivers. The best estimates of the net radiative forcing are shown as black diamonds with corresponding uncertainty intervals; the numerical values are provided on the right of the figure, together with the confidence level in the net forcing (VH – very high, H – high, M – medium, L – low, VL – very low). Albedo forcing due to black carbon on snow and ice is included in the black carbon aerosol bar. Small forcings due to contrails (0.05 W m⁻², including contrail induced cirrus), and HFCs, PFCs and SF₆ (total 0.03 W m⁻²) are not shown. Concentration-based RFs for gases can be obtained by summing the like-coloured bars. Volcanic forcing is not included as its episodic nature makes it difficult to compare to other forcing mechanisms. Total anthropogenic radiative forcing is provided for three different years relative to 1750. For further technical details, including uncertainty ranges associated with individual components and processes, see the Technical Summary Supplementary Material. {8.5; Figures 8.14–8.18; Figures TS.6 and TS.7}

²⁹⁶ *IPCC_WGI_2013* p. 14
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Future Consequences and What to Do About GW

These are substantial and dire (APGW p. 294-301), but I will include only some summary statements.

IPCC5 is cautious in its conclusions:

“Evidence of observed climate-change impacts is strongest and most comprehensive for natural systems. In many regions, changing precipitation or melting snow and ice are altering hydrological systems, affecting water resources in terms of quantity and quality (medium confidence). Many terrestrial, freshwater, and marine species have shifted their geographic ranges, seasonal activities, migration patterns, abundances, and species interactions in response to ongoing climate change (high confidence). Some impacts on human systems have also been attributed to climate change, with a major or minor contribution of climate change distinguishable from other influences... Assessment of many studies covering a wide range of regions and crops shows that negative impacts of climate change on crop yields have been more common than positive impacts (high confidence). Some impacts of ocean acidification on marine organisms have been attributed to human influence (medium confidence)...

Changes in many extreme weather and climate events have been observed since about 1950. Some of these changes have been linked to human influences, including a decrease in cold temperature extremes, an increase in warm temperature extremes, an increase in extreme high sea levels and an increase in the number of heavy precipitation events in a number of regions...

Continued emission of greenhouse gases will cause further warming and long-lasting changes in all components of the climate system, increasing the likelihood of severe, pervasive and irreversible impacts for people and ecosystems. Limiting climate change would require substantial and sustained reductions in greenhouse gas emissions which, together with adaptation, can limit climate change risks.”²⁹⁷

Adverse Effects of Special Importance to Me:

These include rising or worsening of the following:

- high latitude and glacial ice loss, with adverse impacts on certain animals (polar bears) and indigenous peoples
- infectious disease
- heat stress, including from CO₂ domes
- lowland flooding, including island nations such as Tuvulu
- air pollution and mortality (from O₃, CO, BC)
- the effects of ocean acidification. This is especially troubling because it causes coral destruction and damage to shellfish including important food species, and is part of the mass extinction we are causing. Dissolved CO₂ in the oceans has caused falling ocean pH (acidification), from ~8.25 in 1750 to ~8.13 in 2000. (APGW p. 297)

What Should We Do?

I omit discussion of possible methods of slowing GW. Although drastic CO₂ emission reduction is needed long-term, Jacobson favors in the short term the controlling of soot BC aerosols, something which could have significant and rapid beneficial effects. (APGW p. 305)

Details of GW Science

Some of the fascinating details of the science behind GW are presented to follow.

Natural Versus Anthropogenic Greenhouse Effect

Greenhouse gases are those gaseous constituents of the atmosphere (both natural and anthropogenic), that are largely transparent to visible light but that absorb and re-emit the Earth's thermal IR at specific wavelengths. Water vapor (H₂O), carbon dioxide (CO₂), nitrous oxide (N₂O), methane (CH₄) and ozone (O₃) are the primary greenhouse gases in the Earth's atmosphere. Moreover, there are a number of mostly or entirely human-made greenhouse gases in the atmosphere—these include halocarbons and other chlorine- and

²⁹⁷ IPCC_SR_2014 p. 6-8

bromine-containing substances, sulfur hexafluoride (SF₆), hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs). (*IPCC_WGI_2013* p. 1455)

The current 2011 concentrations and radiative forcing for well-mixed greenhouse gases WMGHGs (thus excluding water vapor H₂O, O₃, and BC) are given by the *IPCC_WGI_2013* p. 678 as:

Table 8.2 | Present-day mole fractions (in ppt(pmol mol⁻¹) except where specified) and RF (in W m⁻²) for the WMGHGs. Concentration data are averages of National Oceanic and Atmospheric Administration (NOAA) and Advanced Global Atmospheric Gases Experiment (AGAGE) observations where available. CO₂ concentrations are the average of NOAA and SIO. See Table 2.1 for more details of the data sources. The data for 2005 (the time of the AR4 estimates) are also shown. Some of the concentrations vary slightly from those reported in AR4 owing to averaging different data sources. Radiative efficiencies for the minor gases are given in Table 8.A.1. Uncertainties in the RF for all gases are dominated by the uncertainties in the radiative efficiencies. We assume the uncertainties in the radiative efficiencies to be perfectly correlated between the gases, and the uncertainties in the present day and 1750 concentrations to be uncorrelated.

Species	Concentrations (ppt)		Radiative forcing ^a (W m ⁻²)	
	2011	2005	2011	2005
CO ₂ (ppm)	391 ± 0.2	379	1.82 ± 0.19	1.66
CH ₄ (ppb)	1803 ± 2	1774	0.48 ± 0.05	0.47 ^e
N ₂ O (ppb)	324 ± 0.1	319	0.17 ± 0.03	0.16
CFC-11	238 ± 0.8	251	0.062	0.065
CFC-12	528 ± 1	542	0.17	0.17
CFC-13	2.7		0.0007	
CFC-113	74.3 ± 0.1	78.6	0.022	0.024
CFC-115	8.37	8.36	0.0017	0.0017
HCFC-22	213 ± 0.1	169	0.0447	0.0355
HCFC-141b	21.4 ± 0.1	17.7	0.0034	0.0028
HCFC-142b	21.2 ± 0.2	15.5	0.0040	0.0029
HFC-23	24.0 ± 0.3	18.8	0.0043	0.0034
HFC-32	4.92	1.15	0.0005	0.0001
HFC-125	9.58 ± 0.04	3.69	0.0022	0.0008
HFC-134a	62.7 ± 0.3	34.3	0.0100	0.0055
HFC-143a	12.0 ± 0.1	5.6	0.0019	0.0009
HFC-152a	6.4 ± 0.1	3.4	0.0006	0.0003
SF ₆	7.28 ± 0.03	5.64	0.0041	0.0032
SO ₂ F ₂	1.71	1.35	0.0003	0.0003
NF ₃	0.9	0.4	0.0002	0.0001
CF ₄	79.0 ± 0.1	75.0	0.0040	0.0036
C ₂ F ₆	4.16 ± 0.02	3.66	0.0010	0.0009
CH ₃ CCl ₃	6.32 ± 0.07	18.32	0.0004	0.0013
CCl ₄	85.8 ± 0.8	93.1	0.0146	0.0158
CFCs			0.263 ± 0.026 ^b	0.273 ^c
HCFCs			0.052 ± 0.005	0.041
Montreal gases ^d			0.330 ± 0.033	0.331
Total halogens			0.360 ± 0.036	0.351 ^f
Total			2.83 ± 0.029	2.64

Comparison with 2005 shows how

In the following table from APGW p. 269 and its PowerPoint,²⁹⁸ the contributions to natural greenhouse temp change and to anthropogenic global warming temperature change (beyond natural greenhouse) are listed.

Estimated Global Warming Due to Different Gases and Particles

Chemical	Percent Natural Greenhouse Effect Due to Chemical	Percent Global Warming Due to Chemical
H ₂ O(g)	88.9	0.4
CO ₂ (g)	7.5	46.5
Black carbon (S)	0.2	17
CH ₄ (g)	0.5	14
O ₃ (g)	1.1	11
N ₂ O(g)	1.5	4.2
CH ₃ Cl(g)	0.3	~0
CFCL ₃ (g)	0	1.8
CF ₂ Cl ₂ (g)	0	4.2
CF ₂ ClH(g)	0	0.6
CCl ₄ (g)	0	0.3

Table 12.3

This listing includes non-well-mixed gases such as H₂O and O₃, as well as black carbon BC and CH₃Cl, etc., which are not listed in the IPCC table above. Note that water vapor provides most of the natural greenhouse effect (89%), and there is a modest effect from natural CO₂ (8%). However, Jacobson states that **the leading causes of anthropogenic near-surface global warming is CO₂ at 47%, followed by BC at 17%** (black carbon soot particles prob. also including BrC soot), **methane at 14%, O₃ at 11%, and N₂O at 4.2%**. Anthropogenic water vapor has little effect on GW, but despite complex interactions (heating causes more evaporation and cloud formation etc.), its net effect is mild warming. Several gases, including CH₄, N₂O, and CFCl₃, are much more efficient, molecule for molecule, at causing global warming compared to CO₂, but the effect depends on mixing ratio as well as intrinsic global warming potential GWP.

BrC does not appear explicitly in this table, but is probably lumped with BC. BC absorbs all wavelengths, and BrC absorbs UV and short λ visible light, thus they warm the air by direct absorption of incoming light rather than by the greenhouse mechanism. BC in small amounts and BrC arise naturally from forest fires, but are also anthropogenic. (APGW p. 269) **Cooling particles**, such as sulfate, nitrate, chloride, etc. partially offset the multiple causes of global warming, and thus mask part of the warming effect. Aerosol particles also contribute to air pollution mortality.

It appears that IPCC5 does not agree with Jacobson that aerosols including BC are net positive causes of global warming (see earlier figure). Their global emissions are slowly rising. (APGW p. 275)

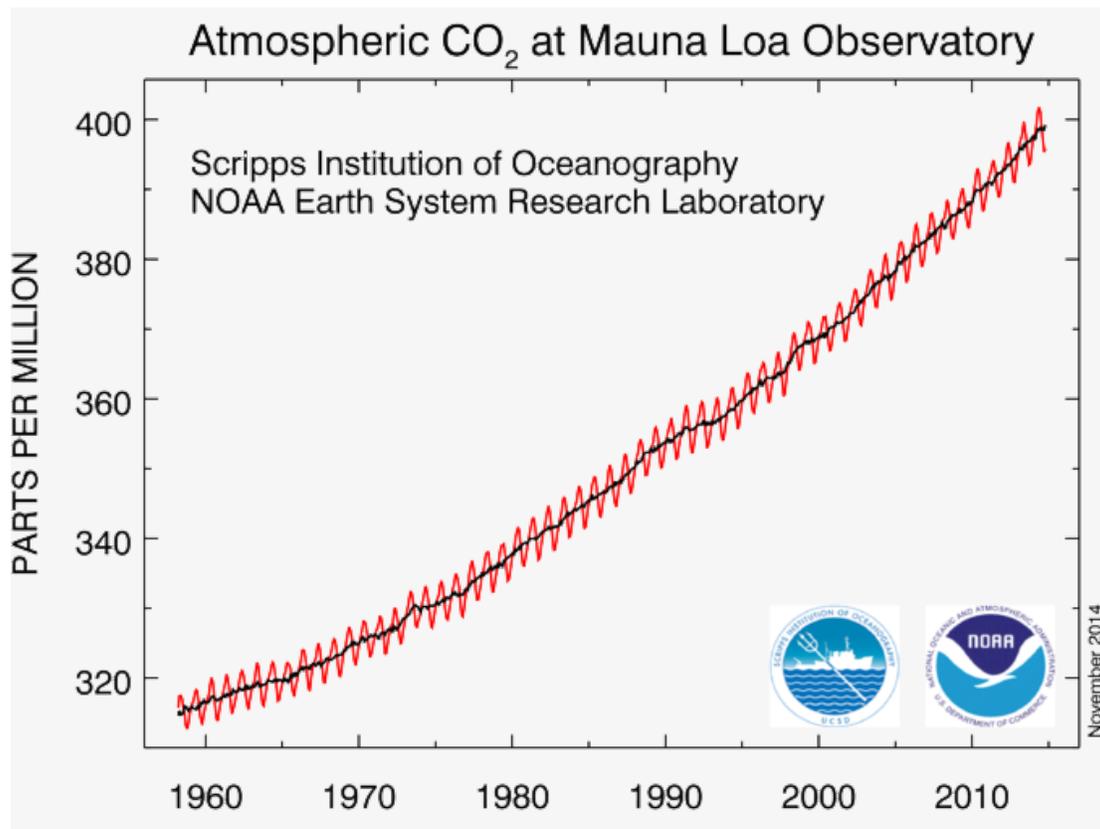
Several greenhouse gases are on the rise, including CO₂, CH₄, N₂O, and a mixture of halogenated hydrocarbons .

Global Distribution of CO₂ and Timeline (Keeling Curve)

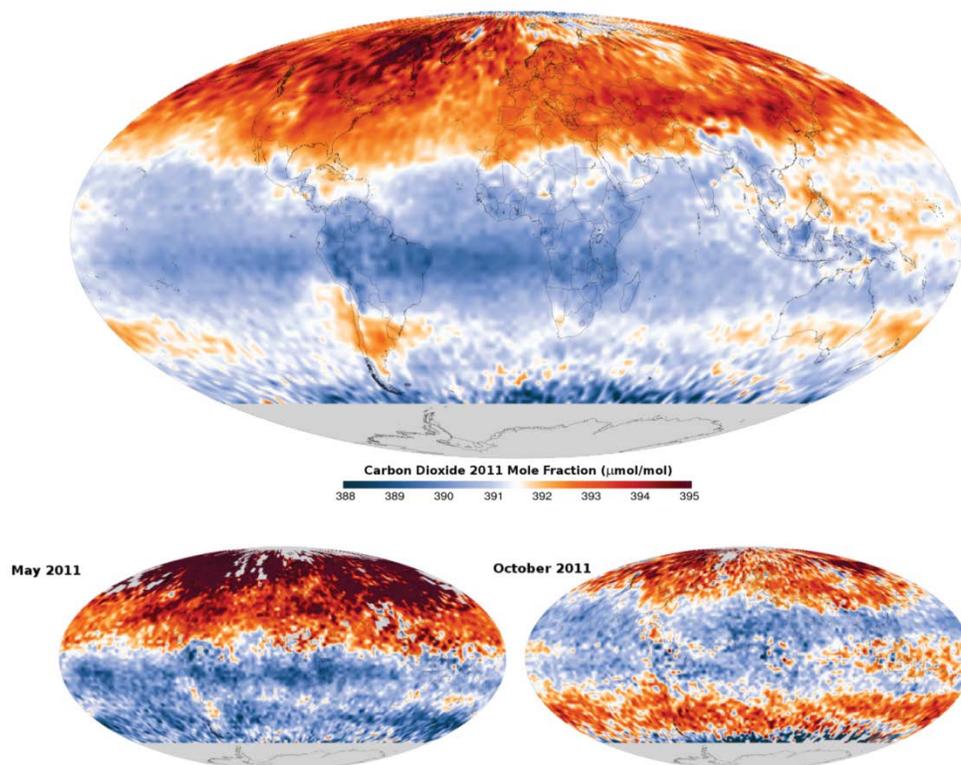
The following graph²⁹⁹ depicts the steady rising of CO₂ since 1980 (the Keeling curve from Mauna Loa Observatory, including superimposed seasonal oscillations):

²⁹⁸ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/APGWCh12Figs.pptx>

²⁹⁹ <http://www.esrl.noaa.gov/gmd/ccgg/trends/>



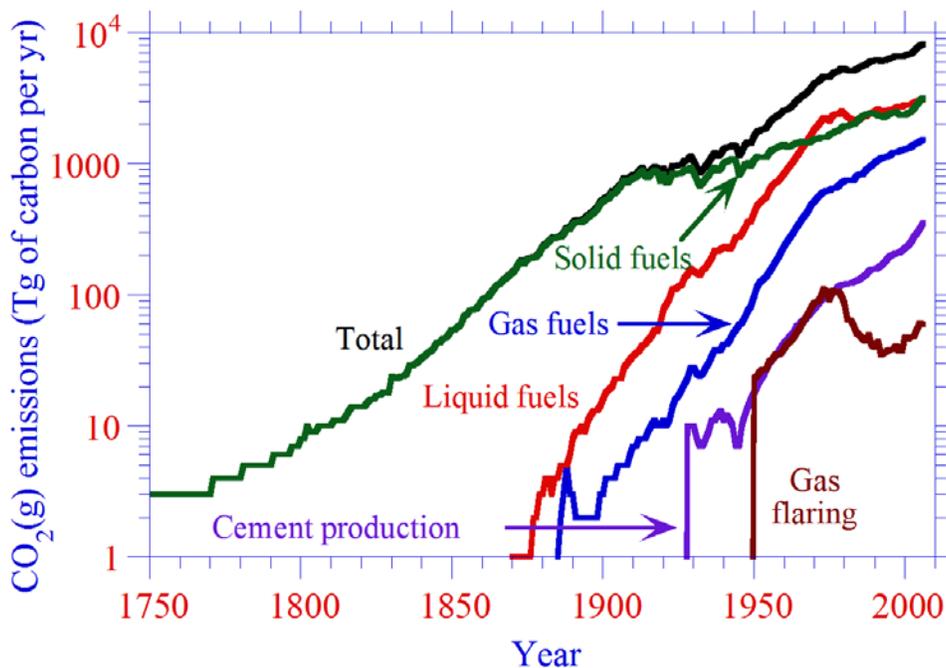
The predominance of CO₂ emission in the Northern Hemisphere is seen in this graph:³⁰⁰



³⁰⁰ http://en.wikipedia.org/wiki/Carbon_dioxide_in_Earth%27s_atmosphere
Page 117 of 141

The following semi-log graph shows the relative contributions of several sources of CO₂ emissions. Historically, this used to be mainly coal and wood (solid fuel), but gaseous (methane, propane, etc.) and liquid fuels (gasoline, diesel, etc.) have risen substantially, and contributions from gas flaring (during oil production) and cement production are also apparent.³⁰¹

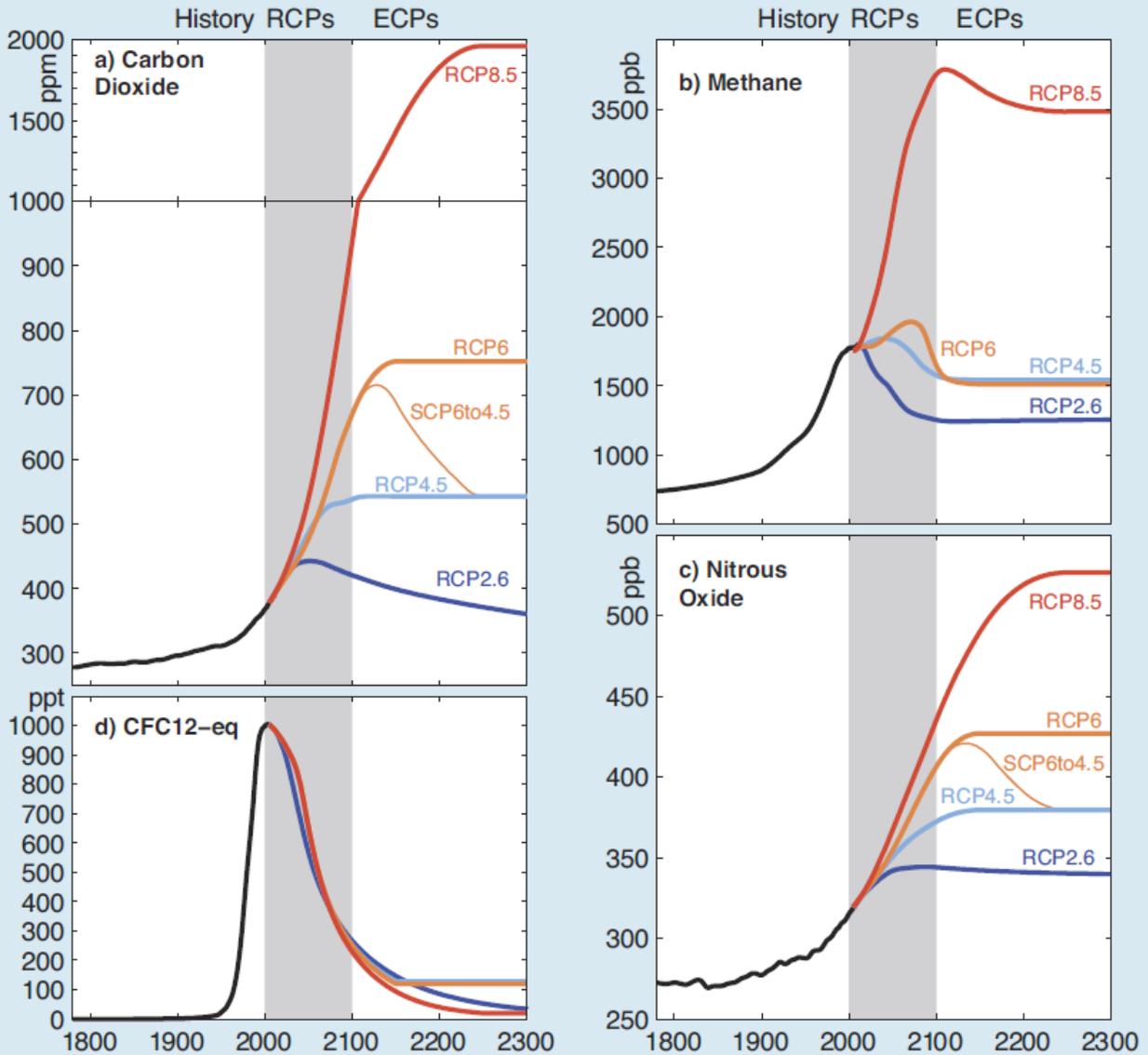
Carbon Dioxide Emission 1750-2008



Other Rising Greenhouse Gases

The following figures show a 200+ year history of rising mixing ratios of CO₂, Methane, N₂O and CFC-12 equivalent (Freon, CCl₂F₂). They also include projections of future trends according to various Representative Concentration Pathway Scenarios RCPs. (*IPCC_WGL_2013* p. 148, see also *APGW* p. 272):

³⁰¹ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/APGWCh12Figs.pptx> fig. 12.9



Box 1.1, Figure 2 | Concentrations of GHG following the 4 RCPs and their extensions (ECP) to 2300. (Reproduced from Figure 5 in Meinshausen et al, 2011.) Also see Annex II Table AII.4.1 for CO₂, Table AII.4.2 for CH₄, Table AII.4.3 for N₂O.

Black Carbon, though not a GHG, is an important contributor to GW, and its emissions have risen substantially from 1850 to 2005. (APGW p. 274-5)

SO₂, which contributes to cooling aerosols, has remained relatively stable in overall emissions 1970 to 2005. (APGW p. 274-5)

The following figure³⁰² depicts another way of presenting the rise in major greenhouse gases, in this case each GHG being expressed quantitatively in CO₂ equivalent values emitted annually.

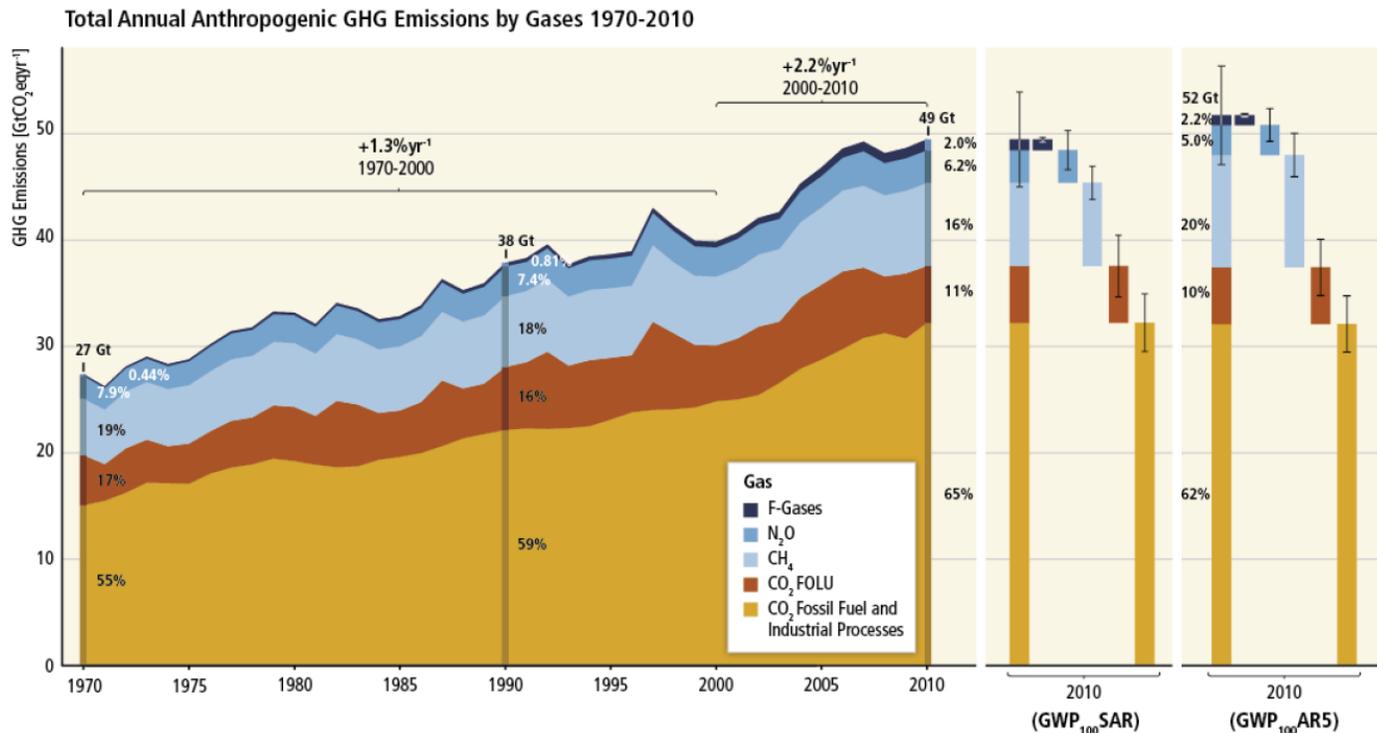


Figure SPM.2: Total annual anthropogenic greenhouse gas (GHG) emissions (gigatonne of CO₂-equivalent per year, GtCO₂-eq/yr) for the period 1970 to 2010 by gases: CO₂ from fossil fuel combustion and industrial processes; CO₂ from Forestry and Other Land Use (FOLU); methane (CH₄); nitrous oxide (N₂O); fluorinated gases covered under the Kyoto Protocol (F-gases). Right hand side shows 2010 emissions, using alternatively CO₂-equivalent emission weightings based on Second Assessment Report (SAR) and AR5 values. Unless otherwise stated, CO₂-equivalent emissions in this report include the basket of Kyoto gases (CO₂, CH₄, N₂O as well as F-gases) calculated based on 100-year Global Warming Potential (GWP₁₀₀) values from the SAR (see Glossary). Using the most recent 100-year Global Warming Potential values from the AR5 (right-hand bars) would result in higher total annual greenhouse gas emissions (52 GtCO₂-eq/yr) from an increased contribution of methane, but does not change the long-term trend significantly. {Figure 1.6, Box 3.2}

Here, SAR = IPCC Second Assessment Report (IPCC2) and AR5 is the current generation of reporting (IPCC5). The graphs show CO₂-equivalent emissions (GtCO₂-eq /yr) using weightings based on the 100 year Global Warming Potentials, using IPCC Second Assessment Report values. The columns of percentages add to 100%. The interval % values at the top (1.3 % /yr and 2.2% /yr) express the annual increase in GHG emissions. It is apparent that emissions are increasing annually, and that the rate of GHG emission has accelerated, at least since 2000.

Astronomical Factors Affecting Hemispheric and Global Temperatures

Seasonal Changes

The overall rate of heating of the Earth depends on its distance from the Sun, and follows the inverse square of distance relationship. The Earth is at a maximal distance and receives the least overall heating in the NH summer. Despite this, the NH is warmer in June than in December because

- (1) the 23.5° obliquity of the Earth's rotational axis with respect to the plane of its orbit about the Sun causes NH summer rays to be more directly overhead and therefore to provide stronger NH heating.
- (2) Days are longer in NH summer, providing longer heating (also arising from the 23.5° obliquity).

(3) Time in NH from vernal equinox to autumnal equinox (4479 h) is longer than NH time from autumnal equinox to vernal equinox (4292 h), a difference of about 8 days, due to the elliptical orbit. (APGW p. 264-5 and 2014-2105 equinox values)³⁰³

Changes in Total Solar Irradiance

See later.

Long-term Milankovitch cycles

These are not responsible for rapid anthropogenic global warming, but do appear to correlate with cyclical paleoclimatic changes.

The Milankovitch cycles result from

- (1) Variation in the eccentricity of Earth's orbit about the Sun (period ~100,000 y)
- (2) Variation in the obliquity of Earth's axis of rotation (period ~41,000 y)
- (3) Precession of the Earth's axis of rotation (period ~22,000 y)

The Milankovitch cycles explain most of the cyclical periodic variation in trapped CH₄, trapped CO₂, and T (measured by δ¹⁸O or δD as seen in Vostok Antarctica ice and deep ocean cores), and correlate with glacial and interglacial periods where adequate data is available.

Equilibrium and Observed Mean Temperature of Earth

Imperfect Black Body Radiator and Kirchhoff's Law

For an imperfect black body radiator (Jacob says "all objects"), the emission spectrum is related to the absorption spectrum by Kirchhoff's Law. (This applies only to a material body in thermodynamic equilibrium, including radiative exchange equilibrium.)³⁰⁴

$$\varphi_{\lambda}(T) = \varepsilon_{\lambda}(T)\varphi_{\lambda}^b(T)$$

where $\varphi_{\lambda}(T)$ = radiation flux as a function of T and wavelength λ

ε_{λ} is emissivity = absorptivity at wavelength λ

$\varphi_{\lambda}^b(T)$ is Planck blackbody radiation flux distribution function (dependent on T and λ)

An example from Jacob illustrates this relationship:³⁰⁵

³⁰³ <http://wwp.greenwichmeantime.com/longest-day/equinox-solstice-2010-2019.htm>

³⁰⁴ "For a body of any arbitrary material, emitting and absorbing thermal electromagnetic radiation at every wavelength in thermodynamic equilibrium, the ratio of its emissive power to its dimensionless coefficient of absorption is equal to a universal function only of radiative wavelength and temperature, the perfect black-body emissive power."

http://en.wikipedia.org/wiki/Kirchhoff%27s_law_of_thermal_radiation

³⁰⁵ Jason, <http://acmg.seas.harvard.edu/publications/jacobbook/bookchap7.pdf> p. 119, 121

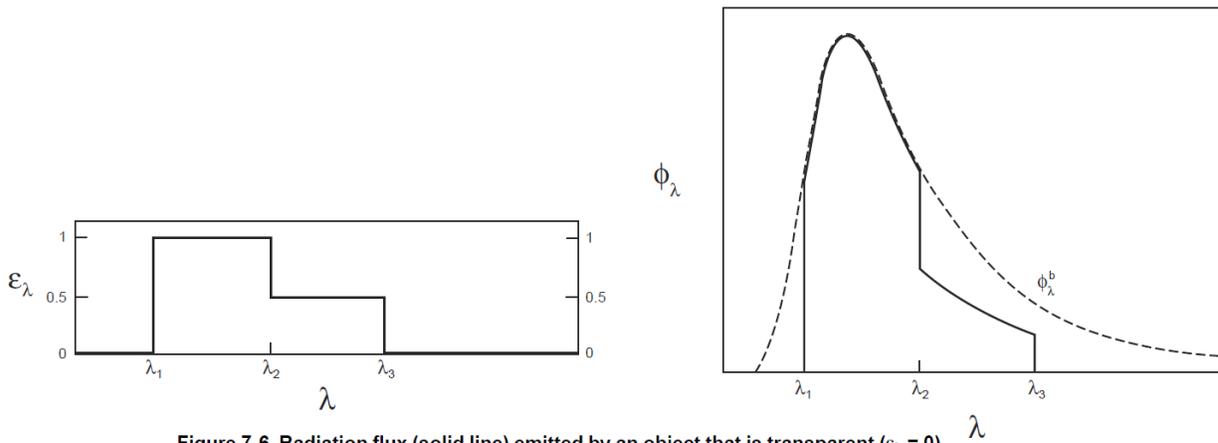


Figure 7-6 Radiation flux (solid line) emitted by an object that is transparent ($\epsilon_\lambda = 0$) for wavelengths shorter than λ_1 or longer than λ_3 , opaque ($\epsilon_\lambda = 1$) for wavelengths between λ_1 and λ_2 , and 50% absorbing ($\epsilon_\lambda = 0.5$) for wavelengths between λ_2 and λ_3 . The dashed line is the blackbody curve for the temperature of the object.

Jacob notes, “the terrestrial [IR] radiation spectrum is a combination of blackbody spectra for different temperatures, ranging from 220 to 320 K in Figure 7-8. The wavelength range of maximum emission is 5-20 mm.”

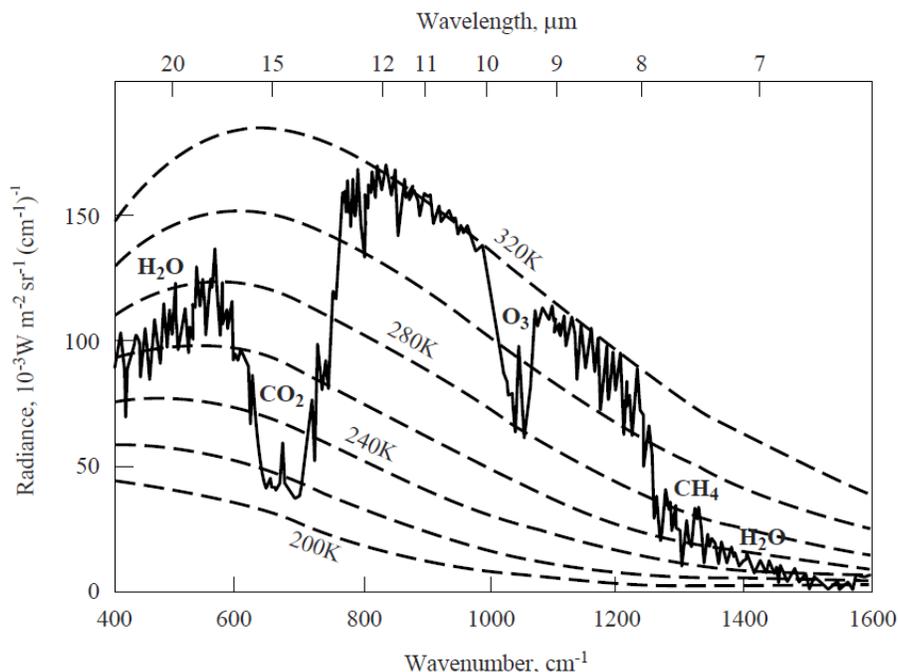


Figure 7-8 Terrestrial radiation spectrum measured from a satellite over northern Africa (Niger valley) at noon. Blackbody curves for different temperatures are included for comparison. The plot shows radiances as a function of wavenumber ($\bar{\nu} = 1/\lambda$). The radiance is the radiation energy measured by the satellite through a viewing cone normalized to unit solid angle (steradian, abbreviated sr). Radiance and $\phi_{\bar{\nu}}$ are related by a geometric factor. Major atmospheric absorbers are identified. Adapted from Hanel, R.A., et al., *J. Geophys. Res.*, 77, 2629-2641, 1972.

In his Fig. 7-8, the emission from the hot land surface of Africa shines through in the atmospheric window (~8 to 12 μm) closely resembling the emission of a blackbody T of 320 K (with the exception of an absorption peak from O_3). At other wavelengths, absorption by water, CO_2 , and CH_4 reduce transmission of surface IR to space—emission in these regions also at equilibrium effectively arise from cooler parts of the atmosphere, thus from higher altitude above the absorbing gases. For instance, the CO_2 absorption is so strong for λ at its peak ~15 μm that the effective Planck blackbody temperature for this segment is about 215 - 220 K, thus at

the tropopause where CO₂ is “thin”. In contrast, the water absorption at 20 μm corresponds to 260 K, thus lower at 5 km and well below the tropopause.³⁰⁶

Calculating Equilibrium T of the Earth

The equilibrium T of the Earth, calculated by ignoring the greenhouse effect of its atmosphere, is obtained by comparing incoming solar EM energy absorbed with the thermal-IR energy emitted. (APGW p. 264-266)

Solar EM radiation at the photosphere has an effective temperature of about 5,785 K and closely follows a blackbody distribution. Using Stefan-Boltzmann, the calculated light energy flux at the photosphere, F_p in W m⁻² is:

$$F_p = \epsilon_p \sigma_B T_p^4$$

where

ε_p = emissivity of solar photosphere (approx. 1)

σ_B = Stefan-Boltzmann constant = 5.6704x10⁻⁸ W m⁻² K⁻⁴

T_p = Average photosphere temperature K

Given the solar photosphere radius R_p and the average Earth-sun distance R_{es} (see Other Information Resources), we may calculate average solar energy flux F_s through a plane perpendicular to the incoming light at the top of the Earth’s atmosphere, namely about 1,365 W m⁻² (APGW p. 264). This quantity was formerly called the **Solar Constant**, but in fact it fluctuates by 0.1% during the sunspot cycle (and even more, up to 0.6%, over many centuries),³⁰⁷ and is currently and preferably called **Total Solar Irradiance**.³⁰⁸ In practice, the Total Solar Irradiance is empirically measured with satellites (see discussion and graphs below).

P_{in} is the total EM solar power in W incoming to Earth, outside the atmosphere and over its cross sectional area πR_e², is given by

$$P_{in} = F_s(1 - A_e)(\pi R_e^2)$$

where

F_s = Solar energy flux (TSI) W m⁻² at top of Earth atmosphere

A_e = Albedo of Earth and atmosphere (details follow)

R_e = Earth radius (average)

The albedo A_e = 0.3 utilized is that of Earth plus its atmosphere, averaged for visible light (i.e., a net 30% of incoming light energy is reflected back to space as shortwave EM). This is apparently the Bond albedo (see glossary), which includes averaging over all astronomical “phase angles” (arising from orbital movement) and also over all wavelengths. NASA states that from 2000 to 2011, there has been no significant change in average global albedo of 0.3.³⁰⁹

The total power P_{out} in W emitted by Earth as thermal-IR spread over its surface area 4πR_e² may be calculated from

$$P_{out} = \epsilon_e \sigma_B T_e^4 (4\pi R_e^2)$$

where

ε_p = emissivity of Earth (average, nearly 1)

T_e = Earth surface equilibrium effective average temperature in K

At equilibrium (again neglecting atmosphere effects), P_{in} = P_{out}, and we may solve for T_e.

$$F_s(1 - A_e)(\pi R_e^2) = \epsilon_e \sigma_B T_e^4 (4\pi R_e^2)$$

$$T_e = \left[\frac{F_s(1 - A_e)}{4\sigma_B} \right]^{1/4}$$

For Earth with F_s=1,365 W and albedo 0.3, this yields a calculated equilibrium temperature T_e=255 K. This is below the freezing point of water. Jason, now regarding a system that does have an atmosphere that includes

³⁰⁶ Jason, <http://acmg.seas.harvard.edu/publications/jacobbook/bookchap7.pdf> p. 129

³⁰⁷ http://science.nasa.gov/science-news/science-at-nasa/2003/17jan_solcon/

³⁰⁸ The TSI was 1360.8 ± 0.5 W m⁻² during the 2008 solar minimum

<http://atmospheres.gsfc.nasa.gov/climate/?section=136>

³⁰⁹ <http://earthobservatory.nasa.gov/IOTD/view.php?id=84499>

GHGs, states, “We should view it [T_e] as an effective temperature for the (Earth + atmosphere) system as would be detected by an observer in space. Some of the terrestrial radiation detected by the observer may be emitted by the cold atmosphere rather than by the Earth’s surface.”³¹⁰

The actual measured globally and annually averaged near-surface temperature is more like 288 K. The additional 33 K is attributable to the greenhouse effect of the atmosphere (natural plus anthropogenic), primarily from water vapor.³¹¹ In Jacob’s simple model, the equation for T_e must be adjusted further for the absorption and emission of radiation by the atmospheric layer by adding a quantity f , the fraction of LWR absorbed by the atmospheric layer, some of which is reemitted upward and some downward. His final formula for global mean surface temperature, assuming by Kirchhoffs law that there is equal absorption and emission, is

$$T_0 = \left[\frac{F_s(1 - A_e)}{4\sigma_B(1 - \frac{f}{2})} \right]^{1/4}$$

This formula yields 288 K (same as the actual observed measured global mean surface temperature of 288 K) for a value of $f = 0.77$.

The physics of how GHGs interact with SWR and LWR warrants considerably more study than I have given it, in particular how the most sophisticated current computer models that project future effects compare to the relatively simple calculations stated here.

Runaway Greenhouse Effect on Venus versus Our Rare Earth

Planets vary in the amount of greenhouse gases and effect on equilibrium temperature T_{eq} that they exhibit:

Venus (has dense atmosphere & a runaway greenhouse)	calc. = 252 K	actual = 730 K
Earth (has greenhouse atmosphere)	calc. = 255 K	actual = 288 K
Mars (has minimal atmosphere)	calc. = 217 K	actual = 218 K
Jupiter (has dense atmosphere w some greenhouse)	calc. = 102 K	actual = 129 K
Saturn (has dense atmosphere w some greenhouse)	calc. = 77 K	actual = 97 K

The runaway greenhouse effect on Venus (actual T - calculated T = 478 K) is due to a CO₂ mixing ratio of 96% at an atmospheric pressure of 90 bars. This arose from³¹²

- Greater surface temperature in early evolution
- Early vaporization of all liquid and ice water
- Photolysis of water vapor from far-UV
- Escape of atomic H to space, preventing recombination with O as water
- CO₂ from volcanoes cannot form carbonate rock or dissolve in an ocean, no other sinks
- CO₂ builds up in atmosphere in a positive feedback loop, increasing greenhouse warming.

Surely, life on Earth is extraordinarily fortunate to have a planet with a temperature varying in so optimal a range for sustaining life, with average T above freezing and well below the boiling point. If all liquid water were vaporized, the enhanced greenhouse effect would make Earth uninhabitable.

Determining Global Temperatures Through Geological History

I will not attempt to review the geological history in *APGW*. A few comments must suffice for now on this rich and complex subject, which includes Paleoclimatology and Thermochemistry.

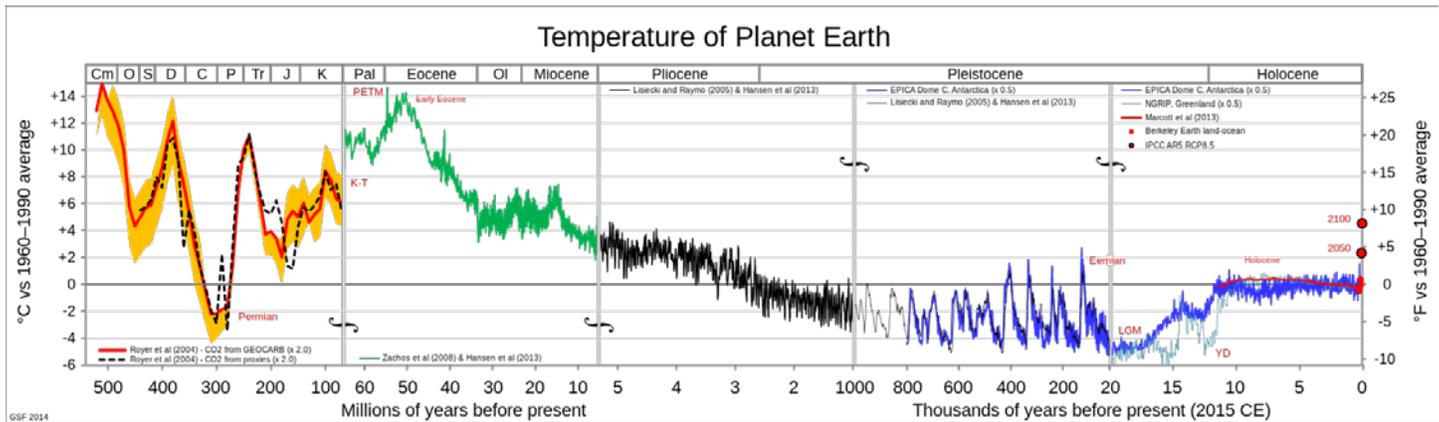
Here is a graph of reconstructed Earth temperatures back to the Cambrian:³¹³

³¹⁰ Jason, <http://acmg.seas.harvard.edu/publications/jacobbook/bookchap7.pdf>

³¹¹ Water vapor is said to cause 89% of natural greenhouse effect on Earth. (*APGW* p. 269)

³¹² *APGW* p. 267

³¹³ <http://en.wikipedia.org/wiki/Paleoclimatology>



The temperatures vary over a range of at least 21 °C.

The following are some of the methods of establishing ages, at least during the Quaternary Period.

The isotope techniques described below are a complex and confusing topic which I have not mastered. The discrepancies in stable isotope ratios are expressed as $\delta^{18}\text{O}$ (delta-O-18), using the formula that follows, and expressed as “per mil” (‰, parts per thousand):³¹⁴

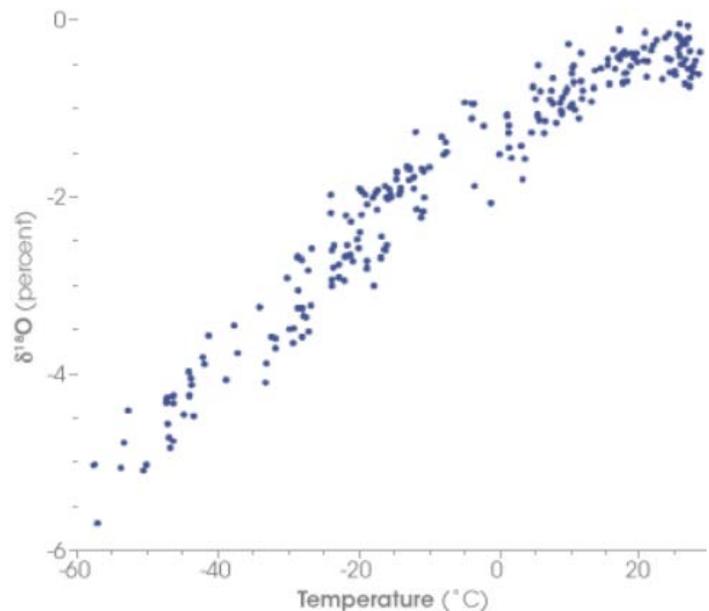
$$\delta^{18}\text{O} = \left(\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}}} - 1 \right) * 1000 \text{ ‰}$$

(Vienna Pee Dee Belemnite VPDB is used as the standard for carbonates and Vienna standard mean ocean water VSMOW is used as the standard for seawater.)

The metric δD , based on the deuterium:protium ratio, is also used as a proxy for T similar to use of $\delta^{18}\text{O}$, or they are both used together.

(1) Ocean Sediments: Water molecules containing ^{16}O evaporate slightly more readily than water molecules containing ^{18}O . At the same time, water vapor molecules containing ^{18}O condense more readily... This causes present-day warmer ocean water to be relatively depleted in ^{16}O relative to ^{18}O , so that $\delta^{18}\text{O}$ (Delta-O-18) is more positive in ocean water compared to water precipitating at high latitude (which has a decreased $\delta^{18}\text{O}$).

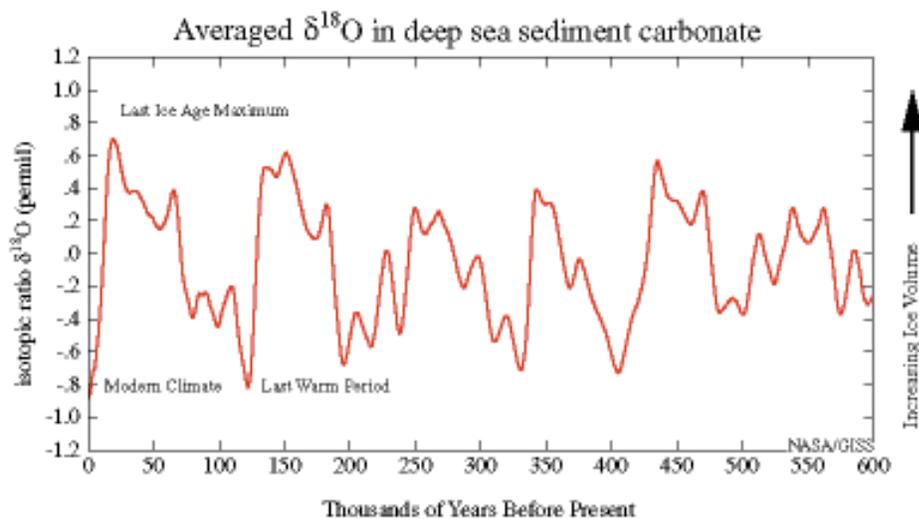
The graph (right) shows how $\delta^{18}\text{O}$ in precipitation varies with average annual T for sites at varying latitudes for modern Earth. “Air becomes progressively depleted in ^{18}O as it travels to high latitudes and becomes colder and drier. In turn, the snow that forms most glacial ice is also depleted in ^{18}O .”³¹⁵ (The vertical axis is labeled percent, and comparison with the original article [Jouzel et al, 1994] indicates the this $\delta^{18}\text{O}$ graph is indeed expressed in units of per cent.) Note that $\delta^{18}\text{O}$ is quite low (nearly -6 %) at the lowest polar temperatures and essentially 0 (no depletion) at the highest temperature latitudes, corresponding to the tropics.



³¹⁴ <http://en.wikipedia.org/wiki/%CE%9418O>

³¹⁵ http://earthobservatory.nasa.gov/Features/Paleoclimatology_OxygenBalance/

In the next graph, the variation in $\delta^{18}\text{O}$ over 600,000 years is shown for carbonate in deep sea sediments. Modern warm interglacial climate is at the far left, and shows the lowest value of $\delta^{18}\text{O}$ (-8), whereas the $\delta^{18}\text{O}$ for the last ice age maximum is maximally positive (+7). This figure is further captioned “The variations of ^{18}O in carbonate averaged over a large number of different cores (in order to isolate a global signal) over the last 600,000 years. Most clear are the regular oscillations of the glacial ice volume which follows small changes to Earth's orbit around the Sun (Milankovitch forcing)... The many records of $\delta^{18}\text{O}$ in ocean sediments and in ice cores, contain information about the temperature, evaporation, rainfall, and indeed the amount of glacial ice — all of which are important to know if we are to understand the changes of climate in the Earth's history. Unfortunately, trying to disentangle these multiple effects is complicated since we have one measurement with many unknowns.”³¹⁶



“Delta-O-18 changes directly as a result of temperature fluctuations, so it provides a very good record of the climate. Oceanic delta-O-18 values that are high represent cold climates, while lower values indicate a warm climate. This trend occurs because of the effects of precipitation and evaporation. Since it is lighter than ^{18}O , ^{16}O evaporates first, so in warm, tropical areas, the ocean is high in ^{18}O . Additionally, as water vapor condenses to form rain, water droplets rich in ^{18}O precipitate first because it is heavier than ^{16}O ... The Tropics possess a large amount of ^{18}O but have little ^{16}O . This state is not permanent, however, because evaporation and precipitation are highly correlated with temperature. Changes in the climate can greatly affect the ratio of ^{18}O and ^{16}O and can alter their distribution throughout the globe. In addition to the effects of evaporation and precipitation, the amount of ice near the poles affects the delta-O-18 ratio. When temperatures are cold in the polar regions, ^{16}O becomes locked in glaciers after it precipitates in the high latitudes. Therefore, in warmer climates when glaciers melt, they release the ^{16}O that is trapped in them, and the oceans become enriched in ^{16}O . As a result, the amount of ice in the high-latitudes plays an important role in regulating the delta-O-18 value.”³¹⁷ Higher delta-O-18 ratios in shell carbonate correlates with higher water temperatures in seawater. (APGW p. 277)

See further information below about *Marine Isotope Stages (MISs)*.

(2) Greenland and Antarctic ice cores: T is inferred from the ratio of stable ^{18}O to ^{16}O expressed as $\delta^{18}\text{O}$ (delta-O-18). A ratio which is higher means increased T, a lower ratio means decreased T. As mentioned above, “The snow [water] that forms most glacial ice is also depleted in ^{18}O . As glacial ice melts, it returns ^{16}O -rich fresh water to the ocean.” “During ice ages, cooler temperatures extend toward the equator, so the water vapor containing heavy oxygen rains out of the atmosphere at even lower latitudes than it does under milder conditions. The water vapor containing light oxygen moves toward the poles, eventually condenses, and falls onto the ice sheets where it stays. The water remaining in the ocean develops increasingly higher concentration of heavy oxygen compared to the universal standard, and the ice develops a higher concentration of light oxygen [thus lower $\delta^{18}\text{O}$]. Thus, high concentrations of heavy oxygen in the ocean tell scientists that light oxygen was trapped in the ice sheets [low $\delta^{18}\text{O}$]. The exact oxygen ratios can show how much ice covered the Earth... As temperatures rise, ice sheets melt, and freshwater runs into the ocean. Melting returns light oxygen to the water [decreasing sea water $\delta^{18}\text{O}$], and reduces the salinity of the oceans worldwide. Higher-than-standard global concentrations of light oxygen in ocean water [decreased ocean water $\delta^{18}\text{O}$] indicate that global temperatures have warmed, resulting in less global ice cover and less saline waters. Because water vapor containing heavy oxygen condenses and falls as rain before water vapor containing light oxygen, higher-than-standard local concentrations of light oxygen [lower water $\delta^{18}\text{O}$] indicate that the watersheds draining into the sea in that region experienced heavy rains, producing more diluted waters.

³¹⁶ http://www.giss.nasa.gov/research/briefs/schmidt_01/

³¹⁷ <http://www.seas.harvard.edu/climate/eli/research/equable/isotope.html>

Thus, scientists associate lower levels of heavy oxygen [$\delta^{18}\text{O}$] ... with fresher water, which on a global scale indicates warmer temperatures and melting, and on a local scale indicates heavier rainfall.”³¹⁸

The following figure uses δD and shows its correlation with trapped Antarctic ice core N_2O , CH_4 , and CO_2 .³¹⁹ (See also APGW p. 283 Fig. 12.20 for similar data):

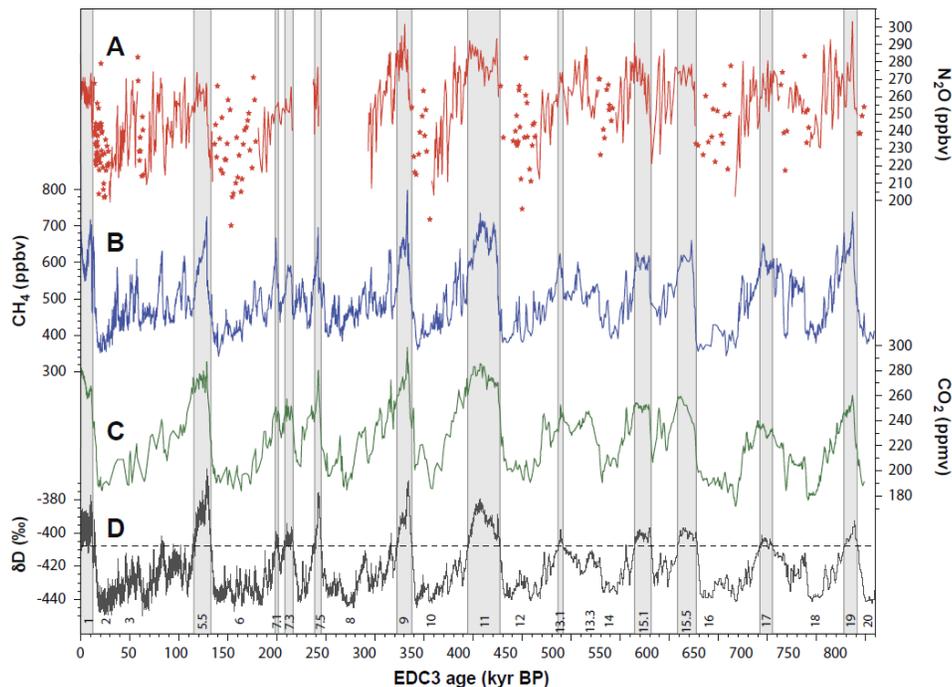


Fig. 9. Variations, over the last 800 000 yr, of deuterium (δD ; black), a proxy for local temperature, and the atmospheric concentrations of the greenhouse gases CO_2 (green), CH_4 (blue), and nitrous oxide (N_2O ; red) derived from air trapped within ice cores from Antarctica (Schilt et al., 2009).

Here, EDC3 ³²⁰ is the latest 800 kyr age scale derived from the EPICA (European Project for Ice Coring in Antarctica) Dome C drilling.

The numbered gray vertical bands apparently represent the warmest interglacial *Marine Isotope Stages (MISs)* of Quaternary geochronology.³²¹ (I hope someday to learn more about this complex subject.) The current *Holocene interglacial warm period* in which we live, beginning 14 kya, is called MIS1, and the most recent ice age is MIS2, beginning 29 kya. More than 100 stages have been identified, alternating odd-numbered warm with even-numbered cold stages, and some are further subdivided into *substages*. Substage MIS 5e (the Eemian or Ipswichian) was the *last interglacial period* before the present, and it is also notated by decimal horizons such as MIS 5.5 representing the peak point or event of MIS 5e.

It seems apparent by inspection that CO_2 , CH_4 , and possibly N_2O peak during the interglacials having highest T (including 5.5, 9, 11, 15.1, 15.5, 17, and 19).

The next graph is from the same source.³²²

³¹⁸ http://earthobservatory.nasa.gov/Features/Paleoclimatology_OxygenBalance/

³¹⁹ Jouzel J, “A brief history of ice core science over the last 50 yr”, *Clim. Past*, 9, 2525–2547, 2013 <http://www.clim-past.net/9/2525/2013/cp-9-2525-2013.pdf>

³²⁰ ftp://ftp.ncdc.noaa.gov/pub/data/paleo/icecore/antarctica/epica_domec/edc3-timescale.txt

EDC3 supersedes EDC2 and EDC1

³²¹ http://en.wikipedia.org/wiki/Marine_isotope_stage

³²² Jouzel J, op. cit.

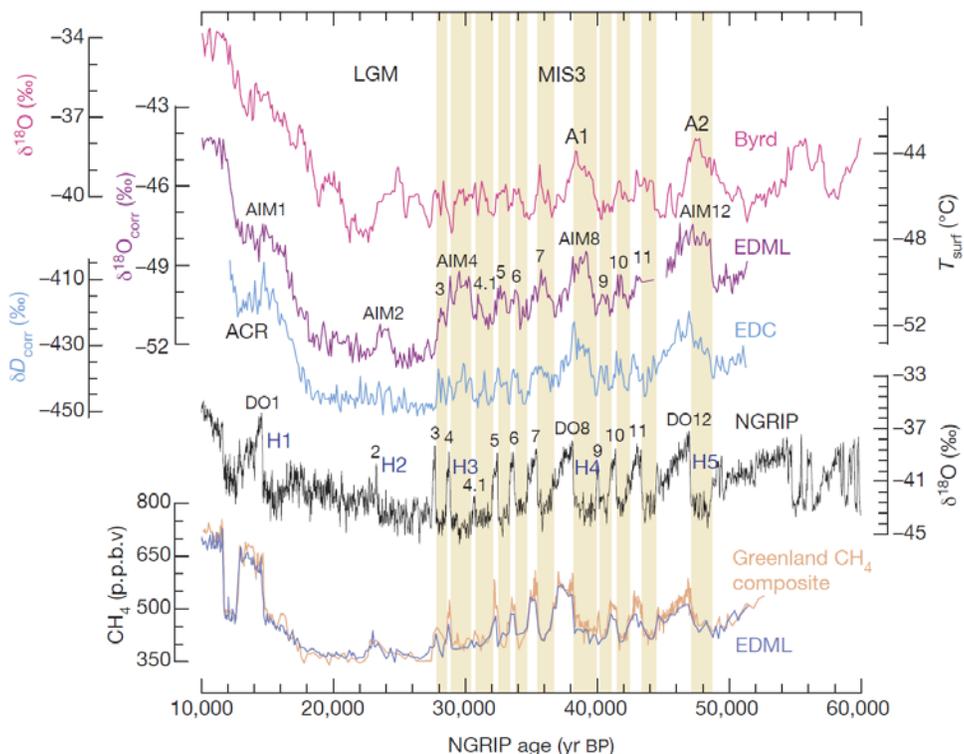


Fig. 10. Methane synchronization of the EDML and the NGRIP records reveals a one-to-one assignment of each Antarctic warming with a corresponding stadial in Greenland (adapted from EPICA Community Members, 2006)

Abbreviations used are as follows:

For Antarctica: EDC = EPICA (European Project for Ice Coring in Antarctica) Dome C ice cores; EDML = EPICA Dronning [Queen] Maud Land Ice cores; Byrd = Byrd Station in West Antarctica; LGM = Last Glacial Maximum (beginning 26.5 kya); MIS3 = Marine Isotope Stage 3 (beginning 57 kya). AIM1 = Antarctic Isotopic Maxima (AIM) 1.

For Greenland: NGRIP = North Greenland Ice Core Project. The terminology uses numbered *stadials* (cold periods or glaciations) and *interstadials* (milder periods)³²³ rather than stages. DO1 = Dansgaard-Oeschger event 1. The DO events are “most clearly observed in the North Atlantic region, [and] are recorded in Greenland ice cores as abrupt temperature increases of 8–16 C in a few centuries from cold periods (Greenland stadials, GS) to warm periods (Greenland interstadials, GI)”.³²⁴ (For example, the DO1 δD peak corresponds to a T peak) H2 = Heinrich event 2. These are rapid “global climate fluctuations which coincide with the destruction of northern hemisphere ice shelves, and the consequent release of a prodigious volume of sea ice and icebergs.”³²⁵

Thus, CH₄ variations from Greenland and Antarctica are correlated and matched against δ¹⁸O and δD (proxies for T).

This is the kind of data used to explore previous periods of warming and cooling, helpful in evaluating our current era of GW.

We are in a period of relatively high Earth temperature. During previous periods of high temperatures, the Earth did not need to support the large human population now present, and global warming arose in most instances much more gradually, on the order of 0.05 °C per century rather than the current 2.2%/yr. (APGW p. 287)

³²³ <http://www.nature.com/nature/journal/v359/n6393/abs/359311a0.html>

³²⁴ <http://www.clim-past.net/9/1733/2013/cp-9-1733-2013.pdf>

³²⁵ http://en.wikipedia.org/wiki/Heinrich_event

Thermal Infrared IR Absorption by Greenhouse Gases

According to *APGW* p. 269, the following IR spectral % absorption curves apply to certain named greenhouse gases (data from Valley 1965):

Percent Absorption of Infrared Radiation by Greenhouse Gases

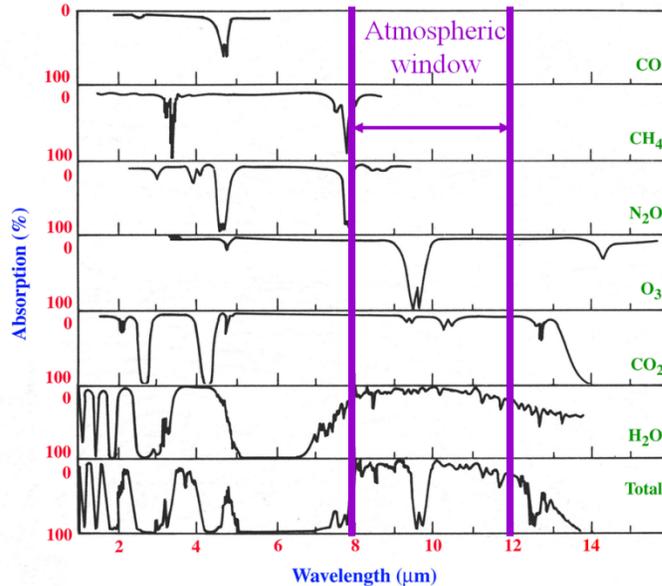


Figure 12.4

This chart includes an “atmospheric window” from 8 to 12 μm which normally is relatively transparent, but several greenhouse gases absorb radiation in this window, namely, O₃, CH₃Cl (not depicted), and marginally N₂O and CH₄. Absorption in this window by added greenhouse gases has a disproportionate effect on warming.

For an imperfect black body radiator, the emission spectrum is related to the absorption spectrum by Kirchhoff's Law.

$$\varphi_{\lambda}(T) = \varepsilon_{\lambda}(T)\varphi_{\lambda}^b(T)$$

where $\varphi_{\lambda}(T)$ = radiation flux as a function of T and λ

ε_{λ} is emissivity = absorptivity at λ

$\varphi_{\lambda}^b(T)$ is Planck black body radiation flux as a function of T and λ

The example from Jacob to follow illustrates this relationship³²⁶

³²⁶ <http://acmg.seas.harvard.edu/publications/jacobbook/bookchap7.pdf>

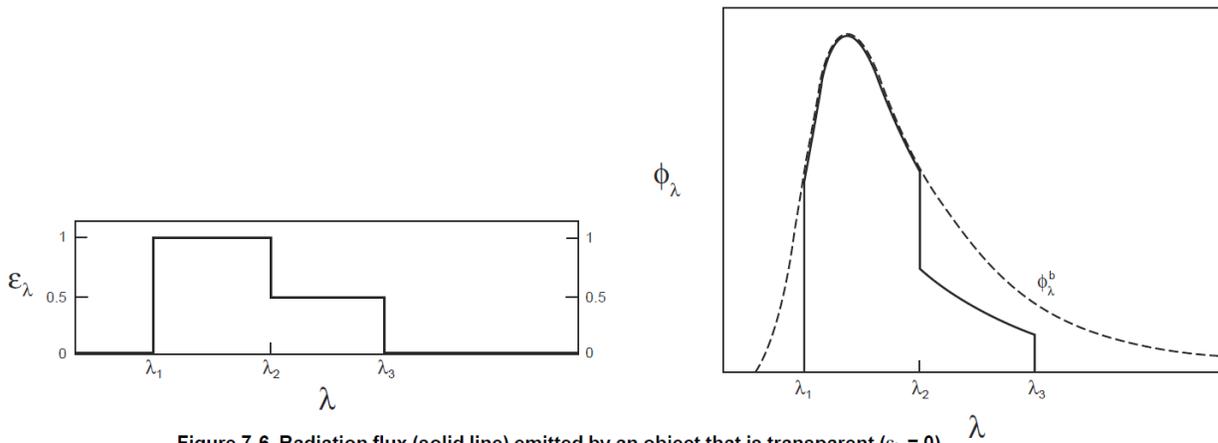


Figure 7-6 Radiation flux (solid line) emitted by an object that is transparent ($\epsilon_\lambda = 0$) for wavelengths shorter than λ_1 or longer than λ_3 , opaque ($\epsilon_\lambda = 1$) for wavelengths between λ_1 and λ_2 , and 50% absorbing ($\epsilon_\lambda = 0.5$) for wavelengths between λ_2 and λ_3 . The dashed line is the blackbody curve for the temperature of the object.

Jacob notes, “the terrestrial [IR] radiation spectrum is a combination of blackbody spectra for different temperatures, ranging from 220 to 320 K in Figure 7-8. The wavelength range of maximum emission is 5-20 mm.”

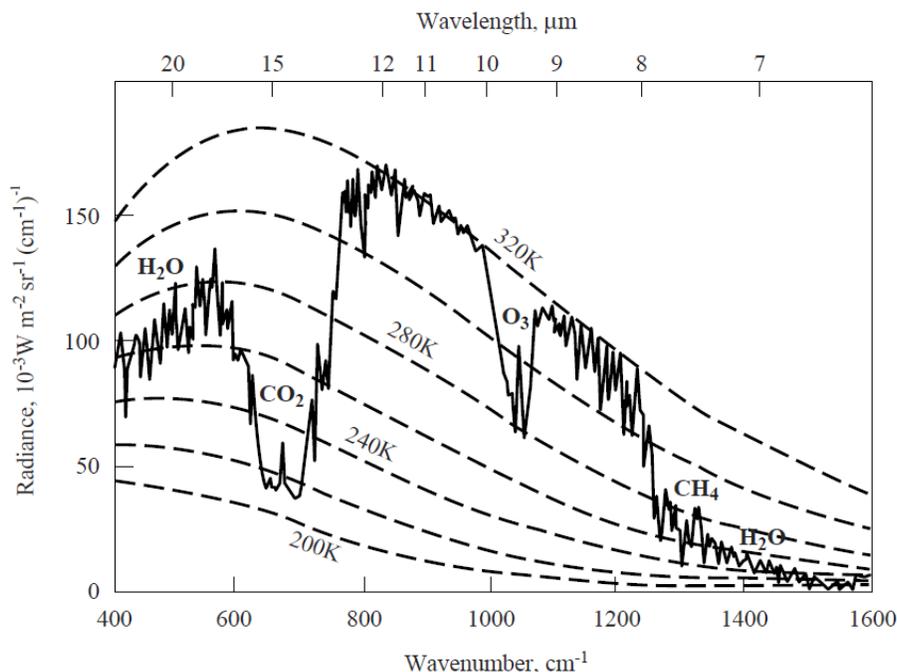


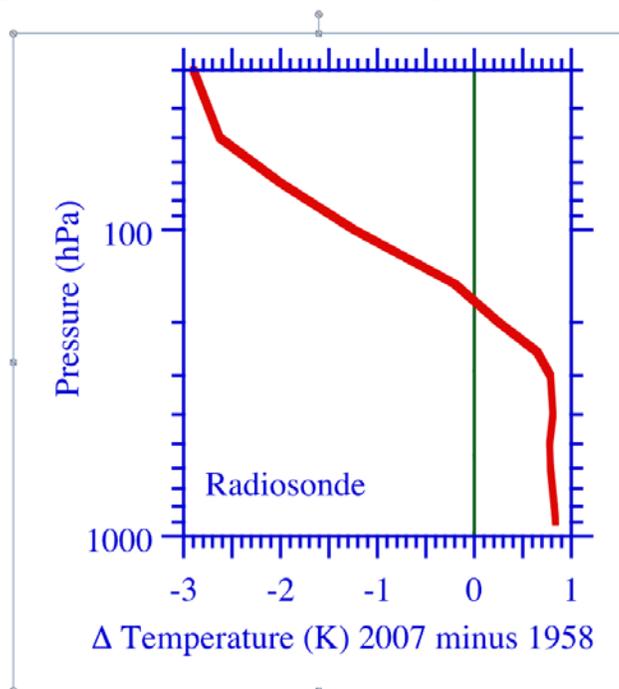
Figure 7-8 Terrestrial radiation spectrum measured from a satellite over northern Africa (Niger valley) at noon. Blackbody curves for different temperatures are included for comparison. The plot shows radiances as a function of wavenumber ($\bar{\nu} = 1/\lambda$). The radiance is the radiation energy measured by the satellite through a viewing cone normalized to unit solid angle (steradian, abbreviated sr). Radiance and $\phi_{\bar{\nu}}$ are related by a geometric factor. Major atmospheric absorbers are identified. Adapted from Hanel, R.A., et al., *J. Geophys. Res.*, 77, 2629-2641, 1972.

Here, the emission from the hot land surface of Africa shines through in the atmospheric window (8 to 12 μm) at a blackbody T of 320 K (with the exception of an absorption peak from O_3). At other wavelengths, absorption by water, CO_2 , and CH_4 reduce transmission of IR to space and effectively show emission as if from cooler parts of the atmosphere and thus at higher altitude, above the absorbing gases. For instance, the CO_2 absorption is so strong that over the range of its absorption peak, the effective Kirchhoff/Planck blackbody temperature is about 220 K, thus in the stratosphere.

What Is Warming Globally?

The warming has taken place globally at the Earth surface and throughout the troposphere (below 200 hPa or about 10 km altitude, the region of the tropopause). A corresponding global **stratospheric cooling** is apparent above 200 hPa in this historical radiosonde data extending back to 1958:³²⁷

Observed Vertical Profile of Temperature Changes 1958-2007

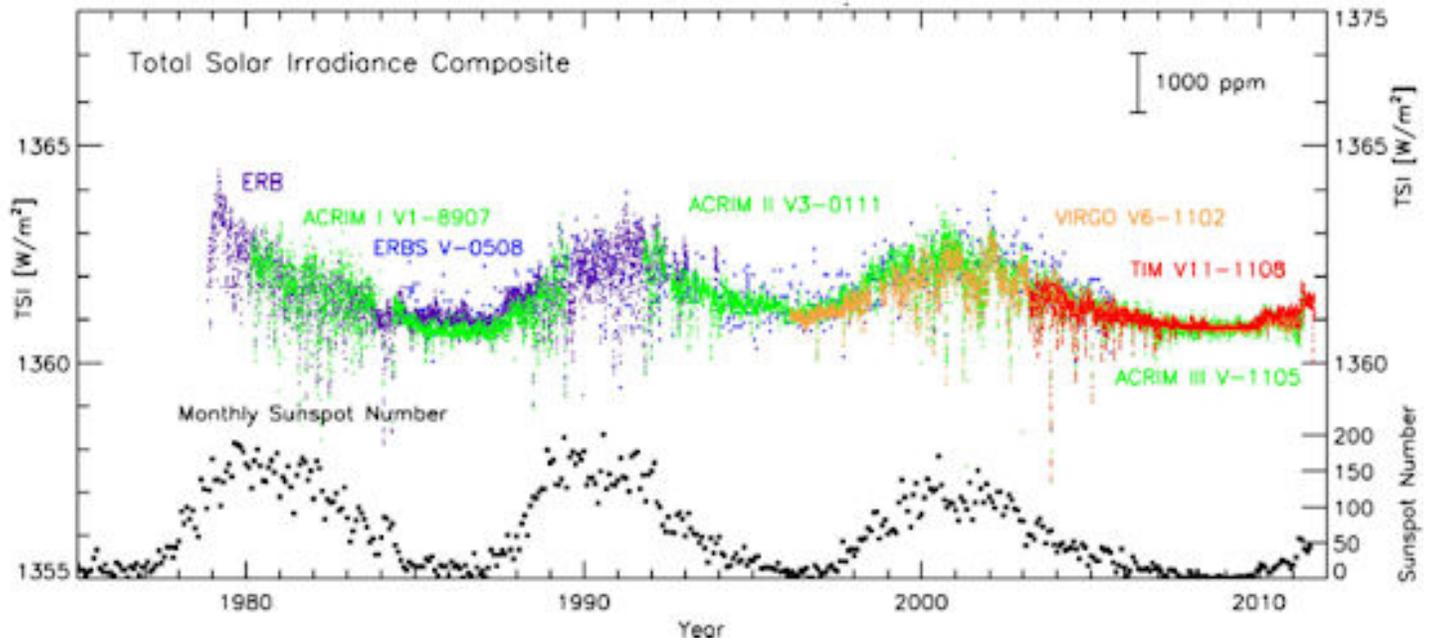


Fluctuation of Total Solar Irradiance TSI

TSI is EM solar radiation measured at the Earth Sun distance and above the effects of the atmosphere, often normalized to a distance of 1 AU. The following graph,³²⁸ with data gathered from a number of successive satellites, shows how normalized TSI varies with the 11-year sunspot cycle.

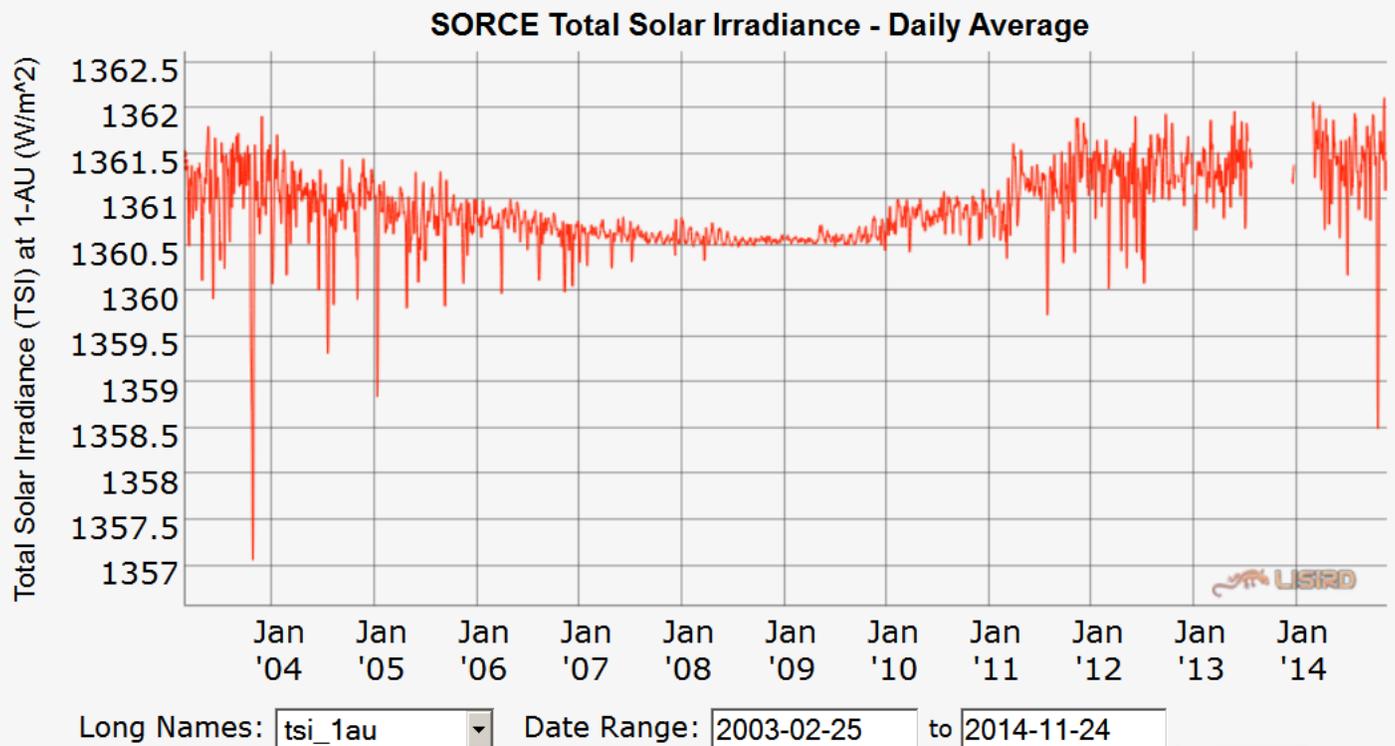
³²⁷ <http://web.stanford.edu/group/efmh/jacobson/POLbook2/APGWCh12Figs.pptx> fig. 12.14

³²⁸ http://science.nasa.gov/science-news/science-at-nasa/2013/08jan_sunclimate/



The current state-of-the-art satellite instrument is the *SORCE* (Solar Radiation and Climate Experiment) *TIM* (Total Irradiance Monitor), which uses a high resolution absolute radiometer to measure total EM radiation. The following is its full data set since 2/25/2003 (with a gap in 2013 due to battery problems). Values shown are daily averages, normalized to 1 AU.³²⁹ Truly, this output is not constant!

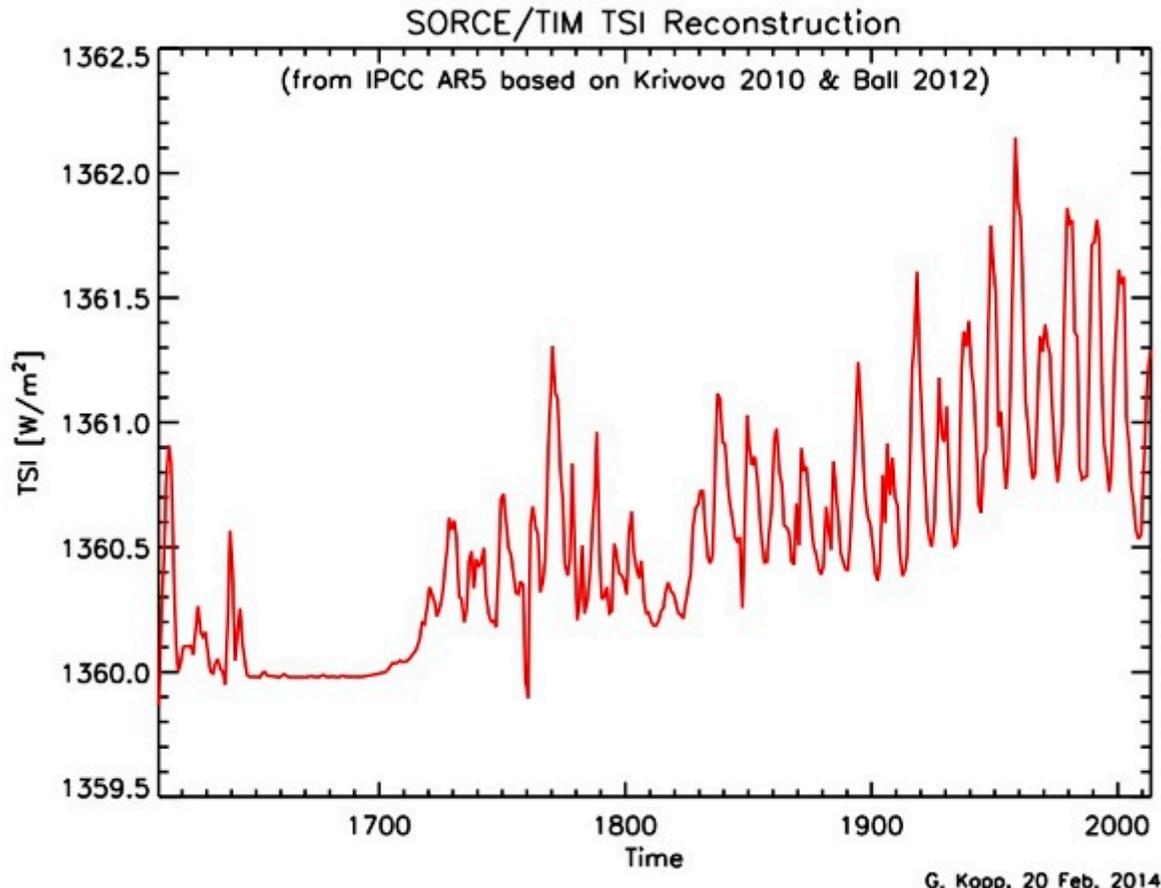
SORCE TOTAL SOLAR IRRADIANCE



TSI, which has been reconstructed back to before 1700, shows a small long-term increase since then:³³⁰

³²⁹ http://lasp.colorado.edu/lisird/sorce/sorce_tsi/

³³⁰ http://lasp.colorado.edu/home/sorce/data/tsi-data/#summary_table



The low value from 1645 to about 1715 is the Maunder Minimum, a time of prolonged sunspot minimum.

APGW p. 288 states, “The difference in solar intensity ... between times of sunspot maxima and minima is about 1.4 W m^{-2} , or only 0.1% of the solar constant... Sunspots cannot cause multi-decade increases in temperatures as have occurred since the 1950s... Peak sunspot intensity declined rather than increased between 1978 and 2003 [when T was rising].”

Regarding the past few decades, the IPCC5 concludes “There is high confidence that changes in total solar irradiance [including from the sunspot cycle] have not contributed to the increase in global mean surface temperature over the period 1986 to 2008, based on direct satellite measurements of total solar irradiance.”³³¹

Energy Solutions to Air Pollution and Global Warming

This topic is presented in *APGW* Chapter 13, , a chapter we did not read in our class and which I am omitting.

³³¹ *IPCC_WGI_2013* p. 17
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Other Information Resources

Basic Facts about the Sun and Earth ⊕

This section was compiled in 2010 for a Space Physics course. The values and references were correct (with rounding) as of 2010.

The solar system formed about 4.6 b.y.a.

Radius of Earth (R_E or R_\oplus per WGS-84)³³²

Mean at Equator: $6.378137 \times 10^6 \text{ m} = 6,378.137 \text{ km}$

Mean at Poles: $6.356752 \times 10^6 \text{ m} = 6,356.752 \text{ km}$

Ellipticity of Earth = 0.00335 = ~0.3% (expressed inverted: 1:298)

Distance from Sun to Earth, average (1 Astronomical Unit = AU):³³³

$1.496 \times 10^{11} \text{ m} = 92.96 \text{ million mi} = 8.32 \text{ lm (light minutes)} = 499 \text{ ls} = 4.8481 \times 10^{-6} \text{ parsec} = 215 R_\odot$

Mass of Earth $M_\oplus = 5.9742 \times 10^{24} \text{ kg}$

Density of Earth ρ_E :³³⁴

Mean: $5.515 \text{ gm/cm}^3 = 5.515 \times 10^3 \text{ kg/m}^3$

Inner Core: $12.8 - 13.1 \text{ gm/cm}^3 = 12.8 \times 10^3 - 13.1 \times 10^3 \text{ kg/m}^3$

Mantle: $3.4 - 5.6 \text{ gm/cm}^3 = 3.4 \times 10^3 - 5.6 \times 10^3 \text{ kg/m}^3$

Crust: $2.2 - 2.9 \text{ gm/cm}^3 = 2.2 \times 10^3 - 2.9 \times 10^3 \text{ kg/m}^3$

Atmosphere (at sea level)³³⁵— $1.2 \times 10^{-3} \text{ gm/cm}^3 = 1.2 \text{ kg/m}^3$

[MCM crude estimate cf. Sun: $\sim 6 \times 10^{26} \text{ particles m}^{-3}$]

Temperature of Sun³³⁶

Surface (effective black body temperature) = 5770 K = 9,930 °F (ISP: 5785 K)

Central or Core = 15,600,000 K = 28,000,000 °F

Luminosity of Sun L_\odot ^{337,338} = $3.846 \times 10^{26} \text{ W} = 3.846 \times 10^{33} \text{ erg/s}$

Total Solar Irradiance (TSI, the not-so-constant “Solar Constant”) is the irradiance (W m^{-2}) at all wavelengths of photons (effectively from about 10,000 nm to about 10 nm) at exactly 1 A.U.³³⁹ on a surface perpendicular to the incoming rays:

Mean is about $1,366 \text{ W m}^{-2}$

Actual solar irradiance³⁴⁰ varies due to changing Earth-Sun distance and solar fluctuations from 1,412 to $1,321 \text{ W m}^{-2}$

(See above for solar spectra)

³³² http://en.wikipedia.org/wiki/World_Geodetic_System

³³³ http://en.wikipedia.org/wiki/Astronomical_unit

³³⁴ <http://en.wikipedia.org/wiki/Earth>

³³⁵ http://en.wikipedia.org/wiki/Earth%27s_atmosphere

³³⁶ <http://solarscience.msfc.nasa.gov/>

³³⁷ <http://solarscience.msfc.nasa.gov/>

³³⁸ Luminosity:

http://en.wikipedia.org/wiki/Solar_luminosity:

Luminosity here is total bolometric (wide spectrum) photon radiant energy output, and does not include neutrino radiant energy, which adds $0.1 \times 10^{26} \text{ W}$

³³⁹ ftp://ftp.ngdc.noaa.gov/STP/SOLAR_DATA/SOLAR_IRRADIANCE/COMPOSITE.v2.PDF

³⁴⁰ http://en.wikipedia.org/wiki/Solar_irradiation

Glossary and Miscellaneous Mini-Topics

Topics and terms are included here for added emphasis or for when they are not fully treated in the body of this summary. Emphasis such as italics may be added by MCM in quoted material.

Adiabat and Adiabatic Lapse Rates

“A line plotted on a thermodynamic diagram ... showing as a continuous sequence the temperature and pressure states of a parcel of air with changing height. Dry adiabats show temperature change at the dry adiabatic lapse rate,”³⁴¹ which represent the adiabatic sequence for dry air lacking water vapor [or moist air that does not attain saturation over the range of pressures under consideration]. Its value is approximately $\Gamma_d = 9.8 \text{ }^\circ\text{C per 1,000 m.}$ ³⁴² The name implies an absence of input or output of heat by the parcel.

Aerosol

“Particles may be further segregated into aerosol particles and hydrometeor particles. An aerosol is an ensemble of solid, liquid, or mixed phase particles suspended in air [or other gas]. An aerosol particle is a single liquid, solid, or mixed-phase particle among an ensemble of suspended particles. (APGW p. 2.)” “An aerosol is a colloid of fine solid particles or liquid droplets, in air or another gas. Examples of aerosols include haze, dust, particulate air pollutants and smoke. The liquid or solid particles have diameter mostly smaller than 1 μm or so; larger particles with a significant settling speed make the mixture a suspension, but the distinction is not clear-cut.”³⁴³ Aerosol includes both the particles and the suspending gas. “To qualify as a colloid, the mixture must be one that does not settle or would take a very long time to settle appreciably.”³⁴⁴ Colloidal systems can be destabilized by particle aggregation, also termed coagulation or flocculation.³⁴⁵

Per the AMS: “A colloidal system in which the dispersed phase is composed of either solid or liquid particles [or both], and in which the dispersion medium is some gas, usually air... There is no clear-cut upper limit to the size of particles composing the dispersed phase in an aerosol, but as in all other colloidal systems, it is rather commonly set at 1 μm . Haze, most smokes, and some fogs and clouds may thus be regarded as aerosols. However, it is not good usage to apply the term to ordinary clouds with drops so large as to rule out the usual concept of colloidal stability. It is also poor usage to apply the term to the dispersed particles alone; an aerosol is a system of dispersed phase and dispersing medium taken together.”³⁴⁶

Air Pollution

“The presence of substances in the atmosphere, particularly those that do not occur naturally. These substances are generally contaminants that substantially alter or degrade the quality of the atmosphere. The term is often used to identify undesirable substances produced by human activity, that is, anthropogenic air pollution. Air pollution usually designates the collection of substances that adversely affects human health, animals, and plants; deteriorates structures; interferes with commerce; or interferes with the enjoyment of life.”³⁴⁷ The term is used by some but not all authors to refer to levels of atmospheric gases and aerosols that are anthropogenic and in excess of natural production (APGW p. 3). “An air pollutant is a substance in the air that can have adverse effects on humans and the ecosystem. The substance can be solid particles, liquid droplets, or gases. A pollutant can be of natural origin or man-made. Pollutants are classified as primary or secondary. Primary pollutants are usually produced from a process, such as ash from a volcanic eruption. Other examples include carbon monoxide gas from motor vehicle exhaust, or the sulfur dioxide released from factories. Secondary pollutants are not emitted directly. Rather, they form in the air when primary pollutants react or interact. Ground level ozone is a prominent example of a secondary pollutant. Some pollutants may be both primary and secondary: they

³⁴¹ <http://www.answers.com/topic/adiabat>

³⁴² http://en.wikipedia.org/wiki/Adiabatic_lapse_rate

³⁴³ • APGW p. 2, also

• <http://en.wikipedia.org/wiki/Aerosol>

• <http://www.nasa.gov/centers/langley/news/factsheets/Aerosols.html>

³⁴⁴ <http://en.wikipedia.org/wiki/Colloid>

³⁴⁵ http://en.wikipedia.org/wiki/Particle_aggregation

³⁴⁶ <http://glossary.ametsoc.org/wiki/Aerosol>

³⁴⁷ APGW p. 3 and http://glossary.ametsoc.org/wiki/Air_pollution

are both emitted directly and formed from other primary pollutants.”³⁴⁸ Air pollution has been described dating back to ancient times (especially Pb and Hg from smelting, and Fe).

Albedo

“The albedo of an object is a measure of how strongly it reflects light from light sources such as the Sun. It is therefore a more specific form of the term reflectivity [which is directional]. Albedo is defined as the ratio of total reflected [in any direction] to incident electromagnetic radiation. It is a unitless measure indicative of a surface’s or body’s diffuse reflectivity. The word is derived from Latin albedo ‘whiteness’... The range of possible values is from 0 (dark) to 1 (bright)... The average albedo of the Earth is about 0.3.”³⁴⁹ There are several types of albedo distinguished in technical treatments, such as “bond albedo” and “geometric albedo”.³⁵⁰ “The Bond albedo, named after the American astronomer George Phillips Bond (1825–1865), who originally proposed it, is the fraction of power in the total electromagnetic radiation incident on an astronomical body that is scattered back out into space. Because the Bond albedo accounts for all of the light scattered from a body at all wavelengths and all phase angles [angle between incident light and reflected light], it is a necessary quantity for determining how much energy a body absorbs.”³⁵¹

Alkane

Saturated acyclic HC with general formula C_nH_{2n+2} , thus containing only H and C.

Anions

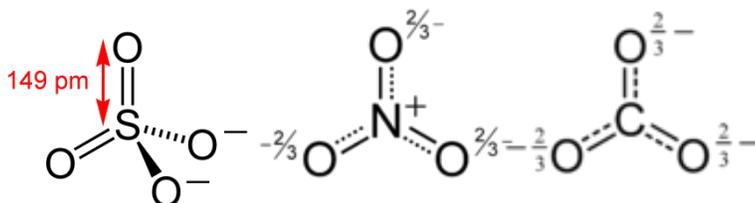
These are ions attracted to the anode (positively charged element) and are thus negatively charged. Important species pertaining to air pollution include

Sulfate: SO_4^{2-}

Nitrate NO_3^-

Carbonate CO_3^{2-}

Others include OH^- (hydroxide), Cl^- , Br^- , PO_4^{3-} , HSO_4^- (hydrogen carbonate), HCO_3^- , CH_3COO^- (acetate), $HCOO^-$ (formate), and $C_2O_4^{2-}$ (oxalate)..³⁵²



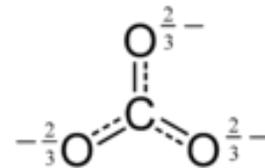
Cations

These are ions attracted to the cathode (negatively charged element) and are thus positively charged. Important species pertaining to air pollution include

Ammonium NH_4^+

Hydronium H_3O^+

Others include many metals: Al^{3+} , Ca^{2+} , Fe^{2+} , Fe^{3+} , Mg^{2+} , Na^+



Cyclone and Anti-Cyclone

Cyclone: “An atmospheric cyclonic circulation, a closed circulation. A cyclone's direction of rotation [is counterclockwise CCW in the Northern Hemisphere NH and clockwise CW in the Southern Hemisphere]. While modern meteorology restricts the use of the term cyclone to the so-called cyclonic-scale circulations, it is popularly still applied to the more or less violent, small- scale circulations such as tornadoes, waterspouts, dust devils, etc. (which may in fact exhibit anticyclonic rotation), and even, very loosely, to any strong wind... Because cyclonic circulation and relative low atmospheric pressure usually coexist, in common practice the terms cyclone and low are used interchangeably...”

Anticyclone: An atmospheric anticyclonic circulation, a closed circulation. The wind in an anticyclone is in the clockwise [CW] direction in the Northern Hemisphere and counterclockwise in the Southern Hemisphere. With respect to the relative direction of its rotation, it is the opposite of a cyclone. Because anticyclonic circulation and relative high atmospheric pressure usually coexist, the terms anticyclone and high are used interchangeably in common practice.³⁵³

Diagmagnetic and Paramagnetic

Diagmagnetic materials create “an induced magnetic field in a direction opposite to an externally applied

³⁴⁸ http://en.wikipedia.org/wiki/Air_pollution

³⁴⁹ <http://en.wikipedia.org/wiki/Albedo>

³⁵⁰ <http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/albedo.html>

³⁵¹ http://en.wikipedia.org/wiki/Bond_albedo

³⁵² Structures images from Wikipedia.

³⁵³ <http://glossary.ametsoc.org/wiki/cyclone> and <http://glossary.ametsoc.org/wiki/Anticyclone>

magnetic field, and are repelled by the applied magnetic field”.³⁵⁴

“Paramagnetism is a form of magnetism whereby certain materials are attracted by an externally applied magnetic field, and form internal, induced magnetic fields in the direction of the applied magnetic field... Paramagnetic materials include most chemical elements and some compounds... Unlike ferromagnets, paramagnets do not retain any magnetization in the absence of an externally applied magnetic field.”³⁵⁵

Dissolution and Solvation

Dissolution is the process by which a solute forms a solution in a solvent. Dissolution is a kinetic process, and is quantified by its rate. The outcome of the process of dissolution ... is governed by the thermodynamic energies involved, such as the heat of solution and entropy of solution, but the dissolution itself (a kinetic process) is not. Solvation is an interaction of a solute with the solvent, which leads to stabilization of the solute species in the solution. Solvation is, in concept, distinct from dissolution and solubility.

e-folding time (or e-folding lifetime) τ_A

For reactions in which a reactant is lost at a rate proportional to the concentration, this is defined as the time τ_A required for the concentration of a substance to decrease to $1/e = 36.79\%$ of the initial amount. It is therefore a little longer than the half-life. The use of the word “fold” is analagous to its use in the phrase “a two-fold decrease”.

Geopotential Height Z, Geometric Height z, Reference Ellipsoid for Mean Sea Level, and Geoid

Geopotential Height is usually symbolized by upper case Z rather than ordinary “geometric” height z. It is “the height of a given point in the atmosphere in units proportional to the potential energy of unit mass (geopotential) at this height relative to sea level. The relations, in SI units, between the geopotential Φ , the geopotential height Z, and the geometric height z are:

$$\Phi = \int_0^z g(\phi, z) dz$$

$$Z = \Phi / g_0$$

$$Z = \frac{1}{g_0} \int_0^z g(\phi, z) dz$$

where Φ = Geopotential (work to lift a unit mass to the geometric height above MSL)
 $g(\phi, z)$ = acceleration of gravity, varying with ϕ and z, in $m s^{-2}$
 g_0 = standard gravity near the Earth's surface, defined as exactly $9.80665 m s^{-2}$
 ϕ = Latitude
 z = geometric height m above the WGS84 datum reference ellipsoid (taken as MSL)
 Z = Geopotential height m

The two heights are numerically interchangeable for most meteorological purposes.”³⁵⁶

The datum surface used to define mean sea level, and therefore the surface for which $z = Z = 0$, is commonly taken to be the reference ellipsoid (oblate spheroid) known as the World Geodetic System 84 Reference Ellipsoid [“WGS 84”]. The WGS 84 datum surface is the reference system used by the Global Positioning System.³⁵⁷ As a mathematically defined ellipsoid, this idealized surface will differ from actual calculated local sea level.

The geoid is “that equipotential surface which would coincide exactly with the mean ocean surface of the Earth, if the oceans were in equilibrium, at rest [no winds or tides], and extended through the continents (such as with very narrow canals [or tunnels])... It is a smooth but highly irregular surface that corresponds not to the actual surface of the Earth's crust, but to a surface which can only be known through extensive gravitational measurements and calculations... The surface of the geoid is higher than the reference ellipsoid wherever there is a positive gravity anomaly (mass excess) and lower than the

³⁵⁴ <http://en.wikipedia.org/wiki/Diamagnetism>

³⁵⁵ <http://en.wikipedia.org/wiki/Paramagnetism>

³⁵⁶ <http://amsglossary.allenpress.com/glossary/search?id=geopotential-height1>

³⁵⁷ http://en.wikipedia.org/wiki/Global_Positioning_System

reference ellipsoid wherever there is a negative gravity anomaly (mass deficit).”³⁵⁸ “Presently WGS 84 uses the 1996 Earth Gravitational Model (EGM96) geoid, revised in 2004. This geoid defines the nominal sea level surface... The deviations of the EGM96 geoid from the WGS 84 reference ellipsoid range from about -105 m to about +85 m.”³⁵⁹

Heat Transfer Relative to the Atmosphere, Methods

- (1) Conduction: Transfer of energy in the conductor from one molecule to the next in the presence of a temperature gradient. The medium does not move. It can occur through soil, air, and particles. Conductive heat flow occurs primarily between the surface and the adjacent 1 mm of air, where the temperature gradient is high.
- (2) Convection: Transfer of energy by the mass movement of air, predominantly in the vertical direction.
- (3) Advection: Horizontal movement of energy, gases, and particles by the wind.
- (4) Radiation: Transfer of energy by electromagnetic waves or photons.

Hydrometeor

“Any product of condensation or deposition of atmospheric water vapor, whether formed in the free atmosphere or at the earth's surface [such as dew and hoarfrost]; also, any water particle blown by the wind from the earth's surface. Hydrometeors may be classified in a number of different ways, of which the following is one example:

- 1) liquid or solid water particles formed and remaining suspended in the air, for example, damp (high relative humidity) haze, cloud, fog, ice fog, and mist;
- 2) liquid precipitation, for example, drizzle and rain;
- 3) freezing precipitation, for example, freezing drizzle and freezing rain;
- 4) solid (frozen) precipitation, for example, snow, hail, ice pellets, snow pellets (soft hail, graupel), snow grains, and ice crystals;
- 5) falling particles that evaporate before reaching the ground, for example, virga;
- 6) liquid or solid water particles lifted by the wind from the earth's surface, for example, drifting snow, blowing snow, and blowing spray.”³⁶⁰ Hydrometeor particles differ from aerosols primarily by having much more water—i.e., they consist predominantly water. (APGW p. 3)

International Union of Pure and Applied Chemistry (IUPAC)

“serves to advance the worldwide aspects of the chemical sciences and to contribute to the application of chemistry in the service of Humankind.”³⁶¹

Isobar

A contour line of equal pressure, usually expressed as surface level pressure after adjustment to mean sea-level (SLP). Surface pressure readings that are not corrected to SLP would have little predictive usefulness, as pressure over the mountains would always be low and pressure over lowlands would always be high. “An isobar ... is a line of equal or constant pressure on a graph, plot, or map; an isopleth [isoline] or contour line of pressure. More accurately, isobars are lines drawn on a map joining places of equal average atmospheric pressure reduced to sea level for a specified period of time. In meteorology, the barometric pressures shown are reduced to sea level, not the surface pressures at the map locations. The distribution of isobars is closely related to the magnitude and direction of the wind field, and can be used to predict future weather patterns...”³⁶²

Wind blows to some extent across isobars from higher to toward lower pressure (but see discussion with Coriolis effect as to how wind is deflected by this effect).

Isoentropic (Isentropic) process

“In thermodynamics, an isentropic process or isoentropic process ... is one in which for purposes of engineering analysis and calculation, one may assume that the process takes place from initiation to completion without an increase or decrease in the entropy of the system, i.e., the entropy of the system remains constant. It can be proved that any reversible adiabatic process is an isentropic process.”³⁶³

³⁵⁸ <http://en.wikipedia.org/wiki/Geoid>

³⁵⁹ http://en.wikipedia.org/wiki/World_Geodetic_System

³⁶⁰ <http://glossary.ametsoc.org/wiki/Hydrometeor>

³⁶¹ <http://www.iupac.org/>

³⁶² http://en.wikipedia.org/wiki/Contour_line

³⁶³ http://en.wikipedia.org/wiki/Isentropic_process

Isohypse

A contour line on a constant pressure height surface (e.g., the 500 mb surface) for which line the height above sea level (typically, the geopotential height above mean sea level) is constant. The pressure along the contour line also happens to be constant, but this applies to the entire constant pressure surface by definition, whereas the different isohypse contours have different geopotential heights. Thus on such a surface, there would only be one isobar.

Isopleth (Isoline)

In meteorology, the word isopleth is used for any type of contour line graph, and is synonymous with isoline. In this document, we encounter this term when two atmospheric pollutants are represented on X and Y axes, and the isopleth lines represent particular values of the concentration of a third variable such as ozone. In contrast, "In geography, the word isopleth (from plethos, meaning 'quantity') is used for contour lines that depict a variable which cannot be measured at a point, but which instead must be calculated from data collected over an area. An example is population density."³⁶⁴

Isotherm

A contour line of constant temperature.

Mixing Ratio

There is an interesting discrepancy in definitions for "mixing ratio" for substances in air such as N₂.

Daniel J. Jacob in *IAC* defines it thus: "The mixing ratio CX of a gas X (equivalently called the mole fraction) is defined as the number of moles of X per mole of air [thus presumably including the N₂]. It is given in units of mol/mol (abbreviation for moles per mole)..."³⁶⁵ By this definition, the mixing ratio for N₂ is 0.78.

But other sources define mixing ratio as

(1) "the dimensionless ratio of the mass of a substance (such as water vapor) in an air parcel to the mass of the remaining substances in the air parcel."³⁶⁶

(2) "the amount of a constituent n_i divided by the total amount of all other constituents in a mixture"³⁶⁷

(3) "The ratio of the weight of water vapor in a specified volume (such as an air parcel) to the weight of dry air in that same volume."³⁶⁸

Using these definitions, the mixing ratio for N₂ would exclude N₂ from the denominator of the ratio and be more like $78/22 = 3.5$.

An unambiguous and clearly better term for this purpose is mole fraction, the definition referred to for mixing ratio by the IPCC.³⁶⁹

Oxidation and Reduction (Redox) Reactions

Redox (shorthand for reduction/oxidation) reactions describe all chemical reactions in which atoms have their oxidation number (oxidation state) changed. This can be either a simple redox process such as the oxidation of carbon to yield carbon dioxide, or the reduction of carbon by hydrogen to yield methane (CH₄), or it can be a complex process such as the oxidation of sugar in the human body through a series of very complex electron transfer processes.

Oxidation describes the loss of electrons by a molecule, atom or ion; Reduction describes the gain of electrons by a molecule, atom or ion. Oxidation and reduction properly refer to a change in oxidation number—the actual transfer of electrons may never occur. Thus, oxidation is better defined as an increase in oxidation number, and reduction as a decrease in oxidation number. In practice, the transfer of electrons will always cause a change in oxidation number, but there are many reactions which are classed as "redox" even though no electron transfer occurs (such as those involving covalent bonds).

Substances that have the ability to oxidize other substances are said to be oxidative and are known as oxidizing agents, oxidants or oxidizers. Put in another way, the oxidant removes electrons from another

³⁶⁴ http://en.wikipedia.org/wiki/Contour_line#Isopleths

³⁶⁵ <http://acmg.seas.harvard.edu/people/faculty/djj/book/bookchap1.html#pgfld=439991>

³⁶⁶ <http://goldbook.iupac.org/M03948.html>

³⁶⁷ http://en.wikipedia.org/wiki/Mixing_ratio

³⁶⁸ <http://forecast.weather.gov/glossary.php?word=mixing%20ratio>

³⁶⁹ *IPCC_WGI_2013* Glossary

substance, and is thus reduced itself. And because it "accepts" electrons it is also called an electron acceptor.³⁷⁰ The substance oxidized is called a reducing agent.

Pressure Height Isohyphse vs. Constant absolute altitude Isobar pressure contours: The isohyphse contour lines (e.g., in m for the 500 mb pressure height surface) follow the same pattern and appear nearly identical compared to the isobar pressure contour lines (in mb) of a constant absolute height map (e.g., the 5600 m surface).³⁷¹ The latter type of graph does not appear to be commonly encountered in routine weather mapping (other than sea level pressure charts described above).

Radical and Biradical

A (free) radical is a molecular entity (atom, molecule, ion, etc.) that has one or more unpaired valence electrons or an open electron shell, and therefore may be seen as having one or more dangling covalent bonds. Many radicals are electrically neutral. Because of the unpaired electron spin, all radicals are paramagnetic (attracted to a magnet), but paramagnetic metal ions are not normally regarded as radicals. For molecular entities, the unpaired electron is often in a singly occupied molecular orbital (SOMO, such as $2p_z$), and are often represented by a dot. With some exceptions, radicals are highly chemically reactive. In some cases they dimerize or polymerize with themselves. Most radicals are reasonably stable only at very low concentrations in inert media or in a vacuum. Examples include:

- the hydroxyl radical ($\text{HO}\cdot$), a molecule that has one dangling bond (unpaired electron) arising from the oxygen;
- the carbene molecule ($:\text{CH}_2$), which has two dangling bonds;
- the superoxide anion ($\cdot\text{O}_2^-$); and
- the oxygen molecule O_2 , said to be a biradical with two unpaired electrons and thus two dangling bonds.

A biradical is a molecular entity with two possibly delocalized radical centers (unpaired electrons), but with an overall even-electron count.

Free radicals may be created in a number of ways, including thermolysis, photolysis, low temperature or other specific chemical reactions, ionizing radiation, electrical discharges, electrolysis, etc. Radicals are intermediate stages in many chemical reactions. Free radicals play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes. Following recent nomenclature revisions, radical now implies free radical.³⁷²

Sea and large lake breezes are a type of thermal circulation. At mid-latitudes these are strongest in spring and summer. When land warms during the day, air rises over this land, a pressure gradient develops, and cooler sea breezes blow inland to replace the air. At night, when the land cools faster than the sea surface, the air rises more over the sea and is replaced by offshore winds from land. (MT8-237)

Troughs and Ridges

Trough: "In meteorology, an elongated area of relatively low atmospheric pressure; the opposite of a ridge. The axis of a trough is the trough line. This term [trough] is commonly used to distinguish [the elongated area of low pressure] from the closed circulation of a low (or cyclone), but a large-scale trough may include one or more lows, an upper-air trough may be associated with a lower-level low, and a low may have one or more distinct troughs radiating from it..."³⁷³ A trough is usually defined on a constant pressure surface, typically 500 mb.

Ridge: "Sometimes called [a] wedge. In meteorology, an elongated area of relatively high atmospheric pressure, almost always associated with and most clearly identified as an area of maximum anticyclonic curvature of wind flow. The locus of this maximum curvature is called the ridge line [i.e., the line connecting the points of maximum anticyclonic curvature in a ridge]. Sometimes, particularly in discussions of atmospheric waves embedded in the westerlies, a ridge line is considered to be a line drawn through all points at which the anticyclonically curved isobars or contour lines are tangent to a latitude circle. The most common use of this term is to distinguish it from the closed circulation of a high (or anticyclone); but a ridge may include a high (and an upper-air ridge may be associated with a surface high)

³⁷⁰ adapted from an earlier version of <http://en.wikipedia.org/wiki/Redox>

³⁷¹ former URL: http://atoc.colorado.edu/~cassano/atoc1050/Lecture_Notes/Chapter03/chapter3.pdf

³⁷² Paraphrased from

- <http://en.wikipedia.org/wiki/Oxygen>
- http://research.cm.utexas.edu/nbauld/unit5_radicals.htm and
- <http://www.britannica.com/EBchecked/topic/488669/radical/6040/Magnetic-properties-of-free-radicals>
- <http://goldbook.iupac.org/R05066.html>

³⁷³ <http://glossary.ametsoc.org/wiki/Trough>

and a high may have one or more distinct ridges radiating from its center. The opposite of a ridge is a trough...”³⁷⁴ A ridge is usually defined on a constant pressure surface, typically 500 mb.

(See also Convergence and Divergence above)

³⁷⁴ <http://glossary.ametsoc.org/wiki/Ridge>