

## Lecture 6: Mass Balance - The Cornerstone of Chemical Oceanography

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The chemical distributions on the earth and in the ocean reflect transport and transformation processes, many of which are cyclic. The cycling of water from the ocean to the atmosphere to land and back to the ocean via rivers is such an example. This basic cycling is often described in terms of the content of the various reservoirs (e.g., the ocean, the atmosphere, etc.) and the fluxes between them (e.g., evaporation, rivers, etc.). A fundamental question is how the rates of transfer between the reservoirs depend on the content of the reservoirs and on other external factors. The details of the distributions within the reservoirs are, for the most part, neglected.

Most oceanographers construct simple models to test their understanding of the essential elements of the system and to predict the response of a system to perturbations and forcing. The two main types of models used. These are:

### **Box (or reservoir) Models and Continuous Transport-Reaction Models**

First some basic definitions related to models in general and box models in particular.

- **Model** – A simplified or idealized description of a particular system or process that is put forward as a basis for calculations, predictions or further investigation. A model should contain only those elements of reality that are needed to solve the problem. A model is an imitation of reality that stresses those aspects that are assumed to be important and omits all properties considered nonessential.
- **Parameter** – A quantity that is constant in a particular case considered, but which varies in different cases.
- **Variable** – A quantity or force that, throughout a mathematical calculation or investigation, is assumed to vary or be capable of varying in value.
- **Closure** – Closure in a modeling sense usually means having the number of unknowns equal the number of equations. Often, closure is achieved by making simplifying assumptions.
- **Reservoir or Box (M)** – The amount of material contained by a defined physical regime, such as the atmosphere, the surface ocean or the lithosphere. The sizes of the reservoirs are determined by the scale of the analysis as well as the homogeneity of the spatial distribution. The units are usually in mass of moles.
- **Flux (F)** – Amount of material transferred from one reservoir to another per unit time.
- **Source (Q)** – A flux of material into a reservoir.
- **Sink (S)** – A flux of material out of a reservoir
- **Budget** – A balance equation of all sources and sinks for a given reservoir.
- **Residence Time or Turnover Time ( $\tau$ )** – The ratio of the content of a reservoir (M) divided by the sum of its sources ( $\Sigma Q$ ) or the sum of its sinks ( $\Sigma S$ ). Thus,  $\tau = M/\Sigma Q$  or  $\tau = M/\Sigma S$ .
- **Cycle** – A system consisting of two or more connected reservoirs where a large fraction of the material is transferred through the system in a cyclic fashion. Budgets and cycles can be considered over a wide range of spatial scales from local to global.

- **Steady State** – When the sources and sinks are in balance and do not change with time.
- **Closed System** – When all the material cycles within the system
- **Open System** – When material exchanges with components outside the system.

### **Mass Balance – Simple Box Models**

Many processes may act to control the distributions of chemicals in the ocean. The method of putting these processes together in a model utilizes the principle of mass balance applied to the system as a whole or some parts of it (control volumes). The system as a whole is linked to the environment by external inputs and outputs. Box models are especially useful for understanding geochemical cycles and their dynamic response to change.

Describing a model first requires choosing a system; that is, the division between what is "in" and what is "out". The second step involves choosing the complexity of the description of the "internal" system (how many components in the system).

The goal in modeling is to analyze all the relevant processes simultaneously. The concept of mass balance serves as a way to link everything together. To use the idea of a mass balance, the system is first divided into one or several "control volumes" which are connected with each other and the rest of the world by mass fluxes. A mass balance equation is written for each control volume and each chemical

The Change in Mass with Time = Sum of all Input Sources + Sum of Internal Sources –  
Sum of Outputs – Sum of all Internal Sinks

Such box models are used to determine the rates of transfer between reservoirs and transformations within a reservoir.

Advantages are:

1. It is easy to conceptualize where material is coming from and where it is going.
2. Provide an overview of fluxes, reservoir sizes, and turnover or residence times ( $\tau$ ).
3. They provide the basis for more detailed quantitative models.
4. They help identify gaps in knowledge.

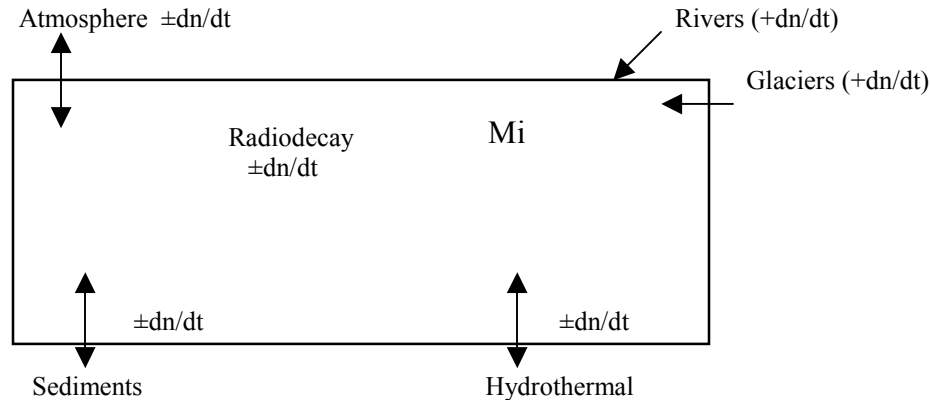
Disadvantages are:

1. The analysis is superficial and over-simplified.
2. Little or no insight is gained into what goes on inside the reservoirs or into the nature of the fluxes between them.
3. They usually assume homogeneous average distributions within reservoirs
4. They can easily give a false impression of certainty, even if all the individual fluxes have solid estimates. Remember, a model is an imitation of reality.

## Steady State and Residence Time

We can draw a one box model of the ocean with the main fluxes indicated. These include river and glacial input, atmospheric exchange, hydrothermal exchange, radioactive activity, and sediment exchange. Rivers and glaciers are shown here as ocean sources. The other fluxes can go both ways. The total dissolved mass in the box is called  $M$  and is assumed to be homogeneously distributed in the box.

Simple 1-Box Ocean



At **steady state** the dissolved concentration ( $M_i$ ) does not change with time:

$$(dn/dt)_{\text{ocean}} = \sum dn_i / dt$$

At steady state the sum of the sources  $\sum(dn_i/dt)_{\text{sources}}$  must equal the sum of the sinks  $\sum(dn_i/dt)_{\text{sinks}}$ .

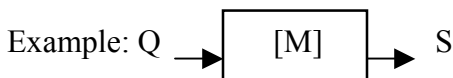
For most elements the main sources are from continents via the atmosphere and rivers. Removal to the sediments is a main sink for most elements. Hydrothermal processes can be both sources and sinks depending on the element. The following balance is a good approximation for most elements in the ocean:

$$(dm/dt)_{\text{ocean}} = F_{\text{atmosphere}} + F_{\text{rivers}} - F_{\text{sediments}} \pm F_{\text{hydrothermal}}$$

If we assume steady state then the change with time is zero or  $dM_i / dt = 0$ .

**Residence Time ( $\tau$ )** The residence time (also called turnover time) is defined as the ratio of the dissolved mass in a reservoir divided by the mass flux in or out of the reservoir. For example, using a simple model with one source and one sink,  $\tau$  can be thought of as the time it would take to fill the reservoir if the source ( $Q$ ) remained constant and the sink was zero (or vice-versa).

$$\tau = \text{mass} / \text{input or removal flux} = M / Q = M / S$$



$Q$  = input rate (e.g., moles  $\text{yr}^{-1}$ )  
 $S$  = output rate (e.g., moles  $\text{yr}^{-1}$ )  
 $[M]$  = total dissolved mass in the box (moles)

Residence time can also be calculated with respect to any one of the individual fluxes ( $Q_i$  or  $S_i$ ) as well, again with all other sources and sinks at zero. For example, you could calculate the residence time of Fe in the ocean with respect to input from either the atmosphere or rivers.

The rate of change equation for this simple model is the difference between the source(s) and the sink(s), thus:

$$d[M] / dt = Q - S$$

If the inflow rate equals the outflow rate, or  $Q = S$ , then  $d[M] / dt = 0$  and we would have steady state

A **zeroth order flux** means that the flux is not proportional to how much M is present in the one-box ocean. For example, river or atmospheric inputs that are not influenced by the oceanic content.

A **first order removal mechanism** means that the flux is proportional to how much is there. Examples of such removal rate mechanisms include: radioactive decay, plankton uptake and adsorption by sediments

These fluxes can be described as:

$$S = k [M] \quad \text{e.g. units for } S \text{ are mol yr}^{-1}$$

Where  $k$  (sometimes called  $\lambda$ ) is a first order removal rate constant ( $\text{t}^{-1}$ ) and  $[M]$  is the total mass ( $m$ ).

When the sink is described in this first order form we can rewrite the mass balance as:

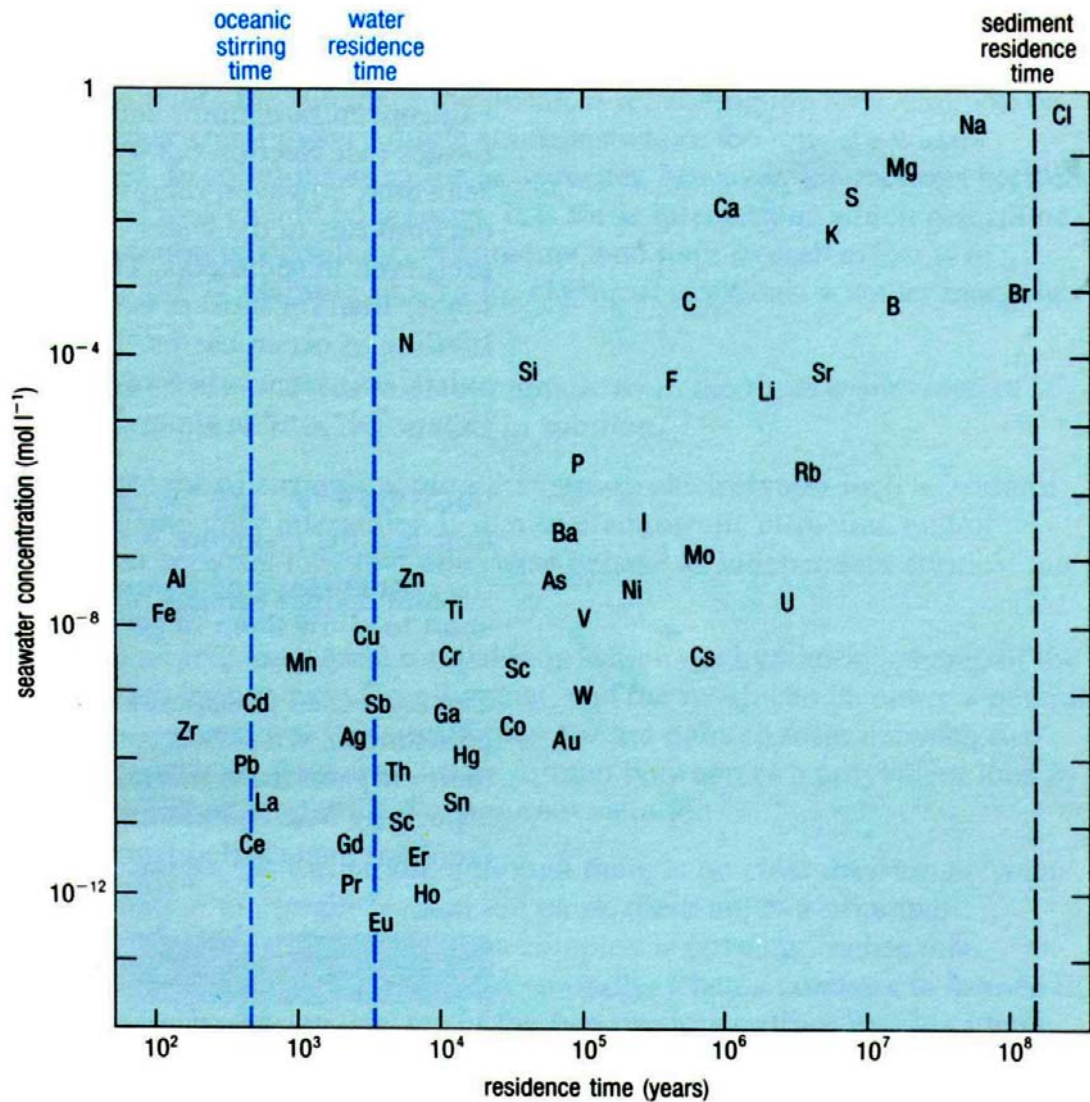
$$d[M] / dt = Q - k [M]$$

At steady state, when  $d[M] / dt = 0$ ,  $[M] / Q = \text{mass present/input} = 1/k = \tau$

This equation predicts an inverse relationship between elemental reactivity ( $k$ ) and residence time  $\tau$ ; as  $k$  goes up,  $\tau$  goes down. Elements will have a short residence time if they are readily incorporated into particles that are removed from the ocean.

If the value of  $\tau$  for a given element is less than the residence time of water, then  $\tau$  can not strictly be interpreted as a residence time and you would expect that the element would not be homogeneously distributed in the ocean.

Such a relationship is supported by a very simple analysis by Whitfield and Turner (1979) who showed that a strong correlation exists between the mean ocean residence time of an element and the element's concentration in seawater or the partitioning of that element between seawater and crustal rock (even though log scales hide a lot of scatter).



Graph showing the broad correlation between concentration ( $\text{mol l}^{-1}$ ) and residence time of several elements in seawater. Note that both scales are logarithmic.

Notice that  $\text{Cl}^-$  is concentrated in seawater and has a long residence time. Aluminum is at the other extreme. This reflects the tendency of  $\text{Cl}^-$  to partition preferentially into seawater (solution) relative to the crustal abundance and of Al to partition into mineral phases and thus have a higher abundance in the crust.

Some dimensions, areas and volumes to use for ocean box models are given in the Table. The simplest models are either whole ocean 1-Box models or 2-Box models where the ocean is divided into surface and deep layers.

<b>Characteristic Data for the Ocean</b>			
<i>Volume</i>	Total	V	1349.3 x 10 <sup>6</sup> km <sup>3</sup>
	Surface ocean (<200m)	V <sub>s</sub>	69.6 x 10 <sup>6</sup> km <sup>3</sup>
	Deep Ocean	V <sub>d</sub>	1279.7 x 10 <sup>6</sup> km <sup>3</sup>
<i>Area</i>	Surface Ocean	A	362.0 x 10 <sup>6</sup> km <sup>2</sup>
	At 200m	A <sub>200</sub>	335.2 x 10 <sup>6</sup> km <sup>2</sup>
<i>Mean Depth</i>	Total	h = V/A	3,727 m
	Surface Ocean	h <sub>s</sub> = V <sub>s</sub> /A	192 m
	Deep Ocean	h <sub>d</sub> = V <sub>d</sub> /A <sub>200</sub>	3,818 m
<i>River Inflow</i>		R	37,400 km <sup>3</sup> yr <sup>-1</sup>

### Dynamic Box Models

In many instances the source (Q) and sink (S) rates are not constant with time or they may have been constant and suddenly change. Here are some examples of how to set up dynamic box models. To describe how the mass in a reservoir changes with time after an increase in source (or sink) for a 1-Box ocean for example receiving anthropogenic contamination. Note that the sink is proportional to the contaminant concentration.

Starting with:

$$dM/dt = Q_0 - S = Q_0 - k M$$

We let the input increase to a new value Q<sub>1</sub> and we assume that the initial amount at t = 0 is M<sub>0</sub>. The new equation is:

$$dM/dt = Q_1 - k M$$

and the solution is:

$$M(t) = M_1 - (M_1 - M_0) \exp(-k t) = M_0 \exp(-k t)$$

This describes how M changes from M<sub>0</sub> to the new equilibrium value M<sub>1</sub>, ( $\Delta M = Q_1 / k$ ) with a response time equal to k<sup>-1</sup> or  $\tau_0$ .

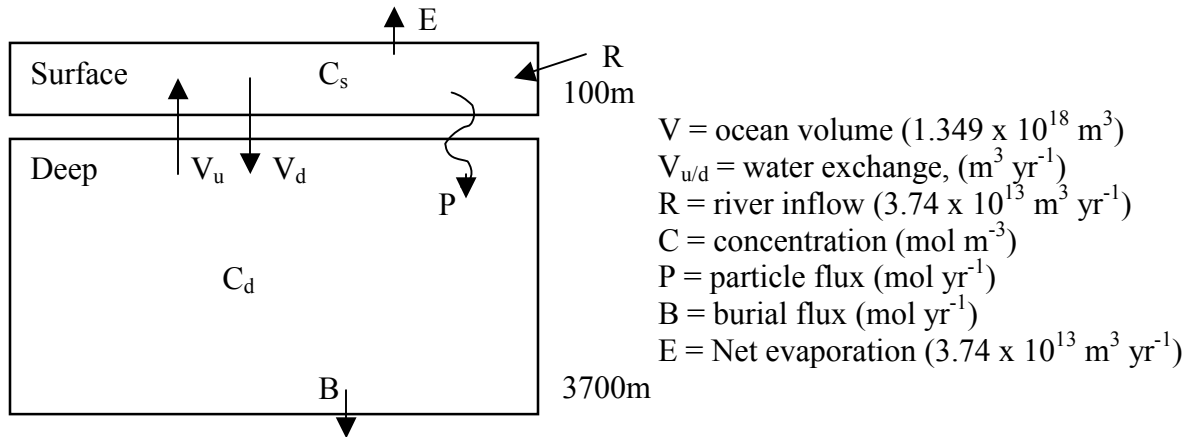
Where the response time is defined as the time it takes to reduce the imbalance to e<sup>-1</sup> or 37% of the initial imbalance (e.g. M<sub>1</sub> - M<sub>0</sub>). This response time-scale is referred to as the "e-folding time". If we assume M<sub>0</sub> = 0, then after one residence time (t =  $\tau$ ) we find that: M <sub>$\tau$</sub>  / M<sub>1</sub> = (1 - e<sup>-1</sup>) = 0.63 (remember that e  $\approx$  2.7). Thus, for a single box with a sink proportional to its content, the response time equals the residence time. Elements with a short residence time will approach their new value faster than elements with long residence times.

### Multi-Box Models

The simple treatment of 1-Box models can easily be generalized to systems with two or more boxes. Most natural systems are sufficiently complex that multi-box models with cyclic fluxes are required. It is simple to view 2- and 3-box models but as more boxes and cycles are added the problems become sufficiently complex that the principles of linear

algebra and matrix methods are required. The matrix methods are at least rotationally simple, especially for linear systems (e.g. when  $S = k M$ ). While this section becomes more mathematically difficult it is possible to read it in a qualitative sense. There are computer programs available for solving coupled box models without knowing how to actually do the math (e.g. STELLA, BOXES (Chameides and Perdue, 1997), MATLAB (the MathWorks, Inc.)).

We can start with a simple 2-box model that is often used to derive insight into the way the ocean works. The approach is deceptively simple and matrix algebra is not required. We assume that the ocean consists of two reservoirs - a surface box (100m) and a deep box (3700m). We assume that each box is well mixed and separated by a thermocline. Transport across the thermocline is approximated as an advection rate (units are volume per unit time, e.g.  $\text{m}^3 \text{yr}^{-1}$ ).



1. First we can write the water conservation balances:

$$E = R \quad \text{river inflow equals net evaporation}$$

$$V_u = V_d = V_{\text{mix}} \quad \text{upwelling and downwelling exchanges are equal}$$

2. The mass balance for an element in the surface layer is:

$$V_{\text{mix}} \{d[C_{\text{surf}}]/dt\} = R [C_{\text{river}}] - V_{\text{mix}} ([C_s] - [C_d]) - P$$

3. The mass balance for the deep layer is:

$$V_{\text{mix}} \{d[C_{\text{deep}}]/dt\} = V_{\text{mix}} ([C_s] - [C_d]) + P - B$$

4. At steady state we have:

$$d[C]/dt = 0 \quad \text{and} \quad R[C_{\text{river}}] = B$$

Two important properties that are derived from the two box model

- $g = \text{efficiency of bioremoval from the surface as particles.}$   
 $= \text{bioremoval/inputs} = \text{the fraction of the total input to the surface box that is removed as particles}$   
 $= P / (R C_{\text{river}} + V_{\text{mix}} C_{\text{deep}})$

2.  $f$  = fraction of particles that is buried. The efficiency of ultimate removal.  
 $f = B/P$  and  $B = R[C_{\text{river}}]$   
 $f = R[C_{\text{river}}] / P$   
 $= R[C_{\text{river}}] / (R[C_{\text{river}}] + V_{\text{mix}} C_{\text{deep}} - V_{\text{mix}} C_{\text{surf}})$   
 $= 1 / (1 + V_{\text{mix}}/R (C_{\text{deep}}/C_{\text{river}} - C_{\text{surf}}/C_{\text{river}}))$

The dynamics of a bioactive element in the ocean can be estimated from known rates of river water input and seawater mixing through the thermocline, plus the average concentrations of that element in river water plus surface and deep seawater, as indicated in this table.

Element Category	Element	$C_s/C_r$	$C_d/C_r$	$g$	$f$	$\tau$ (years)
Bio-limiting	P	0.15	3.0	0.95	0.01	100,000
Bio-limiting	Si	0.02	0.7	0.97	0.05	20,000
Bio-Intermediate	Ba	0.10	0.3	0.70	0.14	10,000
Bio-Intermediate	Ca	24.8	25	0.01	0.14	800,000

From Broecker and Peng (1982).

### Transport-Reaction Models

There are basically two kinds of transport

- 1) Direct transport due to the motion of the medium (e.g. advection) or due to external forces such as gravity (e.g. particle sinking).
- 2) Random transport leading to molecular or turbulent diffusion.

Sources and sinks of chemicals are not homogeneously distributed. The spatial heterogeneity in distribution of a chemical in an environmental system is determined by the ratio of the time-scale of the internal transport to the timescale of chemical reaction (input or removal). Boundary fluxes (e.g., air-sea, sediment-water) and chemical transformations are both important.

Transport time scales may vary with direction but are usually determined by the hydrodynamics of the system and not by the chemical reactivity of the elements. In contrast, time scales of removal are compound specific. We need to develop some tools for analyzing and describing the problem of spatial variation.

Advection-diffusion type models are frequently used by chemical oceanographers. This topic is treated lightly in Libes Ch. 4 (for water column) and in Ch. 12 (for sediments). The concepts and mathematics are largely the same, see also Munk (1966) Deep-Sea Research, 13, 707 and Craig (1969) JGR 74, 5491.



Advection-diffusion models are used to understand and interpret how dissolved species move in three-dimensional coordinates in the ocean. Historically, this has been an important area of overlap between chemical and physical oceanography. This is a tool that can be applied to studies of the distribution and reactions of chemicals of both natural and pollution origin.

Objectives: to quantify a) transport and mixing processes  
b) production/consumption of chemical species

These types of models are solved by fitting curves to empirical data. Start with a 3-dimensional box and consider all possible influences that control the concentration of a substance C within the box

C may be affected by:

1. Advection (currents)
2. Diffusion (random motion)
3. Consumption (scavenging, chemical reaction, radioactive decay)
4. Production (remineralization, chemical reaction, radioactive production)

We combine the effect of the two main transport mechanisms (advection and diffusion) with simple expressions of reaction (movement in 3 directions). The transport can be expressed as the combined action of advective and diffusive transport on the temporal variation of the concentration, C:

$$(\partial c / \partial t)_{\text{trans}} = -(u \partial c / \partial x + v \partial c / \partial y + w \partial c / \partial z) + \partial / \partial x (K_x \partial c / \partial x) + \partial / \partial y (K_y \partial c / \partial y) + \partial / \partial z (K_z \partial c / \partial z)$$

Where u, v and w are the three Cartesian velocity components and  $K_x$ ,  $K_y$  and  $K_z$  are the turbulent diffusion coefficients. The values of K may vary spatially, thus they are inside the parentheses.

The chemical reactivity can be most simply expressed as a combination of zeroth order (J) and first order ( $\lambda C$ ) terms expressed as:

$$(\partial c / \partial t)_{\text{react}} = J - \lambda C$$

Combining transport and reaction gives:

$$\partial c / \partial t = (\partial c / \partial t)_{\text{trans}} + (\partial c / \partial t)_{\text{react}}$$

The general form of the transport or mass balance equation in 3-dimensions, with all terms included is written as:

$$(\partial c / \partial t) = K_x \partial^2 c / \partial x^2 + K_y \partial^2 c / \partial y^2 + K_z \partial^2 c / \partial z^2 - u \partial c / \partial x - v \partial c / \partial y - w \partial c / \partial z + J - \lambda C$$

This general form has 8 unknowns.

Where:  $K_x, K_y, K_z$  - eddy diffusion coefficients (e.g.,  $\text{cm}^2 \text{sec}^{-1}$ )  
 $u, v, w$  - advection velocities (e.g.,  $\text{cm sec}^{-1}$ )  
 $J$  - zeroth order production (+) or consumption (-)  
 $\lambda$  - First order production/consumption rate constant ( $\text{sec}^{-1}$ )  
(e.g. radioactive decay or chemical scavenging)

What is the origin of these terms?

**Diffusion:** The diffusive flux (for each direction) as a function of time is given as:

$$\partial c / \partial t = K_z \partial^2 c / \partial z^2$$

For steady state boundary conditions we can use Fick's First Law where the flux is proportional to the concentration gradient.

$$F_c = K_z \partial c / \partial z$$

Eddy diffusion is treated in an analogous way as molecular diffusion. Note that eddy diffusion is a much more rapid process than molecular diffusion (D).

Vertical eddy diffusion (in the deep sea):  $K_z = 0.1$  to  $10 \text{ cm}^2 \text{sec}^{-1}$

Horizontal eddy diffusion coefficients are typically much larger,  $K_x = K_y = 10^7 \text{ cm}^2 \text{sec}^{-1}$ .

**Advection:** Still in the presence of active currents eddy diffusion is a minor influence – advective transport is usually  $10^3$  to  $10^5$  times faster than eddy diffusion. The time rate of change by advection is written as:

$$\partial c / \partial t = -w \partial c / \partial z \text{ (similar for each direction)}$$

Typical values of  $w$  in the abyssal ocean are  $2 - 11 \text{ m yr}^{-1}$

The complete equation is difficult to solve so we make some assumptions.

1) Steady state  $\partial c / \partial t = 0$

2) The horizontal concentration gradients are small. Thus the model is independent of any considerations of horizontal transport.

$$\partial c / \partial y \text{ and } \partial c / \partial x \ll \partial c / \partial z$$

$$\text{and } v \partial c / \partial y \text{ and } u \partial c / \partial x \ll w \partial c / \partial z$$

The general equation reduces to the form of an ordinary differential equation. This simplified equation has 4 unknowns.

$$K_z \partial^2 c / \partial z^2 + J = w \partial c / \partial z + \lambda c$$

This model can be further simplified to apply to four classes of tracers.

a) Stable conservative profiles like salinity and potential temperature:  $J = \lambda = 0$

b) Stable non-conservative profiles such as  $\text{O}_2$ ,  $\text{PO}_4$  and Cu:  $\lambda = 0$

c) Radioactive conservative profiles such as  $^3\text{H}$  and  $^{137}\text{Cs}$ :  $J = 0$

d) Radioactive and non-conservative profiles like  $^{14}\text{C}$ ,  $^{226}\text{Ra}$ , and  $^{234}\text{Th}$  all terms included.

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