The interactions between the various spheres of the earth system (after Christensen, 1991).

Complex interactions involving biological, geological, and chemical processes operating on a broad range of time scales.

Place yourself on the figure
Why Study Global Biogeochemical Cycles?

Understanding how the world works and how we are changing natural processes.

- Biogeochemical cycles provide the basic framework for investigating global change and its implications for life on earth.
- An understanding of biogeochemical cycles and anthropogenic impacts on them is fundamental for predicting impacts of global climate change.
Atmospheric CO$_2$ concentrations at Mauna Loa, Hawaii
The global biogeochemical cycles of many elements have been altered by human (anthropogenic) activity.

Fossil fuel burning alone accounts for perhaps 80% of sulfur dioxide (SO$_2$) emissions from the land surface to the atmosphere, 50% of carbon monoxide, 50% of NOx, 20% of methane, 5% of ammonia, and 4% of nitrous oxide. It is also responsible for 70–90% of anthropogenic CO$_2$ emissions to the atmosphere. CO$_2$ in the atmosphere increased by 30% since the industrial revolution.
What do we try to understand in these studies?

The present state of the Earth’s surface environment.

What controls it.

How it got to its present state.

How did it change over Earth’s history.

What are the processes/feedbacks that sustain a habitable planet.
Biogeochemical cycles operate on many different spatial and temporal scales
Cycles are fueled by solar and geological energy.
Three basic types of system

A. Isolated system
B. Closed system
C. Open system
A reservoir is a physically well-defined system. A given setting with defined physical and/or biological boundaries. In each reservoir, the relevant chemical, physical and biological properties are assumed to be (reasonably) uniform. A reservoir will contain a collection of matter.

EXAMPLES?
Major Reservoirs

- Atmosphere
- Land/Lithosphere
- Ocean/Hydrosphere
- Sediments
- Deep Earth
Fluxes - Material Transport

*Fluxes* transfer of matter from one reservoir to another. A flux into a reservoir is sometimes referred to as a *source*, a flux out of the reservoir as a *sink*.

For a perfectly mixed reservoir, the concentration of a component in the outflow is equal to the uniform concentration inside the reservoir.

Biogeochemical Cycles – Matter and energy move all the time at different rates from one earth reservoir to another.
Matter and energy flow between and within these reservoirs

- Atmosphere
- Land/Lithosphere
- Ocean/Hydrosphere
- Sediments
- Deep Earth

**EXAMPLES?**
The two main tasks in depicting a biogeochemical cycle is the definition of the reservoirs and the parameterization of the fluxes. There are no magic guidelines, other than to clearly define the goals of the work and system of investigation and to start as simple as possible. Obviously, it is only possible to provide direct information on reservoirs, fluxes and parameters that are explicitly represented.
Steady-state is a common assumption made about the changes in the components of a system (lack of)

For steady-state:

\[ \text{Flux}_{\text{in}} = \text{Flux}_{\text{out}} \]

An equilibrium state
Residence Time

- **Residence Time** – how quickly a substance cycles through a reservoir (exchange rate)
- **Content** – the total amount of any constituent in a reservoir (standing stock)
- **Capacity** – maximum concentration of a substance a reservoir can reach before saturation occurs
- **Rate of In/outflux** – how much of a substance get into/out a reservoir at a given time.

- Residence times for different elements vary widely
- Humans can alter the rate of influx/outflux by our activity (pumping, diversion, adding pollution)
The turnover time is defined as

\[ t_R = \frac{M}{F_{out}} \]

where \( M \) is the mass of the reservoir (say, the total number of moles of organic carbon in marine biota) and \( F_{out} \) is the total flux out of the reservoir (i.e., the sink or source).

Content = 1,000,000 m³
Input = 163 m³/s

Residence Time
1,000,000/163 = 6000 seconds = 1.66 hours
Non Steady State Conditions

• In many instances the source (Q) and sink (S) rates are not constant with time or they may have been constant and suddenly change (transient events or perturbation).

• To describe how the mass in a reservoir changes with time after an increase in source (or sink) for a reservoir

Starting with: \( \frac{dM}{dt} = Q_0 - S = Q_0 - kM \)
We let the input change to a new value \( Q_1 \) and we assume that the initial amount at \( t = 0 \) is \( M_0 \).
The new equation is: \( \frac{dM}{dt} = Q_1 - kM \)
and the solution is: \( M(t) = M_1 - (M_1 - M_0) \exp(-kt) \)
This describes how \( M \) changes from \( M_0 \) to the new equilibrium value \( M_1 (= Q_1 / k) \) with a response time equal to \( k^{-1} \).

For constant exponential change \( Q = Q_0 \exp[m(t-t_0)] \)
The solution for \( \frac{dM}{dt} \) for these conditions is:
\( M = M_0 \{ (m/m+k) \exp[-k(t-t_0)] + k / m+k \exp[m(t-t_0)] \} \) for \( t_0 < t < t_1 \)
Reactive Transport Models

Reactive transport models

\[ \frac{dC_{\text{res}}}{dt} = \frac{1}{t_f} (C_{in} - C_{\text{res}}) + R \]

For a system with a single inlet and a single outlet

where $C_{in}$ is the concentration of the species in the inflow, $R$ is the rate, per unit volume, at which the species is produced in the system (note: when the species is being consumed $R$ is negative), and $t_f$ is the mean residence time (or transit time) of the carrier fluid in the system.
Changes in the Water Cycle
Box models - Reservoirs and Fluxes

Reservoir total inventories (in brackets) in units of $10^6$ km$^3$. Fluxes in units of $10^6$ km$^3$yr$^{-1}$. 
Ocean Flux in = 0.398 (precipitation) + 0.036 (runoff) = 0.434
Flux out = 0.434 (evaporation)
Residence Time 1400/0.434 = 3200 years
Oxygen isotope fluctuations in seawater as recorded in marine sediments can be indicative of ice volume and thus sea level changes. Temperature effects will be included as well. Indicative of exchange among water reservoirs.
65 Million Years of Climate Change
The black numbers indicate how much carbon is stored in various reservoirs, in billions of tons (GigaTons, circa 2004). The purple numbers indicate how much carbon moves between reservoirs each year. The sediments, as defined in this diagram, do not include the ~70 million GtC of carbonate rock and kerogen.
On geologic times scales, the carbon cycle model can be augmented by 3 reservoirs, sedimentary carbonate, sedimentary organic carbon, and the mantle, as well as fluxes between these reservoirs and the oceans and atmosphere.
The Carbon Cycle

The present carbon cycle
Volumes and exchanges in billions of tonnes of carbon

Sources: Center for climatic research, Institute for environmental studies, University of Wisconsin at Madison; Okanagan university college in Canada, Department of geography; World Watch, November-December 1998; Climate change 1995, The science of climate change, contribution of working group 1 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge press university, 1996.
When more C is removed into the reduced organic C reservoir residual C in the ocean and carbonates becomes enriched in $^{13}$C (heavy) and atmospheric CO$_2$ is lower and O$_2$ is higher (less consumed for oxidation).

Figure 38.3. Isotopic compositions of carbon and sulfur in the oceans through Phanerozoic time. After Holser (1984).
The long-term increases in $\delta^{13}$C_carb (e.g. more organic C burial) that began in the Mesozoic were accompanied by major evolutionary changes among the primary producers in the marine biosphere. Three groups of eucaryotic marine phytoplankton (calcareous nannoplankton, dinoflagellates, and diatoms) began their evolutionary trajectories to ecological prominence at ~ 200 Ma. As Pangea fragmented and the Atlantic Ocean basin widened, the total length of coastline increased and sea level rose, flooding continental shelves and low-lying continental interiors. Nutrients that were previously locked up in the large continental interior were transported to newly formed shallow seas and distributed over wider shelf areas and longer continental margins.

Katz et al., 2005
The decline since the late Miocene in addition to changes in ocean circulation could be related to the evolution of C4 plants (less fractionation in organic C burial).

Large perturbations in the global C cycle.
Gas hydrate?

Figure 1. Late Cenozoic carbon isotopic record of bulk marine carbonate averaged in million year increments. Data from Shackleton and Hall [1984].

Figure 1. Carbon and oxygen isotope data for benthic foraminifera spanning the Paleocene-Eocene boundary. The figure is based on data compiled in Zachos et al. (2001). EWI—Eocene Warm Interval; GPTS—geomagnetic polarity time scale; PDB—Pee Dee Belemnite; PETM—Paleocene-Eocene Thermal Maximum.
N is present in many chemical forms, both organic and inorganic, in the atmosphere, biosphere, hydrosphere, and geosphere. It occurs in the gas, liquid (dissolved in water), and solid phases. N can be associated with organic species and with inorganic species. Important inorganic species include N₂, nitric acid (HNO₃), nitrate (NO₃⁻), nitrite (NO₂⁻), nitrous oxide (N₂O), nitric oxide (NO), N dioxide (NO₂), ammonium (NH₄⁺), and ammonia (NH₃). Most organic N species are bio-molecules, such as proteins, peptides, enzymes, and genetic material (RNA and DNA). NO₃⁻ and organic-N species exist in solution and as particulates.

No evidence for change in atmospheric N₂
N₂ is the most abundant gas in the atmosphere (78%). However, most organisms cannot use this ubiquitous nitrogen source to make their essential, nitrogen-containing molecules (e.g., proteins and DNA). The two nitrogen atoms in N₂ are connected by an extremely stable triple bond, which does not easily break.

Just a few species of bacteria, called nitrogen fixers, can break the N₂ triple bond. These bacteria convert N₂ into NH₄, which other bacteria then convert into NO₂ and NO₃. Plants use NO₃ or NH₄ to produce nitrogen-containing organic molecules. Then, by consuming plants, animals also obtain usable forms of nitrogen.
Humans add to the amount of nitrogen fixed on Earth. Through energy-consuming industrial processes, we capture atmospheric N₂ and convert it into NH₄ or NO₃, key components of most artificially made agricultural fertilizers. Some of this nitrogen enters the ocean through runoff.

When organisms die, on land and in the oceans, they liberate their organic stores of nitrogen. Some of this nitrogen is converted to inorganic nitrogen compounds, such as NH₄, NO₃, and NO₂. A number of species of bacteria can then convert these inorganic compounds back into N₂—a process called denitrification.
The Nitrogen Cycle

A large quantity of "fixed" nitrogen does not return to the atmosphere. Before becoming converted to N₂ gas, the small, inorganic molecules (NH₄, NO₂, and NO₃) are taken up again by organisms and used to create organic compounds. This movement accounts for 95% of the flux in the global nitrogen cycle.
Transformations and isotopes in the N cycle
The global sulfur cycle, with two components: gaseous and sedimentary. Human activities which contribute to the cycle include: acid drainage from coal mining and fossil fuel burning.

Teragrams of sulfur
The Sulfur Cycle

A) Pyrite burial
   6x10^19 gSa⁻¹

B) Weathering
   10x10^19 gSa⁻¹

C) Ocean SO₄
   +2% 1.3x10^20 gS

D) Evaporite
   +16% 3x10^21 gS

E) CAS
   +ve%?

Sulfide re-oxidation
24x10^19 gSa⁻¹

BSR
30x10^19 gSa⁻¹

Pyrite
-12% 6x10^21 gS

0%

TECTONIC BURIAL AND UPLIFT
A Representation of the Sulfur Cycle

volcanic \[10, 3\] 

uplift

subduction

weathering \[72\]

0 to +10 (5.7)

seawater \[+21, 128^\circ\text{Tg}\]

burial

 gypsum \[44, +21\]

pyrite \[28, -16\]

hydrothermal

10, 3.5

fluxes in units of Tg (S) yr\(^{-1}\), isotope ratios in \(^\circ\text{CDT}\)

Arthur et al., 1990
Seawater Sulfate S isotope Curve

* Increased ocean crust production
* Active mid plate and plate margin volcanism
* Increased greenhouse gas input to the atmosphere
* Warm Climate
* Increased continental weathering rates

Cretaceous

Cenozoic
steady state mass and isotope balance model

\[ F_{py} = \left( \delta^{34}S_{in} - \delta^{34}S_{SO4} \right) \times \frac{\Delta^{34}S_{sw - py}}{\Delta^{34}S_{sw - py}} \]

Evaluate the change in each of the model parameters needed to explain the difference in \( \delta^{34}S_{SO4} \).

Kump 1989
The biogeochemical cycles of S and C are intimately linked with the principal processes that control the level of atmospheric oxygen.

\[
\text{CO}_2 + \text{H}_2\text{O} = \text{CH}_2\text{O} + \text{O}_2
\]

\[
2\text{Fe}_2\text{O}_3 + 16\text{Ca}^{2+} + 16\text{HCO}_3^- + 8\text{SO}_4^{2-} = 4\text{FeS}_2 + 16\text{CaCO}_3 + 8\text{H}_2\text{O} + 15\text{O}_2
\]

To maintain constant oxygen an periods of organic C burial should be compensated by less pyrite burial resulting in an inverse isotopic relation.
Feedbacks in the Climate System

**Water**
- Initial change
- Climate warming
- Increased warming
- Increased greenhouse trapping of radiation
- Increased atmospheric water vapor

**Ice**
- Initial change
- Climate cooling
- Greater cooling
- Less solar radiation absorbed at surface
- Increased snow and ice: higher reflectivity
\( \text{CO}_2 \uparrow \rightarrow \) Temperature \( \uparrow \)

Precipitation \( \uparrow \)

Weathering \( \uparrow \)

River solute load \( \uparrow \)

Biological Productivity \( \uparrow \)

\( \text{CO}_2 \downarrow \)
The Water Cycle

Global WATER Reservoirs, Fluxes, and Turnover Times

- Atmosphere
  - 13 (0.0009%) (9 d)

- Pools
  - 40,000 y⁻¹

- Ocean
  - 385,000 y⁻¹

- Soil moisture
  - 67 (0.005%) (280 d)

- Groundwater (active)
  - 4000 (0.29%) (300 y)

References:
- Schlesinger, 1993
- Murray, 1992

WSR 1994
The Carbon Cycle

Global CARBON Reservoirs, Fluxes, and Turnover Times

- **Terrestrial**
  - NPP = 50 y\(^{-1}\)
  - Deforestation 1.4 y\(^{-1}\)
  - Combustion (80's) 5.4 y\(^{-1}\)

- **Atmosphere**
  - 750 (3-5 y)
  - Ann. Increment = 3.2 y\(^{-1}\)
  - (~ +1.5 ppmv CO\(_2\) y\(^{-1}\))

- **Marine**
  - NPP = 50 y\(^{-1}\)
  - New production = 10 y\(^{-1}\)

- **Rivers**
  - DOC: 0.2 y\(^{-1}\)
  - POC: 0.2 y\(^{-1}\)

- **Coastal Ocean**
  - 20% of NPP

- **Open Ocean**
  - 80% of NPP

- **Soils (~1m)** 1580
  - peat 360 (>1000 y)
  - mineral 1220
    - microbial* 15-30 (<10 y)
    - POC 250-500 (<100 y)
    - remainder 600-600 (10\(^{2}\)-10\(^{5}\) y)

- **Surface Sediments (~1m)**
  - 150 (0.1-1000 y)
    - 80% coastal
    - 20% deep sea

- **Sediments**
  - kerogen 15x10\(^{6}\) (>>1 my)
  - methane clathrates 11x10\(^{3}\)
  - limestone 60x10\(^{6}\)

- **Respiration ≡ NPP**

References:
Hedges, 1992; Eswaran et al., 1993;
Siegenthaler & Sarmento, 1993;
Schimel et al., 1994

Pools in Gt C, Fluxes in Gt C y\(^{-1}\), Gt = 10\(^{12}\) g:
< living pools; (turnover times)

Ocean CO\(_2\) Exchange
- 90 y\(^{-1}\)
- 92 y\(^{-1}\)

Surface
- 100 m

Deep
- 3.8 km

DOC 40 (? y)
POC 5, Living 2* (0.1-1 y)

DOC 700 (5000 y)
POC 20-30 (10-100 y)
DIC 38000 (~2000 y)

Sedimentation (long-term burial)
- 0.1 y\(^{-1}\)

WSR 1997
The Nitrogen Cycle

Global NITROGEN Reservoirs, Fluxes, and Turnover Times

**Fixation**
- Natural terrestrial 190 yr⁻¹
- Natural oceanic 40 yr⁻¹
- Leguminous crops 40 yr⁻¹
- Chemical fertilizer 20 yr⁻¹
- Combustion 20 yr⁻¹

**Atmosphere**
- \( N_2 \): 3.9-4.0x10⁸ (10⁷y)
- Fixed N: 1.3-1.4x10⁶ (~5 wk)
- \( N_2O \): 1.4x10³ (10²y)

**Terrestrial Biomass**
- 3.5x10⁴ (~50y)

**River runoff**
- 36 yr⁻¹

**Soil**
- 9.5x10⁴ (~2000 y)

**Marine Biomass**
- Plants: 3x10⁸
- Animals: 1.7x10⁸

**Ocean**
- \( N_2 \): 2.2x10⁷
- \( N_2O \): 2.0x10⁴
- Inorganic: 6x10⁵
- Organic: 2x10³

**Sediments**
- 4.0x10⁶ (10⁷y)
- Weathering 5 yr⁻¹

**Denitrification**
- Natural terrestrial 147 yr⁻¹
- Natural ocean 30 yr⁻¹
- Industrial combustion 20 yr⁻¹
- Biomass burning 12 yr⁻¹

**Sedimentation (burial)** 14 yr⁻¹

References:
- Burns & Hardy, 1975; Jaffe, 1992; McElroy et al., 1976; Schlesinger & Hartley, 1992; Stedman & Shetter, 1983; Söderlund & Svensson, 1976; Galloway et al., 1995

- WSR 1994
The Phosphorus Cycle

Global PHOSPHORUS Reservoirs, Fluxes, and Turnover Times

- **Atmosphere**: 0.028 (0.006 y, 53 h)
- **Land Biota**: 3000 (47.2 y)
- **Rivers**: Reactive 1.7-2.7 y⁻¹, Total 20 y⁻¹
- **Land (~60 cm)**: 2x10⁵ (2000 y)
- **Surface Ocean (0.3 km)**: 2700 (2.6 y)
- **Deep Ocean (3.0 km)**: 8.7 x 10⁴ (1500 y)
- **Sediments**: 4x10⁹ (2x10⁶ y)
- **Sedimentation (burial)**: 1.9 y⁻¹

**References**: Jahnke, 1992; Berner & Rao, 1994
The Sulfur Cycle Pre-Industrial

Global SULFUR Reservoirs, Fluxes, and Turnover Times
(Natural)

- Atmosphere
  - Continental: 1.6 (8d)
  - 13 y⁻¹
  - 24 y⁻¹

- Marine: 3.2 (10 d)
  - COS (5-10y)
  - Seashell particles: 140 y⁻¹
  - Biogenic: 15-30 y⁻¹
  - Deposition: 159 y⁻¹

- Lakes & Rivers
  - 300 (3y)
  - River runoff: 104 y⁻¹

- Open Ocean
  - 1.3 x 10⁸ (6.6 x 10⁶ y)

- Ocean Sediments
  - 3 x 10⁸ (4 x 10⁶ y)

- Lithosphere
  - 2.4 x 10¹⁰ (1.8 x 10⁸ y)

- Sedimentation (burial)
  - 135 y⁻¹

Pools in Tg S, Fluxes in Tg S y⁻¹, Tg = 10¹² g.
(Turnover times)

Terrestrial dust: 20 y⁻¹
Biogenic: 2.5 y⁻¹
Volcanoes: 10 y⁻¹
Deposition: 43 y⁻¹

Soils & Land Biota
- 3 x 10⁸ (8.6 x 10³ y)

References:
- Andreae, 1990; Bates et al., 1992;
- Charlson, Anderson & McDuff, 1992

WSR 1994
The Sulfur Cycle (mid 1980's)

Global SULFUR Reservoirs, Fluxes, and Turnover Times (mid-80's)

- **Atmosphere**
  - Continental: 1.6 Tg, 81 y⁻¹
  - Marine: 3.2 Tg, 10 d
  - Terrestrial dust: 20 Tg y⁻¹
  - Biogenic: 2.5 Tg y⁻¹
  - Anthropogenic emission: 93 Tg y⁻¹
  - Deposition: 65 Tg y⁻¹

- **Lakes & Rivers**
  - 300 Tg (3 y)
  - River runoff: 21.3 Tg y⁻¹

- **Ocean**
  - 1.3 x 10⁸ Tg (6.8 x 10⁸ y)
  - Consumption from lithosphere: 150 Tg y⁻¹
  - Weathering: 72 Tg y⁻¹
  - Marine biota: 30 Tg (1 y)
  - Sedimentation (burial): 135 Tg y⁻¹

- **Lithosphere**
  - 2.4 x 10¹⁰ Tg (1.8 x 10¹⁰ y)

- **Open Ocean**
  - CO₂ (5–10 y)
  - Seasalt particles: 140 Tg y⁻¹
  - Biogenic: 15–30 Tg y⁻¹
  - Deposition: 231 Tg y⁻¹

References:
- Andreae, 1990; Bates et al., 1992;
- Charlson, Anderson & McDuff, 1992

WSR 1994