I. Biogeochemical cycles (Saleska)
   A. Method: Box models & Residence time
   B. Budgets and cycles: water, carbon, nitrogen
   C. Ecological Stoichiometry

II. Thermodynamics of Biogeochemical Reactions (guest Prof. Chorover)

I. What is Biogeochemistry?

Biogeochemistry = the study of how the cycling of elements through the earth system (water, air, living organisms, soil and rock) is governed by physical, chemical, geological and biological processes

Key Names

Vladimir Vernadsky (1863-1945): Russian scientist known as the “father of biogeochemistry”, invented the terms geosphere, biosphere, and “noosphere”

G. Evelyn Hutchinson (1903-1991): famous limnologist (considered to be founder of limnology) (also studied the question of how biological species coexist)
A. Box models and Residence times

Steady-state: when flow (of water, nutrients, energy) through a ‘box’ (a lake, the atmosphere, a population or organisms) is steady, i.e.:

\[ \text{inflow } (F_{in}) = \text{outflow } (F_{out}) \]

\[ \rightarrow \text{ box size (or stock } S \text{) doesn't change} \]

Then residence time \( \tau \) (the time it would take for the flow to fill the box if the box were empty) is the ratio of the stock in the box, to the flow:

\[ \tau = \frac{S \text{ grams}}{F \text{ grams sec}^{-1}} = \text{ sec} \]

(Using consistent units)

A. Box models and Residence times

Example 1: Students at University

Given 30,000 student-body population (stock), about how many graduate each year? (what is the flow?)

Example 2: Land and sea autotrophs have roughly equal global productivities (\( \text{NPP}_{\text{land}} \approx 60 \text{ PgC/yr}; \text{NPP}_{\text{sea}} = 50 \text{ PgC/yr} \)), but big differences in total biomass carbon (560 PgC on land vs 3 PgC in the sea)

Why? Residence time! Land: \( \frac{560 \text{ PgC}}{60 \text{ PgC/yr}} \approx 10 \text{ yrs}; \) Sea: \( \frac{3 \text{ PgC}}{50 \text{ PgC/yr}} = 0.06 \text{ yrs} \)

(24 days)

Example 3: Zooplankton (residence time 6 mo) graze phytoplankton (residence time 2 weeks) in a lake. Zooplankton consume 40% of phytoplankton NPP, with a carbon-use efficiency of 25% (meaning 25% is converted to biomass)

What is the ratio of the zooplankton to phytoplankton population biomass?

For more: see J. Harte, 1985. *Consider a Spherical Cow*
B. Budgets and Cycles

How important is your biochemical/microbial process?
-- Compare it to the size of appropriate cycle!
(can be done locally and globally)

Overview: global cycles of nitrogen, water, and carbon (including some associated stock, flow, and residence times)
The Global water cycle

Chapin, et al. 2002

Oceans: 1.350 x 10^9

groundwater: 15.3 x 10^6

Atmosphere: 13,000

Precip: 385,000

Evaporation: 425,000

Runoff: 40,000

Vegetation: 10,000

Soil water: 120,000

Lakes: 230,000

Ice: 33 x 10^6

Atmospheric turnover time: 13,000 / 496,000 = 0.026 yrs ≈ 1 week

Opposite is true over the ocean (precip < evapotranspiration)

40,000

Atmospheric supply to Land (precipitation) is greater than land return to atmosphere (evapotranspiration)

In km³ (pools) and km³/yr (fluxes)
Facts about the global water cycle

496 x 10^3 km^3

- Global precip: 385,000 (ocean) + 111,000 (land)
  \[
  \frac{496 \times 10^3 \text{ km}^3}{510 \times 10^6 \text{ km}^2} = 0.97 \times 10^{-3} \text{ km}
  \]

- Land area is 148 x 10^6 km^2 \rightarrow \frac{111}{148} = 0.75 \text{ m}
  
  average land precip
  - Comparison: Tucson gets 0.30 m,
  - tropical forests 2 or 3 m

\[\approx 1 \text{ meter of precip (global average)}\]

Chapin, et al. 2002
Overview: The Modern Global carbon cycle (1990s)

Values in black are natural, **values in red** are anthropogenic

Note: 1990s values (IPCC 2007, Ch. 7)

What is residence time of C in atmosphere?

One estimate is from land+ocean flux: 120+70=190; 597/190 ≈ 3yrs

**BUT:** this is not an estimate of removal rate to ocean of excess CO₂ (2.2).

Better: 597 / 2.2 = 270 years.

**But in truth, for CO₂, no single residence time.**
What is residence time of C in atmosphere?
One estimate is from land-ocean flux: \(120+70=190; \frac{597}{190} \approx 3 \text{ yrs}\)
BUT: this is not an estimate of removal rate to ocean of excess CO\(_2\) (2.2).
Better: \(\frac{597}{2.2} = 270 \text{ years}\).

BUT in truth, for CO\(_2\), no single residence time.

Carbon Residence times:
Land Veg: (stock)\(560/NPP(60) = 9.3 \text{ yrs}\)
Land Soil: \(1740/60 = 30 \text{ yrs}\)
Marine biota: \(3/50 = 0.06 \text{ y} = 21 \text{ d}\)
All surface ocean: \(900/(70+100) = 5 \text{ yrs}\)
Deep Ocean: \(37,000 / 100 = 370 \text{ years}\)
Geosphere: \(15 \times 10^6 / 0.2 = 75 \text{ Myrs}\)

Values in black are natural, values in red are anthropogenic

Note: 1990s values (IPCC 2007, Ch. 7)

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Biological flows of Nitrogen

\(N_2 (78\%) + \text{trace } N_2O, NH_3, NO_x\)

Soil solution: \(NO_3^- (\text{nitrate}) \quad NH_4^+ (\text{ammonium})\)

Plants/soil organic matter: organic N

Uptake

Mineralization

Uptake

Microbial

Inorganic N (soil solution)
\(NH_4^+ \rightarrow NO_3^- (\text{nitrification})\)

Biological nitrogen fixation

Dissimilative denitrification (N\(_2\), N\(_2O\))
Beyond Carbon: Scientists Worry About Nitrogen’s Effects

“The nitrogen dilemma is not just thinking that carbon is all that matters. But also thinking that global warming is the only environmental issue. The weakening of biodiversity, the pollution of rivers... Smog. Acid rain. Coasts. Forests. It’s all nitrogen.”

- Peter Vitousek

Human alteration of terrestrial N-cycle is LARGE (> 100% in fixation relative to the background rate of 50-100 Tg N/yr):

No place on earth unaffected by this

Anthropogenic N-fixation

Increases since 1850:

- 120 Tg
- 30 Tg
- 25 Tg
Atmospheric N\(_2\): \(3.9 \times 10^9\)

Huge but inaccessible

Reactive N (NO\(_x\), NH\(_3\))

Vegetation: 4,000

Soils: 100,000

Note big difference in N turnover times in terrestrial vs. Marine biota

Terrestrial: 
4000/1200 = 3-4 yrs

Marine: 
300/8000 = 2 weeks

Atmosphere: 
\(3.9 \times 10^9/\sim 300 \approx 10^7\) years!

Units:
Stocks (Tg N) or Flows (Tg N/yr)

The Global Nitrogen Cycle
Atmospheric N$_2$: $3.9 \times 10^9$

Reactive N (NO$_x$, NH$_3$)

Vegetation: 4,000

Soils: 100,000

Units: Stocks (Tg N) or Flows (Tg N/yr)

The Global Nitrogen Cycle

Chapin, et al. 2002
C. Stoichiometry (proportional elemental composition, e.g. C:N:P in biomass) 

(because biogeochemical cycles do not exist in isolation, but are coupled) 

Example: Integrated N-C cycle 

\[
\text{Inorg N} + H_2O + CO_2 \rightarrow C_{106}H_{263}O_{110}N_{16}P_1 
\]

"organic N" and "organic C" are the same stuff!

Stoichiometry: 

Greek: \textit{stoikheion} (element) 

\textit{metron} (measure) 

ecological stoichiometry: definite proportions of elemental combinations, a constraint on biogeochemistry of life, from the cell to the organism to the biosphere 

(broader concept than the stoichiometry of balancing a chemical reaction)
C. Stoichiometry (proportional elemental composition, e.g. C:N:P in biomass)

Originally introduced as an ecological concept by A. Redfield in 1934 in his study of marine phytoplankton. the **Redfield ratio** \( C:N:P = 106:16:1 \)

(relative amounts of C, N, & P in phytoplankton)

Based on what we know now about marine vs terrestrial residence times (and other things we know about these systems), what might we infer/guess about terrestrial vs. marine C:N:P?

**Forest Foliage**
\[ C:N:P = 1200:28:1 \]  
(Global scale)

**Litter**
\[ = 3000:45:1 \] (resorption)

(higher C than in marine phytoplankton: reflecting importance of carbon-rich structural components - e.g. cellulose)

Much more recently applied to terrestrial systems: 

McGroddy et al. 2004
Next...

Thermodynamics of 
Biogeochemical reactions

Fun problem in global biogeochemistry: 
How likely is it that in your next breath, you will inhale at 
least one molecule of nitrogen (N$_2$) that Julius Caesar 
exhaled in his last breath?

(Julius Caesar, the famous Roman emperor, was 
assassinated on March 15, 44 BC by a group of Roman 
senators).

This requires some basic chemistry: 
1 mole of air is 6.02 x 10$^{23}$ molecules 
At STP, 1 mole occupies ~22 liters. 
Also helpful: whole atmosphere: 1.8 x 10$^{20}$ moles of air 
What is atmospheric mixing ratio of N$_2$? 
What is N$_2$ mixing time in the atmosphere? 
What is N$_2$ residence time in the atmosphere?

From J. Harte, 2001. Consider a Cylindrical Cow
First, the concentration, in the whole atmosphere, of Caesar’s last-breath $N_2$ molecules

$$\text{Concentration} = \frac{\# \text{ $N_2$ molecules in Caesar’s last breath}}{\# \text{ molecules in whole atmosphere}}$$

$$= \frac{(1 \text{ L of air in breath}) \left( \frac{3 N_2}{4 \text{ air}} \right) \left( \frac{1 \text{ mol air}}{22 \text{ L air}} \right) \left( 6 \times 10^{23} \text{ molecules / mol} \right)}{(1.8 \times 10^{20} \text{ mols air / atmosphere}) \left( 6 \times 10^{23} \text{ molecules / mol} \right)} \approx 2 \times 10^{-22}$$

Next, the average number you inhale per breath =

$$= \left( 2 \times 10^{-22} \right) \left[ \left( 1L \times \frac{1 \text{ mol air}}{22 \text{ L air}} \right) \left( 6 \times 10^{23} \text{ molecules / mol} \right) \right]$$

$$\approx \left( 2 \times 10^{-22} \right) \times \left( 2.7 \times 10^{22} \right) = 5.4 \approx 5$$

So on average you inhale 5 molecules of Caesar’s-breath $N_2$ in every breath!

From J. Harte, 2001. *Consider a Cylindrical Cow*