

Chapter 2: 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 depends on the content of the reservoirs and on other external factors. The details of the distributions within the reservoirs is 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 forcings. The principal of **Ockham's Razor** has served oceanographers well. This principle states that: When seeking to explain phenomena, start with the simplest theory (see Safire, 1999, for the etymology).

A few words about the scientific method. Some fields of science are advancing more rapidly than others. It is the contention of Platt (1964) that those rapidly advancing fields are those where the method of doing research called "**strong inference**" is systematically used and taught. Strong inference consists of formally and explicitly applying the following steps to every problem.

- 1) Devising alternative hypotheses
 - 2) Devising a crucial experiment (or experiments) with alternative possible outcomes each of which will, as nearly as possible, exclude one or more of the hypotheses
 - 3) Carrying out the experiment so as to get a clean result.
- 1') Recycling the procedure to refine the hypotheses that remain.

Scientific hypotheses are most securely "validated" when (i) they make successful predictions; (ii) there are conceivable observations that could, in principle, refute them, but have not; and (iii) there is a comparably sensible competitor theory that is faring worse. Developing alternative simple models is part of this process.

The purpose of this chapter is to introduce the tools necessary to develop the two main types of models used in chemical oceanography. These are:

- Box (or reservoir) Models
- and
- Continuous Transport-reaction Models

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

- **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. The least necessary model is the best possible model for the purpose. A model is an imitation of reality which stresses those aspects that are assumed to be important and omits all properties considered to be nonessential. A model is like a caricature of a real system.
- **Parameter** - A quantity which is constant (as distinct from ordinary variables) in a particular case considered, but which varies in different cases. An independent variable in terms of which each co-ordinate of a point is expressed.
- **Variable** - A quantity or force which, 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 (M)(also box or compartment)** - The amount of material contained by a defined physical regime, such as the atmosphere, the surface ocean or the lithosphere. The size 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)** - The 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.
- **Turnover Time (τ)** - The ratio of the content (M) of a reservoir divided by the sum of its sources (ΣQ) or sinks (ΣS). 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 outside the system.

A. 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). Control volumes or boxes are connected by internal transport processes such as advection and diffusion. 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.

The framework of box models for geochemical cycles is conceptually similar to chemical kinetic reactions and similar equations are used to describe the stability of chemical and biochemical systems (Prigogine, 1967). The Lotka-Volterra predator-prey model of population dynamics is a classic example of the such equations.

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.

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 Inputs + 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. They are easy to conceptualize and visualize where material is coming from and going to.
2. They provide an overview of fluxes, reservoir sizes and turnover or residence times (τ)
3. They provide the basis for more detailed quantitative models
4. They help identify gaps in knowledge

Disadvantages are:

1. The analysis is superficial
2. Little or no insight is gained into what goes on inside the reservoirs or into the nature of the fluxes between them.
3. It usually assumes 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.

Introduce the concept of 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 and sediment exchange. Rivers and glaciers are shown here as ocean sources. The other fluxes can go both ways. Radioactive decay is a source or sink for radioactive elements in the ocean. The total dissolved mass in the box is called M and is assumed to be homogeneously distributed in the box.