The simultaneous use of chemical tracers in oceanic studies

I. *General theory of reservoir models*[1, 2]

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ABSTRACT

The reservoir, or "box", model is a useful starting point for studies of chemical tracers. The model can be derived from the chemical transport equation for a continuous ocean and thus rests on a sound physical foundation. The assumption that the tracers are well-mixed inside each reservoir is discussed and found unnecessary. The model is well adapted for dealing with sets of chemical tracers which simultaneously undergo chemical reactions, isotopic fractionation, radioactive decay, and exchange with the atmosphere.

In this article we relate the transfer coefficients of the reservoir model to the advective and diffusive coefficients of the space-averaged chemical transport equation for a continuous ocean, and we develop general methods for applying the reservoir model to a large suite of nonconservative chemical tracers. In an article which follows we apply the concepts of this article to a study of eight chemical tracers in the Pacific Ocean.

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[1] Contribution from the Scripps Institution of Oceanography. New Series.

[2] Contribution no. 183. Institute of Meteorology, University of Stockholm.

1. Introduction

1.1. *Introductory remarks*

Oceanic chemical data may be interpreted by relating observed distributions of chemicals in the ocean to sources and sinks of those chemicals and to the motion of the water. From a knowledge of concentrations, sources, and sinks, we can deduce water motion; from a knowledge of concentrations and water motion we can deduce chemical sources and sinks. In both cases the observed chemical species act as *tracers* of the oceanic processes under investigation.

Total ocean salt (or "salinity") has been used extensively as a tracer of water motion. It has no oceanic sources and sinks, and its distribution within the oceans depends solely on transport by the water. For example, a study by Wüst (1935) of the salinity distribution in the South Atlantic Ocean reveals a flow of intermediate water and bottom water northward from the Antarctic Ocean into the South Atlantic Ocean, and the vertical mixing of these waters with an intermediate layer of deep water originating from the North Atlantic Ocean.

The salinity at the ocean surface depends on evaporation and atmospheric precipitation as

well as on water transport. Wüst (1954), for example, from the surface distribution of salinity and the difference between evaporation and precipitation, deduced that the rate of vertical exchange between surface water and intermediate water is roughly the same for all oceanic regions except the Arctic.

The chemical elements nitrogen, oxygen, and phosphorus are linked to the production and decomposition of organic matter in the oceans. A knowledge of their distributions in various chemical forms has been used to deduce both water motion and sources and sinks. Riley 1951), for example, after prescribing the water motion consistent with the distributions of salinity and temperature, calculated biological sources and sinks of inorganic nitrogen, oxygen, and phosphorus. Wyrtki (1962), on the other hand, used Riley's estimate of biological sources and sinks and the distribution of inorganic oxygen and phosphorus to estimate vertical advection and diffusion.

In all such studies the known quantities have been too few to solve the transport equation except after making considerable simplifications or introducing large computational errors. For example, Wyrtki principally considered time averages of vertical motion while Riley considered time averages of both vertical and horizontal motion but attached significance to such small differences in tracer concentrations that his results were unstable to experimental errors. Both Riley and Wyrtki neglected time variations.

Radiocarbon has been used in time-independent transport studies simultaneously with stable tracers by Bolin & Stommel (1961), Eriksson (1962), and Munk (1966). Bolin & Stommel used a reservoir (or "box") model to investigate the relations of salinity, temperature, and radiocarbon to abyssal circulation. They determined the relative contributions of combined intermediate waters, Atlantic deep water, and Antarctic bottom water to the deep water (or "common water") of the Pacific and Indian Oceans. The model was relatively insensitive to small experimental errors. Eriksson, extending an earlier study of stable tracers (Eriksson, 1959), investigated salinity, temperature, oxygen, phosphorus, nitrogen, carbon, carbonate alkalinity, and radiocarbon, using a reservoir model which emphasized transport between the ocean surface and deep water. In both studies, however, he introduced *a priori* assumptions that make his principal conclusions unconvincing. Munk has interpreted the distribution of salinity, temperature, oxygen, radiocarbon, and radon in the Pacific Ocean by considering the vertical transport above and north-south transport below 4000 meters. He represented vertical transport with a second-order differential equation identical to Wyrtki's. His representation of horizontal transport is equivalent to a two reservoir model which exchanges water across the equator.

These studies by no means exhaust the possibilities for using tracers simultaneously. All chemical tracers are transported by the same water, and the more tracers under investigation, the more information should be deducible by applying the transport equation. New data on both well-known and less-familiar tracers are being acquired rapidly, and the prospect of applying the complete transport equation is less distant today than two decades ago when Sverdrup wrote (Sverdrup *et al.*, 1942, p. 162):

> "If the external influences were clear, if processes of diffusion and advection were known, and if biological and organic chemical processes were fully understood, the distribution of all concentrations could be accounted for. It would then be possible not only to explain the average distribution but also to account for all periodic and apparently random changes. This is the distant goal but when working toward it one must be fully aware of the limitations of the different methods of approach."

This final caution might usefully apply to reservoir models as well as to the continuous models Sverdrup had in mind, especially since none of the recent investigators of reservoir models has demonstrated that such models rest on a sound physical foundation. Furthermore, no convincing study with reservoir models has been made of a suite of complicated nonconservative tracers such as Eriksson dealt with, even though such a study would help to demonstrate the advantages and deficiencies in using chemical tracers simultaneously to study transport phenomena. We believe that both demonstrations are overdue. In this article we discuss the theoretical foundations of reservoir models. In a succeeding article

(Bolin & Keeling, 1968) we apply a reservoir model to a suite of nonconservative tracers in the Pacific Ocean.

We shall first consider the ocean as a continuum (section 2). We shall then show that the governing differential equation of transport can be approximated by the algebraic equation which governs the transfer of a tracer in the reservoir model (section 3). We shall next (section 4) develop a formulism for dealing with nonconservative tracers which undergo chemical reactions or radioactive decay within the ocean, volatile tracers which undergo exchange with the atmosphere, and isotopic tracers which undergo fractionation relative to the bulk element.

In the next article we shall illustrate these general methods by considering a specific model of the ocean similar to that proposed by Eriksson (1959) in which the ocean is divided into three reservoirs, two of which interact with the atmosphere. This division, although a crude representation, will test in considerable detail the simultaneous use of oceanic tracers.

Since all readers may not be equally interested in both the general theory of reservoir models and our specific illustration we have arranged the material so that the two articles may be read separately. They are closely linked, however: sections and equations are numbered in a single series, and numerous cross-references are given.

1.2. *List of symbols*

1.2.1. We shall use the following general notations:

A surface area (see subsection 3.2)

F net flux of water from the atmosphere, owing to precipitation and evaporation, into a boundary reservoir of the ocean (cf. 3.22)

h that part of the flux of a rare isotope (e.g., radiocarbon) from the atmosphere into the ocean owing to a difference in the isotopic ratio across the ocean surface (cf. 4.43)

i subscript, denotes an arbitrary region or an average, over the volume of that region

i' subscript, denotes a region adjoining region i ($i' = x, -x, y, -y, z, -z$)

ii' subscript, denotes the surface common to regions i and i', or an average, positive when directed outward, over that surface

$i'i$ subscript, denotes a corresponding average, positive when directed inward

$\mathbf{i}, \mathbf{j}, \mathbf{k}$ unit vectors in the directions of the x, y, and z axes, respectively

k reservoir model transfer coefficient (cf. 3.6)

K_x, K_y, K_z the coefficients of eddy diffusivity in the directions of the x, y, and z axes, respectively (cf. 2.2), and with surface averages, $K_{ii'}$, as defined by (3.4)

p partial pressure of a chemical compound in the atmosphere or in a surface reservoir of the ocean (cf. 4.32)

$^*p$ corresponding partial pressure for a compound involving a rare isotope (cf. 4.36)

q concentration of a chemical tracer in the ocean, defined by (4.7)

Q reservoir source function defined (cf. 3.20) as the local time change of a chemical compound averaged over a region owing to chemical reaction, radioactive decay, and exchange with the atmosphere

R local time change in concentration per unit volume owing to chemical reactions a, b, ..., l, ... and radioactive decay. The function R (cf. 2.1) is the sum of local source terms, $\Sigma_l R_l$, which refer to these processes individually (cf. 4.8 and 4.9)

r rate of a chemical reaction (cf. 4.12)

$^*r$ corresponding rate for a reaction which involves a rare isotope

$\mathcal{R}$ abundance ratio of a rare isotope to the corresponding bulk element, defined by (4.19)

t time

T time interval over which an average value ($\bar{}$) has been computed

V component of $\mathbf{V}$ normal to a surface as specified by a subscript (cf. 3.1 and 3.8)

$\mathbf{V}$ the three-dimensional velocity vector with the components V_x, V_y, and V_z in the directions of the x, y, and z axes, respectively (cf. 2.1)

W the volume of a reservoir in the ocean (cf. 3.1)

α isotopic fractionation factor defined by (4.20)

β reaction coefficient, expressing the power dependence of the reaction rate on the concentration of a specific chemical species (cf. 4.12)

γ source ratio between two tracers, defined by (4.16) for a point and by (4.28) for a reservoir

$\varkappa$ rate coefficient for chemical reaction expressing the dependence of the reaction rate on environmental factors (cf. 4.12)

$^*\varkappa$ corresponding coefficient for a chemical reaction which involves a rare isotope (cf. 4.20)

μ stoichiometric coefficient specifying the number of concentration units of tracer contributed by one concentration unit of a specific chemical species (cf. 4.7)

ν stoichiometric coefficient for a chemical reactant or product (cf. 4.10)

χ a chemical compound, radical, or ion (cf. 4.10)

$^*\chi$ a rare isotopic equivalent of χ (cf. 4.19)

$[\chi]$ the concentration of χ

$(^-)$ denotes a centered time average over a time interval, T

$(\ )'$ denotes an instantaneous departure from the time average denoted by $(^-)$ (cf. 2.1)

$(\ )''$ denotes a spatial departure from a time-space average $(^-)_{ii'}$ (cf. 3.2)

$(\partial/\partial t)_l$ denotes the local rate of change with time owing solely to chemical process l (cf. 4.8) or, with m replacing l, boundary exchange process m (cf. 4.29)

* superscript, denotes a rare isotope (either stable or radioactive)

1.2.2. In subsections 4.3 to 4.7 we shall employ the following subscripts and superscripts:

Superscripts	*Specific notation*	*General notation*
Tracer (letter index)	C (principal tracer)	L
Corresponding rare isotopic tracer	*	L^*
Subscripts		
Location in a reservoir	0, 1, 2, ...	i
Location on a reservoir surface	01, 02, ...12...	ii'
Chemical species	1, 2, ...	j
Reaction component	1, 2, ...	k
Reaction (letter index)		
net or in general:	$a, b, \ldots$	l
forward:	...	$l+$
reverse:		$l-$
Exchange (letter index)		
net or in general:	$f, g, \ldots$	m
evasion:		$m+$
invasion:		$m-$

1.1.3. Mathematics and chemical equations are noted in the text by decimal figures enclosed in parentheses.

2. The general transport equation

Consider an arbitrary point in the ocean. The general equation that governs the distribution of any tracer at that point (cf. Sverdrup *et al.*, 1942, p. 160) reads:

$$\frac{\partial \bar{q}}{\partial t} + \nabla \cdot (\bar{q}\bar{\mathbf{V}}) + \nabla \cdot (\overline{q'\mathbf{V}'}) - \bar{R} = 0 \qquad (2.1)$$

where q denotes the concentration of the tracer, $\mathbf{V}$ the three-dimensional velocity vector for the ocean water, R the local time change of concen- owing to chemical reactions and radioactive decay, a bar $(^-)$ a centered time average over a time interval T, an accent mark $(\ )'$ the departure from this average (for example, $q = \bar{q} + q'$), and $\partial/\partial t$ the local rate of change with time owing to processes with time scales large compared with T. Exchanges with the atmosphere and the ocean bottom are expressed by appropriate boundary conditions. The water is assumed to be incompressible (see subsection 3.5). We will call $\bar{q}\bar{\mathbf{V}}$ the advective transport; $\overline{q'\mathbf{V}'}$ the eddy transport.

According to (2.1) the local time rate of change of tracer concentration, $\partial\bar{q}/\partial t$, depends on:

(a) divergence of the flux owing to mean motion, or advection, expressed by $\nabla\cdot(\bar{q}\bar{\mathbf{V}})$,

(b) divergence of the flux owing to eddy motion, or turbulence, expressed by $\nabla\cdot(\overline{q'\mathbf{V}'})$,

(c) sources, expressed by a local source function, $\bar{R}$ (by "source" we will always imply sources and sinks).

The eddy transport, $\overline{q'\mathbf{V}'}$, depends on the covariance of deviations from the mean of concentration and velocity. Data are not available to compute this averaged product; at best we have only a limited knowledge of *mean* concentrations and velocities. Therefore, as a first approximation in Cartesian coordinates, we put:

$$-\overline{q'\mathbf{V}'} = K_x \frac{\partial \bar{q}}{\partial x}\mathbf{i} + K_y \frac{\partial \bar{q}}{\partial y}\mathbf{j} + K_z \frac{\partial \bar{q}}{\partial z}\mathbf{k} \qquad (2.2)$$

where K_x, K_y, and K_z are coefficients of the so-called "eddy diffusivity" and $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are unit vectors in the axial directions x, y, and z. This assumption is useful if the concentration elements do not influence the motion of the water, or otherwise vary systematically with $\mathbf{V}$ over time scales smaller than T in such a way that the coefficients have different values for different tracers. Therefore, we must not consider heat and momentum as tracers, and even salinity must be used with care since the density of ocean water partially depends on it. Admittedly, we cannot get a complete understanding of the mechanisms of turbulence in the ocean if we make use of (2.2), but we may obtain a general idea of the intensity of the long-term mean eddy transport in various parts of the ocean, and we may at least hope to determine, from the distribution of certain tracers, coefficients which are appropriate to predict the effect of eddy motion on the distribution of other tracers.

With approximation (2.2), the motion of the ocean at a point is described by six scalar fields, $\bar{V}_x$, $\bar{V}_y$, $\bar{V}_z$, K_x, K_y, and K_z, the former three being components of $\bar{\mathbf{V}}$ along the x, y, and z axes.

Each tracer yields one relation in time and space between these six variables; the continuity of water furnishes an additional independent relation. We therefore, in principle, need to know the time dependent distribution of five tracers to determine the six scalar fields of water motion. Even then, the problem is solvable only if the local source functions, $\bar{R}$, are known for all five tracers, and if the distributions of the various tracers are sufficiently different not to yield redundant equations (cf. Bolin & Stommel, 1961). In reality, the source functions are often poorly known, while distributions of many substances, such as the individual chemical species of ocean salt, are so similar that they effectively act as one tracer. On the other hand, sources of tracers are sometimes related. As examples, the formation of organic compounds in the ocean involves carbon, oxygen, phosphorus, and nitrogen in roughly constant proportions (Redfield *et al.*, 1963). Given the distributions of a sufficient number of chemically related tracers we can, in principle, solve both for the six scalar fields of water motion and for certain related source functions.

3. The reservoir model as an approximation of the space-averaged transport equation

3.1. *Introduction*

Owing to experimental limitations, all ocean measurements of concentration, q, and velocity, $\mathbf{V}$, must be reduced to averages in time and space before they are put to use to solve the transport equation. Time averaging was introduced already in section 2. We now consider further approximations which arise from the need to take space averages as well.

We shall use the transport equation to obtain estimates of the components of the mean velocity, $\bar{\mathbf{V}}$, the coefficients of eddy diffusivity, K_x, K_y and K_z and some of the tracer sources, given experimental values of $\bar{q}$ and estimates of other related tracer sources. Two techniques exist for adapting oceanic chemical data for this purpose:

(1) The data may be represented by a series of continuous functions suitably chosen with regard to the oceanic domain.
(2) The data may be represented by discrete values in points in a regular mesh covering the oceanic domain. Derivatives of q, which occur in the transport equation, may be approximated by taking differences between mesh points.

Each technique has certain advantages. For example, we used the first technique in an investigation of atmospheric transport several years ago (Bolin & Keeling, 1963). In this investigation we shall use the difference method, essentially on the grounds that it will be simpler computationally. Subsection 3.2 adapts the general equation for solution by use of finite differences; the remainder of section 3 develops an approximation by differences which is equivalent to the reservoir, or "box", model.

3.2. *The space-averaged transport equation*

Consider an arbitrary region, i, with stationary boundaries within the ocean. (Regions with exterior boundaries will be considered in subsection 3.4.) Denote its volume by W_i, its total surface area by A_i. Integrating (2.1) over W_i and applying the theorem of Gauss [see e.g.,

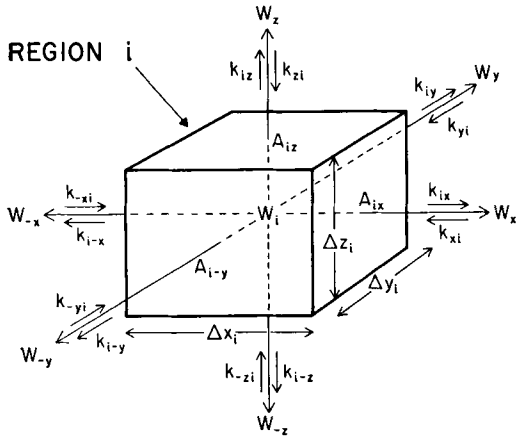

Fig. 1. The general reservoir model of the interior of the ocean. Symbols are explained in the text.

Sokolnikoff, 1939, p. 169) to the integrals of $\nabla\cdot(\bar{q}\bar{\mathbf{V}})$ and $\nabla\cdot(\overline{q'\mathbf{V}'})$:

$$\int_{W_i}\frac{\partial\bar{q}}{\partial t}\,dW+\int_{A_i}(\bar{q}\,\bar{V}+\overline{q'V'})\,dA-\int_{W_i}\bar{R}\,dW=0 \tag{3.1}$$

where $\bar{V}$ and $\overline{q'V'}$ denote the scalar components of $\bar{\mathbf{V}}$ and $\overline{q'\mathbf{V}'}$ normal to surface A_i, counted positive when directed outwards.

For convenience (cf. Fig. 1) let us suppose that region i is rectangular and bounded by surfaces parallel to the x, y, and z axes, and that region i shares its six planar surfaces with six adjoining regions in the abutting directions. (The exact shape of the adjoining regions need not be specified.) Denote these adjoining regions in the positive and negative axial directions by x, $-x$, y, $-y$, z, $-z$, or in general by i'. Denote the six planar surfaces of region i by ix, i–x, iy, i–y, iz, i–z, or in general by ii'. Denote the axial dimensions of region i by Δx_i, Δy_i, Δz_i, or in general by Δr_i, the x dimension of region x by Δx_x, etc.

Let subscript i applied to concentration, eddy velocity, or source function, or to their derivatives or products, denote an average over volume W_i and let subscript ii' denote an average over surface ii', positive when directed outward. Then (cf. 3.1):

$$\frac{\partial\bar{q}_i}{\partial t}W_i+\sum_{i'=x\ldots-z}\{(\bar{q}\,\bar{V})_{ii'}+(\overline{q'V'})_{ii'}\}A_{ii'}-\bar{R}_iW_i=0 \tag{3.2}$$

We next denote spatial departures from a time-space average by a double accent mark $(\ )''$ (for example on surface ii', $\bar{q}=\bar{q}_{ii'}+\bar{q}''$) and we rewrite (3.2):

$$\frac{\partial\bar{q}_i}{\partial t}W_i+\sum_{i'=x\ldots-z}\{\bar{q}_{ii'}\bar{V}_{ii'}+(\bar{q}''\bar{V}'')_{ii'}+(\overline{q'V'})_{ii'}\}A_{ii'}-\bar{R}_iW_i=0 \tag{3.3}$$

The three terms in the bracket express, respectively, the transport across boundary surface ii' of region i by the mean motion, by standing eddies, and by transient eddies.

Finally, we introduce a surface average coefficient of eddy diffusivity, $K_{ii'}$, to express the eddy transport per unit gradient across surface ii'. This approximation implies, instead of (2.2), that we assume

$$(\bar{q}''\bar{V}'')_{ii'}+(\overline{q'V'})_{ii'}=-K_{ii'}\left(\frac{\partial\bar{q}}{\partial r}\right)_{ii'} \tag{3.4}$$

where $(\partial/\partial r)_{ii'}$ denotes $(\partial/\partial x)_{ix}$, ..., $(\partial/\partial z)_{i-z}$. With approximation (3.4) the transport equation becomes:

$$\frac{\partial\bar{q}_i}{\partial t}W_i+\sum_{i'=x\ldots-z}\left\{\bar{q}_{ii'}\bar{V}_{ii'}-K_{ii'}\left(\frac{\partial\bar{q}}{\partial r}\right)_{ii'}\right\}A_{ii'}-\bar{R}_iW_i=0 \tag{3.5}$$

To solve equation (3.5) for the variables of water motion, $\bar{V}_{ii'}$, $K_{ii'}$, requires that we evaluate from oceanic data the time-surface averages $\bar{q}_{ii'}$ and $(\partial\bar{q}/\partial r)_{ii'}$. What approximation of the direct measurements of concentration is most appropriate for this purpose will depend on the problem and region under investigation. In the next subsection we shall show that (3.5) can be replaced by the transfer equation for a reservoir model by the simple expedient of approximating these time boundary averages by linear combinations of the time-volume averages $\bar{q}_i$ and $\bar{q}_{i'}$. The model will suit our needs in later sections, and we shall not investigate alternative approximations in this article.

3.3. *The reservoir model of the interior of the ocean*

The transfer equation for a reservoir model we may write for region i in the form (cf. Welander, 1959):

$$\frac{\partial\bar{q}_i}{\partial t}W_i=\sum_{i'=x\ldots-z}(\bar{q}_{i'}k_{i'i}-\bar{q}_ik_{ii'})+\bar{R}_iW_i \tag{3.6}$$

where $k_{ii'}$ and $k_{i'i}$ are non-negative forward and reverse transfer coefficients with the dimensions of volume of water per unit time and where the other symbols have their former meanings.

The reservoir model transfer coefficients $k_{ii'}$ and $k_{i'i}$ have no clearly defined physical basis, but neither do the eddy diffusivity coefficients $K_{ii'}$, introduced in (3.4). From a knowledge of the concentrations, sources and sinks, and oceanic boundary exchanges of five tracers, we can in principle (cf. section 2) obtain numerical values for either set of parameters. If we express the concentrations as volumetric averages, we evaluate the k's. If we express them as surface averages, we evaluate space averages of K_x, K_y, K_z and $\mathbf{V}$. Which set of transport parameters is superior depends upon which set behaves most nearly like physical constants independent of the tracer under investigation. We cannot presently decide this, because we cannot with existing data solve for even five tracers, much less test the results on additional tracers (cf. subsection 8.9).

We nevertheless attach more meaning to the surface-averaged transport parameters because the average velocities, $\bar{V}_{ii'}$, are clearly defined, and the eddy diffusivity coefficients, $K_{ii'}$, are analogous to molecular diffusivity coefficients, even though they may not be constants in actual situations encountered in the oceans. We, therefore, would like to relate the reservoir model k's of (3.6) to the velocities and eddy diffusivity coefficients of (3.5).

If we subtract (3.6) from (3.5) to eliminate common terms, and then rearrange, we can equate the alternate representations of the total transport in and out of region i:

$$\underbrace{\sum_{i'=x\ldots-z}\left\{\bar{q}_{ii'}\bar{V}_{ii'}-K_{ii'}\left(\frac{\partial\bar{q}}{\partial r}\right)_{ii'}\right\}A_{ii'}}_{\text{surface-averaged continuous model}}=\underbrace{\sum_{i'=x\ldots-z}(\bar{q}_{i'}k_{i'i}-\bar{q}_i k_{ii'})}_{\text{reservoir model}} \qquad (3.7)$$

To reconcile the two models we shall give a physical interpretation to $k_{ii'}$ and $k_{i'i}$ which is consistent with the definition of velocity, $\bar{V}_{ii'}$, and we shall express $\bar{q}_{ii'}$ and $(\partial\bar{q}/\partial r)_{ii'}$ in terms of $\bar{q}_i$ and $\bar{q}_{i'}$.

Of the various physical interpretations which have been given to the transfer coefficients, the interpretation which corresponds most closely to the continuous representation (2.1) and its surface-averaged equivalents (3.2) and (3.5) is to treat the k's as unidirectional average flows of water. If we define $V_{ii'}$ as the instantaneous average of the normal component of velocity over surface ii', then $(k_{ii'}/A_{ii'})$ is the time average of positive $V_{ii'}$, and $(k_{i'i}/A_{ii'})$ is the corresponding average for negative $V_{ii'}$, i.e.:

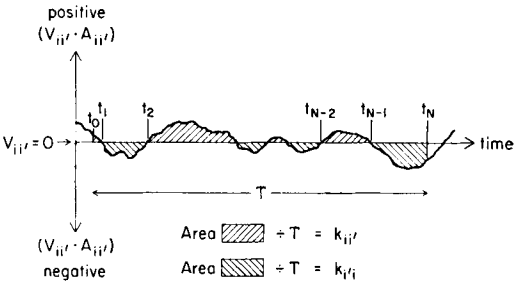

Fig. 2. Physical interpretation of reservoir model transfer coefficients. Symbols are explained in the text.

$$\left.\begin{aligned} k_{ii'} &= \frac{A_{ii'}}{T}\sum_{n=0,2,\ldots N-2}\int_{t_n}^{t_{n+1}} V_{ii'}\,dt \\ k_{i'i} &= \frac{A_{ii'}}{T}\sum_{n=0,2,\ldots N-2}\int_{t_{n+1}}^{t_{n+2}} -V_{ii'}\,dt \end{aligned}\right\} \qquad (3.8)$$

where time interval $t_N - t_0 = T$ has been subdivided into subintervals $t_{n+1}-t_n$, $t_{n+2}-t_{n+1}$, etc., during which $V_{ii'}$ is alternately positive and negative, as shown in Fig. 2. (If $V_{ii'}$ is negative at the beginning of interval T, we set $t_0 = t_1$, if positive at the end we set $t_{N-1} = t_N$.)

It follows that:

$$\bar{V}_{ii'} = \frac{1}{A_{ii'}}(k_{ii'}-k_{i'i}) \qquad (3.9)$$

We next note that assumptions (3.8) provide a reasonable basis for representing the eddy transport. To show this, we eliminate $\bar{V}_{ii'}$ from (3.7) according to (3.9) to obtain:

$$\sum_{i'=x\ldots-z}K_{ii'}\left(\frac{\partial\bar{q}}{\partial r}\right)_{ii'}A_{ii'}=\sum_{i'=x,\ldots-z}\left\{\left(\frac{\bar{q}_{ii'}-\bar{q}_i}{\tfrac{1}{2}\Delta r_i}\right)\frac{k_{ii'}}{2}+\left(\frac{\bar{q}_{i'}-\bar{q}_{ii'}}{\tfrac{1}{2}\Delta r_i}\right)\frac{k_{i'i}}{2}\right\}\Delta r_i \qquad (3.10)$$

where we have introduced the reservoir length Δr_i to emphasize the dimensional relationships. The eddy transport in the reservoir model is thus proportional to a sum of the products of the k's with "model gradients" obtained by comparing the surface average concentrations $\bar{q}_{ii'}$ with the volume average concentrations in the upstream reservoirs. (If $\Delta r_i \neq \Delta r_{i'}$ along a given coordinate, we may, if we prefer, express the model gradients in terms of mean lengths such as $\frac{1}{2}(\Delta r_i + \Delta r_{i'})$.)

If the tracer concentrations vary more or less uniformly over region i and its neighboring region i', as for example when eddy motion is the predominate mode of transport, we expect $\bar{q}_{ii'}$ to equal, approximately, the average of $\bar{q}_i$ and the $\bar{q}_{i'}$, i.e.:

$$\bar{q}_{ii'} \cong \frac{\bar{q}_i + \bar{q}_{i'}}{2} \tag{3.11}$$

and we expect the model gradient obtained by comparing the volume average concentrations between adjacent regions to equal, approximately, the average gradient over the adjoining surface, i.e.:

$$\left(\frac{\partial \bar{q}}{\partial r}\right)_{ii'} \cong \frac{\bar{q}_{i'} - \bar{q}_i}{\Delta r_i} \tag{3.12}$$

Substituting these approximations in (3.10):

$$K_{ii'} \cong \frac{\Delta r_i}{A_{ii'}}\left(\frac{k_{ii'} + k_{i'i}}{2}\right) \tag{3.13}$$

i.e., the eddy diffusivity coefficients, in this instance, are approximately proportional to averages of the forward and reverse reservoir model transfer coefficients. If $\bar{V}_{ii'} = 0$, $k_{ii'}$ and $k_{i'i}$ are equal by (3.9) and identical to $(K_{ii'}A_{ii'}/\Delta r_i)$.

A second possibility is that the tracers are relatively well-mixed within each reservoir in comparison to their mixing between reservoirs, as for example when distinctly different but nearly uniform concentrations are observed in adjacent regions of the ocean. Bolin & Stommel (1961), for example, cite the existence of distinct modes in the distribution of temperature and salinity in the world oceans to justify their using a reservoir model to investigate abyssal circulation. If strong internal mixing occurs, the model gradients which appear on the right side of (3.10) will be much smaller than the true boundary gradients $(\partial \bar{q}/\partial r)_{ii'}$ and the values of the $k_{ii'}$ obtained using (3.13) will be far larger than those which would be obtained from surface averages using (3.5).

Still another possibility is that the tracer concentrations, in one way or another, are significantly influenced by the mean motion. If so, (3.13) is clearly a poor approximation because it predicts that $(K_{ii'}/\Delta r_i)$ approaches $\frac{1}{2}\bar{V}_{ii'}$ as the eddy transport approaches zero, whereas it should approach zero. This unrealistic limit is a result of assumptions (3.8) and (3.11) which imply physically that the water at face ii' is a mixture of equal parts of the average water of both adjacent reservoirs, regardless of the prevailing direction of motion of the water.

More realistically, let us suppose that $\bar{q}_{ii'}$ is influenced more strongly by the volume average concentration in the reservoir which is predominately upstream.

The simplest possibility which yields correct limits for both purely advective and purely eddy transport is that

$$\left.\begin{aligned} \bar{q}_{ii'} &\cong \bar{q}_i \quad \text{when} \quad k_{ii'} > k_{i'i} \\ \bar{q}_{ii'} &\cong \bar{q}_{i'} \quad \text{when} \quad k_{ii'} < k_{i'i} \end{aligned}\right\} \tag{3.14}$$

In this case the transport by the mean motion depends on only the volume-averaged concentration in the upstream reservoir, i.e.:

$$\bar{q}_{ii'}\bar{V}_{ii'}A_{ii'} \begin{cases} \cong \bar{q}_i(k_{ii'} - k_{i'i}) & \text{if} \quad k_{ii'} > k_{i'i} \\ \cong \bar{q}_{i'}(k_{ii'} - k_{i'i}) & \text{if} \quad k_{ii'} < k_{i'i} \\ \cong 0 & \text{if} \quad k_{ii'} = k_{i'i} \end{cases} \tag{3.15}$$

and the eddy transport depends on only the smaller of the transfer coefficients for each face:

$$\sum_{i=x\ldots-z} K_{ii'}\left(\frac{\partial \bar{q}}{\partial r}\right)_{ii'} A_{ii'}$$

$$\begin{cases} \cong \displaystyle\sum_{i'=x\ldots-z} k_{i'i}\left(\frac{\bar{q}_{i'} - \bar{q}_i}{\Delta r_i}\right)\Delta r_i & \text{if} \quad k_{ii'} \geqslant k_{i'i} \\ \cong \displaystyle\sum_{i'=x\ldots-z} k_{ii'}\left(\frac{\bar{q}_{i'} - \bar{q}_i}{\Delta r_i}\right)\Delta r_i & \text{if} \quad k_{ii'} \leqslant k_{i'i} \end{cases} \tag{3.16}$$

It is also possible that

$$\bar{q}_{ii'} \cong \frac{k_{ii'}\bar{q}_i + k_{i'i}\bar{q}_{i'}}{k_{ii'} + k_{i'i}} \tag{3.17}$$

In this case the transport by the mean motion depends on a weighted mean of the volume average concentrations in both reservoirs, where the weighting accords to the relative strengths of the unidirectional average flows $k_{ii'}$ and $k_{i'i}$, while the eddy transport is proportional to a geometric mean of the k's, i.e.:

$$\sum_{i=x\ldots-z} K_{ii'}\left(\frac{\partial\bar{q}}{\partial r}\right)_{ii'} A_{ii'} \cong \sum_{i'=x\ldots-z} \frac{k_{ii'}k_{i'i}}{\frac{1}{2}(k_{ii'}+k_{i'i})}\left(\frac{\bar{q}_{i'}-\bar{q}_i}{\Delta r_i}\right)\Delta r_i \tag{3.18}$$

Since the reservoir model is likely to be useful principally when information on the $\bar{q}_{ii'}$ is lacking, we are not likely to establish a correspondence between the k's and K's that is any more convincing than as given by (3.16) or (3.18). Since the former is slightly simpler and agrees with the latter within a factor of 2, we shall employ it in sections 7 and 8. Since, in addition, we cannot evaluate the gradients $(\partial\bar{q}/\partial r)_{ii'}$, we shall assume that they are roughly equal to the model gradients, $(\bar{q}_{i'}-\bar{q}_i)/\Delta r_i$, whence (3.16) reduces to the set of approximations:

$$K_{ii'}\begin{cases} \cong \dfrac{\Delta r_i}{A_{ii'}}k_{i'i} & \text{if} \quad k_{ii'} \geqslant k_{i'i} \\ \cong \dfrac{\Delta r_i}{A_{ii'}}k_{ii'} & \text{if} \quad k_{ii'} \leqslant k_{i'i} \end{cases} \tag{3.19}$$

3.4. *The reservoir model with exterior boundaries*

For a reservoir which shares a portion of its surface with the atmosphere or ocean bottom, the boundary conditions of (2.1) may be replaced by appropriate averages over the exterior surfaces. A detailed discussion is postponed until subsection 4.7. In preparation we shall now modify (3.6) by defining for reservoir i a *reservoir source function*, $\bar{Q}_i$, which includes expressions for the exchange across whatever external boundaries the reservoir may possess, in addition to the interior sources $\bar{R}_i W_i$, i.e.:

$$\bar{Q}_i = \bar{R}_i W_i + \sum_m \bar{Q}_{im} \tag{3.20}$$

where m sums over all external boundary processes. The mean motion and eddy motion must vanish at the external boundaries and therefore exchange coefficients $k_{ii'}$ and $k_{i'i}$ apply only to interior surfaces. The reservoir model equation thus takes the general form:

$$\frac{\partial\bar{q}_i}{\partial t} W_i = \sum_{i'=x\ldots-z} (\bar{q}_{i'}k_{i'i} - \bar{q}_i k_{ii'}) + \bar{Q}_i \tag{3.21}$$

where the sum is over all adjacent oceanic reservoirs, i'.

3.5. *Use of the principle of continuity of water*

In view of the uncertainties discussed in subsection 3.3, we introduce only negligible error in the transfer equation (3.6) by assuming ocean water to be incompressible. This assumption allows us to express the continuity of water as a special case of equation (3.21) in which the $\bar{q}_i$ are unity. Writing $\bar{F}_i$ in place of $\bar{Q}_i$ to denote specifically the exchange of water at an atmospheric surface of reservoir i:

$$0 = \sum_{i'=x\ldots-z} (k_{i'i} - k_{ii'}) + \bar{F}_i \tag{3.22}$$

where $\bar{F}_i$ vanishes except for atmospheric boundary reservoirs. Combining (3.21) and (3.22) to eliminate the $k_{ii'}$:

$$\frac{\partial\bar{q}_i}{\partial t} = W_i = \sum_{i'=x\ldots-z} (\bar{q}_{i'} - \bar{q}_i)k_{i'i} + \bar{Q}_i - \bar{q}_i\bar{F}_i \tag{3.23}$$

Equation (3.23) shows that the relation between transport and tracer concentration in the reservoir model is fully specified by the inward-directed transfer coefficients $k_{i'i}$, together with the concentrations differences $(\bar{q}_{i'}-\bar{q}_i)$, and the reservoir source functions $\bar{Q}_i$ and $\bar{q}_i\bar{F}_i$. In section 5 (cf. 5.11) we shall employ this equation in a format appropriate for a three-reservoir model.

Of considerable interest is the ratio of the reservoir volume to the sum of the inward directed transfer coefficients, which can be evaluated if we solve (3.23) for a suite of tracers. We shall denote this ratio by the symbol τ_i, i.e.:

$$\tau_i = \frac{W_i}{\sum_{i'} k_{i'i}} \tag{3.24}$$

This mass-flux ratio has often been called a "turn over" or "residence" time (Bolin and

Stommel, 1961, Eriksson, 1962,) and interpreted as a measure of the average time a molecule or fluid element spends in the reservoir before removal to adjacent reservoirs. Such a physical interpretation does not follow directly from a definition of the k's as measures of the average rate at which water enters or leaves the reservoir (cf. 3.8), but requires, also, that the times individual particles spend in the reservoir are temporally distributed in a manner characteristic of a reservoir which is well mixed internally. Again, as in our attempt to relate the k's to eddy diffusivity coefficients (cf. 3.14 and 3.17) we need more information than can be obtained directly from solving the reservoir model equations.

Generally, it is unrealistic to suppose that oceanic reservoirs are well mixed, and since this condition is not a requirement of the reservoir model (cf. subsection 3.3) we shall not confer a meaning on τ_i beyond that implied by (3.24). In sections 7 and 8 we shall employ mass-flux ratios in connection with the conservation equations of radiocarbon (cf. 7.8 and 7.9).

4. Representation of source functions

4.1. *Introduction*

We shall now develop a procedure for simultaneously applying the transport equation to a suite of nonconservative tracers. To do so we shall express $\overline{R}$, the time-averaged change in concentration of a tracer owing to chemical reactions, radioactive decay, and other local processes, by a formula which distinguishes such local processes and also makes clear the chemical relationships between that tracer and other tracers. To produce such a formula, we shall first define a tracer precisely in chemical terms; we shall next introduce the stoichiometry of chemical reactions as applied to tracers; and finally we shall make specific use of *source ratios* between the tracers considered.

We shall distinguish between *elemental tracers*, composed of bulk chemical species, and *isotopic tracers*, equivalent to the former except that, for one element of the tracers, a single, usually rare, isotope is distinguished. We shall thus provide a unified formulism which is sufficiently general to apply to all chemical processes introduced in later sections. Finally, in subsection 4.7, we shall also develop a formulism for dealing with isotopic exchange at the atmospheric boundary.

Before we begin a general discussion, however, let us illustrate what we propose to do, using as an example the most complicated tracer we shall deal with later on: total dissolved inorganic radiocarbon.

We shall define this isotopic tracer as the sum of the inorganic carbon-14 species in ocean water, i.e., its concentration, denoted by $^*q$, is given by:

$$^*q = [^{14}CO_2] + [H^{14}CO_3^-] + [^{14}CO_3^=] \qquad (4.1)$$

where the brackets indicate concentrations of the enclosed chemical species. Justification for this particular definition is given in subsection 6.1. Local changes in the concentration of $^*q$ in the interior of the ocean are brought about principally by three processes which we may represent approximately as follows:

Reaction a: formation and dissolution of calcium carbonate:

$$\underset{\text{(dissolved)}}{^{14}CO_3^=} + Ca^{++} \rightleftharpoons \underset{\text{(precipitated)}}{Ca^{14}CO_3} \qquad (4.2)$$

Reaction b: synthesis and oxidation of organic (bio) carbon:

$$^{14}CO_2 \rightleftharpoons \text{organic-}^{14}C + O_2 \qquad (4.3)$$

Reaction c: radioactive decay:

$$\text{inorganic-}^{14}C \rightarrow {}^{14}N + \beta^- \qquad (4.4)$$

Evidently, $^*\overline{R}$, the time-averaged local time change of concentration of radiocarbon per unit volume owing to chemical reaction and radioactive decay, may be expressed as a series of "local source terms", $^*\overline{R}_a + {}^*\overline{R}_b + {}^*\overline{R}_c$, where superscript * specifies the tracer, and the subscripts denote the individual local processes.

The last term, $^*\overline{R}_c$, may be immediately replaced by the more explicit expression $(-{}^*\lambda {}^*\overline{q})$ where $^*\lambda$ is the radioactive decay constant. The first two terms, $^*\overline{R}_a$ and $^*\overline{R}_b$, have, however, no simple representation. They depend in a complicated way on chemical concentrations, organisms, light, temperature, and other environmental factors. We shall not attempt to evaluate them explicitly, but instead shall express the functional relationships between them and local source terms for other tracers involved in reactions (4.2) and (4.3).

Consider, for example, the relationships between $^{14}CO_2$, stable CO_2, and O_2 gas, implied by (4.3). As it stands, equation (4.3) neglects the organic synthesis of compounds containing nitrogen and phosphorus. A more complete equation which will be satisfactory for the present purpose is ($v \ll w$):

$$v^{14}CO_2 + wCO_2 + (x+y)H_2O + yNO_3^- + zPO_4^{\equiv} \rightleftharpoons {}^{14}C_vC_w(H_2O)_x(NH_2^-)_y(PO_4^{\equiv}) + (w+2y)O_2 \qquad (4.5)$$

With superscripts C and O to denote stable inorganic carbon (bulk $CO_2 + HCO_3^- + CO_3^{=}$) and oxygen (bulk O_2) as tracers, we relate the local source terms for tracers *, C, and O, by the stoichiometric relationships:

$$^*\overline{R}_b = \left(\frac{v}{w}\right)^C\overline{R}_b = \left(-\frac{v}{w+2y}\right)^O\overline{R}_b \qquad (4.6)$$

These relationships are useful because the stoichiometric ratios v/w and $v/(w+2y)$ are measureable even though the associated local source terms are not. Furthermore, these ratios vary less than do the individual source terms and are more readily averaged.

We shall now generalize these ideas for use in later sections.

4.2. *Notation*

We shall classify quantities with respect to tracer location in the ocean, chemical species, reaction component, and chemical process (reaction or ocean surface exchange). For clarity, we shall reserve specific letters L, i, j, k, l, m, to denote general members of each class. To denote forward and reverse chemical reactions and evasive and invasive exchange, we shall place + or − after the letters representing the process. If two or more general members of a class are referred to in the same expression, they will be distinguished by primes, e.g., k, k', and k''. The specific symbols are listed in subsection 1.2.2.

4.3. *Definitions and stoichiometry*

Subscript i will be omitted in subsections 4.3 to 4.5 because all quantities will refer to the same location. We shall also leave out the notation (⁻) for time-averaged quantities.

4.3.1. *Tracer concentration.* The concept of a chemical "tracer" arises in connection with equation (2.1) when, from a knowledge of q, we can deduce information about the motion of water or chemical sources and sinks. All chemicals in the ocean vary in concentration spacially and thus, in principal, can serve as tracers but if we assume that the eddy diffusivity coefficients have the same value for all chemicals considered (cf. 2.2 and 3.10), we ought to choose only those whose presence in the ocean does not systematically influence water motion. Salinity fails in this requirement because it influences the density of water, and thus, the thermohaline circulation (cf. subsection 7.2). The other chemicals which we shall employ meet this condition satisfactorily because they all occur in the ocean in low concentration.

Let χ denote a chemical compound, radical, or an ion (e.g., CO_2, PO_4, or OH^-), and χ_j a specified member of a set of chemical species. The most general chemical tracer we can define will consist of a linear combination of species, χ_j, such that its concentration is defined by:

$$^Lq = \sum_j {}^L\mu_j[\chi_j] \qquad (4.7)$$

where chemical concentrations are shown by brackets [ ], and the coefficients $^L\mu_j$ are, in practical applications, whole number, commonly 1 or 2. (For example, the tracer, dissolved inorganic carbon-14, according to (4.1) consists of two ions and one molecule, each with $^L\mu_j = 1$.)

4.3.2. *Local source terms and functions.* The local time change in concentration of tracer L owing to a single chemical reaction or radioactive decay, "l", we shall call a *local source term* and denote by ^LR_l, i.e.:

$$^LR_l = \left(\frac{\partial {}^Lq}{\partial t}\right)_l \qquad (4.8)$$

where $(\ )_l$ denotes a time change owing solely to process l.

The local source function for L (which without specifying the tracer, appeared as a time average, $\overline{R}$, in (2.1)) is given by:

$$^LR = \sum_l {}^LR_l \qquad (4.9)$$

4.3.3. *Stoichiometry of tracer reactions.* Chemical reaction l may be represented by the reaction equation (cf. Denbigh, 1963, pp. 132–133):

$$-\nu_{1l}\chi_{1l}-\nu_{2l}\chi_{2l} \underset{r_{l-}}{\overset{r_{l+}}{\rightleftharpoons}} \nu_{3l}\chi_{3l}+\nu_{4l}\chi_{4l}, \quad (4.10)$$

where the χ_{kl} are chemical symbols for the various chemical species, the ν_{kl} are stoichiometric coefficients (usually whole numbers), and r_{l+} and r_{l-} are the forward and reverse reaction rates, measured in chemical equivalents per unit time. The species on the left, as usually written, are called "reactants" (ν negative); those on the right "products" (ν positive). (Equation (4.10) could, if required, be extended to more than four species.)

Stoichiometry requires for all subscripts k:

$$\frac{1}{\nu_{kl}}\left(\frac{\partial[\chi_{kl}]}{\partial t}\right)_l = r_{l+}-r_{l-} \quad (4.11)$$

The reaction rates in (4.11) are expressed with considerable generality (cf. Denbigh, 1963, pp. 439–441) by the expressions:

$$\begin{aligned} r_{l+} &= \varkappa_{l+}[\chi_{1l}]^{\beta_{1l}}[\chi_{2l}]^{\beta_{2l}} \\ r_{l-} &= \varkappa_{l-}[\chi_{3l}]^{\beta_{3l}}[\chi_{4l}]^{\beta_{4l}} \end{aligned} \quad [4.12]$$

where the β_{kl} are small powers, usually integers, and the "rate coefficients", $\varkappa_{l+}$ and $\varkappa_{l-}$, are usually independent of the concentrations $[\chi_{kl}]$, or nearly so, but generally vary with temperature, hydrostatic pressure, light intensity, and other environmental factors. As defined, r_{l+} and r_{l-} are always $\geqslant 0$.

If a certain species χ_{kl} which takes part in reaction l is in the set of χ_j which define the concentration of tracer L according to (4.7) and we write μ_{kl} for the corresponding μ_j, the time rate of change in concentration of tracer L owing to reaction l is:

$$\left(\frac{\partial^L q}{\partial t}\right)_l = {}^L\mu_{kl}\left(\frac{\partial[\chi_{kl}]}{\partial t}\right)_l \quad (4.13)$$

More generally, if one or more species belonging to tracer L takes part in reaction l:

$$\left(\frac{\partial^L q}{\partial t}\right)_l = \sum_k {}^L\mu_{kl}\left(\frac{\partial[\chi_{kl}]}{\partial t}\right)_l \quad (4.14)$$

Comparing this second equation with (4.8) and (4.11), we obtain a stoichiometrically explicit relation for the local source term of tracer L in reaction l.

$${}^LR_l = \sum_k {}^L\mu_{kl}\nu_{kl}(r_{l+}-r_{l-}) \quad (4.15)$$

4.4 *Source ratios for elemental tracers*

The quotient of local source terms for two elemental tracers associated with the same chemical reaction, according to (4.15), will depend only on the associated coefficients μ and ν, since the values r_{l+} and r_{l-} are not related to the choice of tracer. To avoid reference to two tracers in specifying this quotient, we shall make the simplification that all source ratios of elemental tracers be of the form:

$${}^L\gamma_l = {}^LR_l/{}^CR_l \quad (4.16)$$

where L refers to any elemental tracer, but C is an invariant "principal tracer".

From (4.15) and (4.16) it follows that:

$${}^L\gamma_l = \frac{\sum_k {}^L\mu_{kl}\nu_{kl}}{\sum_{k'} {}^C\mu_{k'l}\nu_{k'l}} \quad (4.17)$$

where subscripts k and k' refer to the possibly different components χ_{kl} and $\chi_{k'l}$, respectively of reaction l.

The local source function ${}^LR$ may now be expressed in the form:

$${}^LR = \sum_{l'} {}^L\gamma_{l'}{}^CR_{l'} + \sum_{l''} {}^LR_{l''} \quad (4.18)$$

where the sum over l' represents all reactions in which the local source function of tracer L is related to the principal tracer, C, while the sum over l'' represents reactions not related to C.

4.5. *Source ratios for isotopic tracers*

The source ratio of two isotopic tracers, unlike that of elemental tracers, will not depend on the stoichiometric coefficients, μ and ν, which must be the same for isotopes of the same element, but it will depend on the reaction rates r_{l+} and r_{l-} which, in general, show isotopic differences. The resulting expressions for the source ratios will be considerably more complicated and will require that we define additional quantities.

Consider that in reaction equation (4.10) the chemical reactant χ_{1l} and chemical product χ_{3l} are the only species which contain the element whose separate isotopes are of interest. (More complicated possibilities need not be considered here.) With superscript * to denote the rarer isotope, and L^* to denote the rare isotopic tracer corresponding to elemental tracer L, we denote the isotopic ratio of χ_{kl} by:

$$\mathcal{R}_{kl} = [{}^*\chi_{kl}]/[\chi_{kl}] \tag{4.19}$$

we define forward and reverse fractionation factors in terms of corresponding rate coefficients:

$$\left.\begin{aligned} \alpha_{l+} &= {}^*\varkappa_{l+}/\varkappa_{l+} \\ \alpha_{l-} &= {}^*\varkappa_{l-}/\varkappa_{l-} \end{aligned}\right\} \tag{4.20}$$

and we write for the local source term for tracer L^* in reaction l (cf. 4.15):

$${}^{L*}R_l = {}^L\mu_l \nu_l ({}^*r_{l+} - {}^*r_{l-}) \tag{4.21}$$

Comparing (4.12) with (4.19) and (4.20) the forward and reverse reaction rates of reaction l for the rare isotope may be written:

$$\left.\begin{aligned} {}^*r_{l+} &= \alpha_{l+} (\mathcal{R}_{1l})^{\beta_{1l}} r_{l+} \\ {}^*r_{l-} &= \alpha_{l-} (\mathcal{R}_{3l})^{\beta_{3l}} r_{l-} \end{aligned}\right\} \tag{4.22}$$

If we define isotopic source ratios for the forward and reverse reactions by:

$$\left.\begin{aligned} {}^{L*}\gamma_{l+} &= {}^*r_{l+}/r_{l+} \\ {}^{L*}\gamma_{l-} &= {}^*r_{l-}/r_{l-} \end{aligned}\right\} \tag{4.23}$$

we obtain by (4.22):

$$\left.\begin{aligned} {}^{L*}\gamma_{l+} &= \alpha_{l+} (\mathcal{R}_{1l})^{\beta_{1l}} \\ {}^{L*}\gamma_{l-} &= \alpha_{l-} (\mathcal{R}_{3l})^{\beta_{3l}} \end{aligned}\right\} \tag{4.24}$$

In studies of transport, α_{l+}, α_{l-}, and the β_{kl} will usually be known independently of the results deduced by studies of chemical transport in the oceans. The isotopic ratios, $\mathcal{R}_{kl}$, customarily replace bulk concentration as the variables whose distributions are determined in the ocean water.

If we restrict ourselves to the principal tracer, C, and a rare isotopic equivalent of C which we shall denote by the single character *, the local source function $^*R$ may be written (cf. 4.18):

$${}^*R = \sum_{l'} {}^*\gamma_{l'} {}^C R_{l'} + {}^*R_{l''} \tag{4.25}$$

where the sum over l' represents all reactions in which tracer C takes part, $^*R_{l''}$ is non-zero only in the case of radioactive decay, and where $^*\gamma_{l'}$ denotes the isotopic source ratio for tracer * in net reaction l i.e.:

$${}^*\gamma_{l'} = {}^*R_{l'}/{}^C R_{l'} = \frac{{}^*\gamma_{l'+} r_{l'+} - {}^*\gamma_{l'-} r_{l-}}{r_{l+} - r_{l-}} \tag{4.26}$$

The second equality in (4.26) may be derived by the use of (4.15), (4.21), and (4.23).

Whereas the source ratio ${}^L\gamma_l$ for two elemental tracers L and C is determined by stoichiometric quantities likely to be nearly independent of oceanic location and time (cf. 4.17), the isotopic source ratio $^*\gamma_{l'}$ is seen (cf. 4.24) to be dependent on oceanic concentration ratios $\mathcal{R}_{kl}$ and, even more seriously, also on the forward and reverse reaction rates r_{l+} and r_{l-}. We shall be forced to make approximations of (4.26) before we can successfully use an isotopic tracer in an application of the transport equation (cf. subsection 6.3).

4.6. *Reservoir source functions*

In the preceding subsections all processes refer to a single location, and the relations which we derive are directly applicable to the general transport equation (2.1), provided that the concentrations and the variable reaction parameters are treated as functions of the space coordinates.

To adapt these relations to the reservoir model approximation of section 3, we shall specify by a subscript, i, the space averages over reservoir i, of all quantities which vary with location. As before, we consider average conditions over time interval T, but to simplify notation, we shall not take the trouble to note this specifically by a bar as we did in sections 2 and 3.

For reservoir i, of volume W_i, the reservoir source functions for elemental and principal isotopic tracers can be written (cf. 3.20, 4.18, and 4.25):

$${}^L Q_i = \sum_{l'} {}^L\gamma_{il'} {}^C R_{il'} W_i + \sum_{l''} {}^L R_{il''} W_i + \sum_m {}^L Q_{im} \tag{4.27}$$

where L refers either to an elemental tracer or an isotopic equivalent of principal tracer C. The final terms, $({}^L Q_{im})$, refer to exchange across external boundaries as defined in section 3 and developed in the next subsection. The source ratios ${}^L\gamma_{il}$ are quotients of the averages, over reservoir i, of the local source terms, i.e.:

$${}^L\gamma_{il} = {}^L R_{il}/{}^C R_{il} \tag{4.28}$$

4.7. *Gas exchange at the atmospheric boundary*

In the general transport equation (2.1), exchange at the ocean bottom and atmospheric

boundary are accounted for by specifying the boundary conditions. We shall not formulate general cases, but rather shall immediately write expressions in a form useful to the reservoir model of section 5. We shall thus restrict our discussion to the atmospheric boundary.

4.7.1. *Reservoir source terms.* We shall denote the local time change in average concentration of tracer L in reservoir i owing to a single chemical exchange process "m" by:

$$ {}^{L}Q_{im} = W_i \left(\frac{\partial {}^{L}q_i}{\partial t} \right)_m \tag{4.29} $$

where $(\ )_m$ denotes a time change averaged over volume W_i owing to boundary exchange process m.

4.7.2. *Stoichiometry.* The reaction equation which describes the exchange of a gas between the atmosphere (designated as reservoir o) and an oceanic reservoir i may be written:

$$ \underset{(\text{in } i)}{\chi_m} \quad \underset{r_{iom-}}{\overset{r_{iom+}}{\rightleftharpoons}} \quad \underset{(\text{in } o)}{\chi_m} \tag{4.30} $$

since the stoichiometric coefficients (cf. 4.10) always have the values:

$$ \nu_{im} = -1, \quad \nu_{om} = +1 $$

and where subscript m refers to both the species and the process.

Stoichiometry requires:

$$ -W_i \left(\frac{\partial [\chi_m]_i}{\partial t} \right)_m = A_{io}(r_{iom+} - r_{iom-}) \tag{4.31} $$

where A_{io} is the surface area of reservoir i in contact with the atmosphere and where the evasion and invasion rates r_{iom+} and r_{iom-}, are in units of mass per unit area (rather than volume as was the case for r_{i+} and r_{i-}) and are expressed by:

$$ \left. \begin{aligned} r_{iom+} &= \varkappa_{iom+} p_{im} \\ r_{iom-} &= \varkappa_{iom-} p_{om} \end{aligned} \right\} \tag{4.32} $$

Here $\varkappa_{iom+}$ and $\varkappa_{iom-}$ are exchange coefficients for invasion and evasion per unit area, and p_{im} and p_{om} are the average vapor pressures exerted by χ_m at the boundary in reservoirs i and o, respectively.

If χ_m is in the set of χ_j which define the concentration of tracer L according to (4.7) and if we write μ_m for the corresponding μ_j, the time rate of change in concentration of tracer L owing to exchange m is:

$$ \left(\frac{\partial {}^{L}q_i}{\partial t} \right)_m = {}^{L}\mu_m \left(\frac{\partial [\chi_m]_i}{\partial t} \right)_m \tag{4.33} $$

and the reservoir source term for exchange m is:

$$ {}^{L}Q_{im} = -{}^{L}\mu_m A_{io}(r_{iom+} - r_{iom-}) \tag{4.34} $$

Replacing r_{iom+} and r_{iom-} according to (4.32) and noting that ${}^{L}Q_{im}$ must vanish if $p_{om} = p_{im}$, we require $\varkappa_{iom+} = \varkappa_{iom-}$; that is:

$$ {}^{L}Q_{im} = {}^{L}\mu_m A_{io} \varkappa_{iom}(p_{om} - p_{im}) \tag{4.35} $$

where $\varkappa_{iom}$ stands for either $\varkappa_{iom+}$ or $\varkappa_{iom-}$.

In dealing with atmospheric gas exchange, source ratios are of interest only in the case of isotopic tracers. These will be discussed in the next subsection.

4.7.3. *Source ratios for isotopic tracers.* Analogous to (4.19) through (4.24) we denote the isotopic pressure ratio of χ_m in reservoirs i and o by:

$$ \left. \begin{aligned} \mathcal{R}_{im} &= {}^{*}p_{im}/p_{im} \\ \mathcal{R}_{om} &= {}^{*}p_{om}/p_{om} \end{aligned} \right\} \tag{4.36} $$

we define the fractionation factors:

$$ \left. \begin{aligned} \alpha_{iom+} &= {}^{*}\varkappa_{iom+}/\varkappa_{iom+} \\ \alpha_{iom-} &= {}^{*}\varkappa_{iom-}/\varkappa_{iom-} \end{aligned} \right\} \tag{4.37} $$

and (cf. 4.34) we express the source term for the rare isotopic tracer L^* in reaction m by:

$$ {}^{L*}Q_{im} = -{}^{L}\mu_m A_{io}({}^{*}r_{iom+} - {}^{*}r_{iom-}) \tag{4.38} $$

the evasion and invasion rates for the rare isotope by:

$$ \left. \begin{aligned} {}^{*}r_{iom+} &= \alpha_{iom+} \mathcal{R}_{im} r_{iom+} \\ {}^{*}r_{iom-} &= \alpha_{iom-} \mathcal{R}_{om} r_{iom-} \end{aligned} \right\} \tag{4.39} $$

and the separate isotopic source ratios for the forward and reverse reactions by:

$$ \left. \begin{aligned} {}^{L*}\gamma_{im+} &= \alpha_{iom+} \mathcal{R}_{im} \\ {}^{L*}\gamma_{im-} &= \alpha_{iom-} \mathcal{R}_{om} \end{aligned} \right\} \tag{4.40} $$

If we again restrict ourselves to the principal tracer, C, and its rare isotope equivalent, *,

equation (4.38), which expresses the reservoir source term for the rare isotope, may be transformed with the aid of (4.39) and (4.40) to:

$$*Q_{im} = -{}^{c}\mu_m A_{io}({}^{*}\gamma_{im+}\mathfrak{r}_{iom+} - {}^{*}\gamma_{im-}\mathfrak{r}_{iom-}) \tag{4.41}$$

Rearranging, factoring, and replacing $\mathfrak{r}_{iom+}$ and $\mathfrak{r}_{iom-}$ according to (4.32):

$$*Q_{im} = {}^{c}\mu_m A_{io}\varkappa_{iom}\{{}^{*}\gamma_{im+}(p_{om} - p_{im}) + p_{om}({}^{*}\gamma_{im-} - {}^{*}\gamma_{im+})\} \tag{4.42}$$

where $\varkappa_{iom}$ has the same meaning as in (4.35).

The first term in brackets vanishes if $p_{im} = p_{om}$, but the second term is non-zero because the pressure p_{om} of χ_m in the atmosphere and the source ratio difference $({}^{*}\gamma_{im-} - {}^{*}\gamma_{im+})$ are, in general, non-zero. This second term, which represents the flux of the rare isotope owing solely to a difference in isotopic ratio ($\mathcal{R}_{om} - \mathcal{R}_{im}$) corrected for fractionation by factors α_{iom-} and α_{iom+}, we shall denote by a new symbol h_{im}, i.e.:

$$h_{im} = {}^{c}\mu_m A_{io}\varkappa_{iom}p_{om}({}^{*}\gamma_{im-} - {}^{*}\gamma_{im+}) \tag{4.43}$$

Comparing (4.35), (4.42), and (4.43), we obtain:

$$*Q_{im} = {}^{*}\gamma_{im+}{}^{c}Q_{im} + h_{im} \tag{4.44}$$

This linear relation between $*Q_{im}$ and ${}^{c}Q_{im}$ will be useful in later sections.

If we eliminate the unknown, $\varkappa_{iom}$, between equations (4.35) and (4.43) with $L = C$, we obtain an expression for h_{im} in terms of the reservoir source term, ${}^{c}Q_{im}$, and measurable quantities:

$$h_{im} = {}^{c}Q_{im}\cdot\frac{p_{om}({}^{*}\gamma_{im-} - {}^{*}\gamma_{im+})}{p_{om} - p_{im}} \tag{4.45}$$

This equation is, however, valid only of ${}^{c}Q_{im} \neq 0$, and thus $p_{om} \neq p_{im}$.

4.8. *Concluding remarks*

In a succeeding article (Keeling & Bolin, 1968) we will apply the formulism developed above to a suite of tracers which include salinity, oxygen, inorganic phosphorus, organic and inorganic carbon, carbonate alkalinity, and radiocarbon. Extensive use will be made of the relationships of section 4, especially equations (4.17), (4.26), (4.35), 4.43), and (4.45).

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ОДНОВРЕМЕННОЕ ИСПОЛЬЗОВАНИЕ ХИМИЧЕСКИХ ТРАССЕРОВ ДЛЯ ИУЗЧЕНИЯ ОКЕАНА

I. *Общая теоия моделей резервуаров*

Модель резервуаров является полезной отправной точкой при изучении химических трассеров. Эта модель может быть поставлена в соответствие уравнению переноса для непрерывного океана и таким образом основываться на разумном физическом основании. Обсуждается предположение, что трассеры хорошо перемешиваются внутри каждого резервуара, и обнаружено, что такое предположение не является необходимым. Модель хорошо приспособлена для того, чтобы иметь дело с наборами химических трассеров, которые одновременно подвергаются химическим реакциям, разделению изотопов, радиоактивному распаду и обмену с атмосферой.

Развивается общий метод для применения модели резервуаров для изучения большого набора таких трассеров. В последующей статье эти методы будут применены для изучения циркуляции Тихого океана с шестью химическими трассерами.