Geochemical Cycles, Aerosol

Geochemical cycles:

- Reservoirs and exchange
- Carbon
- Nitrogen

Aerosol:

- What is an aerosol?
- Sources and sinks of aerosol particles
- Introducing atmospheric aerosols

Literature connected with today's lecture (see "Reading instructions"):

Geochemical cycles:

Jacob, chapter 6

IPCC AR5, chapter 6 pp. 465-480

Aerosol:

Slides from this presentation (the aerosol part)

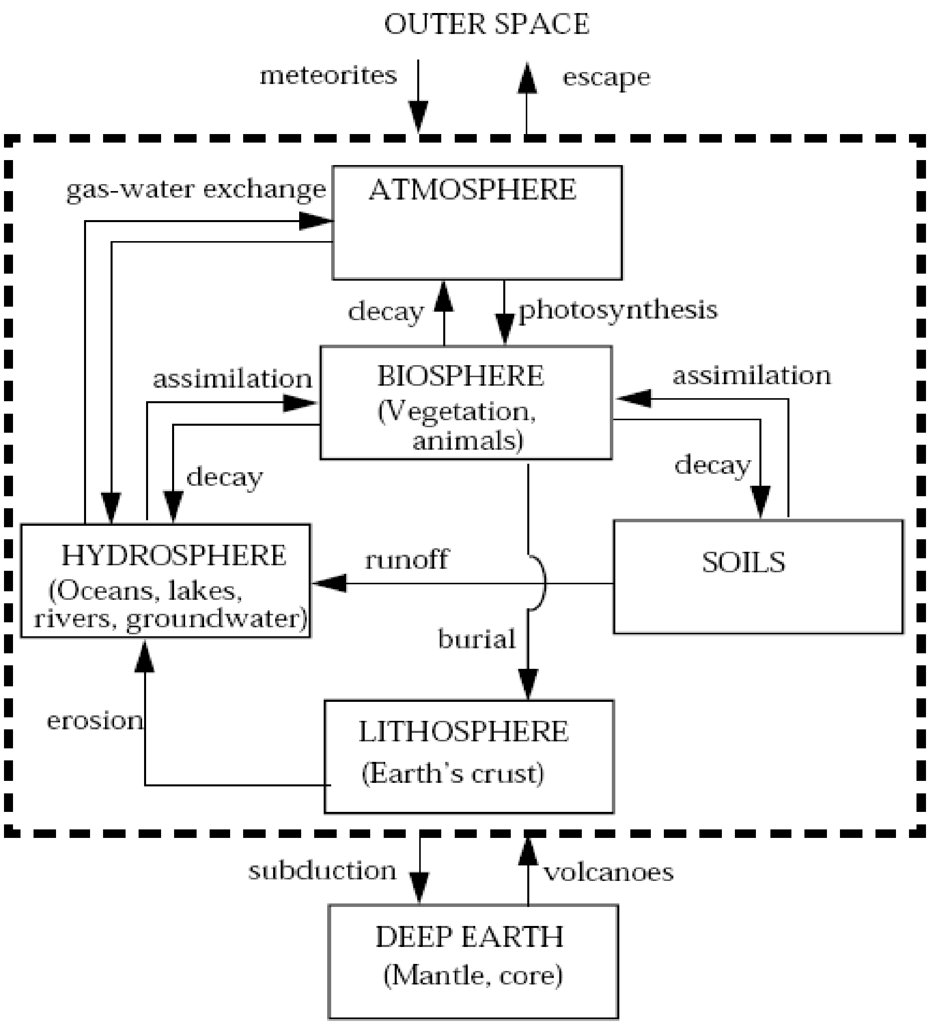
Jacob, chapter 8

Heintzenberg – The Life Cycle of the Atmospheric Aerosol

Exercises:

6:1 – 6:5, 8:1 – 8:6

Geochemical cycles

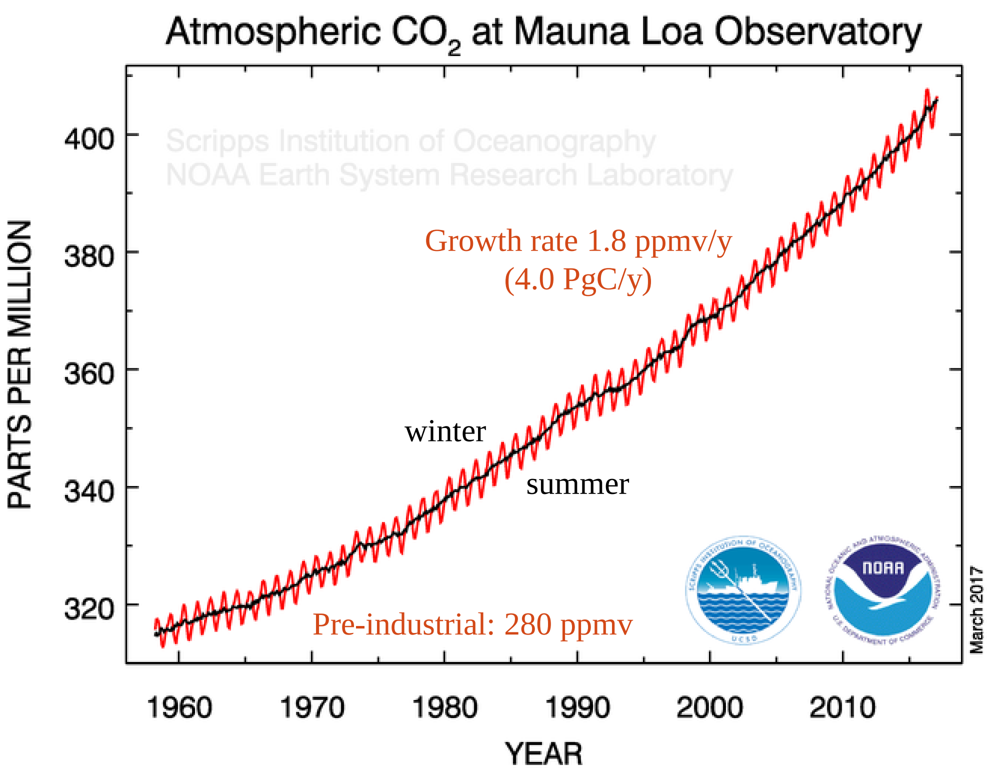


- Geochemical cycle – closed system
  - Chemical elements
  - Not chemical compounds
- Reservoir – Where do we find a chemical element
- Exchange – Describes the element migration between reservoirs
- The earth a closed system for most elements
  - Exchange with space negligible
  - Exchange with deep layers small (volcanism, continental shift)
- In practice: most interaction between surface reservoirs

I will talk much about the Carbon cycle

…why?

C release increases the atm CO_2 conc



- CO_2 sources (anthropogenic):

Fossil fuels: 6.0 ± 0.5 PgC/y

Deforestation: 1.6 ± 1.0 PgC/y

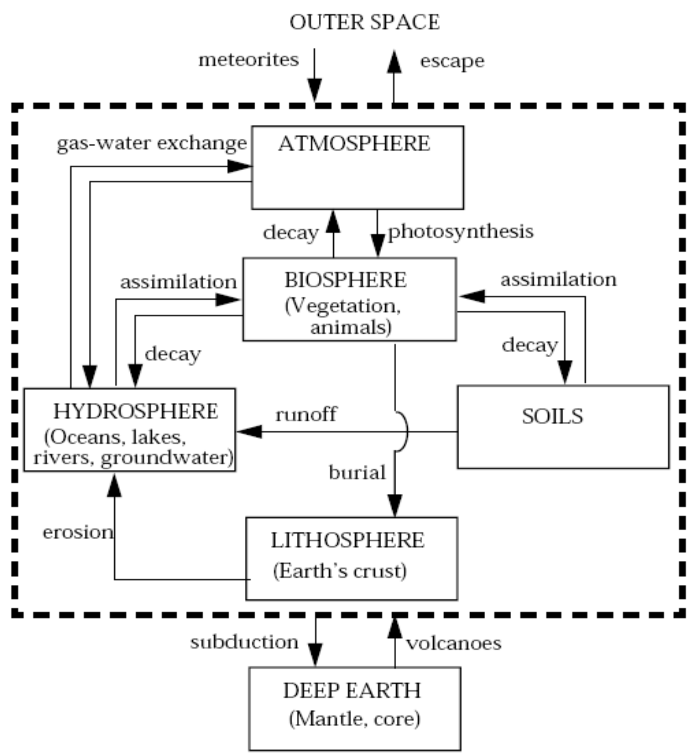
- Mass balance:

$$\frac{dm_{CO_2}}{dt} = \Sigma\text{sources} - \Sigma\text{sinks} = 4\text{PgC/y}$$

Σsinks = 6.0 + 1.6 - 4.0 = 3.6PgC/y

…part of the Carbon goes elsewhere

Which are the largest reservoirs of Carbon?

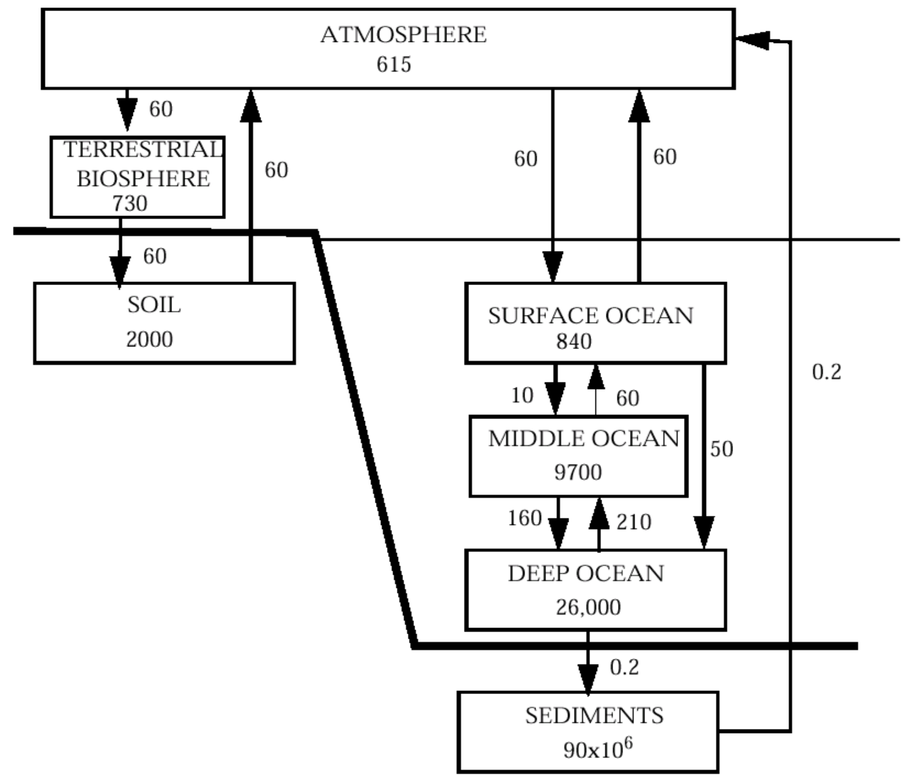


…and which are the sinks?

Pre-industrial Cycle of Carbon

- The carbon cycle
  - The sediments – Dominating carbon reservoir
  - The ocean reservoirs
  - Soil + biosphere
  - Small fraction in the atmosphere (CO_2, CH_4)

Units: Pg; Pg/y



- Uptake of atmospheric CO_2:
  - dissolution in the oceans
  - increased biosphere mass

Exercise

How long time is needed to restore carbon to the sediments after combustion of fossil fuel?

Residence time

- (mass in the box) / outflow

Only one flow to the sediments

- 0.2 Pg C/y from "Deep ocean"

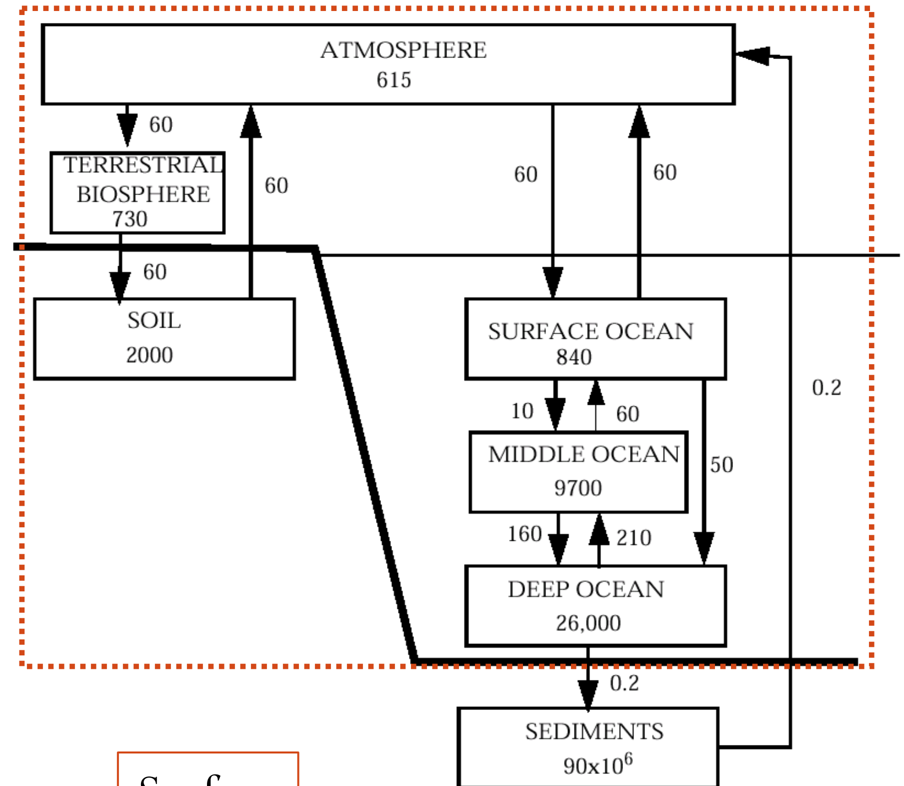
Combine to form reservoir "Surface"

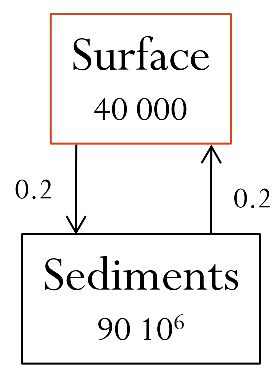
- Exchanges inside box becomes internal
- Sum up the masses of the new reservoirs
- m = 615 + 730 + 2000 + 840 + 9700 + 26 000 =

  = 40 000 Pg C

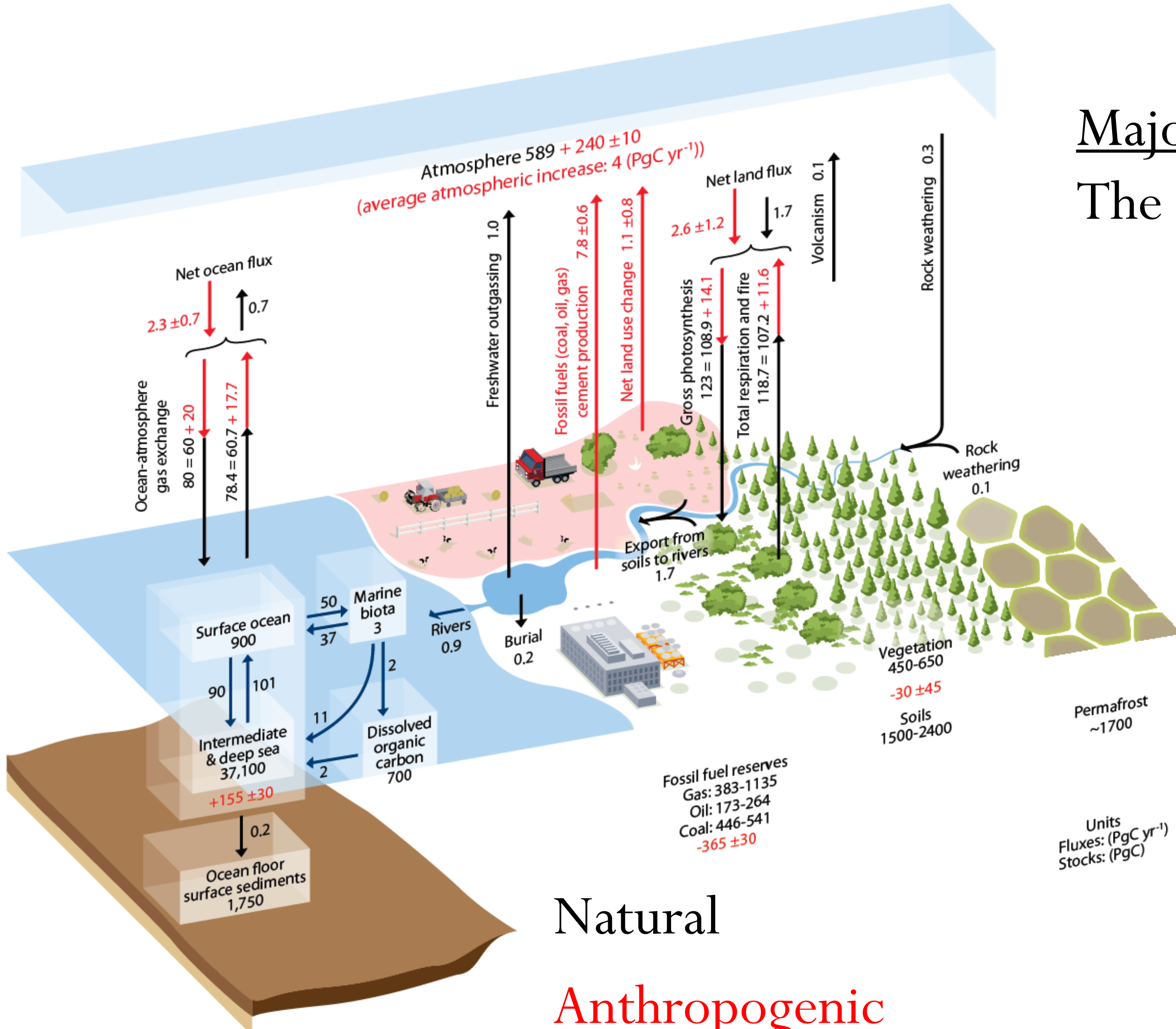
$\tau = m/F_{out} = 40\ 000/0.2 = 200\ 000$ y

Units: Pg; Pg/y





CO_2 Increase Changes the Balance



Natural

Anthropogenic

__Major sinks__

The ocean and vegetation

How much of the CO_2 ends up in the

…atmosphere?

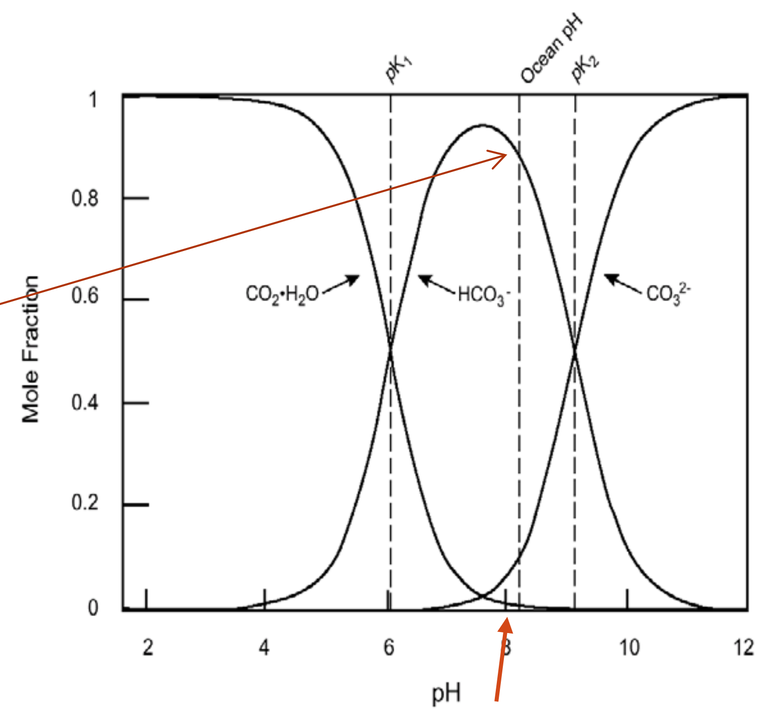
… oceans?

Dissolution of CO_2 in the Oceans

CO_2 dissolution in water …and dissociation

$CO_2 \overset{H_2O}{\Leftrightarrow} CO_2 \bullet H_2O$	Carbonic acid
$CO_2 \bullet H_2O \Leftrightarrow HCO_3^- + H^+$	Bicarbonate
$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$	Carbonate

Get different molar fractions depending on the pH of the ocean



Ocean pH 8.2 - Weathering of basic rocks

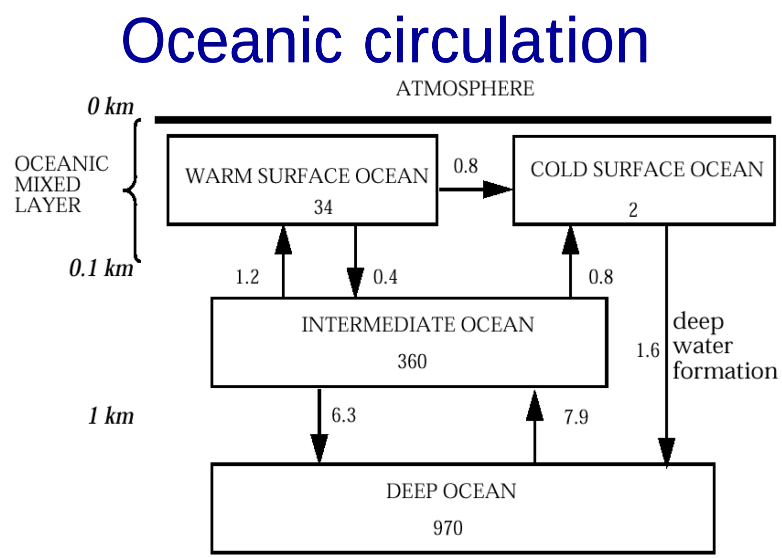
- Fraction atmospheric CO_2 (F)
  - Only 3% @ equilibrium
  - The rest in the ocean
- When considering acidification
  - ~30% of the C dissolves in the ocean

Mixing Within the Ocean

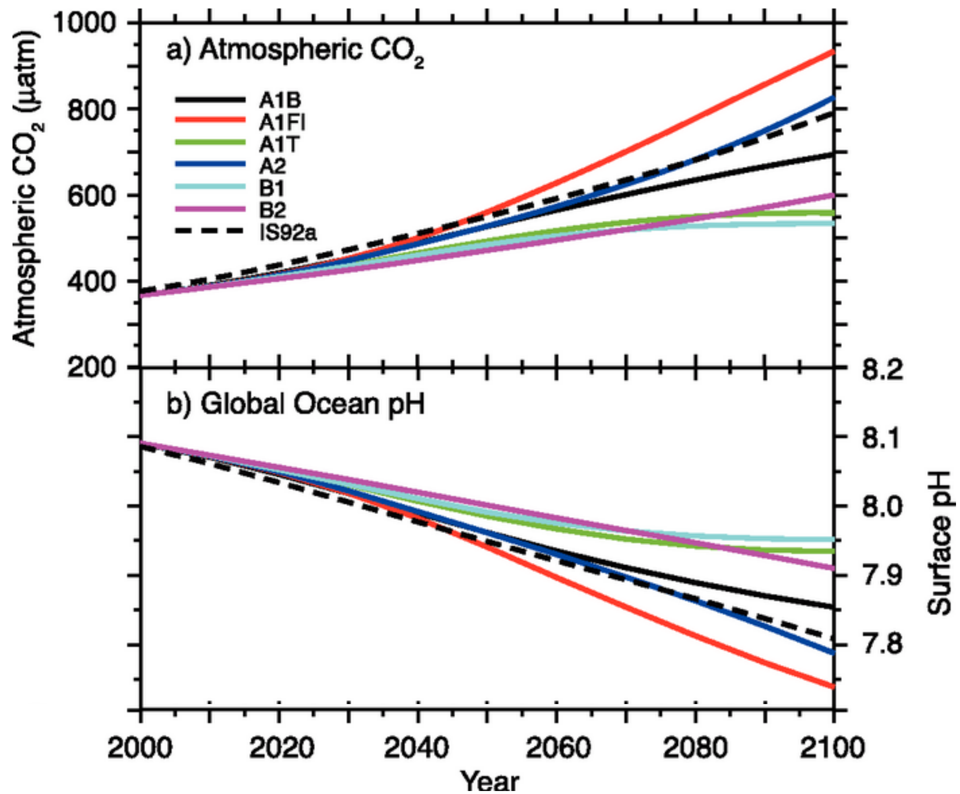
- Residence times
  - 18 y, surface ocean (warm + cold)
  - 40 y, Intermediate ocean
  - 120y, Deep ocean

- Thus, a gradient with more C stored close to the surface
  - Equilibration takes ~200 y

- Further sink of CO_2 by sedimentation of organic matter from phytoplankton photosynthesis



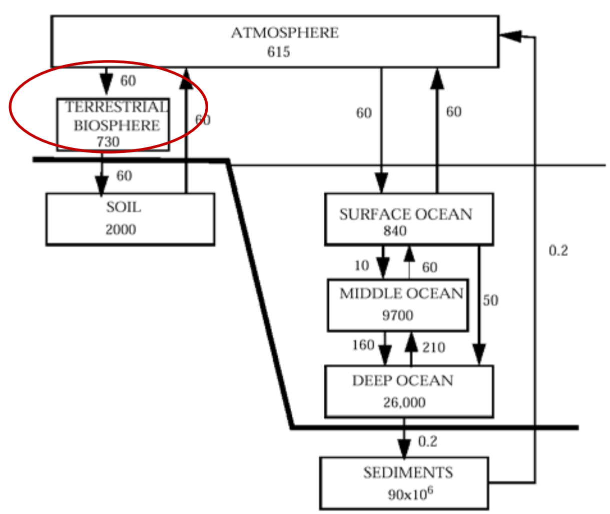
Projections for the Oceans pH



<u>Impact on the sink:</u>

The decrease in pH will result in less solubility of CO_2 leading to a larger fraction in the atmosphere

What about the biosphere?



CO_2 Uptake by the Biosphere

NPP (net primary productivity):

photosynthesis - respiration

NPP ≈ 60 Pg C/y

- Compare fossil fuels 6 Pg C/y

NPP balanced by biological decay

…but human impact increases the NPP

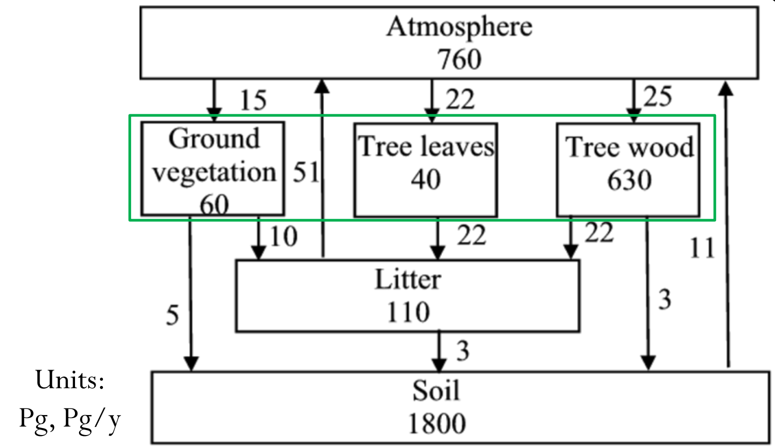
- Possible explanation for the missing sink of 20% (atmosphere 50%, ocean 30%)

NPP increases due to:

- Conversion of agricultural land to forest
- Increased photosynthesis due to climate change (temp)
- Increased CO_2 fertilizes the biosphere

Exercise 6:4

Part of the cycle of carbon is shown. "Ground vegetation", "tree leaves" and "tree wood" represent reservoir "terrestrial vegetation". The inflow of atmospheric CO_2 into this reservoir represents the NPP of the terrestrial biosphere.



a: Calculate the residence time of carbon in the terrestrial vegetation reservoir against transfer to the litter and soil.

Mass in the ***terrestrial vegetation*** reservoir:

- m = 60 + 40 + 630 = 730 Pg C
- Outflows to ***litter*** and ***soil***:

$$F_{out} = 10 + 22 + 22 + 5 + 3 = 62 \text{ Pg C / y}$$

$$\tau = m/F_{out} = 11.8 \text{ y}$$

b: Tree leaves eventually fall to produce litter. What is the dominant fate of carbon in the litter? What fraction is incorporated into the soil?

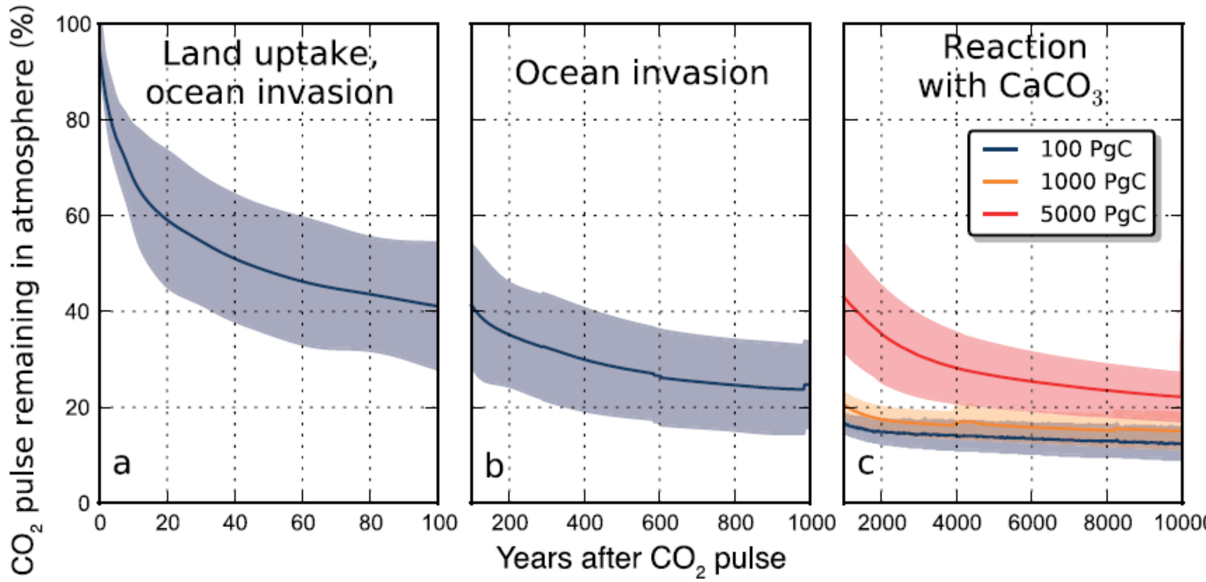
Carbon outflows from ***litter***:

- ***Atmosphere***: 51 Pg C / y
- ***Soil***: 3 Pg C / y

Dominant fate: CO_2 in the ***atmosphere***

Fraction to ***soil***: 3 / (3 + 51) = 5.6%

Time Scales of Carbon Sinks



Box 6.1, Table 1 | The main natural processes that remove CO_2 consecutive to a large emission pulse to the atmosphere, their atmospheric CO_2 adjustment time scales, and main (bio)chemical reactions involved.

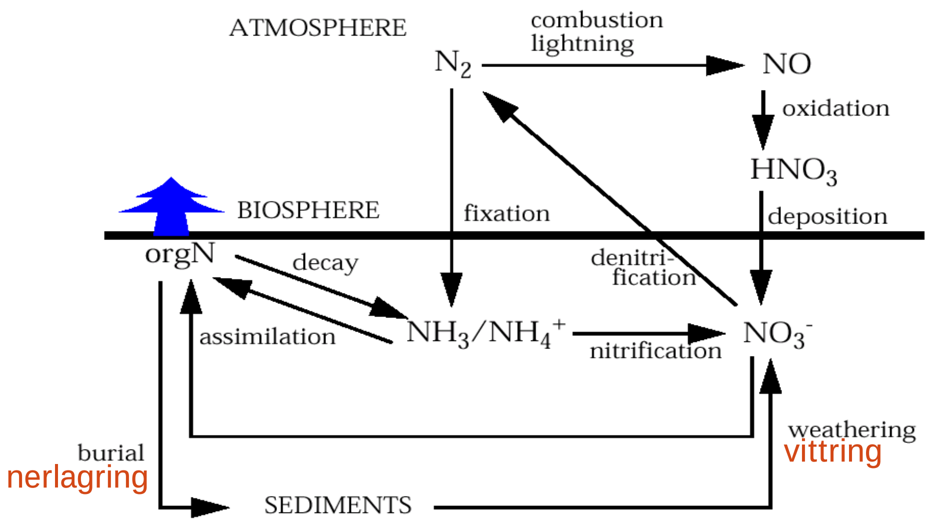
Processes	Time scale (years)	Reactions
Land uptake: Photosynthesis–respiration	$1–10^2$	$6CO_2 + 6H_2O$ + photons $\rightarrow C_6H_{12}O_6 + 6O_2$ $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ + heat
Ocean invasion: Seawater buffer	$10–10^3$	$CO_2 + CO_3^{2-} + H_2O \rightleftharpoons 2HCO_3^-$
Reaction with calcium carbonate	$10^3–10^4$	$CO_2 + CaCO_3 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$
Silicate weathering	$10^4–10^6$	$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2$

Summary of CO_2

- Atmospheric CO_2 conc. increase by 1.8 ppmv/y, corresponding to 4 PgC/y
- CO_2 emissions (7.6 PgC/y) from fossil fuels (6) and deforestation (1.6)
- ~ 50% of emissions stay in the atmosphere
- ~ 30% dissolved in the oceans
- ~ 20% (?) taken up by increased vegetation

The Nitrogen Cycle

- Nitrogen – important as a component in amino acids
- N_2 highly stable to biological conversion
- Important processes making nitrogen chemically and biologically available:



Fixation by specialized bacteria:

- Reduction: $N_2 \rightarrow NH_3$
- Nitrification: $NH_3 \rightarrow NH_4^+ \rightarrow NO_3^-$
- Denitrification: $NO_3^- \rightarrow N_2$

Fixation by high temperature processes and lightening forms NO from N_2

- $NO \rightarrow HNO_3 \rightarrow$ deposition
- Industrial areas: Combustion engines fixates more N_2 than the natural nitrification

- Sediment: exchange by burial (dead organisms) and weathering

NH_3 Ammonia
NH_4 Ammonium
HNO_3 Nitric acid

Problem 6.5 (in Jacob)

6.5.1. What is the residence time of nitrogen in each of the reservoirs?

$\tau = m/F_{out}$

Atmospheric N

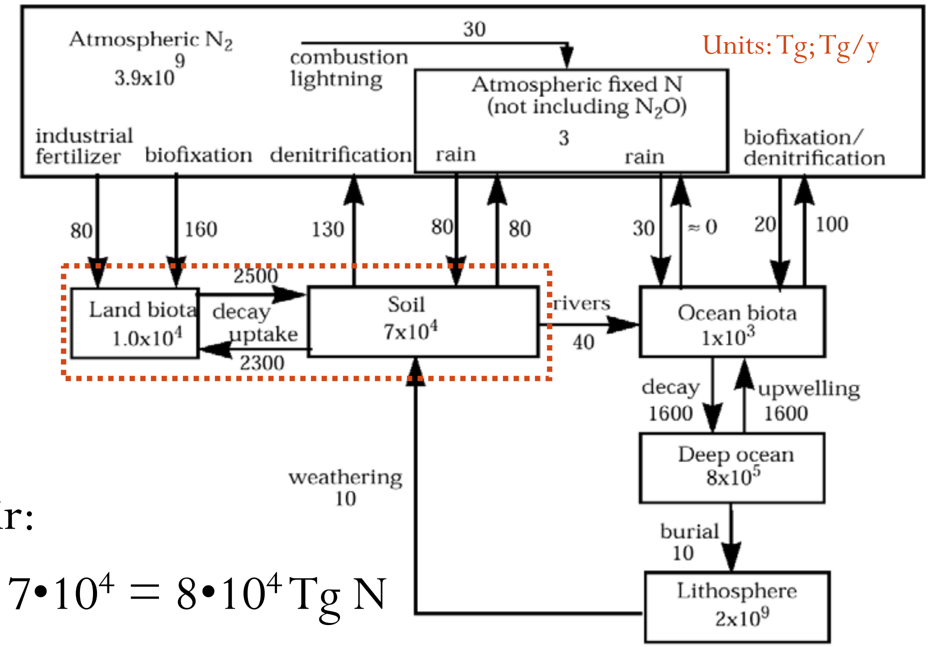
- N_2: $3.9 \bullet 10^9/(80+160+30+20) = 13 \bullet 10^6$ y
- Atmos. fixed N: $3/(80+30) = 0.03$ y (1.5 weeks)

Large N_2 reservoir with small flows → N_2 stability controls atmospheric concentration

The other reservoirs:

- Land biota 4 y
- Soil 27 y
- Ocean biota 0.59 y
- Deep ocean 500 y

6.5.2. Form a "land" reservoir as the sum of "land biota" and "soil". Calculate the residence time in the land reservoir. Why is the residence time much longer in the combined reservoir?



Land reservoir:

$m = 1 \bullet 10^4 + 7 \bullet 10^4 = 8 \bullet 10^4$ Tg N

$F_{out} = 130 + 80 + 40 = 250$ Tg N / y

$\tau = m/F_{out} = 320$ y

Large internal flows of the combined land reservoir do not affect the residence time

Aerosols and Aerosol Particles

An aerosol is a suspension of fine solid or liquid **particles in air** (or another gas).

The suspended particles are called **aerosol particles.**

- Sizes of 0.001 – 100 µm
  - Lower limit: Enough material to form a stable system
  - Upper limit: Low sedimentation velocity ($v < 25$ cm/s)

Atmospheric Aerosol

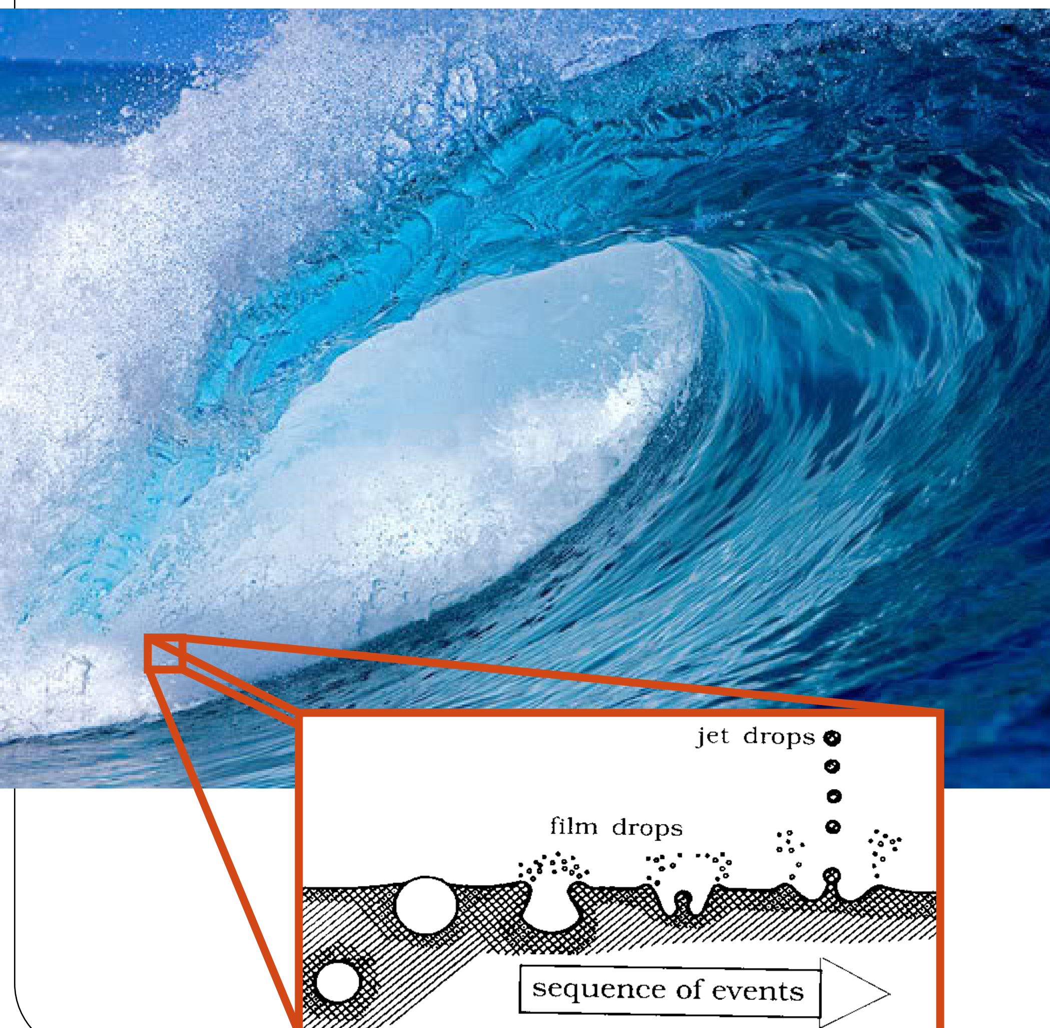
- Particle number concentrations
  - Over the oceans: ~100 cm^{-3}
  - Urban environment: up to 1 million cm^{-3}
- Mass concentrations
  - Over the oceans: ~10 $\mu g/m^3$
  - Urban environment: 10 – 1000 $\mu g/m^3$

- Air close to the Earth's surface: ~1 kg/m^3 $\Rightarrow$ Aerosol Particles are trace constituents in the atmosphere

- Environmental effects
  - Climate
  - Acidification
  - Health
  - Visibility

Natural Aerosol Sources

Sea spray



Windblown dust

Which are the most important

sources

of aerosol particles from

human activities?

Human Activities

- Combustion particles
  - Energy production
  - transportation
- Particle types
  - Primary – Direct emission of particles
  - Secondary – Emission of gases that are transformed in the atmosphere (e.g. SO_2 and NO_x)

Deposition of Particles

Sinks of atmospheric aerosol

Dry deposition

- Sedimentation – important for large particles
- Diffusion (random motion due to collision with molecules) - small particles
- Also: impaction and interception

- Dry deposition
  - Inefficient sink for particles smaller than 1 µm diameter
  - Important for large particles due to sedimentation

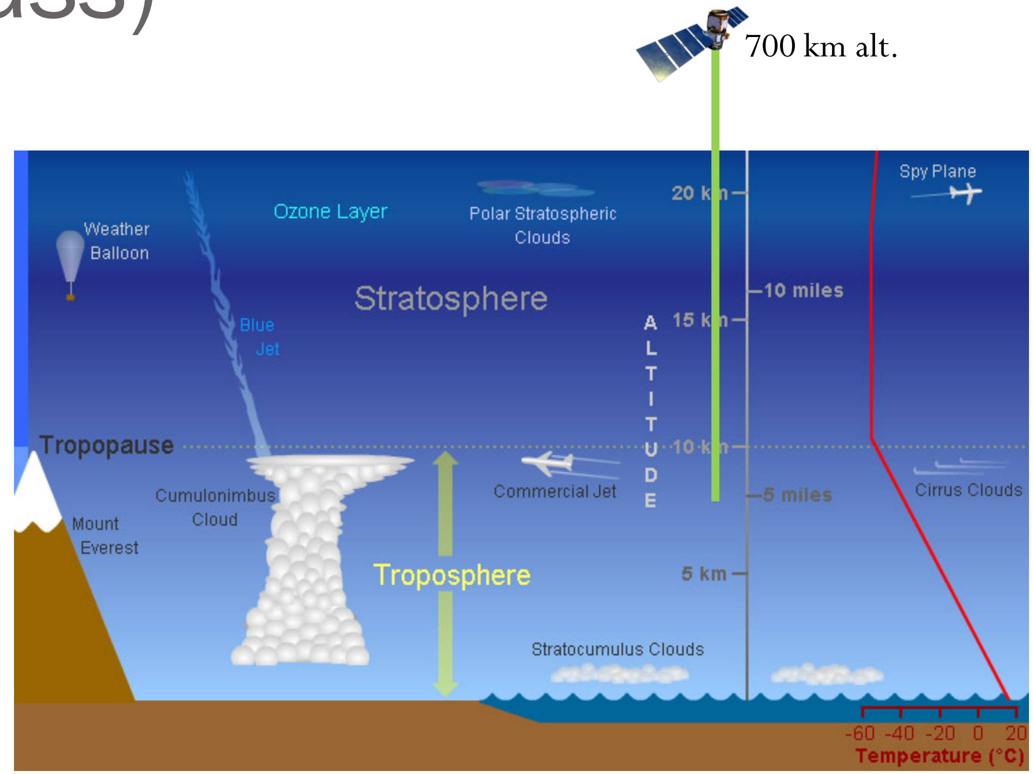
Wet deposition

- Cloud drops form by condensation of water vapour on particles
- Precipitation (~ 10% of all clouds) – particle-containing large drops fall to the ground (in-cloud-scavenging)
- Particles below clouds caught by falling drops (below-cloud-scavenging)

- Precipitation efficiently cleans the atmosphere from particles

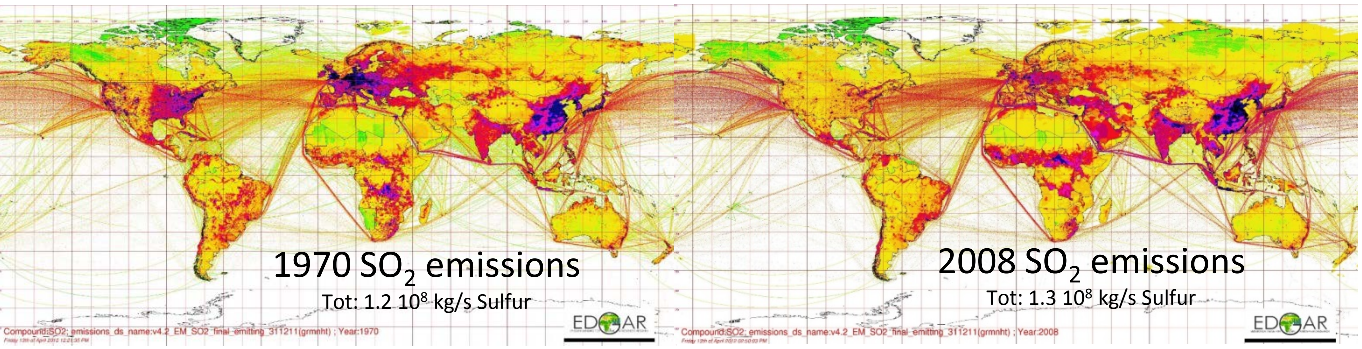
Residence times due to wet deposition (by mass)

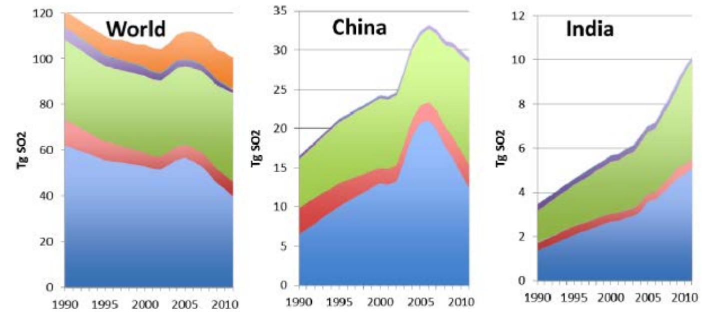
reservoir	τ_{wet}	unit
< 1.5 km	0.5-2	days
lower troposphere	2-7	days
upper troposphere	1-2	weeks
tropopause	3-4	weeks
lower stratosphere	1-2	months
upper stratosphere	1-2	years



Wet deposition dominates over dry deposition for submicron particles

Sulphate in Atmospheric Particles

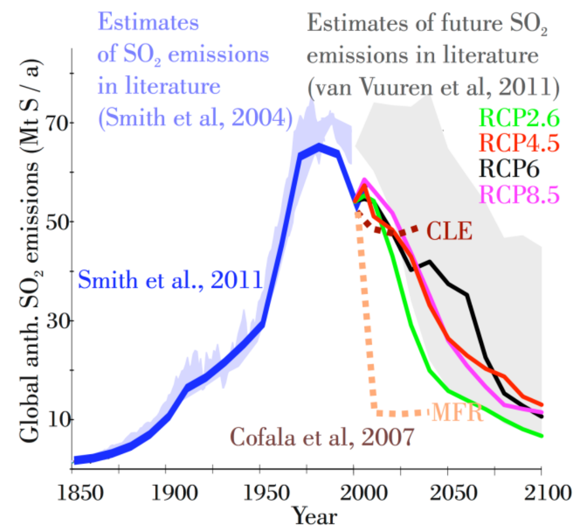




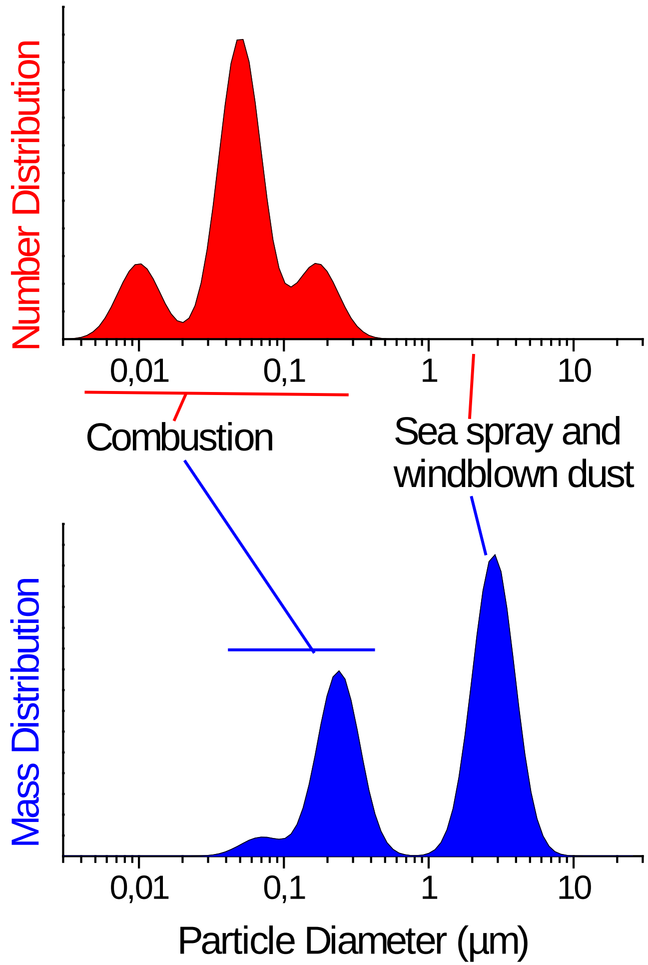
SO$_2$ (gas) and sulphate (particles)

- Sulphate important component of atmospheric aerosol
- Most of the sulphate formed in the atmosphere from gaseous SO$_2$
- Emissions by human activities mainly from industrialized regions
- Many changes over almost 40 years
- Total emissions approximately constant over the same period

- High sulphate conc. in the SO$_2$ emission regions
- Large fraction anthropogenic in these regions



Particle Size Distributions



- Human activity
  - Small particles
  - Large number
  - Components: sulphate, nitrate, organic
  - Contribute more to the total number
- Natural Sources
  - Large particles
  - Small number
  - Examples: mineral, sea spray
  - Contribute more to the total mass

Lecture tomorrow @ 10-12

THE END

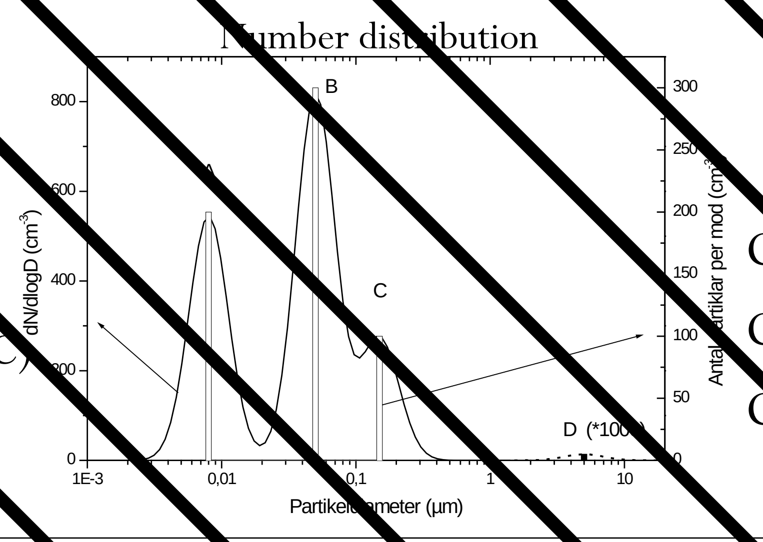
Exercise 8:6

The Figure shows a typical atmospheric aerosol size distribution. Usually 4 modes are present: Ultrafine mode (A), Aitken mode (B), Accumulation mode (C) and Coarse mode (D). The modes result from different types of sources and aerosol-dynamical processes.

a: To which mode (A – D) do the following sources primarily contribute:

Sea-spray (1), formation of new particles in the atmosphere (2), windblown dust (3), combustion (4) and aged particles smaller than 1 µm diameter (5)

1) Coarse mode (D)
2) Ultrafine mode (A)
3) Coarse mode (D)
4) Aitken mode (B)
5)Accumulation mode (C)



b: The bars show the number of particles (right Y axis (C_{ai}): 200, 300, 100 and 0.005 particles/ cm³) at the maximum of each mode (d_i = 0.008, 0.05, 0.15 and 5 µm diameter). Approximate the distribution by these discrete values and calculate the mass concentration C_{mi} of each mode assuming particle density of 1.5 g/cm³.

c: Discuss the sources in (a) with respect to importance in terms of mass and number.

b: $C_{mi} = C_{ai} m_i =$

$= C_{ai} \rho 4\pi (d_i/2)^3/3$

Mode A:

- $C_{ai} = 200\ cm^{-3} = 200 \cdot 10^6\ m^{-3}$
- $\rho = 1.5\ g/cm^3 = 1500\ kg/m^3$
- $d_i = 0.008\ \mu m = 8 \cdot 10^{-9}\ m$

$C_{mA} = 8 \cdot 10^{-14}\ kg/m^3 = 0.08\ ng/m^3$

$C_{mB} = 29\ ng/m^3$, $C_{mC} = 270\ ng/m^3$

$C_{mD} = 490\ ng/m^3$

c: 1) mass
2) number
3) mass
4) number
5) Mass and number