Geochemical Cycles, Aerosol

Geochemical cycles:

- Reservoirs and exchange
- Carbon
- Nitrogen

Aerosol:

- What is an aerosol?
- Sources and sinks of aerosol particles
- Description of the atmospheric aerosol

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

Geochemical cycles:

Jacob, chapter 6

Aerosol:

These overheads – Aerosol part

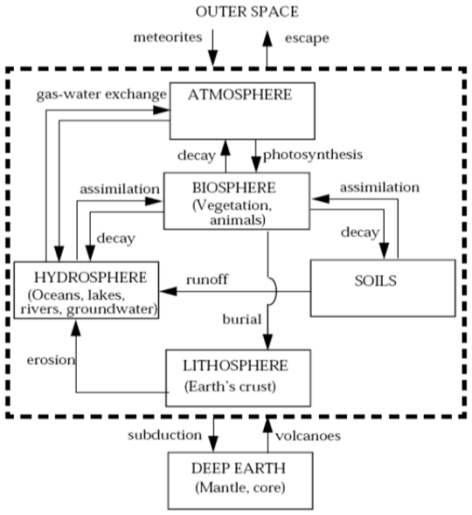
Jacob, chapter 8

Heintzenberg – The Life Cycle of the Atmospheric Aerosol

Exercises:

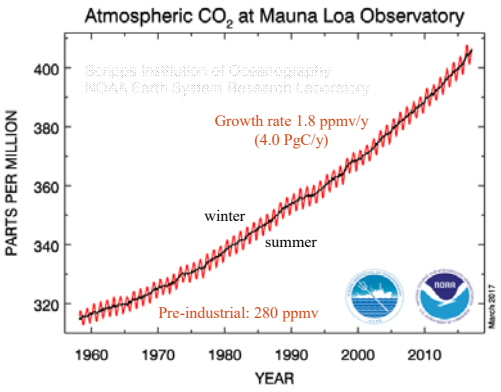
6:1 – 6:5, 8:1 – 8:6

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

Atmospheric CO_2 Concentration



- 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

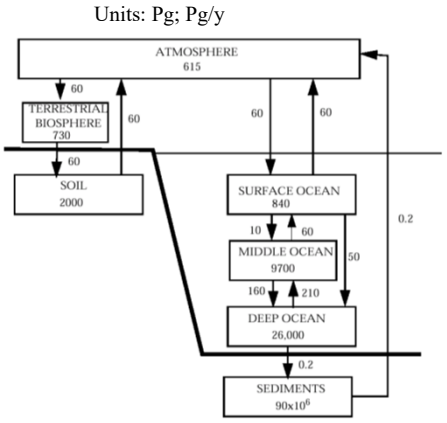
- The entire emission not accumulated in the atmosphere
  - Where does the CO_2 go?
  - → Geochemical cycle of carbon

Problem

1. **Which are the largest carbon reservoirs on earth?**
2. **Which are the main sinks for CO_2?**

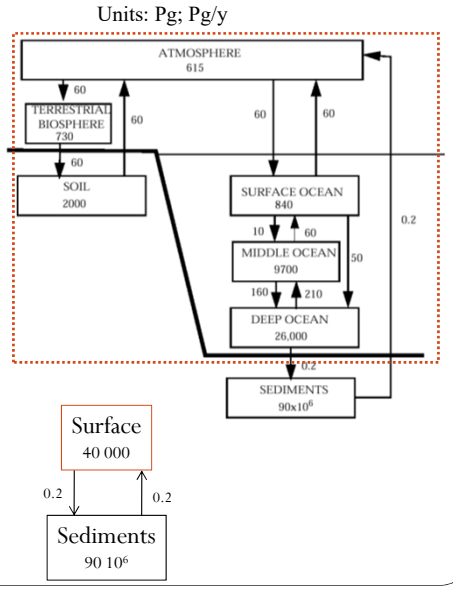
Pre-industrial Cycle of Carbon

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



Fossil fuel combustion

- carbon from the sediments
- emitted to the atmosphere as CO_2

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

Dissolution of CO_2 in the Oceans

CO_2 partial pressure at sea level

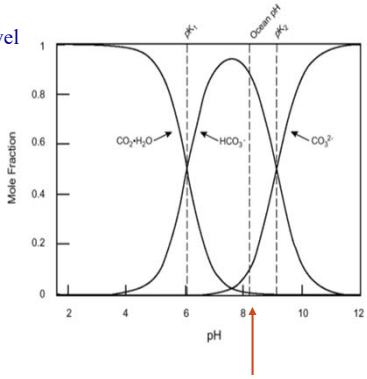
CO_2 dissolution in water

$$CO_2 \overset{H_2O}{\Leftrightarrow} CO_2 \bullet H_2O \qquad K_H = [CO_2 \bullet H_2O]/P_{CO_2}$$

$$CO_2 \bullet H_2O \Leftrightarrow HCO_3^- + H^+ \qquad K_1 = [HCO_3^-][H^+]/[CO_2 \bullet H_2O]$$

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ \qquad K_2 = [CO_3^{2-}][H^+]/[HCO_3^-]$$

- What fraction of atmospheric CO_2 to the oceans?



Ocean pH 8.2 - Weathering of basic rocks

CO_2 Dissolution at Equilibrium

- Fraction atmospheric CO_2 (F):

  $F = n_{CO2}(g)/(n_{CO2}(g) + n_{CO2}(aq))$

- Concentration dissolved CO_2:

  $[CO_2(aq)] = [CO_2 \bullet H_2O] + [HCO_3^-] + [CO_3^{2-}]$

  $= K_H P_{CO2} (1 + K_1/[H^+] + K_1K_2/[H^+]^2)$

- Assume the atm in equilibrium with the entire ocean ($V_{OC} = 1.4 \times 10^{18}$ m^3):

  $n_{CO2}(aq) = V_{OC}[CO_2(aq)]$

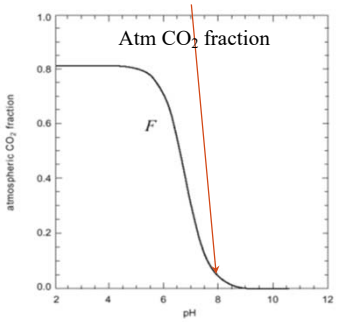
  $n_{CO2}(g) = C_{CO2}(g)n_a = n_a P_{CO2}/P$

- We get:

$$F = \frac{1}{1 + \frac{V_{OC} P K_H}{n_a}\left(1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}\right)}$$

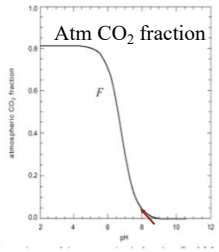
- With typical values of K_H, K_1, K_2

F = 0.03 !???



Dissolved CO_2 Fraction

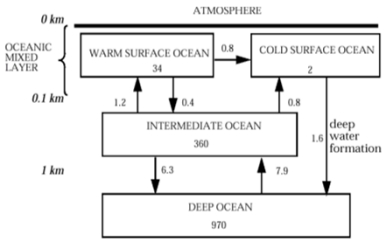
- F = 0.03, but
- CO_2 affects oceanic pH
  - Increased CO_2 ⇒ lower **pH** ⇒ incr. F
- Re-formulate question: What fraction of a CO_2 increase is taken up?
  - Form $f = dn_{CO2}(g)/(dn_{CO2}(g) + dn_{CO2}(aq))$
  - In a similar manner: $f = 0.28$
- Exchange with the entire ocean crude approximation
  - Well mixed 100 m deep surface layer
  - Mix the entire ocean: ~ 200 years
- Best estimate: $f = 0.7$, i.e.
- Oceanic uptake by 30 % of the CO_2 emissions



$$f = \frac{1}{1 + \frac{V_{OC} P K_H K_1 K_2}{n_a (1 + 4K_2/[H^+])[H^+]^2}}$$

Small change of pH and F induced:
f >> F due to the entire population affected

Oceanic circulation



Units: 10^{15} m^3, 10^{15} m^3 / y

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

Possible explanation for the missing sink of 20%:

Indications of increased NPP due to:
- Conversion of agricultural land to forest
- increased photosynthesis due to climate change (temp)
- Increased CO_2 might fertilize the biosphere

Summary 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

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.

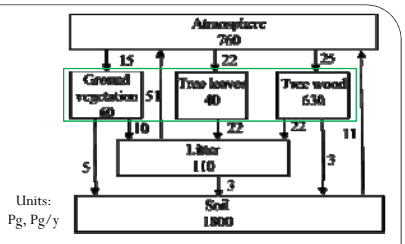
a: Calculate the residence time of carbon in the terrestrial vegetation reservoir against transfer to the litter and soil.

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 Pg C / y

$\tau = m/F_{out} = 11.8$ 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***:

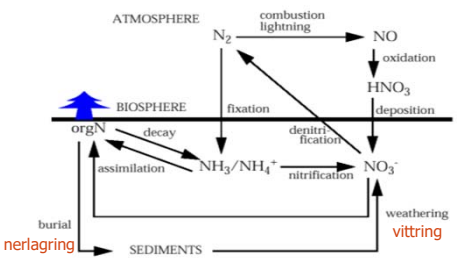
- ***Atmosphere***: 51 Pg C / y
- ***Soil***: 3 Pg C / y

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

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

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

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

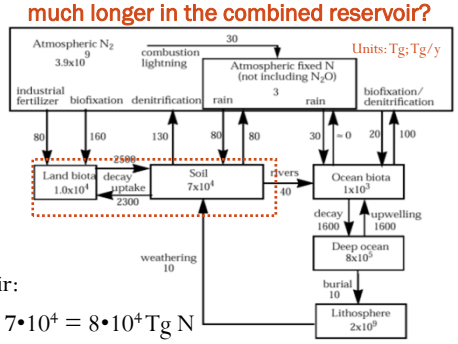
- N_2: $3.9 \cdot 10^9/(80+160+30+20) = 13 \cdot 10^6$ y
- Atmos. fixed N: $3/(80+30) = 0.03$ y (1.5 weeks)

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:

$m = 1 \cdot 10^4 + 7 \cdot 10^4 = 8 \cdot 10^4$ 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

Problem 6.5.3

Humans last century have affected the nitrogen cycle by cultivation of N-fixing crops and use of industrial fertilizers. As a result the land biofixation rate increased from 110 to 240 Tg N / y. Fossil fuel combustion has increased N-fixation from 5 to 30 Tg N / y. Estimate the resulting percentage increases over the past century in the global nitrogen contents of the land and the ocean reservoirs. Conclude as to the extent of global fertilization of the earth's biosphere by human activity.

Increased biofixation affects the land reservoir: $F_{bio}(land) = 240 - 110 = 130$ Tg N / y

Fossil fuel combustion produces fixed N in the atmosphere: 80 Tg N/y to ***land***, 30 Tg N/y to ***ocean***

=> $F_{fossil}(land) = (30 - 5) \cdot 80/(80+30) = 18$ Tg N / y

$F_{land} = 130 + 18 = 148$ Tg N / y

$\tau_{land} = 320$ y => Most of the N accumulates over 100 y

$\Delta m = 100 \cdot 148 = 14\,800$ Tg N over 100 y

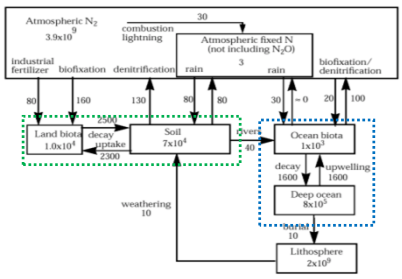
$m_{land} = 80\,000$ Tg N

Increase: $80\,000 / (80\,000 - 14\,800) = 1.23$; 23% increase

$F_{ocean} = (30 - 5) - 18 = 7$ Tg N / y

$\tau_{ocean} = 8 \cdot 10^5/(100 + 10) = 7000$ y >> 100 y => $\Delta m = 700$ Tg

causing ocean fixed N a 0.1% increase

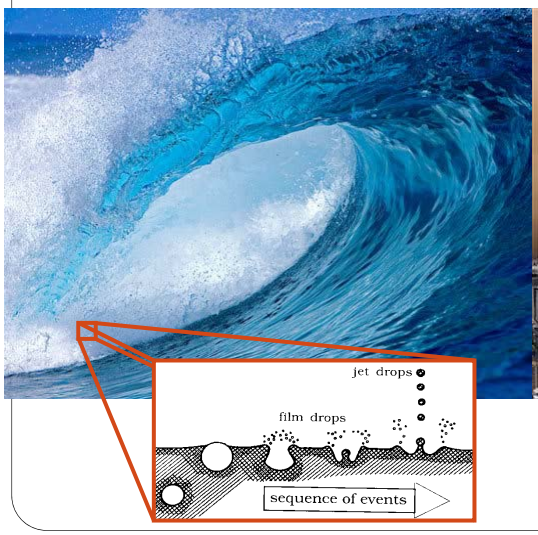


Atmospheric Aerosol

- **Aerosol:** Multiphase system consisting of solid or liquid particles suspended in a gas
  - 0.001 – 100 µm particles
    - Lower limit: Enough material to form a stable system
    - Upper limit: Low sedimentation velocity (v < 25 cm/s)
- 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 ⇒ Aerosol Particles are trace constituents in the atmosphere
- Environmental effects
  - Climate
  - Acidification
  - Health

Natural Aerosol Sources

Sea spray



Windblown dust

Problem

Which, do you think, are the most important sources of aerosol particles from human activities?

Human Activities

- Combustion particles
  - Energy production
  - transportation
- Particle types
  - Primary – 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

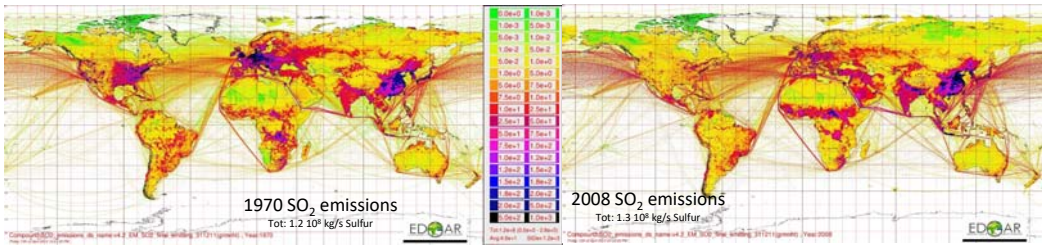
- Cloud drops form by condensation of water vapour on particles
- Precipitation (~ 10% of all clouds) – particle-containing large drops fall to the ground (in-cloud-scavenging)
- Particles below clouds caught by falling drops (below-cloud-scavenging)

- 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

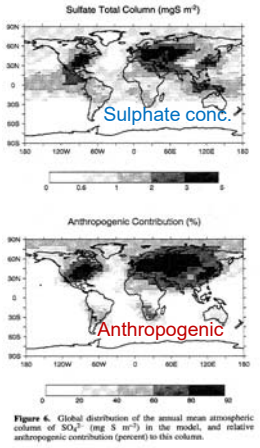
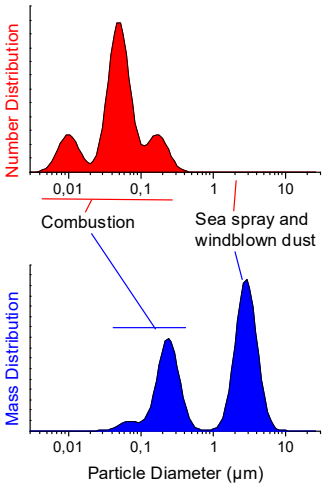


Figure 6. Global distribution of the annual mean atmospheric column of SO_4^{2-} (mg S m^{-2}) in the model, and relative anthropogenic contribution (percent) to this column.

Particle Size Distribution



- Natural Sources
  - Large particles
  - Small number
  - Examples: mineral, sea spray
- Human activity
  - Small particles
  - Large number
  - Components: sulphate, nitrate, organic

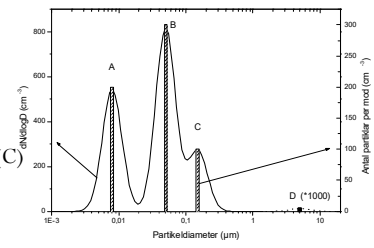
Exercise 8:6

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/ cm^3) 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/cm^3.

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