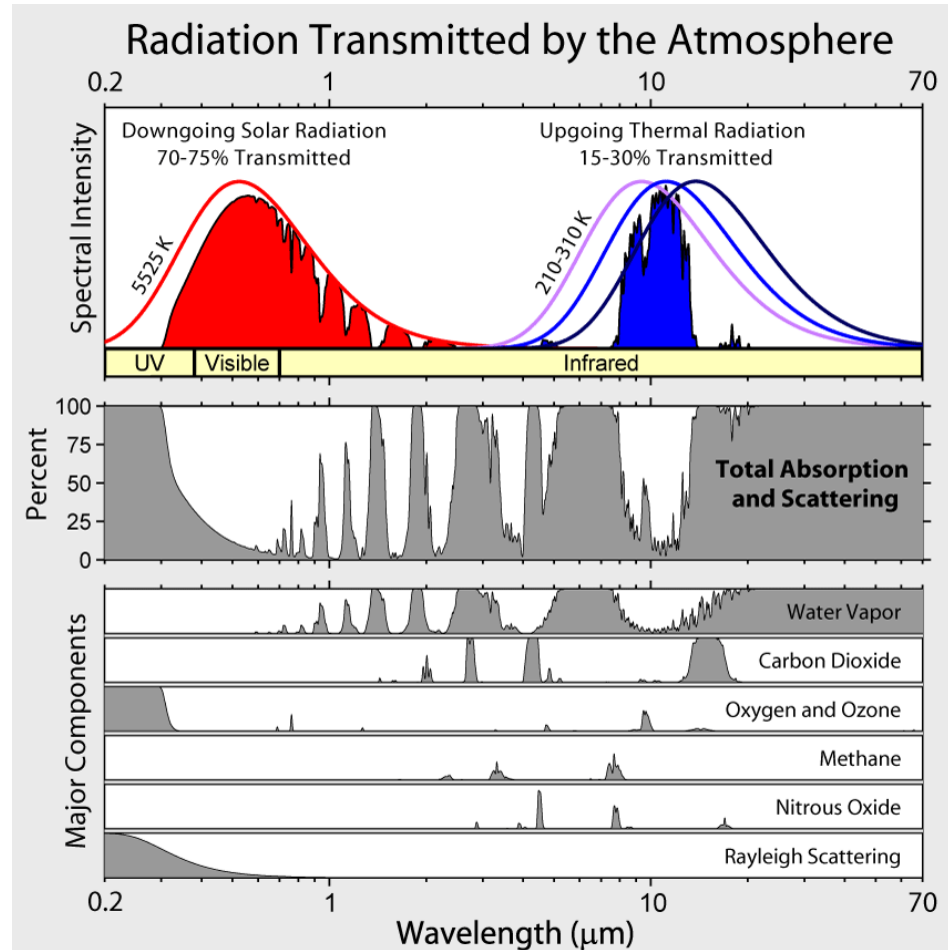


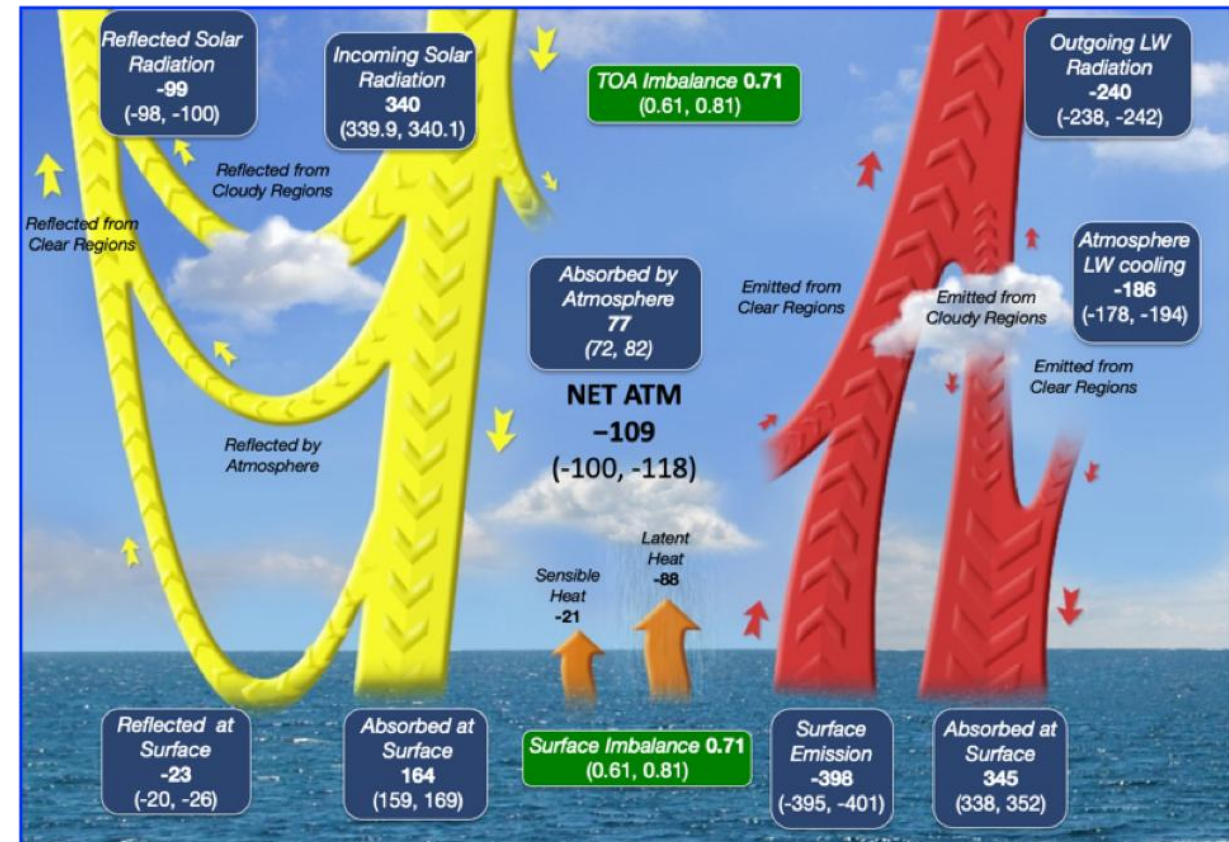
# Take home messages from previous lecture

- Check out: <https://ceres.larc.nasa.gov/science/>
- What are atmospheric windows?
- What are key properties of greenhouse gases?
- The warming and cooling effects of clouds and aerosols.
- Unit optical depth as key parameter for temperature profile retrieval.
- Top of atmosphere radiation balance.
- Radiative forcing and the challenge of climate science.

# Recap previous lecture



Atmospheric windows (shortwave, longwave)



Earth's radiation balance, net atmospheric heat loss, sensible and latent heat flux re-create the equilibrium

[responseware.eu](http://responseware.eu)

env320

# Overview on 2nd half of the course: Atmospheric Chemistry

- Atmospheric composition
  - Geochemical cycles, concept of lifetime
- Stratospheric chemistry
  - Ozone chemistry
- Tropospheric chemistry
  - Main oxidants and pollutants
- Aerosols
  - Microphysics and chemistry
- Clouds
  - Aerosol-cloud interactions

A dramatic industrial scene at sunset. Several tall, dark smokestacks are silhouetted against a bright, orange, and red sky. Thick plumes of dark smoke are rising from the stacks, drifting into the sky. The sun is a bright, glowing orb positioned centrally behind the stacks, creating a strong lens flare and illuminating the clouds with a fiery orange light. The overall atmosphere is one of intense industrial activity and environmental impact.

# Atmospheric composition



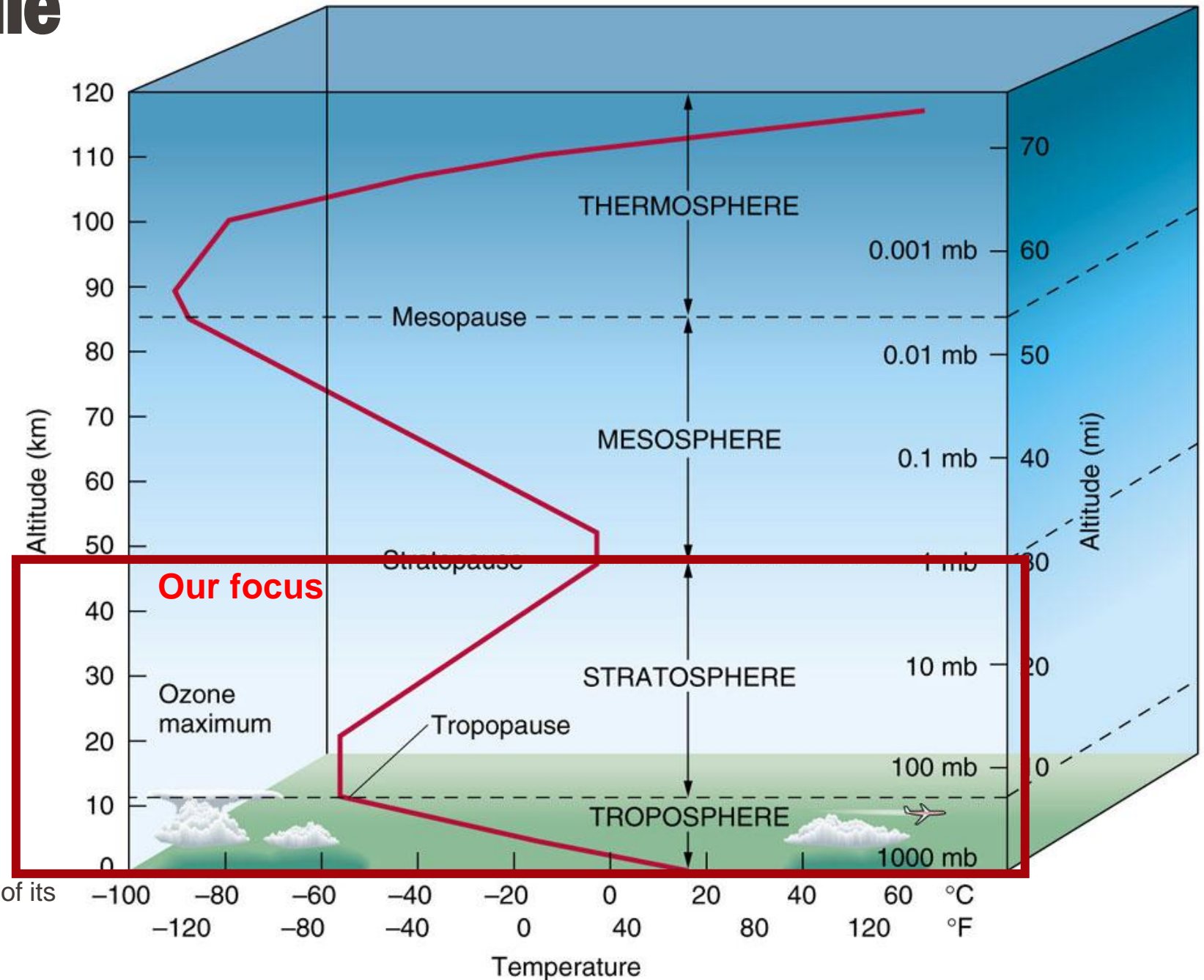
The vertical temperature profile provides basis for dividing the atmosphere into four layers:

- *Troposphere*: average lapse rate of  $-6.5\text{ }^{\circ}\text{C km}^{-1}$ .
- *Stratosphere*: dry and ozone-rich; vertical mixing strongly inhibited.
- *Mesosphere*: temperature decreases to a minimum at top
- *Thermosphere*: increase in temperature due to absorption of solar radiation and photodissociation of nitrogen and oxygen molecules (radiation lecture)

We care about the troposphere, because

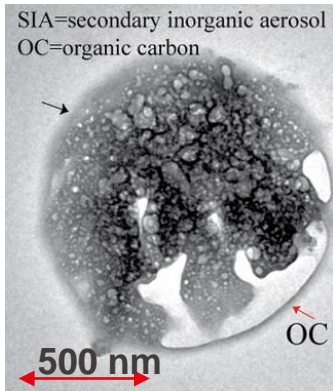
- 85 % of atmospheric mass is in the troposphere,
- most emissions are at the surface.

We care about the stratosphere, because of its role in UV absorption.

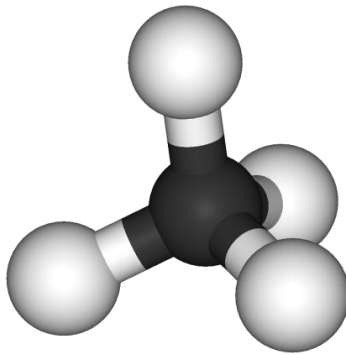


# Atmospheric processes at a glance

## Aerosols



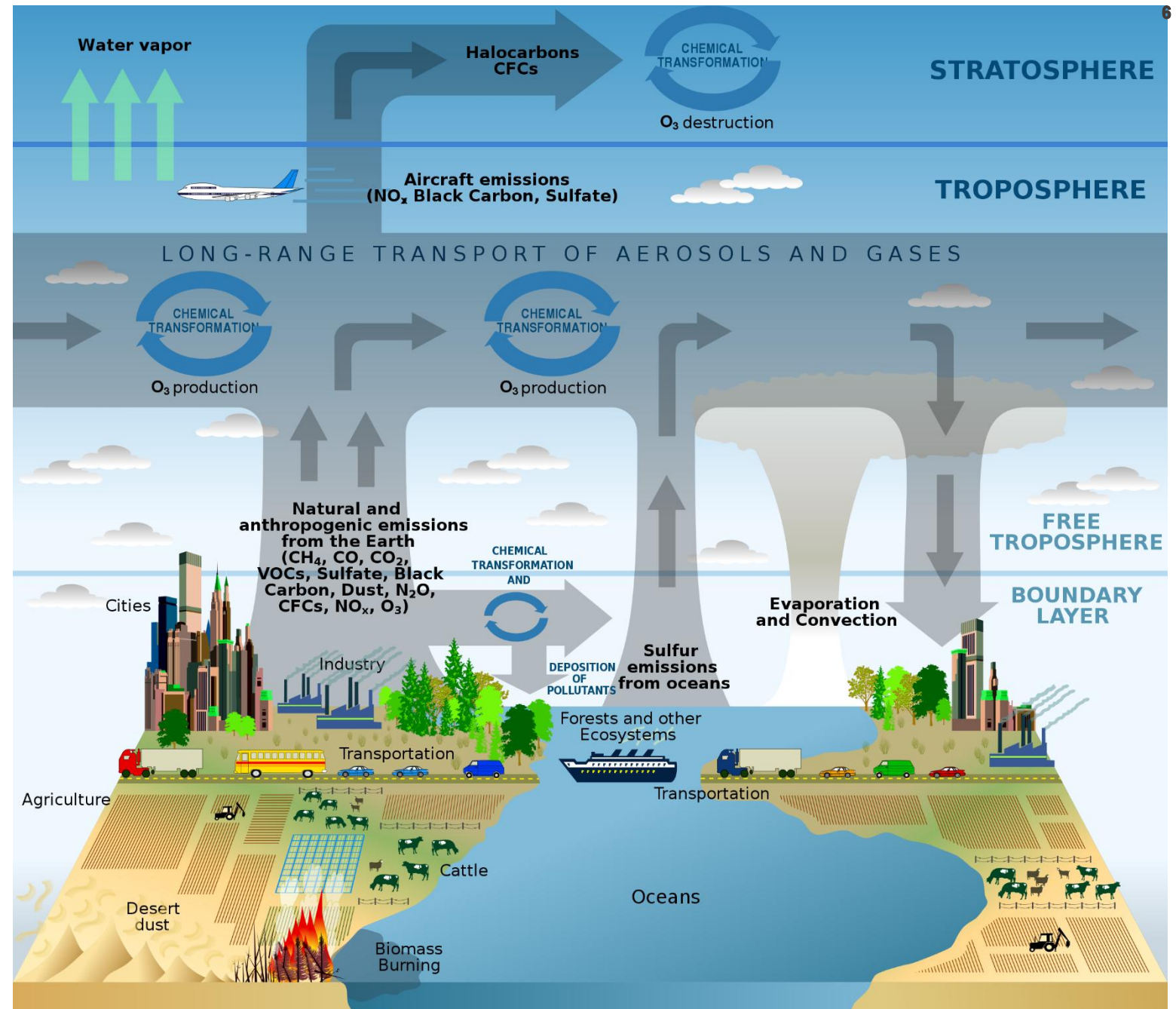
## Gases



## Why study these?

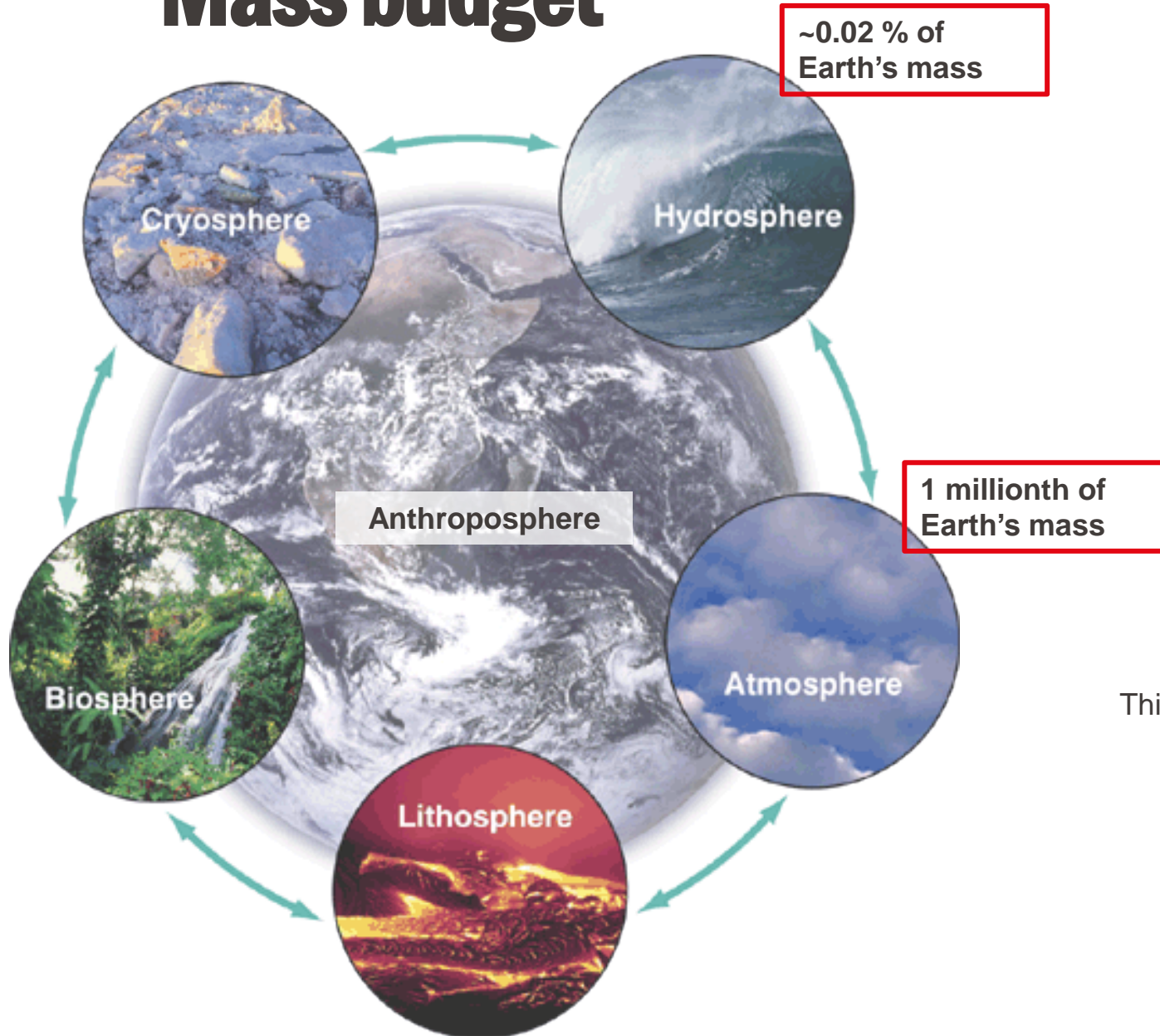
How do our anthropogenic activities influence atmospheric chemical composition and what are the implications?

What is the «natural» or preindustrial state of the atmosphere, which we need to compare against to estimate the impacts?

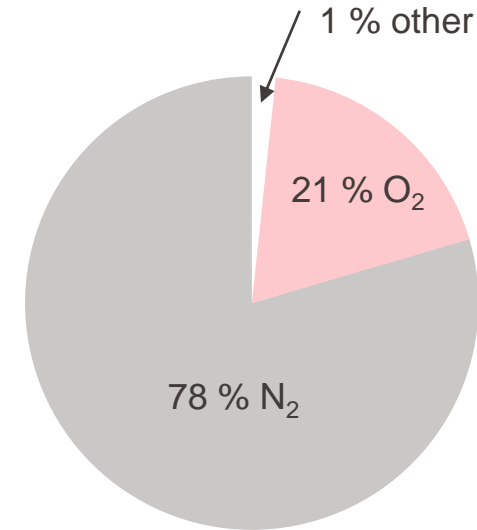




# Mass budget



Dry air composition



This course is about trace compounds (1 % level)!

## Air pollution

7 million premature deaths each year, life quality reduction, cardiovascular & respiratory diseases, mainly PM and ozone

relative global crop losses for soy 6-16%, wheat 7-12% and maize 3-5%, mainly ozone

... and biodiversity – acid rain, eutrophication, and cell damage, mainly sulphur, nitrogen and ozone

shorter term and regional effects, direct interaction with solar radiation, interaction with clouds, overall cooling effect, largest uncertainty of anthropogenic climate forcing

lives, work ability, food production, damage to historical monuments, ecosystems services, (economic damage from air pollution in Europe is close to USD 1.6 trillion)

## Climate Change

increasing allergens, malnutrition, mental health, heat, vector diseases (Malaria in Ticino)

weather extremes (hail), drought, shifting vegetation zones, water resources

coral bleaching, invasive species, loss of wetlands, loss of Arctic tundra, fires...

exacerbation of pollution (enhanced ozone production, fires), combined health effects

climate refugees, work ability, adaptation measures, cost of food and water, ...



Check out: <https://ccacoalition.org/en>



# Implications of emissions to the atmosphere

## Air pollution

7 million premature deaths each year, life quality reduction, cardiovascular & respiratory diseases, mainly PM and ozone

relative global crop losses for soy 6-16%, wheat 7-12% and maize 3-5%, mainly ozone

... and biodiversity – acid rain, cell damage, mainly sulphur

shorter term and regional effects, direct interaction with solar radiation, interaction with clouds, overall cooling effect, largest uncertainty of anthropogenic climate forcing

lives, work ability, food production, damage to historical monuments, ecosystems services, (economic damage from air pollution in Europe is close to USD 1.6 trillion)

## Climate Change

increasing allergens, malnutrition, mental health, heat, vector diseases (Malaria in Ticino)

weather extremes (hail), drought, shifting vegetation zones, water resources

... species, loss of wetlands, ...

exacerbation of pollution (enhanced ozone production, fires), combined health effects

climate refugees, work ability, adaptation measures, cost of food and water, ...

Health

Food

The atmosphere is highly non-linear:  
**Small amounts of trace compounds can have large effects.**



Economy

Check out: <https://ccacoalition.org/en>



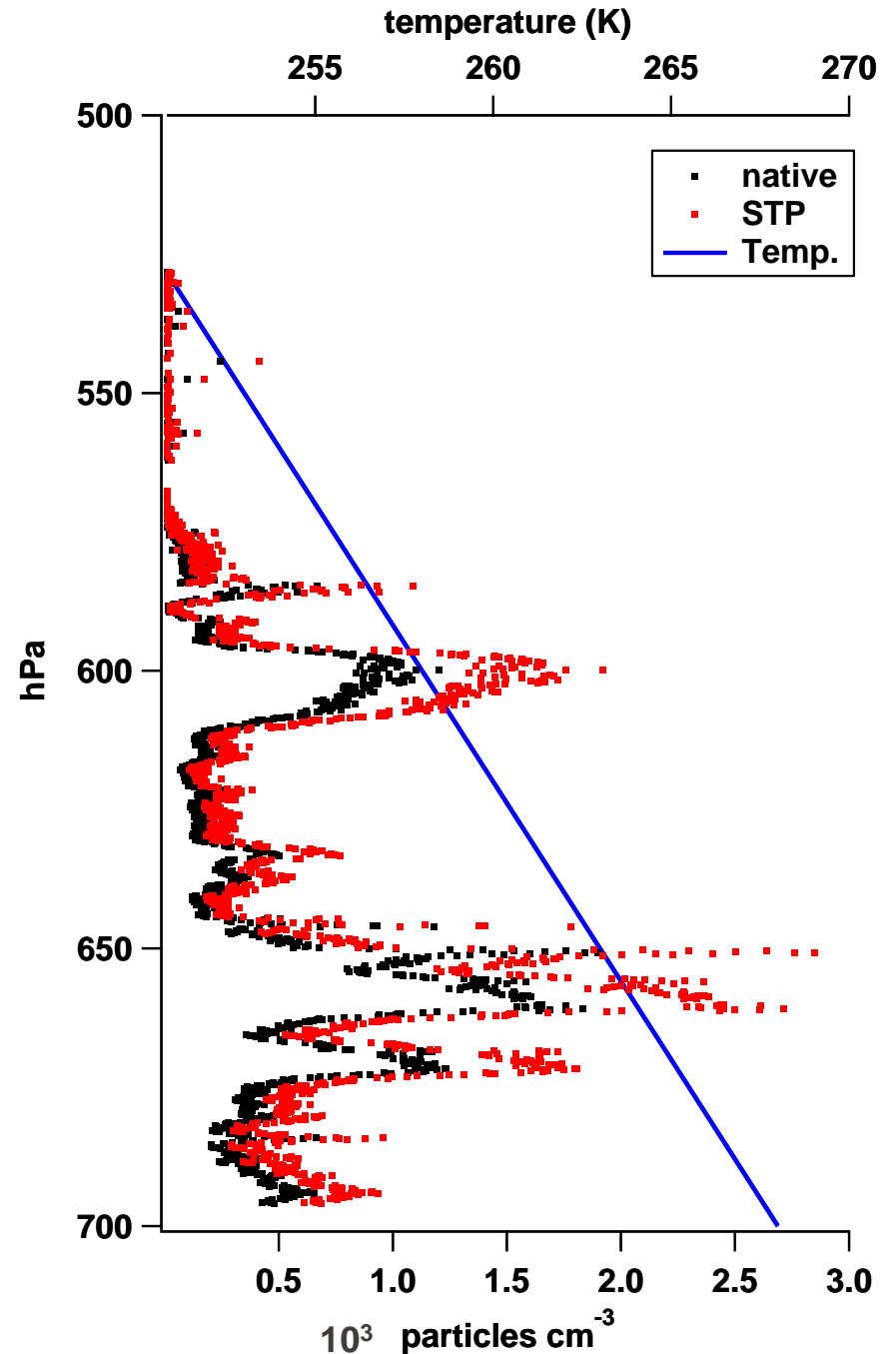
# Units



- Number concentration

- Molecules per volume (molecules / cm<sup>-3</sup>)
- Particles per volume (# / cm<sup>-3</sup>)

**Caveat:** the volume changes with pressure.  
For comparability conversion to  
**standard temperature and pressure (STP)**.  
T = 273.15 K  
P = 1013.25 hPa





Mixing ratios provide a robust measure of atmospheric composition, because they remain constant with changing pressure.

- Partial pressure (ideal gas law)

$$PV = nRT$$

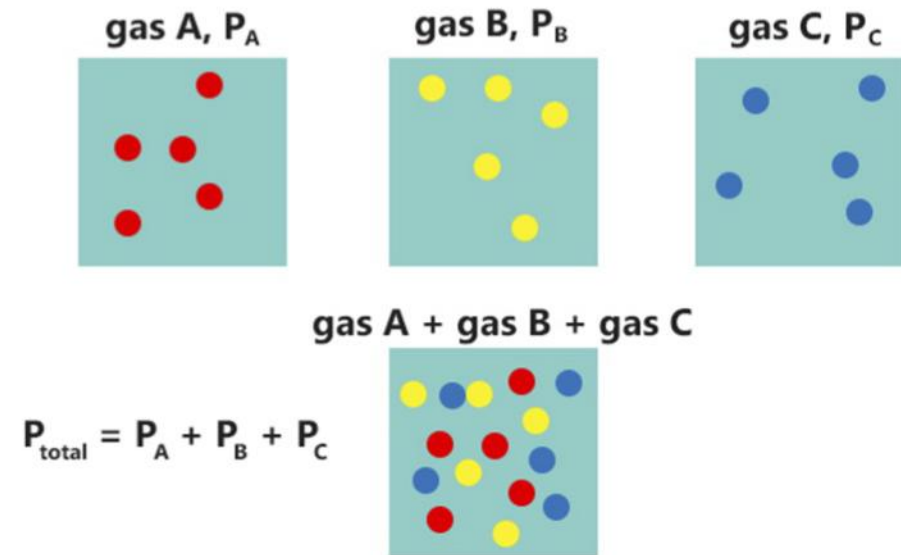
$$x_i = \frac{p_i}{p_{tot}} = \frac{n_i}{n_{tot}} = \frac{V_i}{V_{tot}}$$

$x_i$  mole fraction of gas (species) i

$n_i$  mole number of species i

$p_i$  partial pressure of species i

$V_i$  partial volume of species i



[https://en.wikipedia.org/wiki/Partial\\_pressure#/media/File:Schematic\\_Depicting\\_Dalton's\\_Law.jpg](https://en.wikipedia.org/wiki/Partial_pressure#/media/File:Schematic_Depicting_Dalton's_Law.jpg)

## ■ Partial pressure (ideal gas law)

$$PV = nRT$$

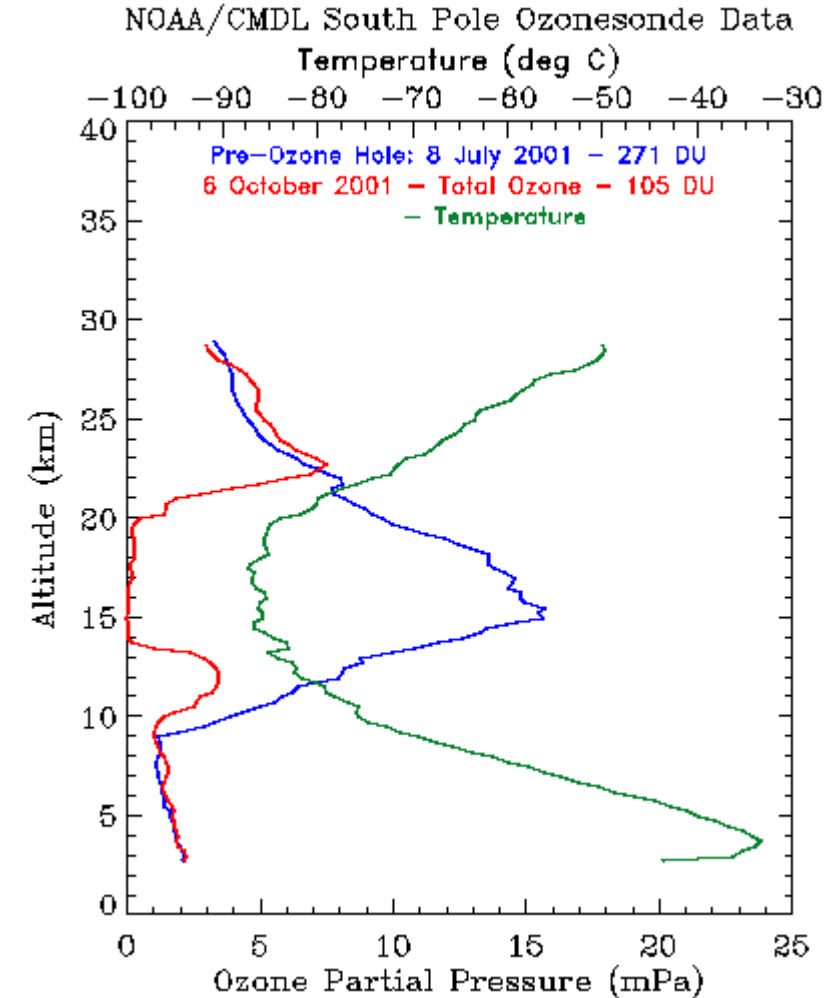
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$n_i$  mole number of species i

$p_i$  partial pressure of species i

$V_i$  partial volume of species i



<https://serc.carleton.edu/download/images/776/OzoneVertProfile.gif>

## ■ mixing ratios (dimensionless)

- Molar mixing ratio  $r_i$

$$r_i = \frac{n_i}{n_{air}}$$

- Volume mixing ratio

$$VMR = \frac{V_i}{V_{air}}$$

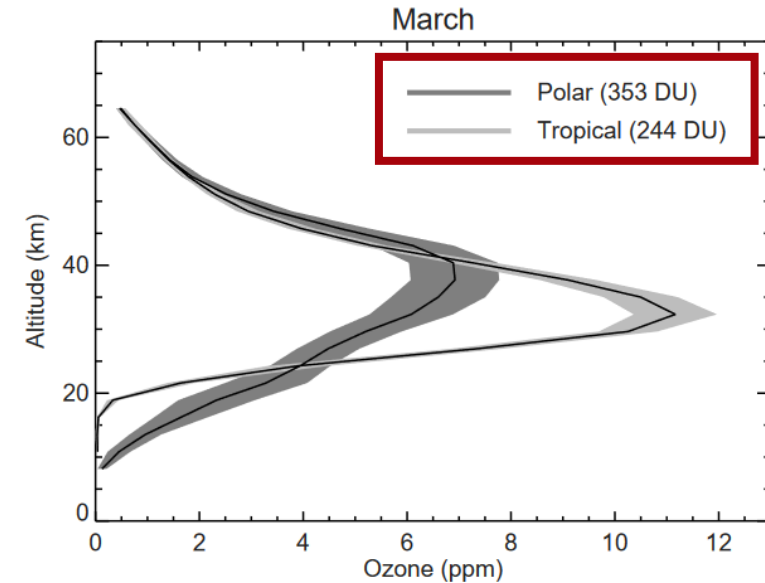
- Mass mixing ratio

$$MMR = \frac{M_i}{M_{air}}$$

parts per million ppm (ppmv, ppmm)

parts per billion ppb

parts per trillion ppt

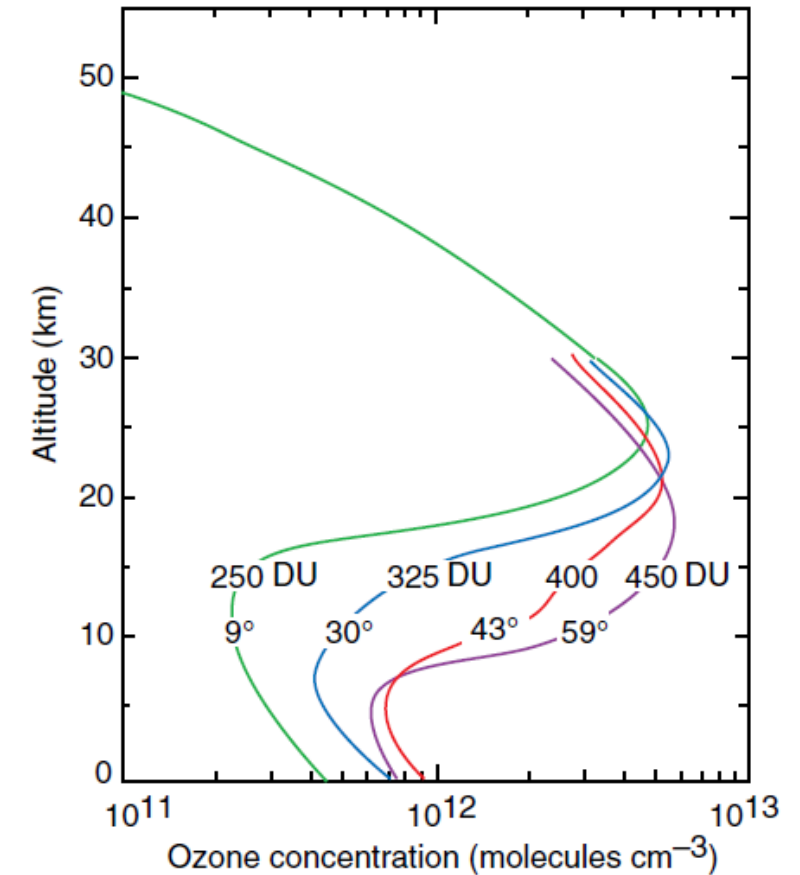


**Figure 1.6:** The vertical profile of ozone mixing ratio against altitude for polar (equivalent latitude 72.5°N) and tropical (equivalent latitude 2.5°N) conditions in March. The ozone data are from the climatology of Grooß and Russell (2005).

[https://www.researchgate.net/publication/48693158\\_Tracer-tracer\\_Relations\\_as\\_a\\_Tool\\_for\\_Research\\_on\\_Polar\\_Ozone\\_Loss](https://www.researchgate.net/publication/48693158_Tracer-tracer_Relations_as_a_Tool_for_Research_on_Polar_Ozone_Loss)



- Amount of gas per vertical column, commonly used for ozone
- Definition: thickness (in 10  $\mu\text{m}$ ) of layer that a gas throughout the entire column would form at STP.
  - 250 DU:  $250 * 10 \mu\text{m} = 2.5 \text{ mm}$
  - $1 \text{ DU} = 2.687 \times 10^{20} \text{ (molecules m}^{-2}\text{)}$
  - Ozone hole:  $< 220 \text{ DU}$



**Fig. 5.16** Mean vertical distributions of ozone concentrations based on measurements at different latitudes (given in degrees). Note the increase in the total ozone column abundance (given in DU) with increasing latitude. [Adapted from G. Brasseur and S. Solomon, *Aeronomy of the Middle Atmosphere*, D. Reidel Pub. Co., 1984, Fig. 5.7, p. 215. Copyright 1984 D. Reidel Pub. Co., with kind permission of Springer Science and Business Media.]

## ■ Particulate matter (PM)

- $\leq 10 \mu\text{m}$ :  $\text{PM}_{10}$
- $\leq 2.5 \mu\text{m}$ :  $\text{PM}_{2.5}$

## ■ Swiss standard

- $\text{PM}_{2.5}$  :  $10 \mu\text{g m}^{-3}$  (annual mean),  
 $25 \mu\text{g m}^{-3}$  (daily mean)
- $\text{PM}_{10}$  :  $20 \mu\text{g m}^{-3}$  (annual mean),  
 $50 \mu\text{g m}^{-3}$  (daily mean)

## ■ Ozone

### CH:

- $< 100 \mu\text{g m}^{-3}$  (98 % of  $\frac{1}{2}$  -h averages in one month)
- $120 \mu\text{g m}^{-3}$  hourly average, only to be surpassed once per year

### USA

- $0.070 \text{ ppm}$  (8-hour average)

## ■ Emission Rates

- Tg / year  
or similar units

1 billion t / year

$10^9$  t / year

1 t =  $10^6$  g

$10^6 * 10^9$  g / year =  $10^3$  Tg/y

Mega:  $10^6$

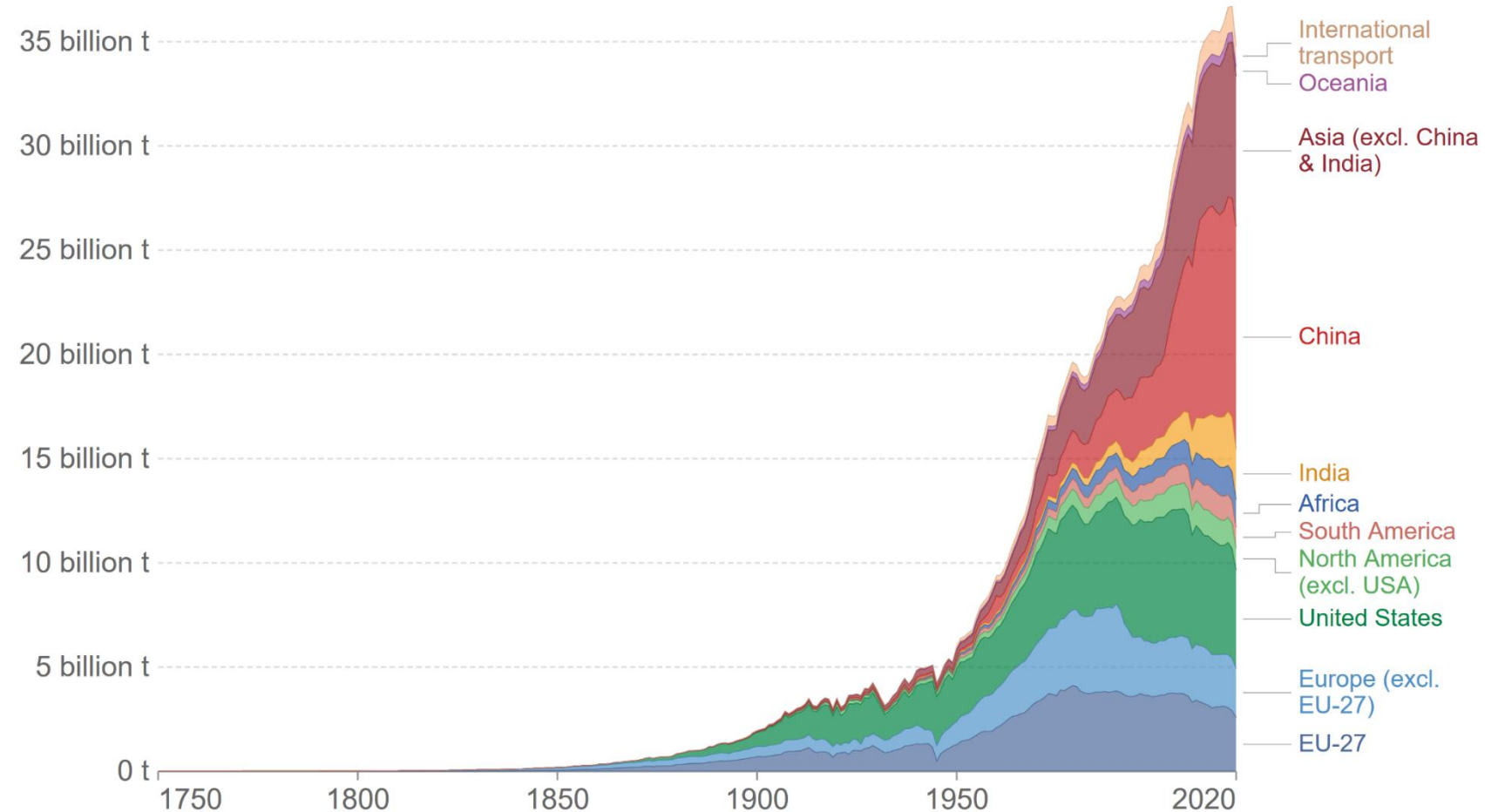
Giga (G):  $10^9$

Tera (T):  $10^{12}$

Peta (P):  $10^{15}$

Annual CO<sub>2</sub> emissions from fossil fuels, by world region

Our World  
in Data



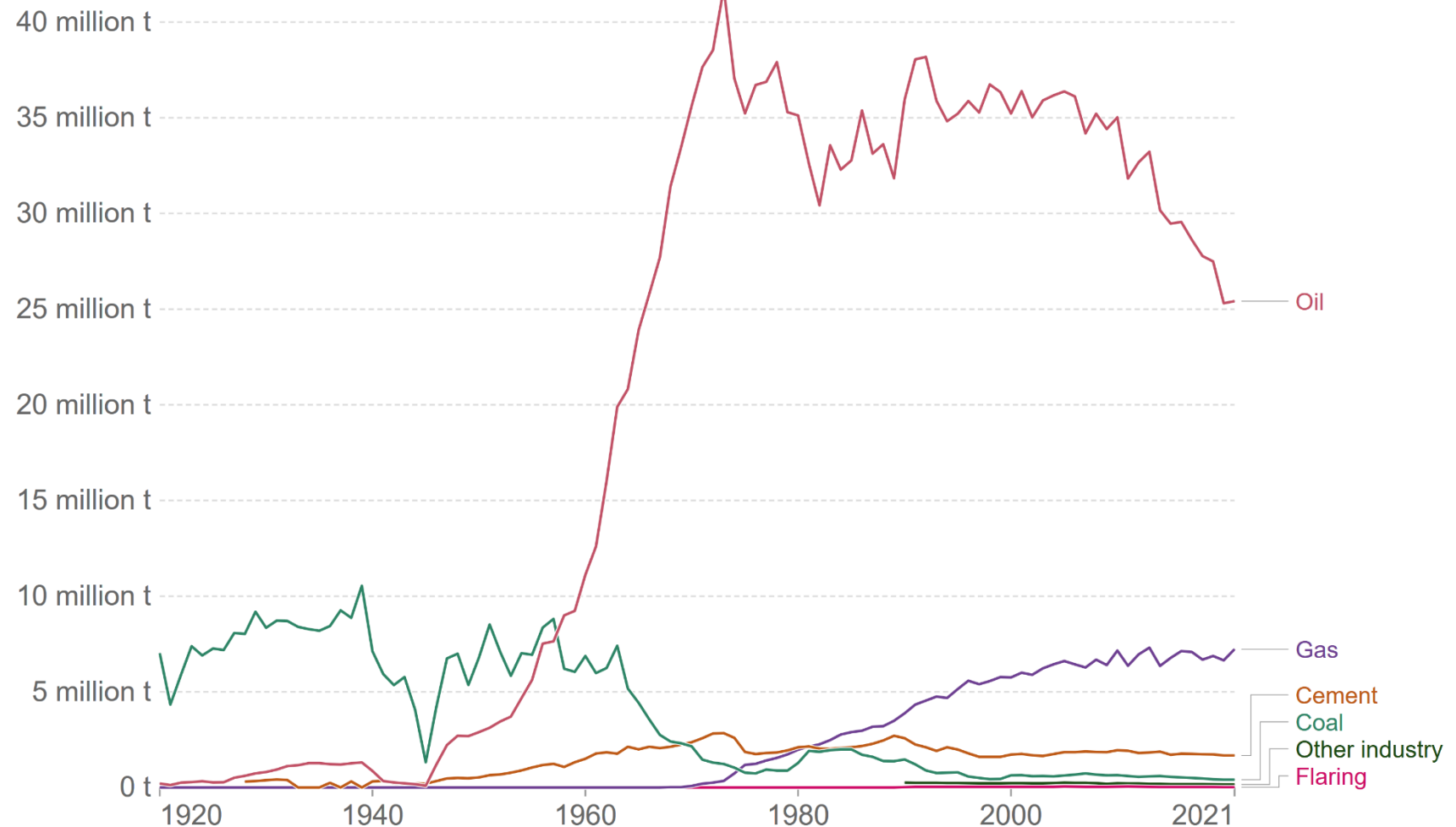
Source: Global Carbon Project

Note: This measures CO<sub>2</sub> emissions from fossil fuels and cement production only – land use change is not included. 'Statistical differences' (included in the GCP dataset) are not included here.

OurWorldInData.org/co2-and-other-greenhouse-gas-emissions • CC BY



## CO<sub>2</sub> emissions by fuel or industry, Switzerland

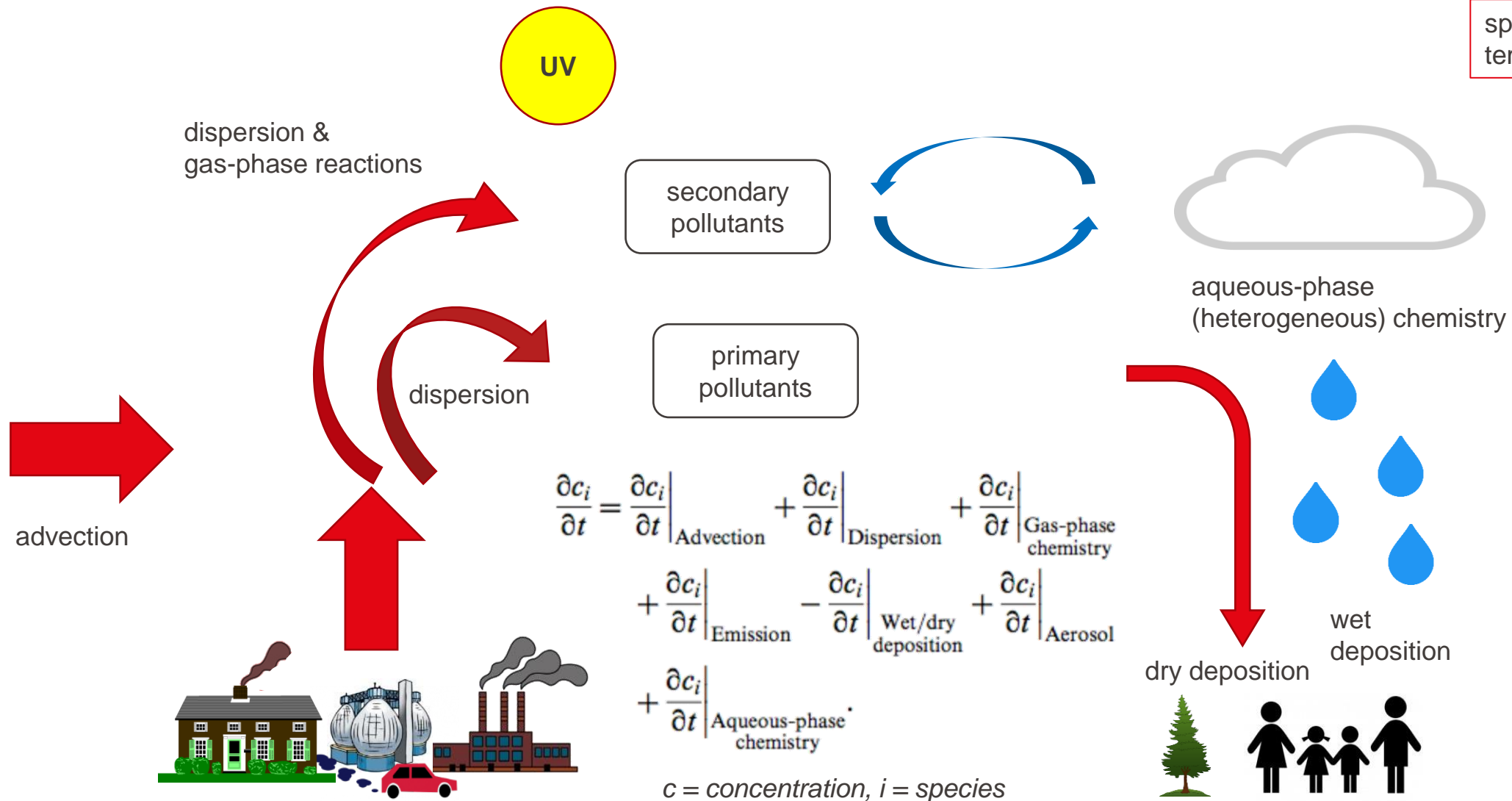
Our World  
in Data

Europe total 5 billion tons  
Switzerland total: ~0.05  
billion tons

# Main compounds and oxidants



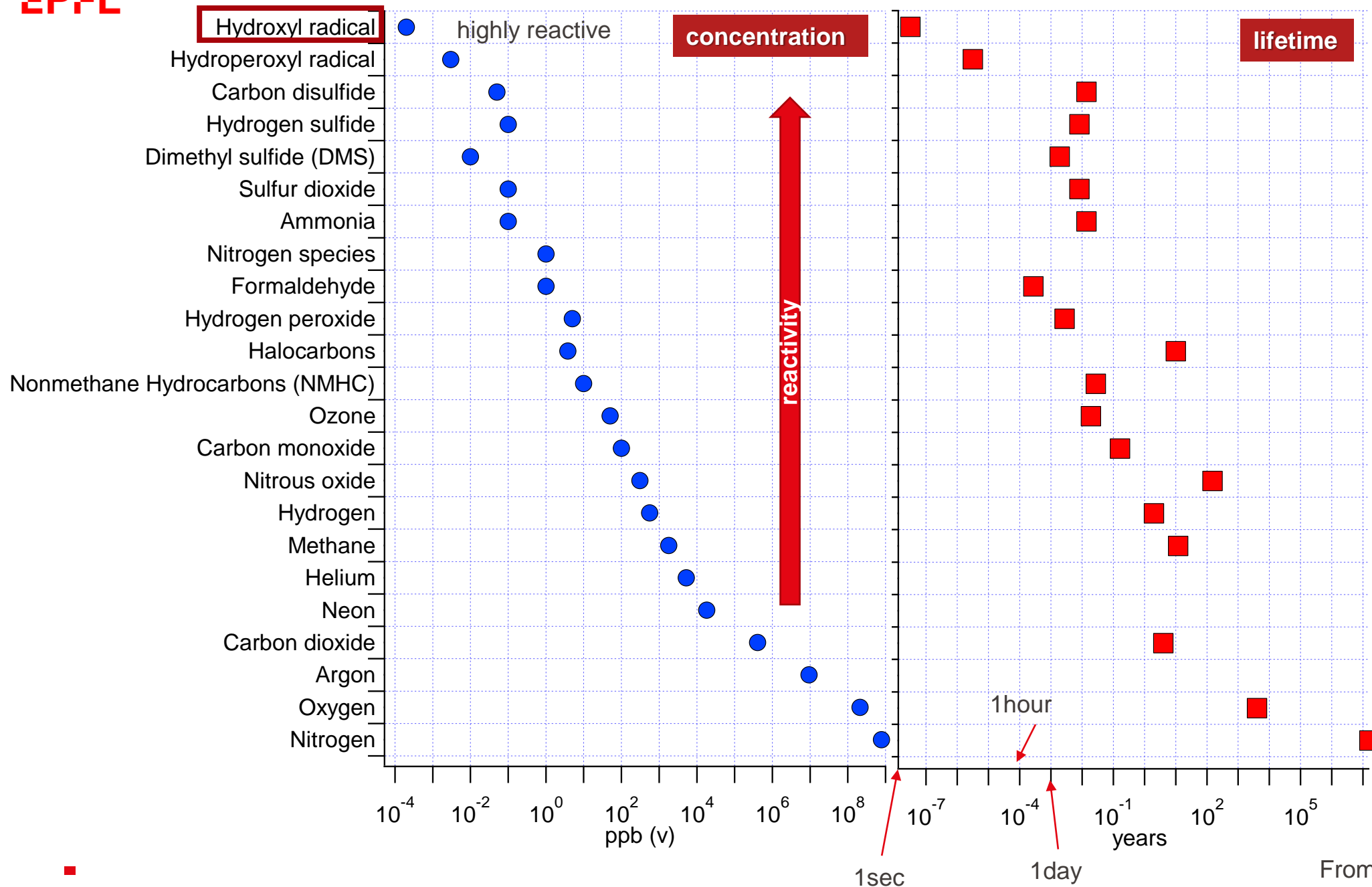
# The atmosphere is a chemical reactor



EMISSION/SOURCE

TRANSFORMATION

DEPOSITION/SINK



Very large ranges of mixing ratios and lifetimes.

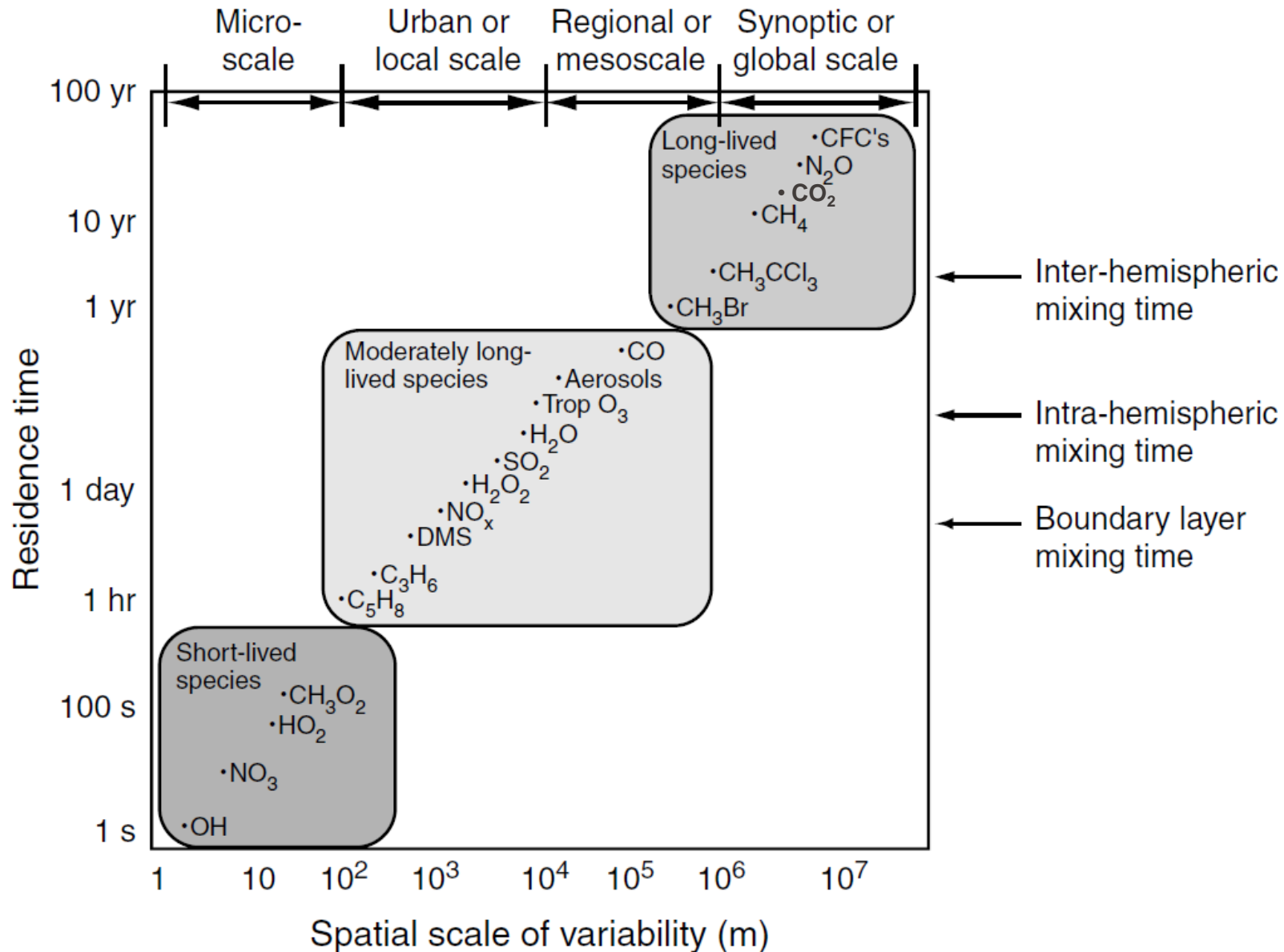
Greenhouse gases have typically longer lifetimes than air pollutants.

Some atmospheric oxidants have extremely short lifetimes (seconds).

Concentrations are driven by emission and deposition processes as well as chemical transformation.



# Lifetime and dispersion



Greenhouse gases are mostly globally dispersed.

Air pollutants play a role on a local and regional scale.

The chemical transformations play a large role for the lifetime and spatial dispersion.

Fig. 5.1 Wallace and Hobbs (2006)

# Atmospheric lifetime

Mass balance for species  $X$  in the (well-mixed) box:

$$\frac{dm}{dt} = F_{\text{in}} - F_{\text{out}} + E + P - L - D \quad m = \text{mass of species}$$

The lifetime or residence time in the box:

$$\tau = \frac{m}{F_{\text{out}} + L + D}$$

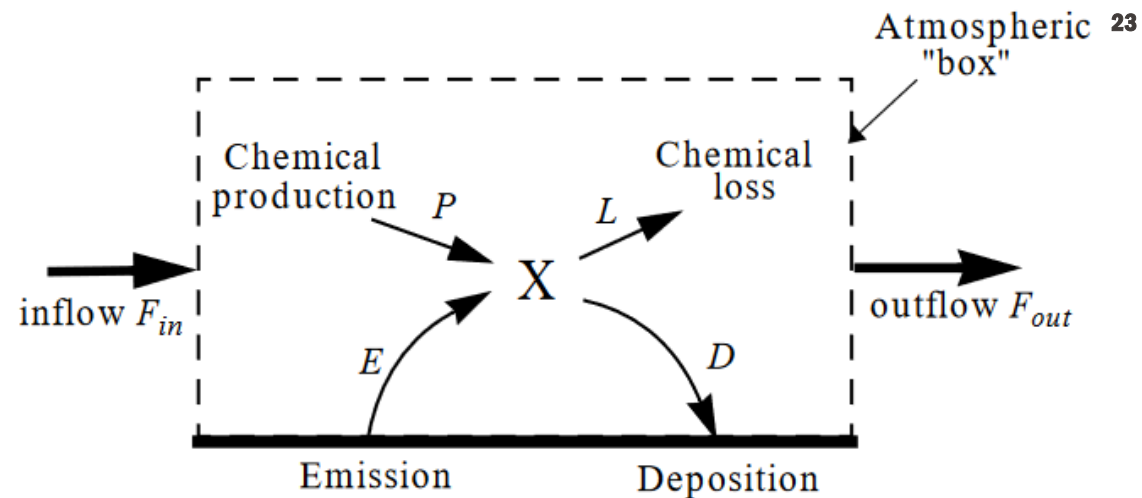


Figure 3-1 One-box model for an atmospheric species  $X$

# Atmospheric lifetime

Mass balance for species  $X$  in the (well-mixed) box:

$$\frac{dm}{dt} = F_{in} - F_{out} + E + P - L - D \quad m = \text{mass of species}$$

The lifetime or residence time in the box:

$$\tau = \frac{m}{F_{out} + L + D}$$

We are often interested in determining the relative importance of different sinks contributing to the overall removal of a species:

$$f_{out} = \frac{F_{out}}{F_{out} + L + D}$$

Lifetime with respect to various sinks:

$$\tau_{out} = \frac{m}{F_{out}} \quad (\text{export})$$

$$\tau_c = \frac{m}{L} \quad (\text{chemical loss})$$

$$\tau_d = \frac{m}{D} \quad (\text{deposition})$$

which can be combined using a harmonic sum:

$$\frac{1}{\tau} = \frac{1}{\tau_{out}} + \frac{1}{\tau_c} + \frac{1}{\tau_d}$$

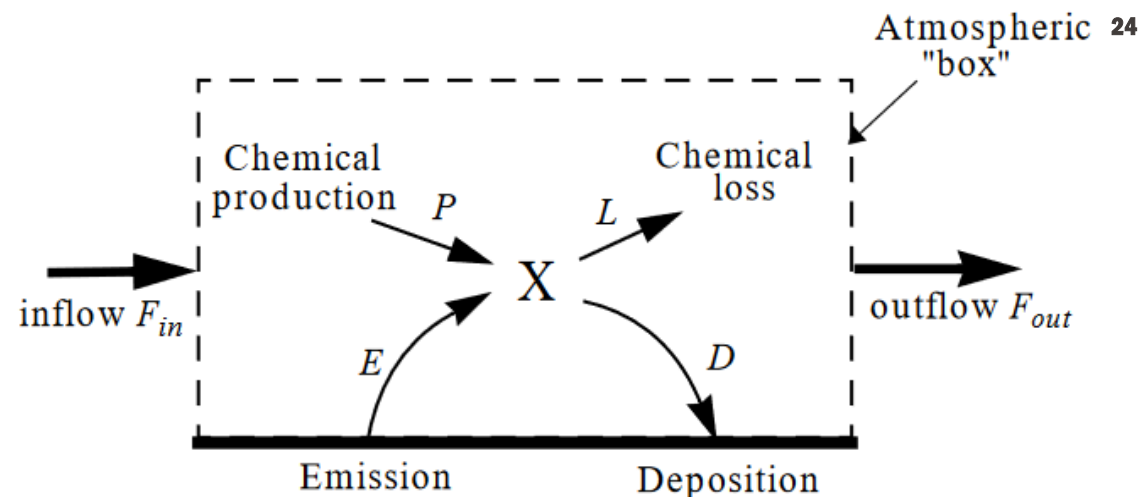


Figure 3-1 One-box model for an atmospheric species  $X$

Consider a first-order chemical loss for  $X$  with rate  $L = k_c m$ .

$$\tau_c = \frac{m}{L} = \frac{1}{k_c}$$

We can generalize the notion of chemical rate constants to define rate constants for each loss mechanism:

$$k_{out} = \frac{1}{\tau_{out}}$$

$$k_c = \frac{1}{\tau_c}$$

$$k_d = \frac{1}{\tau_d}$$

and an overall loss rate constant can be obtained by an arithmetic sum:

$$F_{out} + L + D = (k_{out} + k_c + k_d) m = km$$

"Introduction to  
Atmospheric  
Chemistry" by  
Daniel J. Jacob  
Princeton  
University Press,  
1999

Example of a first order loss process: dry deposition

$$D = - \left[ \frac{dm}{dt} \right]_d = \frac{v_d}{H} m$$

D Depositional loss rate (kg/s)

H is a representative lengthscale (e.g., boundary layer height (m))

$v_d$  deposition velocity (m/s)

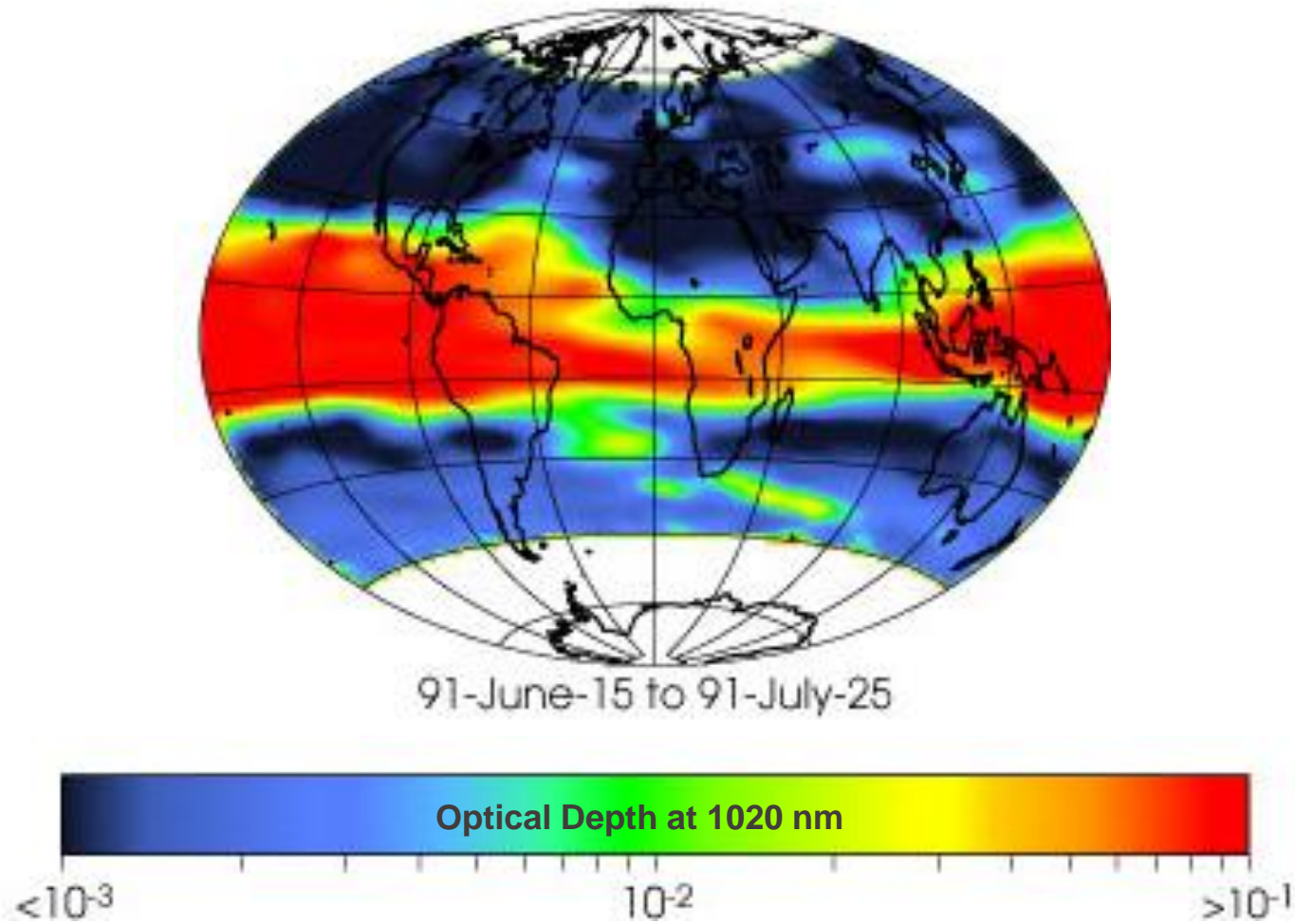
m is mass of a substance (kg)

Characteristic time:  $\tau_d = \frac{m}{D} = \frac{H}{v_d}$



# Mt. Pinatubo eruption

15 June 1991



# How long did it take until the Pinatubo layer was dissolved?

- Assume the layer was 2 km thick
- Assume a sensible particle diameter

Characteristic time:  $\tau_d = \frac{m}{D} = \frac{H}{v_d}$

1

**TABLE 3.1 Effect of Pressure on Terminal Settling Velocity of Standard Density Spheres at 293 K [20°C].**

| Particle Diameter<br>( $\mu\text{m}$ ) | $V_{\text{TS}}$ at the Indicated Pressure (m/s) |                       |                       |
|--|---|-----------------------|-----------------------|
|  | $P = 0.1 \text{ atm}$                           | $P = 1.0 \text{ atm}$ | $P = 10 \text{ atm}$  |
| 0.001                                  | $6.9 \times 10^{-8}$                            | $6.9 \times 10^{-9}$  | $6.9 \times 10^{-10}$ |
| 0.01                                   | $6.9 \times 10^{-7}$                            | $7.0 \times 10^{-8}$  | $8.7 \times 10^{-9}$  |
| 0.1                                    | $7.0 \times 10^{-6}$                            | $8.8 \times 10^{-7}$  | $3.5 \times 10^{-7}$  |
| 1                                      | $8.8 \times 10^{-5}$                            | $3.5 \times 10^{-5}$  | $3.1 \times 10^{-5}$  |
| 10                                     | 0.0035  | 0.0031                | 0.0029                |
| 100                                    | 0.29  | 0.25                  | 0.17                  |

Now we can use the loss term to calculate lifetime.  
Lifetimes are defined by the e-folding or half-lifetimes.

Consider a first order reaction for X:

$$\frac{d[X]}{dt} = -k[X]_0$$

The solution is:

$$[X] = [X]_0 e^{-kt} \quad [X]_0 \dots \text{initial concentration}$$

The e-folding lifetime ( $\tau_e$ ) is the time at which:

$$\frac{[X]}{[X]_0} = e^{-1} = e^{-k\tau_e}$$

The characteristic lifetime, e-folding lifetime  
is hence:

$$\tau_e = \frac{1}{k}$$

More common

The half-lifetime can be defined as:

$$\frac{[X]}{[X]_0} = \frac{1}{2} = e^{-k\tau_{(1/2)}}$$

$$\text{Then} \quad \tau_{(1/2)} = \frac{\ln(2)}{k}$$

Units: PgC (1 PgC =  $10^{15}$  gC), PgC yr<sup>-1</sup>

Black: reservoir or fluxes prior to 1750 (pre-industrial),  
reservoir also called «carbon stock»

Red: «anthropogenic» fluxes 2000-2009

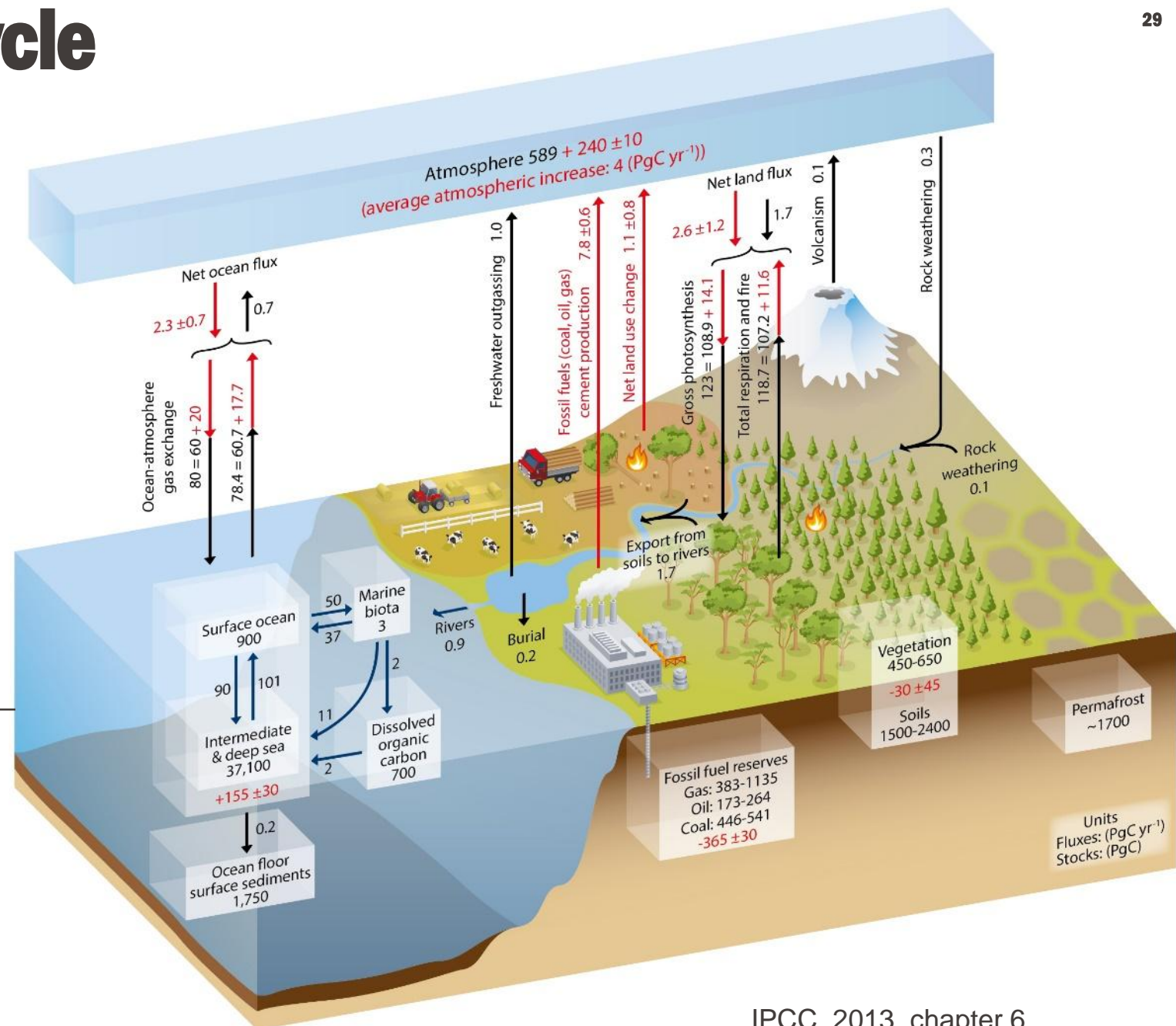
Two domains:

«Fast»: carbon in the atmosphere, the ocean,  
surface ocean sediments and on land in  
vegetation, soils and freshwaters

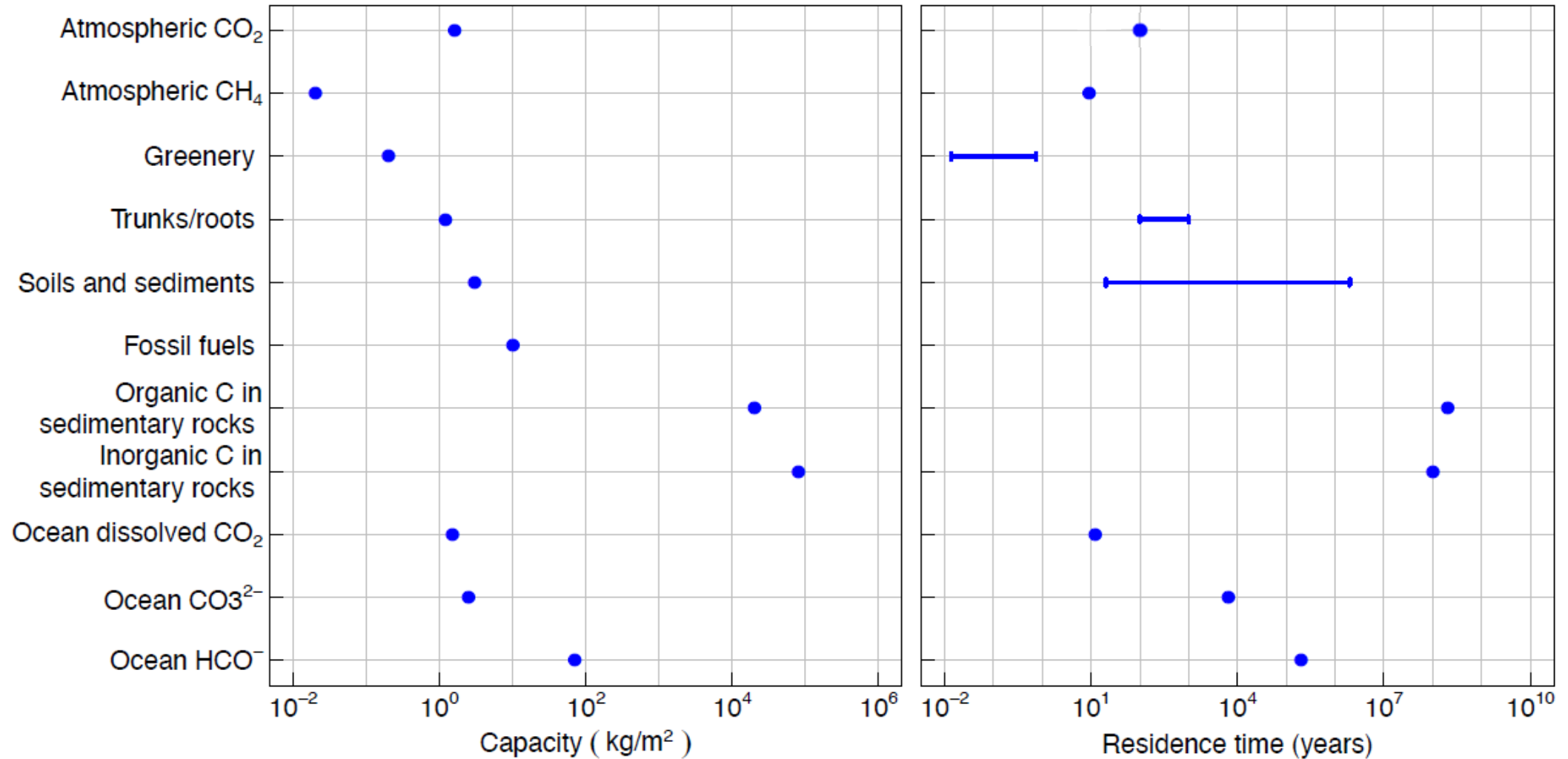
Slow: carbon stores in rocks and sediments

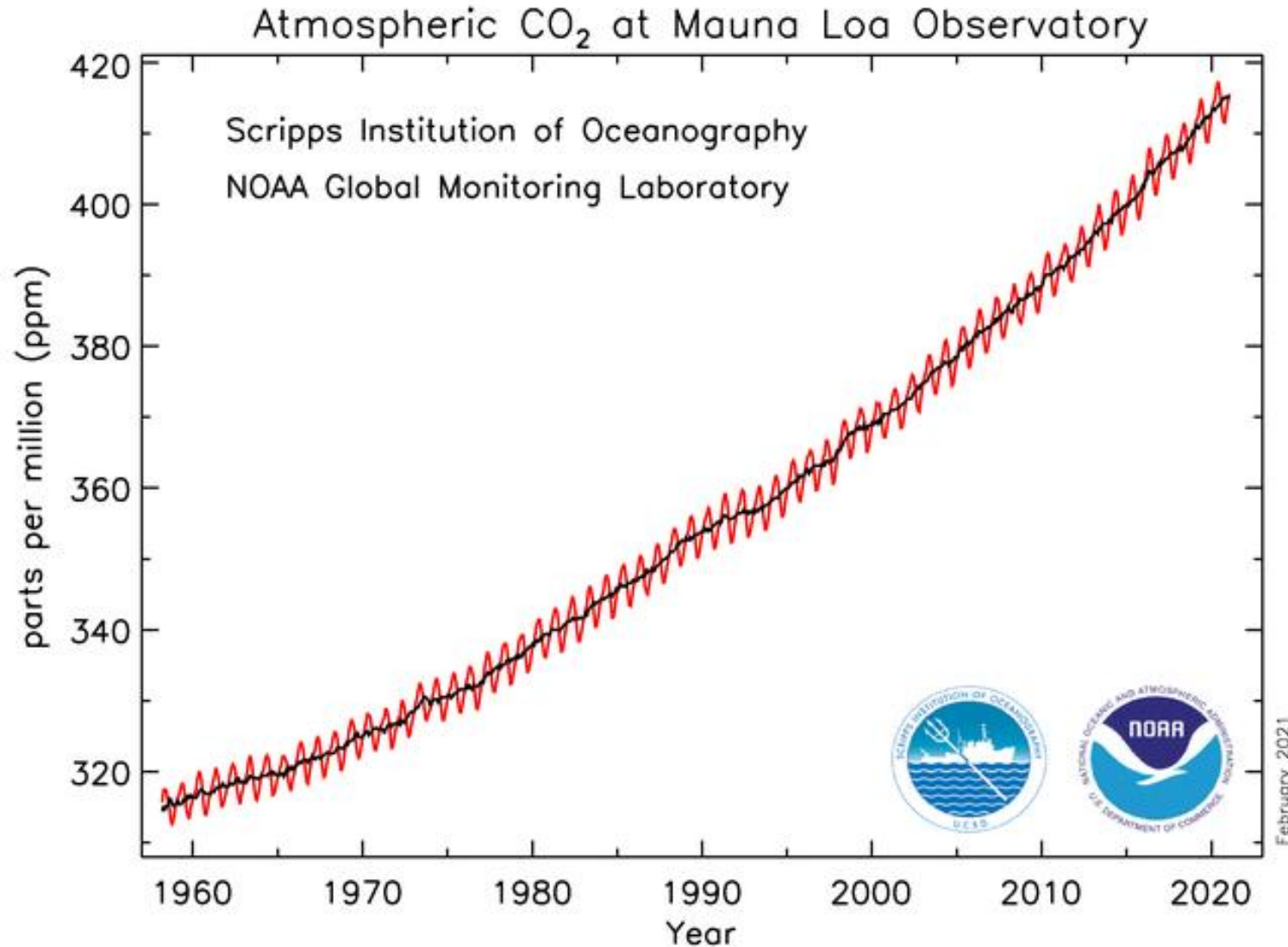
They exchange via volcanic eruptions and  
chemical weathering of rock.

| Location    | % C    | Type of carbon   |
|-------------|--------|--|
| Lithosphere | 99.985 | fossil, sediments, organic carbon, marine sediments          |
| Hydrosphere | 0.0076 | carbonate ions, dissolved CO <sub>2</sub> , bicarbonate ions |
| Pedosphere  | 0.0031 | soil organisms, plant remains                                |
| Cryosphere  | 0.0018 | frozen mosses  |
| Atmosphere  | 0.0015 | gaseous carbon   |
| Biosphere   | 0.0012 | living plants and animals                                    |









**Keeling curve**

**Daily observations at Mauna Loa (Hawaii) since 1958.**

**One of the most important scientific records of the 20th century.**

# Explore on your own

Historical Emissions

Equity Explorer

Emission Projections

Pre-2020 Pledges Map

Paris Contributions Map

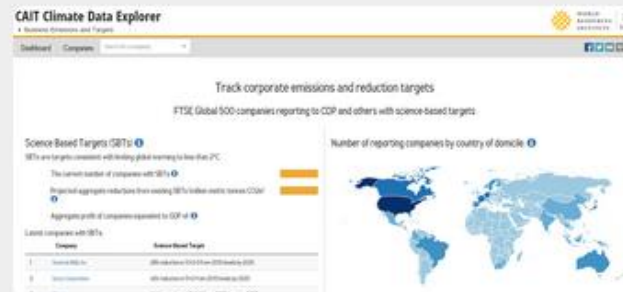
Business Emissions and Targets

Google Public Data Explorer



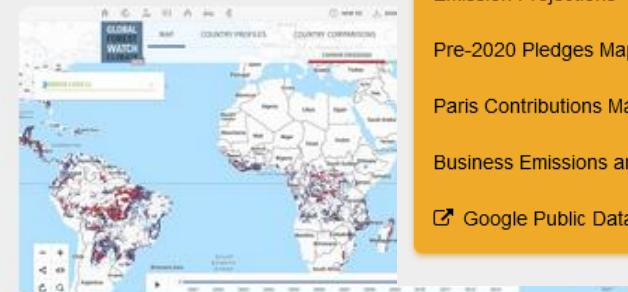
## Google Public Data Explorer\*

Dive deeper into the CAIT Historical Emissions data with the Google Public Data Explorer. Use it to compare country-level and region-level emissions by gases, sectors, per capita information, GDP and other socio-economic indicators and create your own visualizations and animations.

[Go to Google Public Data Explorer »](#)


## Business Emissions and Targets\*

CAIT Business offers the most trusted, decision-relevant data on how companies are contributing and responding to climate change. Full transparency empowers public and private sector leaders, civil society, NGOs and the media to take action to manage companies' climate impacts.

[Start Business Emissions and Targets »](#)


## Global Forest Watch Climate\*

GFW Climate is mapping platform that increases transparency about the climate impacts of tropical deforestation and gives access to comprehensible data on carbon emissions. It provides a benchmark for measuring countries' emissions and tracking progress toward meeting emissions-reduction goals.

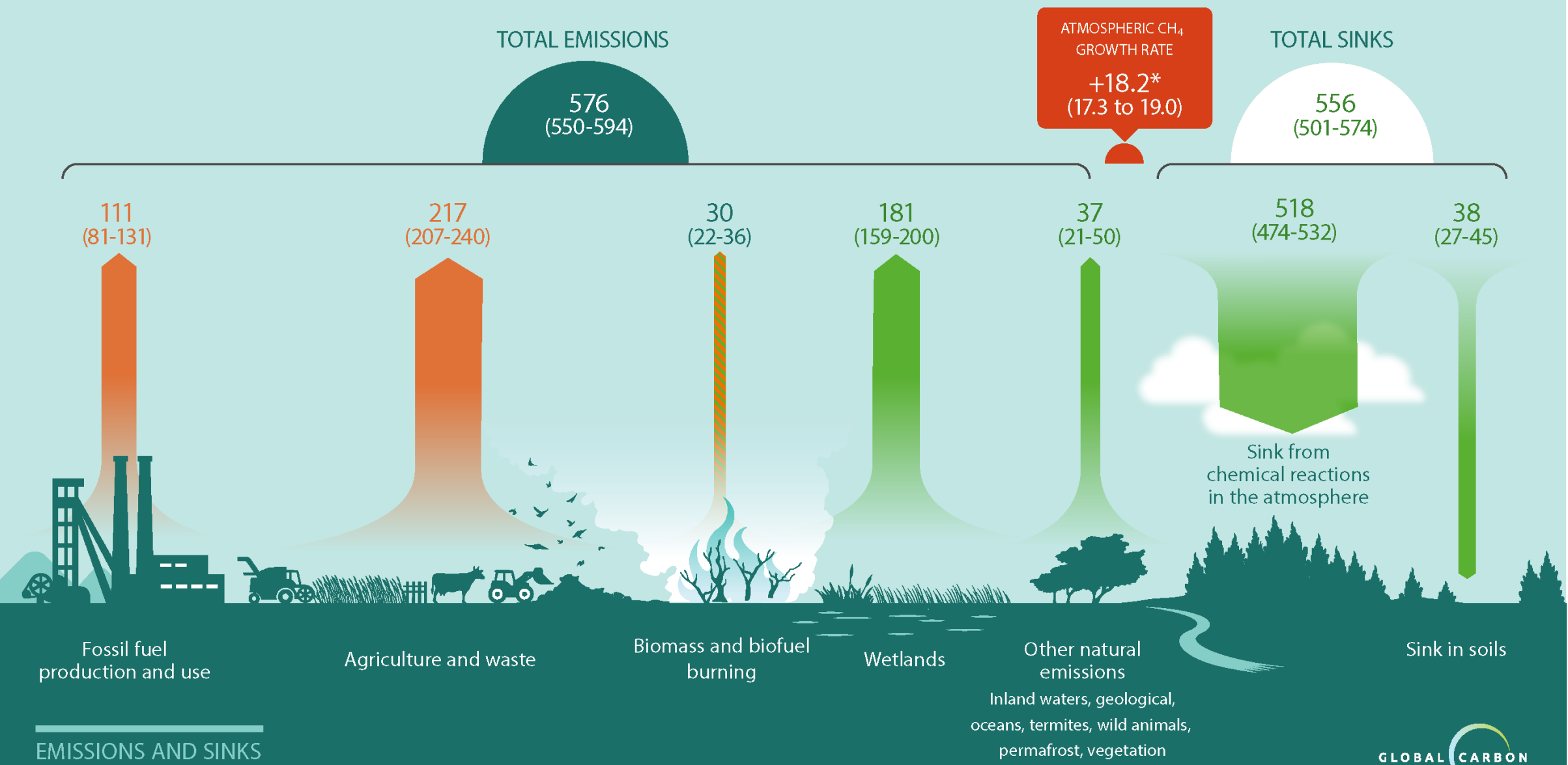
[Start GFW Climate »](#)

\* These CAIT Tool will no longer be updated. Please refer to Climate Watch for latest data.

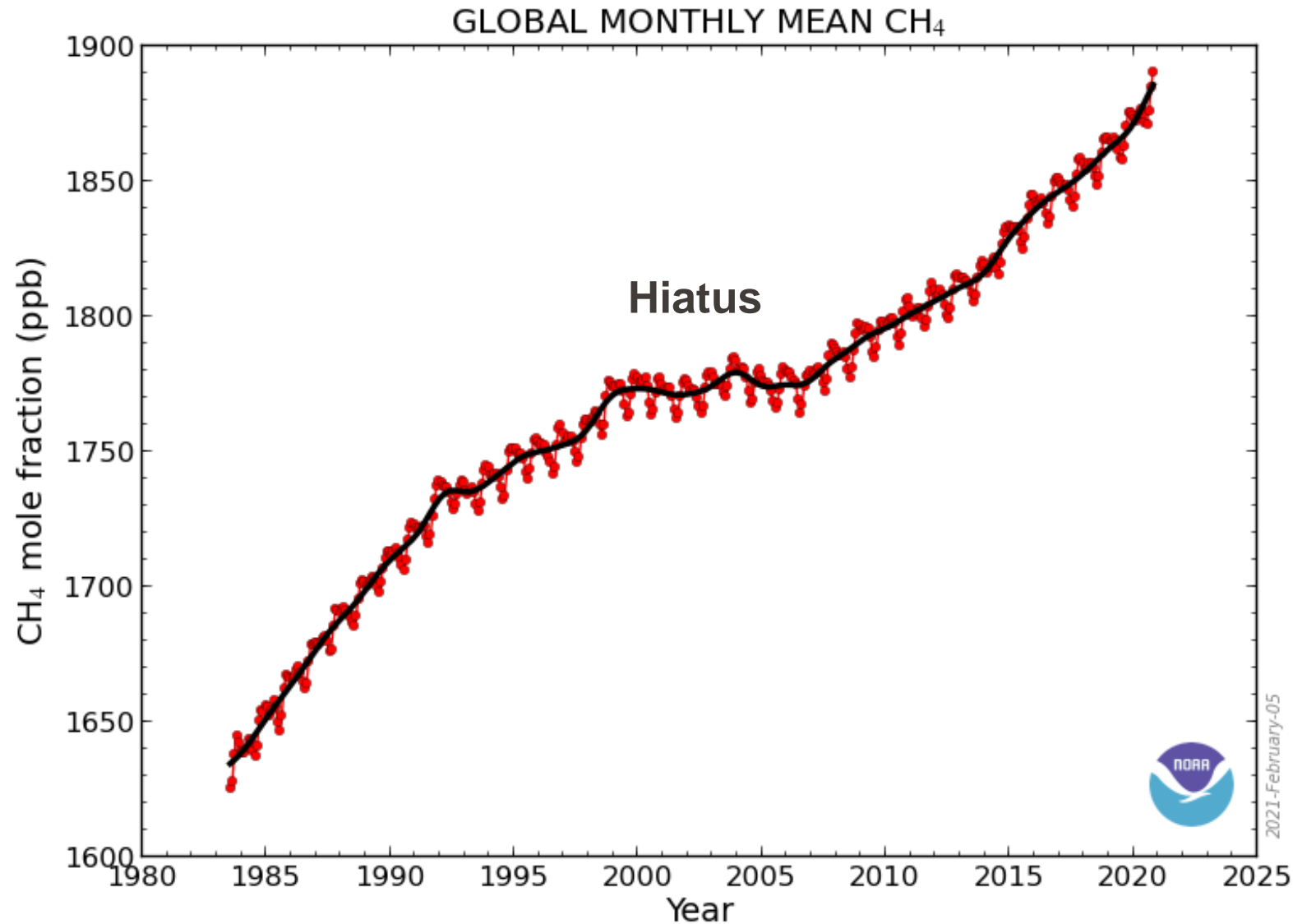
## Watch out for the differences:

- Carbon vs CO<sub>2</sub> emissions
- Greenhouse gas vs CO<sub>2</sub> emission
- CO<sub>2</sub> vs CO<sub>2</sub> equivalent

# GLOBAL METHANE BUDGET 2008-2017







Is there something «strange» in the curve?

Stagnation not yet resolved:

- More anthropogenic emissions in that period.
- Main sink process with OH saw little change.

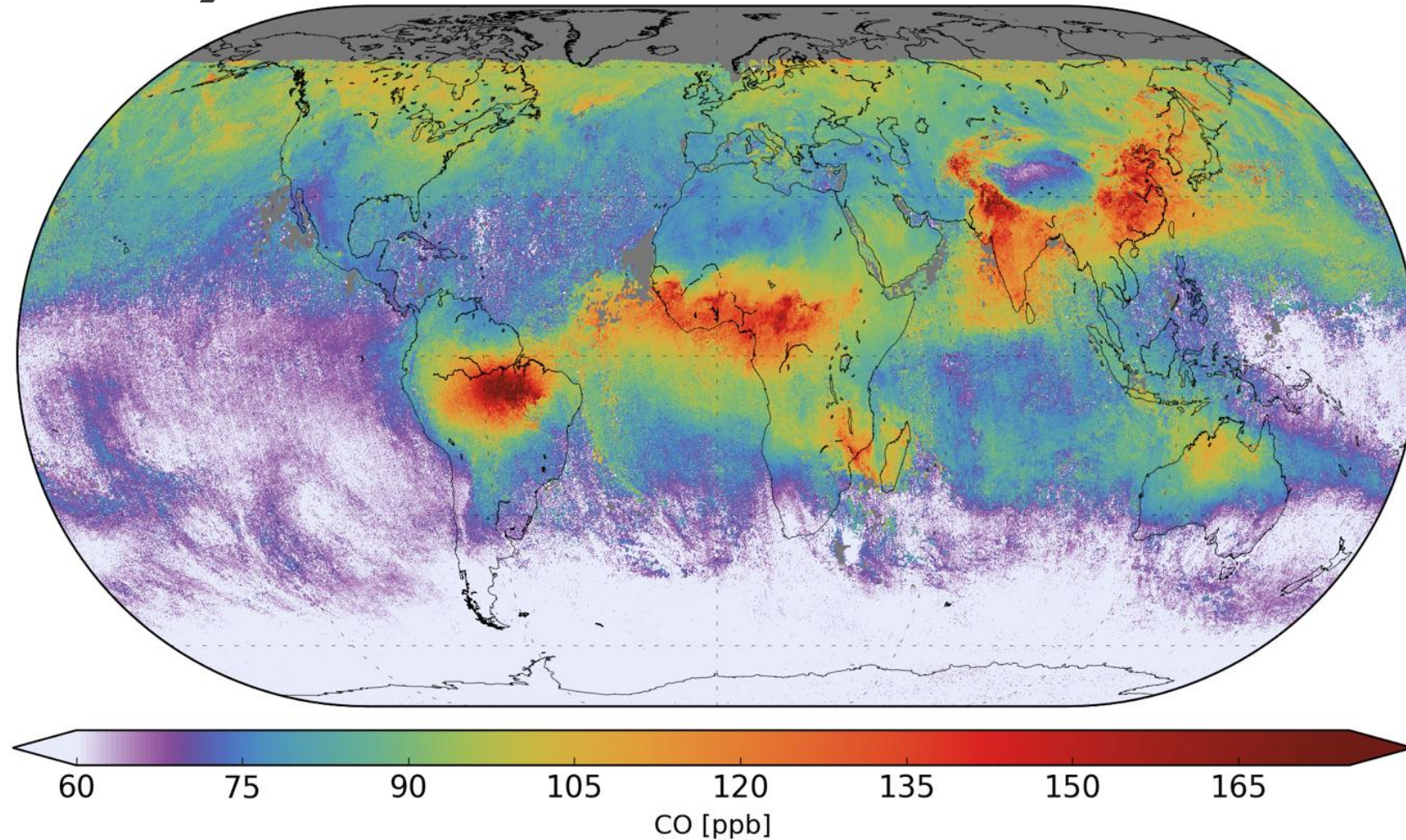
**TABLE 2.15 Estimates of Global Tropospheric CO Budget [in Tg(CO) yr<sup>-1</sup>] and Values Adopted by IPCC (2001)**

|                            |                                | Hauglustaine et al.<br>(1998) | Bergamaschi et al.<br>(2000) | WMO<br>(1998) | IPCC<br>(2001) |
|----------------------------|--------------------------------|-------------------------------|------------------------------|---------------|----------------|
| <b>Sources</b>             |                                |                               |                              |               |                |
| anthropogenic contribution | → Oxidation of CH <sub>4</sub> |                               | 795                          |               | 800            |
|                            | Oxidation of isoprene          |                               | 268                          |               | 270            |
|                            | Oxidation of terpenes          |                               | 136                          |               | ~0             |
|                            | → Oxidation of industrial NMHC |                               | 203                          |               | 110            |
|                            | Oxidation of biomass NMHC      |                               | —                            |               | 30             |
|                            | Oxidation of acetone           |                               | —                            |               | 20             |
|                            | Subtotal in situ oxidation     | 881                           | 1402                         |               | 1230           |
|                            | Vegetation                     |                               | —                            | 100           | 150            |
|                            | Oceans                         |                               | 49                           | 50            | 50             |
|                            | → Biomass burning              |                               | 768                          | 500           | 700            |
|                            | → Fossil and domestic fuel     |                               | 641                          | 500           | 650            |
|                            | Subtotal direct emissions      | 1219                          | 1458                         | 1150          | 1550           |
|                            | Total sources                  | 2100                          | 2860                         |               | 2780           |
| <b>Sinks</b>               |                                |                               |                              |               |                |
|                            | Surface deposition             | 190                           |                              |               |                |
|                            | OH reaction                    | 1920                          |                              |               |                |

# CO seen from satellite (TROPOMI)

$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$   
Lifetime of ~2 months

36



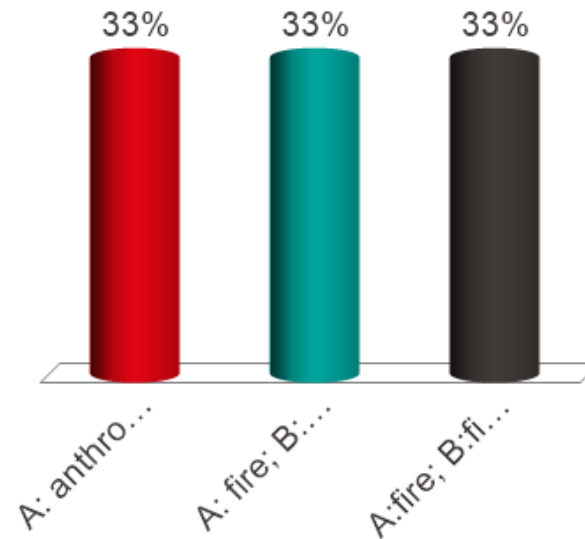
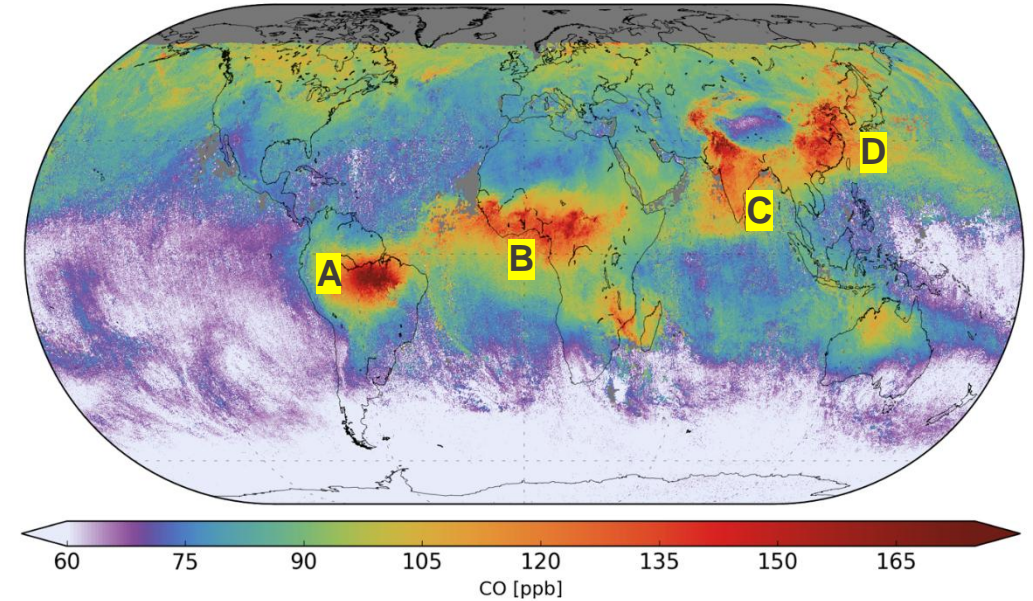
■ (Borsdorff et al., GRL, 2018), Nov. 13-19, 2017

<http://www.tropomi.eu/data-products/carbon-monoxide>  
Measured at 2.3μm, total column, sensitive to boundary layer



# What are the high emissions?

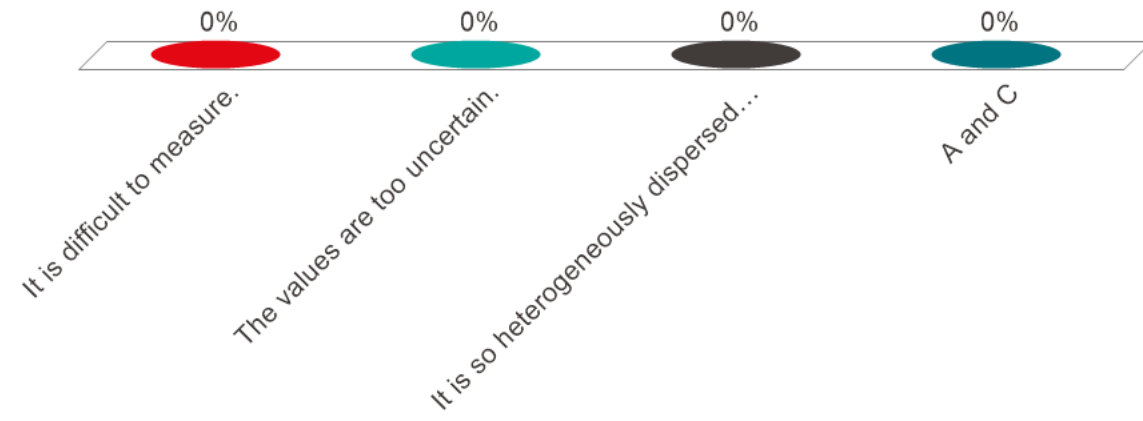
- A. A: anthropogenic, B: fire, C: fire, D: anthropogenic
- B. A: fire; B: fire; C: volcano; D: fire
- C. A: fire; B: fire; C: anthropogenic; D: anthropogenic

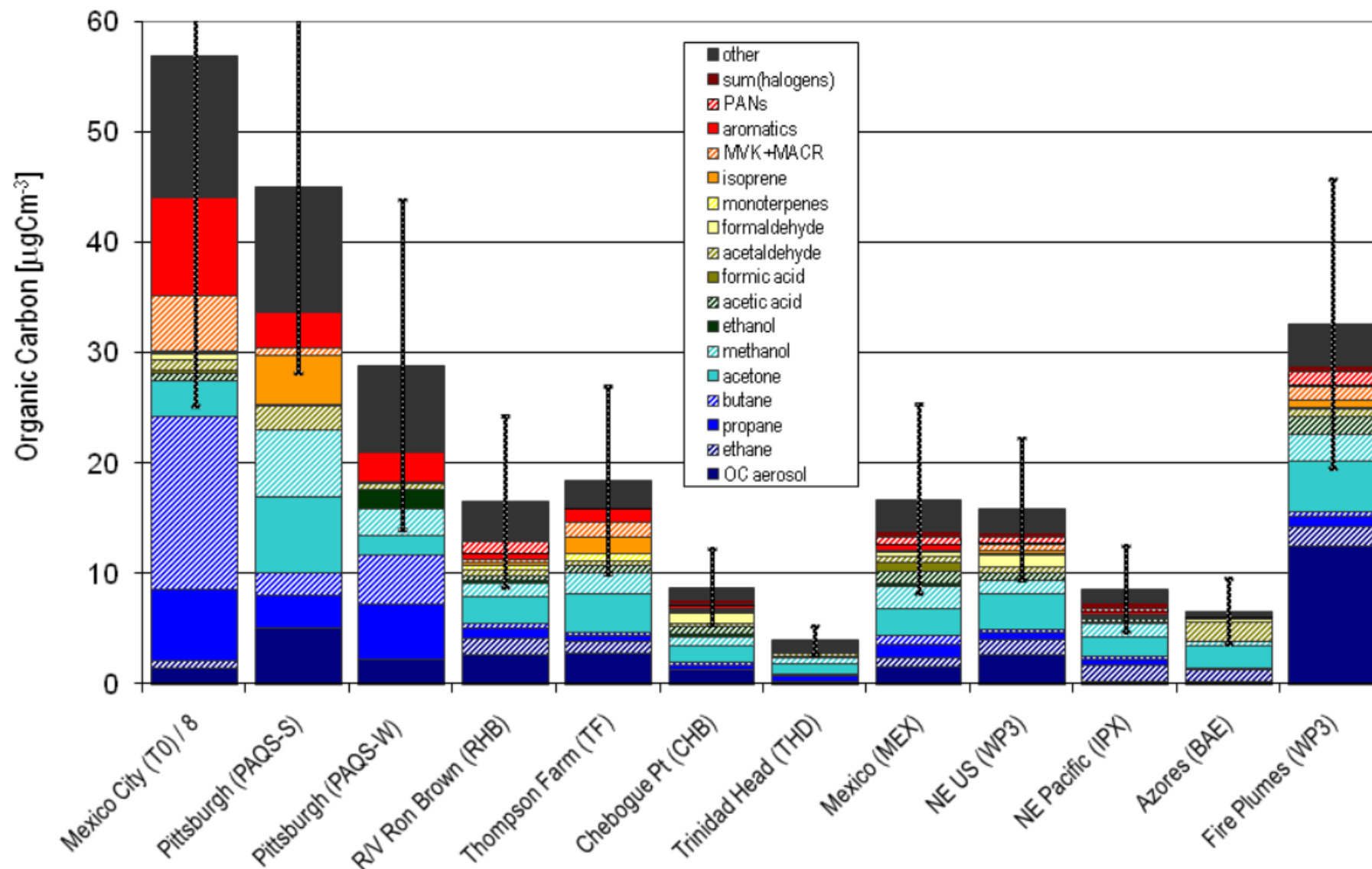




# Why do you not find global concentration trends for CO?

- A. It is difficult to measure.
- B. The values are too uncertain.
- C. It is so heterogeneously dispersed that a global average does not make much sense.
- D. A and C



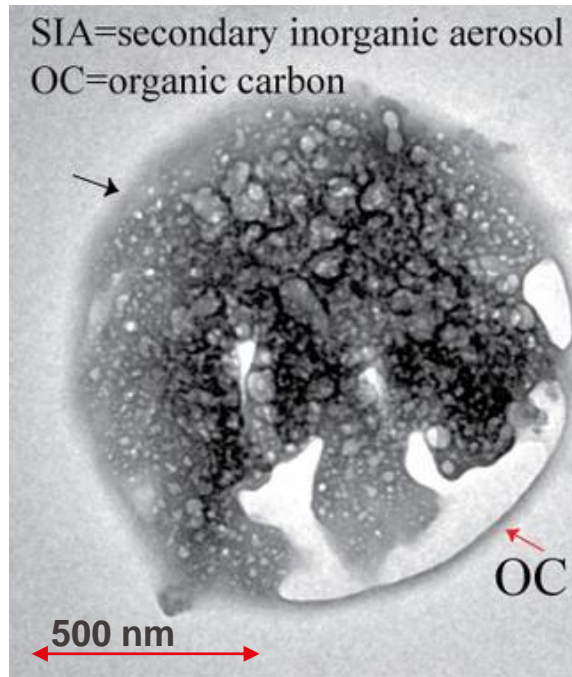


Also called NMHC (non-methane hydrocarbons)

TOC is total organic carbon

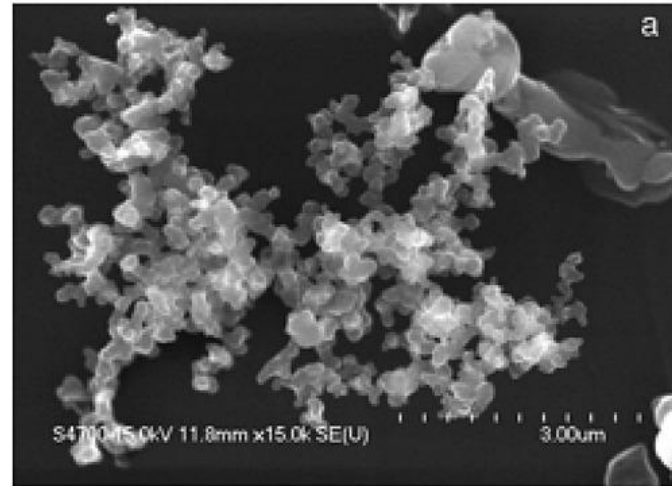
Form organic aerosol particles

# Carbon in the atmosphere is not only contained in gases but also particles



DOI:[10.5194/acp-15-13365-2015](https://doi.org/10.5194/acp-15-13365-2015)

Black carbon aggregates



Sources are combustion processes (fossil and biogenic)



Daily fire radiative power in  
watts per square metre

01/12/2018

## Fires: large source of atmospheric carbon

Emissions of :  
CO<sub>2</sub>, CO, CH<sub>4</sub>, NMHC (VOCs), aerosols: OA, BC





# The global carbon cycle includes...

- A. Only CO<sub>2</sub>.
- B. CO<sub>2</sub> and CH<sub>4</sub>.
- C. Only gases that contain C.
- D. Gases and particles that contain C.
- E. Aerosol organic carbon is not part of the carbon cycle.
- F. NMHCs.

# Nitrogen Cycle

Denitrification produces  $N_2$  and  $N_2O$  from  $NO_3$  and  $NO_2$   
 Fixation is the incorporation of N into living organisms  
 $NO + NO_2$  is  $NO_x$

$N_2$  makes up > 99.99 % of atmospheric N  
 $N_2O$  makes up > 99 % of the remaining N  
 $NH_3$  is of crucial importance, only basic gas (neutralization of aerosols)  
 $NO + NO_2$  play a critical role in tropo- and stratospheric chemistry  
 Atmosphere is the main source of N for ecosystems.

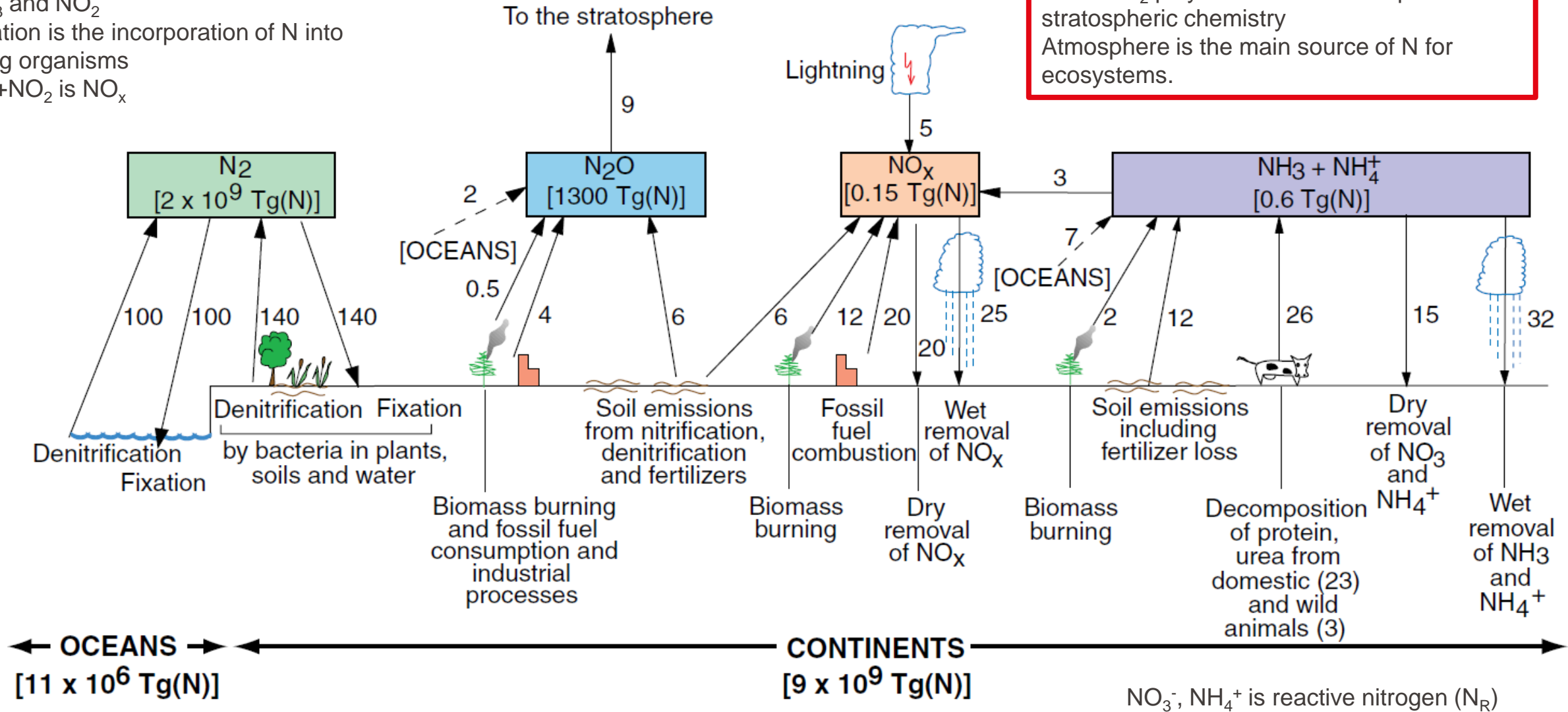
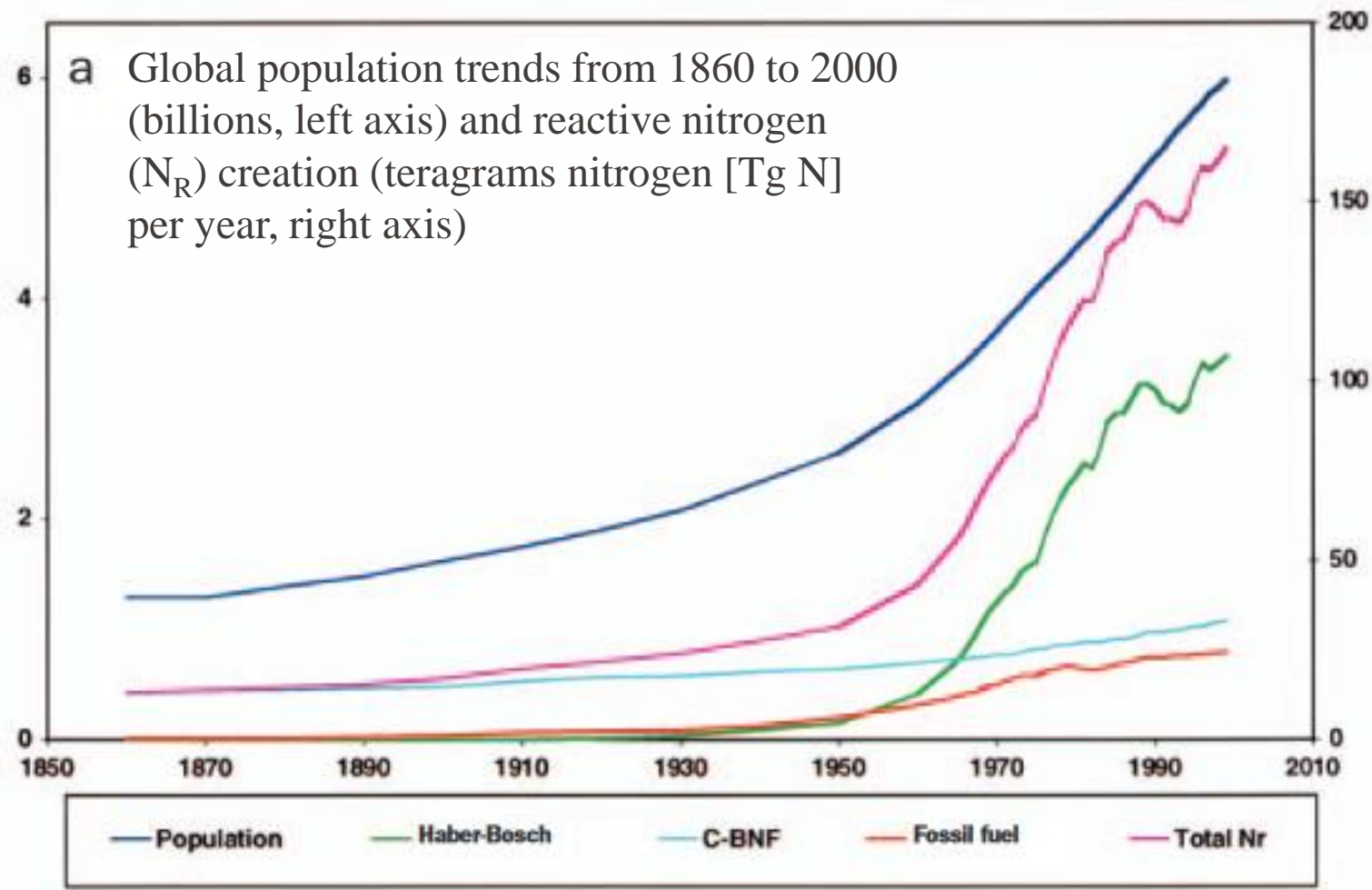
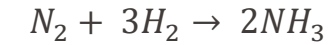


Figure 5.14, Wallace and Hobbs, 2006



**Haber-Bosch process:**

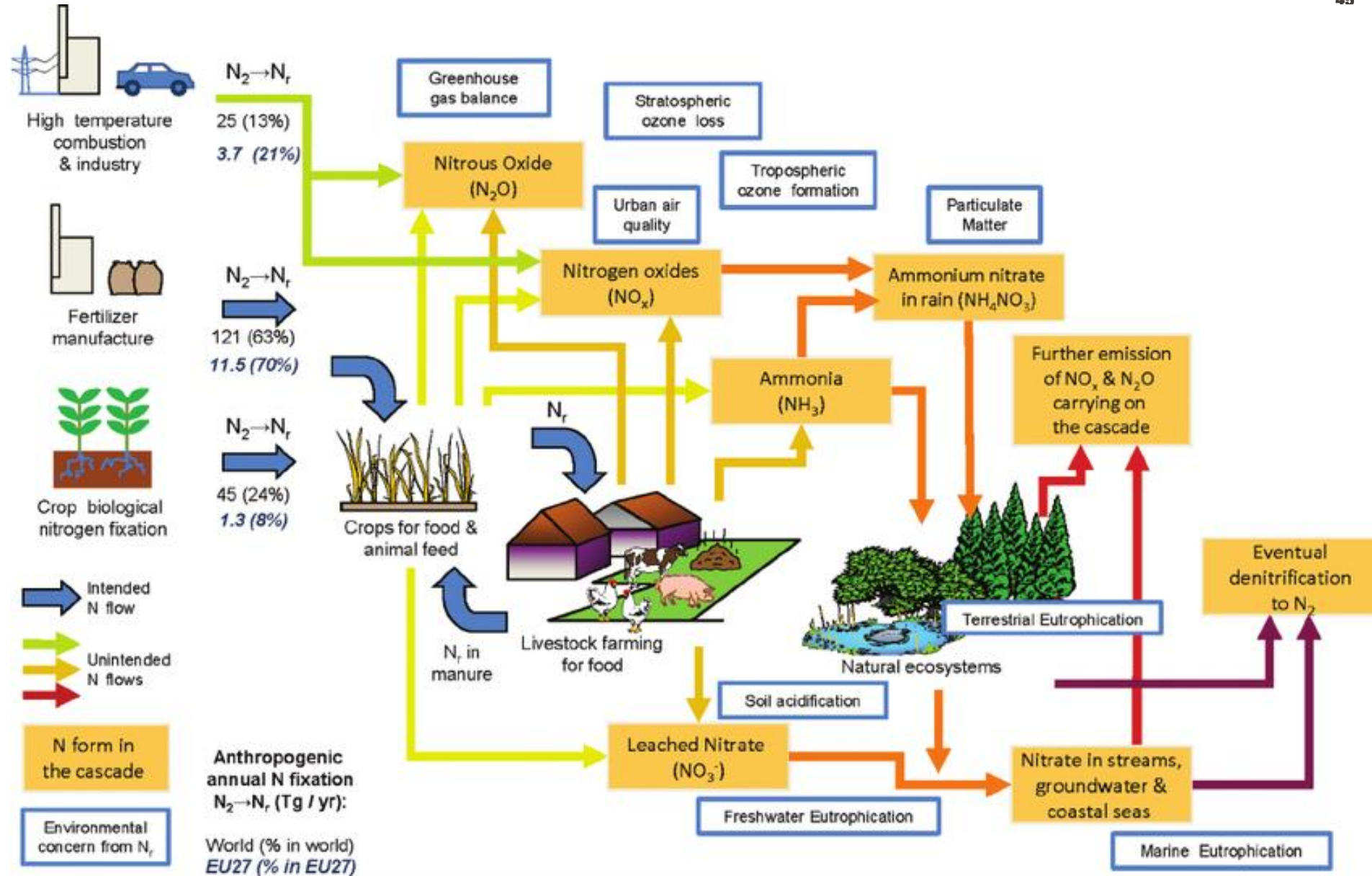


Ammonia as fertilizer (Nobel prize in 1918 and 1931)

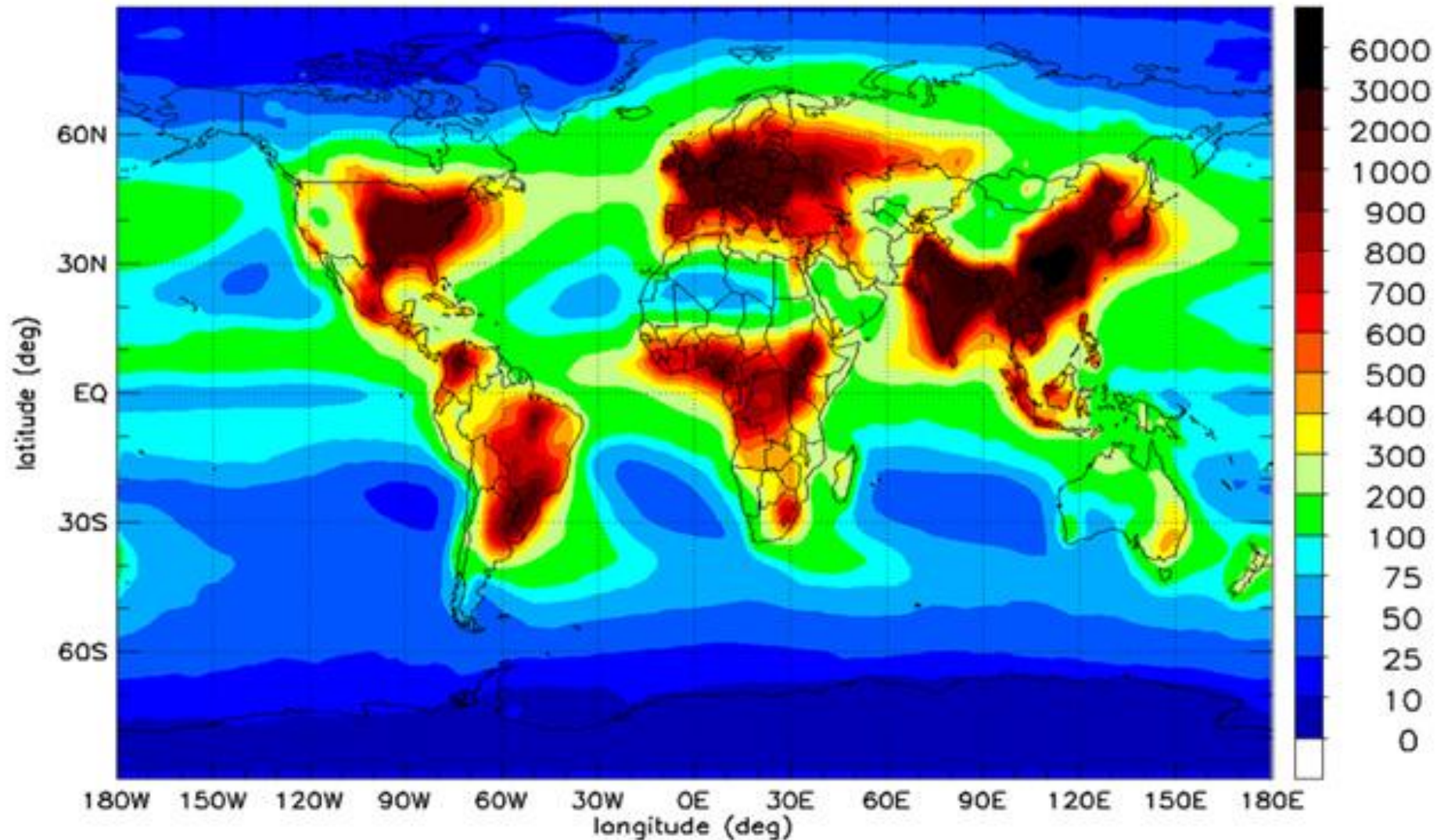
# Nitrogen Cascade

- $N_R$  is released to the environments
- Effects are magnified the longer  $N_R$  stays in the environment, because the same atom of  $N_R$  can cause effects in the atmosphere, terrestrial ecosystems and in freshwater/marine systems

Integrated measures in agriculture to reduce ammonia emissions







Estimated N deposition from global total N (NO<sub>y</sub> and NH<sub>x</sub>) emissions, totaling 105 Tg N y<sup>-1</sup>. The unit scale is kg N ha<sup>-1</sup> y<sup>-1</sup>, modified from the original units (mg m<sup>-2</sup> y<sup>-1</sup>)

# The main air pollutants containing nitrogen are

- A.  $\text{N}_2\text{O}$
- B.  $\text{NO}_x$
- C. Nitrate aerosols
- D.  $\text{N}_2$
- E. Ammonium
- F. A and D
- G. A, B, C, E
- H. B, C, E

The diagram illustrates the sulfur cycle with the following components and fluxes:

- Reservoirs (Tg(S)):**
  - $\text{H}_2\text{S}$ : 0.03
  - $\text{SO}_4^{2-}$ : 1.2
  - $\text{SO}_2$ : 0.3
  - $\text{CS}_2$ : 0.1
  - DMS: 0.05
  - COS: 2.5
- Continents ( $2 \times 10^{10}$  Tg(S)):**
  - Inputs:**
    - Soils and marshlands: 7 (to  $\text{H}_2\text{S}$ )
    - Volcanoes: 3 (to  $\text{SO}_4^{2-}$ )
    - Biomass burning: 3 (to  $\text{SO}_2$ )
    - Volcanoes: 10 (to  $\text{SO}_2$ )
    - Anthropogenic (fossil fuel combustion): 75 (to  $\text{SO}_2$ )
  - Outputs:**
    - Wet deposition: 73 (from  $\text{SO}_4^{2-}$ )
    - Dry deposition: 10 (from  $\text{SO}_4^{2-}$ )
    - Dry deposition: 40 (from  $\text{SO}_2$ )
- Oceans ( $1.6 \times 10^9$  Tg(S)):**
  - Inputs:**
    - Biogenic: 0.7 (to  $\text{CS}_2$ )
    - Biogenic: 0.3 (to  $\text{SO}_2$ )
    - Biogenic: 25 (to DMS)
    - Sea-salt: 40–320 (to  $\text{SO}_4^{2-}$ )
  - Outputs:**
    - Biogenic: 0.5 (from  $\text{CS}_2$  to COS)
    - Biogenic: 25 (from  $\text{SO}_2$  to COS)
    - Biogenic: 0.3 (from COS to  $\text{SO}_4^{2-}$ )
- Continents (Right):**
  - Inputs:**
    - Soils: 0.3 (to COS)
  - Outputs:**
    - Dry deposition: 0.9 (from COS)

■ Figure 5.15, Wallace and Hobbs, 2006

# Oxidation state

TABLE 2.1 Atmospheric Sulfur Compounds

| Oxidation State | Compound                    |                                   | Chemical Structure   | Usual Atmospheric State     |
|-----------------|-----------------------------|-----------------------------------|--|-----------------------------|
|                 | Name                        | Formula                           |  |                             |
| -2              | Hydrogen sulfide            | H <sub>2</sub> S                  | H-S-H  | Gas                         |
|                 | Dimethyl sulfide (DMS)      | CH <sub>3</sub> SCH <sub>3</sub>  | H <sub>3</sub> C-S-CH <sub>3</sub>   | Gas                         |
|                 | Carbon disulfide            | CS <sub>2</sub>                   | S=C=S  | Gas                         |
|                 | Carbonyl sulfide            | OCS                               | O=C=S  | Gas                         |
|                 | Methyl mercaptan            | CH <sub>3</sub> SH                | H <sub>3</sub> C-S-H   | Gas                         |
| -1              | Dimethyl disulfide          | CH <sub>3</sub> SSCH <sub>3</sub> | H <sub>3</sub> C-S-S-CH <sub>3</sub>   | Gas                         |
| 0               | Dimethyl sulfoxide          | CH <sub>3</sub> SOCH <sub>3</sub> | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{S}-\text{CH}_3 \end{array}$                        | Gas                         |
| 4               | Sulfur dioxide              | SO <sub>2</sub>                   | O=S=O  | Gas                         |
|                 | Bisulfite ion               | HSO <sub>3</sub> <sup>-</sup>     | $\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{S}-\text{O}^- \end{array}$                                  | Aqueous                     |
| 6               | Sulfuric acid               | H <sub>2</sub> SO <sub>4</sub>    | $\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{S}-\text{OH} \\ \parallel \\ \text{O} \end{array}$          | Gas/aqueous/aerosol         |
|                 | Bisulfate ion               | HSO <sub>4</sub> <sup>-</sup>     | $\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{S}-\text{O}^- \\ \parallel \\ \text{O} \end{array}$         | Aqueous/aerosol             |
|                 | Sulfate ion                 | SO <sub>4</sub> <sup>2-</sup>     | $\begin{array}{c} \text{O} \\ \parallel \\ ^-\text{O}-\text{S}-\text{O}^- \\ \parallel \\ \text{O} \end{array}$        | Aqueous/aerosol             |
|                 | Methane sulfonic acid (MSA) | CH <sub>3</sub> SO <sub>3</sub> H | $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{S}-\text{OH} \\ \parallel \\ \text{O} \end{array}$ | Gas/aqueous Also as aerosol |



**TABLE 2.2 Global Sulfur Emissions Estimates [Tg(S) yr<sup>-1</sup>]**

| Source   | H <sub>2</sub> S | DMS                  | CS <sub>2</sub> | OCS <sup>a</sup> | SO <sub>2</sub> <sup>b</sup> | Sulfate | Total <sup>c</sup>               |
|--|------------------|----------------------|-----------------|------------------|------------------------------|---------|----------------------------------|
| Fossil fuel combustion + industry              |                  | Total reduced S: 2.2 |                 |                  | 56.3                         | 2.2     | 71–77 (mid-1980s) (68/6)         |
| Biomass burning                                | <0.01?           | —                    | <0.01?          | 0.075            | 1.3                          | 0.1     | 2.2–3.0 (1.4/1.1)                |
| Oceans   | <0.3             | 15–25                | 0.08            | 0.08             | —                            | 40–320  | 15–25 (8.4/11.6) <sup>d</sup>    |
| Wetlands                                       | 0.006–1.1        | 0.003–0.68           | 0.0003–0.06     | —                | —                            | —       | 0.01–2 (0.8/0.2)                 |
| Plants + soils                                 | 0.17–0.53        | 0.05–0.16            | 0.02–0.05       | —                | —                            | 2–4     | 0.25–0.78 (0.3/0.2) <sup>e</sup> |
| Volcanoes                                      | 0.5–1.5          | —                    | —               | 0.01             | 6.6                          | 2–4     | 9.3–11.8 (7.6/3.0)               |
| → Anthropogenic (total)                        |                  |                      |                 |                  |                              |         | 73–80                            |
| Natural (total, without seasalt and soil dust) |                  |                      |                 |                  |                              |         | 25–40                            |
| Total  |                  |                      |                 |                  |                              |         | 98–120                           |

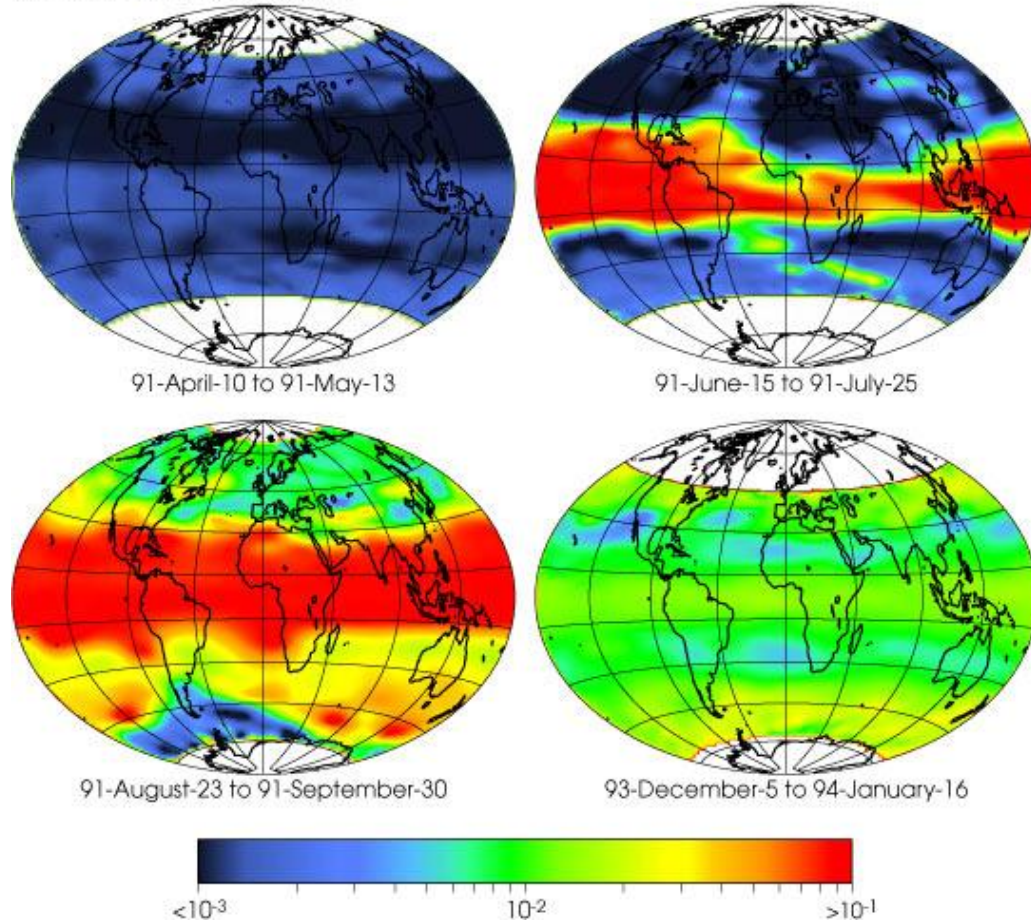
<sup>a</sup>Andreae and Crutzen (1997).<sup>b</sup>Lee et al. (2011).<sup>c</sup>Numbers in parentheses are fluxes from Northern Hemisphere/Southern Hemisphere.<sup>d</sup>Excluding seasalt contributions.<sup>e</sup>Excluding soil dust contributions.

Source: Berresheim et al. (1995).

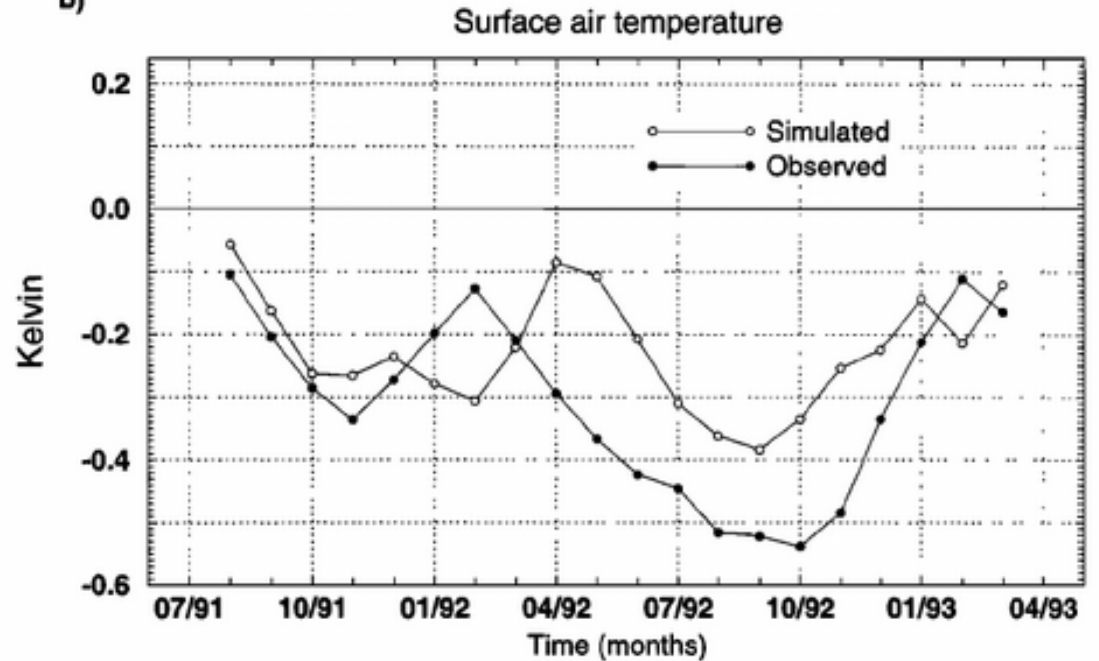
# Mt. Pinatubo eruption

15 June 1991

SAGE II 1020 nm Optical Depth



b)



<https://earthobservatory.nasa.gov/images/1510/global-effects-of-mount-pinatubo>

<https://agupubs.onlinelibrary.wiley.com/doi/epdf/10.1029/1999JD900213>, Kirchner et al., 1999, JGR

# Why does SO<sub>2</sub> survive longer in the stratosphere?

- A. There is less OH.
- B. There is less UV radiation.
- C. There are no clouds.

- We talk about 1% of a millionths of Earth's mass, i.e. 1% of the atmospheric mass.
- We care about atmospheric composition because it affects air quality, ecosystems and climate change.
- The atmosphere is a chemical reactor: emission, advection, production, decomposition, deposition.
- Atmospheric constituents have a lifetime. Greenhouse gases are generally long-lived, while air pollutants are shorter-lived.
- Air pollutants and greenhouse gases play a role in global climate forcing.