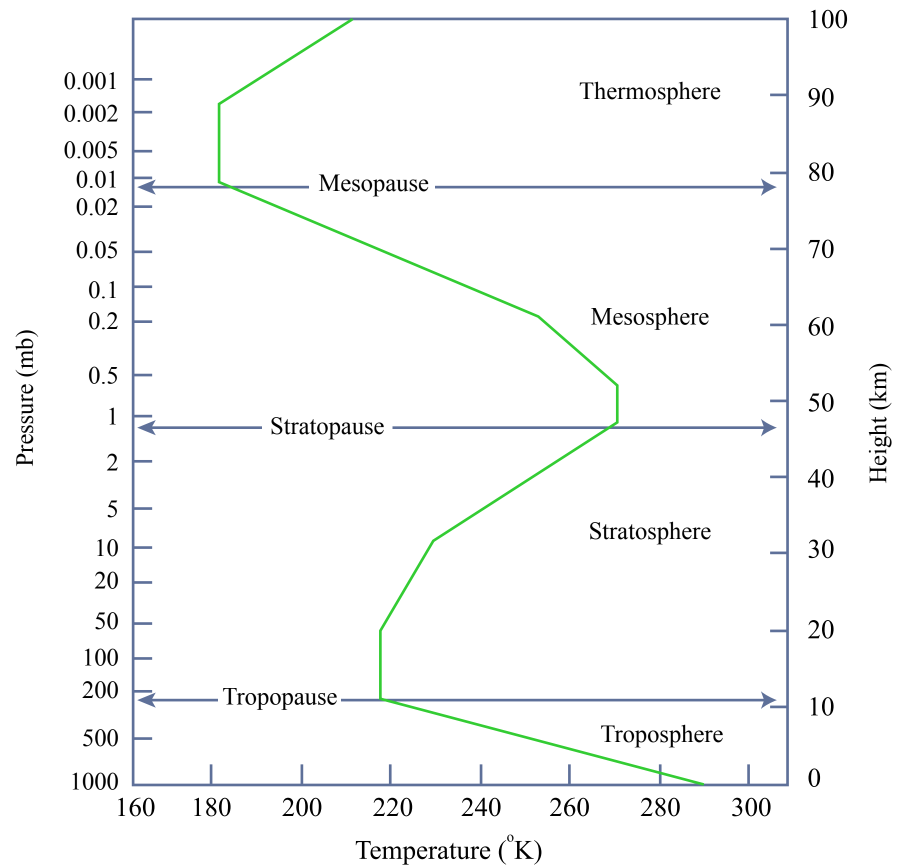
Introduction to Atmosphere – Ocean Interactions

- Atmospheric composition
- Aerosols & greenhouse gases
- UV radiation and ozone
- Some examples:
  - Sulfur cycling
  - Dust (iron)
  - Acid rain
  - Halogen chemistry & sea salt particles

Vertical levels of the atmosphere



Idealized vertical temperature profile according to the U.S. Standard Atmosphere (1976). Also shown are the names commonly used for the various layers and pauses in the atmosphere.

Figure by MIT OCW.

Boundary Layer: ~ 1 km

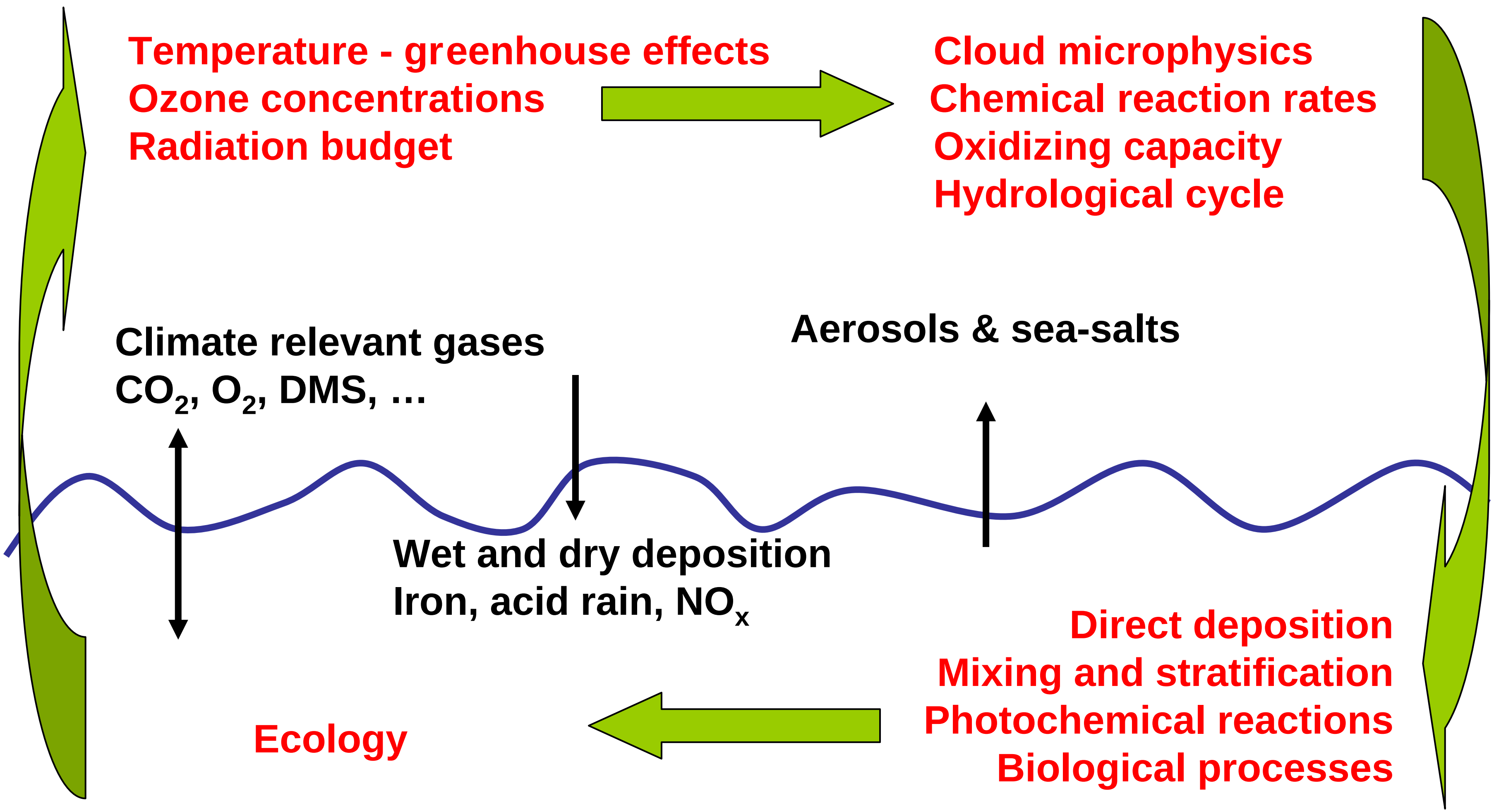
Troposphere: region of strong vertical mixing

Stratosphere: region of weak vertical mixing

Considerable differences in size, chemical nature, sources of the aerosols and gases

Transport across tropopause via large scale ascent in the tropics / descent in the poles, cloud convection, or tropopause folding

Atmosphere – Ocean Interactions in a Nutshell



Sunlight is a powerful structuring agent

Components of atmosphere

N_2	780840
O_2	209460
H_20	0 - 40000
Ar	9340
$C0_2$	350
H_2	0.53
CH_4	1.7
N_20	0.3
CO	0.04 – 0.2
SO_2	10^{-4}
H_2S	10^{-4}
O_3	.1

ppmv

- ~ 78% nitrogen, 21% oxygen
- Water vapor is the most variable component
- Trace components can have enormous impacts on the radiation budget and inputs to the ocean
- Lifetimes (residence times) vary from 10^7 – 10^9 years for N_2 to days for ozone at high altitudes
- Sources and sinks vary spatially and temporally

Aerosols

- Aerosol = suspension of particles in a gas
    - Liquid = cloud or mist
    - Solid = dust or smoke

- The direct effect relates to the changes in net radiative fluxes in the atmosphere caused by the modulation of atmospheric scattering and absorption properties due to changes in aerosol concentration and optical properties

- The indirect effect relates to the changes in net radiative transfer in the atmosphere caused by the modulation of cloud properties due to changes in the concentration of cloud condensation nuclei, CCN

4 types of aerosol reactions

1) *Homogeneous, homomolecular* = the condensation of a single gaseous component to form a new suspended particle (H_20 molecules forming droplets)

2) *Homogeneous, heteromolecular* = reaction of 2 or more gases to form a new particle

$$NH_{3(g)} + HNO_{3(g)} \Rightarrow NH_4NO_{3(s)}$$

3) *Heterogeneous, heteromolecular* = reaction of gases on a pre-existing particle

$$NaCl_{(s)} + HNO_{3(g)} \Rightarrow HCl_{(g)} + NaNO_{3(s)}$$

4) Chemical reactions within the aerosols themselves to form particles of changed composition (oxidation of SO_2 to sulfate ions in clouds)

Absorption and scattering

- Different gases & aerosols absorb at different λs:

  Direct absorption of UV by ozone (< 290 nm)

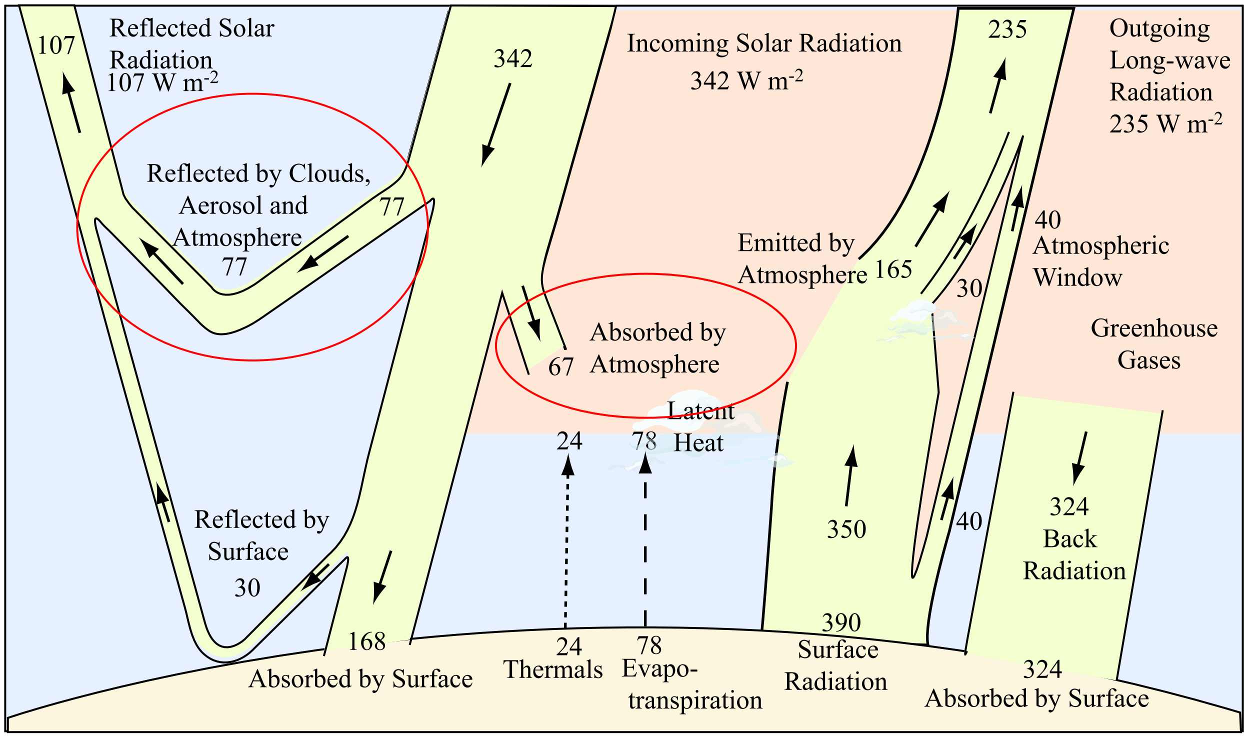
- Scattering is a function of particle size relative to the λ of radiation:

Rayleigh scattering: particles are generally small compared to the λs of light (gases)

Mie scattering: particles are generally equal to or greater than the λs of light (aerosols & droplets)

CCNs are ~0.1 μm containing 10^8 H_20 molecules per drop

Earth’s energy budget



Schematic showing the atmospheric and surface processes determining the earth's annual global mean energy budget . Unit are W m^{-2}

Figure by MIT OCW.

Greenhouse gas warming

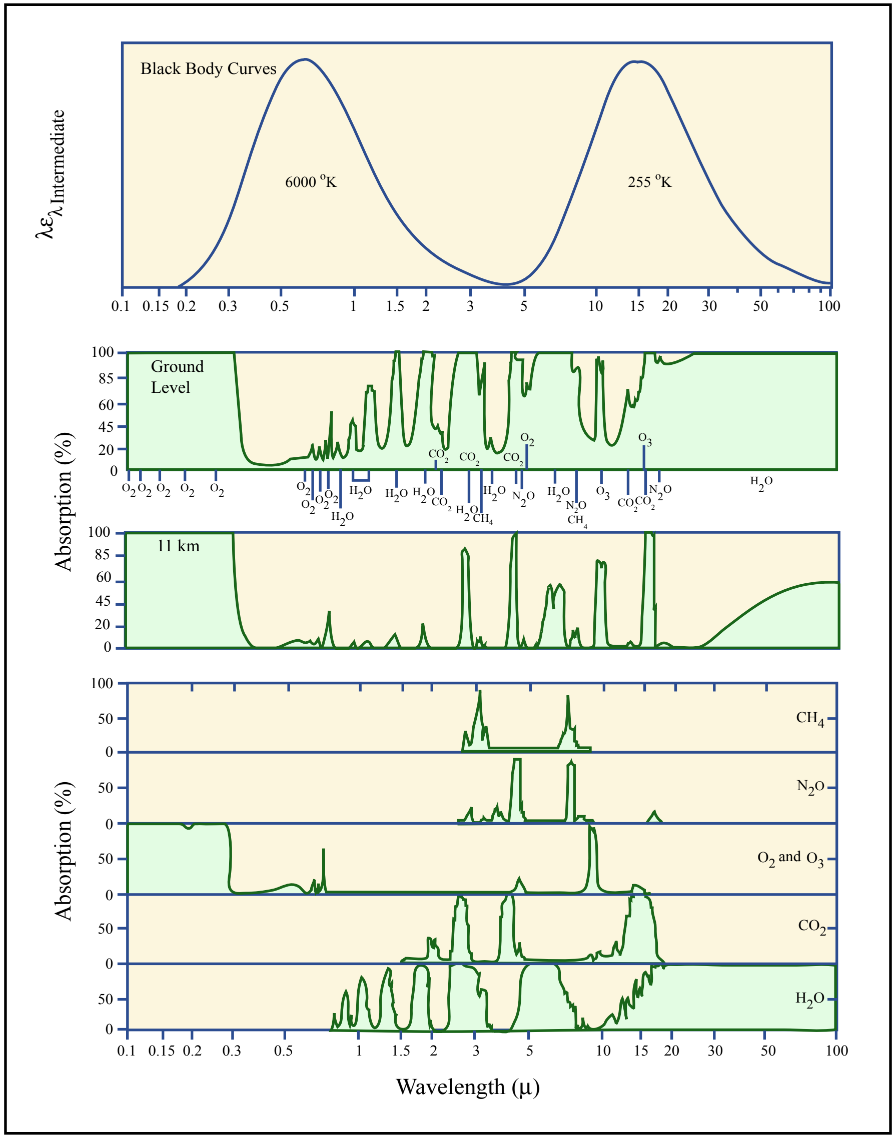


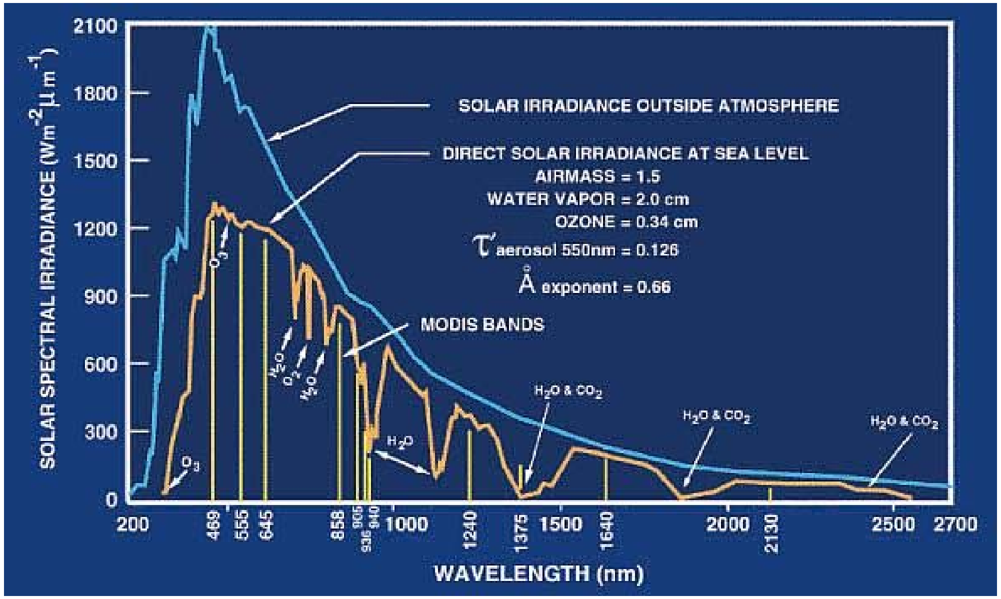
Figure by MIT OCW.

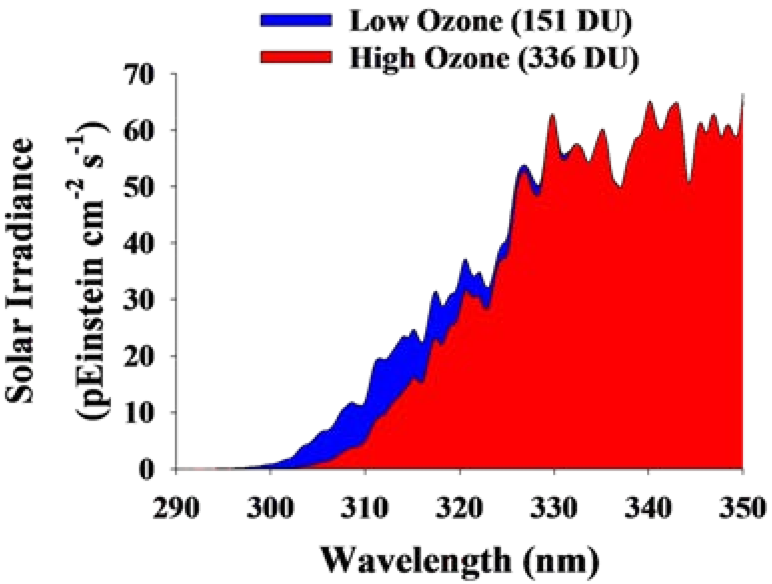
Peixoto and Oort, 1992

- Absorb incoming photons and dissipate energy as heat
- Greenhouse gases have overlapping infrared bands

Species removed	% trapped radiation remaining
None	100
O_3	97
CO_2	88
Clouds	86
H_2O	64
H_2O, CO_2, O_3	50
H_2O,O_3,clouds	36
All	0

Radiation at the ocean surface





From Palmer Station, 2000

- UV-C = λs < 280 nm
- UV-B = λs 280 – 320 nm
- UV-A = λs 320 – 400 nm
- Visible = λs 400 – 700 nm
- IR = λs 700 nm – 1 mm

The importance of UV radiation in the ocean

- Overall a very small % of total solar flux but:
  - Affects biology – protein & nucleic acid damage, inhibits photosynthesis, bacterial production, photoenzymatic repair, etc.
  - Causes photochemical reactions
    - Inorganic – Nitrate/nitrite photolysis, Fe(III) reduction to Fe(II)
    - Organic – DOM breakdown & alteration

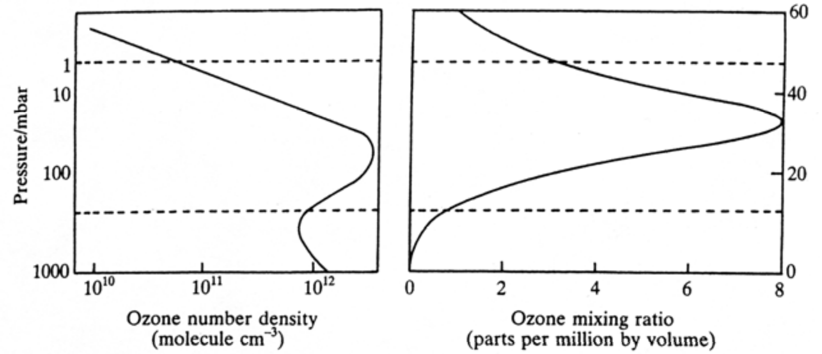


Fig. 1.2. Variation of atmospheric ozone concentration with altitude, expressed as an absolute number density and as a mixing ratio. From *Stratospheric Ozone 1988*, UK Stratospheric Ozone Research Group, HMSO, London, 1988.

Flux regulated by **OZONE** concentrations

Stratosphere ozone chemistry

- Stratosphere is dominated by oxygen atoms and ozone related reactions

$$O_2 + h\nu\ (\lambda < 240\ \text{nm}) \Rightarrow O(^1D) + O(^1D)$$

$$O(^1D) + O_2 + M \Rightarrow O_3 + M$$

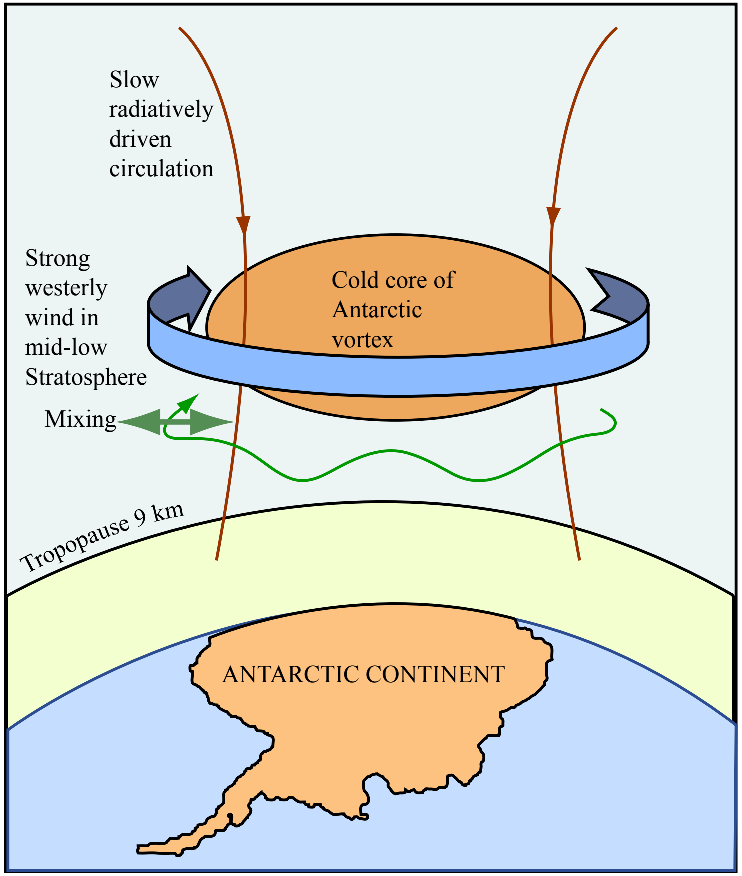
$$O_3 + h\nu\ (\lambda < 240\ \text{nm}) \Rightarrow O(^1D) + O_2$$

$$O(^1D) + O_3 \Rightarrow 2O_2$$

- UV light converted into heat
- Ozone can be destroyed by a number of free radical catalysts: OH, NO, Cl, and Br
- OH and NO are predominately natural while Cl and Br have anthropogenic origins from CFCs

Antarctic ozone hole

- Very low temps (< -80 C) lead to formation of polar stratospheric clouds
- A vortex forms as air cools and descends in winter
- Strong westerly circulation isolates the region from lower latitudes

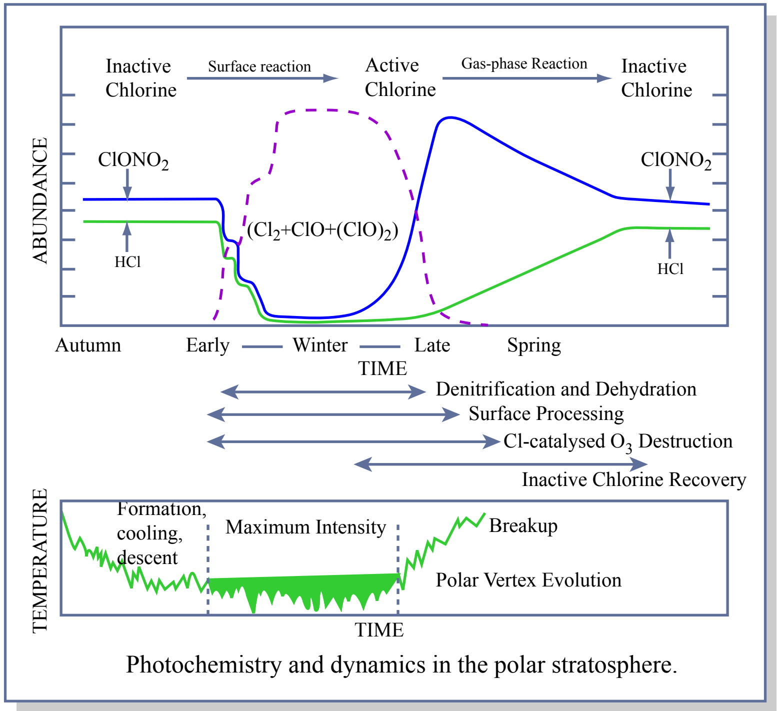


The winter vortex over Antarctica. The cold core is almost isolated from the rest of the atmosphere, and acts as a reaction vessel in which the constituents may become chemically 'preconditioned' during the long polar night.

Figure by MIT OCW.

Antarctic ozone hole

- PSCs provide surfaces for chemical reactions
- Highly deficient in oxides of nitrogen
- Very dry → condensation of water
- Catalytic destruction of ozone



Photochemistry and dynamics in the polar stratosphere.

Figure by MIT OCW.

$$Cl_2 + h\nu \Rightarrow Cl + Cl$$

$$Cl + O_3 \Rightarrow ClO + O_2$$

$$ClO + O \Rightarrow Cl + O_2$$

Antarctic stratospheric ozone hole 2005

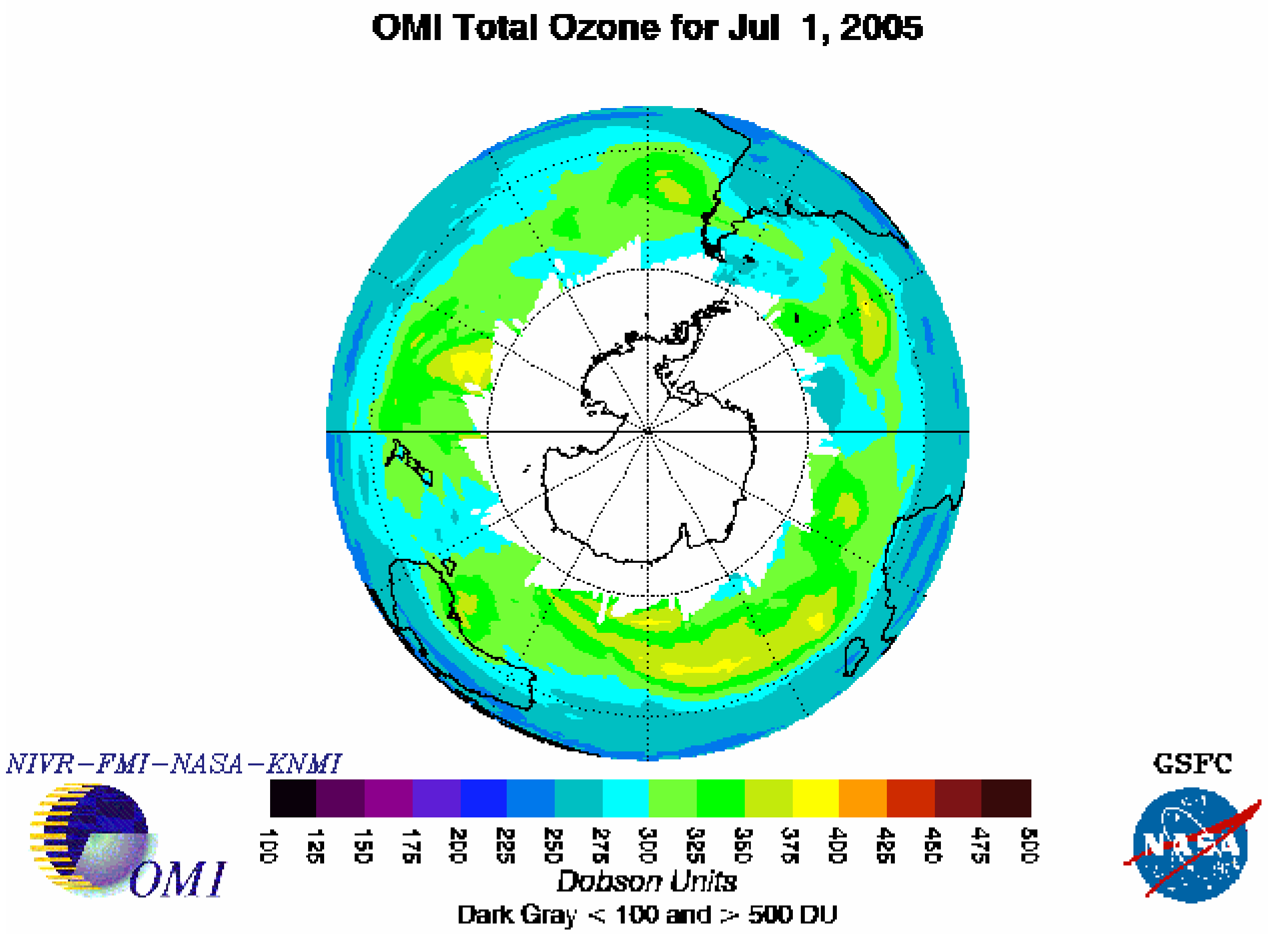


Figure courtesy NASA GSFC

1 Dobson unit = column ozone compressed to 10 um thick at STP

Chemistry in the troposphere

- Troposphere oxidation reactions are initiated by the highly reactive hydroxyl radical (OH) during the day

$$O_3 + h\nu \Rightarrow O_2 + O(^1D)$$

an electronically excited state of the oxygen atom, $O(^1D)$ can then react with methane or water

$$O(^1D) + H_2O \Rightarrow OH + OH$$

$$O(^1D) + CH_4 \Rightarrow OH + CH_3$$

- And nitrate radicals at night (nitrate is rapidly photolyzed)

$$NO_2 + O_3 \Rightarrow NO_3 + O_2$$

- Govern fates of almost all trace gases in the troposphere

Radiation Forcing

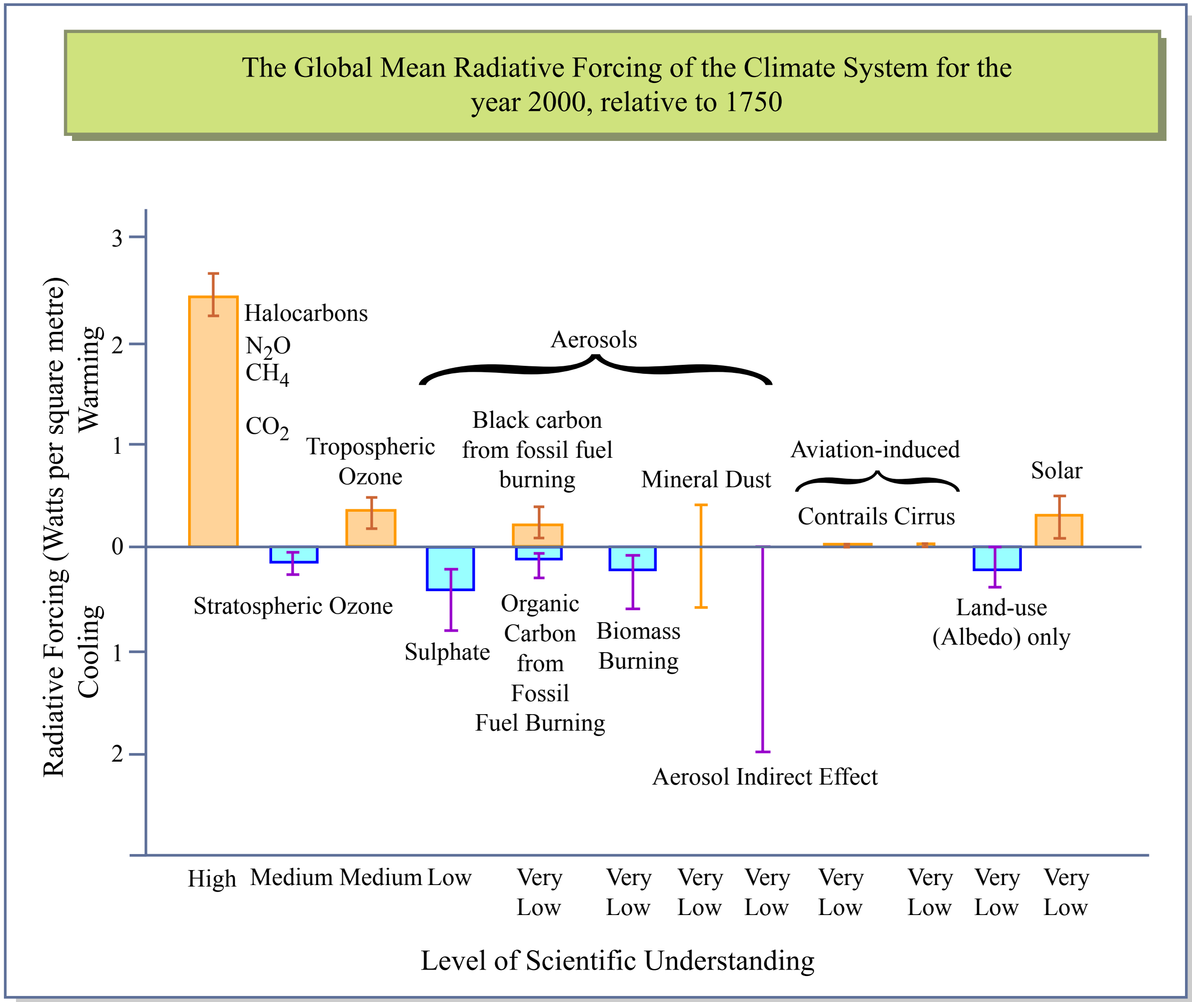


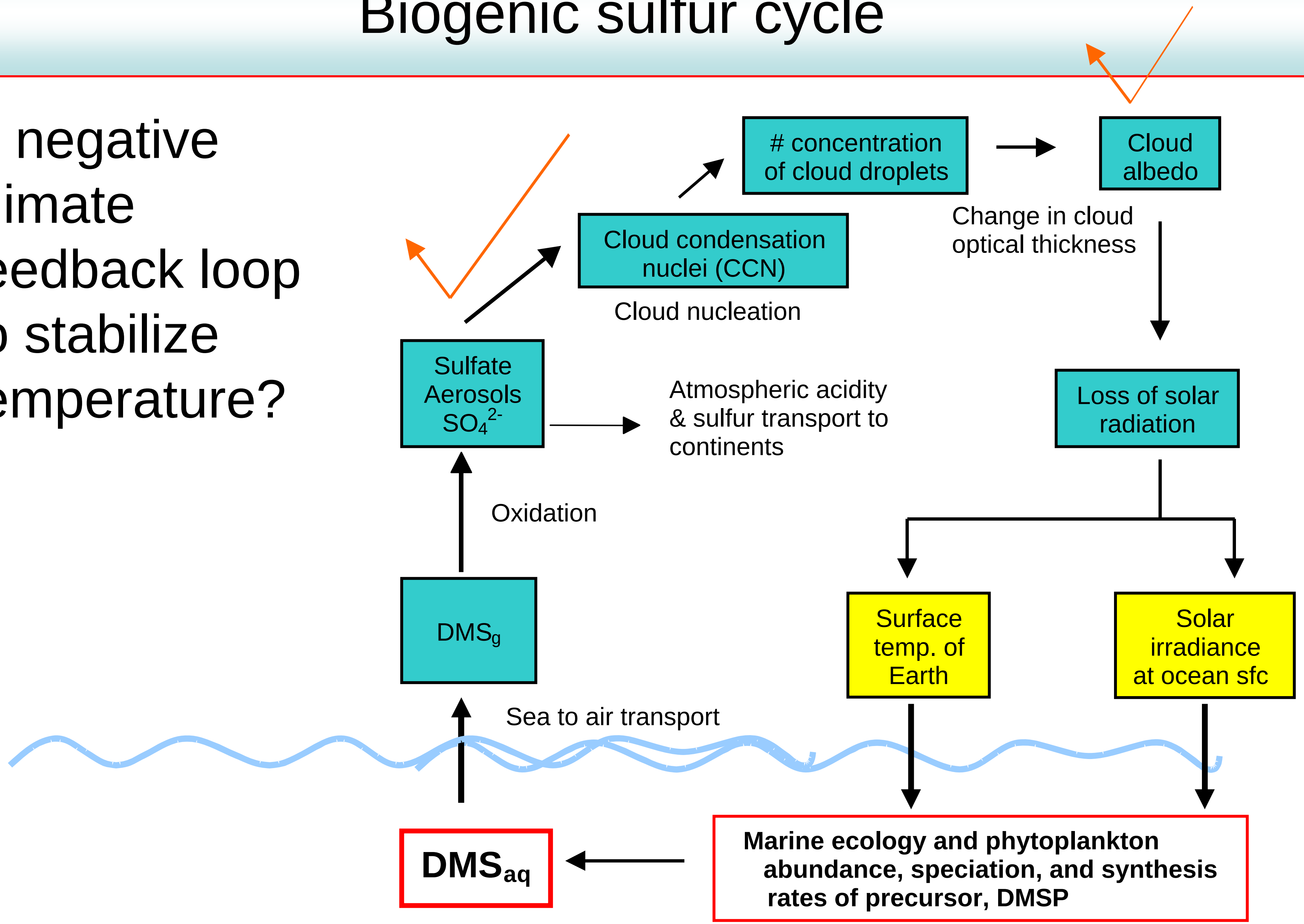
Figure by MIT OCW.

- Our estimates are ‘best’ for the greenhouse gases and decrease in certainty for ozone processes and mineral and sulfate aerosols

Now some examples of compounds that are of great interest in the ocean….

Biogenic sulfur cycle

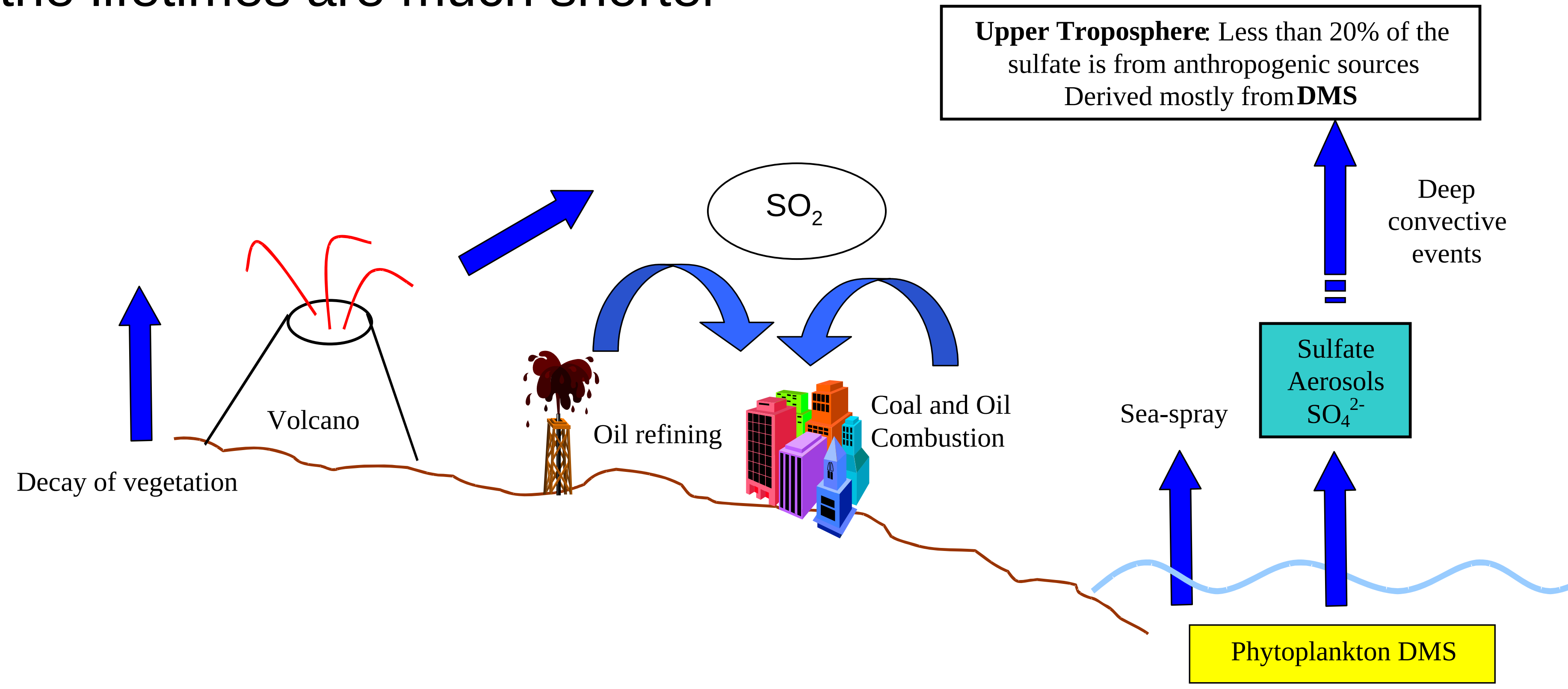
A negative climate feedback loop to stabilize temperature?



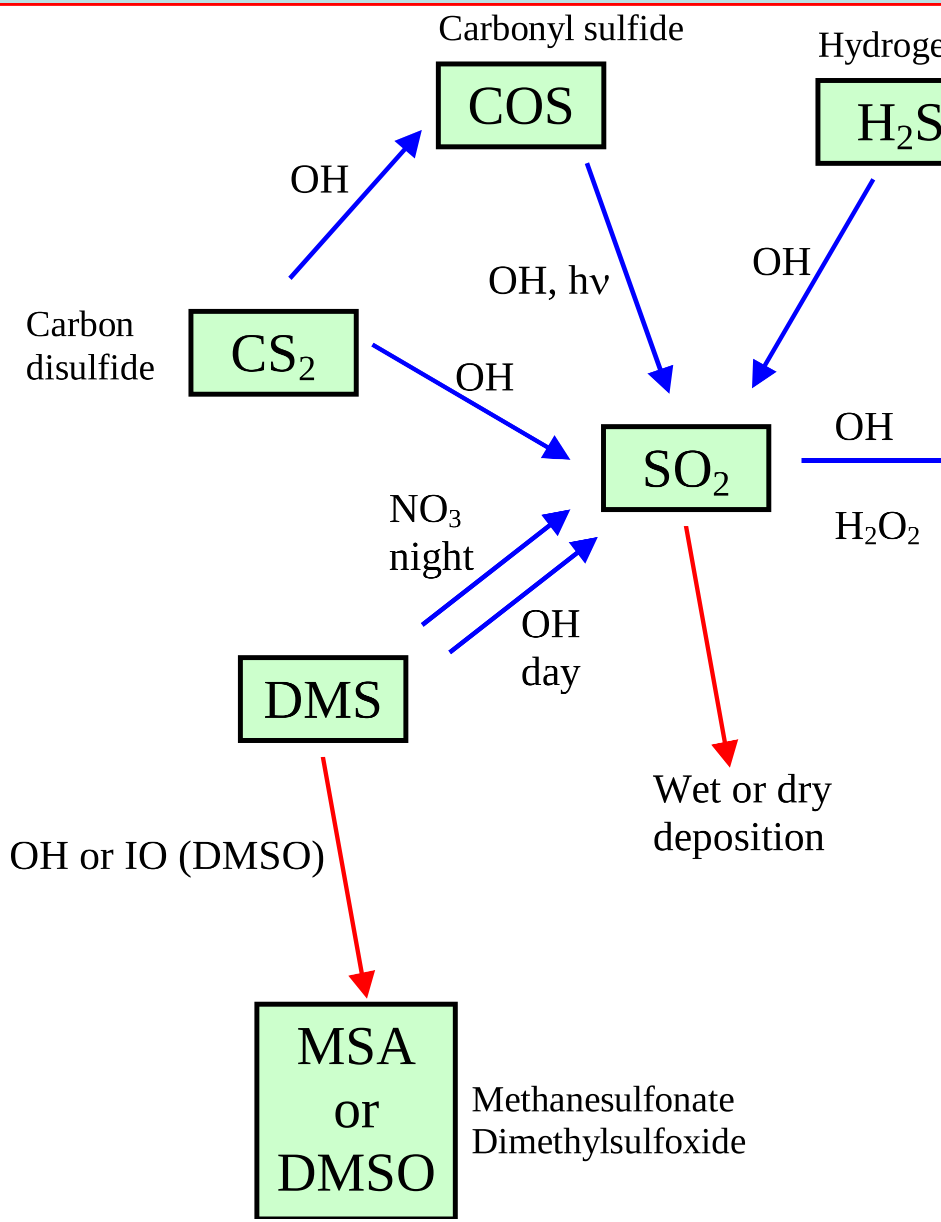
CLAW hypothesis after Charlson et al., 1987

Sulfur flux

- DMS contributes > 90% of the oceanic sulfur flux and > 50% of the global biogenic flux
- Estimated anthropogenic sources of sulfur are approximately three times larger than biogenic sources BUT the lifetimes are much shorter



DMS impacts atmospheric chemistry



- Acid rain - in the North Sea region DMS can account for up to 25% of the tropospheric H_2SO_4 over Europe
- Is thought to be the source of the stratospheric COS layer and background atm. levels of MSA, SO_2, and nssSO_4^{2-}

Iron Cycling – Mineral aerosols

- In the equatorial Pacific, the subarctic Pacific, and the Southern Ocean nitrate and phosphate concentrations are high year round and standing stocks of phytoplankton are always low =

High Nitrate Low Chlorophyll (HNLC) regions

- Iron limitation?? (1988, Martin and Fitzwater)
- Fe(III) versus Fe(II)

Source	Flux
Fluvial particulate total iron	625 to 962
Fluvial dissolved iron	1.5
Glacial sediments	34 to 211
Atmospheric	16
Coastal erosion	8
Hydrothermal	14
Authigenic	5

Figure by MIT OCW.

Jickells et al., 2005

Input of new iron to the surface waters is dominated by the **atmospheric deposition of soluble iron in mineral aerosols** (wet & dry deposition)

Iron in the ocean

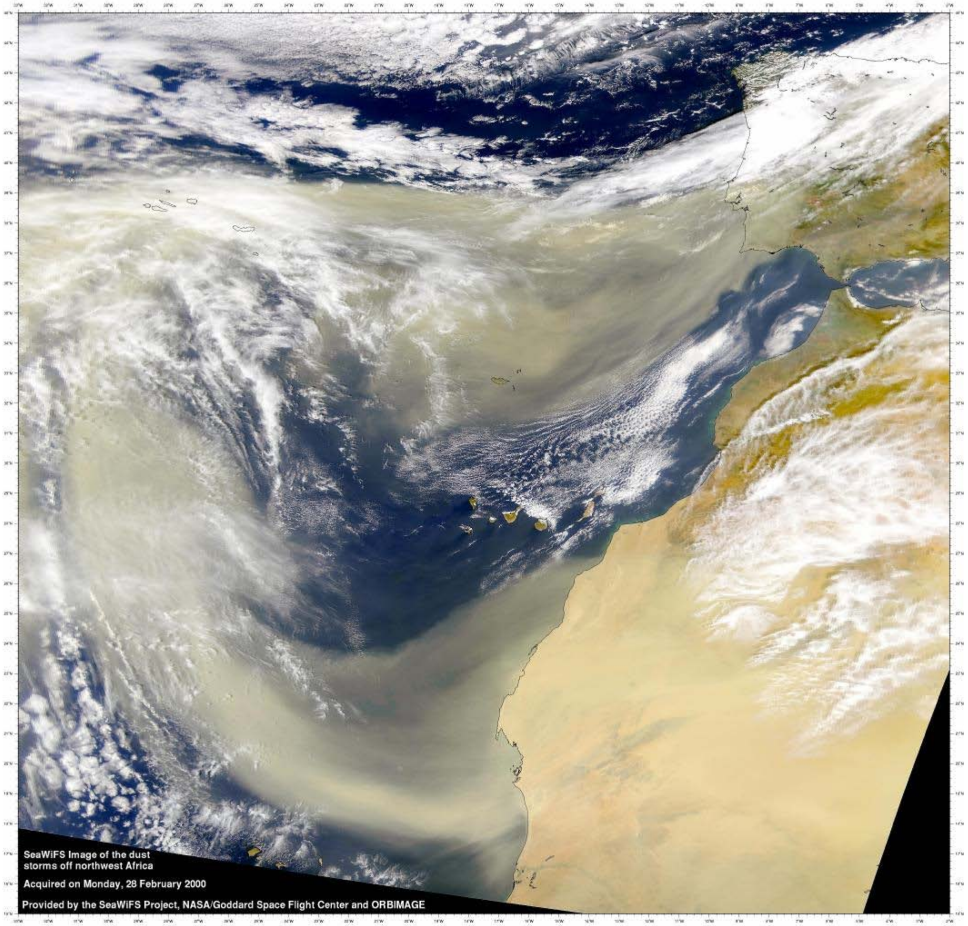
- Sub-nanomolar concentrations in surface waters
- Fe is extremely insoluble in oxygenated seawater, so the bio availability of Fe is controlled by presence of organic ligands that enhance Fe solubility

Dust variability

Image removed due to copyright restrictions.

- Dust (iron) input to the ocean is highly variable:
  - Spatially
  - Seasonally (rainfall & transport patterns) & glacial-interglacial
  - Episodic (wind speed)
  - Solubility

Dust transport examples



SeaWiFS image from Feb 28, 2000

Image Courtesy NASA GSFC

Rainfall sample from Sargasso Sea, July 2004

Nitrogen deposition

- Nitrous oxide from the ocean contributes ~4 Tg yr^{-1} to the atmosphere (upwelling and deep convective areas)

$$O(^1D) + N_2O \Rightarrow NO + NO$$

- Anthropogenic sources of NO_x ($NO_x = NO + NO_2$) are fossil fuels, biomass burning, and fertilizer
- NO_x chemistry in stratosphere:

$$NO + O_3 \Rightarrow NO_2 + O_2$$

$$OH + NO_2 + M \Rightarrow HNO_3 + M$$

(M = species which dissipates energy)

- HNO_3 nitric acid is highly soluble in droplets = wet depositions
- Photolysis of NO_2 is the only known way of producing ozone in the troposphere

Acid Rain

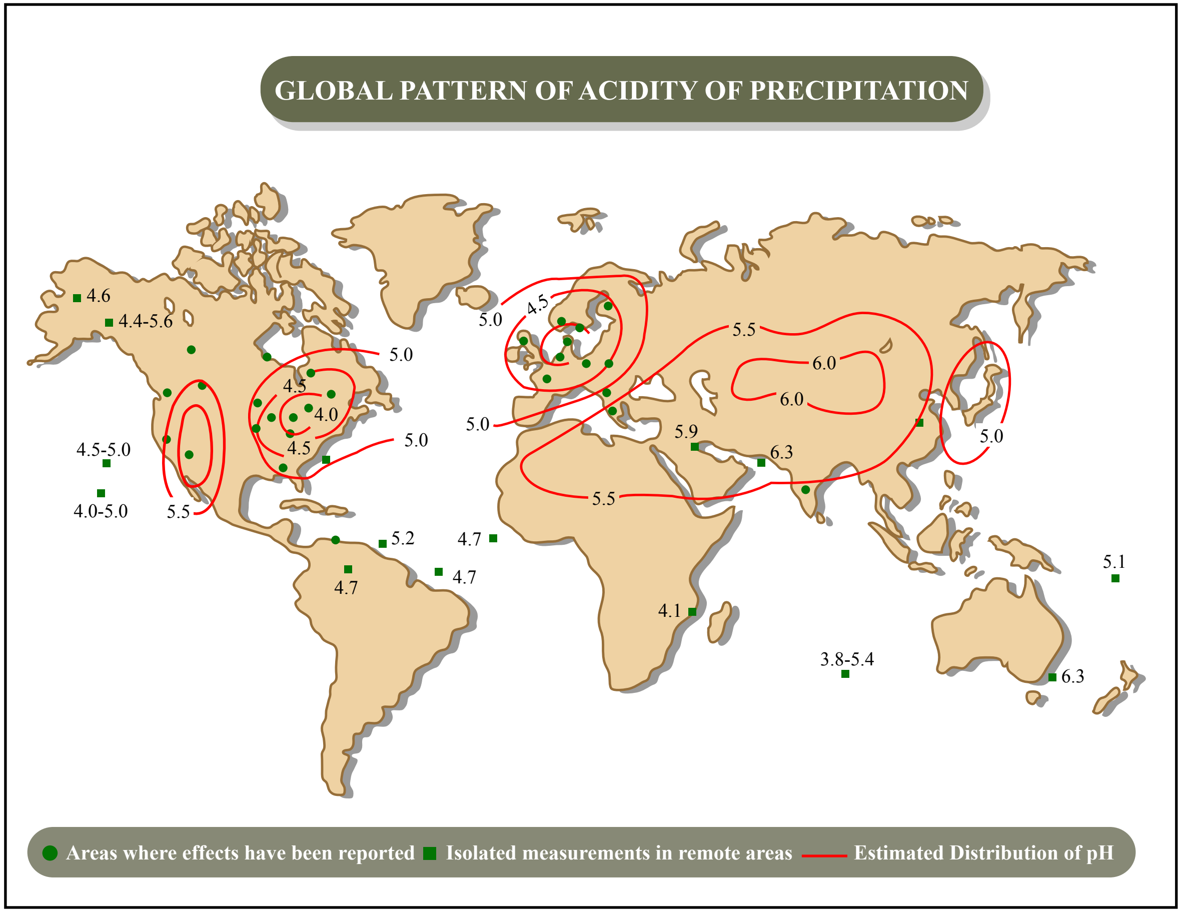


Figure by MIT OCW.

- Natural precipitation is slightly acidic (~ 5.6)
- HNO_3 & H_2SO_4 decrease pH & deliver N and S to the surface ocean

Halogen chemistry

- Organic biogenic oceanic sources: methyl halides CH_3Cl, CH_3Br, CH_3I
- CH_3Cl, CH_3Br have lifetimes > 1 year wrt OH so they can reach the stratosphere and function as catalytic species in O_3 chemistry
- Inorganic sources: sea salt which is ‘activated’

$$NaCl_s + ClONO_{2g} \Rightarrow Cl_{2g} + NaNO_{3s}$$

Cl_2 is readily photolyzed in the troposphere

- Sea-salt particles are an important removal pathway (reaction surface) of nitrogen oxides in the marine troposphere:

$$HNO_{3(g)} + NaCl_{(s,aq)} \text{ --> } NaNO_{3(s,aq)} + HCl_{(g)}$$

This affects the NO_x partitioning and the ozone chemistry

Summary

- Atmospheric gases and aerosols impact the global radiation and heat budget
- Trace constituents dominate these effects
- The reaction pathways and feedback mechanisms are often complex, interrelated, and cyclical making climate change estimates difficult
- Many biogeochemical cycles deliver key substances to the ocean (iron, nitrogen, sulfur) and vice versa