University of Crete

Human Impact on Atmospheric Composition

University of Bremen

Why do we care about Atmospheric composition?

> impacts on

1- climate

2- visibility

2- health (human & ecosystems)

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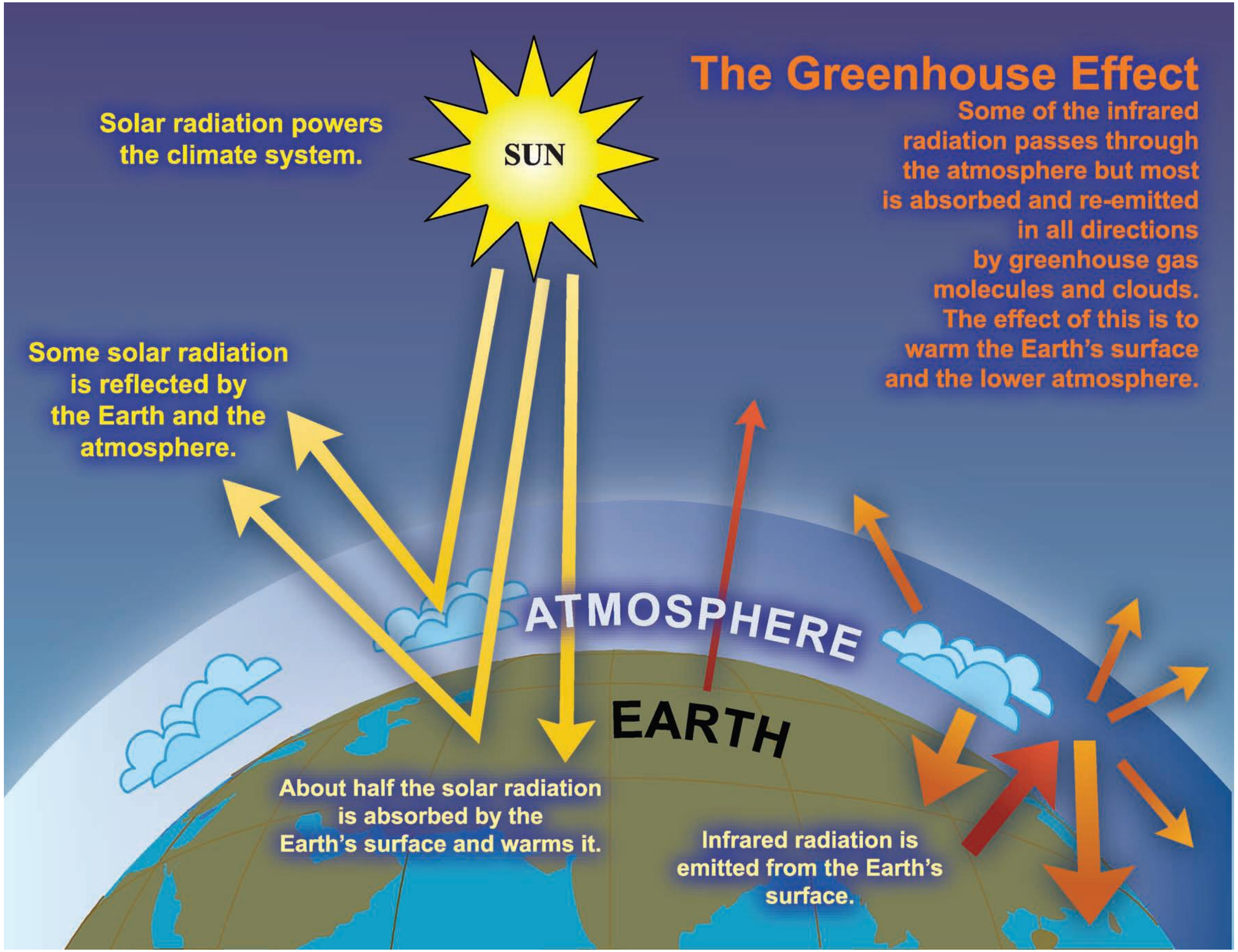
Vila Monastero, Varenna, Italy, 17 July 2023

Sun is the main source of energy maintaining life in our planet and controlling climate

Energy balance of the atmosphere – a tender equilibrium

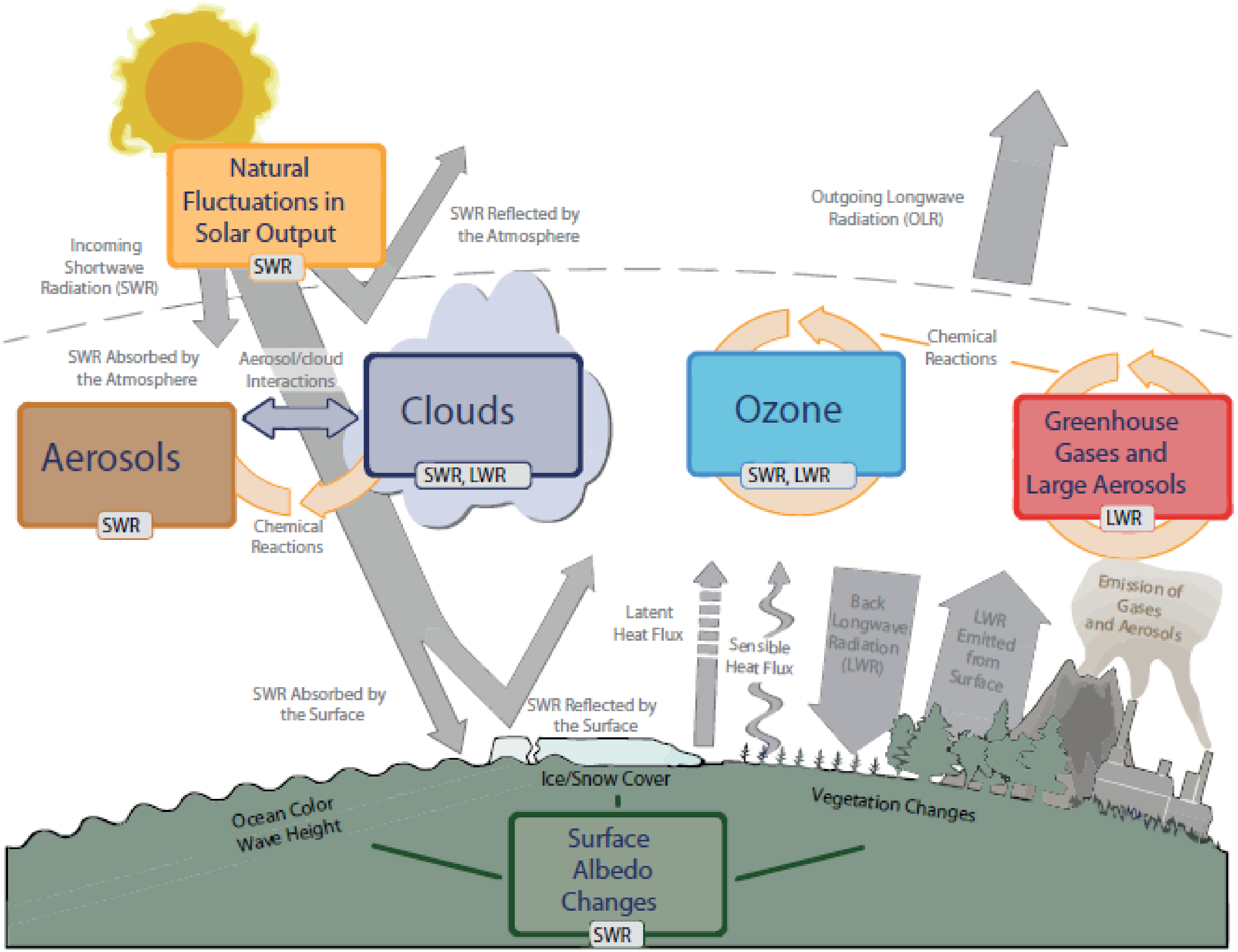


Earth is receiving solar radiation and is sending back to space IR radiation.

If all IR radiation emitted by the Earth was going back to space then T~ -18°C

Part of the outgoing radiation from Earth is trapped in its atmosphere and is warming Earth. Thus the actual T is T_{mean} Earth ≈15°C

Main drivers of climate change



GHG:

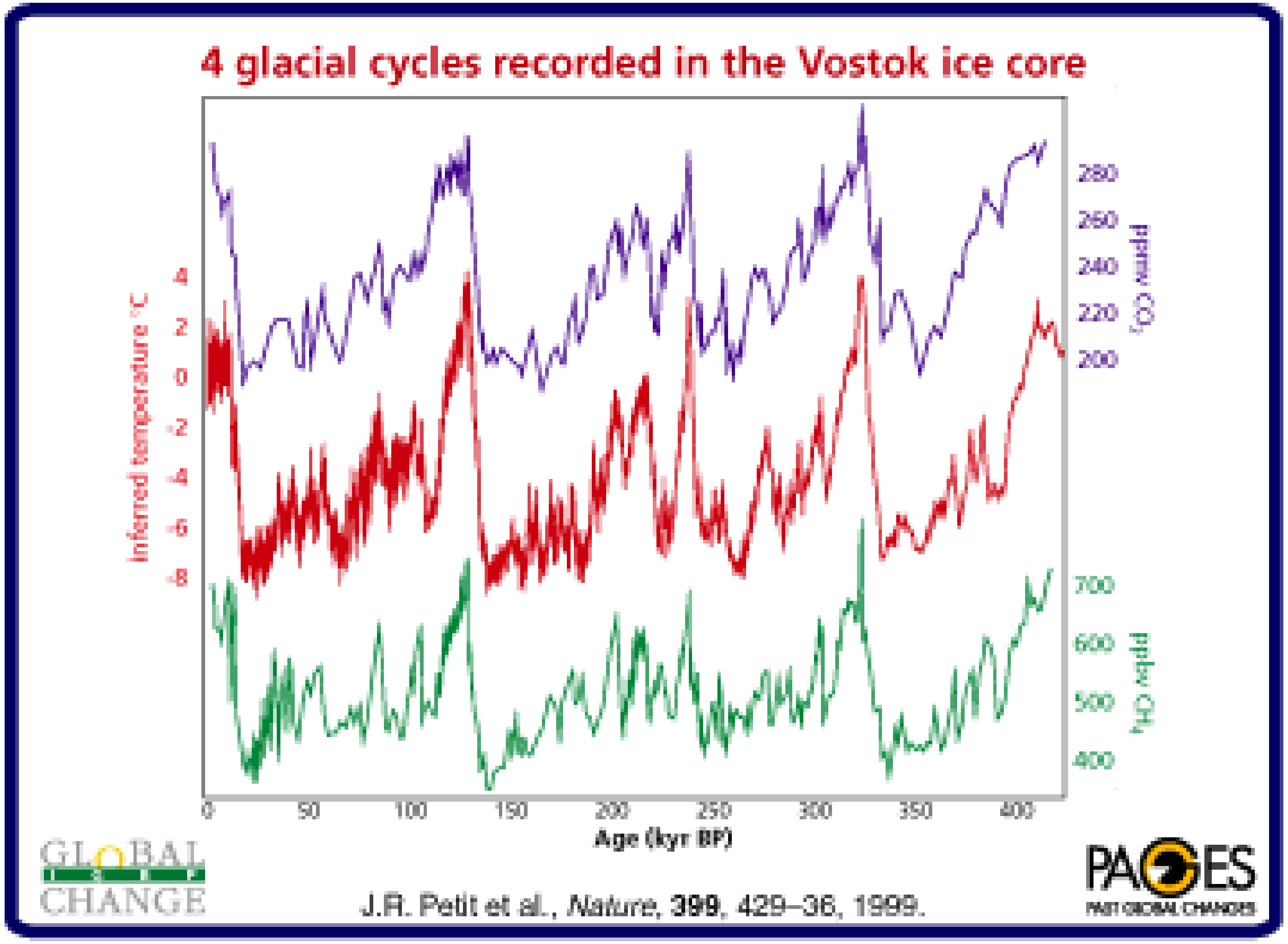
CO_2 CH_4 O_3 H_2O

N_2O CFCs

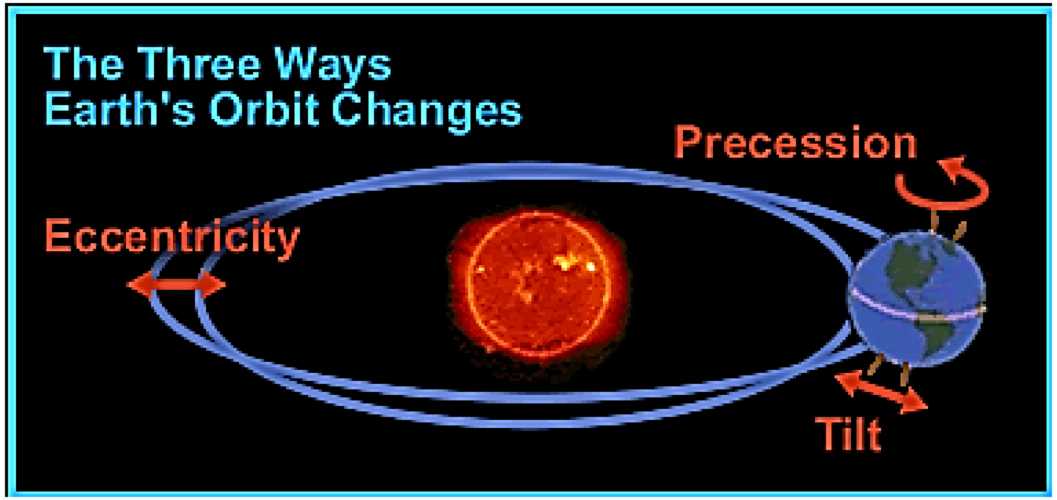
IPCC AR5 Working Group I
Climate Change 2013: The Physical Science Basis

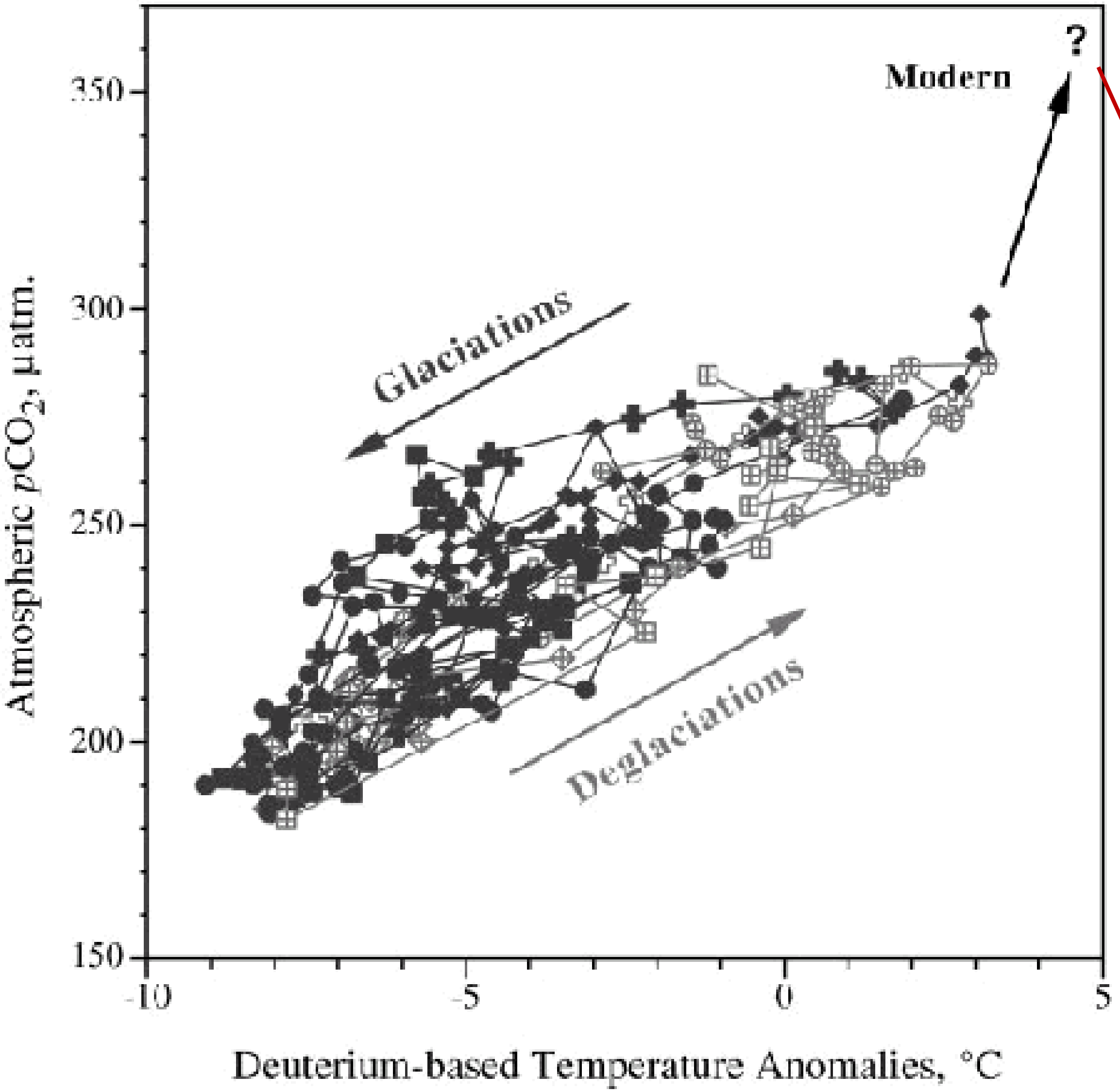
INTERGOVERNMENTAL PANEL ON climate change

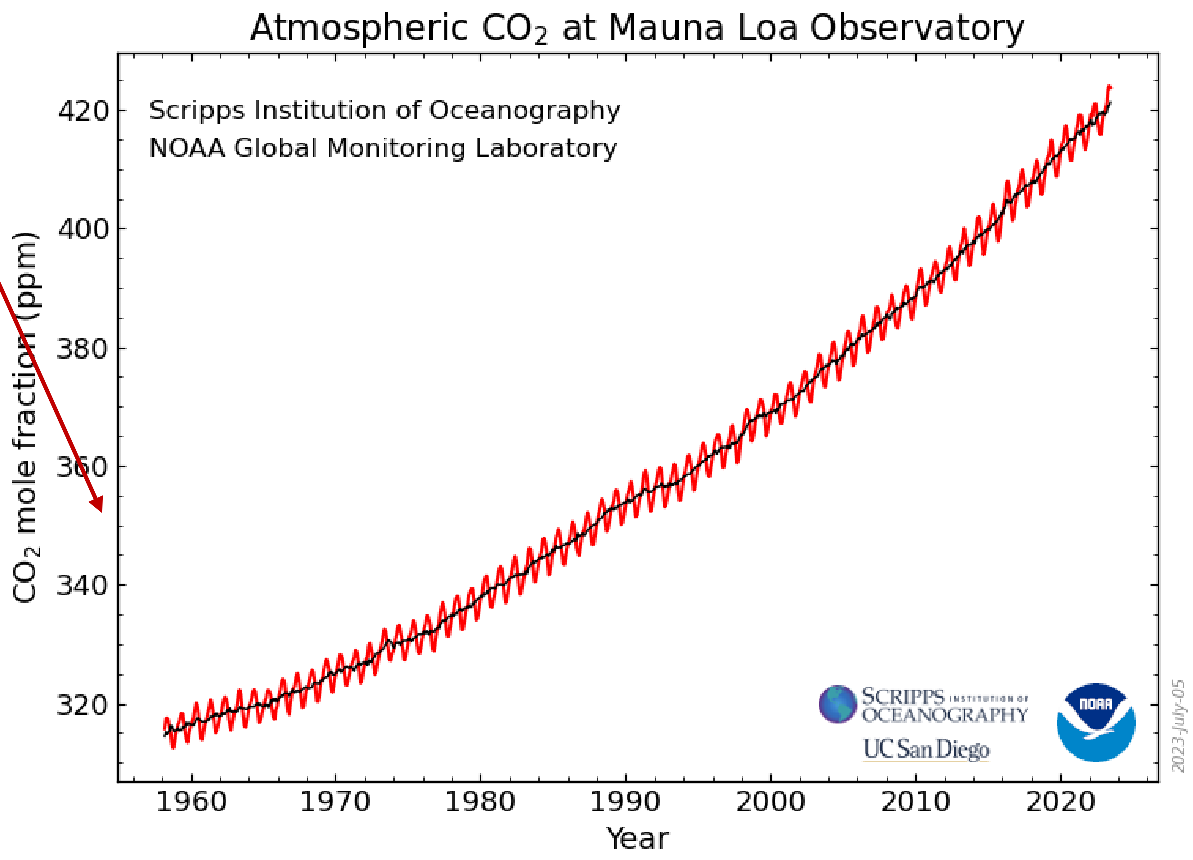
What do we learn from the past - ice core records ?



Geological periods - Periodicities
100 000 yrs
41 000 yrs
21 000 yrs

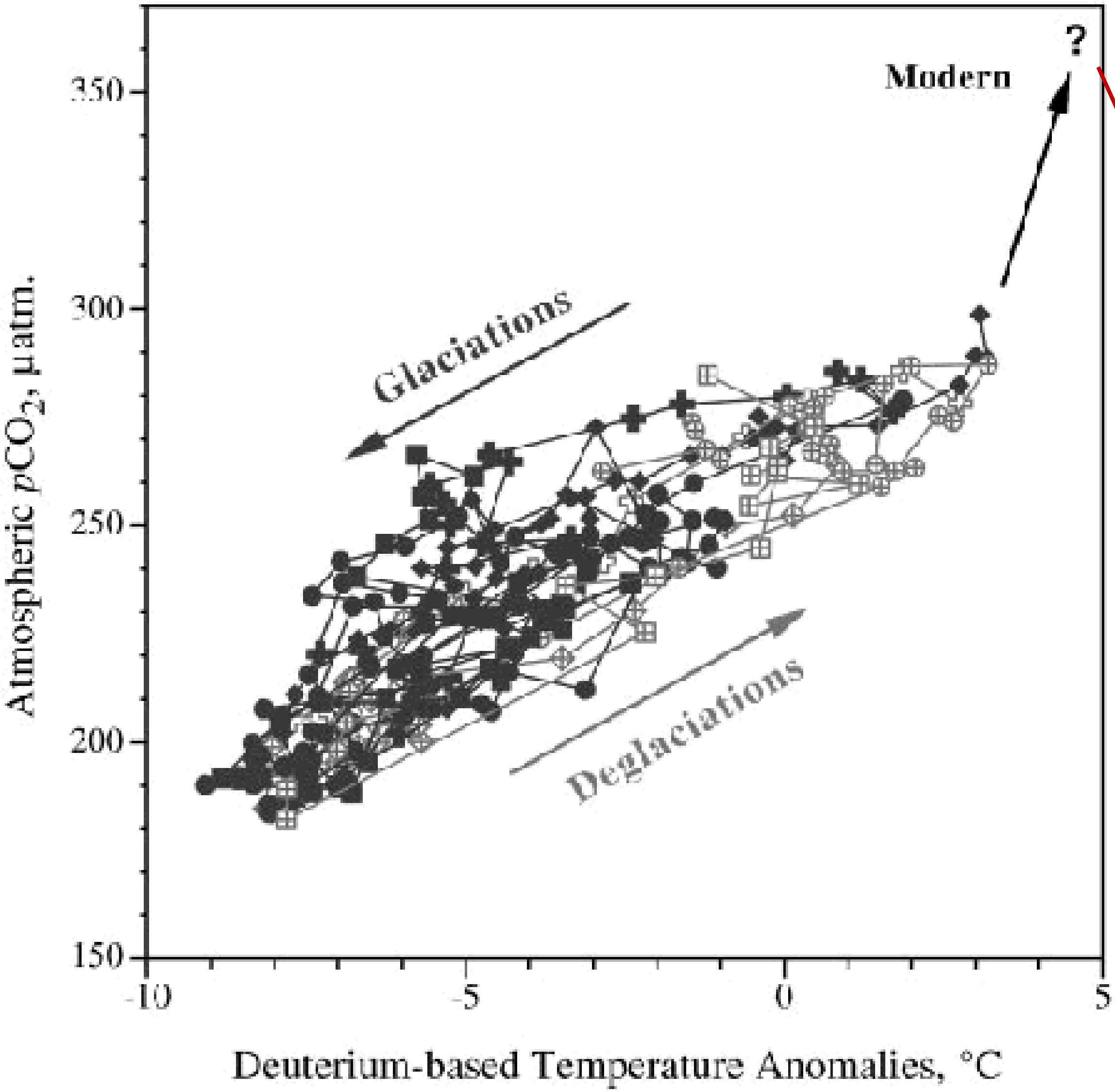


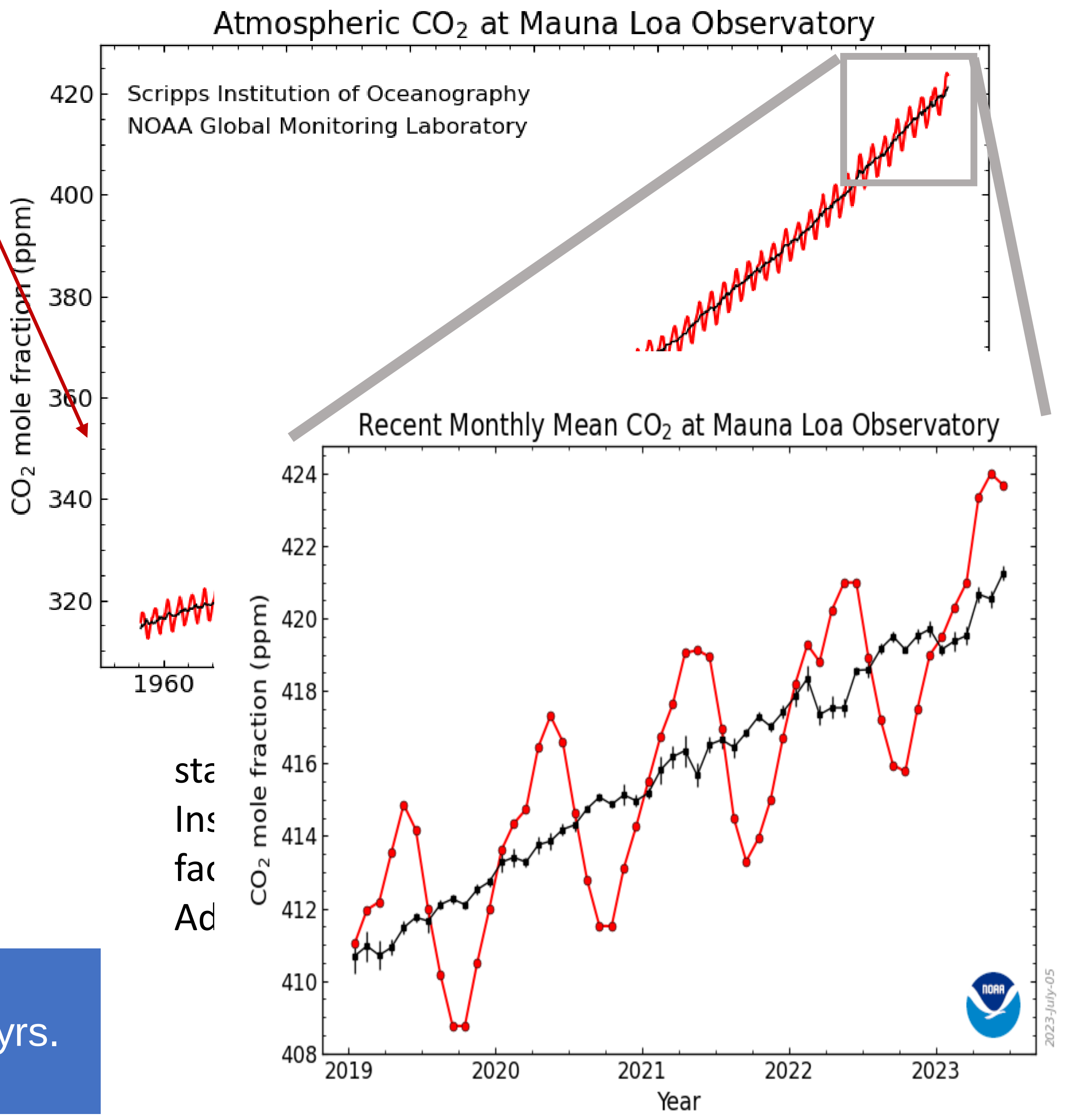




started by C. David Keeling of the Scripps Institution of Oceanography in March of 1958 at a facility of the National Oceanic and Atmospheric Administration *[Keeling, 1976]*

We are currently out of this 'safe' zone (CO_2, T) →.
CO_2 >100 ppm higher than max CO_2 the last 420 000 yrs.
Increasing rate of CO_2 10 - 100 times higher





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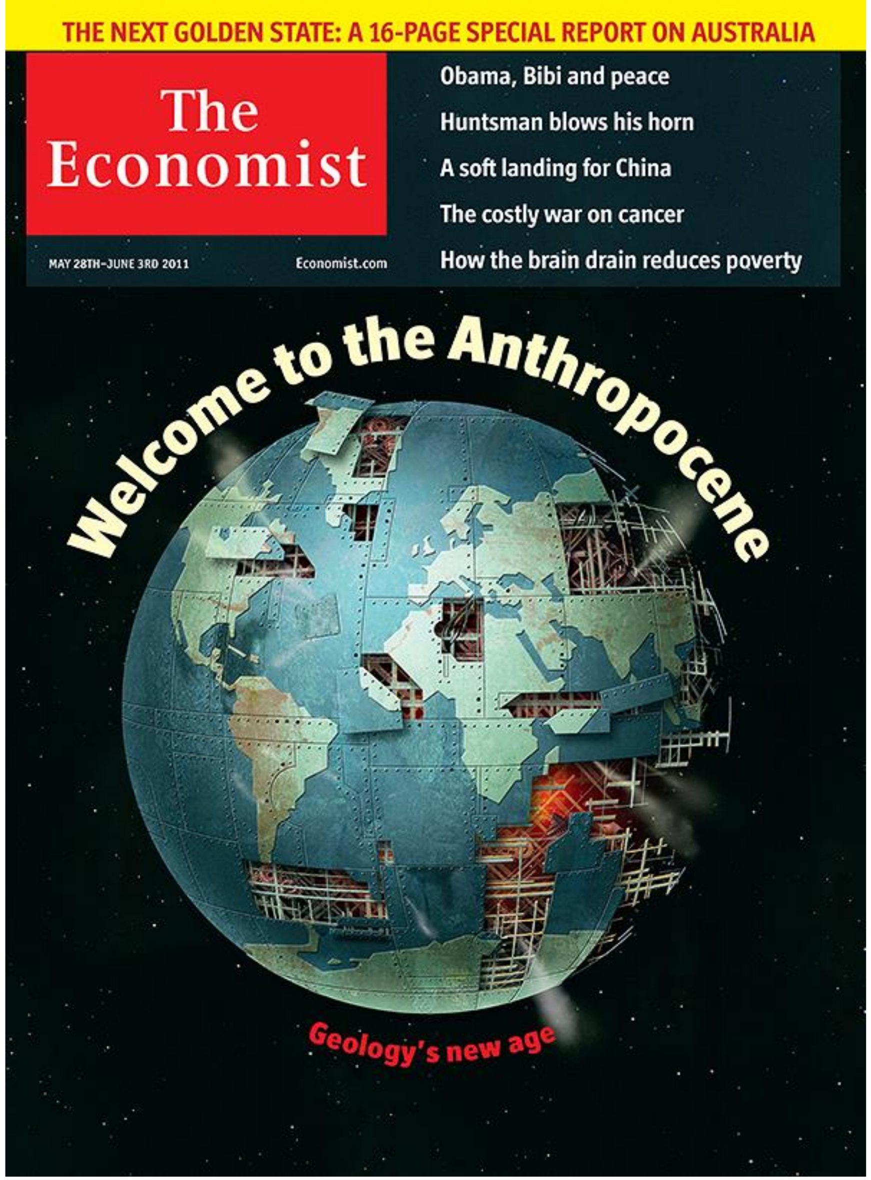
13 OCTOBER 2000 VOL 290 SCIENCE www.science



The **Anthropocene** is proposed as the new geological epoch where **human-influence will dominate the fossil records**. There is overwhelming global evidence that atmospheric, geologic, hydrologic, biospheric and other Earth system processes are now modified by human activity. (E. F. Stoermer and P. J. Crutzen 2001 IGBP)[Slide courtesy of J.P.Burrows]

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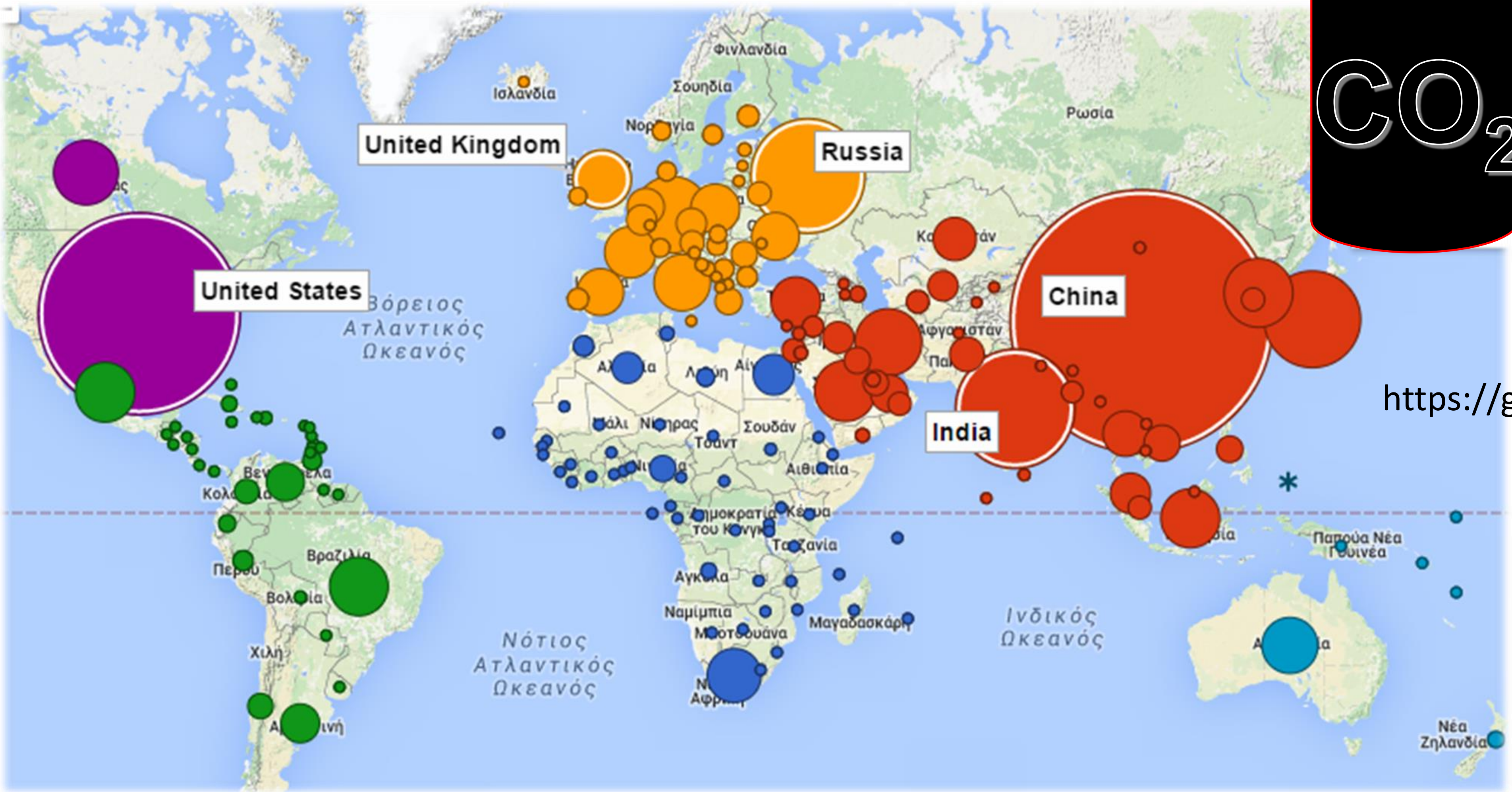
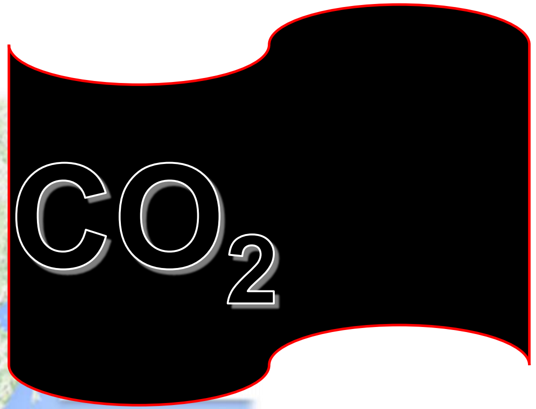
Large emitters of CO_2





https://globalcarbonatlas.org/

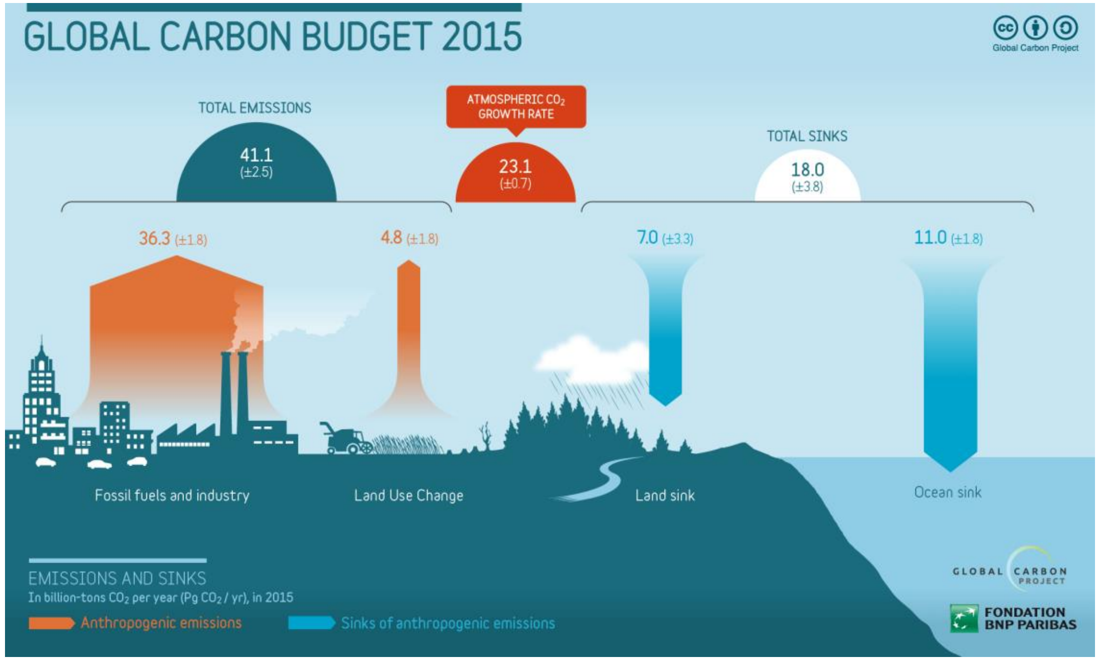
The world's top 1% of emitters produce over 1000 times more CO_2 than the bottom 1% (www.iea.org)

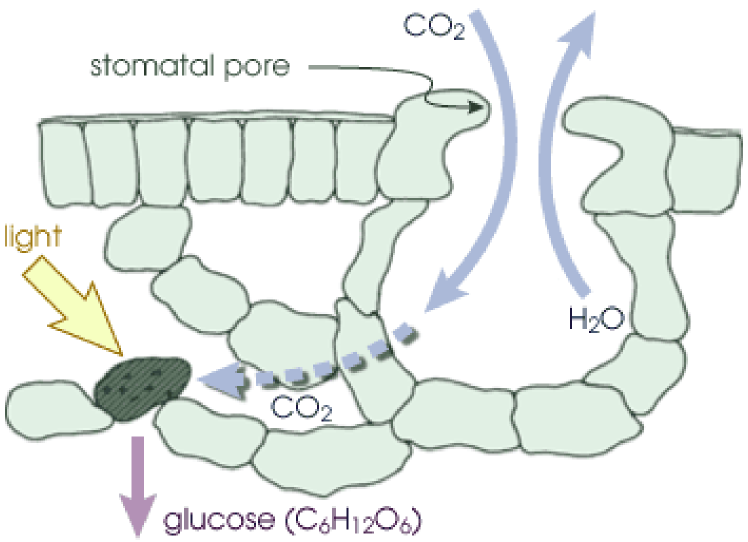
The richest 0.1% of the world's population emitted 10 times more than all the rest of the richest 10% combined.

CO_2 sources and sinks

CO_2 sources

- **Energy - Fossil fuels**
- **Cement Production**
- **Deforestation**
- Respiration
- Sea emissions

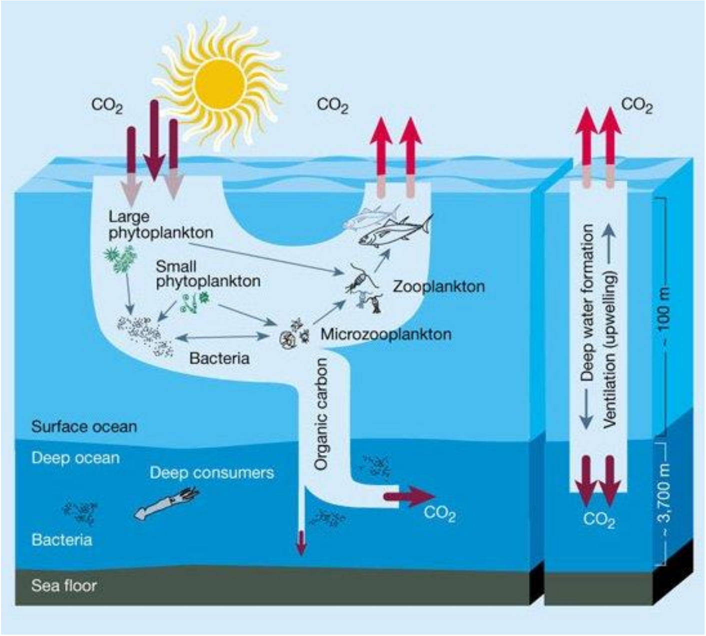




CO_2 sinks

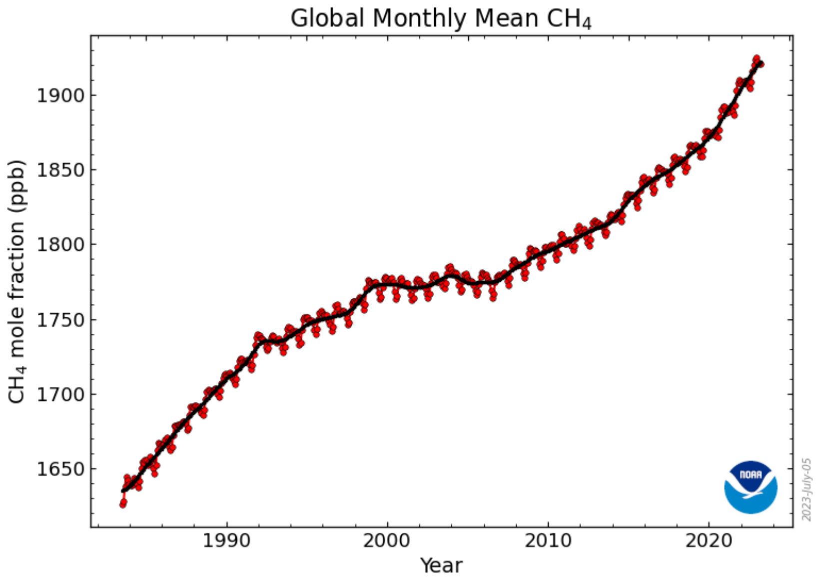
- Photosynthesis
- Ocean Uptake (biological and carbonate pumps)

very long lifetime in the atmosphere ~ century



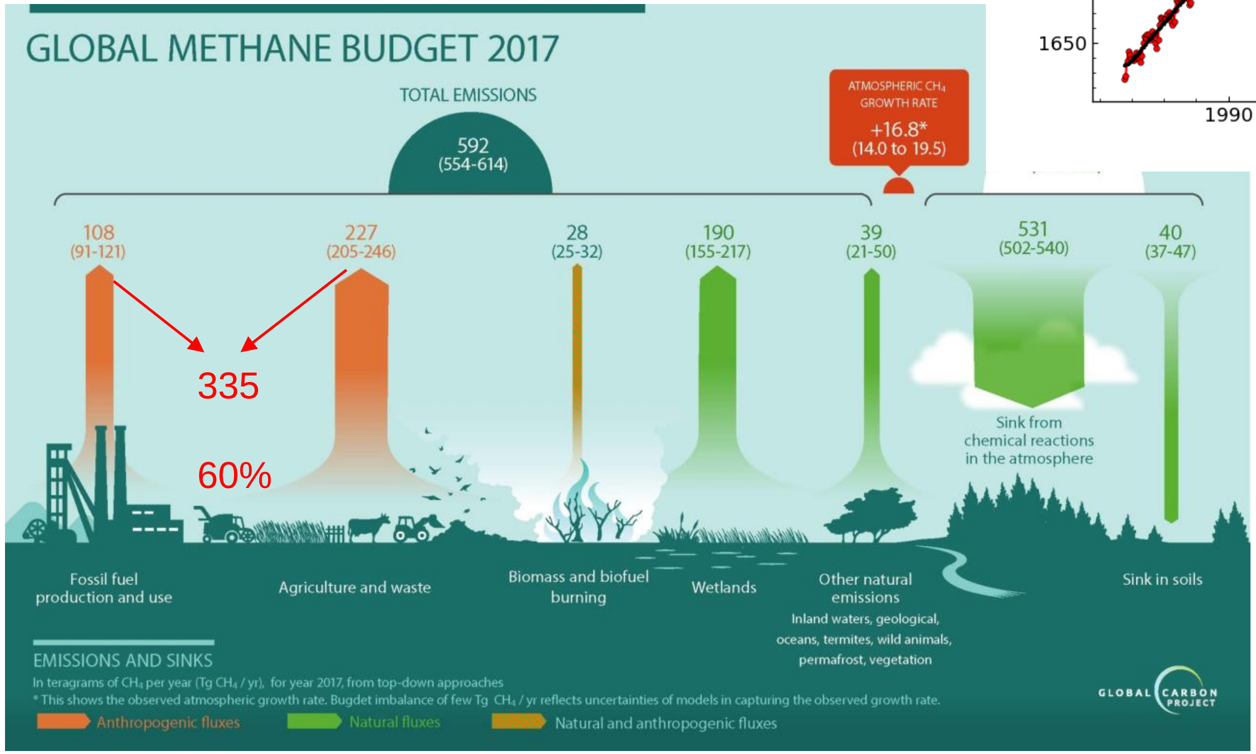
airs.jpl.nasa.gov

CH_4 sources and sinks



CH_4 sources

- Microbial activity in soil (Methanogens)
- Plant decay in wetlands and rice paddies
- Digestive processes in domestic animals and termites
- **Landfills**
- **Fossil Fuels**
- **Biomass Burning**
- Thawing Permafrost



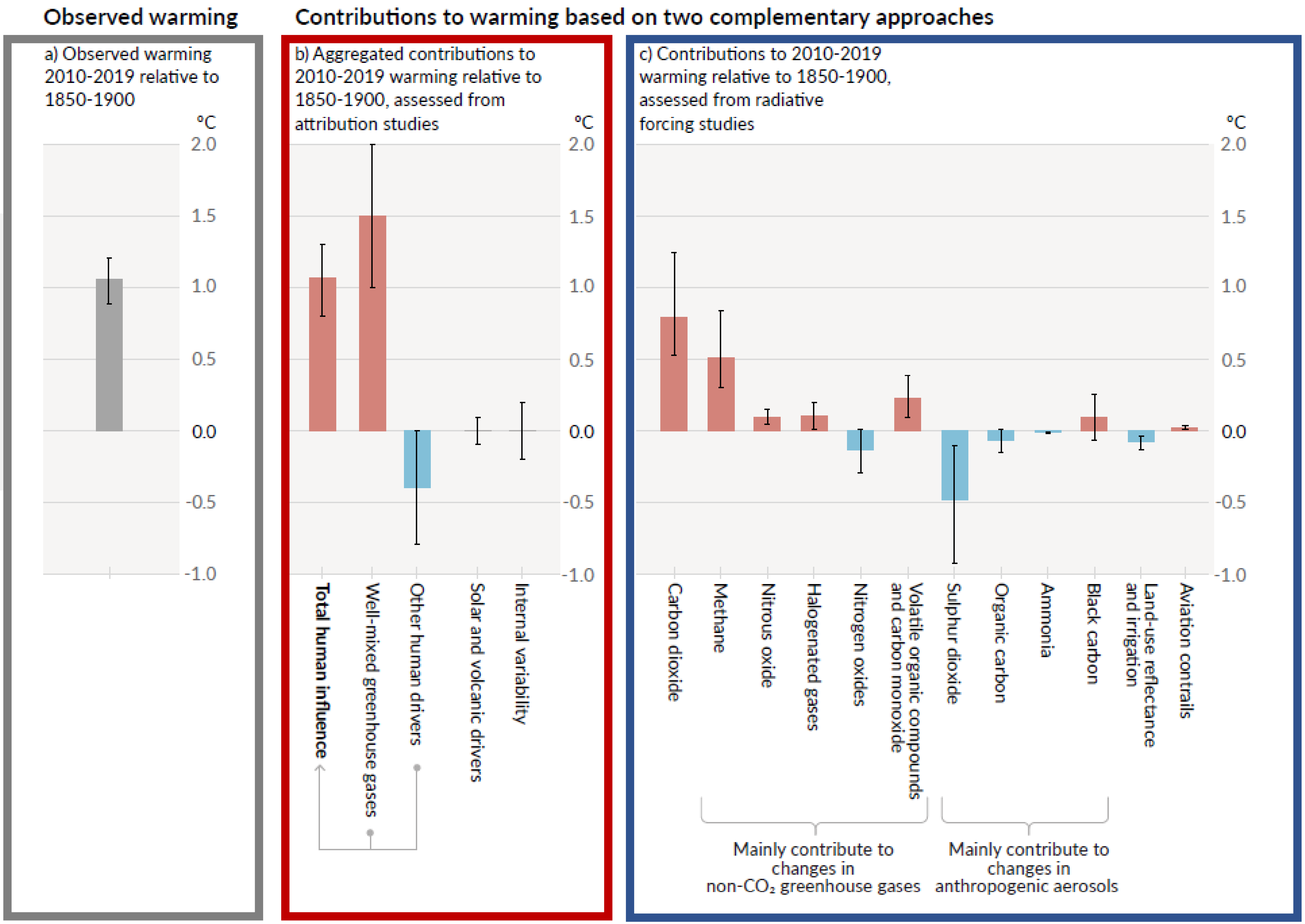
long lifetime in the atmosphere ~ 10 yrs

CH_4 sinks

- Oxidation by ·OH (producing H_2O)
- Methanotrophic Bacteria
- Reactions with Cl· και O· in the stratosphere
- Reactions with Cl· from the sea

B. Riley Berkley Uni.
https://newscenter.lbl.gov/2020/08/13/global-methane-emissions-soaring-but-how-much-was-due-to-wetlands/

Temperature anomaly in 2010-2019 compared to 1850-1900



IPCC, 2021

Human activities emit not only GHG but also aerosols and precursor gases

Short lifetimes of aerosols, O_3, and their precursors

Aerosols: suspended in air, solid or liquids, of <100 µm diameter

- Impact on health
- Scatter or absorb solar radiation – large uncertainty
- Carry trace elements - nutrients or toxic

Kanakidou et al., Envir. Res. Let., 2018

Air pollution : What are we talking about ?

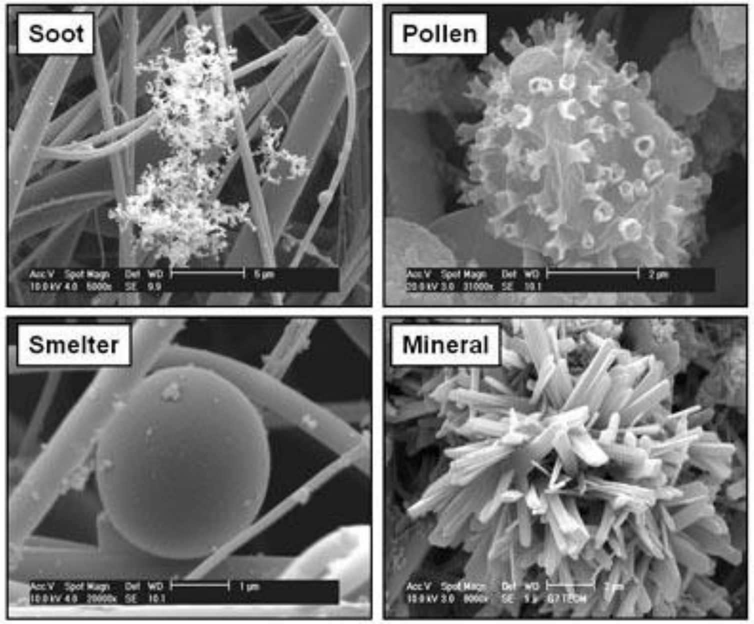
Gases & aerosols

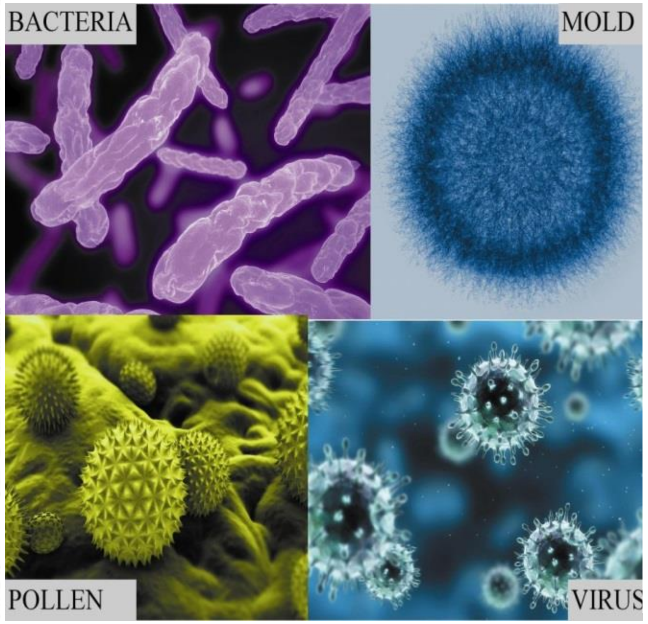
Anthropogenic

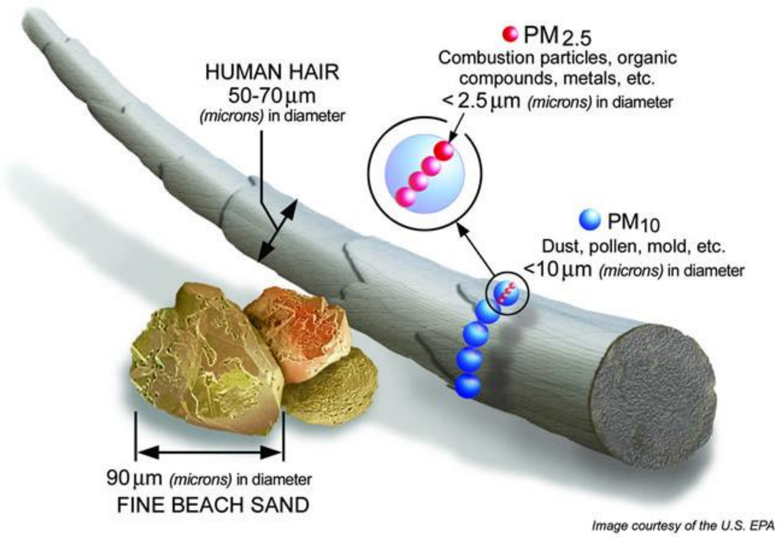
Aerosols:
sulfates, nitrates, ammonium, black carbon, organic aerosol (primary & secondary), metals

Natural

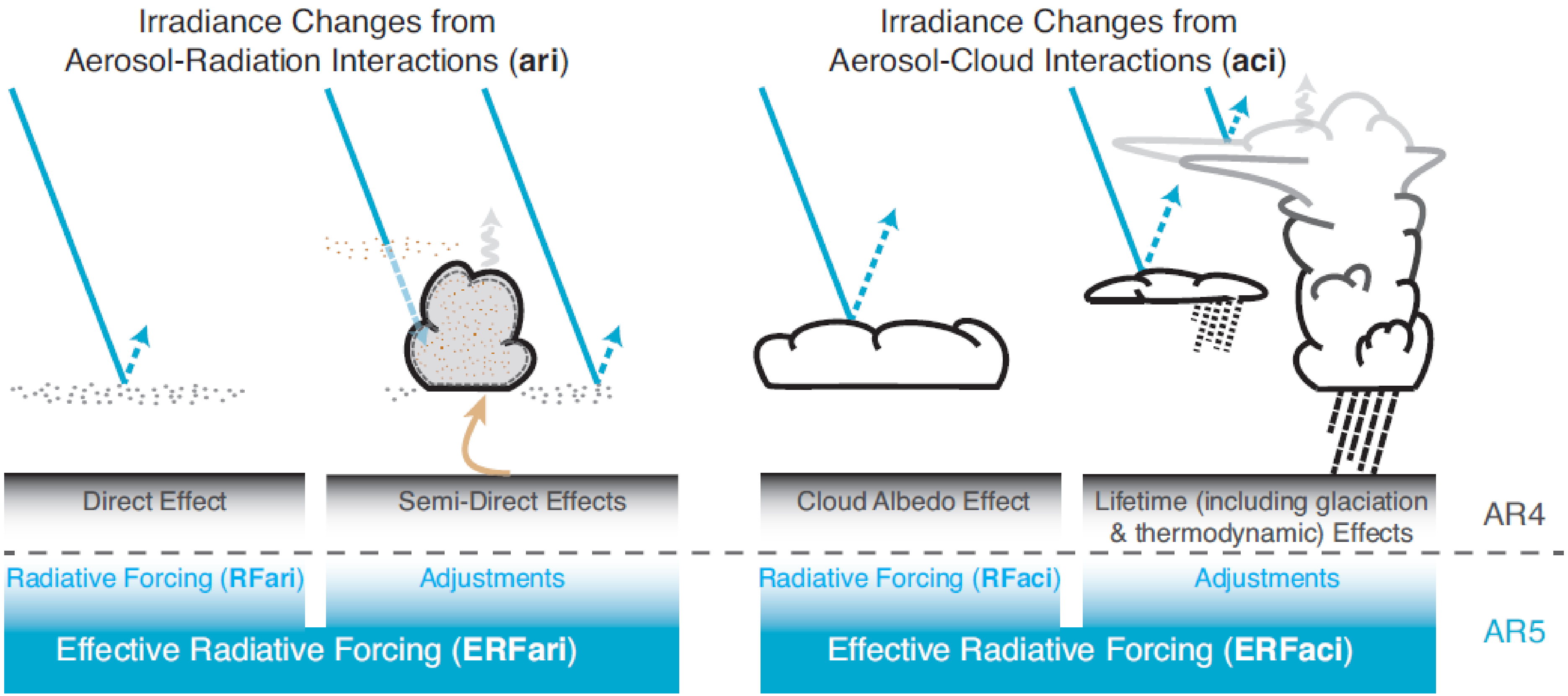
dust, sea-salt, bioaerosols, volcanic aerosols, secondary aerosols







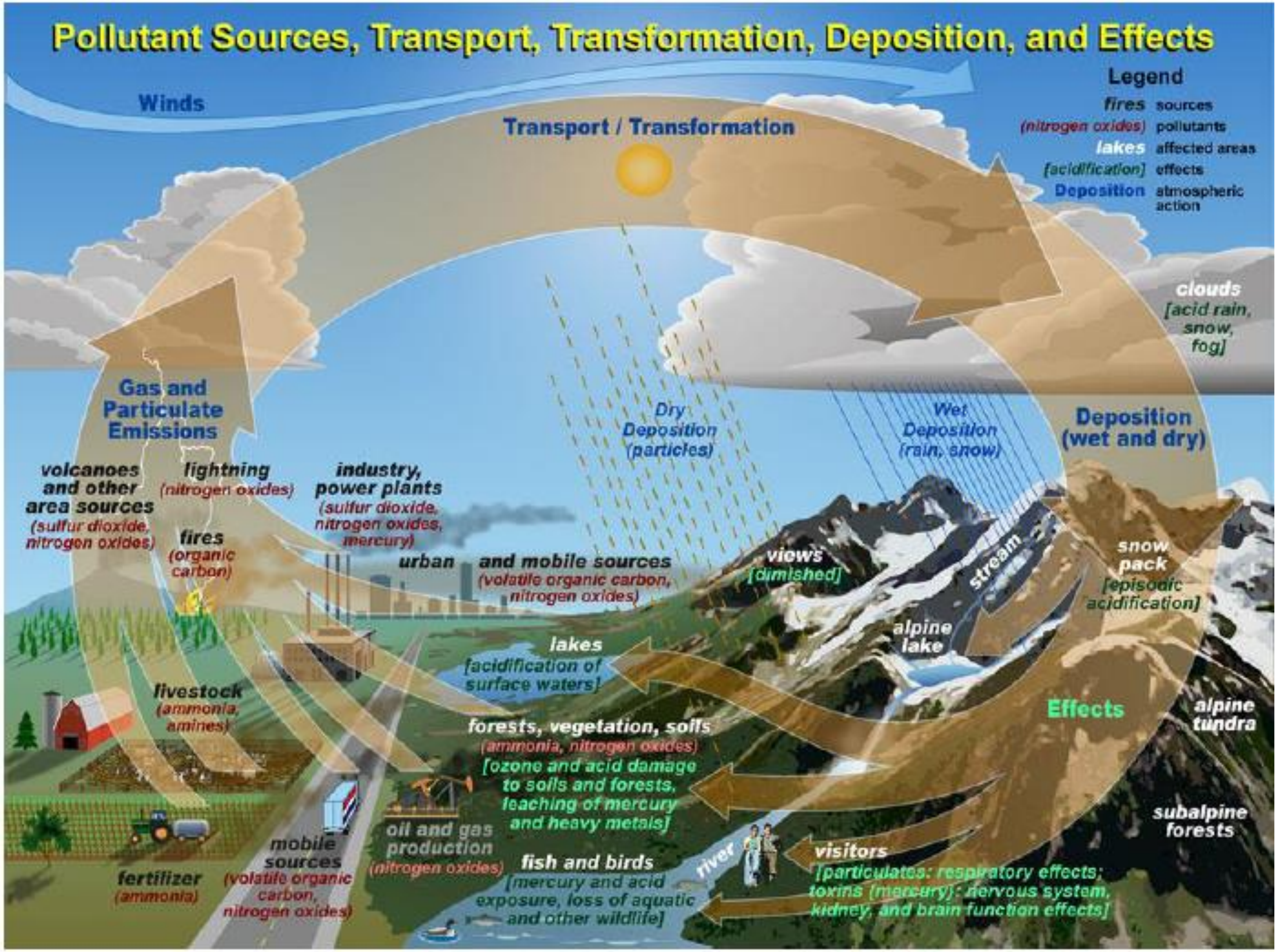
aerosol–radiation and aerosol–cloud interactions



The blue arrows depict solar radiation, the grey arrows terrestrial radiation and the brown arrow symbolizes the importance of couplings between the surface and the cloud layer for rapid adjustments.

Globally, between 20 and 40% of aerosol optical depth (medium confidence) and between 1/4 and 2/3 of cloud condensation nucleus (CCN) concentrations (low confidence) are of anthropogenic origin

ipcc INTERGOVERNMENTAL PANEL ON climate change WMO UNEP



Atmospheric cycle of air pollutants.

Emission, transport and transformation, deposition.

(https://www.fws.gov/refuges/AirQuality/sources.html)

Photochemical smog in megacities

Cocktail of gases and aerosols

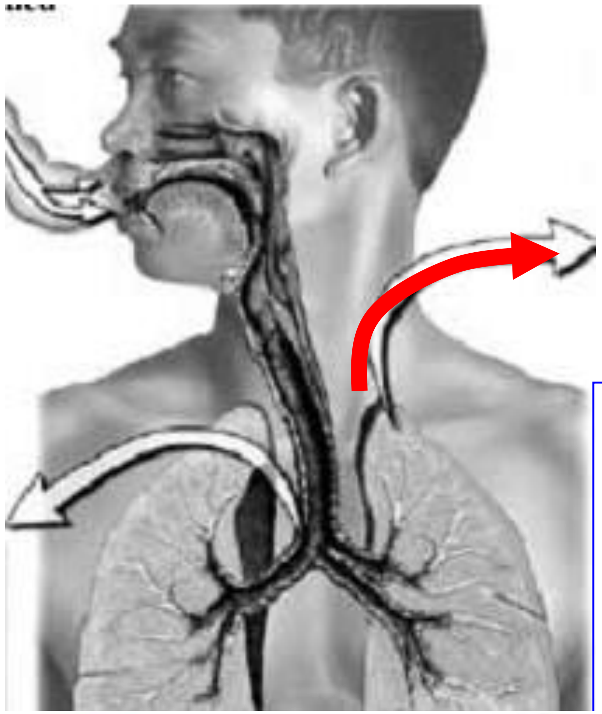
Financial crisis – Low Economy level

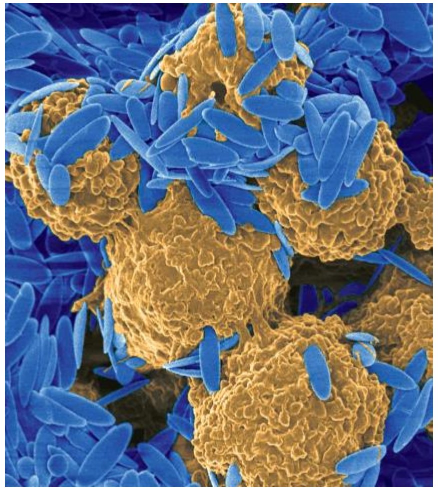
Increasing use of Domestic wood burning -

Air pollution issue mainly during winter

Impact of aerosols on human -health

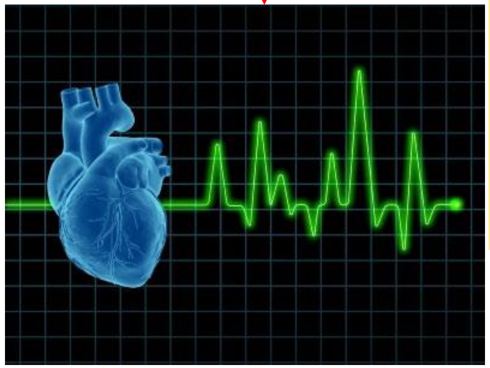
Smaller particles penetrate deeper in the human bronchial





Oxidative stress

Every day, we breath ~ 12000 liters of air that are filtered in our lugs through a surface equivalent to one tennis court.



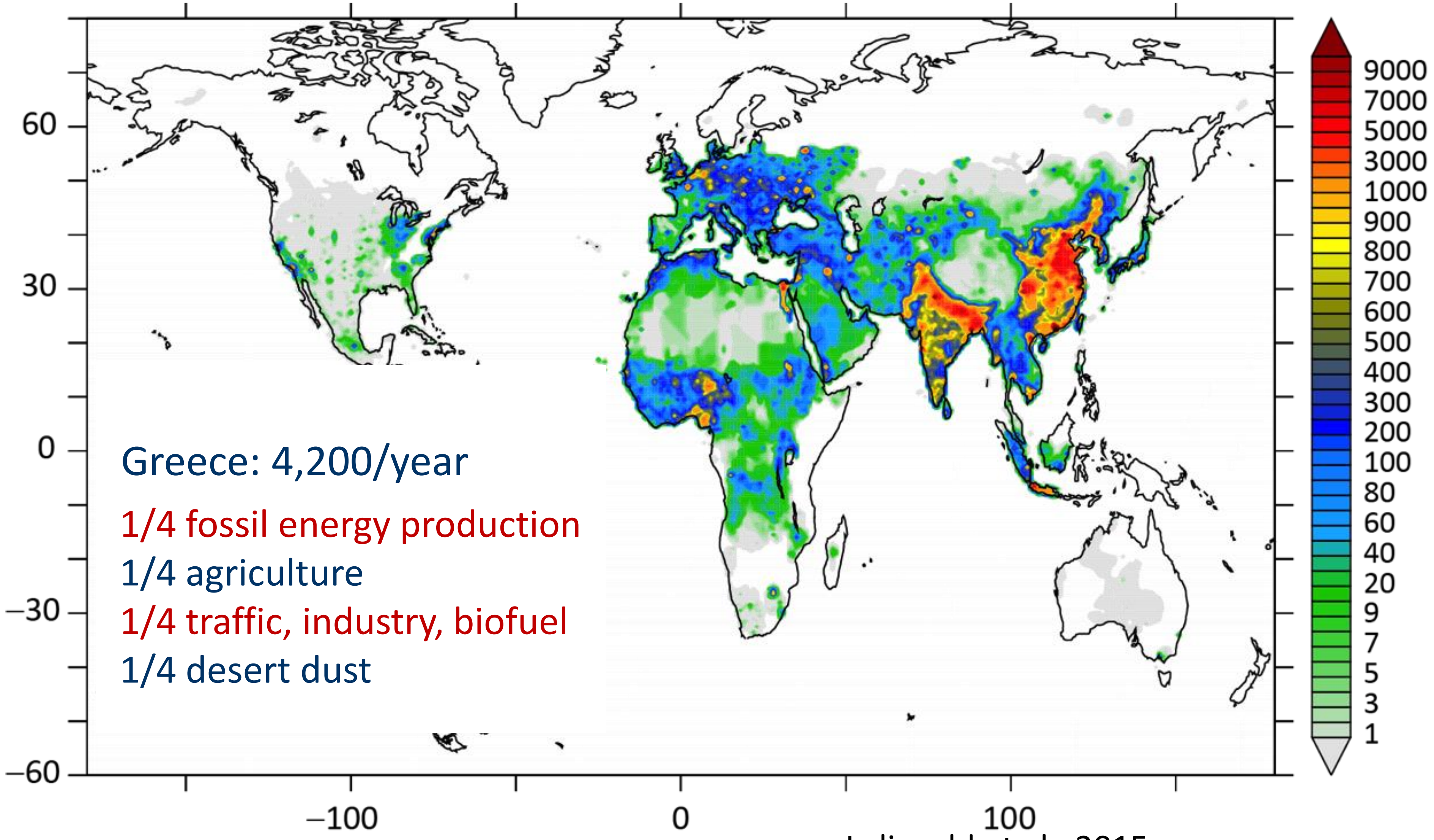
Air pollution leads to reduction in expectance of life
2.9 years globally
2.2 years in Europe

Lelieveld 2019

- ✓ In polluted areas, Black Carbon are among the smallest particles (< 100nm) and have been classified recently by WHO as cancerogenic
- ✓ Ultra fine particles (UFP) from transportation & combustion or chemically produced are the most aggressive for health.

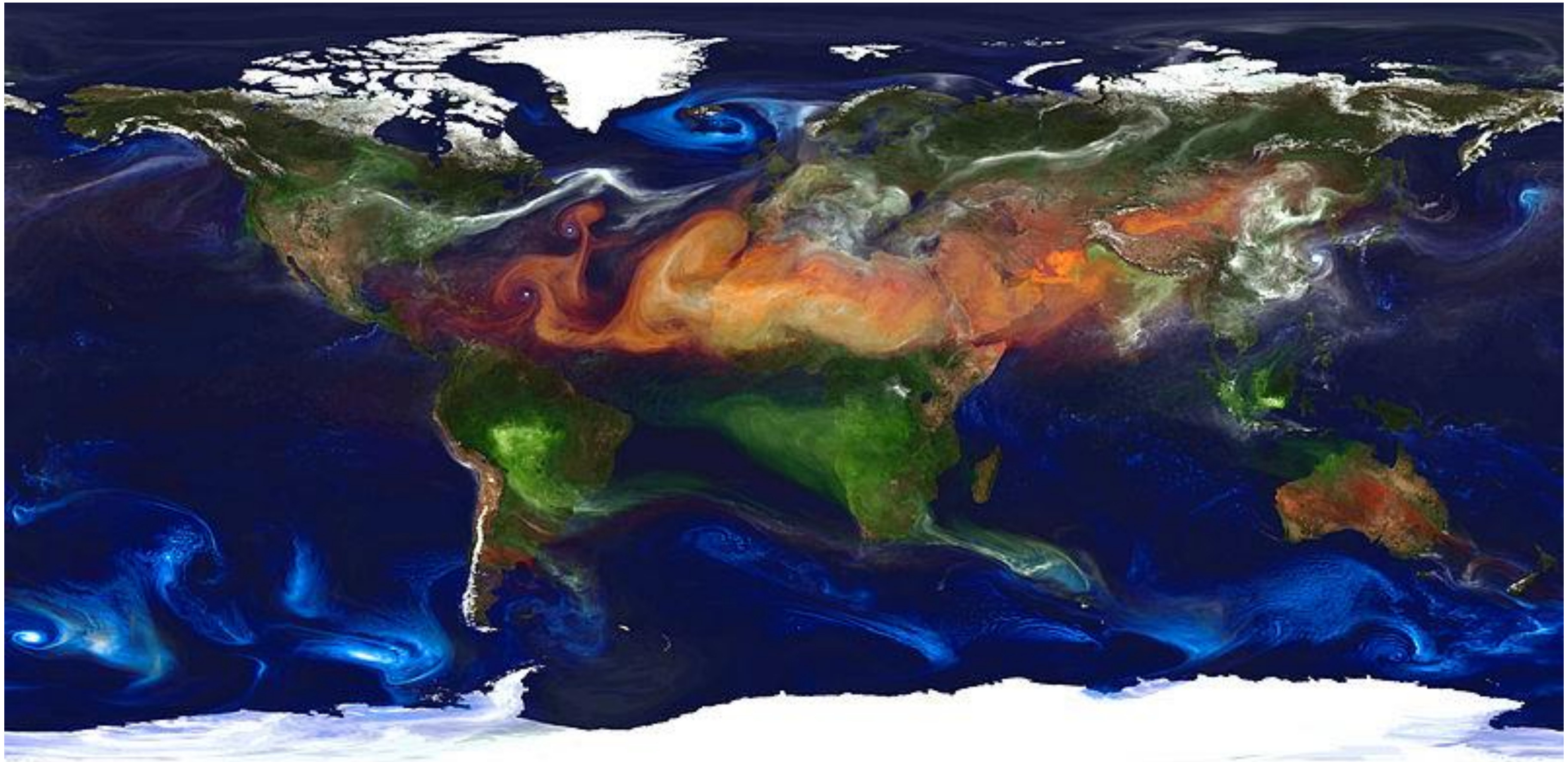
Annual premature mortality attributable to outdoor air pollution

Individuals per 100 × 100 km^2 – **Globally 3.3 million/year**



Lelieveld et al., 2015

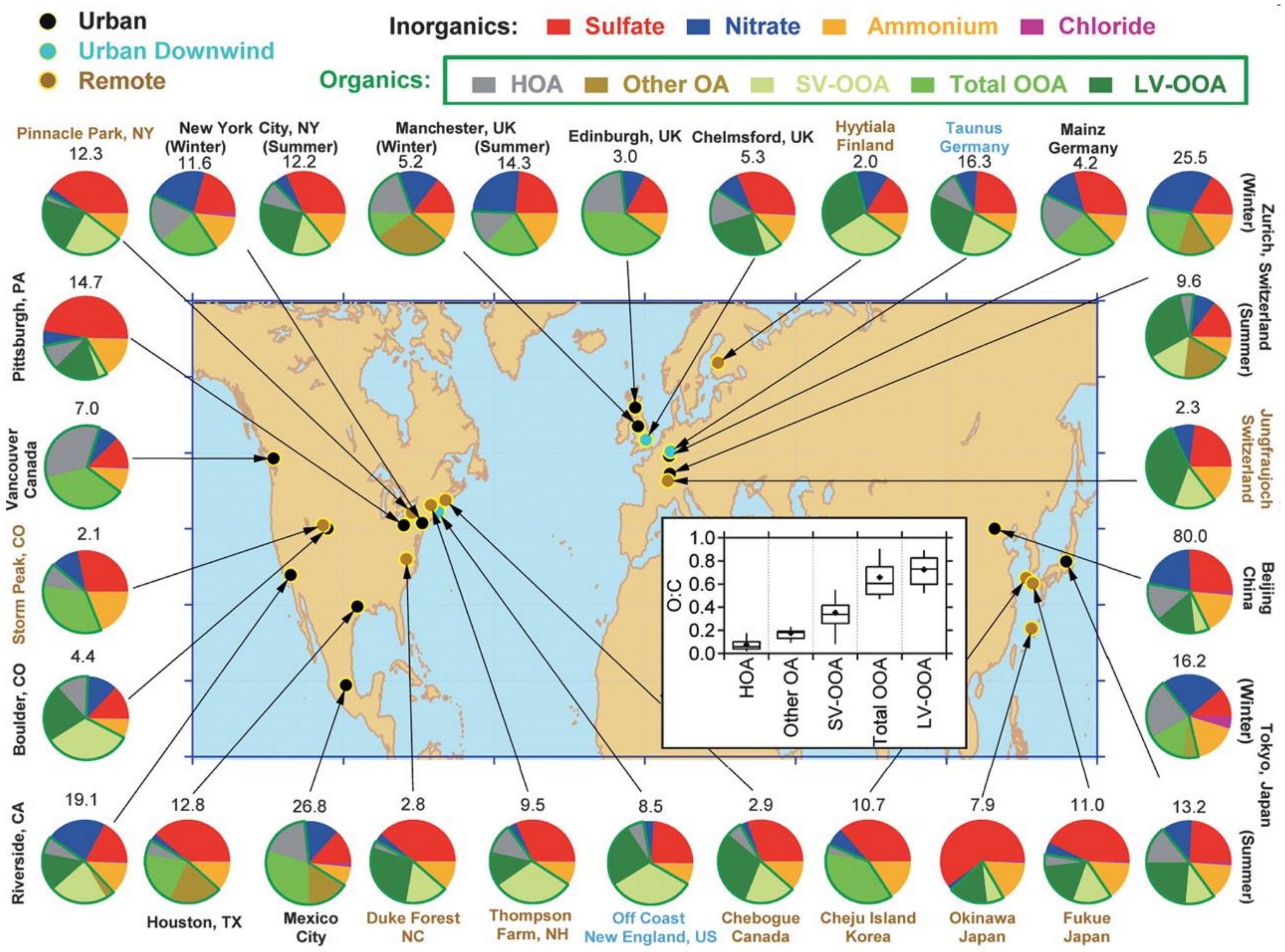
Global distribution of aerosols at surface



https://youtu.be/oRsY_UviBPE

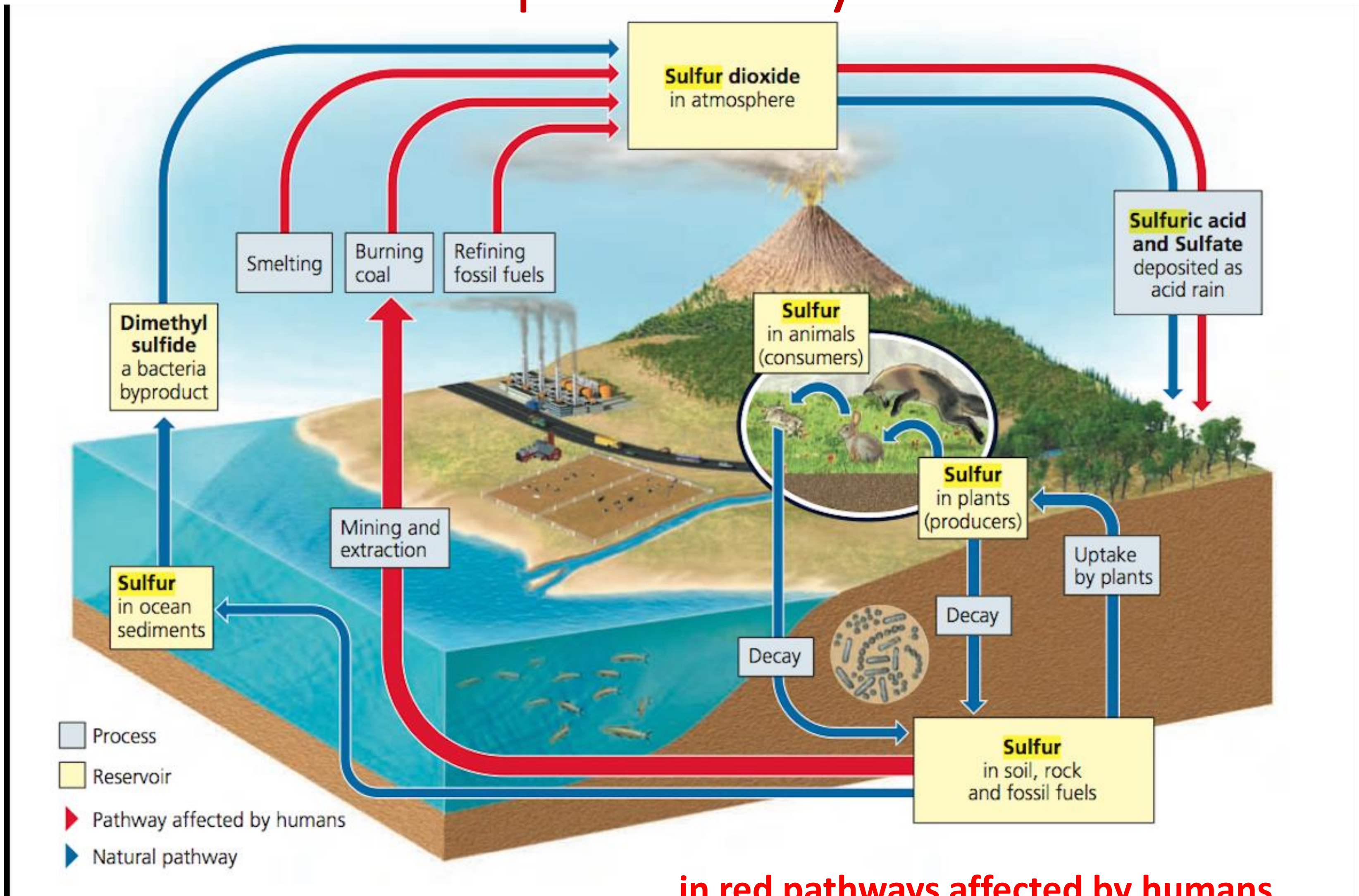
Courtesy NASA, the Image of the Day Gallery
NASA Center for Climate Simulation at Goddard Space Flight Center

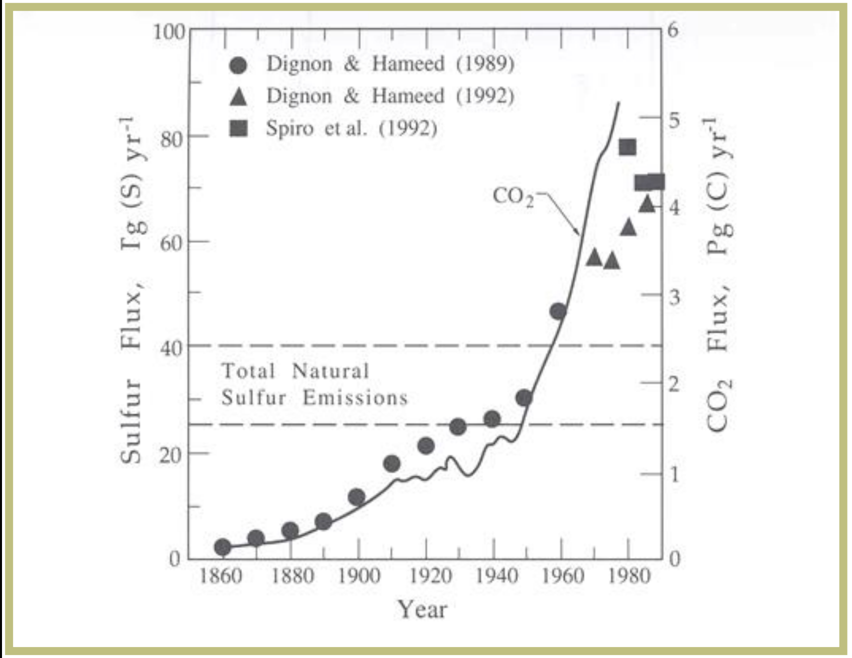
PM1 Aerosol Composition Worldwide



Jimenez, Canagaratna, Donahue, et al., Science 326, 1525 (2009)

Sulfur atmospheric cycle





Carolina Eduardo
https://www.emaze.com/@AWILICQ

in red pathways affected by humans

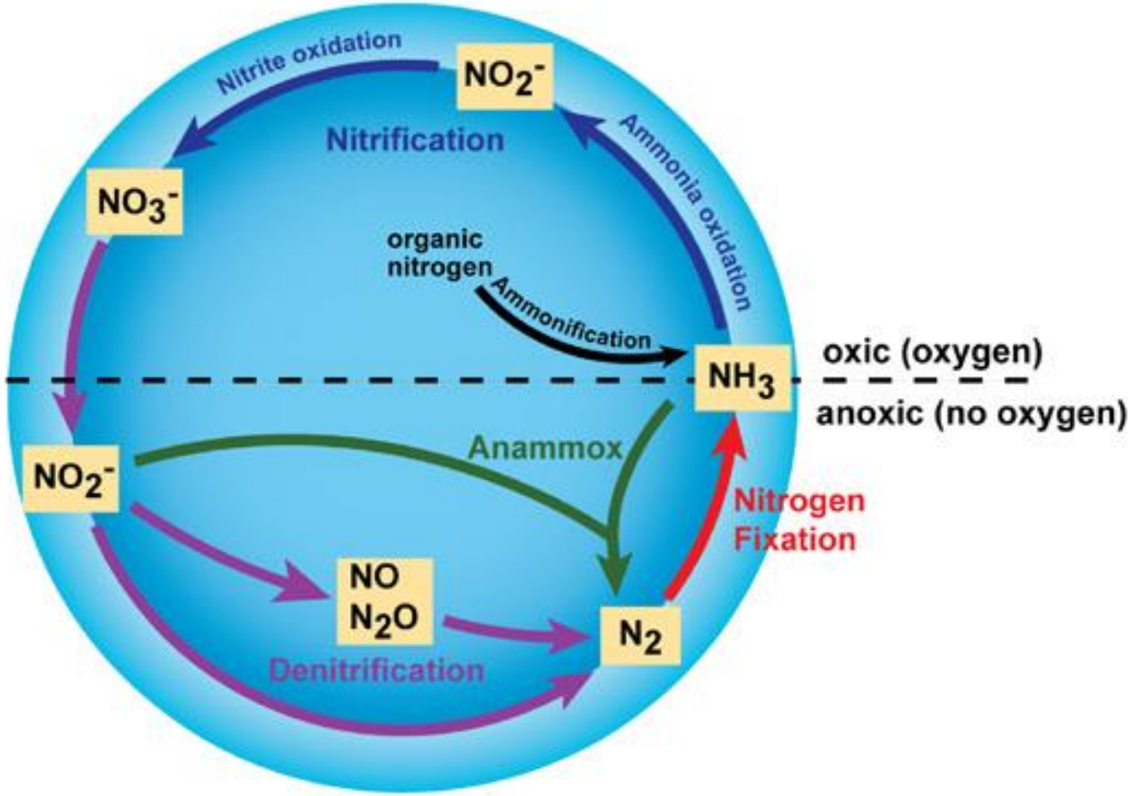
>70% of emissions are human driven

The increase in SO_2 since 1860 followed that of CO_2

Combustion of coal, fossil fuels, wood, smelting, H_2SO_4 production, refineries. ~80 Tg-S/yr

Ocean, volcanoes, soil/vegetation ~ 30 Tg-S/yr

Nitrogen atmospheric cycle



Transformations in the ecosystems

https://www.nature.com/scitable/knowledge/library/the-nitrogen-cycle-processes-players-and-human-15644632/

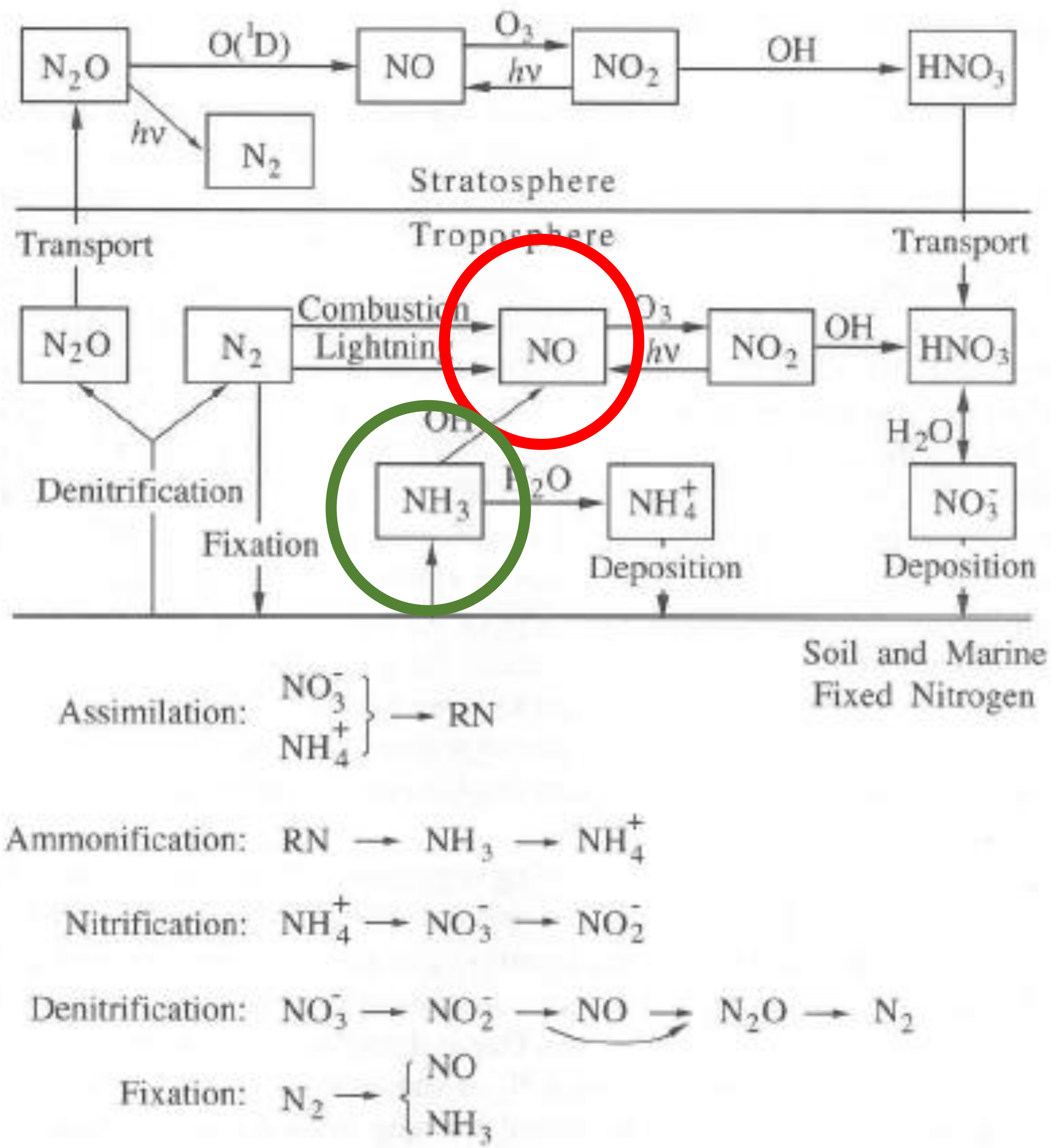


FIGURE 2.4 Processes in the atmospheric cycle of nitrogen compounds. A species written over an arrow signifies reaction with the species from which the arrow originates.

Transformations in the atmosphere

Nitrogen atmospheric cycle –impacts of interest

- N_2O is a greenhouse gas
- NOx (= NO + NO_2) impact on ozone (O_3) → photochemical smog

  & nitric acid (HNO_3) formation → acid rain
- NH_3 & amines neutralize atmospheric acids
- Aerosol formation (NH_4^+ NO_3^-)
- Nitrogen is the most important nutrient for ecosystems (if too much → eutrophication, acidification) – necessary to cover humanity's needs in food (NH_3 industrial production)

N_2O emissions	**~6% fossil & industry, 43% anthropogenic**
NH_3 emissions	**~20% combustion, remaining livestock, agriculture, soils**
NOx emissions	**~75% combustion, remaining lightning, soils**

Geographical distribution of NOx emissions from anthropogenic sources in 2000.

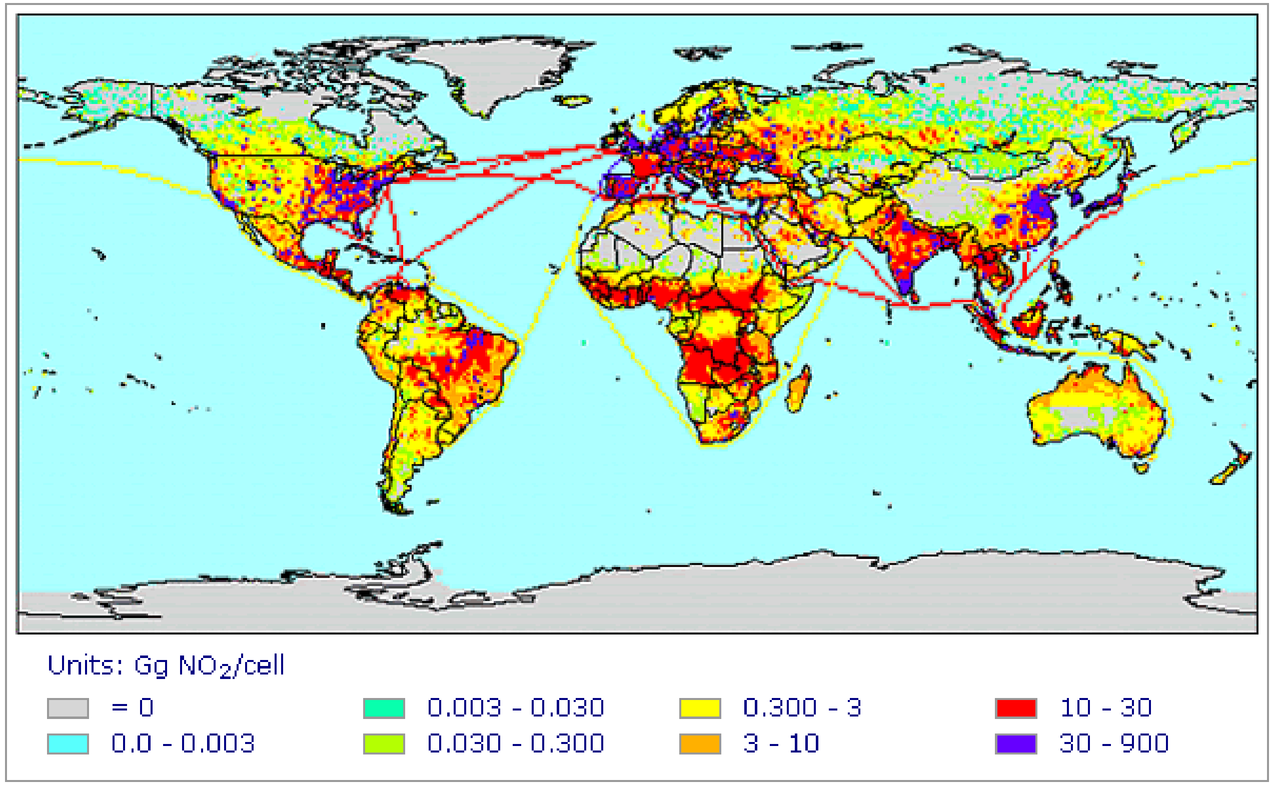
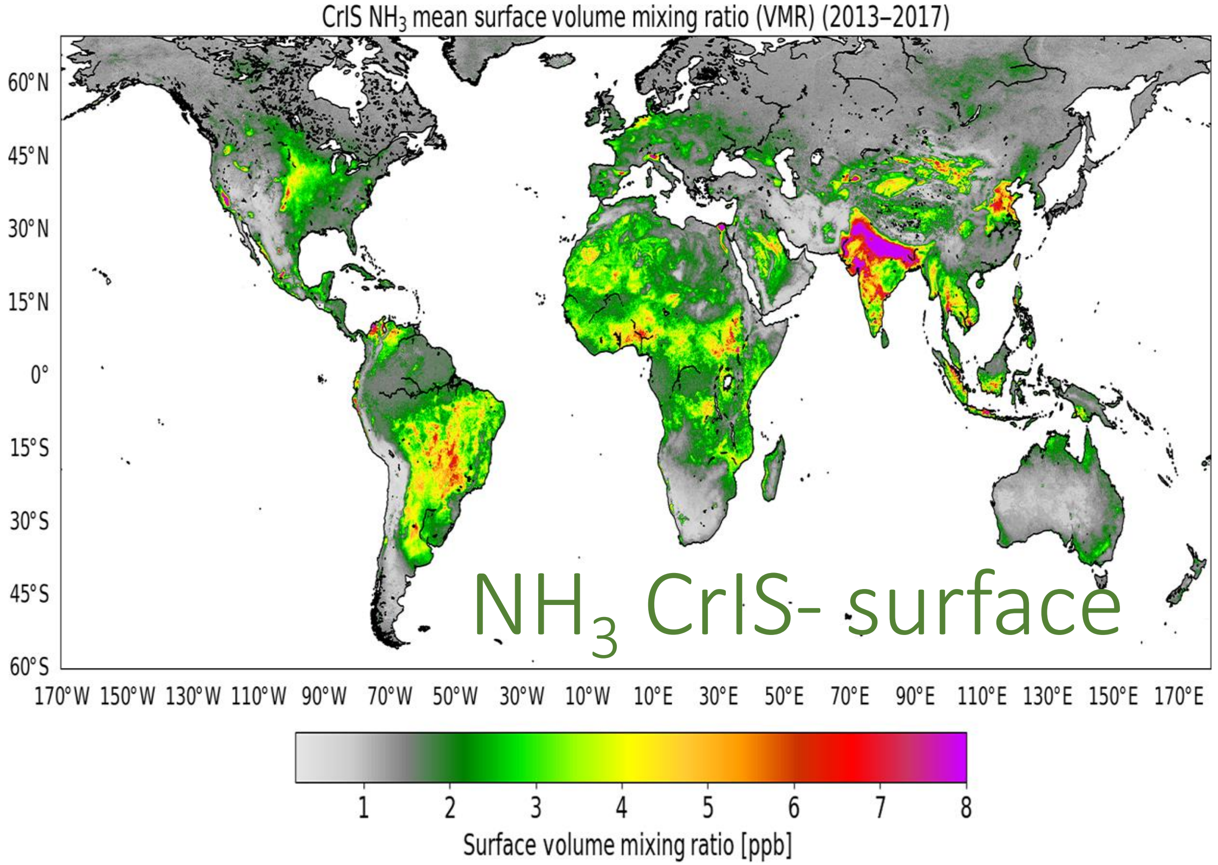


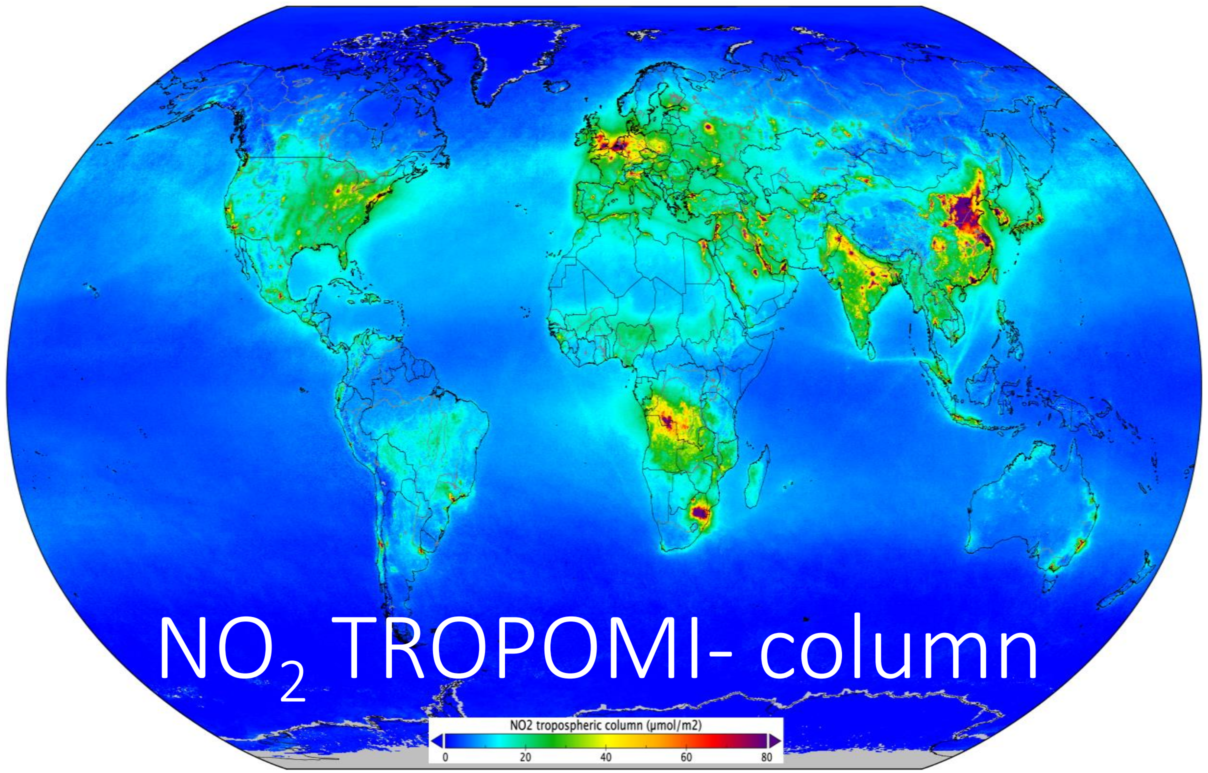
Image after: [**Netherlands Environmental Assessment Agency: Edgar32FT2000**]()

Vertical distribution of NOx emissions

Image: AT2-ELS

Atmospheric NH_3 & NO_2 seen from space





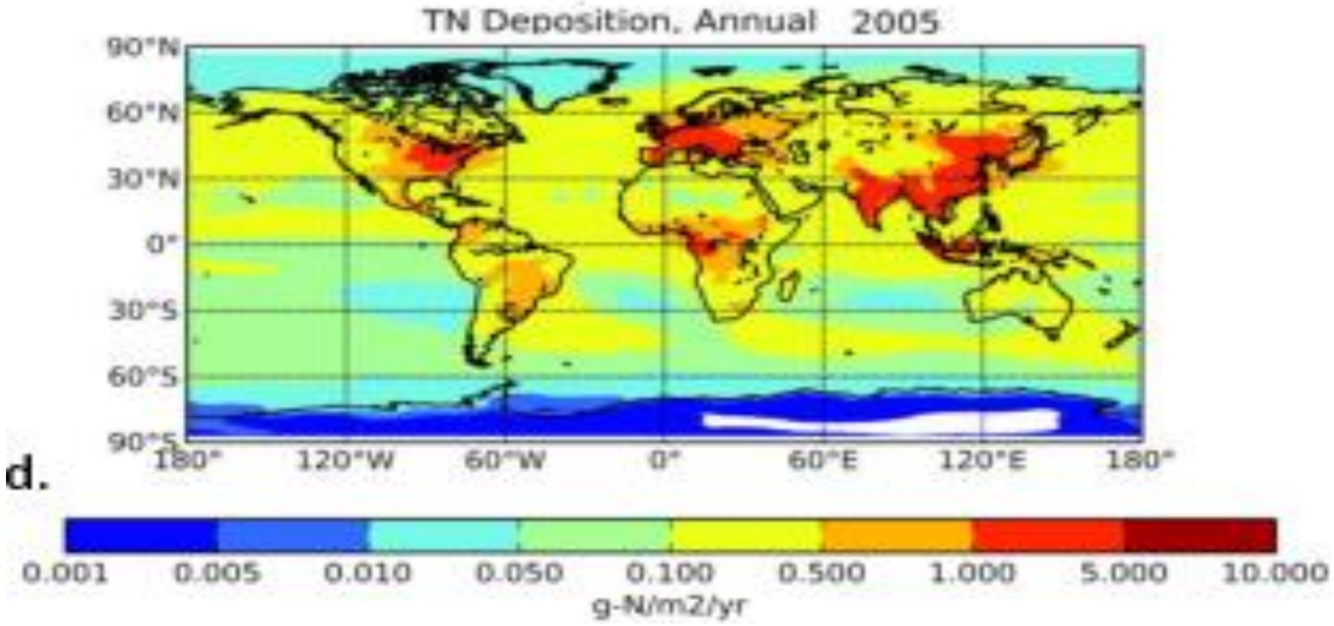
CrIS 5-year mean (2013–2017) of surface ammonia globally over land. The CrIS mean gridded Level 3 values are generated on a uniform 0.05° x 0.05° (5km x 5km) grid with a quality flag of 5.

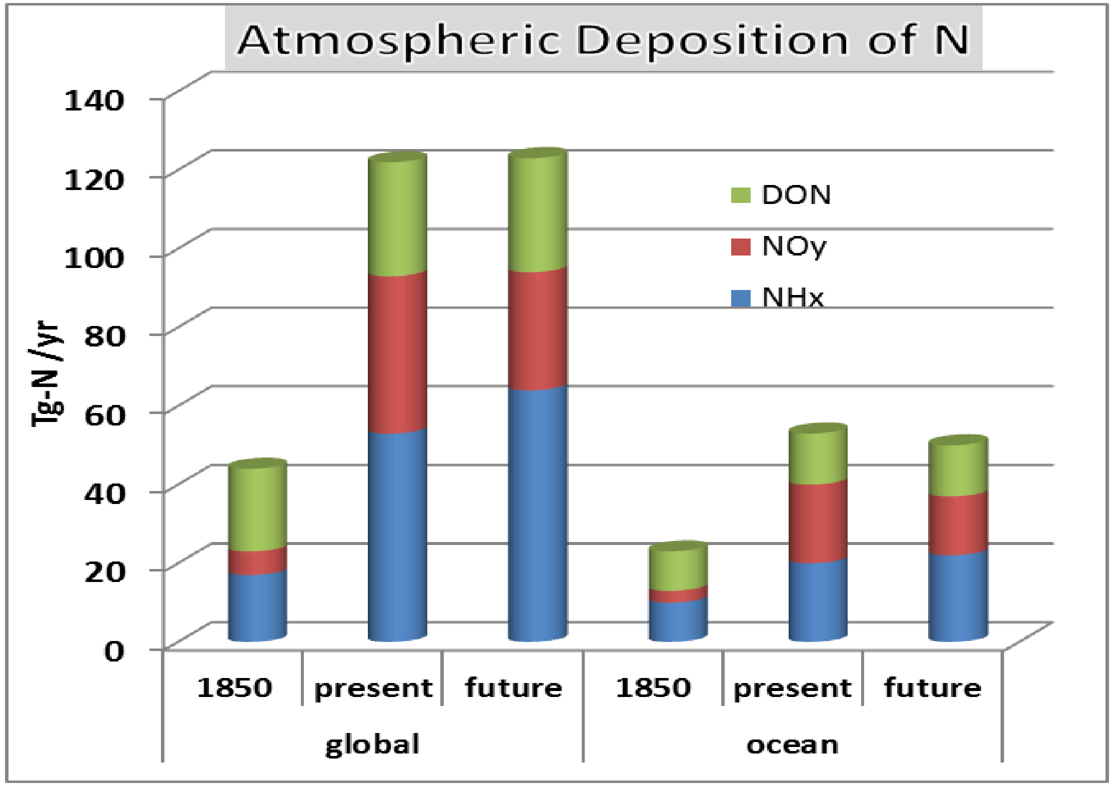
M. W. Shephard et al., 2020

Data between April and September 2018 averaged & regridded on a regular latitude-longitude grid of about 2 x 2 km.

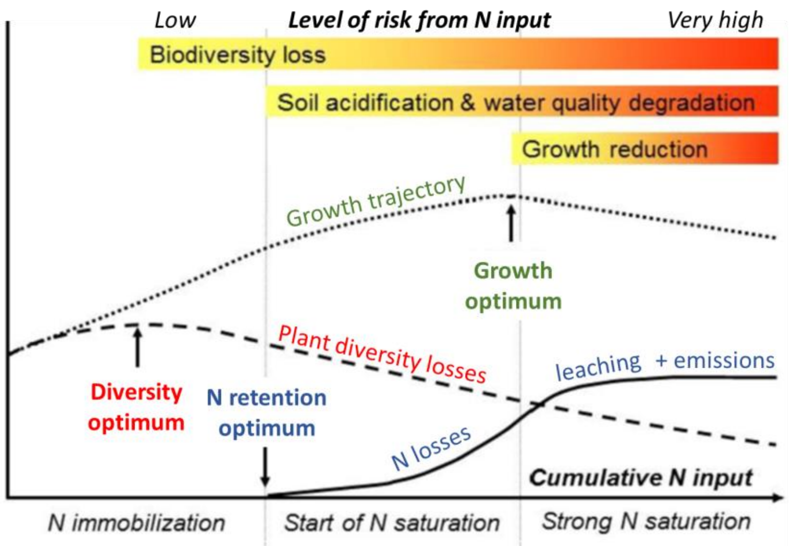
- https://www.esa.int/Applications/Observing_the_Earth/Copernicus/Sentinel-5P/Nitrogen_dioxide_pollution_mapped

Atmospheric N deposition and simulated changes





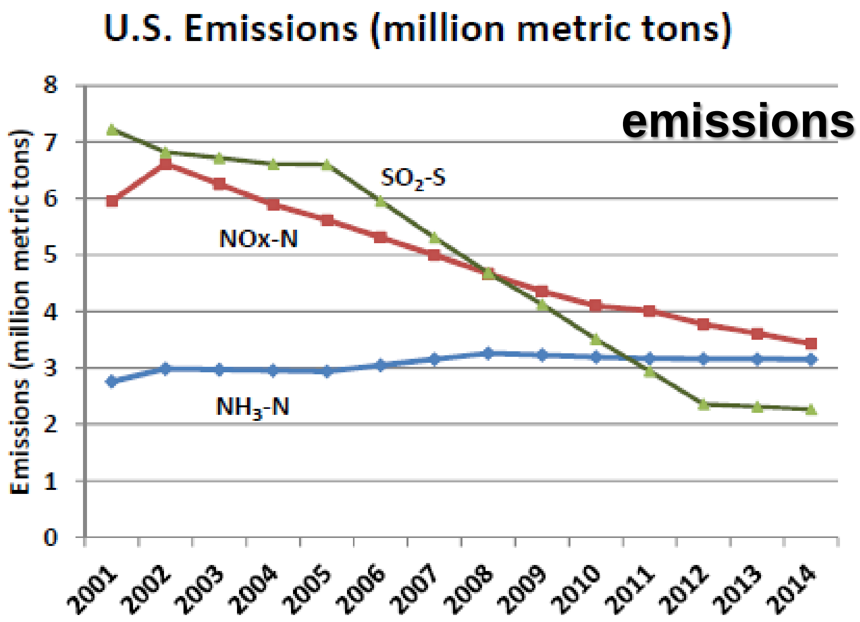
Kanakidou et al., J. Aerosol Science, D150278, 2016

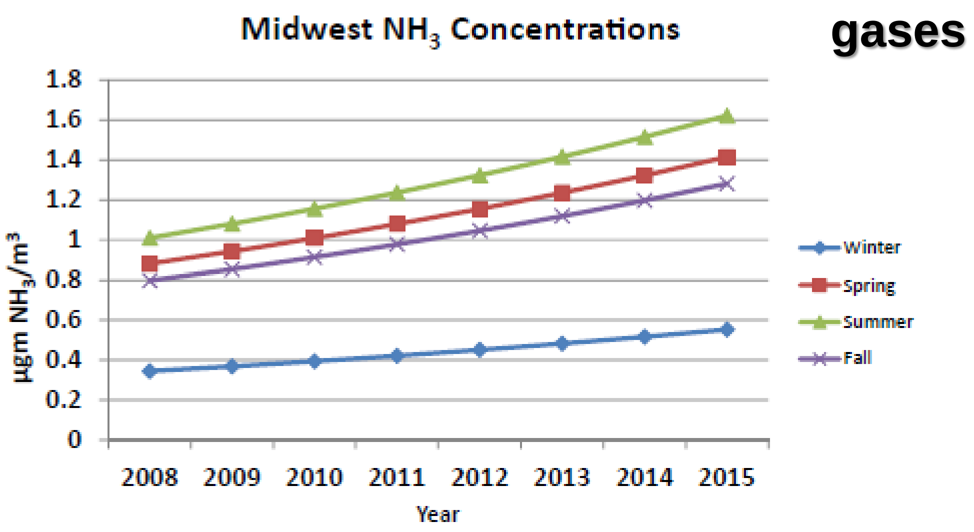


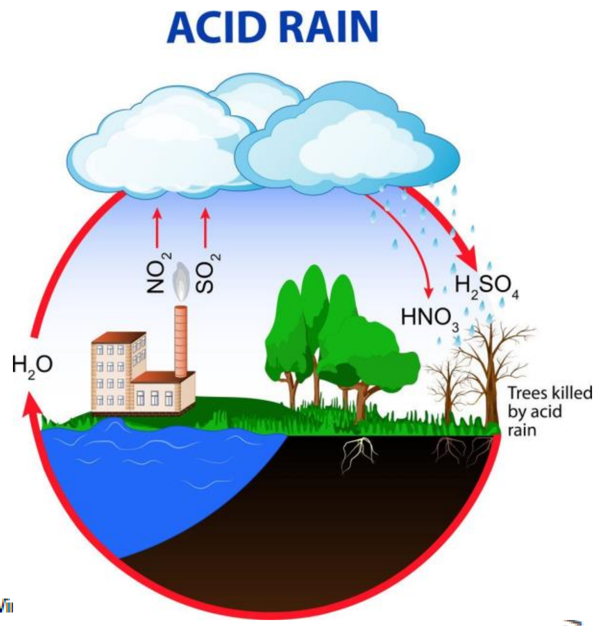
Nitrogen saturation effects on ecosystems (modified from Schmitz et al., 2019 in GAW Report No. 269

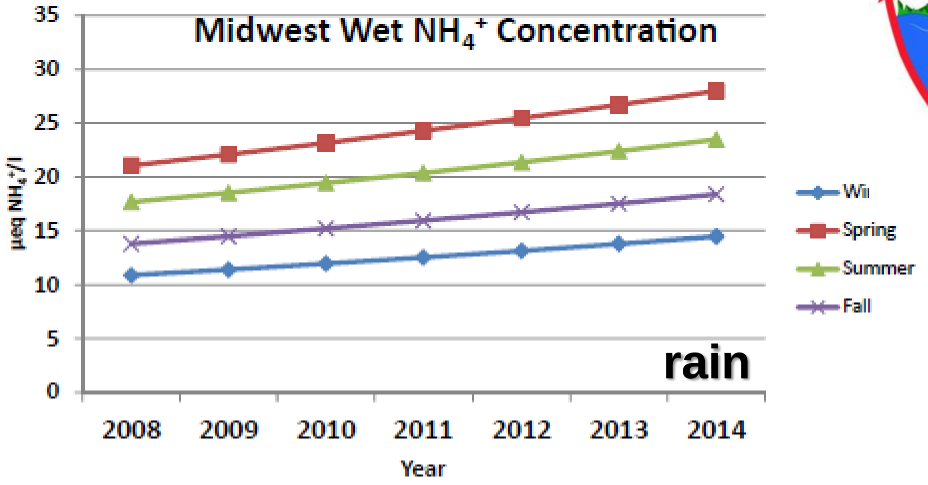
- Large uncertainties associated with the estimates
- What is the impact on the ecosystems?
- biodiversity loss?

Impact of emission changes on atmospheric acidity

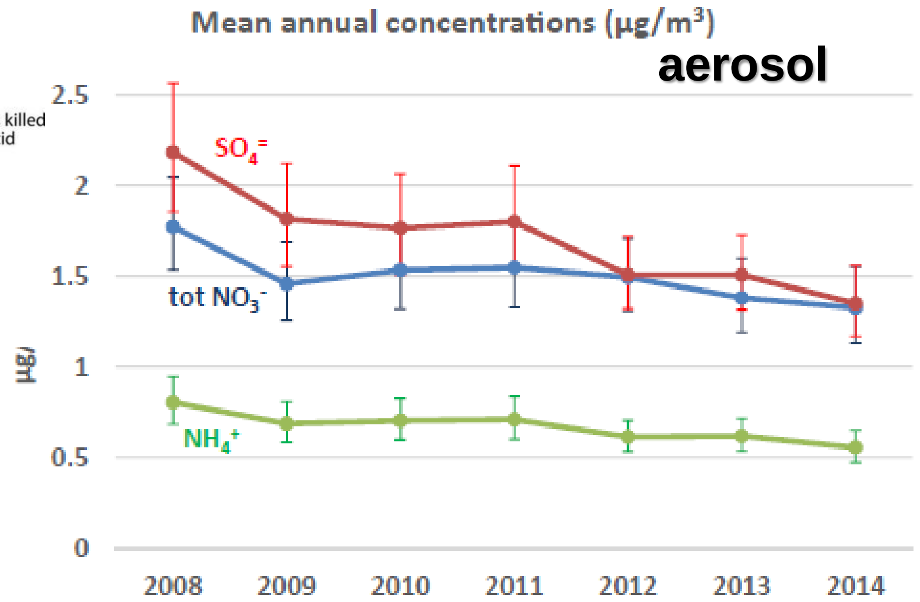






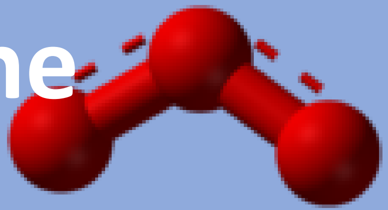


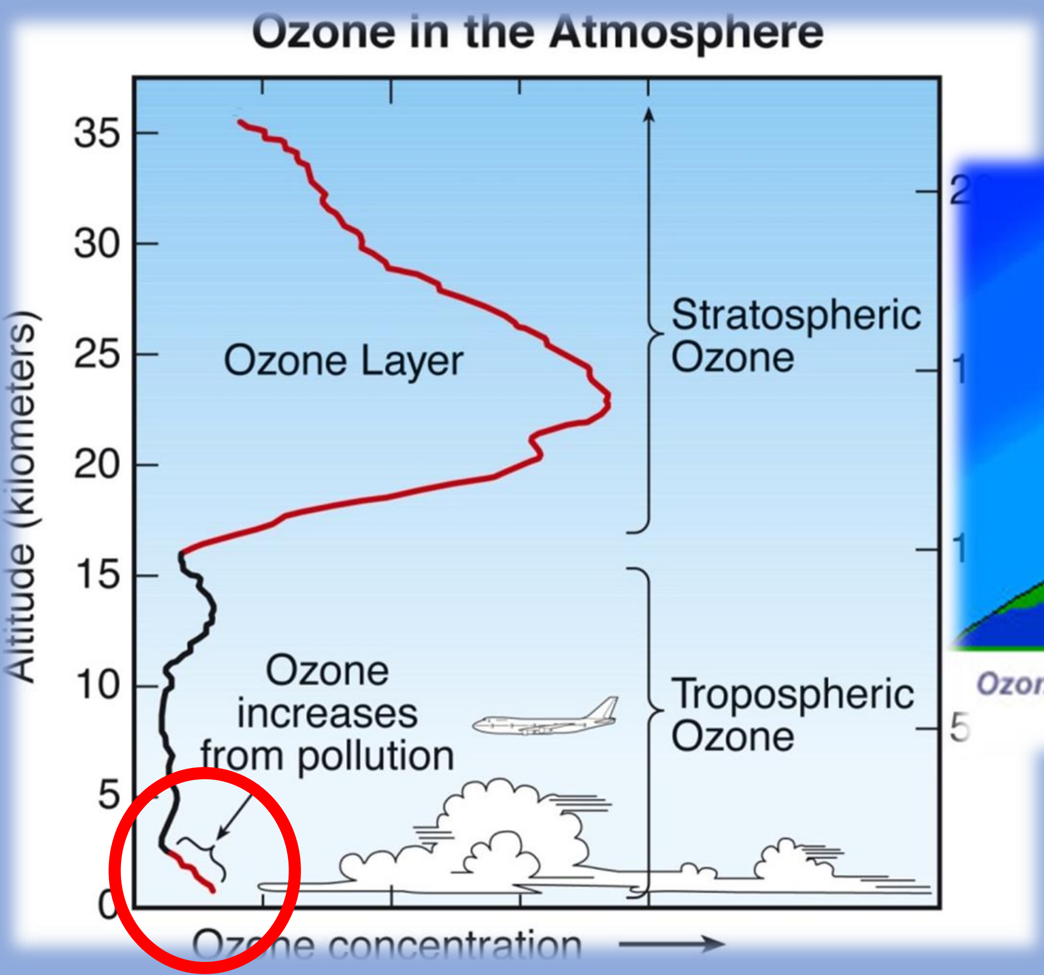
https://www.internet
geography.net/topics/
what-is-acid-rain/

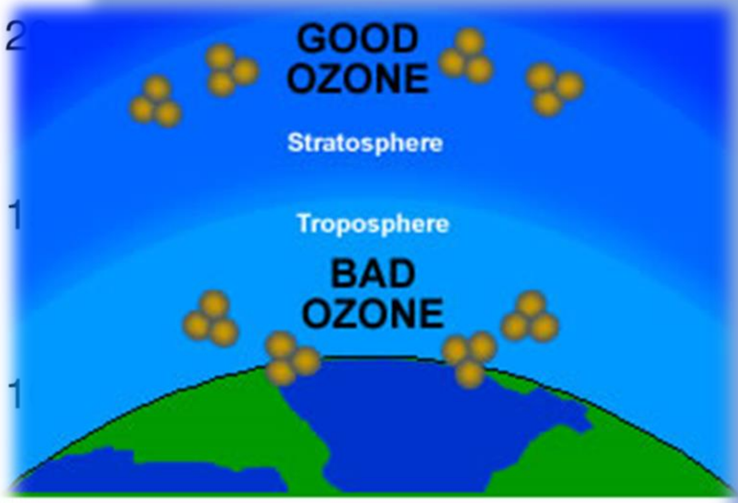


T. Butler et al. / Atmospheric Environment 146 (2016) 132–140

Ozone







Ozone in the stratosphere protects Earth but in the troposphere, it is harmful.

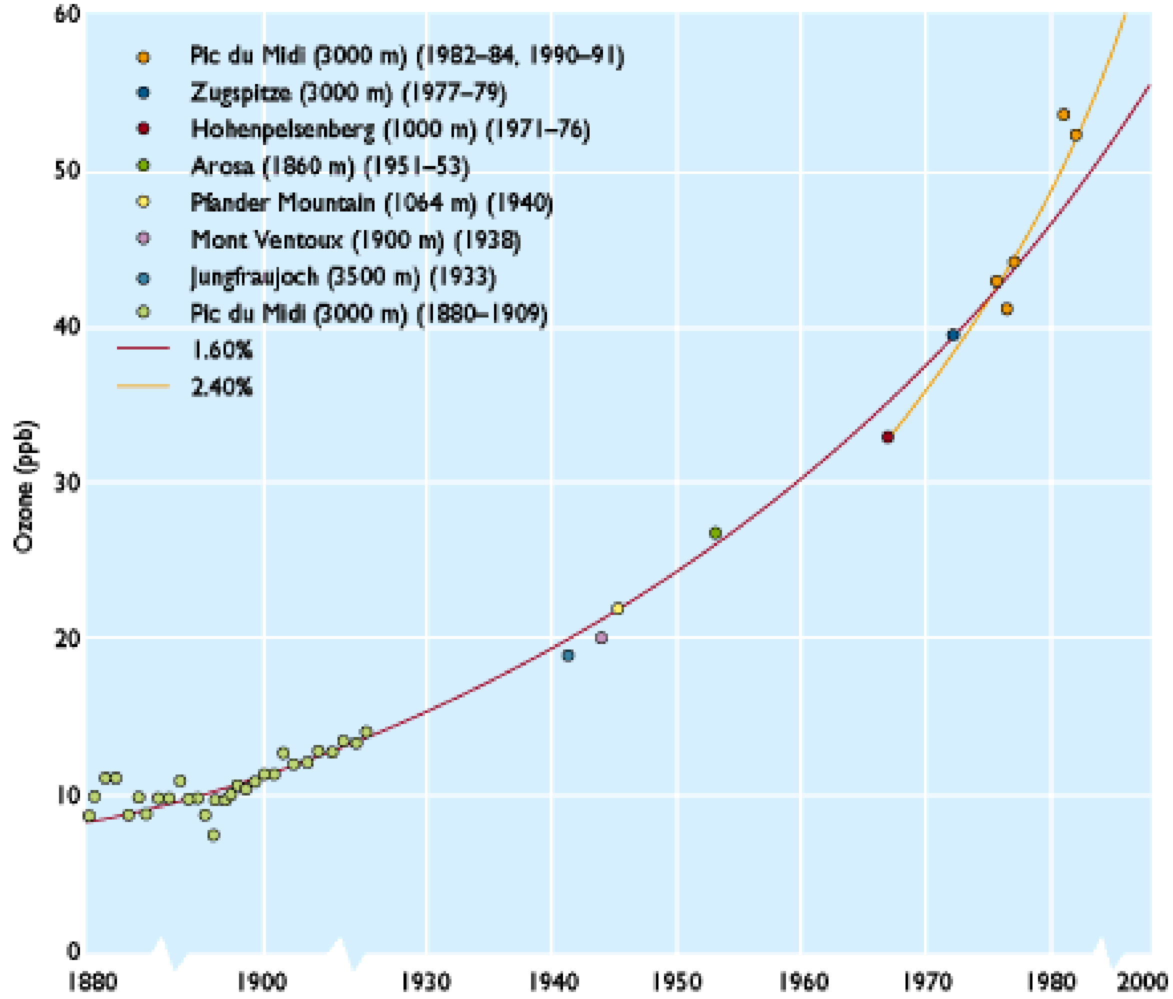
UCAR©2003

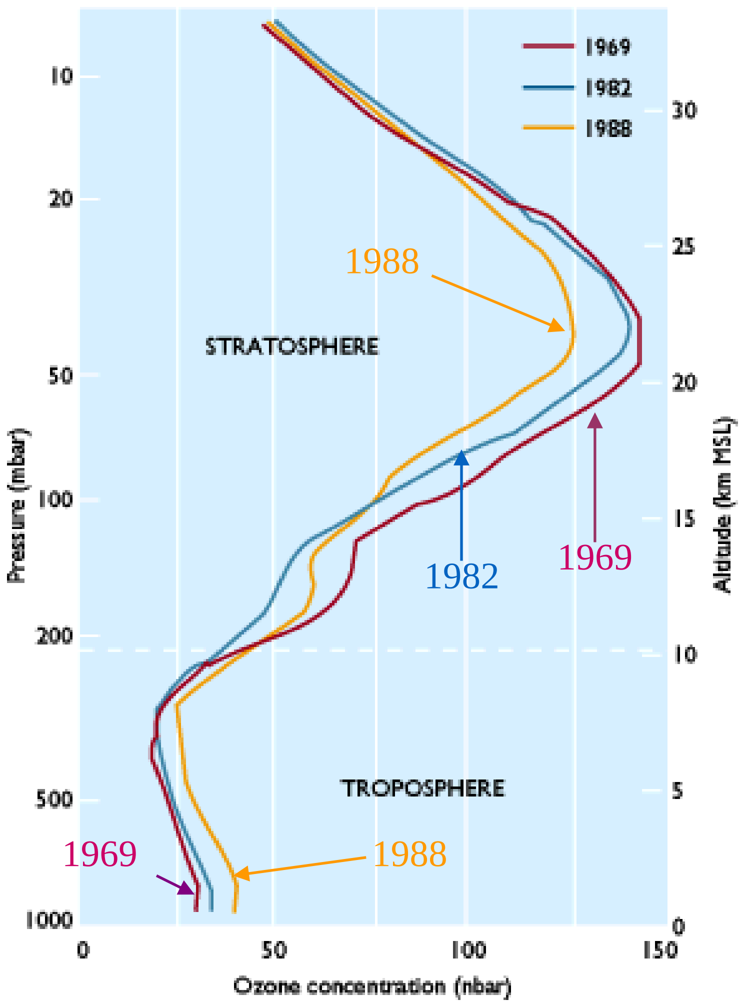
90% of O_3 in the stratosphere
Ozone hole (thinner O_3 layer in the stratosphere)
Cooler stratosphere
Penetration of UV => cancer

Phytotoxicity
Premature deaths
High values spring & summer

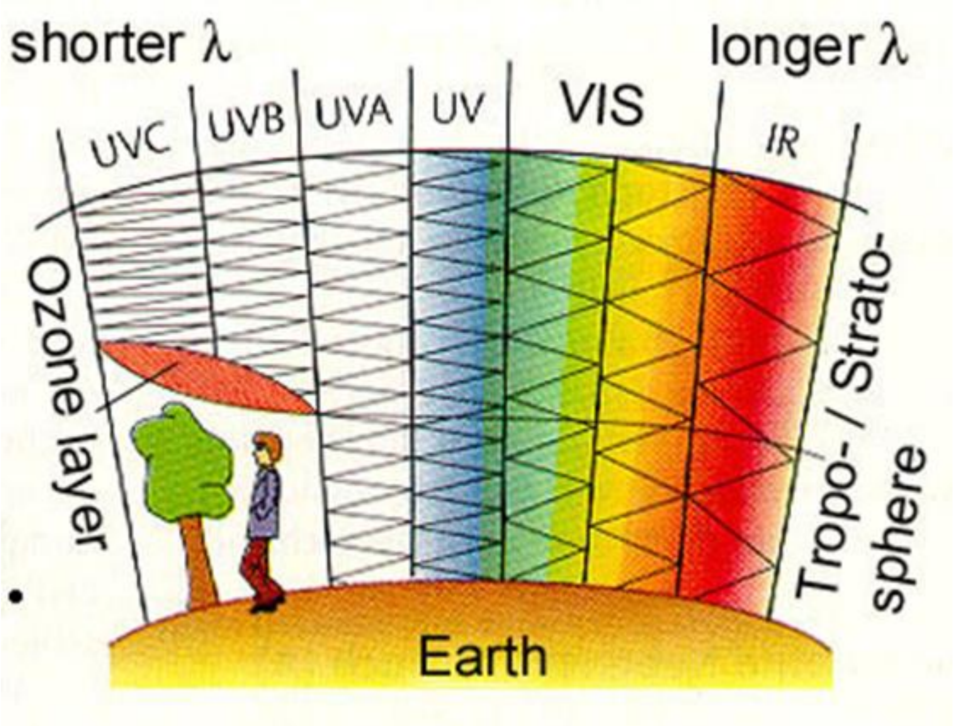
Secondary pollutant is difficult to control – needs coordination between countries.

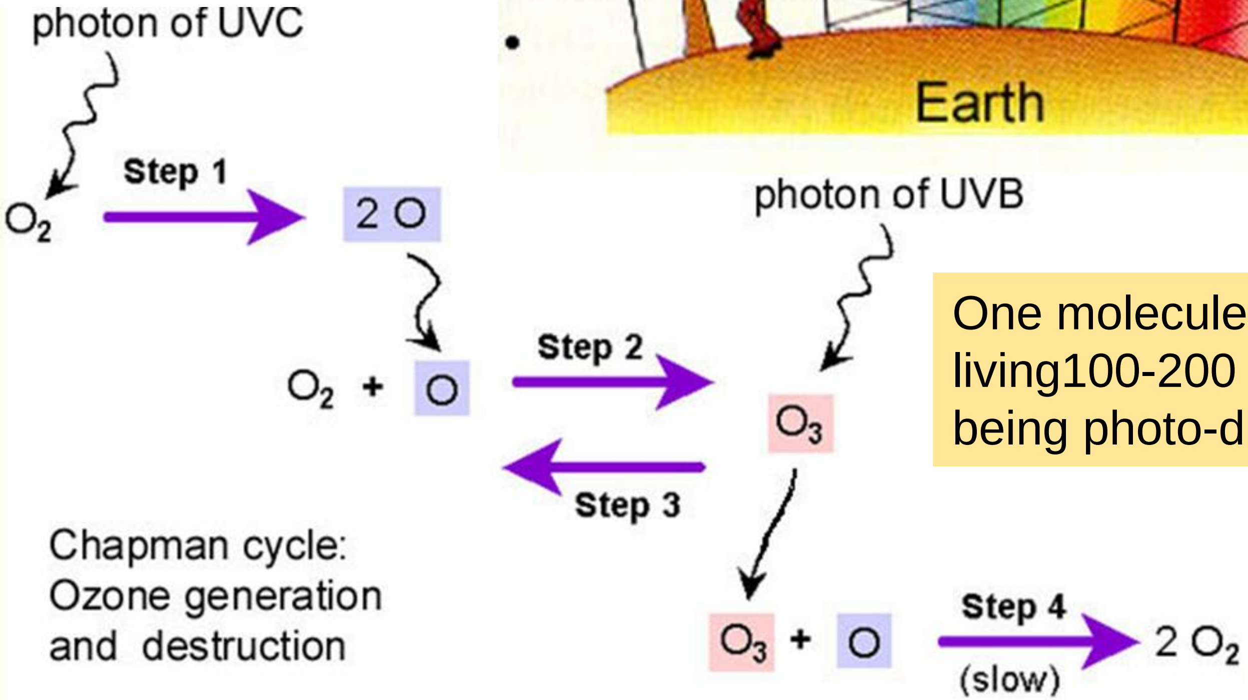
Historic data for O3





Formation and destruction of ozone in the stratosphere

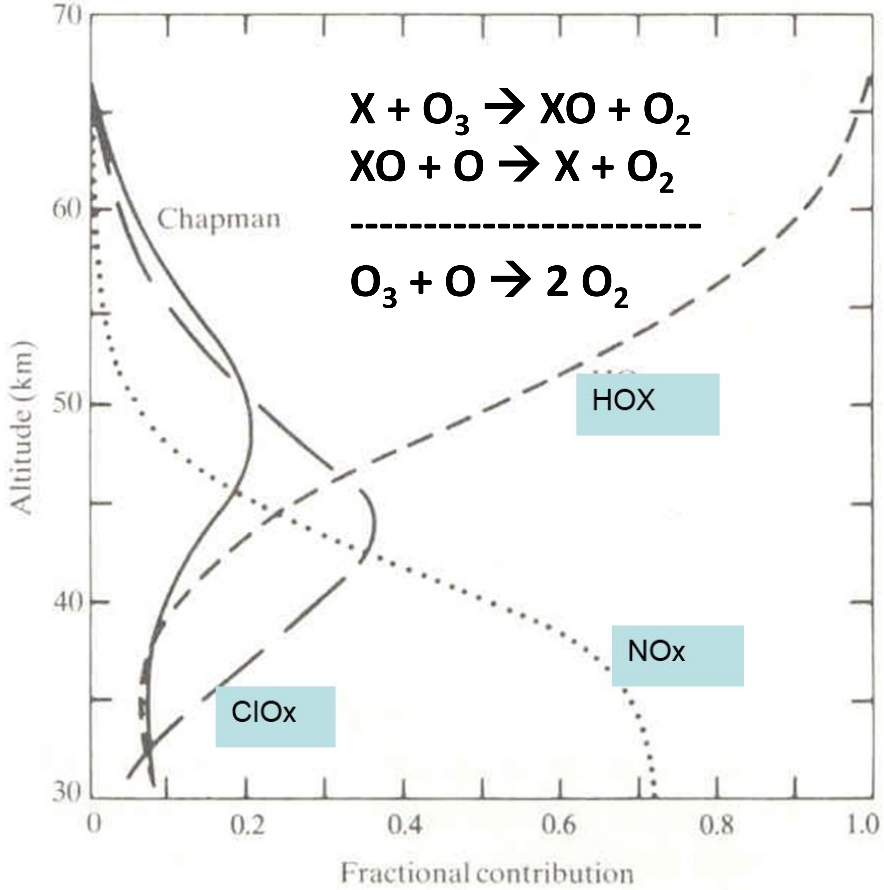




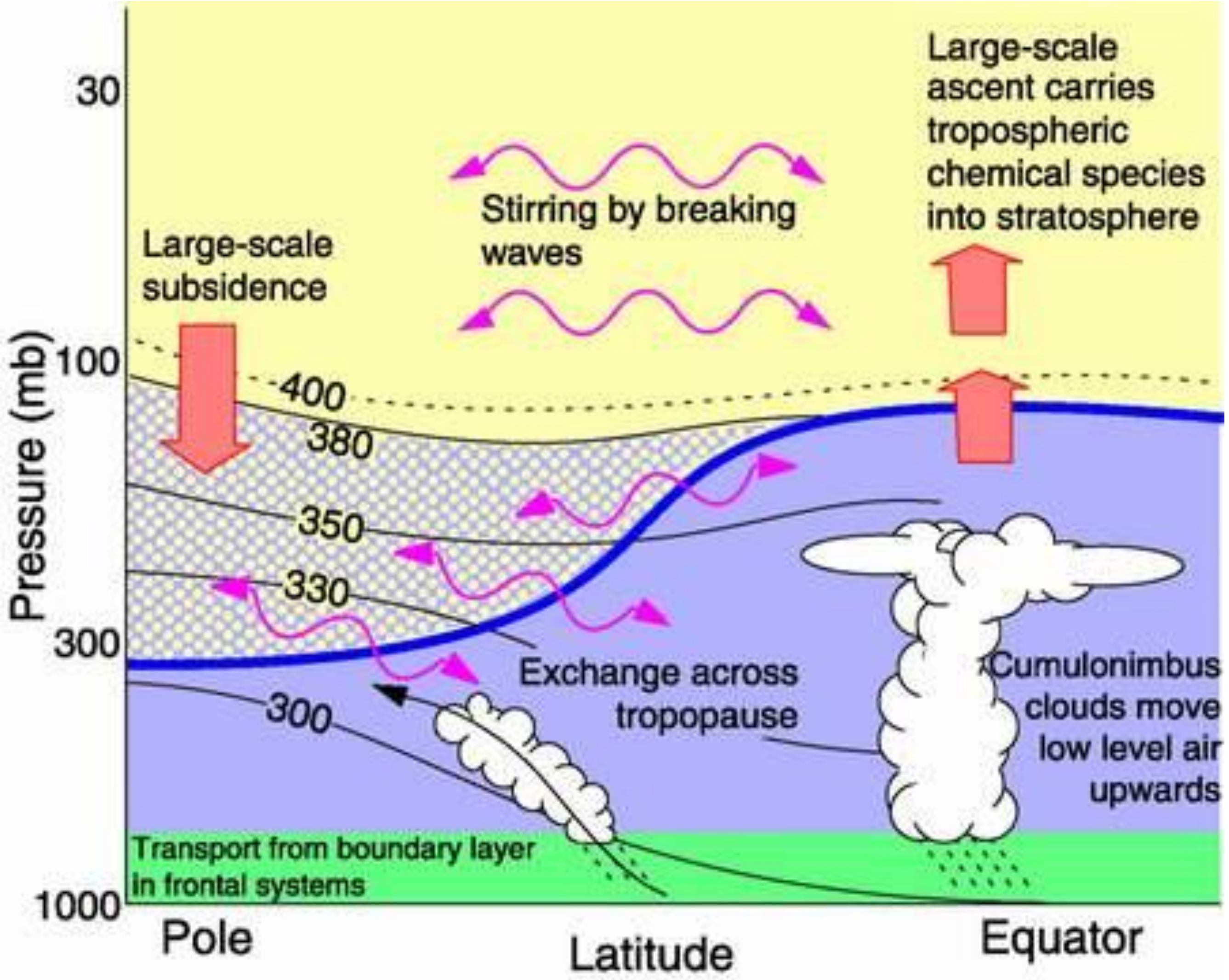
One molecule of O_3 is living100-200 s before being photo-dissociated

R. Wayne, Chemistry of Atmospheres

O_3 depletion : catalytical cycles



Origins and fate of O_3 in the troposphere?



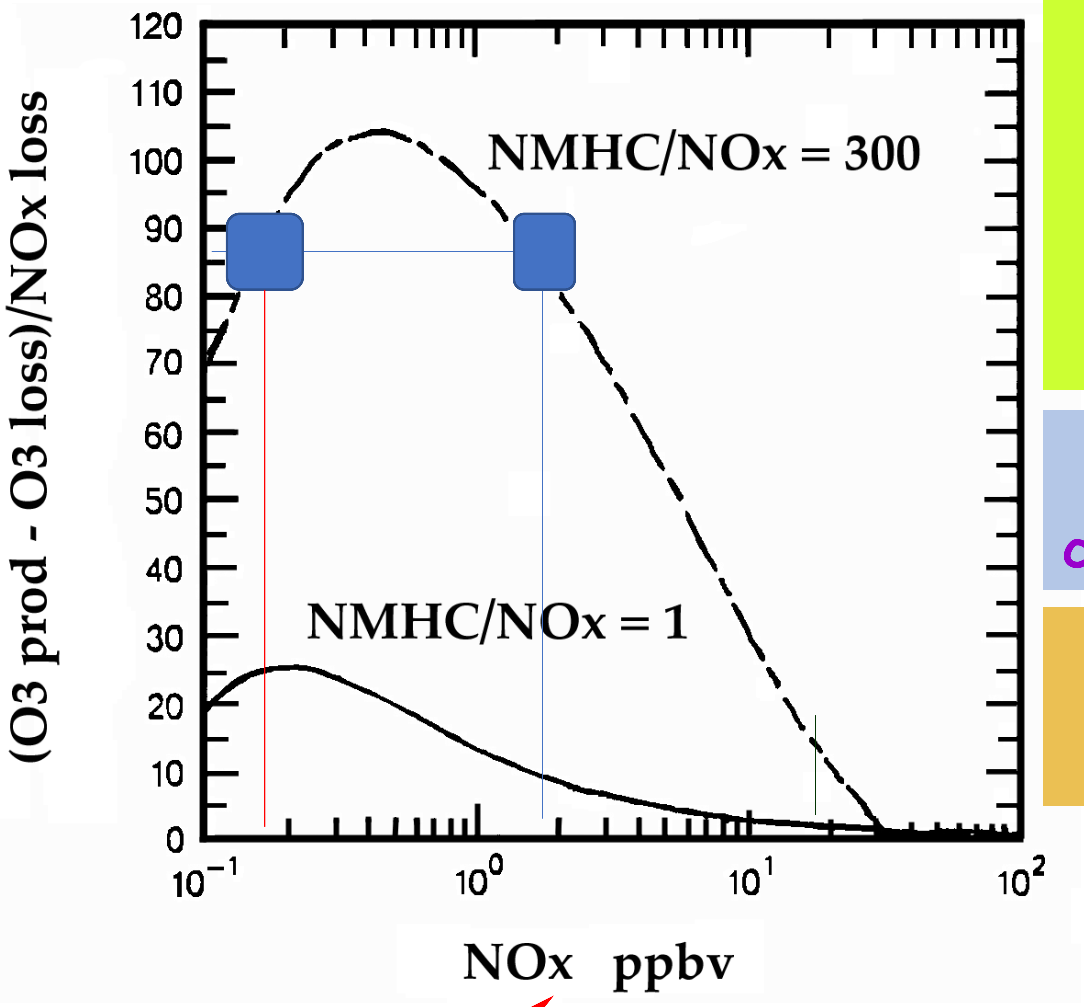
Mechanisms affecting tropospheric Ozone

1. transport from the stratosphere

2. photochemistry in the troposphere

3. deposition

O_3 chemical production in the troposphere – Complexity
Non-linearity in chemical processes



Ageing pollution plume

Requires NO_2

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 \rightarrow O_3$

emissions of NOx occur mainly in the form of NO

$NO + RO_2^{\cdot} \rightarrow NO_2 + RO^{\cdot}$

catalytic cycle forming O_3

$NO + O_3 \rightarrow NO_2 + O_2$

Zero catalytic cycle for O_3

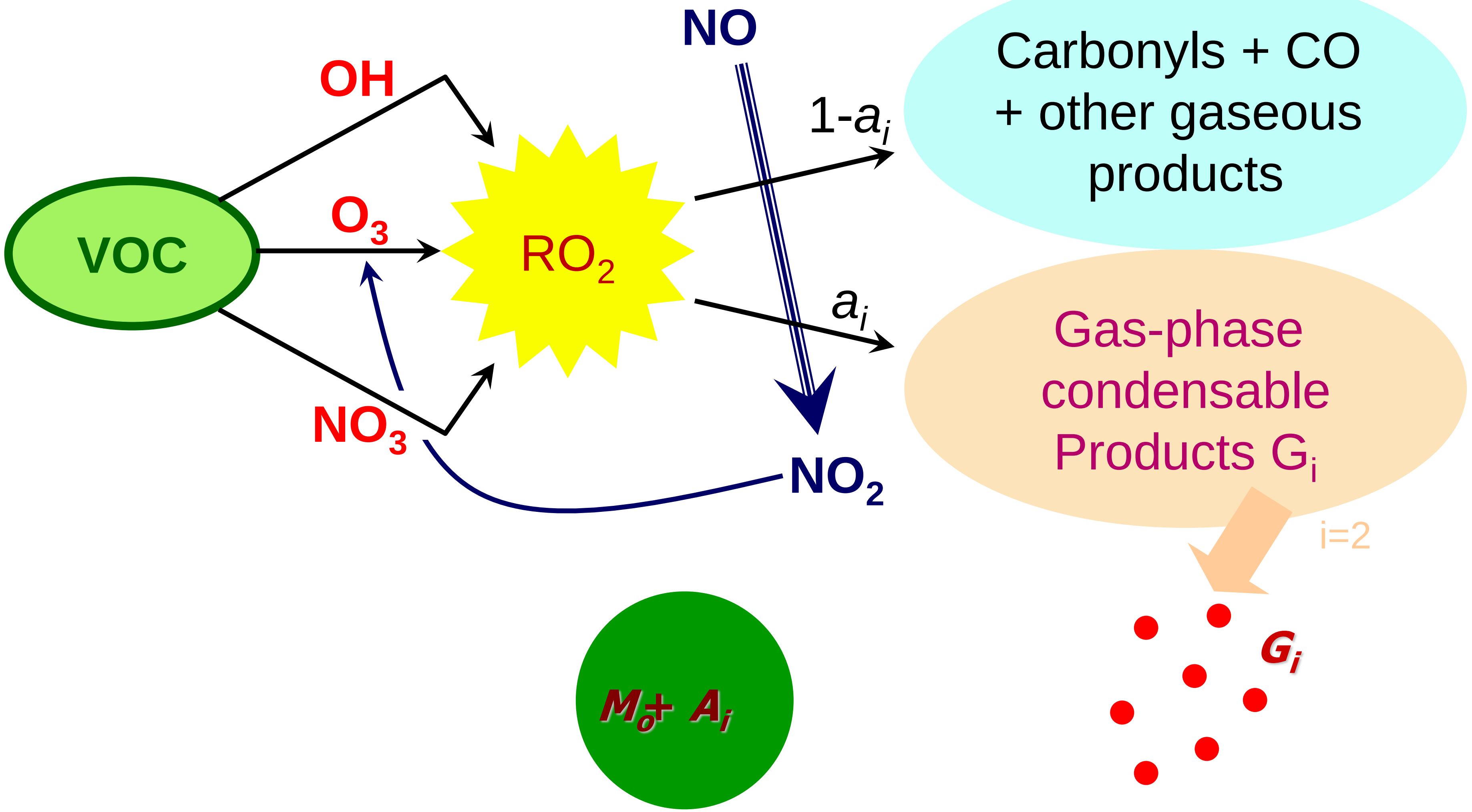
$NO_2 + OH \rightarrow HNO_3$

Termination of catalysis

Acid formation

Calculated O3 production efficiency as a function of the concentration of NOx for NMHC/NOx =1 and for NMHC/NOx=100 (NMHC=non methane hydrocarbon). Lin et al. JGR. 1988.

Where RO_2 come from ? CO & VOC oxidation chemistry



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Where RO_2 come from ? CO & VOC oxidation chemistry

VOC + oxidant + NOx → **O_3 + aerosols + …**

CO + oxidant + NOx → **O_3 + CO_2**

VOC (except CH_4) is 90% natural

CO is 50% anthropogenic

NOx is 75% anthropogenic

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Dependence of O_3 formation on the ratio of VOC/NOx

(1) VOC + OH $\rightarrow$ RO_2 $\rightarrow$ -$\rightarrow$ O_3
(2) NO_2 + OH $\rightarrow$ HNO_3

Ratio of reaction rates (1)/(2) is proportional to VOC/NOx

NOx $\uparrow$ $\rightarrow$ VOC/NOx $\downarrow$ $\rightarrow$ O_3 $\downarrow$

NOx $\downarrow$ $\rightarrow$ VOC/NOx $\uparrow$ $\rightarrow$ O_3 $\uparrow$

city versus suburbs

Downtown : high NOx & HNO_3

Downwind : high O_3

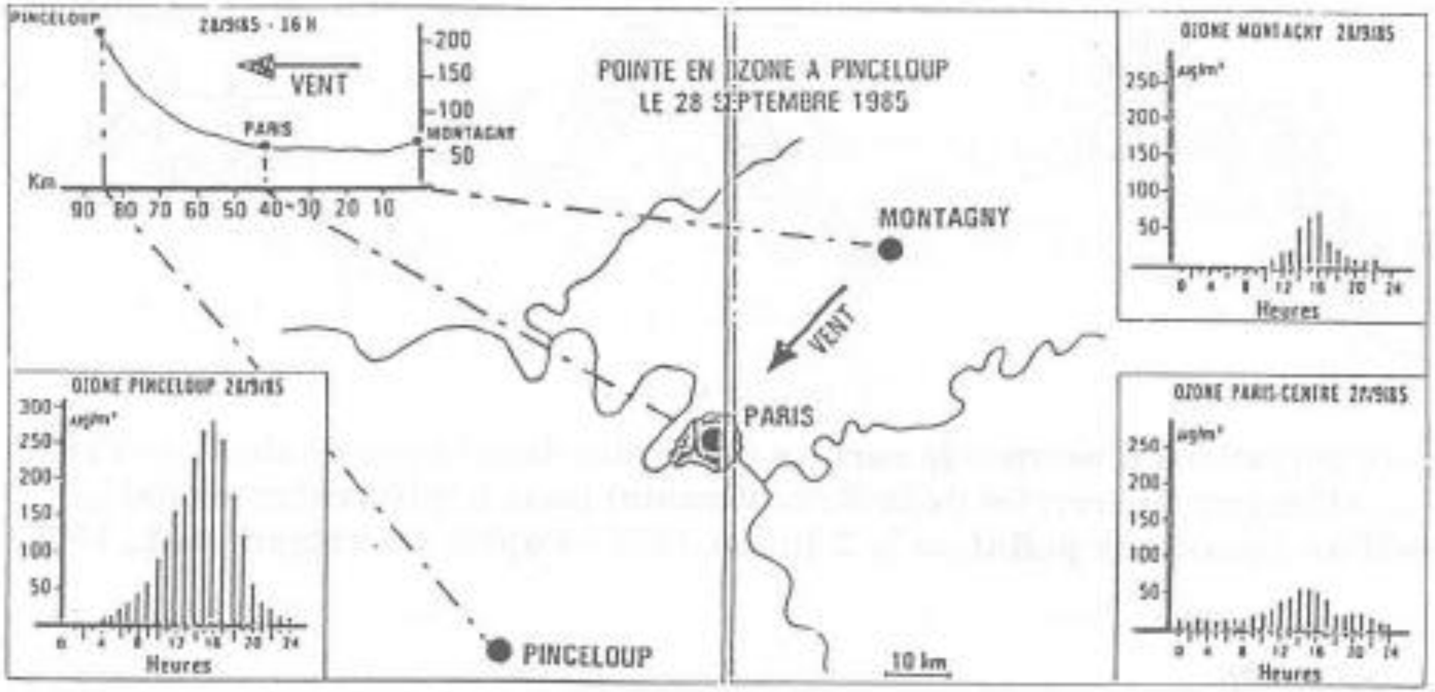
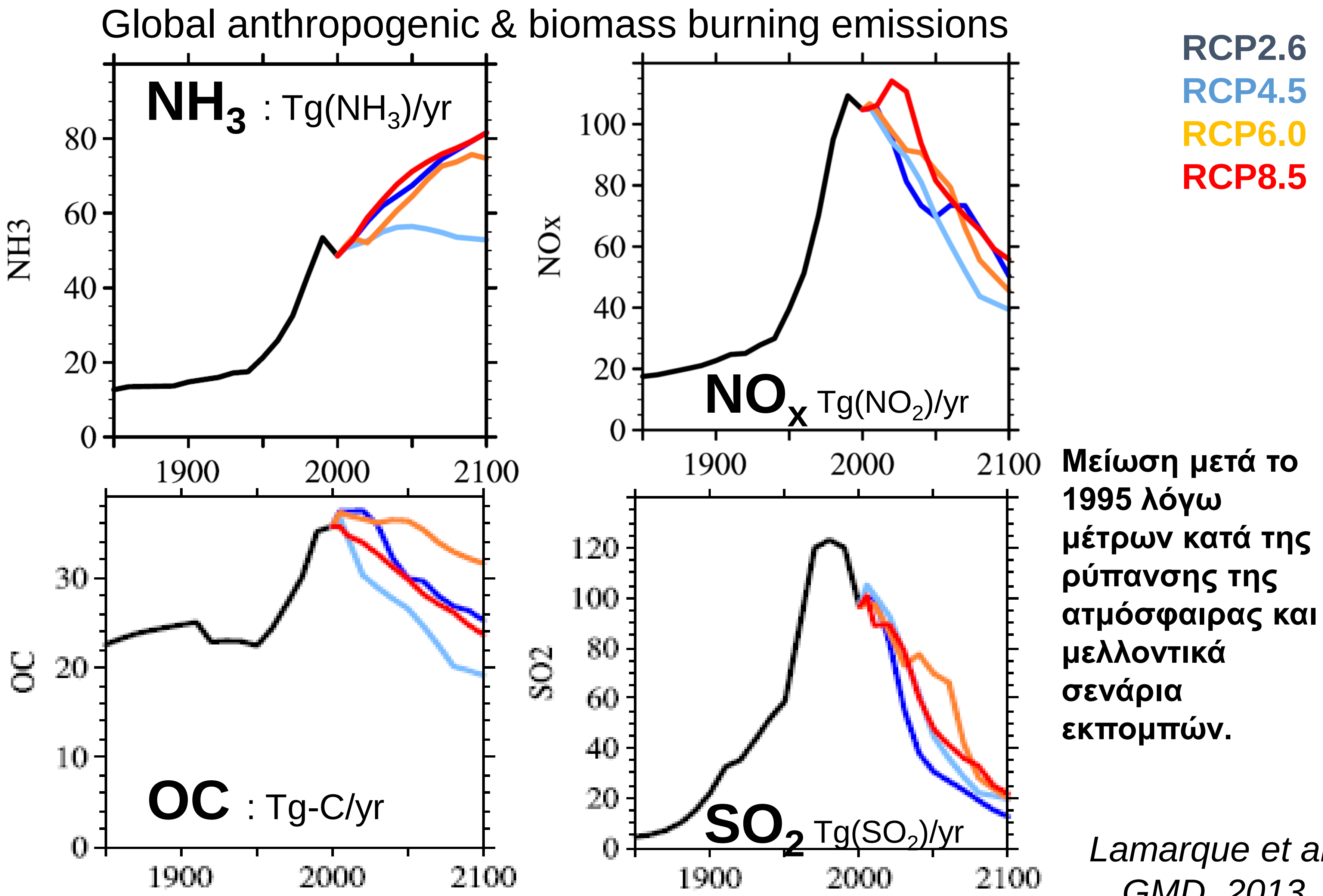


Figure V-8
Concentrations d'ozone à la surface (en $\mu g.m^{-3}$, 100 $\mu g.m^{-3}$ = 50 ppbv) observées lors d'un épisode de pollution photochimique en région parisienne (coupe Nord-Est/Sud-Ouest) , le 28 Mai 1985 (d'après Toupance et al., 1986)

Trends:
past ?
Where are we heading ?

Anthropogenic emission changes

what is their impact on atmospheric acidity and nutrients?

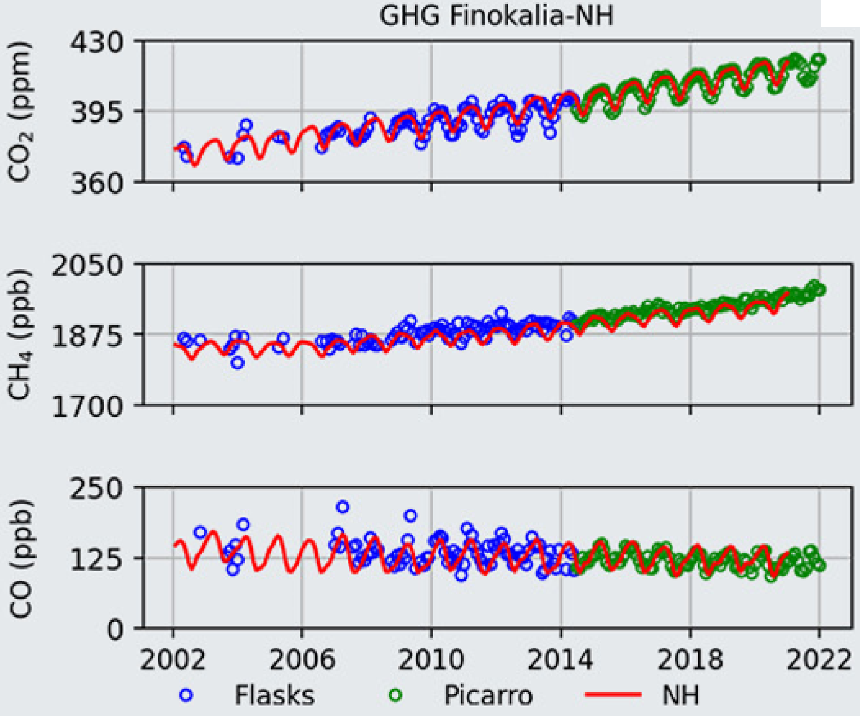


Μείωση μετά το 1995 λόγω μέτρων κατά της ρύπανσης της ατμόσφαιρας και μελλοντικά σενάρια εκπομπών.

Lamarque et al. GMD, 2013

A twenty years record of greenhouse gases in the Eastern Mediterranean

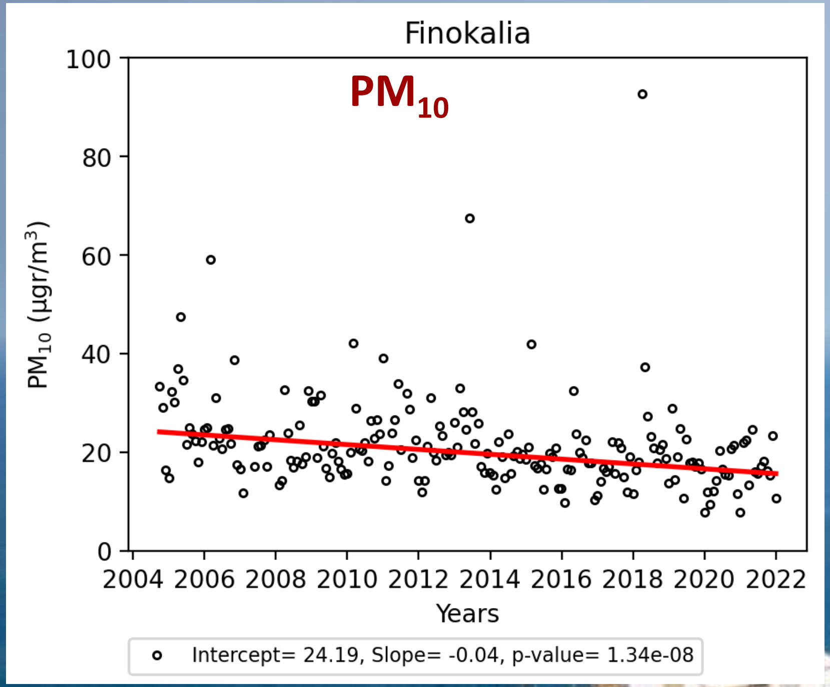
University of Crete

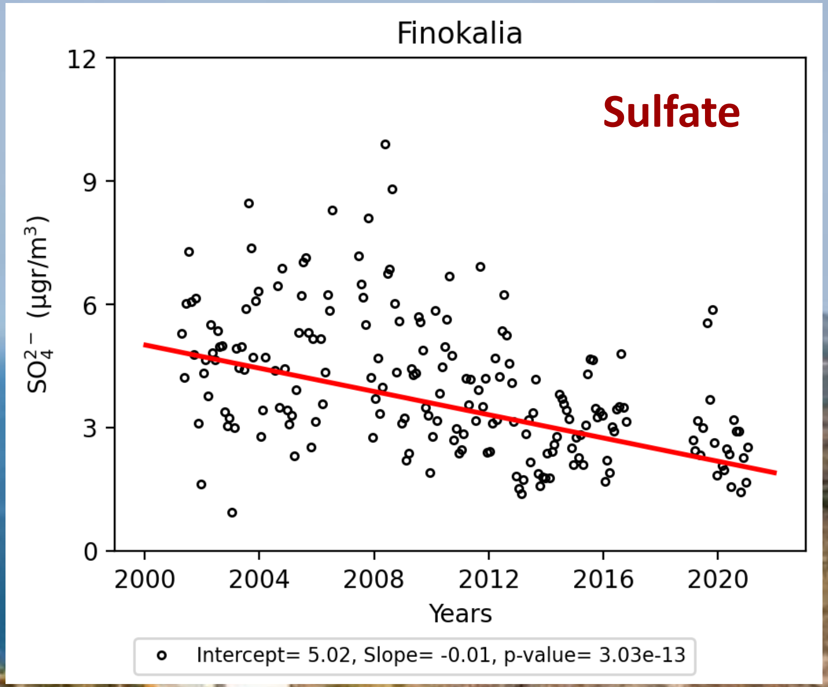


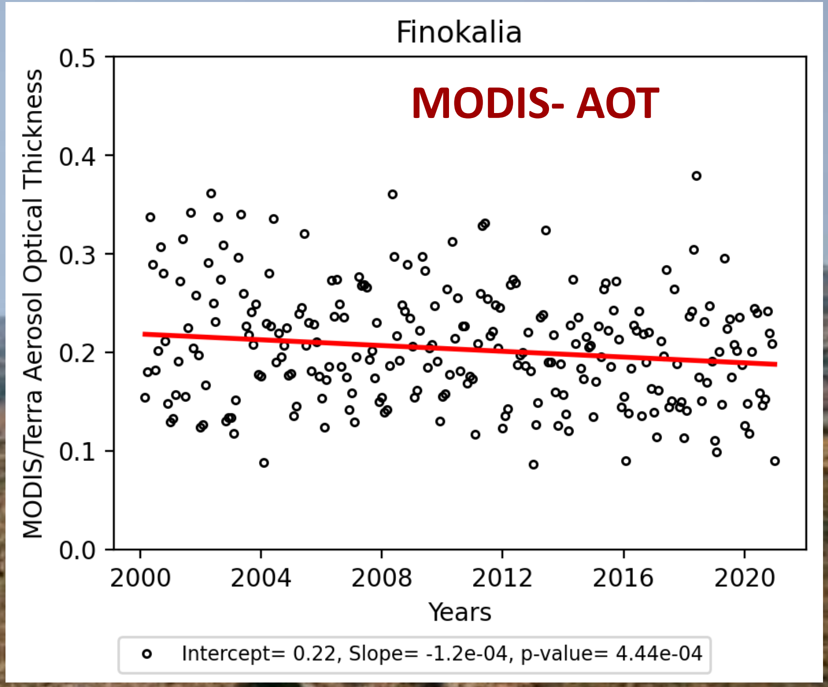
Conclusion: Since 2002, CO_2 and CH_4 concentrations at Finokalia station increased by 2.4 ppm·y^{-1} and 7.5 ppb·y^{-1} respectively, while CO concentrations decreased by 1.6 ppb·y^{-1}. Since 2018, CH_4 increase accelerated (12.4 ppb·y^{-1}).

Gialesakis et al., STOENV 2023

Trends in Aerosols at Finokalia, Crete, Greece & Trends in AOT





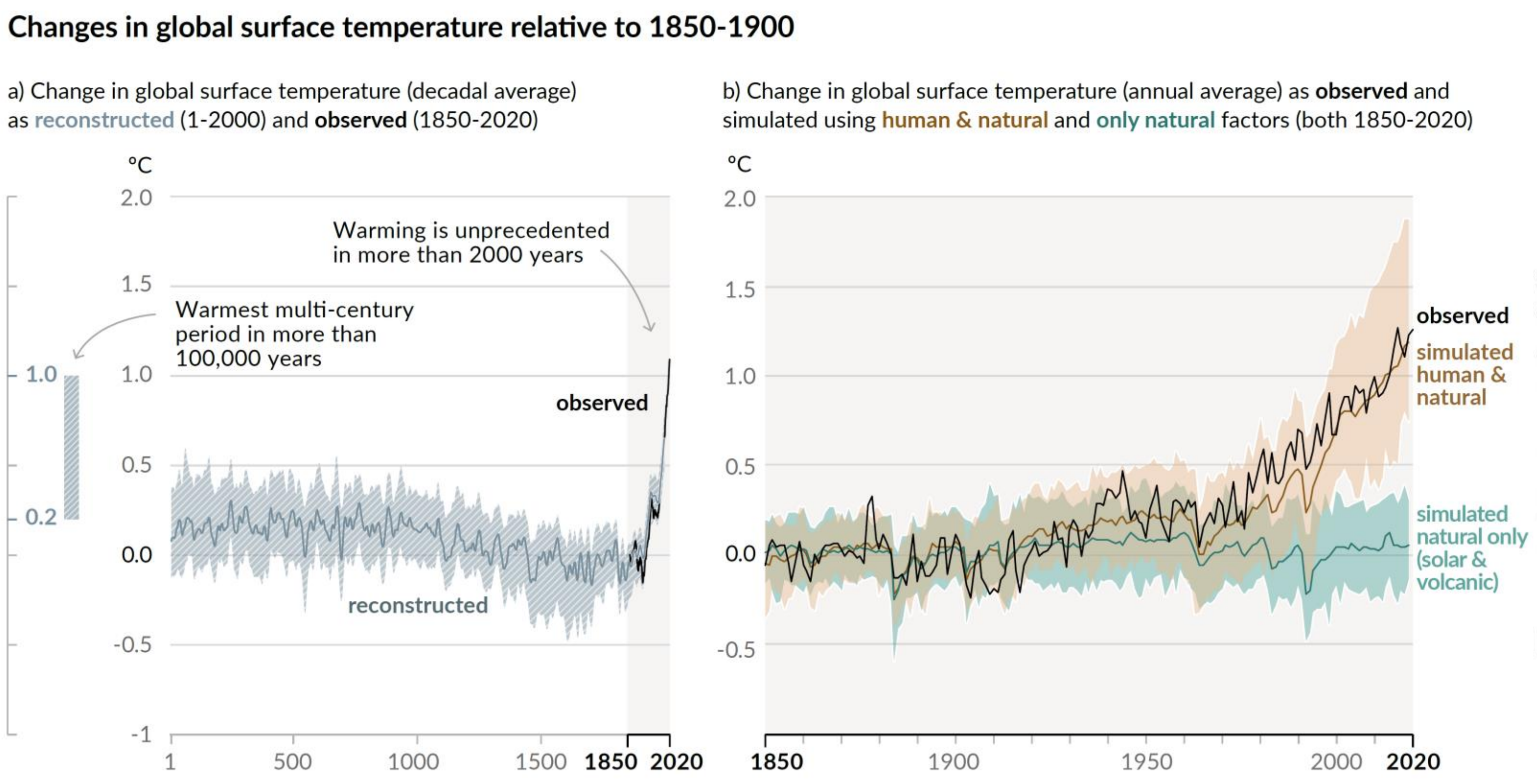


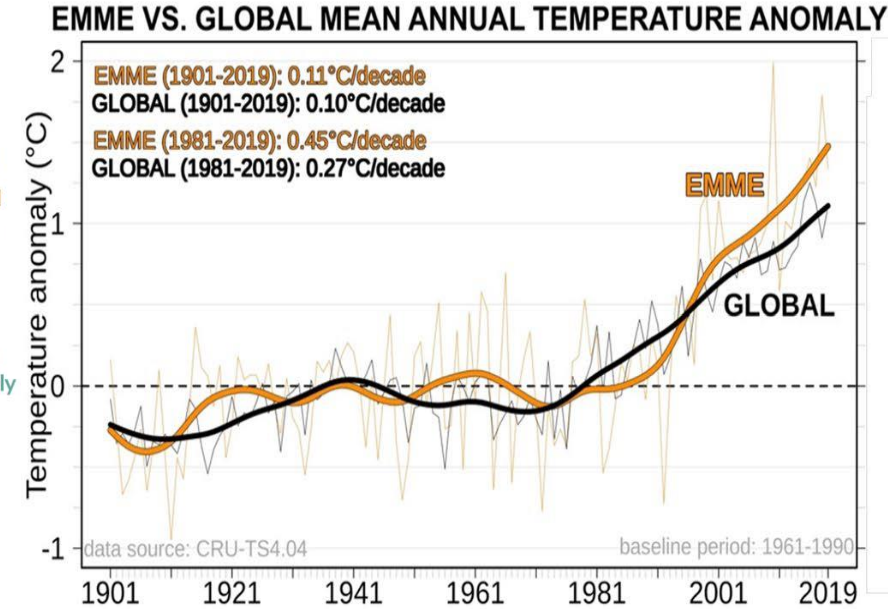
- At the Finokalia station a statistical significant decreasing trend in PM_{10} has been observed that could explain the trend of AOT observed by MODIS (Mann Kendall Trend test)
- The decrease in particulate mass observed is not attributed only to the decrease of dust but also other constituents as sulfate and organic matter.

Kalivitis et al., IAC 2022

Human driven global warming

The Eastern Mediterranean is warming faster than the global mean

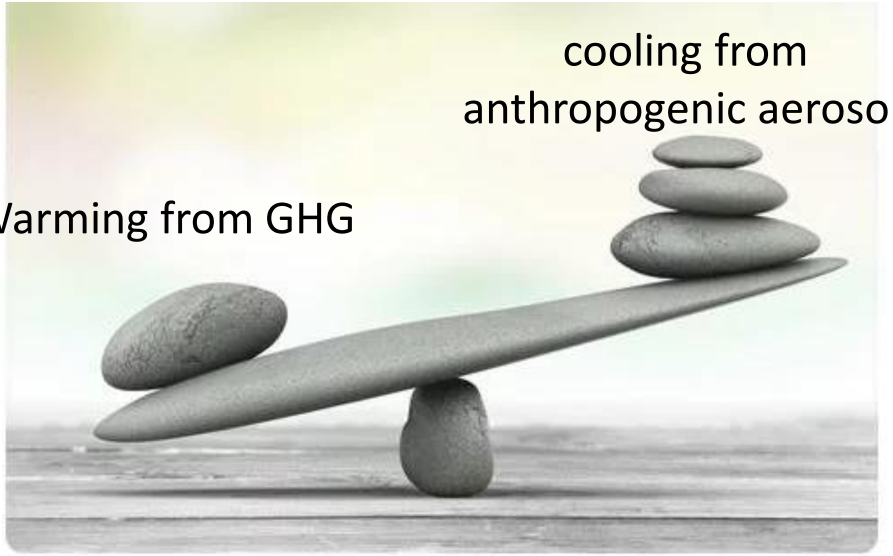


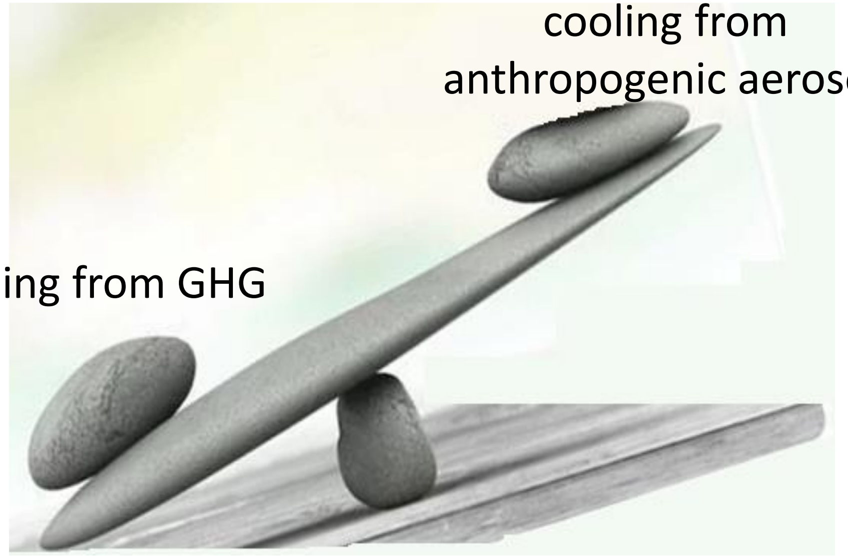


IPCC, 2021

Zittis et al., Reviews of Geophysics, 2021, 10.1029/2021RG000762

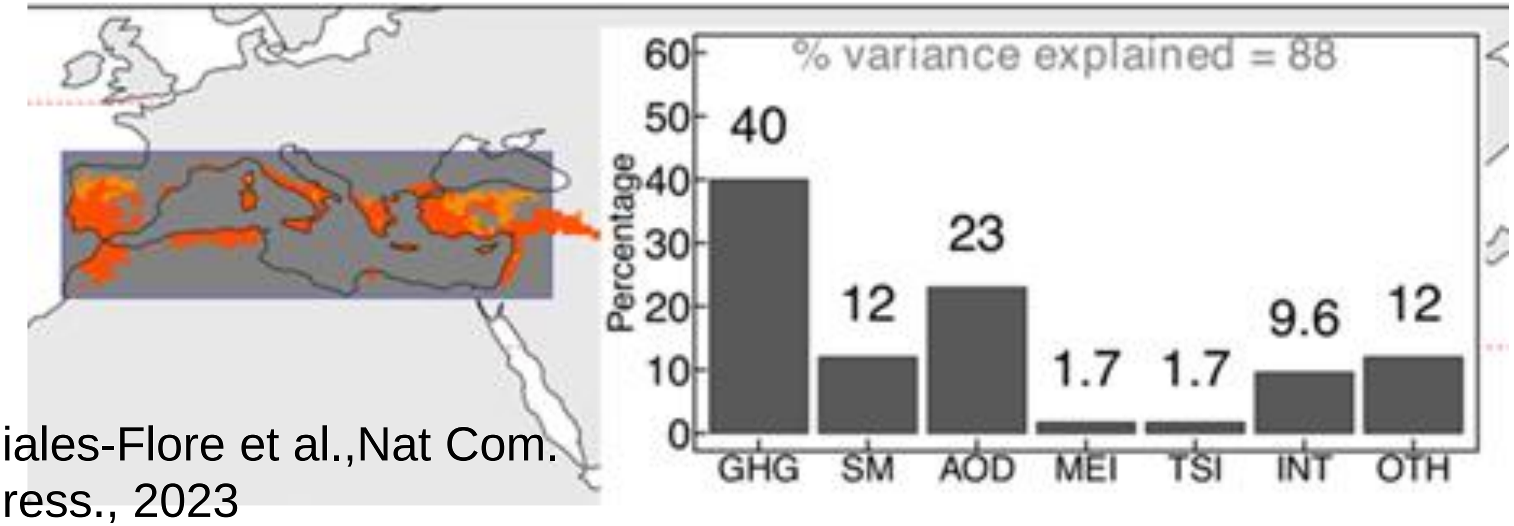
The rapid warming of the Mediterranean: a key role for aerosols?





In the Mediterranean Basin, the recent warming acceleration is largely due to the combined effect of declining **aerosols** and a negative trend in **soil moisture**.

Red: dry summer climate & hot summers; Orange: warm summer for 1981-2020



Urdiales-Flore et al.,Nat Com. in press., 2023

Take home messages

- ✓ The development of human civilization with increasing population and **needs for energy, food and comfort** led to the production of numerous air pollutants as products, or-by products of energy production and industrial activities.

- ✓ **Greenhouse gases** are a major category with impacts on climate and ecosystem development, **short-lived pollutants** like aerosols, are another important category of air pollutants with multiple impacts on **climate, and human and ecosystem health.**

- ✓ **Non-linear relationships** imply careful design of measures for AQ mitigation.

- ✓ In the **Anthropocene era** we live, all these pollutants have a large fraction of their sources associated to **energy production and use, and transportation.**

- ✓ **Observed trends** of air pollutant levels show that clean air quality has been efficient in limiting air pollution by short-lived species, with mean atmospheric lifetimes of less than a year.

- ✓ For greenhouse gases that have **long lifetimes** in the atmosphere, i.e. decades or centuries are required to reduce their atmospheric levels, **immediate action** is needed to support future sustainability.

- ✓ **Targeting Carbon-free economical growth** will contribute in mitigating air pollution by reducing these air pollutants and their undesirable effects. Renewable energies, new technologies and change in life-style is the way forward.

University of Bremen

University of Crete

Thank you for your attention

Ευχαριστώ για τη προσοχή σας

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https://finokalia.chemistry.uoc.gr