Water: Universal Solvent

Covalent Bonding

Polarity

Excellent Solvent!
Unique Properties of Water

- Hydrogen Bonding
- Cohesion → Surface Tension!
- Capillarity
- Hydration Spheres
Color and Transparency

Hydration Spheres

Garrett & Grisham: Biochemistry, 2/e
Figure 2.4
Salts and Salinity

- **Salts**
  - Replacement of acidic proton donor by charged particle (usually a metal)
  - \( \text{HCl} + \text{Na}^+ \rightarrow \text{NaCl} + \text{H}^+ \)

- **Salinity**
  - Total dissolved salts in a liquid
  - Measured by weight (ppt, ‰)

Seawater Salinity

Global Average: 35 ‰
**Constancy of Composition**

- Salinity changes, *Proportions DON’T*
- 6 Elements = 99% salts in seawater
  - Chloride
  - Sodium
  - Sulfur
  - Magnesium
  - Calcium
  - Potassium

**Measuring Salinity**

- Chloride easiest component
  - Salinity (‰) = 1.80655 x [Cl\(^-\)]

- Conductivity
  - Presumed Salinity Units (psu)
  - Presumed Salinity Scale (pss/ no units)
Ocean Salinity Variations

- Increase
  - Evaporation
  - Sea Ice Formation
- Decrease
  - Precipitation
  - Runoff (Rivers)
  - Melting Icebergs/ Sea Ice

The Hydrologic Cycle describes the circulation of water on the planet.
Density

• Mass per unit volume (g/mL or g/cm³)
• Difficult to measure *in situ*
• Pure water: 1.000 g/cm³
  – Max density: ~ 4°C (Not Ice!)
• Seawater: 1.022 - 1.030 g/cm³
  – $\sigma = [\text{density} - 1.000] \times 10^3$
    • Thus, range from 22 - 30 (easier units)
  – Density increases until frozen

Vertical Profiles

*Density* always increases with depth in a stable ocean.

Density decreases with increasing temperature, and decreasing salinity.

Temperature is *much* more important than salinity!
**T-S Plots**

Antarctic Bottom Water (AABW)

N Atlantic Deep Water (NADW)

Ant Intermediate Water (AAIW)

Surface Water

**Vertical Structures**

-CLINE means slope

**Pycno:** Density Slope

**Thermo:** Temp. Slope

**Halo:** Salinity Slope

**Nutri:** Nutrient Slope

**ISO-** means constant
Units for Elements

• Depending on what area of oceanography you are working in, there are different units for measuring concentrations of elements in the ocean….but they are all based on **mass per unit volume**

  - ppm -- parts per million (also ppb, etc.)
  - µM -- $10^{-6}$ moles per liter of seawater
  - nM -- $10^{-9}$ moles per liter of seawater

Vertical Profiles in the Ocean

- Bio-Limiting (Nutrient Type)
- Bio-Unlimiting (Conservative)
- Bio-Intermediate (Mixed)
- Scavenged
Vertical Profiles in the Ocean

- Bio-Limiting (Nutrient Type)
  - NO₃, PO₄, Fe
- Bio-Unlimiting (Conservative)
- Bio-Intermediate (Mixed)
- Scavenged

Depth (m)
Vertical Profiles in the Ocean

- **Bio-Limiting** (Nutrient Type)
- **Bio-Unlimiting** (Conservative)
  - Na, Cl, K, Mg
- **Bio-Intermediate** (Mixed)
- **Scavenged**

[Graph showing depth (m) vs. [element] (µM)]

- **Mixed Layer**
- **Nutricline**
Vertical Profiles in the Ocean

- Bio-Limiting (Nutrient Type)
- Bio-Unlimiting (Conservative)
- Bio-Intermediate (Mixed)
  - Cd, C, Ca
- Scavenged

[Graph showing concentration changes with depth]
Vertical Profiles in the Ocean

- Bio-Limiting (Nutrient Type)
- Bio-Unlimiting (Conservative)
- Bio-Intermediate (Mixed)
- Scavenged – Pb, Th

Chemical Profiles
The Biological and Solubility Pumps
**Stokes Law**

Q: How long does it take for a particle to sink in the ocean?

A: We need to know 3 things:
   1) density of the particle
   2) radius of the particle
   3) density of seawater

Then we use Stokes Law:

\[ V = \frac{2}{9} \cdot g \cdot r^2 \cdot \frac{(\rho' - \rho)}{\rho \cdot v} \]

**Stokes Law and Coccolithophores**

\[ V = \frac{2}{9} \cdot g \cdot r^2 \cdot \frac{(\rho' - \rho)}{\rho \cdot v} \]

\[ V = 2.62 \cdot 10^4 \cdot r^2 \]

r = 3 to 40 microns
r = 3 to 40 x10^-4 cm

*Simplification for spherical particles with densities near that of rock*
Box Models

1) Define your problem
   - We want to model the goldfish bowl
   - What happens to the food?

2) Define your assumptions
   - Steady State
     - Integrated over long spatial and temporal scales
     - INS=OUTS

3) Define your goals

Box Model Goldfish

Assumptions:
- There's only one goldfish
- It doesn't get bigger (or spontaneously reproduce)
- We feed it a constant amount daily
Flux In: $1 \text{ g C d}^{-1}$

Flux Out: $1 \text{ g C d}^{-1}$

Box 1

Box 2 (microbial degradation)

10% to 90%

90% to 9%

9% to 99%

1% to 100%
Sources into and Sinks out of Ocean

Land (via rivers) to atmosphere to Ocean

OCEAN

hydrothermal

Ocean is in “Steady State” or “Dynamic Equilibrium”:

Chemistry of ocean is not changing

Input fluxes = Output fluxes
OR
Sources = Sinks

Sediments

Organisms create material that is buried in sediments = Primary way that dissolved constituents are removed from ocean

Box Models

- Sources
- Sinks
- Reactivity

[Diagram of box models showing various processes and interactions]
Phosphorous comes mostly from rocks
The Nitrogen Cycle

Many sources and sinks

Controlled largely by biological processes

The Silica Cycle

Rapid export to depth

Major external source is river water
Residence Time

Total Fluxes In

Inventory
(totals amount in ocean)

Total Fluxes Out

Fluxes are in units of amount per time (e.g. grams/year)

Inventory is total amount (e.g. grams)

Residence time = Inventory / Flux In

The average amount of time one atom of constituent spends in ocean

Approx. the amount of time it takes for the concentration of a constituent to significantly change
TABLE 6-2 Annual fluxes between reservoirs

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Volume (10^3 km^3 yr^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere to ocean</td>
<td>398</td>
</tr>
<tr>
<td>Atmosphere to continent</td>
<td>107</td>
</tr>
<tr>
<td>Continent to atmosphere</td>
<td>71</td>
</tr>
<tr>
<td>Ocean to atmosphere</td>
<td>434</td>
</tr>
<tr>
<td>Continent to ocean</td>
<td>36</td>
</tr>
</tbody>
</table>

(Berner and Berner, 1987; 1996; Drever, 1988)

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TABLE 6-1 Reservoirs of the hydrosphere

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Volume (10^6 km^3)</th>
<th>Percent of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceans and sea ice</td>
<td>1400</td>
<td>95.96</td>
</tr>
<tr>
<td>Glaciers and land ice</td>
<td>43.4</td>
<td>2.97</td>
</tr>
<tr>
<td>Surface waters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lakes</td>
<td>0.125</td>
<td>0.009</td>
</tr>
<tr>
<td>Rivers</td>
<td>0.0017</td>
<td>0.0001</td>
</tr>
<tr>
<td>Subsurface waters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Groundwater</td>
<td>15.3</td>
<td>1.05</td>
</tr>
<tr>
<td>Soil Moisture</td>
<td>0.065</td>
<td>0.0045</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>0.0155</td>
<td>0.001</td>
</tr>
<tr>
<td>Biosphere</td>
<td>0.002</td>
<td>0.0001</td>
</tr>
<tr>
<td>Total</td>
<td>1459</td>
<td>100</td>
</tr>
</tbody>
</table>

(Berner and Berner, 1987; 1996; Drever, 1988)
Residence Time:

\[ RT = \frac{\text{Reservoirs}}{\text{Fluxes}} = \frac{1400 \times 10^6 \text{ km}^3}{434 \text{ km}^3 \text{ yr}^{-1}} = 3226 \text{ years} \]

-OR-

\[ RT = \frac{4000 \text{ m}}{1 \text{ m yr}^{-1}} = 4000 \text{ years} \]
Summary

- We can think of the oceans as a “box model”, which means it is in steady state

- Bio-limiting/Nutrient-type elements (N, P, Fe) have short residence times and tend to be removed (to the sediments)

- Bio-unlimiting/Conservative elements (Chloride) have long residence times and tend to be constant with depth

- The top “box” is where most of the biology occurs, and the flux (removal) is dominated by repackaging rather than sinking

- The amount of time it takes to remineralize an element can be called its “remineralization length scale” and we’ll find out that process regulates large-scale biological patterns