Biogeochemistry: Key concepts and methods

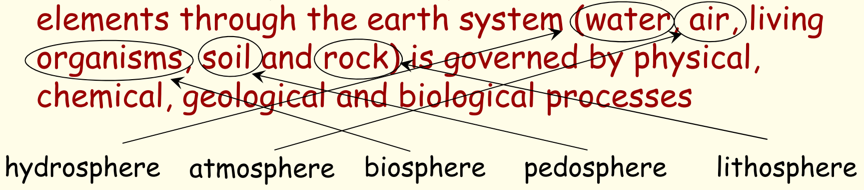
SWES 410/510
Jan. 31, 2014

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.:

inflow (F_{in}) = outflow (F_{out})
→ box size (or stock S) doesn't change

Then residence time τ (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:

(using consistent units)

$$\tau = \frac{S}{F} \quad \frac{\cancel{\text{grams}}}{\cancel{\text{grams}}\ \text{sec}^{-1}} = sec$$

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 ($NPP_{land} \approx 60$ PgC/yr; $NPP_{sea} \approx 50$ PgC/yr), but big differences in total biomass carbon (560 PgC on land vs 3 PgC in the sea)

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

(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*

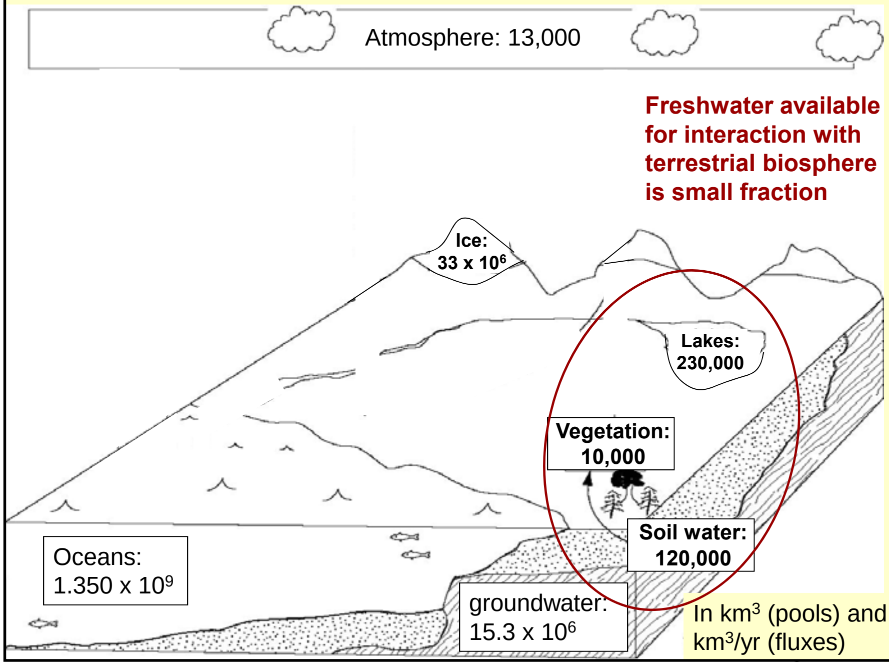
B. Budgets and Cycles

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



Atmosphere: 13,000

Freshwater available for interaction with terrestrial biosphere is small fraction

Ice: 33 x 10^6

Lakes: 230,000

Vegetation: 10,000

Soil water: 120,000

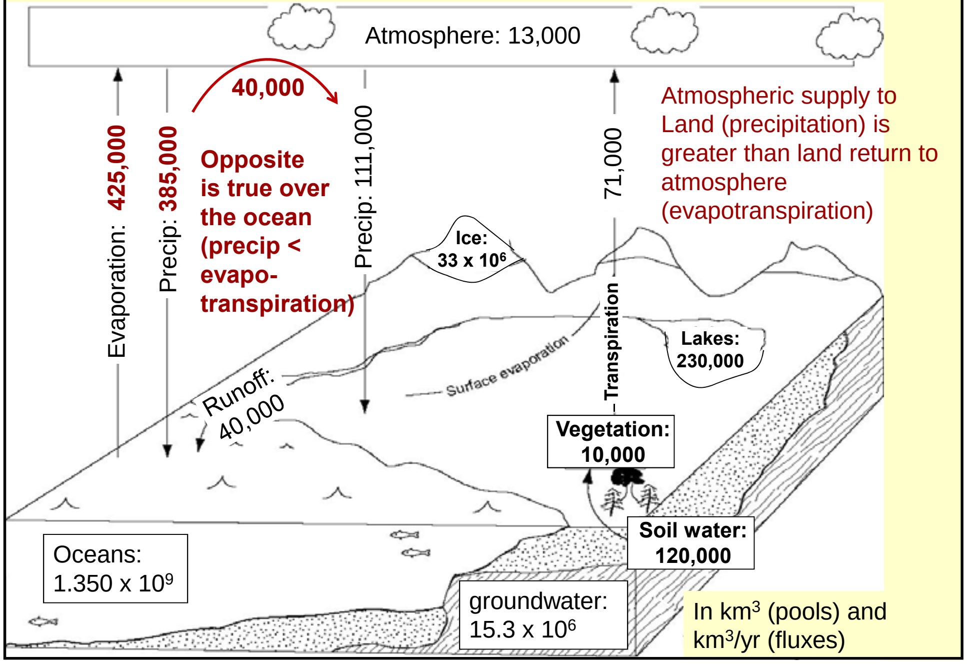
Oceans: 1.350 x 10^9

groundwater: 15.3 x 10^6

In km^3 (pools) and km^3/yr (fluxes)

The Global water cycle

Chapin, et al. 2002



Atmosphere: 13,000

Evaporation: **425,000**

Precip: **385,000**

40,000

Opposite is true over the ocean (precip < evapo-transpiration)

Precip: 111,000

71,000

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

Ice: 33×10^6

Transpiration

Lakes: 230,000

Surface evaporation

Runoff: 40,000

Vegetation: 10,000

Soil water: 120,000

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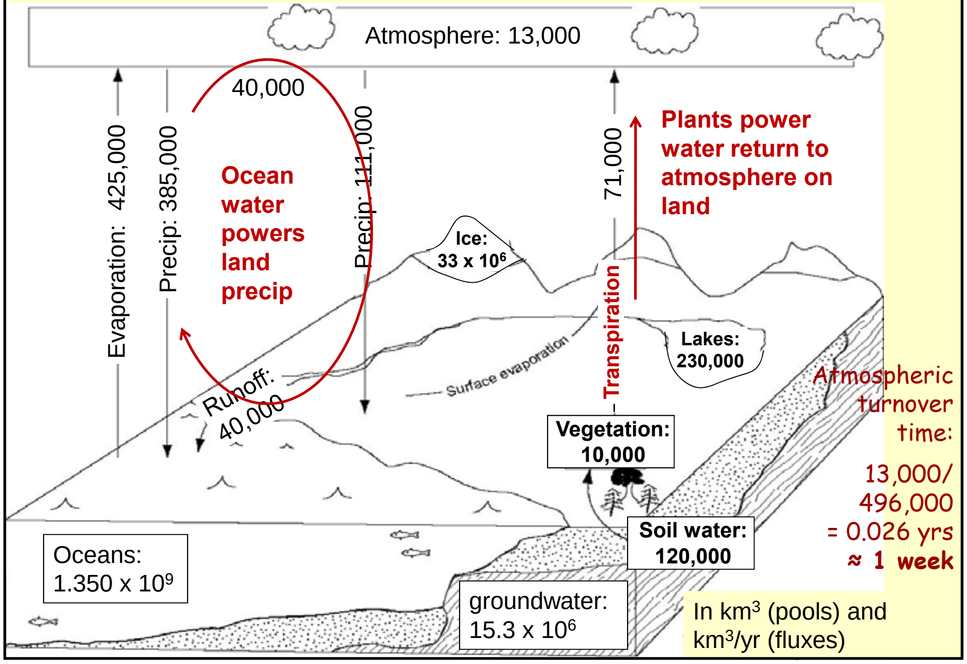


Atmosphere: 13,000

Evaporation: 425,000

Precip: 385,000

40,000

Ocean water powers land precip

Precip: 111,000

71,000

Plants power water return to atmosphere on land

Ice: 33×10^6

Transpiration

Lakes: 230,000

Surface evaporation

Runoff: 40,000

Vegetation: 10,000

Soil water: 120,000

Oceans: 1.350×10^9

groundwater: 15.3×10^6

In km^3 (pools) and km^3/yr (fluxes)

Atmospheric turnover time:

13,000/ 496,000 = 0.026 yrs ≈ **1 week**

Facts about the global water cycle

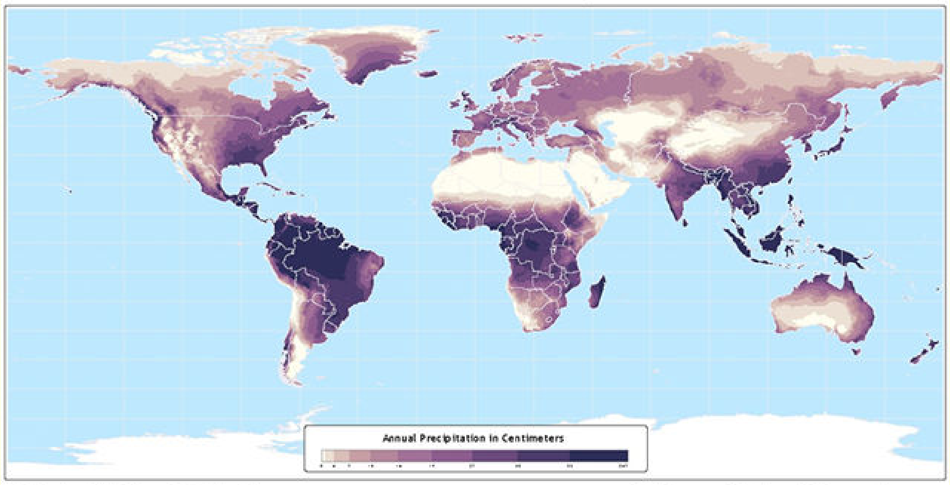
- Global precip: $\overbrace{385{,}000\ \text{(ocean)} + 111{,}000\ \text{(land)}}^{496 \times 10^3\ \text{km}^3}$

  $496 \times 10^3\ \text{km}^3 \div \underbrace{510 \times 10^6\ \text{km}^2}_{\text{Earth surface area}} = \underbrace{0.97 \times 10^{-3}\ \text{km}}_{\boxed{\approx 1 \text{ meter of precip (global average)}}}$

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

Chapin, et al. 2002

Annual Total Precipitation

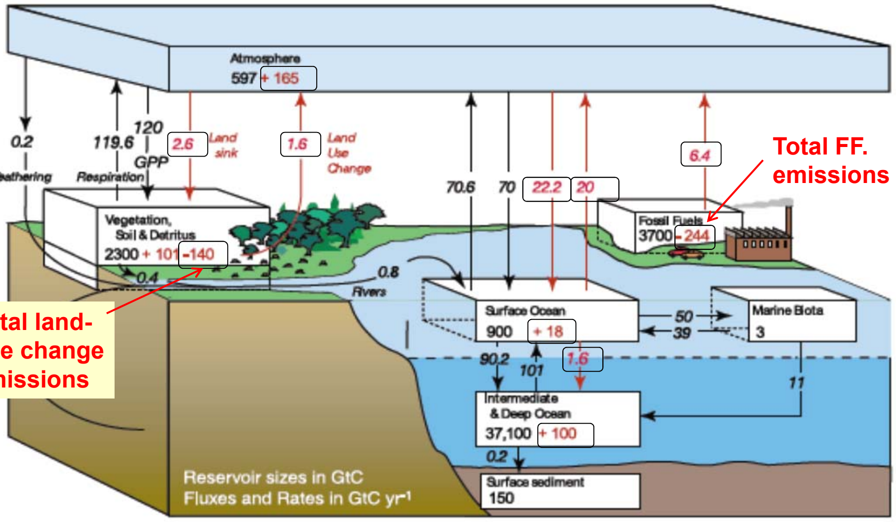


Data taken from: CRU 0.5 Degree Dataset (New et al)

Atlas of the Biosphere

Center for Sustainability and the Global Environment
University of Wisconsin - Madison

Overview: The Modern Global carbon cycle (1990s)



Total FF. emissions

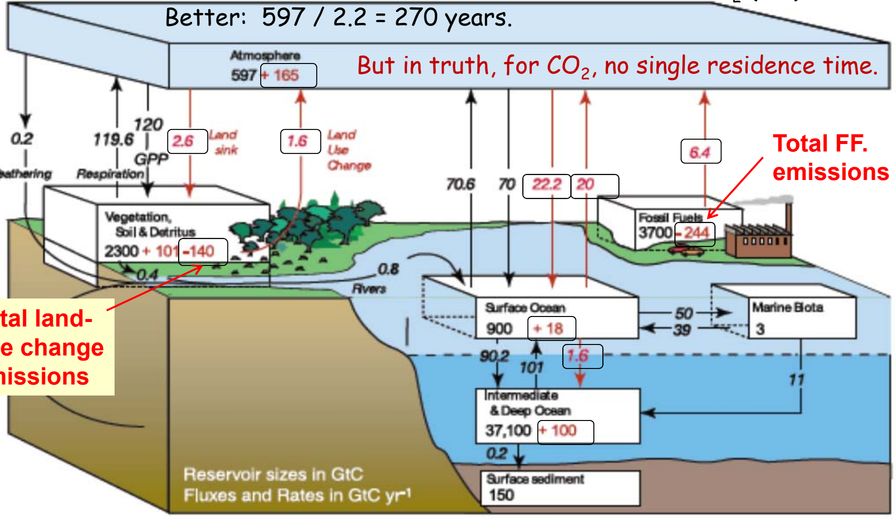
Total land-use change emissions

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 CO_2 (2.2).
Better: 597 / 2.2 = 270 years.

But in truth, for CO_2, no single residence time.



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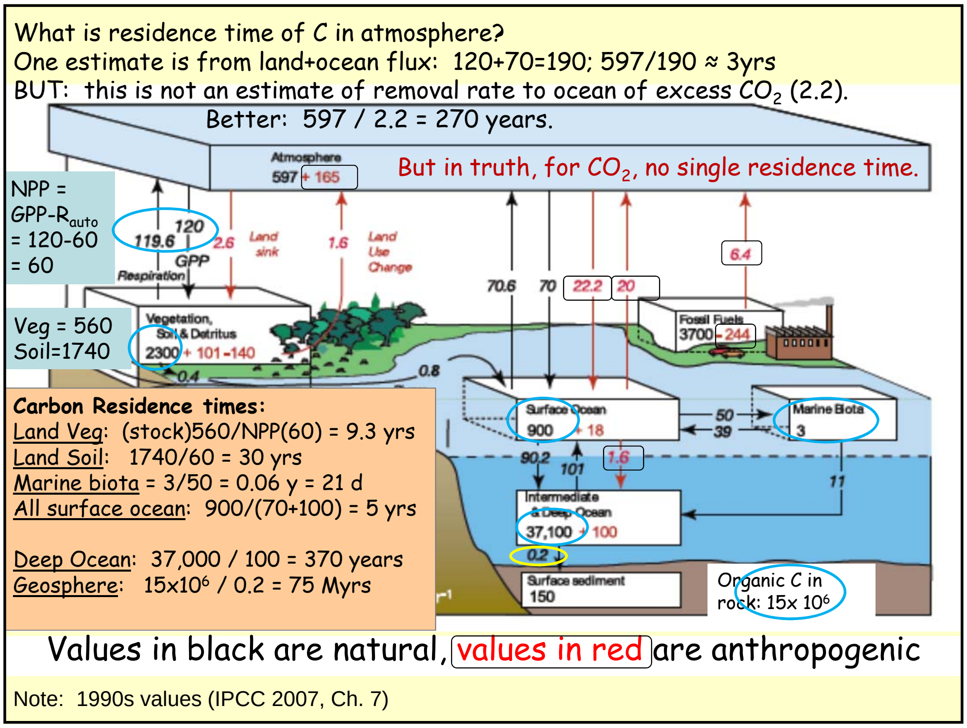

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NPP = $GPP-R_{auto}$ = 120-60 = 60

Veg = 560
Soil=1740

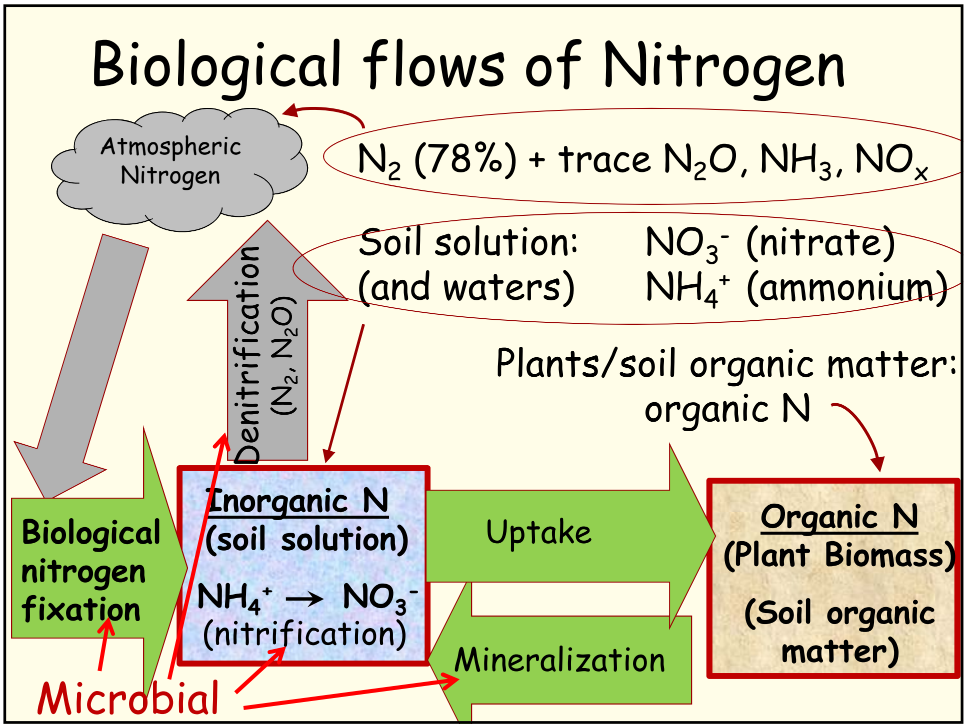
Carbon Residence times:
Land Veg: (stock)560/NPP(60) = 9.3 yrs
Land Soil: 1740/60 = 30 yrs
Marine biota = 3/50 = 0.06 y = 21 d
All surface ocean: 900/(70+100) = 5 yrs

Deep Ocean: 37,000 / 100 = 370 years
Geosphere: 15×10^6 / 0.2 = 75 Myrs

Organic C in rock: 15×10^6

Values in black are natural, values in red are anthropogenic

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



Biological flows of Nitrogen

Atmospheric Nitrogen

N_2 (78%) + trace N_2O, NH_3, NO_x

Soil solution: (and waters)
NO_3^- (nitrate)
NH_4^+ (ammonium)

Plants/soil organic matter: organic N

Denitrification (N_2, N_2O)

Biological nitrogen fixation

Inorganic N
(soil solution)
$NH_4^+ \rightarrow NO_3^-$
(nitrification)

Uptake

Mineralization

Organic N
(Plant Biomass)
(Soil organic matter)

Microbial

Global Change and the N-cycle

The New York Times

Science

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Beyond Carbon: Scientists Worry About Nitrogen's Effects

Nir Elias/Reuters

A woman clears away algae in Quindao, China, a buildup caused by too much nitrogen in the Yellow Sea.

By RICHARD MORGAN
Published: September 1, 2008

E-MAIL
PRINT
REPRINTS

Correction Appended

TOOLIK FIELD STATION, Alaska — As Anne Giblin was lugging

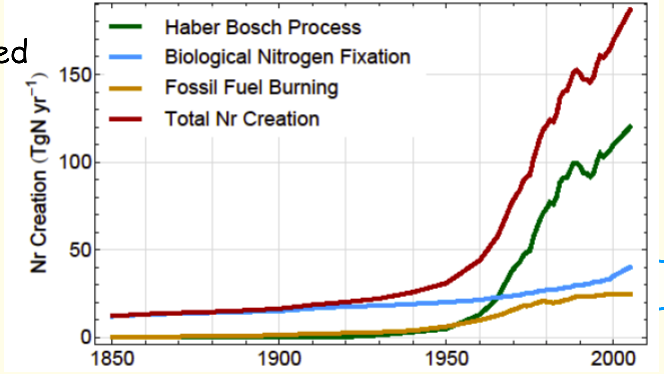
"The nitrogen dilemma is not just thinking that carbon is all that matters. But also thinking that global warming is the only environmental issue. The weakening of biodiversity, the pollution of rivers... Smog. Acid rain. Coasts. Forests. It's all nitrogen."
- Peter Vitousek

Global Change and the N-cycle

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



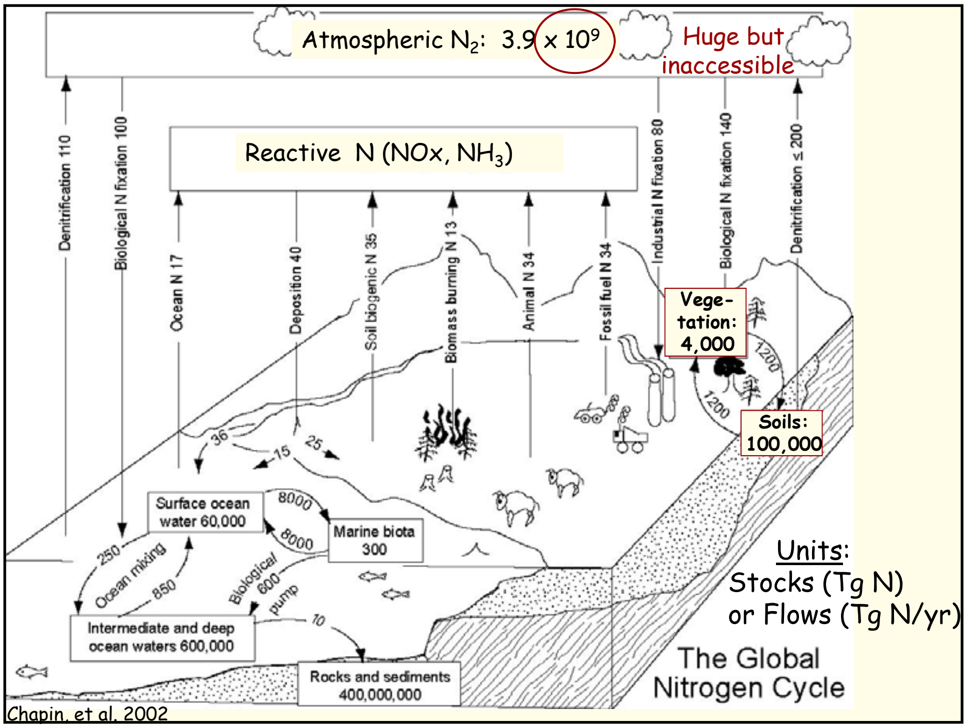
IPCC
AR5 (2013)

Increases since 1850:

120Tg

30 Tg

25 Tg



Atmospheric N_2: 3.9×10^9

Huge but inaccessible

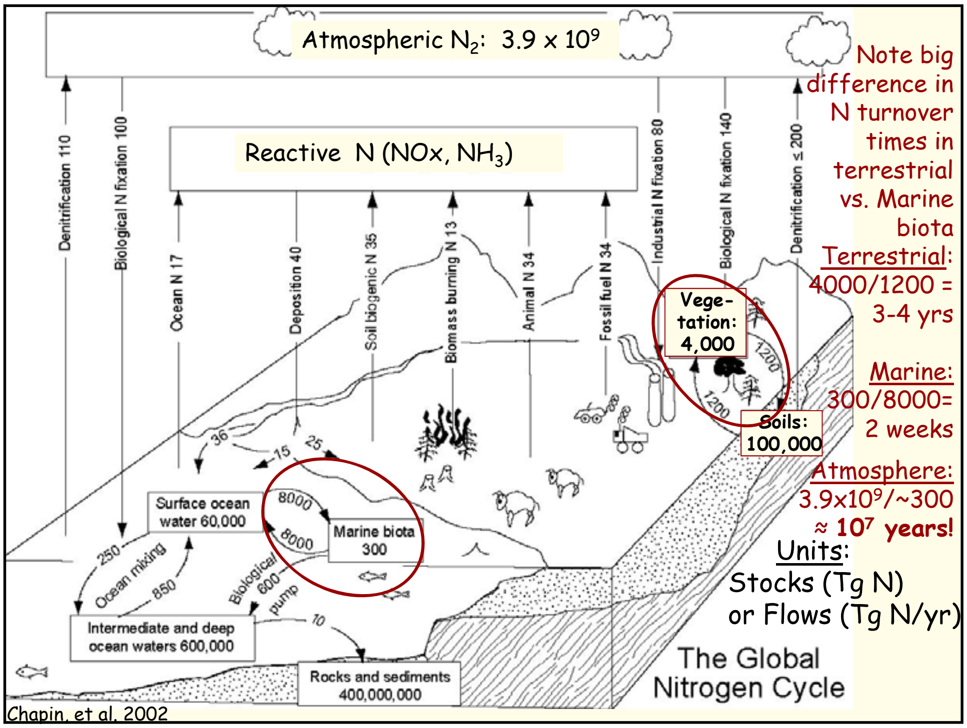
Reactive N (NOx, NH_3)

Vege-tation: 4,000

Soils: 100,000

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

Chapin, et al. 2002



Atmospheric N_2: 3.9×10^9

Reactive N (NOx, NH_3)

Vege-tation: 4,000

Soils: 100,000

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

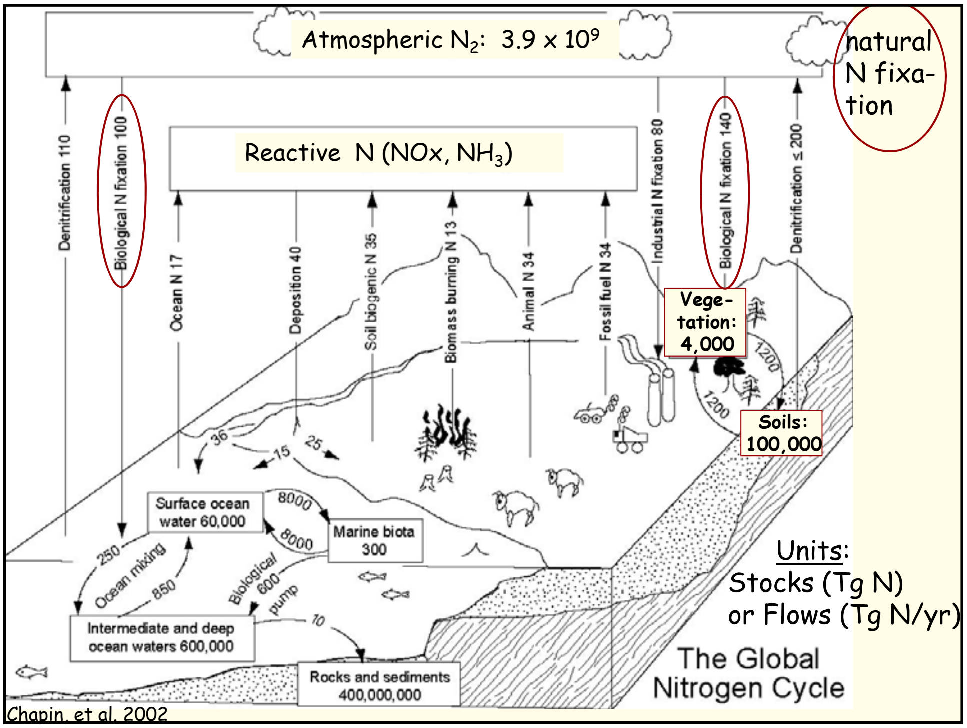
Terrestrial: 4000/1200 = 3-4 yrs

Marine: 300/8000= 2 weeks

Atmosphere: 3.9×10^9/~300 ≈ **10^7 years!**

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

Chapin, et al. 2002



Atmospheric N_2: 3.9×10^9

Reactive N (NO_x, NH_3)

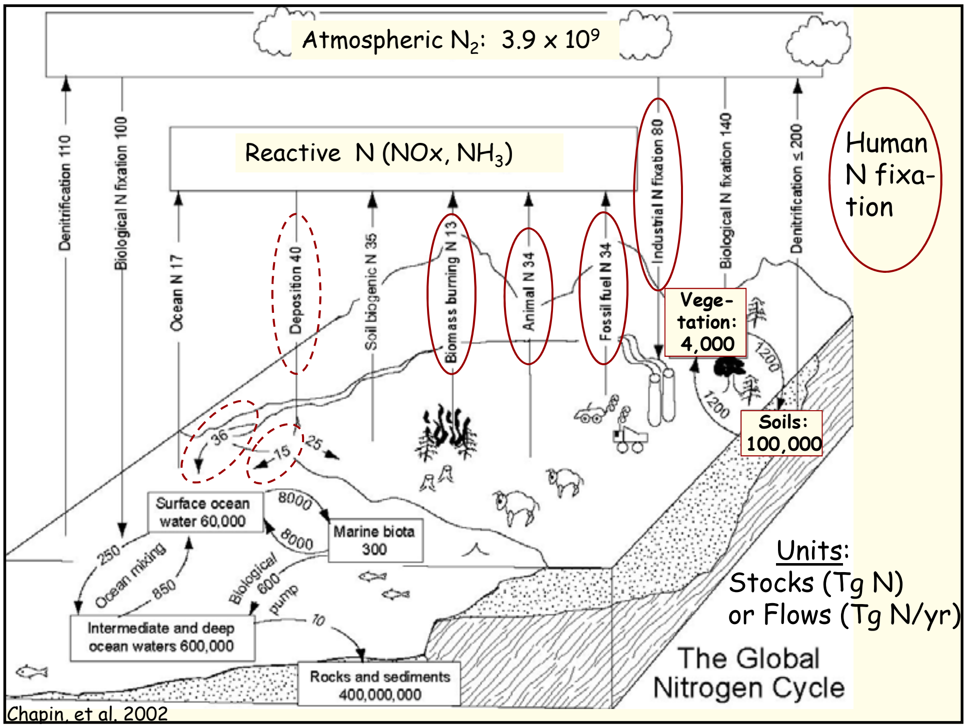
natural N fixation

Vegetation: 4,000

Soils: 100,000

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

Chapin, et al. 2002



Atmospheric N_2: 3.9×10^9

Reactive N (NO_x, NH_3)

Human N fixation

Vegetation: 4,000

Soils: 100,000

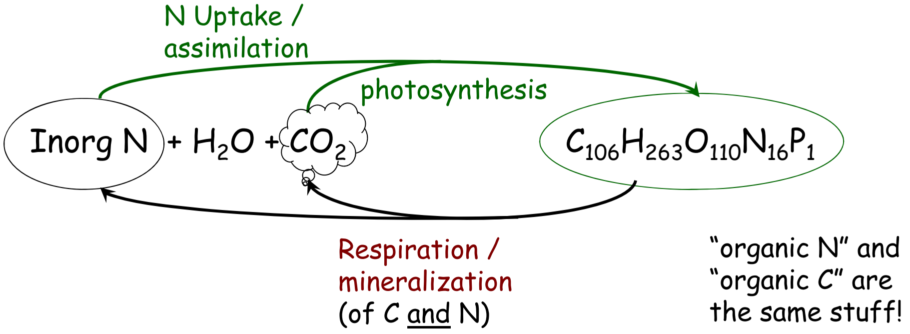
Units:
Stocks (Tg N)
or Flows (Tg N/yr)

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



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

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

Stoichiometry:

Greek: *stoikheion* (element)
+ *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 v terrestrial residence times (and other things we know about these systems), what might we infer/guess about terrestrial vs. marine C:N:P ?

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)

Much more recently applied to terrestrial systems:

McGroddy et al. 2004

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)

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 6.02×10^{23} molecules
At STP, 1 mole occupies ~22 liters.
Also helpful: whole atmosphere: 1.8×10^{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

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

$$= \frac{\left(1L\ of\ air\, in\, breath\right)\frac{3N_2}{4\,air}\left(\frac{1\,mol\,air}{22\,L\,air}\right)\left(6\times10^{23}\,molecules/mol\right)}{\left(1.8\times10^{20}\,mols\,air/atmosphere\right)\left(6\times10^{23}\,molecules/mol\right)} \approx 2\times10^{-22}$$

Next, the average number you inhale per breath =

$$Concentration\,(molecules\,Caesar's\,N2/molecules\,air)\times\left(\#\ molecules\ inhaled\right)$$

$$= \left(2\times10^{-22}\right)\times\left[\left(1L\times\frac{1\,mol\,air}{22\,L\,air}\right)\left(6\times10^{23}\,molecules/mol\right)\right]$$

$$\approx \left(2\times10^{-22}\right)\times\left(2.7\times10^{22}\right) = 5.4 \approx 5$$

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

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