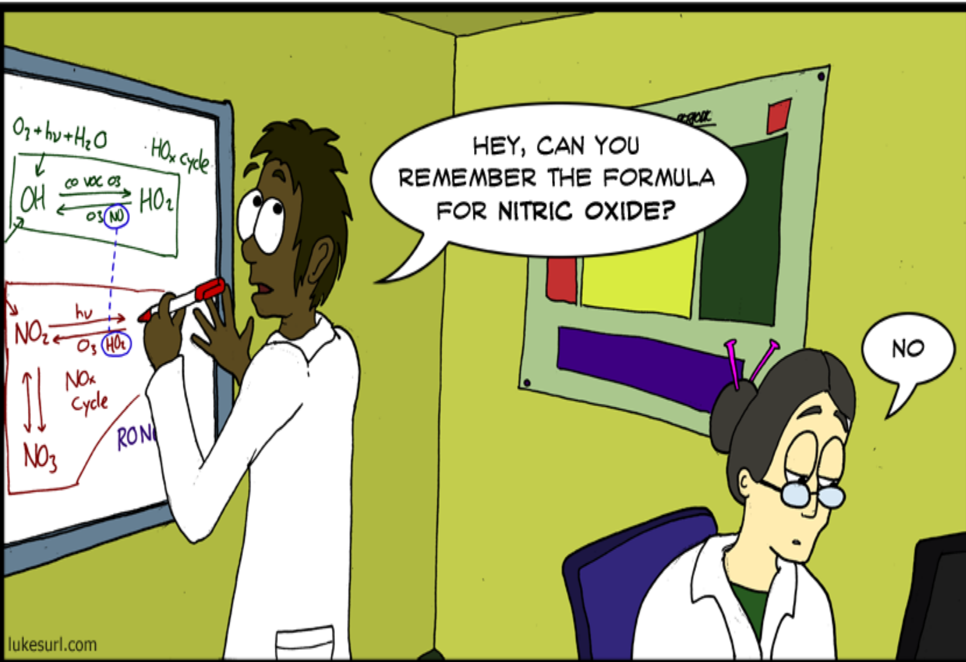
Atmospheric Composition

An Introduction

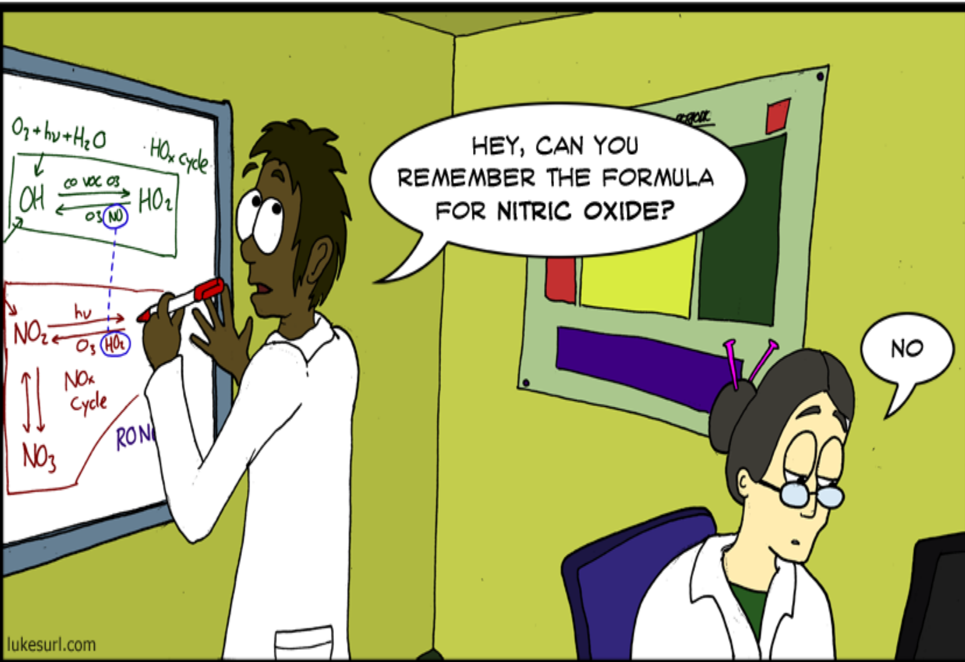
Peer Nowack

PG Lectures, 27th November 2017

Not an atmospheric chemist?



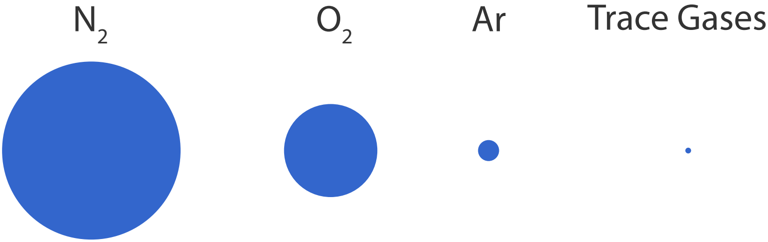
Not an atmospheric chemist? - Not a problem!



Outline

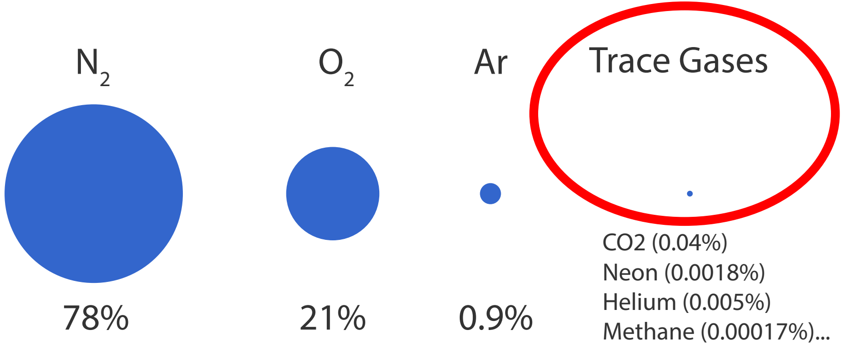
The '101' of atmospheric composition

(for dry air)



The '101' of atmospheric composition

(for dry air, by volume)



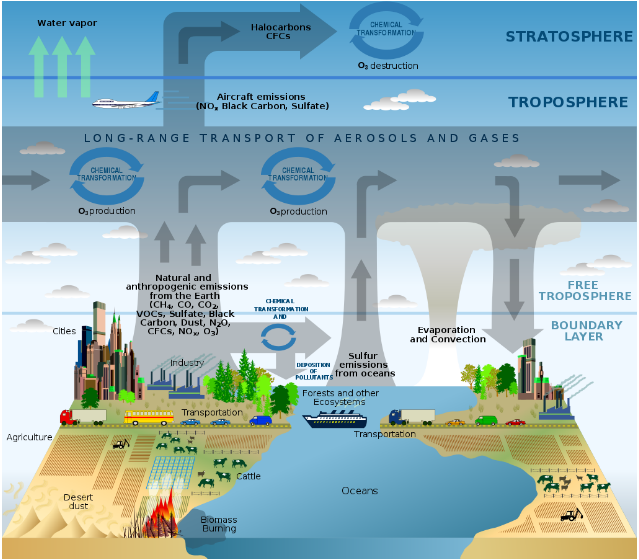
Important trace gases

Impacts: climate, air pollution, UV radiation...

- Carbon dioxide (CO_2)
- Methane (CH_4)
- Nitrous oxide/laughing gas (N_2O)
- Ozone (O_3) $\rightarrow$ section 2
- Water vapour: highly variable concentrations!
  Trace gas in the stratosphere (section 2) and over arid land areas

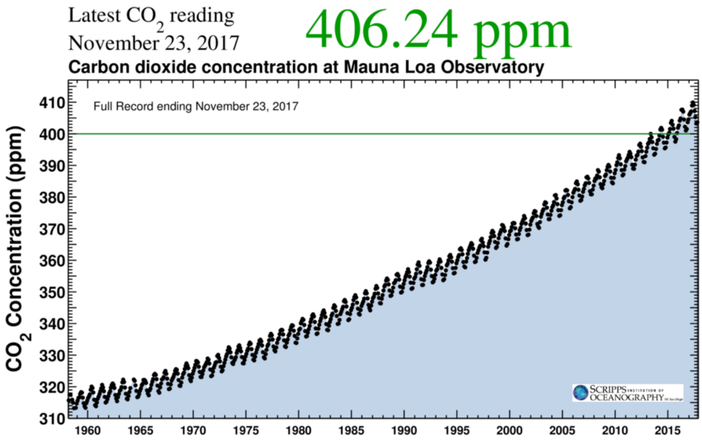
Not included: **aerosols** $\rightarrow$ section 3

The complex composition-climate system



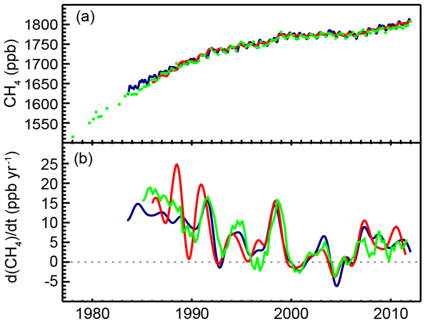
Strategic Plan for the US Climate Change Science Program

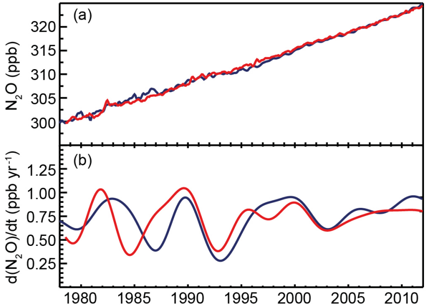
The atmospheric composition is changing - CO_2



https://scripps.ucsd.edu/programs/keelingcurve/

The atmospheric composition is changing - CH_4, N_2O



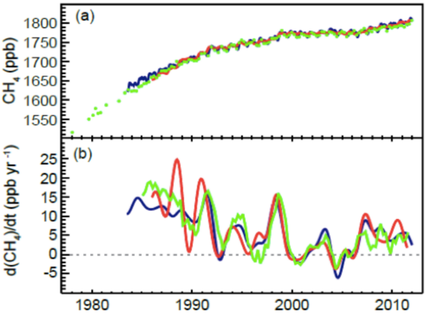


- CH_4: +150% since the year 1750.
- N_2O: +20%.

IPCC AR5, WG1, Chapter 2.

CH_4 - Very active field of research!

slide from A. Voulgarakis



IPCC (2013)

SOURCES

- Bacteria (wetlands, landfills, rice paddies, cattle)
- Natural gas leaks
- Oceans & permafrost
- Fossil fuels, biofuels
- Atmospheric chemistry (minor)

SINKS

- Atmospheric chemistry
- Surface deposition
- Bacteria

Jacobson (2012)

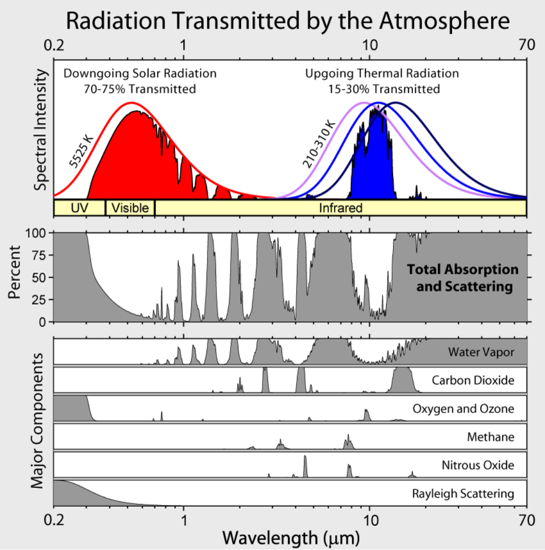
- Upward trend in general (anthropogenic).
- Slowdown in the 2000s (due to fossil fuel & wetland emission reductions).

Breakdown CH_4 budget:

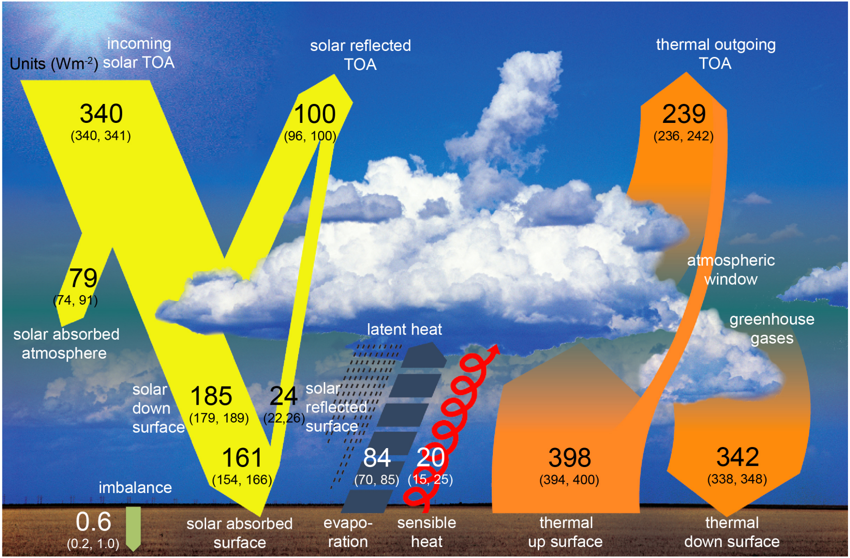
Anthropogenic sources (in Tg/year)		Natural sources (in Tg/year)		Sinks (in Tg/year)	
Fossil (coal/oil/gas)	102	Wetlands	145	Tropospheric OH	523
Rice	80	Termites	20	Soils	30
Burning	45	Ocean	15	Stratospheric	40
Animals	98	Geologic	18		
Waste	70	Plants	?		
Totals	395		198		593

Van Weele (2010)

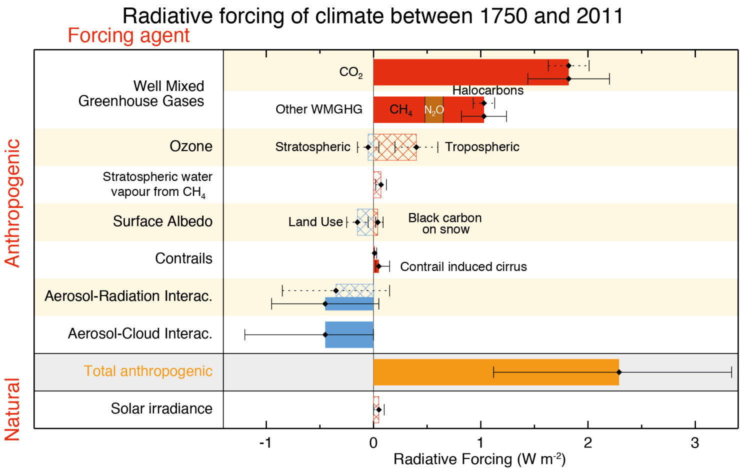
Trace gases absorb radiation at very different wavelengths



The key role of composition in the global energy budget



Radiative forcing measures the energy budget change



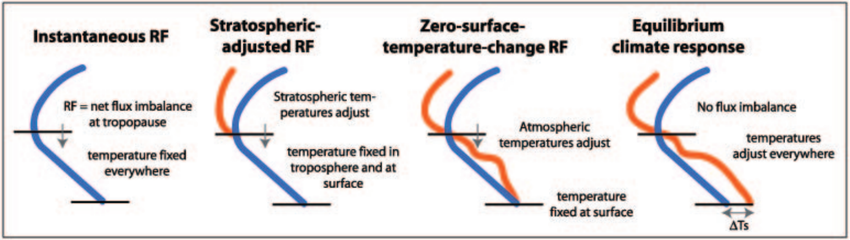
IPCC AR5, WG1, Chapter 8.

What is radiative forcing?

IPCC 2007

The change in net irradiance (solar plus longwave; in W m^{-2}) at the top of the atmosphere after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values.

Note 1: There are actually several RF definitions!



IPCC 2007

Equilibrium definition:

$$\Delta T = \lambda \cdot \mathrm{RF}$$

λ is referred to as the equilibrium climate sensitivity parameter.

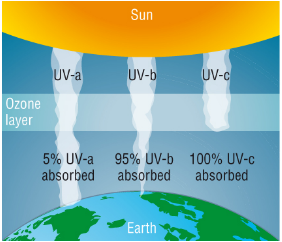
Note 2: RF is not always very useful!

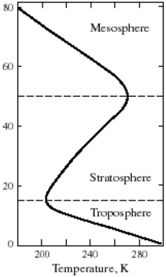
- There is no unique relationship between global RF and the global mean surface temperature response (RF *efficacy*).
- Regional climate impacts are even more dependent on the type and location of the trace gas or aerosol perturbation (e.g. Hansen 1997, Hansen 2005, *Voulgarakis & Shindell 2010*).
- The spatial pattern of RF due to short-lived species such as O_3 and aerosols is far less spatially homogeneous than for CO_2 (e.g. *Shindell & Faluvegi 2009*).
- Regional forcings in turn tend to emphasise the response of local feedback mechanisms (e.g. oceanic vs land, sea-ice albedo)

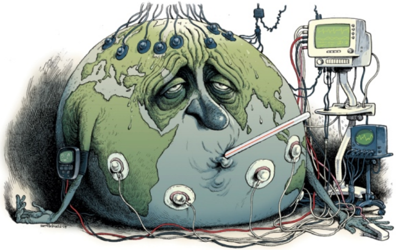
  $\rightarrow$ complex patterns of forcing and response!

Ozone - A Multifunctional Molecule

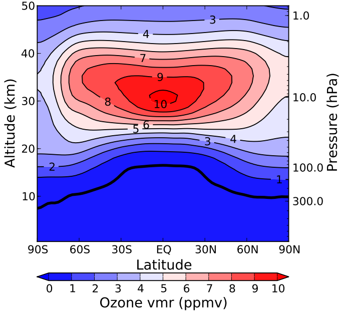
- Absorbs shortwave radiation from the Sun
  $\rightarrow$ T-profile of the atmosphere.
  $\rightarrow$ Major absorber of harmful UV-B radiation.
- Absorbs longwave (infrared) radiation
  $\rightarrow$ Ozone is a greenhouse gas!
- Pollutant in the troposphere.







Stratospheric ozone: sources and sinks



Stratospheric ozone: sources and sinks

Background Ozone - Factors

Chapman Cycle

$$O_2 + h\nu \rightarrow O + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$O_3 + h\nu \rightarrow O + O_2$$
$$O + O_3 \rightarrow O_2 + O_2$$

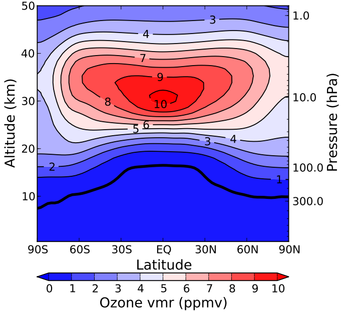
Catalytic O_3 Depletion Cycles

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$

X = NO, OH, Cl, Br,..

Chemical lifetime vs. transport

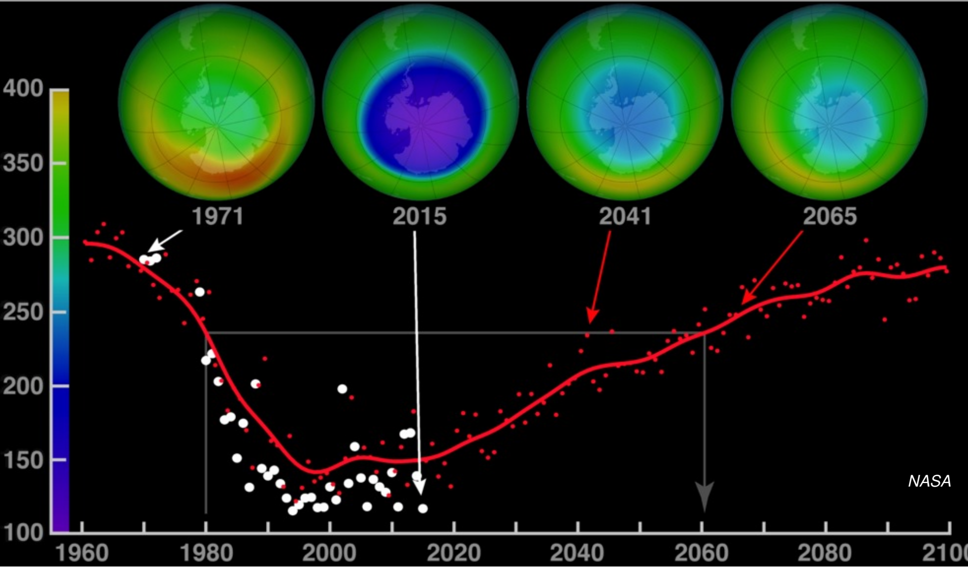
Dynamically ($\sim <$ 30km) vs. photochemically controlled regimes.



$[O_3]$ is affected by changes in

- temperature
- insolation
- composition (NO, OH, Cl, Br...)
- the atmospheric circulation

The ozone hole - a threat to life on Earth (VIDEO)



Chronology of the science

The Ozone (O_3) Hole: Chronology of the science

P. Crutzen, S. Rowland, M. Molina

→ Predicted it (early '70s)

CFCs
↓

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

$$ClO + O \rightarrow Cl + O_2$$

J. Farman

→ Observed it (mid '80s)

S. Solomon

→ Perfected (almost!) the theory (late '80s)

A. Voulgarakis

Chronology of the science

P. Crutzen, S. Rowland, M. Molina

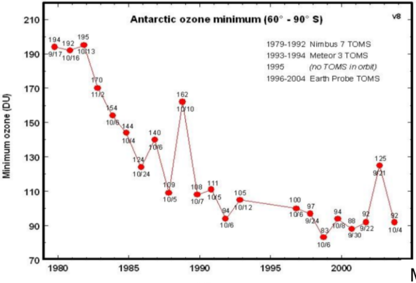
MONTREAL PROTOCOL 1989

The Nobel Prize in Chemistry 1995
Paul J. Crutzen, Mario J. Molina, F. Sherwood Rowland

"…we have left the Holocene and had entered a new Epoch—the ***Anthropocene****—because of the global environmental effects of increased human population and economic development…"*

A. Voulgarakis

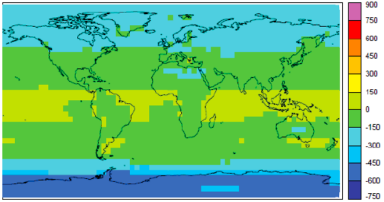
The ozone hole in terms of RF



http://toms.gsfc.nasa.gov Year

- Large depletion in the Antarctic after the 1980s (occurs mostly between 14-18km altitude).
- Stabilization later, due to Montreal Protocol measures.

Modelled stratospheric ozone forcing (mW m^{-2})



Cionni et al. (2011), ACP (for IPCC AR5)

- Ozone loss causes negative radiative forcing (ozone is a warming gas, both in trop. and in strat.).
- Particularly large over the Antarctic.

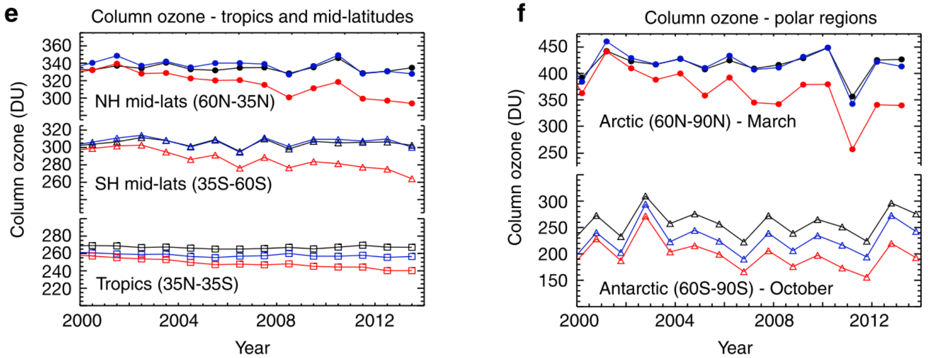
A. Voulgarakis

The World Avoided

Chipperfield et al. (2015)

Policy measures have already prevented:

- The occurrence of a deep 'Arctic ozone hole' (< 120 DU in 2011!).
- Large Northern Hemisphere mid-latitudes ozone depletion (15%)
- Antarctic ozone hole would have grown in size by > 40%.

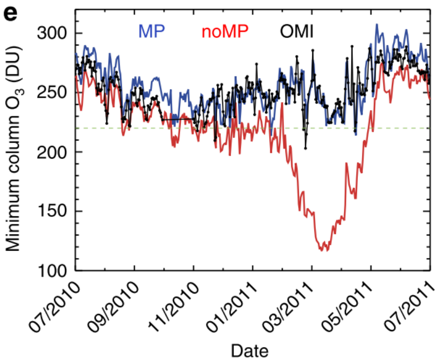


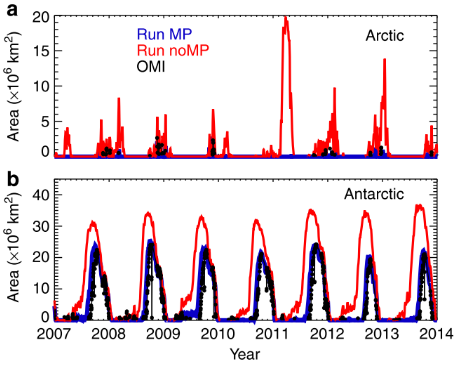
The World Avoided

Chipperfield et al. (2015)

Policy measures have already prevented:

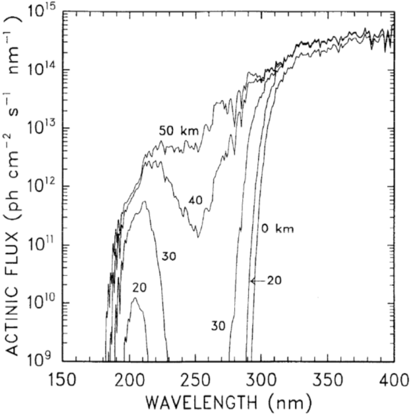
- The occurrence of a deep 'Arctic ozone hole' (< 120 DU in 2011!).
- Large Northern Hemisphere mid-latitudes ozone depletion (15%)
- Antarctic ozone hole would have grown in size by > 40%.





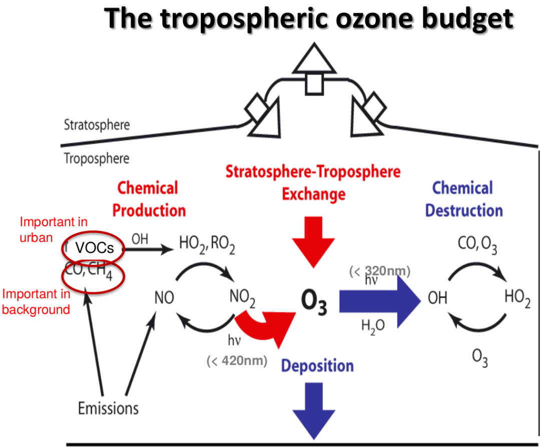
Tropospheric chemistry is fundamentally different

Radiation that drives the photochemistry of the stratosphere is not available in the troposphere → other chemical reactions drive the much smaller tropospheric ozone formation



deMore et al. 1997, JPL

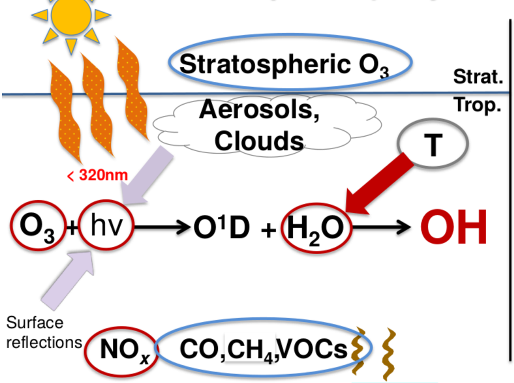
Tropospheric ozone chemistry is complex

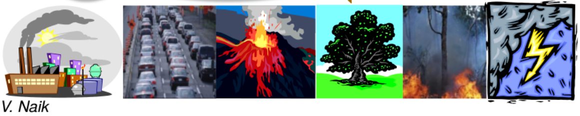


The review by *Monks (2005)* provides a good introduction.

Graph from A. Voulgarakis.

Gases: Hydroxyl Radical (OH): The detergent of the atmosphere (very short lived)



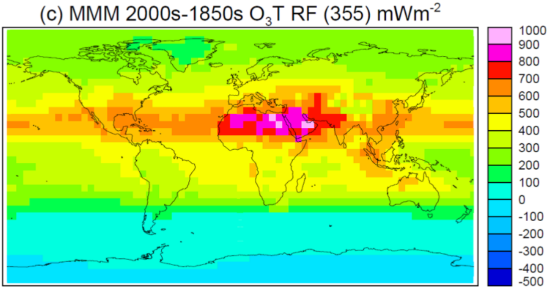


- OH is a major tropospheric oxidant.
- It removes CO/VOCs, is involved in tropospheric ozone (O_3) production, and in aerosol formation.
- It is the major sink of CH_4 in the atmosphere: OH determines CH_4 lifetime.

A. Voulgarakis

Tropospheric ozone RF

- Mostly positive since pre-industrial times, except for the Antarctic.
- It is spatially highly inhomogeneous, just as for aerosols (see below).

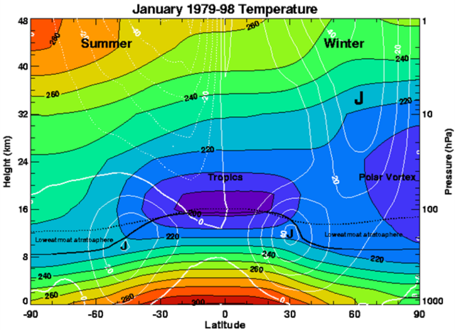


Stevenson (2013)

- Future changes strongly depend on the emission scenario
  → in particular of ozone-precursor methane (*Young, 2013*).

The tropical Upper Troposphere to Lower Stratosphere (UTLS)

Also known as **Tropical Tropopause Layer**, *Fueglistaler (2009)*.

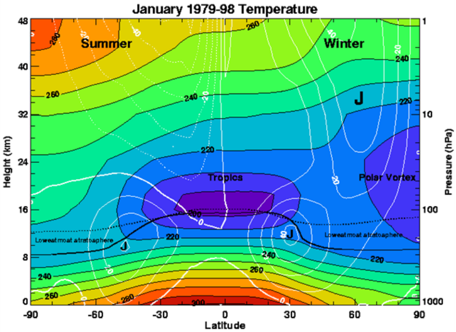


NASA

The tropical Upper Troposphere to Lower Stratosphere (UTLS)

Also known as **Tropical Tropopause Layer**, *Fueglistaler (2009)*.

- Tropical region between around 14 km-19 km altitude, laterally bounded by the subtropical jets.
- Very cold region despite being located in the tropics!
- Large T difference to surface $\rightarrow$ increases RF magnitudes.
- Marked by sharp composition gradients (O_3 $\uparrow$, water vapour $\downarrow$).



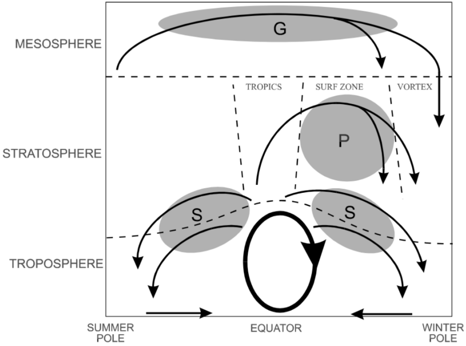
NASA

- Difficult to model (and to observe) $\rightarrow$ interactions between many large and small scale processes such as clouds, dynamics, composition...

Why is the tropical UTLS so cold?

Mainly for dynamical reasons:

- Tropospheric air enters the stratosphere almost exclusively through the tropical UTLS.
- As the air rises, it cools while expanding in lower pressure.
- The ascent is part of the larger scale Brewer-Dobson circulation.
- Dehydration of air within the tropical UTLS → extremely dry stratosphere ($[H_2O] < 10$ ppm).



Sketch from Plumb 2002, see also Butchart 2014

- Ozone modulates tropical UTLS temperatures and thus stratospheric water vapour concentrations (*Fueglistaler 2011*, *Nowack et al. 2015*).

Aerosols introduction

Definition

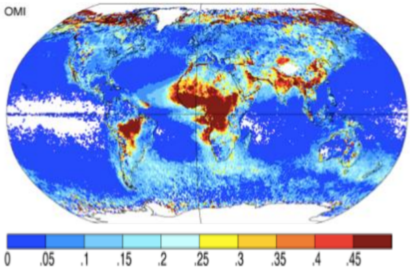
Atmospheric aerosol is a complex and dynamic mixture of solid and liquid particles dispersed in air.

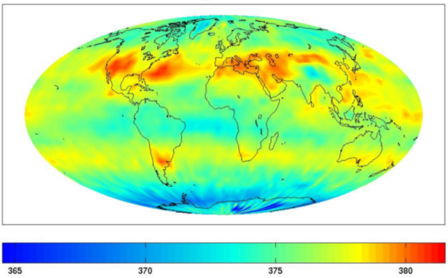
- Division into primary aerosols (directly emitted at the surface) and secondary aerosols (formed by reactions in the atmosphere).
- Aerosols occur naturally, but human activities have led to highly significant increases in their abundance.
- There are many different types of aerosols which vary in terms of size, chemical composition.
- Different aerosol types cause different radiative forcings, climatic impacts and health effects.

Major aerosol components & their sources

Type	Anthropogenic	Natural
Sulphate (SO_4)	✓	✓ (mainly oceans, volcanoes)
Black carbon (BC)	✓	✓ (natural fires)
Organic carbon	✓	✓ (sec. form. from VOCs over forests)
Mineral dust	✗ (very minor)	✓
Sea-salt	✗	✓
Nitrate	✓	✓

Aerosols emissions are highly regional (VIDEO)





- Aerosols (and also some gases) have a very ingomogeneous geographical distribution due to their short lifetime (SLCP).
- CO_2 is much more homogeneous it has a long lifetime (LLCP).

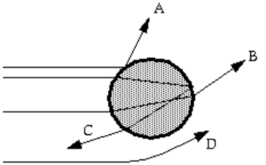
A. Voulgarakis

Aerosol-type-dependent absorption & scattering

Absorption

- Black carbon: the main aerosol absorber in all solar wavelengths (then re-emits thermal). Also some absorption by dust and a bit by organic carbon.
- Dust & sea-salt absorb substantially in thermal wavelengths (3,000-15,000 nm).

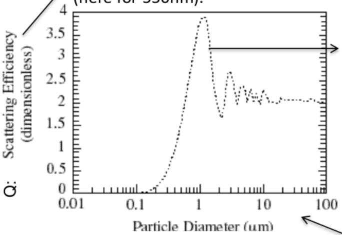
Scattering (only for solar)



A: Reflection B: Refraction
C: Refraction & internal reflection
D: Diffraction

(Their combination results in scattering)

Fraction of light scattered (here for 550nm).



Accumulation mode aerosols are the best scatterers (e.g. sulphate etc).

Jacobson (1998)

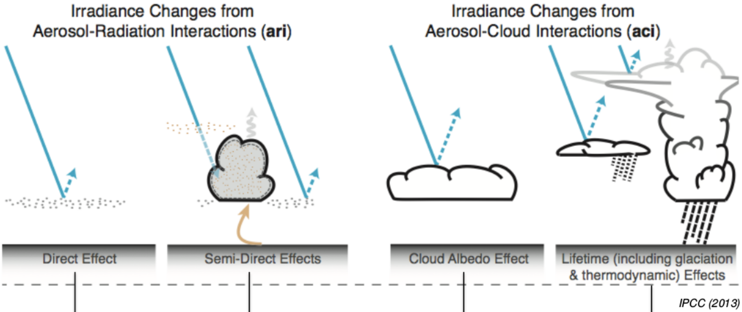
$$\tau_\lambda = \int_0^z k_\lambda(z)\rho(z)dz = \int_0^z \alpha_\lambda(z)dz$$

$$\tau_\lambda = \int_0^z n(z)\pi r^2 Q_\lambda(z)dz = \int_0^z n(z)\sigma_\lambda(z)dz$$

$$\alpha_\lambda = n\pi r^2 Q_\lambda$$

A. Voulgarakis

Aerosol radiative effects (indirect, i.e. through clouds)



The effects mentioned in the previous slide.

Less strong lapse rate ($\Gamma = -dt/dz$), due to cooling of surface and warming of atmosphere (especially true for black carbon). Leads mainly to cloud reductions, and surface warming.

More cloud condensation nuclei (CCN), more cloud droplets and of smaller size, thus greater cross sectional area and greater reflectivity, and surface cooling.

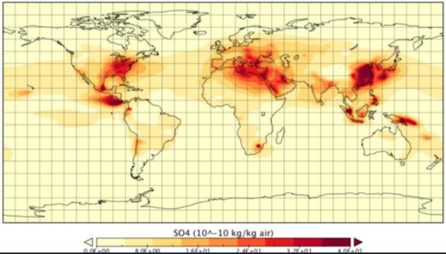
Smaller cloud particles decrease precipitation efficiency, thus prolong cloud lifetime, and so more reflections, and surface cooling.

A. Voulgarakis

Sulphate aerosols

- Sulphate particles are produced from gases (through **OH** oxidation) in the atmosphere.
- Their main precursors are:
  a) anthropogenic or volcanic sulphur dioxide (SO_2),
  b) dimethyl sulfide (DMS) from biogenic sources, especially marine plankton.
- Sulphate is mostly scattering (cooling).

Present-day surface sulphate concentration (NASA GISS model)

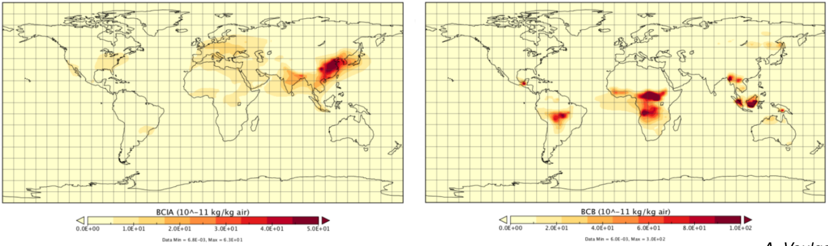


A. Voulgarakis

Black carbon aerosols

- Primary aerosols, i.e. emitted at the surface; no gas precursors.
- The main sources are fossil fuel combustion and biomass burning.
- Are mostly absorbing (black) and thus have a warming impact
  - in contrast to sulphate aerosols.
- Can cause large local albedo changes, e.g. if covering snow.

Present-day surface anthropogenic (left) and biomass burning (right) BC concentration (NASA GISS model)



A. Voulgarakis

Air pollution

The Bird's Nest, Beijing, on two different days in 2014

NO_x

PM2.5

PM10

Ozone

SO_x

Air pollution is a worldwide key public health issue in urban areas

Causes ca. 500,000 premature deaths in Europe each year and health-related economic costs reached EUR 330-990 billion in 2010 (EEA 2016).

Aerosol pollution is grouped into PM2.5 and PM10 depending on the particle diameters ($d < 2.5\,\mu m$ and $2.5\,\mu m < d < 10\,\mu m$, respectively).

Premature mortality linked to air pollution

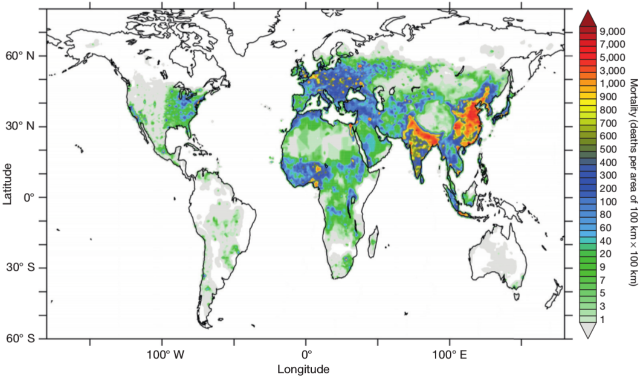


Figure 1 | Mortality linked to outdoor air pollution in 2010. Units of mortality, deaths per area of 100 km × 100 km (colour coded). In the white areas, annual mean $PM_{2.5}$ and O_3 are below the concentration–response thresholds where no excess mortality is expected.

Lelieveld (2015)