12.742 - Marine Chemistry Fall 2004

Lecture 1 - Determinants of Seawater Composition

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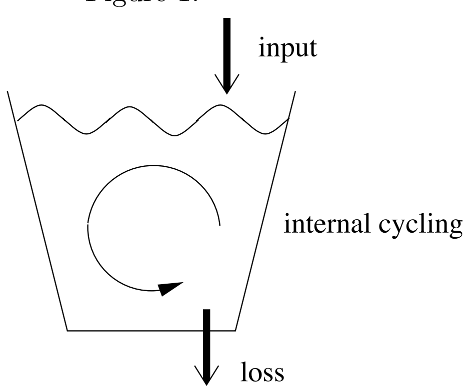
We start off discussing sources and sinks for major ions. Today we focus on box models, residence times, and distributions.

- Main points
  - Box models/residence times
  - Groupings of chemical elements (major vs. minor)
  - Spatial gradients (vertical / horizontal)
  - Resources:
    - Y. Nozaki et. al. "A fresh look at element distributions in the North Pacific", EOS, May 1997. `http://www.ajn.org/eos_elec/97025e.html`
    - MBARI periodic table of the elements. `http://www.mbari.org/chemsensor/pteo.htm`

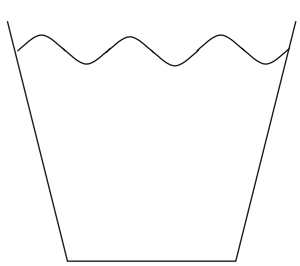
- Box Model

Figure 1.



  - Assume for the moment, a well mixed box

Figure 2.



Concentration $= C_i$
Volume $= V_0$
Inventory $= C_i V_0$

$$\frac{d(C_i V_0)}{dt} = \text{input} - \text{loss}$$

- Assume loss rates are proportional to the inventory - negative feedback

$$\frac{d(C_i V_0)}{dt} = I_i - k_i C_i V_0$$

where k_i has units of $\frac{1}{\text{time}}$: $k_i = \frac{1}{\tau_i}$

Units:

$$\frac{\text{mol}}{\text{m}^3} \cdot \text{m}^3 \cdot \frac{1}{\text{s}} = \frac{\text{mol}}{\text{s}} = \frac{1}{\text{s}} \cdot \frac{\text{mol}}{\text{m}^3} \cdot \text{m}^3$$

Can solve for a "steady state solution":

$$\frac{d(C_i V_0)}{dt} = 0 = I_i - k_i C_i^* V_0$$

$$C_i^* = \frac{I_i}{k_i V_0} \qquad \tau_i = \frac{1}{k_i} = \frac{C_i^* V_0}{I_i} \qquad \text{residence time}$$

bigger input $\rightarrow$ bigger C_i^*

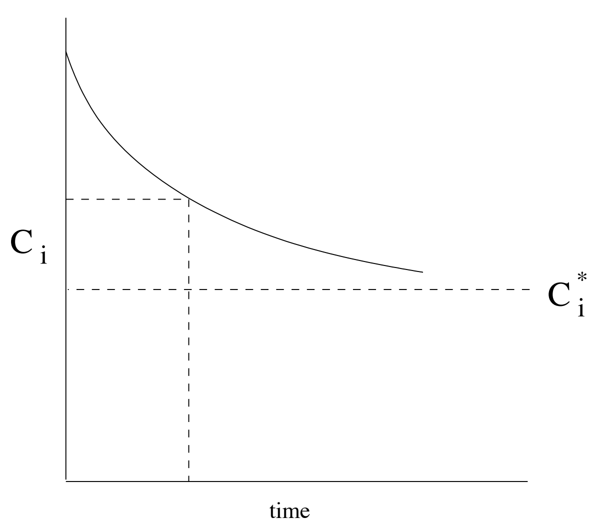
bigger τ_i (smaller k_i) $\rightarrow$ bigger C_i^*

- Time evolving system:

  C_i^0 is C_i at time zero.

$$C_i = (C_i^0 - C_i^*) e^{-k_i t} + C_i^*$$

as $t \rightarrow \infty, C_i \rightarrow C_i^*$



Exponentially approach C_i^*

Figure 3.

At $t = \tau$ have approached 63% of the way from C_i^0 to C_i^*, and at $t = 3\tau$ have approached 95%.

· τ_i and k_i functions of constituent (not reservoir)

$$\frac{C_i - C_i^*}{C_i^0 - C_i^*} = e^{-k_i t}$$

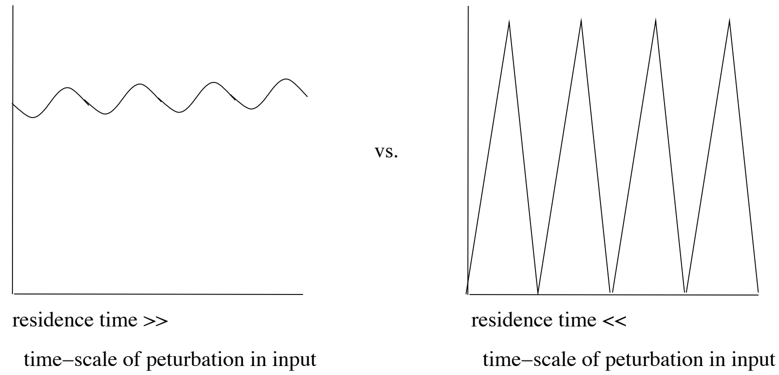


Figure 4.

- · sets up lag in ocean response - characteristic time-scales
- · very different spatial distributions depending upon sources and sinks, time-scales/residence times

- Sources and sinks

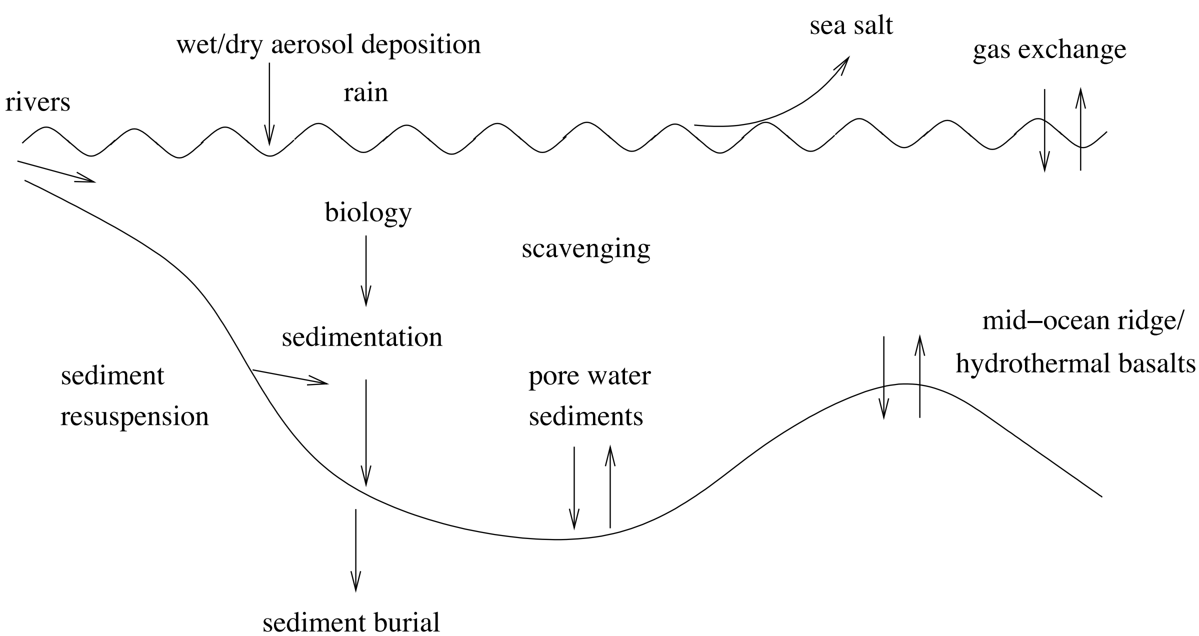


Figure 5.

For most elements, rivers are the primary sources, while sedimentation/burial are the primary sinks.

Estimating residence times:

$$\tau = \frac{\text{amount in ocean}}{\text{input}} = \frac{\text{amount in ocean}}{V_{\text{river}} \times C_{\text{river}}}$$

Complications and issues:

- River inventories highly variable
- Cyclic salts
- Anthropogenic activities (positive bias), these bias pre-industrial estimates
- Other sources

$$\tau = \frac{\text{amount in ocean}}{\sum \text{inputs}}$$

- Estimate using outputs instead

$\tau \leftrightarrow$ chemical reactivity $\qquad$ τ is $\mathcal{O}(10^2) - \mathcal{O}(10^8)$ years

- Major ions (those with high quantities), with residence times of $0.5 - 200 \times 10^6$ years

  Na, Mg, Ca, K, Sr, Cl, SO_4^{2-}, Br, F $\qquad$ $\tau \gg 1000$ years (overturning circulation timescale of ocean)

- Trace elements with long residence times

  Rb, Li, Mo, Cs, U $\qquad$ $0.3 - 3 \times 10^6$ years

  Low quantities because there are low quantities in source rocks

  Solubilized by stable oxyanions

- Trace elements with short residence times

  $\tau < 1000$ yrs, $50 - 1000$ yrs
  No longer "well-mixed"
  Fe, Ag, Hg, Th, Pa, Al, Pb, REE (Rare Earth Elements)

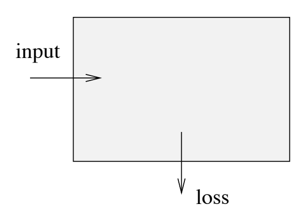


Figure 6.

Elements can also be categorized based on source and internal cycling pathways

- Aeolian (dust) deposited and water-column scavenged elements

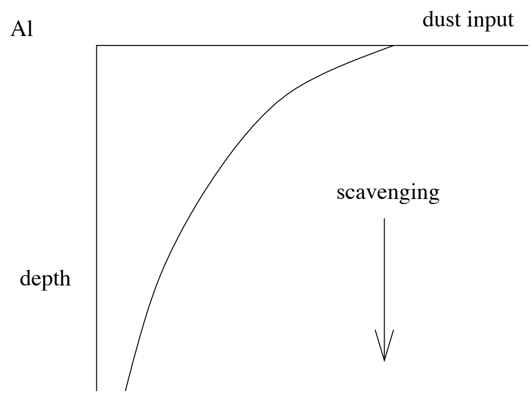


Figure 7.

Atlantic versus Pacific - large differences in dust deposition

- Biologically recycled elements

  Intermediate residence times/rapid uptake and recycling in the water column

  C, N, P (along with many trace elements) taken up by organism

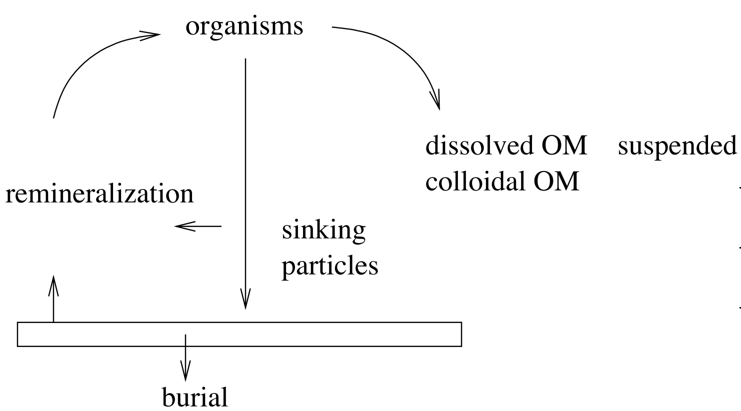


Figure 8.

- Rapid biological uptake
- Almost complete remineralization
- Only $\sim 1\%$ sediment burial

- Two components of biologically produced material

  - "Soft organic matter" - cells, carcasses, mucus, etc.

    C, N, P (O_2)

    Simple respiration and photosynthesis:

    $O_2 + CH_2O \rightleftharpoons CO_2 + H_2O$

    Elemental stoichiometry for marine plankton (Redfield ratios):

    $106\,CO_2 + 16\,NO_3^- + HPO_4^{2-} + 122\,H_2O + 18\,H^+ \rightarrow C_{106}H_{263}O_{110}N_{16}P_1 + 138\,O_2$

    Shallow remineralization

– "Hard organic matter" - shells, tests
  $CaCO_3$ - forams, coccoliths, pteropods, corals
  Si - diatoms, radiolarians
  $SrSO_4$ - Acantharia
  Deep remineralization

"Nutrient-like" elements associated with both "soft" and "hard" biological material

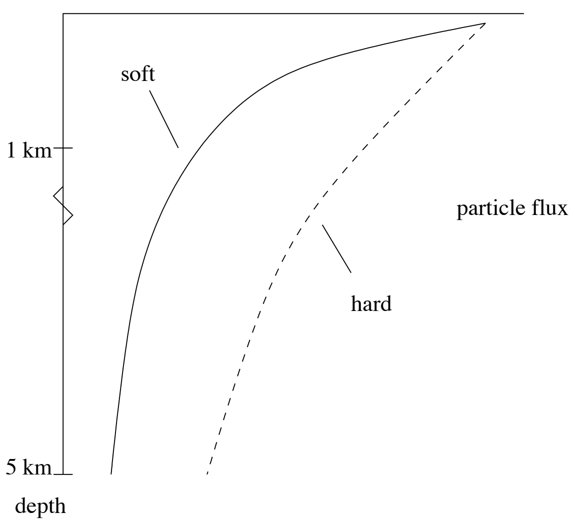


Figure 9.

Concentration profile of "Nutrient-like" elements

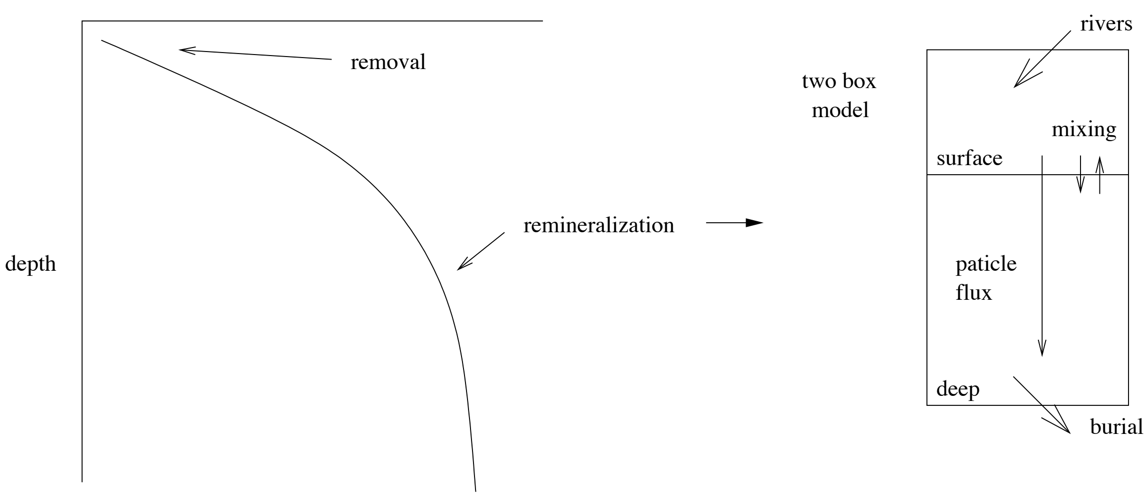


Figure 10.

$$
\begin{aligned}
f_{\text{rivers}} &\approx f_{\text{burial}} \\
\text{net upward mixing flux} &\approx \text{particle flux}
\end{aligned}
$$

$$
\begin{aligned}
\text{fluxes into surface box} &= \text{fluxes out of surface box} \\
V_R[C_R] + V_{\text{mix}}[C_{\text{deep}}] &= V_{\text{mix}}[C_{\text{shallow}}] + F_{\text{sink}}
\end{aligned}
$$

$$
\begin{aligned}
\text{fluxes into deep box} &= \text{fluxes out of deep box} \\
V_{\text{mix}}[C_{\text{shallow}}] + \gamma F_{\text{sink}} &= V_{\text{mix}}[C_{\text{deep}}] \\
\frac{V_{\text{mix}}}{V_R} &\approx 30
\end{aligned}
$$

$$
\begin{aligned}
\gamma &= \text{ fraction of sinking particle flux that remineralizes in deep box} \\
(1-\gamma) &= \text{ fraction that is buried}
\end{aligned}
$$

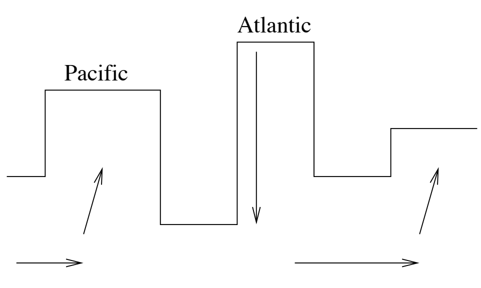


Figure 11.

Deep waters form in North Atlantic and Southern Ocean. Oldest deep waters are in the North Pacific

Ocean Conveyor Belt Circulation:

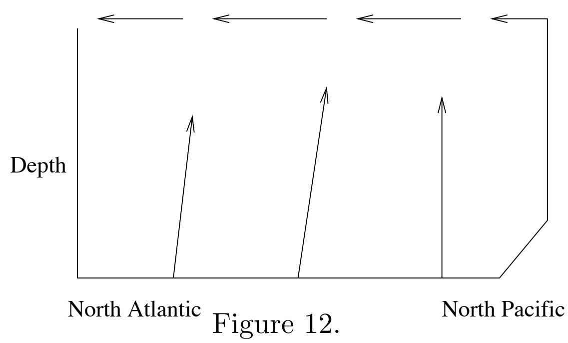


Figure 12.

Elevated concentrations of "nutrient-like" elements are found in the deep North Pacific because of continued organic matter remineralization along the deep-water circulation path

An example is NO_3^-, O_2, silicate from Broecker and Peng (1982).

Start building more complex box models.