The simultaneous use of chemical tracers in oceanic studies

II. *A three-reservoir model of the North and South Pacific Oceans*[1, 2]

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ABSTRACT

Salinity, oxygen, inorganic phosphorus, organic and inorganic carbon, carbonate alkalinity, insoluble carbonate, and radiocarbon are used simultaneously as tracers to investigate oceanic circulation, chemical processes within the ocean and chemical exchange at oceanic boundaries. Estimates of the rates of these processes are made using the equation for chemical transport in the simplest approximation which recognizes spatially variable exchange at the ocean-atmosphere boundary, horizontal and vertical advective and eddy diffusive transport, and gravitational settling of insoluble chemicals within the oceans. This approximation is a cyclic model with one atmospheric and three oceanic reservoirs between which tracers exchange by first-order kinetics. Data for the Pacific Ocean are used after having been averaged over time and the regions: warm surface water, cold surface water, and deep water. Northern and southern cold surface waters are treated as alternate cases.

We deduce that:

(1) The mass of deep water in the Pacific Ocean divided by its rate of production is about 1100 years, a time interval in close agreement with its average radiocarbon age relative to that of cold surface water.

(2) In the South Pacific Ocean, the transfer of water between the deep ocean and the surface is principally by exchange with cold surface water. A small net circulation from warm surface water to cold surface water is suggested by the model, but the rate cannot be calculated with existing information.

(3) The three-reservoir model cannot, even to a first approximation, explain the circulation of the North Pacific Ocean, because it overlooks the flow of deep water into the North Pacific Ocean from the South Pacific Ocean.

(4) Both oxygen and carbon dioxide are evolved from surface waters at low latitudes and absorbed at high latitudes. The rates of exchange from warm surface water to cold surface water are of the order of 10^{17} mmol yr^{-1}.

(5) About 10 % of the inorganic carbon in deep water arrives there from surface water by gravitational settling of organic carbon and insoluble carbonate. The other 90 % is transported there by the water itself.

(6) The use of pH measurements to assay for dissolved inorganic carbon and alkalinity seriously limits the reliability of carbon data in the present study. Small errors in pH result in large uncertainties in the deduced rates of gravitational transport of organic carbon and insoluble carbonates and in the rate of exchange of CO_2 with the atmosphere.

[1] Contribution from the Scripps Institution of Oceanography. New Series.
[2] Contribution no. 184, Institute of Meteorology, University of Stockholm.

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5. Formulation of the three-reservoir model

5.1. *Introductory remarks*

In the preceding article (Keeling & Bolin, 1967) we showed that the equation for the transfer of an oceanic chemical tracer in a multiple reservoir ("box") model is an approximation of the space-averaged equation describing the transport of that tracer in the continuous ocean. We also formulated equations to be employed when tracers undergo chemical transformation within the oceans or exchange with the atmosphere.

[1] Figures, sections, and equations are each numbered in series with the preceding article.

In this article we present a detailed example of the simultaneous use of oceanic chemical tracers in order to investigate the advantages and deficiencies of the multiple reservoir model and to illustrate techniques for solving the model with a suite of complicated non-conservative tracers. Specifically (Fig. 3), we shall divide the ocean into reservoirs to emphasize the transport of chemicals north and south within the surface layer of the ocean and between this surface layer and the atmosphere above and deep waters below. To preserve the oceanic details which we wish to emphasize, but otherwise to simplify the problem as much as possible, we shall assume that the distributions of tracers are symmetrical about the equator. We shall then consider the transport at steady state between (1) warm (temperate and tropical) surface water, (2) cold (temperate and polar) surface water, and (3) (cold) deep water lying below the surface water. The vertical boundary between the surface reservoirs we shall place at 40°, the latitude where the north-south temperature gradient is largest. The surface area of warm water in one hemisphere will thus be approximately twice that of cold water in that hemisphere. We shall choose 75 meters as the depth of the surface reservoirs to conform roughly with the depth of the so-called "mixed layer" (cf. Craig, 1957).

In all the above respects our model agrees closely with that employed by Eriksson (1959). Unlike Eriksson, however, who considered average concentrations and transport for all of the oceans in both hemispheres, we shall focus our attention on the Pacific Ocean alone and shall consider, as separate cases, cold waters having characteristics of the North and South Pacific Ocean. For warm surface waters and deep waters, however, we shall average the data over both hemispheres. As an aid in comparing our results with previous investigations we shall set the volumes and areas of the reservoirs numerically equal to the values for the world oceans. The deduced transfer rates are directly proportional to the volumes assumed, and since the true volumes for the North or South Pacific ocean do not differ markedly, the results of the model may be readily converted to true volumes.

As illustrative tracers we shall use carbonate alkalinity (denoted by A), dissolved inorganic bulk carbon (C) and radiocarbon (C^*), oxygen

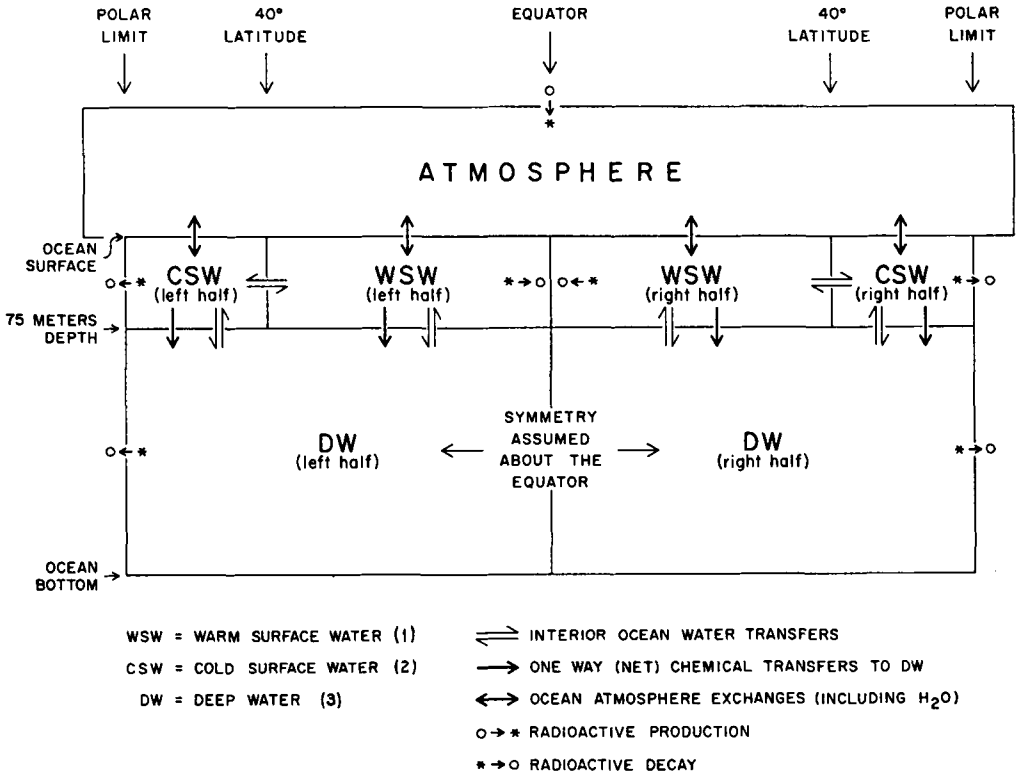


Fig. 3. Two-dimensional representation of the three-reservoir model. Vertical scale of the oceanic surface reservoirs is more highly exaggerated than of the atmosphere and the deep water.

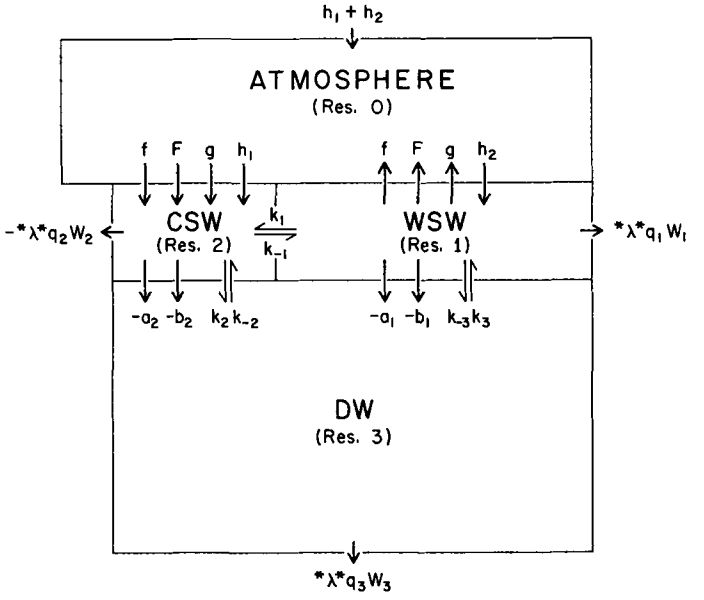


Fig. 4. Diagrammatic representation of the three-reservoir model. Arrows (→) between reservoirs point in the direction of net transport of chemicals: $-a_i$, insoluble carbonate; $-b_i$, biocarbon; f, CO_2; F, H_2O (vapor); g, O_2; h_i, ^{14}C (divided by a standard $^{14}C/^{12}C$ ratio, $\mathcal{R}_\bullet$). The products $*\lambda*q_iW_i$ indicate losses of radiocarbon by radioactive decay. Twin arrows (⇌) refer to reservoir transfer coefficients k_i, k_{-i}. For more complete definitions, see subsections 5.2.1, 5.2.5, and 5.2.6.

gas (O), and inorganic phosphorus (P). We shall also make limited use of organic carbon (B), insoluble carbonate (IC), and salinity (S). All of these tracers except salinity undergo chemical transformations. Two (IC and an insoluble fraction of B) are transported from surface to deep water by gravitational settling. Three (C, C^*, and O) exchange volatile components with the atmosphere. Radiocarbon (C^*) undergoes isotopic fractionation with bulk carbon and is slowly destroyed in all reservoirs by radioactive decay. Except for radioactive decay, we shall treat all these processes as unknown sources and sinks to be solved for in the calculations. Whenever possible, however, we shall insert correct values, or estimates, of the ratios of sources and sinks for different tracers, based on a knowledge of the chemistry and biology of the processes involved. The essential physical and chemical features of the model are depicted in Fig. 4.

5.2. *List of symbols*

5.2.1. We shall use the following general notations:

A_{io} ($i = 1, 2$) the area exposed to the atmosphere, in cm², of surface reservoir i

i subscript, denotes the reservoir: o = the atmosphere; 1 = WSW (warm surface water); 2 = CSW (cold surface water); 3 = DW (deep water). The transfer processes as depicted in Fig. 4 permit us formally to treat the i's for the water reservoirs as cyclic: $(i+1)_{i=3} = 1$; $(i-1)_{i=1} = 3$

k_i, k_{-1} ($i = 1, 2, 3$) the flux of water in liters per year from reservoir i to $(i+1)$ and from $(i+1)$ to i, respectively

Δk net cyclic flow of water in the direction WSW to CSW to DW (cf. 5.10)

L superscript, denotes an unspecified elemental (bulk chemical) or isotopic tracer

L^* superscript, denotes an isotopic tracer corresponding to the elemental tracer, L, except that a rare isotope of one chemical element substitutes for the bulk element

pH negative logarithm to base 10 of the hydrogen ion activity (see subsection 6.1)

${}^Lq_i$ ($i = 1, 2, 3$) the average concentration of tracer L in reservoir i in chemical units per liter. (See below for specific units.)

${}^LQ_i$ reservoir source function of tracer L in reservoir i in chemical units per year. (By "source" we imply either a positive source or a "sink".)

${}^LQ_{il}$ a reservoir source term defined as that portion of ${}^LQ_i$ owing solely to a certain net process l.

${}^LQ_{iL}$, ${}^LQ_{Li}$ corresponding source terms for forward and reverse processes treated separately (cf. subsection 5.2.7).

t time

T temperature in °C

W_i ($i = 1, 2, 3$) the total volume of water in liters in reservoir i

α isotopic fractionation factor defined by (4.20)

${}^L\gamma_{il}$ ($= {}^LQ_{il}/{}^CQ_{il}$) the source ratio of tracer L for process l where C (defined in subsection 5.2.2) is designated as the principal tracer. (${}^L\gamma_{il}$ is a quotient of average source terms over reservoir i; cf. 4.28.)

${}^L\delta_i$ the concentration decrease of tracer L from reservoir i to $(i+1)$ thus:

$$ {}^L\delta_i = {}^Lq_i - {}^Lq_{i+1} \tag{5.1} $$

$$ {}^L\delta_1 + {}^L\delta_2 + {}^L\delta_3 = 0 \tag{5.2} $$

$\varkappa$ rate coefficient for chemical reaction or gas exchange at the atmospheric boundary expressing the dependence of the rate on environmental factors (cf. 4.12)

${}^*\varkappa$ corresponding coefficient for a rare isotope (cf. 4.20)

${}^{L*}\lambda$ radioactive decay constant of a radioactive isotopic tracer L^*

μ stoichiometric coefficient specifying the number of tracer concentration units contributed by one mole of a given chemical compound (cf. 4.7)

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

τ_i mass-flux ratio, in years, of water in reservoir i as defined by (7.4)

${}^*\tau_i$ age, in years, of inorganic radiocarbon in reservoir i as defined by (8.1)

${}^{IC}\tau_3$, ${}^{B}\tau_3$ mass-flux ratio, in years, of insoluble carbonate and biocarbon in deep water as defined by (7.5) and (7.6)

[ ] the concentration of the enclosed chemical species

5.2.2. We shall employ the following elemental tracers:

Symbol	*Name*	*Concentration units*
A	carbonate alkalinity	milliequivalents per liter
B	biocarbon (dissolved and particulate organic carbon)	milligram-atoms per liter
C	inorgan carbon (all dissolved species)	milligram-atoms per liter
IC	insoluble carbonate	millimoles per liter
O	oxygen (dissolved gas)	millimoles per liter
P	inorganic phosphorus	milligram-atoms per liter
S	salinity	grams per kilogram of ocean water (‰)

5.2.3. We shall employ the following isotopic tracers:

Symbol	*Name*	*Concentration units*
A^*	radioalkalinity	milliequivalents per liter divided by an arbitrary standard $^{14}C/^{12}C$ ratio, $\mathcal{R}_\bullet$
B^*	radiobiocarbon	milligram-atoms per liter divided by $\mathcal{R}_\bullet$
C^* or *	inorganic radiocarbon (all dissolved species)	milligram-atoms per liter divided by $\mathcal{R}_\bullet$
IC^*	insoluble radiocarbonate	millimoles per liter divided by $\mathcal{R}_\bullet$

(To simplify the notation in referring to inorganic radiocarbon, we will usually write * for C^*.)

5.2.4. For carbon and radiocarbon we introduce the specific symbols:

p_i the average partial pressure of CO_2 in atm $\times 10^6$ in the atmosphere ($i = o$) or in surface reservoir i ($i = 1, 2$)

$^*p_i$ the average partial pressure of $^{14}CO_2$ in atm $\times 10^6$ in the atmosphere ($i = o$) or in surface reservoir i ($i = 1, 2$) divided by an arbitrary standard $^{14}C/^{12}C$ ratio, $\mathcal{R}_\bullet$, i.e.:

$$^*p_i = (^{CO_2}\mathcal{R}_i/\mathcal{R}_\bullet)p_i = {}^C\alpha_i[1 + {}^L(\delta^{14}C)_i]p_i \tag{5.3}$$

$^{L*}q_i$ ($i = 1, 2, 3$) the average concentration of isotopic tracer $^*L$ in reservoir i in chemical units per liter, evaluated by the formula:

$$^{L*}q_i = (^L\mathcal{R}_i/\mathcal{R}_\bullet)^Lq_i = [1 + {}^L(\delta^{14}C)_i]^Lq_i \tag{5.4}$$

$^L\mathcal{R}_i$ the $^{14}C/^{12}C$ ratio of elemental carbon tracer L in the atmosphere ($i = o$) or reservoir i ($i = 1, 2, 3$)

$^{CO_2}\mathcal{R}_i$ ($i = 1, 2$) the $^{14}C/^{12}C$ ratio of dissolved CO_2 in surface reservoir i (cf. 4.36)

$\mathcal{R}_\bullet$ the $^{14}C/^{12}C$ ratio of an arbitrary radiocarbon standard

$^C\alpha_i$ ($= {}^{CO_2}\mathcal{R}_i/{}^C\mathcal{R}_i$) ($i = 1, 2, 3$) the equilibrium fractionation ratio for dissolved CO_2 with respect to inorganic carbon, C ($^C\alpha_i$ is not a true fractionation factor since its value depends on the relative concentrations of CO_2, HCO_3^-, and $CO_3^=$. See subsection 6.1)

$^L(\delta^{14}C)_i$ ($i = 1, 2, 3$) the departure (often expressed in per mil, ‰) of the $^{14}C/^{12}C$ ratio of elemental carbon tracer L in reservoir i from the standard value $\mathcal{R}_\bullet$.

5.2.5. We note specific reservoir source terms by:

a_i ($i = 1, 2, 3$) net addition of inorganic carbon, C, in milligram-atoms per year to reservoir i by the formation and dissolution of insoluble carbonate (see reaction equation 6.5)

b_i ($i = 1, 2, 3$) net addition of inorganic carbon, C, in milligram-atoms per year to reservoir i by the synthesis and oxidation of biocarbon (see reaction equation 6.6)

f_i ($i = 1, 2, 3$) net additon of inorganic carbon, C, in milligram-atoms per year to reservoir i, by exchange of CO_2 with the atmosphere (see reaction equation 6.7, $f_3 = 0$)

F_i ($i = 1, 2, 3$) net addition of water in liters per year to reservoir i by evaporation and precipitation at the ocean surface ($F_3 = 0$)

g_i ($i = 1, 2, 3$) net addition of oxygen, O, in millimoles per year to reservoir i by exchange with the atmosphere ($g_3 = 0$)

h_i ($i = 1, 2, 3$) the portion of the flux of inorganic radiocarbon, C^* (in the form of $^{14}CO_2$), in milligram-atoms per year from the atmosphere to reservoir i owing to the isotopic gradient at the ocean surface as defined by (4.43) ($h_3 = 0$)

$^*\lambda {}^*q_i W_i$ ($i = 1, 2, 3$) the rate of radioactive decay of inorganic radiocarbon, C^*, in millimoles per year, divided by an arbitrary standard $^{14}C/^{12}C$ ratio, $\mathcal{R}_\bullet$, in reservoir i, where $^*\lambda$ is the decay constant of radiocarbon and $^*q_i$ the concentration of inorganic radiocarbon. (Similar products apply to radioalkalinity, radiobiocarbon, and insoluble radiocarbonate.)

5.2.6. We denote specific fluxes between WSW and CSW via the atmosphere by the following symbols without subscripts:

f the net flux of inorganic carbon, C (in the form of CO_2), in milligram-atoms per year, from WSW to the atmosphere and thence to CSW ($f = -f_1 = f_2$; compare Table 1)

F the net flux of water in liters per year from WSW to the atmosphere and thence to CSW ($F = -F_1 = F_2$; compare Table 1)

g the net flux of oxygen, O, in millimoles per year from WSW to the atmosphere and thence to CSW ($g = -g_1 = g_2$; compare Table 1).

5.2.7. For the carbonate and biocarbon source terms we denote the loss of carbon owing to forward reaction and the gain of carbon owing to reverse reaction in milligram-atoms per year in reservoir i by:

a_{iA}, a_{Ai} forward and reverse source term associated with a_i

b_{iB}, b_{Bi} forward and reverse source term associated with b_i

These source terms are defined (cf. 4.12) as positive for the stated direction of chemical reaction as prescribed by (6.5) and (6.6). It follows that:

$$a_i = -a_{iA} + a_{Ai} \qquad (5.5)$$
$$b_i = -b_{iB} + b_{Bi}$$

Correspondingly, we denote forward and reverse source terms for any other tracer L by symbols $^LQ_{iA}$, $^LQ_{Ai}$, $^LQ_{iB}$, and $^LQ_{Bi}$.

5.2.8. We denote the forward and reverse rate coefficients associated with the reservoir source terms a_i, b_i, and f_i by the symbols:

$\varkappa_{iA}$, $\varkappa_{Ai}$ forward and reverse rate coefficients associated with a_i (cf. 4.12 and 6.5 units need not be specified because we shall only be concerned with ratios, cf. subsection 5.2.9).

$\varkappa_{iB}$, $\varkappa_{Bi}$ forward and reverse rate coefficients associated with b_i (cf. 4.12 and 6.6 units need not be specified because we shall only be concerned with ratios, cf. subsection 5.2.9).

$\varkappa_{io}$, $\varkappa_{oi}$ forward and reverse rate coefficients in milligram-atoms year^{-1} cm^{-2} atm$^{-1} \times 10^{-6}$ associated with f_i (cf. 4.3.2 and 6.7)

5.2.9. For radiocarbon, we define the following fractionation factors associated with reservoir source terms a_i, b_i, and f_i:

$\alpha_{iA} = {}^*\varkappa_{iA}/\varkappa_{iA}$ factor for carbonate formation in the ocean

$\alpha_{Ai} = {}^*\varkappa_{Ai}/\varkappa_{Ai}$ factor for carbonate dissolution in the ocean

$\alpha_{iB} = {}^*\varkappa_{iB}/\varkappa_{iB}$ factor for biocarbon synthesis in the ocean

$\alpha_{Bi} = {}^*\varkappa_{Bi}/\varkappa_{Bi}$ factor for biocarbon oxidation in the ocean

$\alpha_{io} = {}^*\varkappa_{io}/\varkappa_{io}$ factor for evasion of CO_2 at the ocean-atmosphere boundary

$\alpha_{oi} = {}^*\varkappa_{oi}/\varkappa_{oi}$ factor for invasion of CO_2 at the ocean-atmosphere boundary

$\alpha_{i,\,eq} = \alpha_{io}/\alpha_{oi}$ equilibrium factor for CO_2 exchange at the ocean surface

5.2.10. We denote the following net source ratios associated with reservoir source terms a_i, b_i (defined for elemental tracers by 4.16; for isotopic tracers by 4.26 with $R_{il} = Q_{il}/W_i$)

$^L\gamma_{ia} = {}^LQ_{ia}/a_i$ ($i = 1, 2, 3$; $L = A, O, P, {}^*$) net source ratio associated with carbonate formation and dissolution (see subsection 5.2.5)

$^L\gamma_{ib} = {}^LQ_{ib}/b_i$ ($i = 1, 2, 3$; $L = A, O, P, {}^*$) net source ratio associated with biocarbon synthesis and oxidation

5.2.11. We denote the following forward and reverse source ratios of inorganic radiocarbon:

${}^*\gamma_{iA}$, ${}^*\gamma_{Ai}$ $(i = 1, 2, 3)$ source ratios for forward, respectively reverse, reaction associated with carbonate formation and dissolution $({}^*\gamma_{iA} = {}^*Q_{iA}/a_{iA}$, etc.)

${}^*\gamma_{iB}$, ${}^*\gamma_{Bi}$ $(i = 1, 2, 3)$ source ratio for forward, respectively reverse, reaction associated with biocarbon synthesis and oxidation $({}^*\gamma_{iB} = {}^*Q_{iB}/b_{iB}$, etc.)

${}^*\gamma_{io}$, ${}^*\gamma_{oi}$ $(i = 1, 2)$ source ratio for evasion and invasion of CO_2 at the ocean-atmosphere boundary (cf. 4.4)

These are evaluated for source terms a_i and b_i by (4.24) and for source term f_i by (4.40), except that the products of $\mathcal{R}$ and α are to be divided by an arbitrary standard $^{14}C/^{12}C$ ratio, $\mathcal{R}_\bullet$, consistent with the definitions of subsection 5.2.3. We shall, furthermore, only be concerned with chemical reactions in which, for all chemical species involving carbon, the $\beta_{kl} = 1$ (cf. 4.12 and 6.5 to 6.7 below).

We obtain, specifically:

$$\left.\begin{aligned}
{}^*\gamma_{iA} &= ({}^C\mathcal{R}_i/\mathcal{R}_\bullet)\alpha_{iA} \quad (i = 1, 2, 3)\\
{}^*\gamma_{Ai} &= ({}^{IC}\mathcal{R}_i/\mathcal{R}_\bullet)\alpha_{Ai} \quad (i = 1, 2, 3)\\
{}^*\gamma_{iB} &= ({}^C\mathcal{R}_i/\mathcal{R}_\bullet)\alpha_{iB} \quad (i = 1, 2, 3)\\
{}^*\gamma_{Bi} &= ({}^B\mathcal{R}_i/\mathcal{R}_\bullet)\alpha_{Bi} \quad (i = 1, 2, 3)\\
{}^*\gamma_{io} &= ({}^{CO_2}\mathcal{R}_i/\mathcal{R}_\bullet)\alpha_{io} = ({}^C\mathcal{R}_i\,{}^C\alpha_i/\mathcal{R}_\bullet)\alpha_{io} \quad (i = 1, 2)\\
{}^*\gamma_{oi} &= ({}^C\mathcal{R}_i/\mathcal{R}_\bullet)\alpha_{oi} \quad (i = 1, 2)
\end{aligned}\right\} \qquad (5.6)$$

5.2.11. Mathematic and chemical equations are cited in the text by decimal figures enclosed in parentheses.

5.3. *The transport equation applied*

The continuity of tracer L in reservoir i of the three-reservoir model is expressed as follows (see Fig. 5; cf. 3.21):

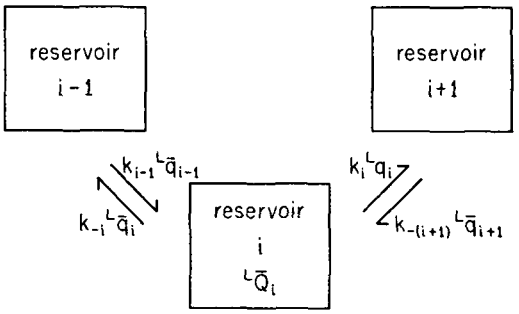


Fig. 5. Transport relationships for reservoir i of the cyclic three-reservoir model. The products $k^L\bar{q}$ denote transport between reservoirs in the directions shown by the arrows. ${}^L\bar{Q}_i$ is the reservoir source function (see text).

$$\frac{\partial {}^L\bar{q}_i}{\partial t} W_i = k_{i-1}\,{}^L\bar{q}_{i-1} + k_{-(i+1)}\,{}^L\bar{q}_{i+1} - (k_i + k_{-i})\,{}^L\bar{q}_i + {}^L\bar{Q}_i \qquad (5.7)$$

where bars denote time averages (see text following equation 2.1).

Since very little information is available on time variations of the concentration of non-conservative tracers in the ocean, we consider a steady state, i.e., we set:

$$\frac{\partial {}^L\bar{q}_i}{\partial t} = 0 \qquad (5.8)$$

We shall further simplify (5.7) by making use of the principle of continuity of water. Although, as in the derivation of (3.23), we could derive an equation which states that water in a given reservoir is conserved, let us alternatively fix our attention on the transfer of water between any pair of reservoirs. If the atmospheric water vapor flux, $\overline{F}$, were equal to zero, the continuity requirements for all pairs $(i = 1, 2, 3)$ would be:

$$\Delta k = k_i - k_{-i} \qquad (5.9)$$

where Δk, a constant, denotes the net cyclic flow of water in the direction WSW to CSW to DW $(1 \to 2 \to 3)$. The presence of a non-zero atmospheric flux of water vapor increases the flow between reservoirs 1 and 2 by $\overline{F}$ so that the appropriate continuity equation is instead:

$$\Delta k = k_1 - k_{-1} + \overline{F} = k_2 - k_{-2} = k_3 - k_{-3} \qquad (5.10)$$

With the aid of (5.8) and (5.10), using the notations of subsection 5.1, and dropping the use

Table 1. *Specific reservoir source terms*

Reservoir No.	Net addition of C owing to formation and dissolution of insoluble carbonate	Net addition of C owing to synthesis and oxidation of "biocarbon"	Net addition of C owing to exchange of CO_2 with the atmosphere	Net addition of O owing to exchange of O_2 with the atmosphere	Net addition of C^* owing to isotopic gradient at the ocean surface
1	a_1	b_1	$f_1 = -f$	$g_1 = -g$	h_1
2	a_2	b_2	$f_2 = f$	$g_2 = g$	h_2
3	$a_3 = -(a_1 + a_2)$	$b_3 = -(b_1 + b_2)$	$f_3 = 0$	$g_3 = 0$	$h_3 = 0$

C = inorganic carbon. C^* = inorganic radiocarbon. O = oxygen gas.

of bars to denote time averages, we may transform (5.7) into:

$$k_{i-1}\,{}^L\delta_{i-1} - k_{-i}\,{}^L\delta_i + {}^LQ_i - F_i\,{}^Lq_i = 0 \qquad (5.11)$$

where $F_1 = -F$, $F_2 = +F$, $F_3 = 0$. Equation (5.11) is the three-reservoir steady state analogue of the general reservoir equation (3.23). It relates the water transfers *into* reservoir i, k_{i-1}, k_{-i}, and F_i, to the concentrations ${}^Lq_i$, concentration differences ${}^L\delta_i$, and the reservoir source functions, ${}^LQ_i$. If all ${}^Lq_i$ and ${}^LQ_i$ are known for *two* tracers (either isotopic or bulk) and if the water source F is also known, (5.10) and (5.11) provide sufficient relationships (six equations) to solve for all k_i and k_{-i}. Thus, the three-reservoir model is drastically simpler than the general case (see section 2) in which knowledge of ${}^Lq_i$ and ${}^LQ_i$ for five chemical tracers is required, together with the requirement of continuity of water. The ${}^LQ_i$ are generally not known, however, except where they are equal to zero, nor is the value of F well established. To solve for some of the ${}^LQ_i$ and F as well as the k_i we shall consider the physical and chemical processes that occur between eight tracers: A, B, C, C^*, IC, O, P, and S. The formulism of section 4 provides a basis by which we can compare reservoir source terms and thereby reduce the number of unknowns. From the assumption of steady state (5.8), an additional restraint is imposed that the sum of all sources be zero for every tracer, i.e.:

$$\sum_{i=1,2,3} {}^LQ_i = 0 \qquad (5.12)$$

as may be deduced by summing (5.11) over i and simplifying by the use of (5.2). It follows that independent equations are obtained only from the application of (5.11) to two of the three reservoirs since one equation can always be obtained by adding the two others and making use of (5.12).

To specify the reservoir source functions (${}^LQ_i$) of elemental tracer L ($=A$, C, O, or P) or an isotopic equivalent (${}^*Q_i$) of principal tracer C, denoted by *, we introduce from subsection 5.1 the specific reservoir source terms a_i, b_i, f_i, g_i, and h_i, and the corresponding source ratios ${}^L\gamma_{il}$ and ${}^*\gamma_{il}$. Thus:

$$\left.\begin{aligned} {}^LQ_i &= {}^L\gamma_{ia}a_i + {}^L\gamma_{ib}b_i + {}^L\gamma_{if}f_i + g_i \\ {}^*Q_i &= {}^*\gamma_{ia}a_i + {}^*\gamma_{ib}b_i + {}^*\gamma_{io}f_i + h_i - \\ &\qquad - {}^*\lambda\,{}^*q_i\,W_i \end{aligned}\right\} \qquad (5.13)$$

where ${}^L\gamma_{if} = 0$ for $L \neq C$, ${}^C\gamma_{ia} = {}^C\gamma_{ib} = {}^C\gamma_{if} = 1$, and g_i appears only for oxygen, O. In the present model all nonzero ${}^L\gamma_{il}$ and ${}^*\gamma_{il}$ are positive (associated with reactants) except for ${}^O\gamma_{ib}$ (below denoted by ${}^O\gamma$) which is negative because O_2 is a product in the formation of biocarbon (cf. 6.18).

The specific sources and source ratios which we shall consider are set forth in Tables 1 and 2, respectively, where simplified notations for the source ratios ${}^L\gamma_{il}$ are also introduced, since many of them are zero. Condition (5.12) is fulfilled for all sources except the radiocarbon sources, h_i. The conservancy for radiocarbon is expressed by (6.39).

The numerical evaluation of the source ratios is considered in the next section.

6. Specification of chemical processes

We shall now describe in more detail the chemical basis for the reservoir model as summarized by equations (5.11), (5.13) and Tables 1 and 2 of section 5. For radiocarbon we shall

Table 2. *Source ratios relative to inorganic carbon, C*

	Reservoir No.	Carbon source a_i	b_i	f
Carbonate alkalinity, A	1 = WSW	${}^{A}\gamma$	0	0
	2 = CSW	${}^{A}\gamma$	0	0
	3 = DW	${}^{A}\gamma$	0	0
Oxygen gas, O	1 = WSW	0	${}^{O}\gamma$	0
	2 = CSW	0	${}^{O}\gamma$	0
	3 = DW	0	${}^{O}\gamma$	0
Inorganic phosphorus, P	1 = WSW	0	${}^{P}\gamma$	0
	2 = CSW	0	${}^{P}\gamma$	0
	3 = DW	0	${}^{P}\gamma$	0
Inorganic radiocarbon, C^*	1 = WSW	${}^*\gamma_{1A}$, ${}^*\gamma_{A1}$	${}^*\gamma_{1B}$, ${}^*\gamma_{B1}$	${}^*\gamma_{1o}$, ${}^*\gamma_{o1}$
	2 = CSW	${}^*\gamma_{2A}$, ${}^*\gamma_{A2}$	${}^*\gamma_{2B}$, ${}^*\gamma_{B2}$	${}^*\gamma_{2o}$, ${}^*\gamma_{o2}$
	3 = DW	${}^*\gamma_{3A}$, ${}^*\gamma_{A3}$	${}^*\gamma_{3B}$, ${}^*\gamma_{B3}$	(0)

also justify several simplifications of the chemical relationships in preparation for numerical calculations in section 7.

6.1. *Inorganic carbon*

Inorganic carbon in ocean water exists principally in three forms: dissolved carbon dioxide, CO_2; biocarbonate ion, HCO_3^-; and carbonate ion, $CO_3^=$. Together these constitute what we shall call the "inorganic carbon system". (Our definition fails to recognize explicitly the hydrated form of CO_2 denoted by H_2CO_3, and various metal complexes such as $CaHCO_3^+$. These, however, play no special part in the reactions we shall consider (Skirrow, 1965, pp. 257 and 278) and for simplicity are not further discussed.)

Owing to the reversible chemical reactions:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \qquad (6.1)$$

$$HCO_3^- \rightleftharpoons CO_3^= + H^+ \qquad (6.2)$$

the concentrations of CO_2, HCO_3^-, $CO_3^=$, and hydrogen ion, H^+, cannot all vary independently. Each reaction is associated with one thermodynamic mass law constant which relates the concentrations of products and reactants at a given temperature, pressure, and salinity. The concentrations of all four species are prescribed if any two species, or linear combination of species, are known by measurement together with the temperature, pressure, and salinity. Thus the inorganic carbon system is chemically bivariant. The time to establish the equilibria described by (6.1) and (6.2) is very short compared with the rates of exchange in our model. These two reactions may therefore be considered to occur instantaneously.

To characterize the inorganic carbon system, oceanographers often measure the pH (related to the concentration of H^+) and the alkalinity (more precisely, the carbonate alkalinity corrected for the influence of borate, hydroxide, and hydrogen ion on the total). The carbonate alkalinity is defined by:

$${}^{A}q = [HCO_3^-] + 2[CO_3^=] \qquad (6.3)$$

where, as in (4.7), brackets denote concentrations of individual chemical species. From values of the pH and alkalinity, and with the use of special tables based on data collected in the laboratories of K. Buch (Harvey, 1955), the concentrations or pressures of other species or combinations of species may be calculated. Two such quantities are of special interest in the present case: the partial pressure of CO_2, which in subsection 5.2 we designated by p_i; and the concentration of all species of dissolved inorganic carbon combined, which is defined by:

$${}^{C}q = [CO_2] + [HCO_3^-] + [CO_3^=] \qquad (6.4)$$

Because of its chemical bivariance, the inorganic carbon system poses a more difficult problem in evaluating chemical transport than tracers such as salinity and oxygen. This perhaps explains the reluctance of oceanographers to give to carbon, the element most intimately and fundamentally involved in organic processes in the oceans, the same degree of attention that they have devoted to the related tracers, oxygen and phosphorus (Redfield *et al.*, 1963).

All oceanic tracers, including those of carbon, should obey the transport equation (2.1). The complicated electrochemical property, pH (see Skirrow, 1965, pp. 231–240), and quotients of chemical concentrations such as "specific" alkalinity (alkalinity divided by salinity) (see Koczy, 1956) are therefore unacceptable as tracers. No confusion in selecting carbon tracers arises if we choose stoichiometric quantities whose concentrations are independent of the ionic reactions (6.1) and (6.2).

The most directly applicable stoichiometric tracer is the *inorganic carbon*, C, defined by (6.4). It can be accurately, and could be routinely, measured by acidifying ocean water and then determining the quantity of evolved CO_2 (Skirrow, 1965, p. 251).

Local changes in the concentration of inorganic carbon, C, are a result principally of three chemical processes:

$$\text{In ocean water: } Ca^{++} + CO_3^{=} \underset{\varkappa_{Ai}}{\overset{\varkappa_{iA}}{\rightleftharpoons}} \underset{\text{insoluble carbonate}}{CaCO_3} \tag{6.5}$$

(other metal ions may substitute for Ca^{++})

$$\text{In ocean water: } CO_2 \underset{\varkappa_{Bi}}{\overset{\varkappa_{iB}}{\rightleftharpoons}} \text{organic C} + O_2 \tag{6.6}$$

At the ocean surface:

$$\underset{\text{(in the water)}}{CO_2} \underset{\varkappa_{oi}}{\overset{\varkappa_{io}}{\rightleftharpoons}} \underset{\text{(in the air)}}{CO_2} \tag{6.7}$$

The concentration of inorganic carbon, C, responds directly to net rates of change owing to these reactions. The reservoir source function for C in reservoir i ($i = 1, 2, 3$) (cf. 5.13 and Table 1) is thus given by:

$${}^{C}Q_i = a_i + b_i + f_i \tag{6.8}$$

where

reaction a:

$$a_i = \left(\frac{\partial[CO_3^{=}]}{\partial t}\right)_{\substack{\text{rate owing to net} \\ \text{reaction (6.5)}}} \tag{6.9}$$

reaction b:

$$b_i = \left(\frac{\partial[CO_2]}{\partial t}\right)_{\substack{\text{rate owing to net} \\ \text{reaction (6.6)}}} \tag{6.10}$$

reaction c:

$$f_i = \left(\frac{\partial[CO_2]}{\partial t}\right)_{\substack{\text{rate owing to net} \\ \text{reaction (6.7)}}} \tag{6.11}$$

Writing f for f_2, noting that $f_3 = 0$ (no atmospheric exchange for the deep water, DW), and observing (5.12), we obtain the specific source terms of C in Table 1. In these equations and in Table 1, we recognize the central importance of inorganic carbon as a non-conservative tracer in the oceans by designating it as the 'principal tracer' in the sense of subsection 4.4.

The *carbonate alkalinity* (Skirrow, 1965, p. 250) is a second stoichiometric tracer which is useful because of the simple form of its reservoir source function. Its numerical value according to (6.3) is proportional to the total negative charge owing to the inorganic carbon system (whether complexed with metal ions or not). Its value is, thus, unaffected by addition or subtraction of the electrically neutral species, CO_2, and, since the change in concentration of hydrogen ion with CO_2 under oceanic conditions is negligible, its value is unaltered by processes (6.6) and (6.7). The reservoir source function for carbonate alkalinity thus takes the simple form:

$${}^{A}Q_i = {}^{A}\gamma a_i = 2\left(\frac{\partial[CO_3^{=}]}{\partial t}\right)_{\substack{\text{rate owing to net} \\ \text{reaction (6.5)}}} \tag{6.12}$$

Since a gain or loss of one mole of $CO_3^{=}$ results in a gain or loss of two equivalents of negative

charge, the source ratio ${}^{A}\gamma$ has always the numerical value 2. It will, nevertheless, be useful to retain ${}^{A}\gamma$ in our equations to identify concentration units.

6.2. *Organic carbon, oxygen, and inorganic phosphorus*

The tracers, inorganic phosphorus and oxygen, we define by:

$$ {}^{P}q = [PO_4^{\equiv}] \tag{6.13} $$

$$ {}^{O}q = [O_2] \tag{6.14} $$

where $PO_4^{\equiv}$ stands for all inorganic forms of phosphorus measured in the conventional analysis of phosphate in ocean water (Barnes, 1959, p. 151).

To determine the source ratios associated with these tracers we shall adopt the opinion of Redfield *et al.* (1963) that the average proportion of phosphorus to carbon in the organic material formed in surface waters of the open ocean (forward reaction 6.6) is nearly constant from region to region, and that oxidation of organic material in surface and deep water uses up oxygen in nearly a fixed ratio to the carbon (reverse reaction 6.6). We shall initially accept Redfield's atomic ratios $P:C:O$ in plankton formation (Redfield *et al.*, 1963, p. 32) $1:106:-276$. We rewrite the reversible equation (4.5) for synthesis of organic carbon, omitting radiocarbon:

$$ wCO_2 + (x+y)H_2O + yNO_3^- + zPO_4^{\equiv} $$

$$ \rightleftharpoons C_w(H_2O)_x(NH_2^-)_y(PO_4^{\equiv})_z + (w+2y)O_2 \tag{6.15} $$

where w, x, y, and z are averages over all of the individual chemical reactions of organic synthesis. Because we deal only with carbon, phosphorus, and oxygen as tracers, this equation is sufficiently accurate for our present purpose. We note that the atomic ratios $P:C:O$ are as $z:w:-2\ (w+2y)$ whereas the stoichiometric coefficients (cf. 4.7) are given by:

$$ \nu_{PO_4} = -z, \quad \nu_{CO_2} = -w, \quad \nu_{O_2} = w+2y. $$

We further note that the tracer coefficients (cf. 4.10) ${}^{P}\mu_{PO_4}$, ${}^{C}\mu_{CO_2}$ and ${}^{O}\mu_{O_2}$ are all equal to unity. Thus we obtain the following values of the source ratios by substitution in (4.17):

$$ {}^{P}\gamma = \frac{\nu_{PO_4}}{\nu_{CO_2}} = \frac{-z}{-w} = \frac{1}{106} = 0.0094 \tag{6.17} $$

$$ {}^{O}\gamma = \left(\frac{\nu_{O_2}}{\nu_{PO_4}}\right)\cdot\left(\frac{\nu_{PO_4}}{\nu_{CO_2}}\right) = \left(\frac{w+2y}{-z}\right)\cdot\left(\frac{-z}{-w}\right) = $$

$$ = \frac{-138}{1}\cdot\frac{1}{106} = -1.30 \tag{6.18} $$

These values are, of course, only rough averages. The possible relative error in ${}^{P}\gamma$ is larger than for ${}^{O}\gamma$, but the average magnitude of neither is well established.

The three-reservoir model does not require that the ratios be the same for WSW and CSW, but this approximation will be used (see Table 2). As we shall see in section 7, if a sufficient number of tracers is chosen, the ratios we compute for ${}^{O}\gamma$ and ${}^{P}\gamma$ are not independent of the concentrations of the tracers that are assigned to the three reservoirs, and we must modify Redfield's ratios to be consistent with our concentration data.

6.3. *Radiocarbon*

6.3.1. *Introduction.* A full account of the distribution of radiocarbon in the oceans requires the most detailed description of local processes of any tracer we shall consider. In our formulation of local processes for radiocarbon, as for bulk carbon (6.5, 6.6, 6.7), we must distinguish between inorganic, organic, and insoluble carbonate. Furthermore, radiocarbon, being a rare isotope, undergoes fractionation relative to the abundant isotope ^{12}C. Hence both forward and reverse reactions must be explicitly considered. Finally, being a radioisotope, it undergoes radioactive decay. In spite of this complexity, if the concentration of oceanic radiocarbon in all its forms were known in details, radiocarbon would present an exceedingly useful tracer, not only because its known rate of radioactive decay establishes absolute rates of change, but also because of the multiplicity of relationships for radiocarbon which supplement those for bulk carbon without introducing new unknown sources. Furthermore, should the distribution of the rare stable isotope, ^{13}C, also be investigated in the same detail as ^{14}C, all isotopic effects could be precisely separated from effects owing to radioactive decay (e.g., see Craig, 1954, p. 133).

It is not practical to discuss here all these possible relationships since our aim is to solve the three-reservoir model with the limited existing data. The reader, by applying the general equations (3.21), and (4.27) or their three-reservoir steady state analogues (5.11), (6.8), and (6.19) to each form of carbon and comparing common factors can, however, satisfy himself that new information on tracer transport could be gained if stable and radioisotopic data were available for all forms and for all regions of the ocean where the distribution of bulk carbon has been investigated.[1]

If we accept (6.8) as the reservoir source function for total dissolved inorganic carbon, the corresponding equation for radiocarbon reads:

$$^*Q_i = {}^*\gamma_{ia} a_i + {}^*\gamma_{ib} b_i + {}^*\gamma_{io} f_i + h_i - {}^*\lambda\, {}^*q_i W_i \tag{6.19}$$

where according to (4.26) and (4.43) and the definitions in subsection 5.2:

$$^*\gamma_{ia} = \frac{{}^*\gamma_{iA} a_{iA} - {}^*\gamma_{Ai} a_{Ai}}{a_{iA} - a_{Ai}} \quad (i = 1, 2, 3) \tag{6.20}$$

$$^*\gamma_{ib} = \frac{{}^*\gamma_{iB} b_{iB} - {}^*\gamma_{Bi} b_{Bi}}{b_{iB} - b_{Bi}} \quad (i = 1, 2, 3) \tag{6.21}$$

$$h_i = A_{io} \varkappa_{io} p_o ({}^*\gamma_{oi} - {}^*\gamma_{io}) \quad (i = 1, 2) \tag{6.22}$$

(A_{io} is the surface area of reservoir i exposed to the atmosphere, $\varkappa_{io}$ the gas exchange coefficient for CO_2 defined by (4.3.2), p_o the average partial pressure of CO_2 in the atmosphere, and γ_{oi}, γ_{io} the source ratios for invasion and evasion of CO_2 at the ocean-atmosphere boundary).

6.3.2. *Source ratios related to a_i and b_i.* The primary production of biocarbon in the ocean, given in our notation by b_{iB}, takes place near the surface of the ocean where sufficient radiant energy is received from the sun to support photosynthesis (Ryther, 1963). Gravitational settling of particulate organic detritus transports a portion of this biocarbon to the deep water. As indicated below, the transport of dissolved biocarbon upward from deep water to surface waters is small compared to the flux of detritus downward. Thus, in the surface reservoirs, the net source function b_i is negative, i.e.:

$$\left.\begin{aligned} b_{iB} &> b_{Bi} \\ b_i &< 0 \end{aligned}\right\} \quad (i = 1, 2) \tag{6.23}$$

Although we lack direct evidence, we may expect similar relations to hold for insoluble carbonate.

In deep water, DW, the production of insoluble carbonate and of biocarbon is very small, or zero. Thus we assert:

$$a_{3A} \cong 0, \quad b_{3B} \cong 0. \tag{6.24}$$

Simplifying (6.20) and (6.21) as applied to the deep water ($i = 3$):

$$^*\gamma_{3a} \cong {}^*\gamma_{A3} \tag{6.25}$$

$$^*\gamma_{3b} \cong {}^*\gamma_{B3} \tag{6.26}$$

For the surface reservoirs, WSW and CSW, neither the forward nor reverse reactions are negligible. We are, nevertheless, forced to make simplifying assumptions to solve our model, and the problem is to use the meager existing data to avoid serious errors.

Taking up biocarbon first, recent results of Williams (1965) indicate that the average concentration of dissolved organic carbon of surface Pacific Ocean water is likely not to exceed 1 mg per liter (0.08 milligram-atoms/l) while the average concentration of particulate organic carbon is less than 0.1 mg per liter.

A rough estimate of the vertical transport

[1] In this connection the tracer equations are instructive in prescribing what quantities should be measured and reported by radiocarbon laboratories. The quantities which must be known experimentally are the source ratios defined by (4.24). These require a determination of the isotopic ratios of substances *as they exist in the oceans* together with fractionation factors which can be determined in the laboratory or deduced from oceanic measurements of ^{13}C. Investigators who report their experimental data "corrected" to an arbitrary standard $^{13}C/^{12}C$ ratio (e.g., Broecker, 1963*a*) are providing numbers in which these simple relationships are obscured. Such "corrected" values do not obey a simple equation of continuity. If the laboratory method for preparing a sample for radiocarbon determination results in isotopic fractionation, the procedure which is called for by the oceanic relationships is to measure the $^{13}C/^{12}C$ ratio of the sample and of the original material and to correct the radiocarbon value to the latter. In any case, all relevant laboratory measurements should be reported. Because Broecker (1963*a*) did not report his measurements of $^{13}C/^{12}C$ ratios, we have been obliged in the next section to guess at his correction factors.

of alkalinity, inorganic carbon, and biocarbon, using Williams's data for biocarbon and the data of section 7 for alkalinity and inorganic carbon indicates that the vertical gradient in biocarbon is too small (even if the concentration in deep water should be near zero) for advective or eddy transport to account for more than a small part of the vertical biocarbon flux. The latter must be largely a gravitational flux of particulate organic carbon which falls through the water, as assumed by Eriksson (1959).

If we now write down the complete set of equations for inorganic carbon, biocarbon, alkalinity, and their radiocarbon equivalents, in the framework of a two-reservoir model consisting of one surface reservoir ($i=1$) and one deep water reservoir ($i=2$) (cf. Craig, 1963), and if we allow for a gravitational flux, b_G, we can solve for the source terms b_{1B}, b_{B1}, $b_{B2}\cong b_2$, the flux b_G, and the radiobiocarbon concentrations ${}^{B}\mathcal{R}_1 \cdot {}^{B}q_1$ and ${}^{B}\mathcal{R}_2 \cdot {}^{B}q_2$ as functions of Williams's estimates of concentrations of biocarbon ${}^{B}q_1$ and ${}^{B}q_2$, and various arbitrarily assigned relative magnitudes of the reverse reaction of biocarbon in the surface reservoir b_{B1}/b_1

Using data for either WSW or CSW, such a calculation indicates that the radiocarbon age of biocarbon relative to inorganic carbon in the surface water is very low even if the reverse reaction rate, b_{B1}, is zero. For increasing b_{B1}/b_1 the age of biocarbon relative to inorganic carbon tends towards zero. Thus we will not produce serious error in the radiocarbon balance if we set $b_{B1}=0$. Furthermore, since the principal mode of transport of biocarbon is a gravitational flux, the model is not sensitive to the assumed vertical gradient of biocarbon, and we shall further simplify the calculation by assuming ${}^{B}q_i$ to be constant.

In the case of the alkalinity sources, a_i, since the concentration of insoluble carbonate (although not known) should be still less than that of biocarbon, the reverse reaction can again be neglected without serious error in the radiocarbon balance. Thus, for surface reservoirs we set the a_{Ai} and b_{Bi} ($i=1, 2$) equal to zero in (6.20) and (6.21) and obtain:

$$ {}^{*}\gamma_{ia} = {}^{*}\gamma_{iA} \quad (i=1, 2) \tag{6.27} $$

$$ {}^{*}\gamma_{ib} = {}^{*}\gamma_{iB} \quad (i=1, 2) \tag{6.28} $$

6.3.3. *Exchange between the atmosphere and the ocean: f.* The specific reservoir source term of inorganic carbon owing to a flux of CO_2 between the atmosphere and surface reservoir i, according to (4.35), (6.11), and the notations of subsection 5.2, is given by:

$$ f_i = A_{io}\varkappa_{io}(p_o - p_i) \quad (i=1, 2) \tag{6.29} $$

Similarly (cf. equations 4.32, 4.41, 4.44, and 6.22) the corresponding source term for total dissolved inorganic radiocarbon is given by:

$$ {}^{*}f_i = A_{io}\varkappa_{io}({}^{*}\gamma_{oi}p_o - {}^{*}\gamma_{io}p_i) \quad (i=1, 2) \tag{6.30} $$

$$ = {}^{*}\gamma_{io}f + h_i \quad (i=1, 2). \tag{6.31} $$

If we eliminate $\varkappa_{io}$ between (6.22) and (6.29) we obtain an expression for h_i in terms of f and measurable quantities, valid if $p_o \neq p_i$:

$$ h_i = f_i\left(\frac{p_o}{p_o - p_i}\right)({}^{*}\gamma_{oi} - {}^{*}\gamma_{io}) \quad (i=1, 2) \tag{6.32} $$

6.3.4. *Reservoir source functions and conservancy equations for radiocarbon.* With the simplifying assumptions of subsection 6.3.2, we revise (6.19) as it applies to each reservoir:

$$ {}^{*}Q_1 = {}^{*}\gamma_{1A}a_1 + {}^{*}\gamma_{1B}b_1 - {}^{*}\gamma_{1o}f + h_1 - {}^{*}\lambda {}^{*}q_1 W_1 \tag{6.33} $$

$$ {}^{*}Q_2 = {}^{*}\gamma_{2A}a_2 + {}^{*}\gamma_{2B}b_2 + {}^{*}\gamma_{2o}f + h_2 - {}^{*}\lambda {}^{*}q_2 W_2 \tag{6.34} $$

$$ {}^{*}Q_3 = {}^{*}\gamma_{A3}a_3 + {}^{*}\gamma_{B3}b_3 - {}^{*}\lambda {}^{*}q_3 W_3 \tag{6.35} $$

From the requirement, at steady state, that radiocarbon be separately conserved in the forms of insoluble carbonate, biocarbon, and inorganic carbon:

$$ {}^{*}\gamma_{1A}a_1 + {}^{*}\gamma_{2A}a_2 + {}^{*}\gamma_{A3}a_3 + {}^{*}\lambda \sum_{i=1}^{3} {}^{IC*}q_i W_i = 0 \tag{6.36} $$

$$ {}^{*}\gamma_{1B}b_1 + {}^{*}\gamma_{2B}b_2 + {}^{*}\gamma_{B3}b_3 + {}^{*}\lambda \sum_{i=1}^{3} {}^{B*}q_i W_i = 0 \tag{6.37} $$

$$ {}^{*}Q_1 + {}^{*}Q_2 + {}^{*}Q_3 = 0 \tag{6.38} $$

Employing (6.33) to (6.38) simultaneously to eliminate the a_i and b_i:

$$({}^*\gamma_{20} - {}^*\gamma_{10})f + h_1 + h_2 = {}^*\lambda \sum_{i=1}^{3} ({}^{IC*}q_i + {}^{B*}q_i + {}^*q_i) W_i \tag{6.39}$$

The terms on the left side give the net flux of radiocarbon entering the oceans from the atmosphere and those on the right side give the total decay of radiocarbon in the oceans.

6.3.5. *Comparison of the two surface reservoirs.* We lack precise values of the fractionation factors for radiocarbon and shall not be justified in distinguishing between the values assigned to the separate reservoirs. Specifically, we shall assume:

$$\alpha_{1A} = \alpha_{2A}, \quad \alpha_{1B} = \alpha_{2B} \tag{6.40}$$

$$\left.\begin{aligned} {}^C\alpha_1 \alpha_{01} &= {}^C\alpha_2 \alpha_{02}, \\ {}^C\alpha_1 \alpha_{1,eq} &= {}^C\alpha_2 \alpha_{2,eq}. \end{aligned}\right\} \tag{6.41}$$

Furthermore, we shall not introduce serious error in evaluating ${}^*\gamma_{A3}$ and ${}^*\gamma_{B3}$ from (6.36) and (6.37) if we simplify these two equations by assuming:

$${}^C\mathcal{R}_1 = {}^C\mathcal{R}_2 \tag{6.42}$$

even though we do not make this assumption elsewhere. Observing (6.40), (6.41), and (6.42) and the definitions of ${}^*\gamma_{ia}$ and ${}^*\gamma_{ib}$ in subsection 5.2:

$${}^*\gamma_{1A} = {}^*\gamma_{2A} \tag{6.43}$$

$${}^*\gamma_{1B} = {}^*\gamma_{2B} \tag{6.44}$$

Substituting for ${}^*\gamma_{2A}$ and ${}^*\gamma_{2B}$ in (6.36) and (6.37) and noting that (5.12) applies to the sums of the a_i and b_i:

$$({}^*\gamma_{A3} - {}^*\gamma_{1A})a_3 + {}^*\lambda \sum_{i=1}^{3} {}^{IC*}q_i W_i = 0 \tag{6.45}$$

$$({}^*\gamma_{B3} - {}^*\gamma_{1B})b_3 + {}^*\lambda \sum_{i=1}^{3} {}^{B*}q_i W_i = 0 \tag{6.46}$$

7. Numerical calculations and results

7.1. *Data*

We begin by assigning average values to the concentrations of the various tracers in the different reservoirs using data for the Pacific Ocean. It is difficult to say whether this leads to any more serious inconsistencies than were introduced by Eriksson (1959), who estimated averages for WSW, CSW, and DW from data of all the oceans. Our choice is influenced by the availability of extensive new observations on the carbon system in the Pacific Ocean. We shall consider three cases:

Case I: for WSW, observations within a few degrees of the equator; for CSW, observations near Antarctica.

Case II: for WSW, averages of observations between 40° N and 40° S; for CSW, averages of observations south of 40° S.

Case III: for WSW, same values as Case II; for CSW, averages of observations north of 40° N;

All cases: for DW, average values as described below.

This selection allows us to compare results for different regions to gain some understanding of the limitations of the model. The third case is of course not realistic, since the northern part of the Pacific Ocean is not a source for deep. The three cases do, however, together produce an interesting illustration of the three-reservoir model.

As Figs. 6–13 show, the surface distributions of the tracers we have chosen do not suggest any particular preference for dividing the surface water into reservoirs at any specific latitudes. The choice of 40°, N and S, is based essentially on a consideration of temperature, these latitudes having the maximum temperature gradients (see subsection 5.1).

Surface water values for temperature and all chemical tracers except inorganic radiocarbon, are based on observations from Russian cruises during 1957–1959. Surface radiocarbon isotopic ratios are based on reports by Broecker (1963*a*) and Bien *et al.* (1963) with ${}^C\mathcal{R}_\bullet = {}^C\mathcal{R}_\circ$ (see subsection 5.2.4). Tables 3, 4, and 5 list the Russian data as reported to the U.S. National Oceanographic Data Center, Washington, D.C. The tables also list concentrations for borate, carbonate alkalinity, the Harvey inorganic carbon factor, and the concentration of inorganic carbon calculated from the Russian values for salinity, temperature, pH, and titration alkalinity according to the methods of Harvey (1955, pp. 160–175). Borate concentrations are determined from Harvey's Table 20 (pp. 164–165); the Harvey factor is based on his

Table 3. *Station data for North Pacific cold surface water (CSW)*

Col.: 1	2	3	4	5	6	7	8	9	10	11	12
Lat. (deg, min)	Stn No.[a]	Temp. (°C)	Salinity (‰)	Oxygen (ml/l)	Inorganic phosphorus (μg-at/l)	pH	Titration alkalinity (meq/l)	Borate (meq/l)	Carbonate alkalinity (meq/l)	Harvey factor	Inorganic carbon (mg-at/l)
54 27	4124	6.42	34.47	6.72	1.29	8.07	2.27	0.06	2.21	0.94	2.08
54 25	4123	7.35	32.53	6.70	1.02	8.09	2.27	0.06	2.21	0.93	2.06
54 22	4121	6.73	31.84	6.55	1.19	8.12	2.23	0.06	2.17	0.93	2.02
53 29	4120	7.13	32.64	6.71	1.28	8.10	2.28	0.06	2.22	0.93	2.06
52 09	4118	7.01	32.72	6.73	1.40	8.06	2.30	0.06	2.24	0.93	2.08
52 24	4117	7.34	32.67	6.74	—	—	—	0.06	—	—	—
50 38	4116	7.35	32.68	6.83	1.23	8.11	2.30	0.06	2.24	0.93	2.08
49 55	4115	7.45	32.73	6.72	—	—	—	0.06	—	—	—
49 10	4114	7.61	32.74	6.68	1.34	8.07	2.32	0.06	2.26	0.93	2.10
48 16	4113	7.68	32.79	6.72	—	—	—	0.06	—	—	—
47 27	4112	7.81	32.89	6.70	1.53	8.07	—	0.07	—	—	—
45 52	4110	8.95	33.03	6.53	1.16	8.12	2.30	0.07	2.23	0.93	2.07
44 37	4108	10.49	33.06	6.29	0.99	8.09	2.31	0.07	2.24	0.93	2.08
42 33	4106	11.85	33.27	6.15	0.78	8.18	2.32	0.08	2.24	0.91	2.04
41 08	4104	14.44	33.71	5.78	0.31	8.17	2.32	0.08	2.24	0.90	2.02
Average		8.37	32.92	6.570 (0.293 mmol/l)	1.13	8.10	2.293		2.227		2.063
No. of samples		15	15	15	12	12	11		11		11

[a] Station Numbers 4124 through 4104, Vityaz Cruise 589.

Table 4. *Station data for Pacific warm surface water (WSW)*

Col.: 1	2	3	4	5	6	7	8	9	10	11	12
Lat. (deg, min)	Stn. No.[a]	Temp. (°C)	Salinity (‰)	Oxygen (ml/l)	Inorganic phosphorus (μg-at/l)	pH	Titration alkalinity (meq/l)	Borate (meq/l)	Carbonate alkalinity (meq/l)	Harvey factor	Inorganic carbon (mg-at/l)
39 33 N	4102	14.94	33.84	5.80	0.27	8.18	2.33	0.09	2.24	0.90	2.02
38 00 N	4100	17.79	34.18	5.50	0.10	8.17	2.34	0.09	2.25	0.90	2.03
36 36 N	4098	18.89	34.31	5.08	0.05	8.14	2.35	0.09	2.26	0.90	2.03
35 55 N	4097	20.82	34.56	—	—	—	—	0.10	—	—	—
34 56 N	4096	20.62	34.46	5.22	0.10	8.18	2.37	0.10	2.27	0.89	2.02
32 48 N	3777	18.78	34.81	5.36	0.10	8.22	2.36	0.10	2.26	0.89	2.01
31 13 N	3778	20.08	34.90	5.18	0.04	8.21	2.37	0.10	2.27	0.89	2.02
29 22 N	3779	22.15	35.26	4.98	0.13	8.20	2.40	0.10	2.30	0.88	2.02
27 37 N	3780	23.28	35.44	4.89	0.07	8.19	2.42	0.10	2.32	0.88	2.04
25 50 N	3781	25.03	35.46	4.76	0.13	8.27	2.41	0.10	2.31	0.88	2.03
24 03 N	3782	25.55	35.47	4.65	0.06	8.19	2.40	0.10	2.30	0.88	2.02
23 12 N	3783	25.71	35.44	4.68	0.07	8.20	—	0.10	—	—	—
20 22 N	3784	26.83	35.14	4.58	0.09	8.19	2.41	0.11	2.30	0.88	2.02
18 56 N	3785	27.13	34.99	4.56	0.11	8.20	—	0.11	—	—	—
16 51 N	3786	27.33	35.05	—	0.03	8.20	2.40	0.11	2.29	0.88	2.02
15 49 N	3787	27.61	34.83	4.47	0.07	8.18	2.35	0.11	2.24	0.88	1.97
14 04 N	3788	27.81	34.67	4.44	0.04	8.18	2.36	0.11	2.25	0.88	1.98
12 32 N	3790	27.91	34.54	4.56	0.10	8.16	—	0.11	—	—	—
11 03 N	3791	28.01	34.60	4.31	0.03	8.18	2.37	0.11	2.26	0.87	1.97
9 48 N	3792	28.26	34.50	4.51	0.17	8.19	2.38	0.11	2.27	0.87	1.97
8 34 N	3793	28.65	34.14	4.35	0.36	8.20	2.33	0.11	2.22	0.87	1.93
7 17 N	3794	28.95	34.28	4.38	0.16	8.21	2.33	0.11	2.22	0.87	1.93
5 58 N	3795	28.43	34.33	4.48	0.17	8.22	2.35	0.11	2.24	0.87	1.95
3 09 N	3796	29.19	34.81	4.38	0.22	8.15	2.35	0.11	2.24	0.87	1.95
1 58 N	3797	29.04	35.03	4.45	0.32	8.20	2.39	0.11	2.28	0.87	1.98
1 08 N	3798	28.56	34.75	4.45	0.32	8.17	2.36	0.11	2.25	0.87	1.96

1 06 S	3800	29.19	35.06	4.34	0.26	8.18	2.39	0.11	2.28	0.87	1.98
2 25 S	3801	29.39	35.66	—	0.27	8.22	2.43	0.11	2.32	0.87	2.02
3 20 S	3802	29.44	35.59	4.32	0.32	8.19	2.42	0.11	2.31	0.87	2.01
4 32 S	3803	29.53	35.62	4.42	0.42	8.10	2.42	0.10	2.32	0.88	2.04
4 57 S	3804	29.33	35.62	4.32	0.29	8.15	2.42	0.10	2.32	0.88	2.04
6 48 S	3805	29.68	35.54	4.38	0.45	8.17	2.42	0.11	2.31	0.88	2.03
8 36 S	3807	29 31	35.31	4.42	0.28	8.16	2.40	0.11	2.29	0.88	2.02
10 07 S	3808	28.73	35.57	4.42	0.26	8.18	2.44	0.11	2.33	0.87	2.06
11 50 S	3810	28 35	35.53	4.45	0.30	8.19	2.57	0.11	—	—	—
13 26 S	3811	28.11	35.81	—	0.42	8.23	2.46	0.11	2.35	0.86	2.02
14 49 S	3812	27.81	35.83	4.51	0.18	8.24	2.45	0.11	2.34	0.86	2.01
17 57 S	3814	26.21	35.74	4.66	0.18	8.24	2.43	0.11	2.32	0.87	2.02
18 49 S	3815	26.22	35.67	4.67	0.32	8.26	2.42	0.11	2.31	0.87	2.01
18 03 S	3816	26.95	36.05	4.54	0.22	8.22	2.45	0.11	2.34	0.87	2.04
20 08 S	3818	25.76	35.56	4.73	0.11	8.22	2.41	0.10	2.31	0.88	2.03
21 15 S	3819	25.27	35.52	4.77	0.08	8.20	2.41	0.10	2.31	0.88	2.03
21 35 S	3820	25.04	35.55	4.76	0.05	8.23	2.42	0.10	2.32	0.88	2.04
22 34 S	3821	25.08	35.66	4.75	0.13	8.20	2.42	0.10	2.32	0.88	2.04
23 17 S	3823	24.88	35.59	4.75	0.19	8.19	2.41	0.10	2.31	0.88	2.03
23 53 S	3824	24.82	35.50	4.84	0.16	8.22	2.42	0.10	2.32	0.88	2.04
25 39 S	3825	23.10	35.66	5.00	0.13	8.23	2.43	0.10	2.33	0.88	2.05
27 16 S	3826	22.55	35.81	5.03	0.09	8.24	2.43	0.10	2.33	0.88	2.05
28 55 S	3827	22.36	35.73	5.10	0.11	8.23	2.42	0.10	2.32	0.88	2.04
30 32 S	3829	21.50	35.74	5.10	0.17	8.21	2.49	0.10	—	0.88	—
32 00 S	3831	21.78	35.76	5.06	0.12	8.22	2.43	0.10	2.33	0.88	2.05
33 51 S	3832	19.38	35.55	5.34	0.21	8.18	2.43	0.10	2.33	0.89	2.07
35 24 S	3833	19.16	35.51	5.31	0.25	8.19	2.43	0.10	2.33	0.89	2.07
37 04 S	3834	18.52	35.54	5.35	0.25	8.19	2.44	0.09	2.35	0.89	2.09
Average		25.27	35.20	4.747 (0.212 mmol/l)	0.18	8.20	2.405		2.296		2.017
No. of samples		54	54	50	53	53	50		48		48

[a] Station Numbers 4102 through 4096, Vityaz Cruise 589.
Station Numbers 3777 through 3834, Vityaz Cruise 862.

Table 5. *Station data for South Pacific cold surface water (CSW)*

Col.: 1	2	3	4	5	6	7	8	9	10	11	12
Lat. (deg, min)	Stn. No.[a]	Temp. (°C)	Salinity (‰)	Oxygen (ml/l)	Inorganic phosphorus (μg-at/l)	pH	Titration alkalinity (meq/l)	Borate (meq/l)	Carbonate alkalinity (meq/l)	Harvey factor	Inorganic carbon (mg-at/l)
40 11	3837	16.85	35.38	5.53	0.13	8.20	2.41	0.09	2.32	0.90	2.09
41 19	3838	16.23	35.52	5.79	0.17	8.16	2.43	0.08	2.35	0.91	2.12
44 28	396	12.73	34.45	6.08	0.46	8.10	2.335	0.07	2.27	0.92	2.09
46 19	395	12.12	34.56	6.15	0.45	8.12	2.336	0.07	2.27	0.92	2.09
47 21	394	12.41	34.60	6.11	0.48	8.13	2.337	0.07	2.27	0.92	2.09
48 24	393	11.37	34.63	6.22	0.52	8.12	2.330	0.07	2.26	0.92	2.08
50 21	392	10.70	34.50	6.34	0.61	8.08	2.326	0.07	2.26	0.93	2.10
52 24	391	8.81	34.29	6.60	0.99	8.05	2.325	0.06	2.27	0.94	2.13
54 17	390	6.79	34.05	6.72	1.16	8.09	2.321	0.06	2.26	0.94	2.12
56 18	389	5.39	33.85	7.10	1.61	8.07	2.320	0.06	2.26	0.94	2.12
57 58	388	4.15	33.85	7.30	1.65	8.04	2.316	0.05	2.27	0.94	2.13
58 57	387	3.19	33.84	7.40	1.80	8.02	2.328	0.05	2.28	0.95	2.17
60 17	386	2.46	33.88	7.55	1.82	8.04	2.326	0.05	2.28	0.95	2.17
62 38	385	1.78	33.91	7.65	1.86	8.04	2.333	0.05	2.28	0.95	2.17
64 01	384	0.49	34.27	7.85	1.82	8.06	2.364	0.05	2.31	0.96	2.22
66 02	383	0.03	34.14	7.90	2.10	8.03	2.358	0.05	2.31	0.96	2.22
67 59	382	−0.42	33.94	8.02	1.61	8.03	2.334	0.05	2.28	0.96	2.19
69 59	381	−1.11	33.80	8.00	1.84	8.04	2.336	0.05	2.29	0.96	2.20
Average		6.89	34.30	6.906 (0.308 mmol/l)	1.17	8.08	2.342		2.283		2.139
No. of samples		18	18	18	18	18	18		18		18

[a] Station Numbers 3837 through 3838, Vityaz Cruise 862.
Station Numbers 396 through 381, Ob Cruise 5.

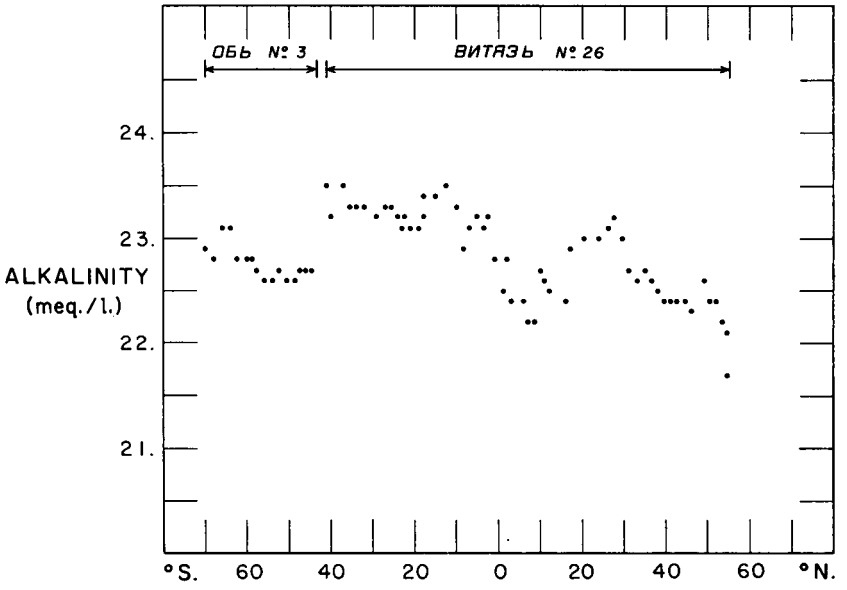


Fig. 6. Surface distribution of carbonate alkalinity.

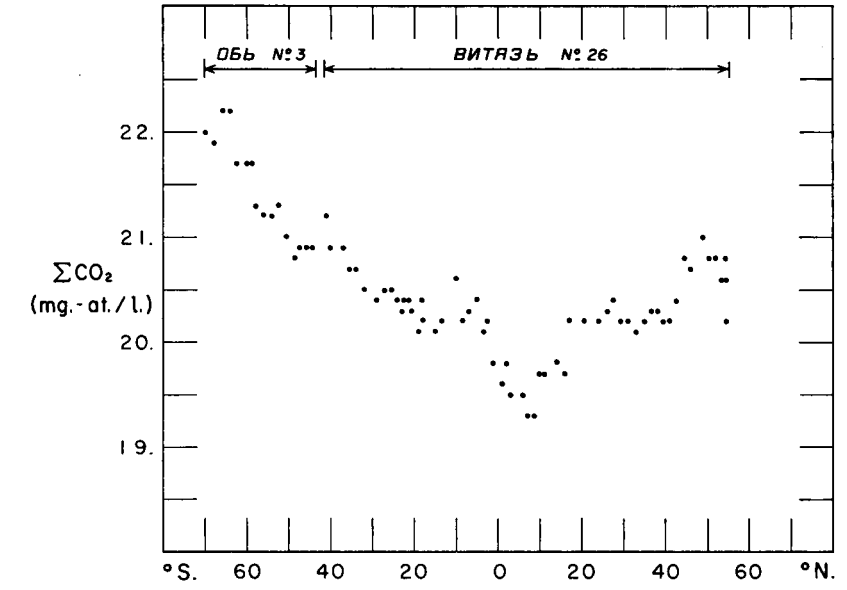


Fig. 7. Surface distribution of dissolved inorganic carbon.

Table 26 (pp. 174–175); salinity values were converted to chlorinities by Harvey's equation (p. 126). The tables list average values used for Cases II and III. (The oxygen concentrations in mmol/l are obtained from values in μg atoms/l using the factor of Sverdrup *et al.* (1942, p. 188).) The data for Case I were selected by inspection of the surface distributions plotted in Figs. 6–13.

For deep water, DW, we have not taken the trouble to average the Russian Pacific Ocean data but have accepted average values from various references listed in Table 6. Some of these selections require additional comment.

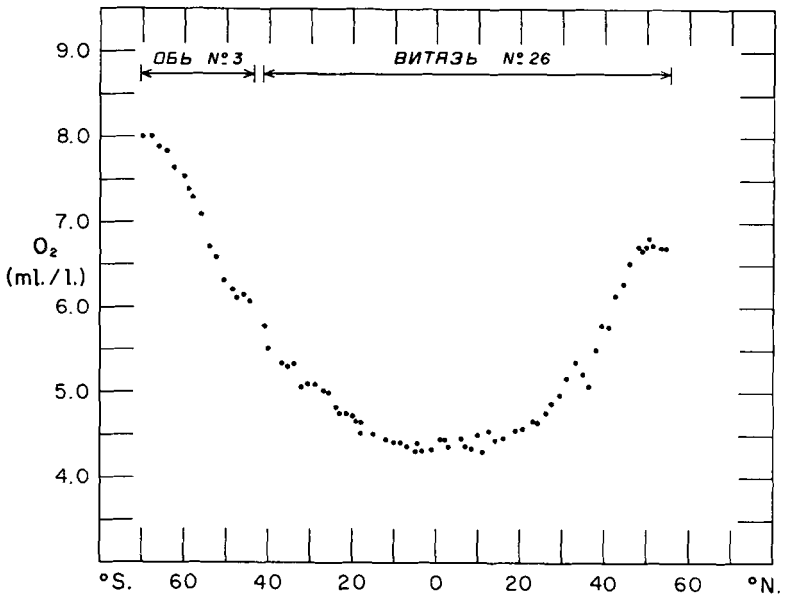


Fig. 8. Surface distribution of dissolved oxygen.

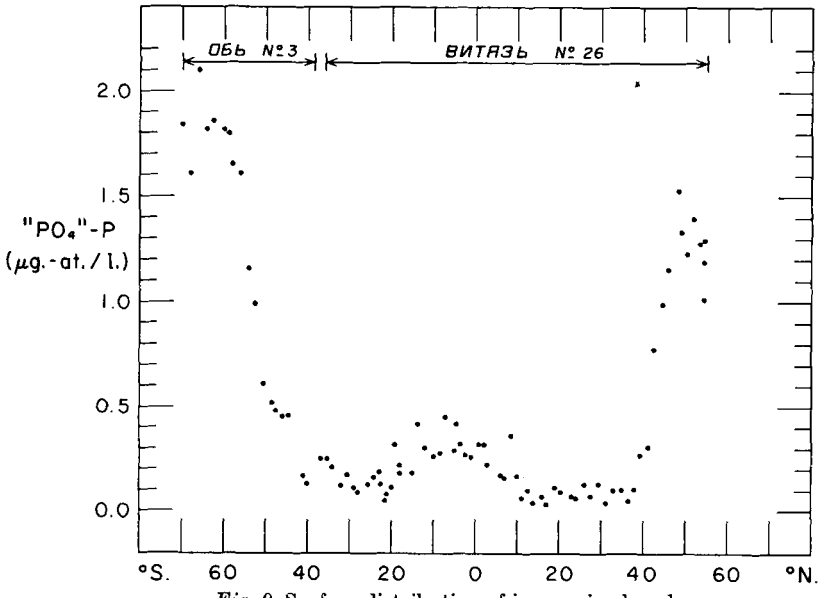


Fig. 9. Surface distribution of inorganic phosphorus.

To determine the carbonate alkalinity, we take 0.005 as the difference in specific alkalinity, A_{sp}, between WSW and DW. We convert the carbonate alkalinity to specific alkalinity (titration alkalinity divided by chlorinity) and the reverse by the method of Harvey (1955, pp. 160–175). For WSW we obtain from the data of Table 4 $A_{sp} = 0.1233$, in good agreement with Wattenburg's value of 0.123 (Skirrow, 1965, p. 248). Hence to DW we assign $A_{sp} = 0.1283$. This value agrees closely with the value of Koczy (1956, p. 283) for deep Pacific Ocean water (0.1285), although Koczy's value for Pacific Ocean surface water (0.120) is significantly lower than our value for WSW.

For oxygen in waters below 2000 meters,

Table 6. *Data for Pacific deep water (DW)*

Carbonate alkalinity	2.423 meq/l	Sverdrup *et al.* (1942, p. 208)
Inorganic carbon	2.330 mg atoms/l	Eriksson (1962, p. 4)
Oxygen	0.18 mmol/l	Eriksson (1962, p. 4)
Inorganic phosphorus	2.58 μg atoms/l[a]	Eriksson (1962, p. 4)
Salinity	34.70g/kg	Bolin & Stommel (1961, p. 96)
Inorganic radiocarbon ratio	0.810	Broecker (1963 *a*, p. 145)
Temperature	1.50°C	Bolin & Stommel (1961, p. 96)

[a] Reference quotes 0.80 μg/liter.

Eriksson (1959) computed an average concentration of 0.18 mmol/l. He noted that waters above 2000 meters are generally lower in oxygen concentration than deeper waters and arbitrarily (as far as we can tell) reduced the value he assigned to DW in his model to 0.17 mmol/l. Our model is not sensitive to such a small adjustment and we initially adopt Eriksson's original value.

For salinity and temperature we take the values which Bolin & Stommel (1961) quote for "common water".

For inorganic radiocarbon the isotopic ratios assigned to all reservoirs, based on data of Broecker (1963*a*), are raised by 10‰ to account for isotopic fractionation at the ocean surface, given in our notation by $\alpha_{i,\mathrm{eq}} \cdot {}^{C}\alpha_i$ (cf. footnote of subsection 6.3).

The values assigned to the various reservoirs are listed in Table 7. The values assigned for pH and p_i were calculated from the assigned values of inorganic carbon and carbonate alkalinity according to the method of Harvey (1955, pp. 160–175).

Because of insufficient data, we cannot make full use of insoluble carbonate, *IC*, and biocarbon, *B*, as tracers. To treat the radiocarbon budget of the ocean adequately, however, we need some idea about existing concentrations. As quoted in subsection 6.3.2, we assume:

$$ {}^{B}q_i \cong 0.08 \text{ mg atoms/l} \quad (i = 1, 2, 3) $$

$$ {}^{IC}q_i \ll {}^{B}q_i \quad (i = 1, 2, 3) $$

In estimating the concentration of radiocarbon in insoluble carbonates and biocarbon ($^{IC}*q_i$ and $^{B}*q_i$), it is sufficient to note that the uncertainty of the values just quoted does not justify us in assuming ${}^{IC}\mathcal{R}_i/\mathcal{R}_\bullet$ and ${}^{B}\mathcal{R}_i/\mathcal{R}_\bullet$ to be different from unity.

For the isotopic fractionation factors, a study by Craig (1954) indicates the following average values:

$$ \alpha_{iA} = 1.000 \quad (i = 1, 2) $$

$$ \alpha_{iB} = 0.980 \quad (i = 1, 2) $$

$$ \alpha_{oi} = 0.972 \quad (i = 1, 2) $$

$$ {}^{C}\alpha_i \cdot \alpha_{i,\mathrm{eq}} = 0.988 \quad (i = 1, 2) $$

Table 7. *Data for three-reservoir model*

Case:	I	II, III	I	II	III	I, II, III
Reservoir name:	WSW	WSW	CSW	CSW	CSW	DW
Reservoir index:	1	1	2	2	2	3
Property						
${}^{A}q$, carbonate alkalinity (meq/l)	2.249	2.296	2.298	2.283	2.227	2.423
${}^{C}q$, inorganic carbon (mg atoms/l)	1.950	2.017	2.200	2.139	2.063	2.330
${}^{O}q$, oxygen (mmol/l)	0.196	0.212	0.357	0.308	0.293	0.180[a]
${}^{P}q$, inorganic phosphorus (μg atoms/l)	0.40	0.18	1.80	1.17	1.13	2.58[a]
${}^{S}q$, salinity (g/kg)	35.00	35.20	34.00	34.30	32.92	34.70
${}^{C}\mathcal{R}_i/\mathcal{R}_\bullet$, inorganic radiocarbon ratio	0.955	0.955	0.925	0.925	0.925	0.810
$*q$, inorganic radiocarbon (mmol/l)	1.862	1.926	2.035	1.979	1.908	1.887
T, temperature (°C)	29.00	25.27	0.00	6.89	8.37	1.50
pH	8.20	8.20	8.04	8.08	8.10	7.98
p_i (atm × 10^6)	319	317	402	374	365	504

[a] Case II′ employs 0.150 for oxygen, no change for inorganic phosphorus; Case III′ employs 0.105 for oxygen, 3.00 for phosphorus, cf. subsection 7.2.

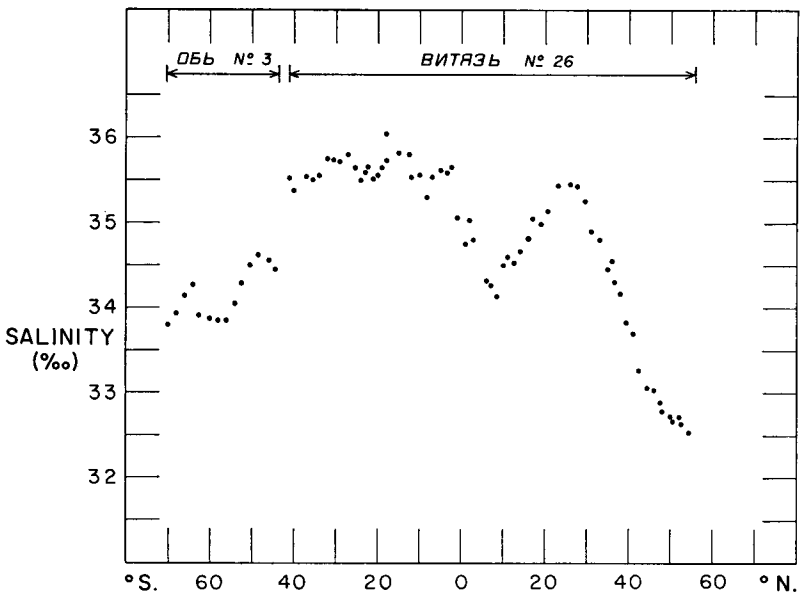


Fig. 10. Surface distribution of salinity.

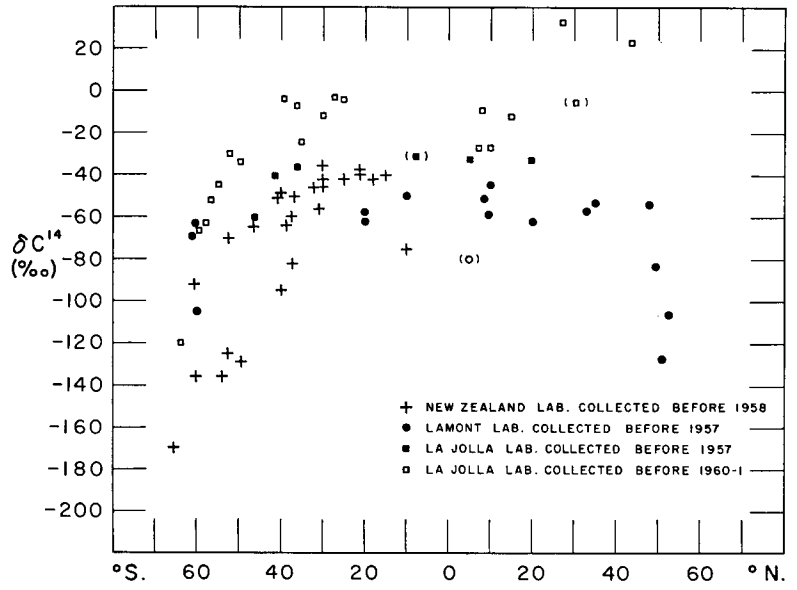


Fig. 11. Surface distribution of dissolved inorganic radiocarbon.

As stated in subsection 6.3.5, differences in isotopic fractionation between the two surface reservoirs are neglected. Using these values, values of ${}^{C}\mathcal{R}_i/\mathcal{R}_\bullet$ of Table 7, and the definitions of subsection 5.2:

$$*\gamma_{1A} = 0.955 \qquad *\gamma_{2A} = 0.925$$
$$*\gamma_{1B} = 0.936 \qquad *\gamma_{2B} = 0.906$$
$$*\gamma_{1o} = 0.917, \qquad *\gamma_{2o} = 0.888$$

For deep water the dissolution of carbonate and oxidation of biocarbon proceed irreversibly (cf. 6.24, 6.25, 6.26), hence:

$$\alpha_{A3} = 1.000 \qquad \alpha_B{}^3 = 1.000$$

and thus

$$*\gamma_{3a} = {}^{IC}\mathcal{R}_3/\mathcal{R}_\bullet \qquad *\gamma_{3b} = {}^{B}\mathcal{R}_3/\mathcal{R}_\bullet$$

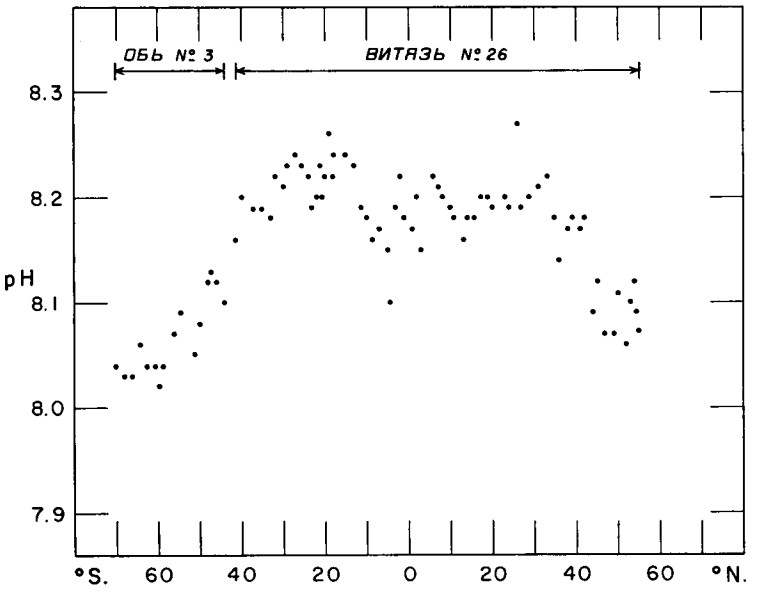


Fig. 12. Surface distribution of pH.

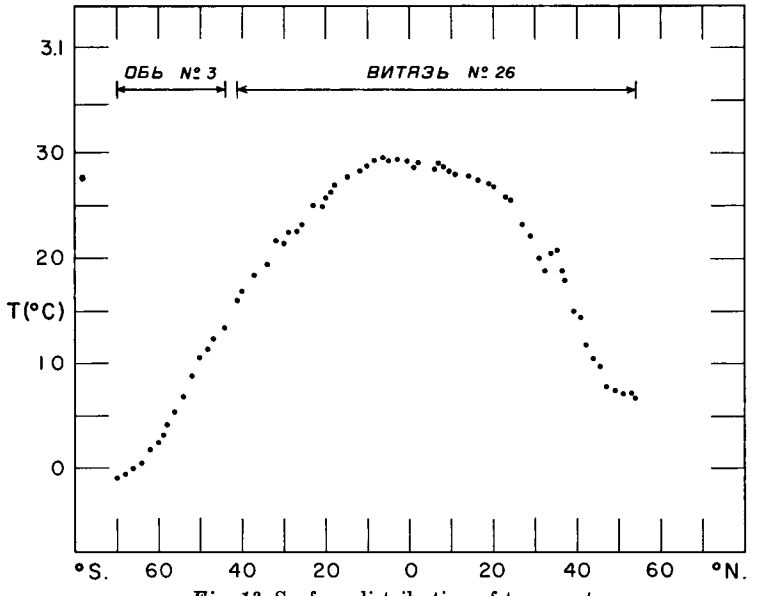


Fig. 13. Surface distribution of temperature.

For the radiocarbon decay constant, we use the value of Craig (1957):

$$*\lambda = (8{,}033 \text{ years})^{-1}$$

We have, finally, assumed (cf. Sverdrup *et al.*, 1952, p. 15) as values for the world oceans:

WSW: $W_1 = 160 \cdot 10^{17}$ liters
CSW: $W_2 = 80 \cdot 10^{17}$ liters
DW: $W_3 = 12{,}980 \cdot 10^{17}$ liters
WSW: $A_{10} = 2.4 \cdot 10^{17}$ cm²
CSW: $A_{20} = 1.2 \cdot 10^{17}$ cm²

10^{18}

Table 8. *Computations for the deep water (DW)*

Column:	1	2	3	4	5	6
Case:	I	II	II	III	II′	III′
${}^{O}\gamma$	−1.3	−1.3	−1.1	−1.3	−1.3	−1.1
k_2 (10^{17} l/yr)	9.0	13.3	12.0	21.0	11.7	11.5
k_{-3} (10^{17} l/yr)	2.2	−1.3	−0.3	−7.7	0.03	0.1
a_3 (10^{17} mg-at/yr)	0.76	0.85	0.83	1.57	0.82	1.13
b_3 (10^{17} mg-at/yr)	1.26	1.28	1.39	1.64	1.42	1.97
${}^{P}\gamma$ ($\times 10^3$)	9.44	12.18	11.74	7.37	11.64	11.07
${}^{*}\gamma_{A3}$	0.955	0.955	0.955	0.955	0.955	0.955
${}^{*}\gamma_{B3}$	0.836	0.838	0.845	0.859	0.847	0.872
τ_3 (yr)	1150	1080	1100	970	1110	1120
${}^{B}\tau_3$ (yr)	860	840	780	660	760	550
${}^{S}q_2$ (‰)	34.63	34.75	34.71	34.88	34.70	34.70

The difference in relative size of the North and South Pacific CSW will not influence critically any of our general conclusions. For simplicity we shall use the above values for all three cases as explained in subsection 5.1. Thus, we shall calculate source terms for a series of model world oceans having the average properties listed in Table 7.

7.2. *Calculation for the deep water reservoir (DW)*

Since processes in the deep water, DW, do not depend directly on exchange at the air-ocean boundary, the system of equations obtained from applying (5.11) to this reservoir is comparatively simple. It can be solved explicitly and gives an insight which is of considerable value when treating the more complex surface reservoirs.

$$\left.\begin{aligned}
&{}^{A}\delta_2 k_2 - {}^{A}\delta_3 k_{-3} + {}^{A}\gamma\ a_3 = 0 && (A)\\
&{}^{C}\delta_2 k_2 - {}^{C}\delta_3 k_{-3} + a_3 + b_3 = 0 && (C)\\
&{}^{O}\delta_2 k_2 - {}^{O}\delta_3 k_{-3} + {}^{O}\gamma\ b_3 = 0 && (O)\\
&{}^{P}\delta_2 k_2 - {}^{P}\delta_3 k_{-3} + {}^{P}\gamma\ b_3 = 0 && (P)\\
&{}^{S}\delta_2 k_2 - {}^{S}\delta_3 k_{-3} = 0 && (S)\\
&{}^{*}\delta_2 k_2 - {}^{*}\delta_3 k_{-3} + {}^{*}\gamma_{A3} a_3 + {}^{*}\gamma_{B3} b_3 = {}^{*}\lambda\, {}^{*}q_3 W_3 && (*)
\end{aligned}\right\} \quad (7.1)$$

In addition to the four unknowns k_2, k_{-3}, a_3, and b_3 which express transfers into DW, we do not *a priori* know the source ratios ${}^{*}\gamma_{A3}$ and ${}^{*}\gamma_{B3}$ which relate the source terms of inorganic radiocarbon in DW to those of inorganic bulk carbon (a_3 and b_3). This is because the former terms depend on the radioactivity of insoluble carbonate and biocarbon in the deep water. Equations (6.45) and (6.46), however, yield two further relations based on the requirement of conservation of radiocarbon in insoluble carbonate and biocarbon.

Combining (6.45), (6.46), and the six equations, (7.1), we have eight equations and six unknowns, k_2, k_{-3}, a_3, b_3, ${}^{*}\gamma_{A3}$, and ${}^{*}\gamma_{B3}$. The system is, thus, overdetermined. This implies that we cannot independently specify the concentrations ${}^{L}q_i$ and all of the source ratios, ${}^{A}\gamma$, ${}^{O}\gamma$, and ${}^{P}\gamma$. The value of ${}^{A}\gamma$ is uniquely given as 2 by the stoichiometry of the inorganic carbon system, but ${}^{O}\gamma$ and ${}^{P}\gamma$ are weighted space and time averages whose values must be estimated from oceanographic data. Since we expect ${}^{O}\gamma$ to vary over a narrower range than ${}^{P}\gamma$, we shall now consider ${}^{P}\gamma$ as an unknown rather than assume Redfield's value (see subsection 6.2). Also, we shall for the moment disregard the salinity equation 7.1*S*.

We now use the values given in Table 7 for the concentrations of *A*, *O*, *C*, *P*, *; we exclude equations (7.1*S*) and (7.1*P*); and we solve the six remaining first-order equations (considering ${}^{*}\gamma_{A3}\cdot a_3$ and ${}^{*}\gamma_{B3}\cdot b_3$ as unknowns). We thus obtain for Cases I, II, and III (see subsection 7.1) the results given in Table 8, columns 1, 2, and 4. Source ratio ${}^{P}\gamma$ was afterwards computed from equation (7.1*P*) using the values for k_2, k_{-3}, and b_3 already obtained. In column 3 we show the results of a computation for Case II using ${}^{O}\gamma = -1.1$ instead of -1.3. The values in columns 5 and 6 are explained below.

The results for the North Pacific Ocean (Case III) are impossible to reconcile with a three-

reservoir model: we obtain a large negative value for the transfer coefficient k_{-3} in violation of (3.8). Even for Case II, k_{-3} is negative, but a moderate increase in ${}^{O}\gamma$ to -1.1, within the uncertainties for this source ratio, yields an almost acceptable value. The source terms a_3 and b_3 (except for a_3 in Case III) are insensitive to the differences in assigned concentrations. The ratio ${}^{P}\gamma$ is in fair agreement with the value 0.0094 based on Redfield *et al.* (1963) (see subsection 6.2).

The negative values for k_{-3} found for Cases II and III need further explanation. With ${}^{P}\gamma$ regarded as an unknown (see above) the ratio k_2/k_{-3} depends only on the distributions A, C, and O, and the source ratio ${}^{O}\gamma$. This is seen if we eliminate a_3 and b_3 between (7.1A), (7.1C), and (7.1O) thus:

$$\left({}^{C}\delta_2 - \frac{{}^{A}\delta_2}{{}^{A}\gamma} - \frac{{}^{O}\delta_2}{{}^{O}\gamma}\right)k_2 - \left({}^{C}\delta_3 - \frac{{}^{A}\delta_3}{{}^{A}\gamma} - \frac{{}^{O}\delta_3}{{}^{O}\gamma}\right)k_{-3} = 0 \tag{7.2}$$

The sum of terms enclosed in the second parentheses is clearly positive for all cases considered. Therefore to obtain $k_{-3} \geqslant 0$ requires:

$${}^{C}\delta_2 - \frac{{}^{A}\delta_2}{{}^{A}\gamma} - \frac{{}^{O}\delta_2}{{}^{O}\gamma} \geqslant 0 \tag{7.3}$$

If we accept the data of Table 7 we obtain, as a condition on the source ratio for O:

$$\text{Case II: } {}^{O}\gamma \geqslant -1.06$$

$$\text{Case III: } {}^{O}\gamma \geqslant -0.67$$

The concentration data themselves are uncertain, however, and we could choose to fix ${}^{O}\gamma$ and vary one or more concentrations so as to preserve a positive value for k_{-3}. For example, Eriksson (1959) adjusted downward the DW value of oxygen to allow for the influence of intermediate waters. If we fix all concentrations except ${}^{O}q_3$, the condition $k_{-3} \geqslant 0$ leads to:

$$\text{If } {}^{O}\gamma = -1.3\text{: Case II: } {}^{O}q_3 \leqslant 0.151$$

$$\text{Case III: } {}^{O}q_3 \leqslant 0.073$$

$$\text{If } {}^{O}\gamma = -1.1\text{: Case II: } {}^{O}q_3 \leqslant 0.175$$

$$\text{Case III: } {}^{O}q_3 \leqslant 0.107$$

The model clearly prefers lower values of oxygen for Case III than for Case II. This is consistent with oceanographic observations (Reid, 1965) that the intermediate waters of the North Pacific Ocean are distinctly lower in oxygen than those of the South Pacific Ocean.

In Table 8, columns 5 and 6, we show results based on lower values for ${}^{O}q_3$; using primes after the case numbers to indicate adjusted data. We have chosen as Case II′, data of Case II except ${}^{O}q_3 = 0.15$; as Case III′, data of Case III except ${}^{O}q_3 = 0.105$, and ${}^{P}q_3 = 3.00$. (The latter change, which preserves a reasonable value for ${}^{P}\gamma$, is in line with oceanographic observations (Reid, 1965).) In the computation for Case III′ we use ${}^{O}\gamma = -1.1$.

For the South Pacific Ocean, fixing ${}^{O}\gamma = -1.3$ and reducing ${}^{O}q_3$ to 0.15 yields values indistinguishable from preserving ${}^{O}q_3 = 0.18$ and changing ${}^{O}\gamma$ to -1.1. Either choice lies within the uncertainty of the oxygen data and source ratios. For the North Pacific Ocean, ${}^{O}q_3 = 0.105$ is too low, and we are hard pressed to find any realistic combination of values, even if, as in Case III′, we both reduce ${}^{O}q_3$ and raise ${}^{O}\gamma$. We conclude that the three reservoir model yields reasonable results for DW employing slightly adjusted data for the South Pacific Ocean, but does not satisfactorily explain the deep water transport in the North Pacific Ocean. The model for the North Pacific Ocean falls short of reality in many ways, but, in particular, it neglects the influence on tracer concentrations of northward flowing water from the South Pacific Ocean (Knauss, 1962). This neglect is so serious that we shall not pursue Cases III or III′ further.

The values in Table 8 were obtained excluding the salinity equation (7.1S). The ratio k_2/k_{-3} may be calculated directly from (7.1S), but the values obtained in this way for both the North and South Pacific Oceans do not agree even approximately with the values based on tracers A, C, and O. This is not entirely unexpected, since the exchange between CSW and DW is highly selective with respect to S in that for a given temperature the most saline surface water preferably sinks. The salinity values assigned to CSW in Cases I and II are clearly not representative of the water that sinks to form DW. Table 8 shows the calculated salinity for CSW that is consistent with the results based on data for A, C, and O. We find approximate agreement between these calculated salinities

and the observed salinity of the waters which oceanographers regard as the immediate sources of Pacific deep water (cf. Sverdrup *et al.*, 1942, p. 611; and Bolin & Stommel, 1961, p. 96).

The solution of the system of equations (7.1) also allows us to calculate a mass-flux ratio[1] for DW, τ_3, defined (with $i=3$) as:

$$\tau_i = \frac{W_i}{k_{i-1}+k_{-i}} \tag{7.4}$$

and a mass-flux ratio for the insoluble carbonate and biocarbon which pass into deep water, DW, from the surface reservoirs WSW and CSW:

$${}^{IC}\tau_3 = \frac{{}^{IC}q_3\, W_3}{a_3} \tag{7.5}$$

$${}^{B}\tau_3 = \frac{{}^{B}q_3\, W_3}{b_3} \tag{7.6}$$

Using the values for W_3 and ${}^{B}q_3$ quoted above, we obtain:

$$\tau_3 = 1100 \text{ years}$$
$${}^{IC}\tau_3 = 0 \text{ years}$$
$${}^{B}\tau_3 = 800 \text{ years}$$

with only minor variation about these values for the individual cases (cf. Table 8).

We may better understand the significance of these numbers if we derive an analytic expression for τ_3 in terms of the input data of the model. To do so we eliminate a_3 and b_3 between (7.1A), (7.1C), and (7.1*) and rearrange:

$$\tau_3 = \frac{1}{{}^{*}\lambda}\left\{\left(\frac{{}^{C}\mathcal{R}_2-{}^{C}\mathcal{R}_3}{{}^{C}\mathcal{R}_3}\right)+\left(\frac{{}^{C}\mathcal{R}_2-{}^{B}\mathcal{R}_3}{{}^{C}\mathcal{R}_3}\right)\frac{{}^{C}\delta_2}{{}^{C}q_3} + \left(\frac{{}^{B}\mathcal{R}_3-{}^{IC}\mathcal{R}_3}{{}^{C}\mathcal{R}_3}\right)\frac{{}^{A}\delta_2}{{}^{A}\gamma^{C}q_3}\right\} \tag{7.7}$$

where we have simplified the expression by setting $k_{-3}=0$. This condition holds approximately for Cases I and II and is imposed for Cases II′ and III′ by equality (7.3). In (7.7) we have also replaced ${}^{*}\gamma_{A3}$ and ${}^{*}\gamma_{B3}$ by ${}^{IC}\mathcal{R}_3/\mathcal{R}_\bullet$ and ${}^{B}\mathcal{R}_3/\mathcal{R}_\bullet$ as prescribed in subsection 7.1. The latter ratios can be related to the inorganic radiocarbon ratio of surface water by (5.6), (6.45), and (6.46). Using the values for ${}^{IC}{}^{*}q_i$ and ${}^{B}{}^{*}q_i$ of subsection 7.1, we derive the relationships:

$${}^{IC}\mathcal{R}_3 = \alpha_{1A}\,{}^{C}\mathcal{R}_1 - {}^{IC}\tau_3{}^{*}\lambda \tag{7.8}$$

$${}^{B}\mathcal{R}_3 = \alpha_{1B}\,{}^{C}\mathcal{R}_1 - {}^{B}\tau_3{}^{*}\lambda \tag{7.9}$$

where we assume (7.3) to be an equality, hence $k_{-3}=0$, and where subscript 1, in a practical sense, designates an average over all surface water because isotopic differences between WSW and CSW are neglected (cf. 6.42, 6.43, and 6.44).

Neither ${}^{IC}\mathcal{R}_3$ nor ${}^{B}\mathcal{R}_3$ is well determined by the model because of insufficient data. Lack of information on insoluble carbonate led us to assert ${}^{IC}{}^{*}q_i = {}^{IC}q_i = 0$, equivalent to assuming a mass-flux ratio, ${}^{IC}\tau_3$, of zero. No direct measurements of the $^{14}C/^{12}C$ ratios of biocarbon are available, and the existing measurements of bulk biocarbon in deep water are too few to be sure of the numerical value of ${}^{B}\tau_3$ evaluated by (7.6). The average concentration of biocarbon in deep water is probably less than the figure used, however,[2] while the concentration of insoluble carbonate is certainly so low that ${}^{IC}\tau_3$ is considerably less than ${}^{B}\tau_3$.

Thus, the insoluble radiocarbon and the radiobiocarbon in deep water very probably have average $^{14}C/^{12}C$ ratios intermediate between those of inorganic radiocarbon in surface and deep water, and the differences, $({}^{B}\mathcal{R}_3 - {}^{IC}\mathcal{R}_3)$ and $({}^{C}\mathcal{R}_2 - {}^{B}\mathcal{R}_3)$, which appear in (7.7) are not likely to exceed $({}^{C}\mathcal{R}_2 - {}^{C}\mathcal{R}_3)$. Since ${}^{C}\delta_2/{}^{C}q_3$ and ${}^{A}\delta_2/{}^{A}\gamma^{C}q_3$ are small compared to unity, τ_3 depends principally on the ratio $({}^{C}\mathcal{R}_2 - {}^{C}\mathcal{R}_3)/{}^{C}\mathcal{R}_3$, i.e., the mass-flux ratio of deep water is prescribed principally by the radiocarbon ratios of inorganic carbon (cf. subsection 8.8).

7.3. *Calculation for the surface reservoirs (WSW and CSW)*

The equations obtained by applying (5.11) to the surface reservoirs permit us to calculate additional transfer rates within the ocean and to estimate several atmospheric fluxes. The latter results may be compared with independent estimates of the net evaporation-precipitation, F, and of the CO_2 transfer through the

[1] If the deep water could be shown to be randomly or well mixed internally, this ratio could be interpreted as an average "turn over" or "residence" time of the deep water (cf. 3.24).

[2] Recent data by P. Williams (private communication) indicate that 0.08 mg l^{-1} (cf. subsection 7.1) is too high for deep water by at least a factor of 2.

atmosphere between polar and equatorial regions, f.

As pointed out in subsection 5.3, the application of (5.11) yields independent equations for only two of the three reservoirs. We may thus consider one of the surface reservoirs in combination with the deep water reservoir, or alternatively, we can solve the equations obtained from the two surface reservoirs without making use of those for the deep water.

If we adopt the latter approach with ${}^{P}\gamma$ as an unknown (as in subsection 7.2), the equations for inorganic phosphorus, P, will contain products of two unknowns, ${}^{P}\gamma \cdot b_1$ and ${}^{P}\gamma \cdot b_2$, and the equations cannot be solved as a linear set. Furthermore, the overdeterminacy of the equations for deep water is implicitly contained in the set of equations for the surface reservoirs, but the means of eliminating the redundancy is not obvious on first inspection. We have found several ways around these difficulties, but to describe them here is unnecessary.

We shall instead adopt the simpler procedure of solving the equations for one of the surface reservoirs, using the results already obtained for the deep water reservoir.

We obtain for reservoir 1 (WSW):

$$\left.\begin{aligned}
&{}^{A}\delta_3 k_3 - {}^{A}\delta_1 k_{-1} + {}^{A}q_1 F + {}^{A}\gamma a_1 = 0 \quad \text{(A)}\\
&{}^{C}\delta_3 k_3 - {}^{C}\delta_1 k_{-1} + {}^{C}q_1 F + a_1 + b_1 - f = 0 \quad \text{(C)}\\
&{}^{O}\delta_3 k_3 - {}^{O}\delta_1 k_{-1} + {}^{O}q_1 F + {}^{O}\gamma b_1 - g = 0 \quad \text{(O)}\\
&{}^{P}\delta_3 k_3 - {}^{P}\delta_1 k_{-1} + {}^{P}q_1 F + {}^{P}\gamma b_1 = 0 \quad \text{(P)}\\
&{}^{S}\delta_3 k_3 - {}^{S}\delta_1 k_{-1} + {}^{S}q_1 F = 0 \quad \text{(S)}\\
&{}^{*}\delta_3 k_3 - {}^{*}\delta_1 k_{-1} + {}^{*}q_1 F + {}^{*}\gamma_{1A} a_1 \\
&\qquad + {}^{*}\gamma_{1B} b_1 - {}^{*}\gamma_{10} f + h_1 - {}^{*}\lambda\, {}^{*}q_1 W_1 = 0 \quad (^{*})
\end{aligned}\right\} \tag{7.10}$$

These six equations contain eight unknowns, k_3, k_{-1}, F, a_1, b_1, f, g, and h_1.

The six tracers considered are thus insufficient to determine all the transfer rates in our model. We may at this stage use (6.32) to relate the h_i to f on the basis of the partial pressure differences of stable and radioactive CO_2 across the ocean surface. The partial pressures which appear in these equations vary considerably, however, for small variations of ${}^{A}q_i$ and ${}^{C}q_i$, and we cannot rely on the values we calculate for the partial pressures from these data, using the tables of Harvey (1955) (see subsection 6.1).

We also prefer not to insert estimates of the atmospheric water flux or source terms based on other investigations since, firstly, these estimates are themselves uncertain, and secondly, to whatever extent they can be relied upon they are needed to compare with the results of our model. We are left with the alternative to solve for prescribed values of two of the eight variables; and we choose, for convenience, Δk as defined by (5.10), and k_{-1}, the transfer coefficient from CSW to WSW. If we adopt the interpretation of reservoir models which leads to (3.19), the former is equal to the net flux of water which circulates through the reservoirs in the direction WSW to CSW to DW, and is thus a measure of advection; while the latter, for positive values of Δk, is proportional to the eddy transport coefficient between the surface reservoirs. These two quantities, together with the two water transfer coefficients already calculated for the DW reservoir, completely specify the water transfer between oceanic reservoirs.

After (7.10) is solved, we solve for remaining unknown transfer coefficients and source terms associated with reservoir 2 by using the source conservation equations: we obtain k_1 and k_{-2} from (5.10); a_2 and b_2 from (5.12); and h_2 from (6.39). We also compute the partial pressure differences of stable CO_2 across the ocean surface from (6.32) and the ratio of the CO_2 exchange coefficients between CSW and WSW, $\varkappa_{20}/\varkappa_{10}$, by the use of (6.29) applied to the two surface reservoirs.

We sample all the physically realistic solutions of the model by selecting, for Δk, values from -4 to 10×10^{17} l/yr; for k_{-1} 0 to 20×10^{17} l/yr. Values outside these ranges produce solutions with negative values of $-b_i$, for one or more of the k_i, $k_{i'}$, in violation of (3.8) and (6.23).

The calculations were performed by a Control Data Corporation 3600 computer at the University of California, San Diego.[1] A summary

[1] A more detailed form of this paper (or extended version, or material supplementary to this article) has been deposited as Document number *9833* with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D.C. 20540. A copy may be secured by citing the Document number and by remitting $ 5.00 for photoprints or $ 2.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 9. *Solutions of the three-reservoir model for Cases I and II′*

	Case I			Case II′						
Column:	1	2	3	4	5	6	7	8	9	10
Given: Δk (10^{17} l/yr)	2	0	0	4	2	2	2	0	0	0
k_{-1} (10^{17} l/yr)	0	0	4	0	0	4	8	8	12	16
$-a_1$ (10^{17} mg-at/yr)	0.41	0.21	0.36	0.32	0.16	0.20	0.24	0.08	0.12	0.16
$-a_2$ (10^{17} mg-at/yr)	0.35	0.54	0.40	0.50	0.66	0.62	0.58	0.74	0.70	0.66
$-b_1$ (10^{17} mg-at/yr)	0.97	0.51	1.11	0.83	0.42	0.76	1.10	0.69	1.03	1.37
$-b_2$ (10^{17} mg-at/yr)	0.28	0.74	0.15	0.59	1.00	0.66	0.32	0.73	0.39	0.05
f (10^{17} mg-at/yr)	0.29	0.15	0.49	0.22	0.11	0.34	0.56	0.45	0.67	0.89
F (10^{17} l/yr)	0.04	0.02	0.06	0.06	0.03	0.09	0.14	0.11	0.17	0.23
g (10^{17} mmol/yr)	1.20	0.63	2.06	0.84	0.42	1.26	2.10	1.69	2.52	3.36
h_1 (10^{17} mg-at/yr	1.43	0.77	1.01	1.38	0.71	0.95	1.20	0.53	0.77	1.02
h_2 (10^{17} mg-at/yr)	1.81	2.47	2.24	1.86	2.52	2.29	2.05	2.71	2.48	2.24
k_1 (10^{17} l/yr)	2.0	0.0	3.9	3.9	2.0	5.9	9.9	7.9	11.8	15.8
k_{-1} (10^{17} l/yr)	0.0	0.0	4.0	0.0	0.0	4.0	8.0	8.0	12.0	16.0
k_2 (10^{17} l/yr)	9.0	(Invariant)		11.7	(Invariant)					
k_{-2} (10^{17} l/yr)	7.0	9.0	9.0	7.7	9.7	9.7	9.7	11.7	11.7	11.7
k_3 (10^{17} l/yr)	4.2	2.2	2.2	4.0	2.0	2.0	2.0	0.0	0.0	0.0
k_{-3} (10^{17} l/yr)	2.2	(Invariant)		0.0	(Invariant)					
p_1-p_o (ppm)	3.5	3.4	8.5	2.8	2.7	6.1	8.1	14.5	14.9	15.2
p_2-p_o (ppm)	−4.2	−1.6	−5.9	−3.2	−1.2	−3.9	−7.2	−4.3	−7.1	−10.5
$\varkappa_{20}/\varkappa_{10}$	1.7	4.2	2.9	1.8	4.6	3.1	2.3	6.7	4.2	2.9
Water exchanges[a]	0 C↔W 7 D 2	0 C↔W 9 D 2	4 C↔W 9 D 2	0 C↔W 8 D 0	0 C↔W 10 D 0	4 C↔W 10 D 0	8 C↔W 10 D 0	8 C↔W 12 D 0	12 C↔W 12 D 0	16 C↔W 12 D 0
Advection[a]	2	0	0	4	2	2	2	0	0	0

[a] The symbolic representation of water exchange and advection is an attempt to show the approximate physical character of the reservoir transfer coefficients. We adopt the view (for $k_i \geqslant k_{-i}$) that $\Delta k (\approx k_i - k_{-i})$ is a measure of the net flux of water which circulates in the direction WSW to CSW to DW and that the k_{-i} are measures of the water which exchanges between reservoirs (cf. subsection 3.2).

of the results is shown in Table 9. We exclude Cases III and III′ because unrealistic results were already obtained from considering the deep water reservoir. Case II, with ${}^{O}\gamma = -1.1$ is not reproduced since it yields results indistinguishable from Case II′ with ${}^{O}\gamma = -1.3$. In Table 10 we show additional results obtained by modifying Case II′ (as in column 6, Table 9) in various ways. We increase the $^{14}C/^{12}C$ ratio, ${}^{C}\mathcal{R}_2$, to become equal to ${}^{C}\mathcal{R}_1$ (column 2), and we change the ${}^{A}q_i$ and ${}^{C}q_i$ slightly (columns 3 to 6) to investigate how sensitive the results are to different surface values of inorganic radiocarbon, ^{14}C, and to pH. We also vary ${}^{S}q_i$ (columns 7 to 10) to investigate how sensitive the atmospheric fluxes f and F are to difference values of the surface salinity gradient, ${}^{S}\delta_1$.

7.4. *Preliminary analysis of the results*

Parameterization of two of the eight unknowns in (7.10) results in a bewildering array of permissible mathematical solutions to the three-reservoir model even after we impose the restriction based on (3.8) that all k_1 and k_{-1} are nonnegative. We shall therefore appeal to independent oceanographic evidence to restrict the range of possibly valid solutions to the equations. As we show below, little reliance may be placed on the values of the source terms for inorganic carbon a_i, owing to uncertain pH data. Also, the magnitudes of the atmospheric oxygen flux, g, and the CO_2 partial pressure difference in high southern latitudes, $p_2 - p_o$, are unknown. However, for all other tracer quantities listed in Table 9 we possess knowledge independent of our model. Furthermore, groups of these quantities are interrelated or show similar behavior with respect to Δk and k_{-1}, owing partly to the demands of our model, partly to the particular concentrations we have assigned in Table 7. For either Case I or II′, f, g, and F vary linearly with Δk and k_{-1},

Table 10. *Solutions of the three-reservoir model for Case II', modified*

Modification	None	${}^{C}\mathcal{R}_2 = {}^{C}\mathcal{R}_1$	pH				None	${}^{S}q_1$	None	${}^{S}q_1$
Column:	1	2	3	4	5	6	7	8	9	10
Δk (10^{17} l/yr)	2	2	2	2	2	2	2	2	0	0
k_{-1} (10^{17} l/yr)	4	4	4	4	4	4	4	4	16	16
Given: WSW pH	8.20	8.20	8.20	8.19	8.20	8.19				
CSW pH	8.08	8.08	8.16	8.16	8.15	8.15				
${}^{S}q_1$							35.20	36.20	35.20	36.20
$-a_1$ (10^{17} mg-at/yr)	0.20	0.20	0.29	0.49	0.10	0.28	0.20	0.39	0.16	0.66
$-a_2$ (10^{17} mg-at/yr)	0.62	0.46	0.15	−0.03	0.66	0.46	0.62	0.43	0.66	0.16
$-b_1$ (10^{17} mg-at/yr)	0.76	0.76	0.81	0.81	0.67	0.68	0.76	0.76	1.37	1.38
$-b_2$ (10^{17} mg-at/yr)	0.66	0.39	0.57	0.58	0.82	0.81	0.66	0.66	0.05	0.04
f (10^{17} mg-at/yr)	0.34	0.34	0.35	0.47	0.14	0.24	0.34	0.48	0.89	1.26
F (10^{17} l/yr)	0.09	0.09	0.09	0.09	0.07	0.07	0.09	0.25	0.23	0.67
g (10^{17} mmol/yr)	1.26	1.26	1.30	1.30	1.18	1.19	1.26	1.30	3.36	3.47
h_1 (10^{17} mg-at/yr)	0.95	0.70	1.10	1.09	0.73	0.75	0.95	0.95	1.02	1.00
h_2 (10^{17} mg-at/yr)	2.29	2.54	2.14	2.16	2.51	2.49	2.29	2.30	2.24	2.27
k_1 (10^{17} l/yr)	5.9	5.9	5.9	5.9	5.9	5.9	5.9	5.8	15.8	15.3
k_{-1} (10^{17} l/yr)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	16.0	16.0
k_2 (10^{17} l/yr)	11.7	9.4	11.2	11.2	12.5	12.4	11.7	11.7	11.7	11.7
k_{-2} (10^{17} l/yr)	9.7	7.4	9.2	9.2	10.5	10.4	9.7	9.7	11.7	11.7
k_3 (10^{17} l/yr)	2.0	2.0	2.5	2.4	1.3	1.4	2.0	2.0	0.0	0.0
k_{-3} (10^{17} l/yr)	0.0	0.0	0.5	0.4	−0.7	−0.6	0.0	0.0	0.0	0.0
$p_1 - p_o$ (ppm)	6.1	8.3	5.5	7.4	3.2	5.7	6.1	8.7	15.2	21.8
$p_1 - p_o$ (ppm)	−3.9	−2.3	−4.4	−5.7	−1.4	−2.6	−3.9	−5.4	−10.5	−14.7
$\varkappa_{1o}/\varkappa_{1o}$	3.1	7.3	2.5	2.6	4.5	4.4	3.1	3.2	2.9	3.0

the sum of the b_i are invariant, and the sum of the h_i nearly so, while the CO_2 partial pressure difference, $p_1 - p_1$, is proportional to the quotient f/h_1. Also from (6.29) and (6.32) we obtain:

$$\frac{h_2}{h_1} = \frac{A_{2o}\varkappa_{2o}}{A_{1o}\varkappa_{1o}}\left(\frac{{}^{*}\gamma_{o2} - {}^{*}\gamma_{2o}}{{}^{*}\gamma_{o1} -}\right) \qquad (7.11)$$

i.e., h_2/h_1 for a given case is prescribed by the CO_2 exchange coefficient ratio $\varkappa_{2o}/\varkappa_{1o}$, or vice versa. To restrict further the range of mathematical solutions, it will suffice to consider limits on the values of only three variables. We choose for analysis $b_1/(b_1 + b_2)$, $\varkappa_{2o}/\varkappa_{1o}$, and F.

Measurements of the primary production of organic carbon in surface waters, averages of which are denoted in our model by b_{1B} and b_{2B}, suggest that the average annual production in high latitudes exceeds that in low latitudes. Ryther (1963) reports:

North Sea (55° N)	45–110 g m^{-2} yr^{-1}
West Atlantic (45° N)	120 g m^{-2} yr^{-1}
Sargasso Sea (30° N)	70 g m^{-2} yr^{-1}
Tropical Oceans	18–48 g m^{-2} yr^{-1}

These values are highly uncertain, but suggest that the primary production poleward of 40° will exceed that between 40° N and 40° S by a factor of about 2. If we choose as representative values 100 g m^{-2} yr^{-1} for CSW, 50 g m^{-2} yr^{-1} for WSW, we obtain with $A_{1o} = 2A_{2o}$ (see subsection 7.1): $b_{1B} = b_{2B} = 10 \times 10^{17}$ mg-atom/yr. We have no data to calculate the ratios of primary production to net synthesis of biocarbon in the separate surface reservoirs, b_{1B}/b_1 and b_{2B}/b_2, although we note that the sum, $b_{1B} + b_{2B}$, is more than ten times the net production for both surface reservoirs together, numerically equal to b_2; so that b_1 and b_2 are both almost sure to be less than zero (cf. 5.5). Thus, we can assert little more than that the $b_1/(b_1 + b_2)$ must be between the limits 0 and 1.

The magnitude of the CO_2 exchange coefficients $\varkappa_{2o}$ and $\varkappa_{1o}$ cannot be estimated reliably from any data independent of that used in this model, but the ratio can be estimated if we accept the conclusion of Kanwisher (1963), based on laboratory data, that the exchange varies approximately as the square of the wind speed. From a plot of the square of the mean wind versus latitude (Kanwisher, 1963, p. 3923)

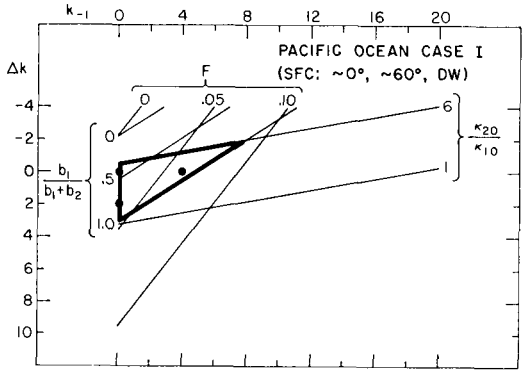


Fig. 14. Parametric plot for Case I. The three sets of parallel lines give the values for the parameters $b_1/(b_1+b_2)$, F, and $\varkappa_{20}/\varkappa_{10}$ for various values of Δk and k (cf. text).

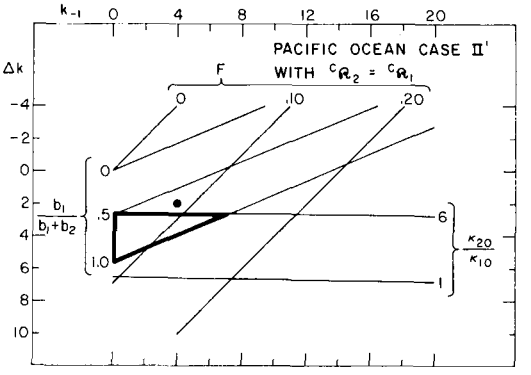


Fig. 16. Parametric plot for Case II' assuming the inorganic radiocarbon ratio of CSW equal to that of WSW (cf. Fig. 14 and the text).

we expect a value for $\varkappa_{20}/\varkappa_{10}$ between 2 and 3. We cannot be confident that the true value is in this range, but we are probably justified to exclude values outside the range 1–6.

Regarding the atmospheric water flux, it is sufficient at this stage to say that all values obtained are considerably smaller than direct estimates based on evaporation and precipitation (cf. subsection 8.2).

In Figs. 14 and 15 we plot for Case I and II′ lines of constant $b_1/(b_1+b_2)$, F, and $\varkappa_{20}/\varkappa_{10}$ versus the parameters Δk and k_{-1}. Owing to the linear relationships between the source terms and water transfer coefficients (cf. 5.11 and 5.13) all the lines for a given quantity are straight and parallel. We see, firstly, that the ratio $\varkappa_{20}/\varkappa_{10}$ varies strongly with Δk but scarcely at all with k_{-1}. This we expect from the small isotopic ratio gradient we have assigned between WSW and CSW. Indeed, as Fig. 16 indicates, if we deliberately set ${}^{C}\mathcal{R}_2 = {}^{C}\mathcal{R}_1$, the ratio $\varkappa_{20}/\varkappa_{10}$ varies almost exclusively with Δk. Secondly, the computed atmospheric water flux, F, is nearly equally sensitive to the values of both surface water fluxes and hence to both Δk and k_{-1}. Thirdly, the model for reasonable values of $b_1/(b_1+b_2)$ and $\varkappa_{20}/\varkappa_{10}$ delivers unreasonably low values for F and, within the limits we have set for $\varkappa_{20}/\varkappa_{10}$, the model favors values for $b_1/(b_1+b_2)$ which tend to be too high. Our preferences for low $b_1/(b_1+b_2)$ and high F are seen to be incompatible demands on the model.

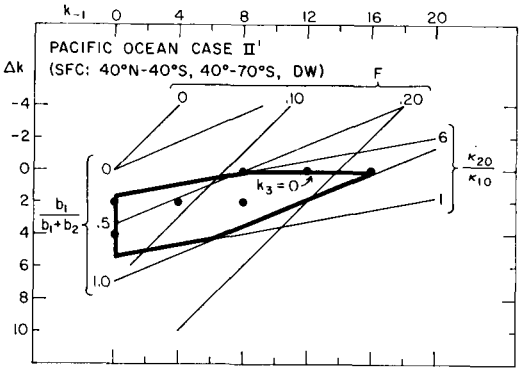


Fig. 15. Parametric plot for Case II′ (cf. Fig. 14 and the text).

In the figures a heavy line encloses the solutions which obey the restrictions $k_{-1} \geqslant 0$, $k_3 \geqslant 0$, $0 \leqslant b_1/(b_1+b_2) \leqslant 1$, $1 \leqslant \varkappa_{20}/\varkappa_{10} \leqslant 6$. These we shall refer to as "preferred solutions". An effective lower limit on $b_1/(b_1+b_2)$ of about 0.3 is set by our demand that $\varkappa_{20}/\varkappa_{10}$ not exceed 6. In Table 9 we have listed at intervals of 2×10^{17} l/yr for Δk and 4×10^{17} l/yr for k_{-1}, nearly all the preferred solutions for Case I and II′ arranged in order of decreasing Δk and increasing k_{-1}. These solutions are indicated in the figures by heavy dots.

When we compare Cases I and II′ at similar positions within the zone of preferred solutions the values obtained in Table 9 are remarkably similar. (Compare, for example, Case I with Δk, $k_{-1} = (2, 0)$[1] with Case II′ (4, 0), or Case I (0, 4) with Case II′ (0, 8). Only one significant difference exists between the cases: for Case I

[1] We shall refer to paired values of Δk and k_{-1} in units of 10^{17} l/yr in this abbreviated notation.

the preferred solutions comprise values for Δk and k_{-1} about half as large as for Case II′. This implies that a three-reservoir ocean having surface reservoirs with the extreme characteristics of equatorial and antarctic surface water will maintain its distribution of tracers including radiocarbon with considerably less surface water transport than an ocean having a more average character, where the gravitational transfers and atmospheric fluxes are nearly the same for both cases.

8. Discussion

8.1. *Introduction*

To evaluate the three-reservoir model we shall now compare the results obtained by the model with independent oceanographic evidence. We shall consider only Case II′ since it utilizes values of the concentrations which are averages over all latitudes south of 40° N and therefore may slightly better represent the Pacific Ocean than Case I (Case III and III′ were rejected in subsection 7.2).

8.2. *The atmospheric water flux, F*

The atmospheric water flux, F, was estimated from data on evaporation and precipitation by Wüst (1954) and from atmospheric water vapor by Peixoto (1958). Wüst found that the net evaporation from the world ocean between 40° N and 40° S is 0.77×10^{17} l/yr and the net gain by precipitation in polar regions is 0.50×10^{17} l/yr. He assumed that the difference is accounted for by runoff from the continents. Peixoto's data are only from the Northern Hemisphere. He obtains a value for the net evaporation of 0.43×10^{17} l/yr for the latitude belt 0–40° N (i.e., half the tropical belt) based on data from the Northern Hemisphere winter, when the evaporation reaches its maximum. On this basis we may accept, as a reasonable estimate for F, $0.6\text{–}0.8 \times 10^{17}$ l/yr.

The values of F that we obtain from Case II′ are less than the lower value just quoted by factors of 3 to 40.

Wüst showed that his estimates of the net water vapor flux in different latitude zones corresponded closely to variations in the observed salinity of the surface water. Averaged over the zones of our model, his salinity data yield ${}^{S}q_1 = 35.2‰$ and ${}^{S}q_2 = 33.9‰$; i.e., ${}^{S}\delta_1 = 1.4‰$. Our salinity values for CSW were adjusted to maintain internal consistency with other tracers when considering DW (cf. Tables 7 and 8). They imply for Case II′ ${}^{S}\delta_1 = 0.50‰$. Equation (7.4S) shows that variations in ${}^{S}\delta_1$ will have direct influence on the value of F obtained from the model. If we recompute with a value of ${}^{S}\delta_1$ consistent with Wüst's, by raising ${}^{S}q_1$ by 1.0‰, with ${}^{S}q_2$ still equal to 34.70‰, for compatibility with the tracer balance for the deep water, we obtain the results shown in Table 10, columns 8 and 10. For given values of the water transfer parameters Δk and k_{-1}, the value of F increases by a factor of nearly 3 as expected. The computed value for the atmospheric flux of CO_2, f, also increases, but only by about 40%. The relative magnitudes of the inorganic carbon source terms, a_1 and a_2, also are considerably influenced owing to the similarity of the distribution of alkalinity to that of salinity. On the other hand, the reservoir transfer coefficients, k_f, k_{-f}, and the other source terms, including b_1 and b_2, remain essentially unchanged. If we adopt the extreme set of values $\Delta k, k_{-1} = (0,\ 16)$, we obtain rough agreement with the transport of water through the atmosphere as estimated by Wüst and Peixoto.

Clearly, the use of salinity as a tracer in the three-reservoir model yields results inconsistent with expectations based on other evidence. Only by adjusting two of the three salinities originally assigned as Case II do we obtain reasonable values for the water transfer coefficients and the atmospheric water flux.

8.3. *The atmospheric carbon dioxide flux, f*

The values for the atmospheric CO_2 flux, f, given in Table 9 for Case II′ ($0.1\text{–}0.9 \times 10^{17}$ mg-atoms/yr) agree poorly with a value of 5×10^{17} mg-atoms (2×10^{10} ton/yr) estimated from atmospheric data (Bolin & Keeling, 1963). Even if the assumed salinity difference ${}^{S}\delta_1$ is increased from 0.5 to 1.5‰, the upper limit for f is increased only to 1.3×10^{17} mg-atoms/yr (see Table 10).

In this instance we cannot trust either of our estimates of f. Firstly, the atmospheric data do not offer a reliable estimate because the observed difference of the CO_2 content of the air between northern polar and equatorial regions upon which the estimate essentially depends is so small (about 1 ppm) that its

Table 11. *Original and adjusted values of the concentrations of inorganic carbon and carbonate alkalinity from Case II′*

WSW			CSW		
pH	${}^{C}q_1$	${}^{A}q_1$	pH	${}^{C}q_2$	${}^{A}q_2$
(Adjusted values: $(p_1 = 325;\ p_2 = 310)$					
8.19	1.991	2.257	8.15	2.135	2.296
8.20	2.042	2.321	8.16	2.179	2.348
Original values: $(p_1 = 317;\ p_2 = 374)$					
8.20	2.017	2.296	8.08	2.139	2.283

value is highly uncertain. Secondly, the basic data for inorganic carbon are remarkably uncertain as discussed in the next subsection.

8.4. *Sensitivity of the results for carbon to small errors in pH*

The values of carbonate alkalinity, ${}^{A}q_i$, and inorganic carbon, ${}^{C}q_i$, in Table 7 are based on observed values of titration alkalinity and pH and were computed using the tables of Harvey (1955). With the same tables and data we may calculate p_i, the average partial pressure of CO_2 in warm and cold surface waters. Adopting the values for temperature and salinity of Table 7, we obtain the values shown on the bottom line of Table 7. The world-wide average atmospheric CO_2 concentration is $p_o = 315 \times 10^{-6}$ atm (Bolin & Keeling, 1963). The values of p_i in Table 7 imply a net release of CO_2 from both CSW and WSW to the atmosphere but primarily from CSW. This is contrary to all other available evidence.

To determine how seriously observational errors in pH may affect our model, we have made four additional computations where we have assumed p_i known and computed ${}^{A}q_i$ and ${}^{C}q_i$ using the tables of Harvey. In approximate agreement with Keeling *et al.* (1965) we assign:

for WSW: $p_1 = 325$ ppm; $T = 26°C$; chlorinity = 19‰

for CSW: $p_2 = 310$ ppm; $T = 6°C$; chlorinity = 19‰

To obtain values for ${}^{A}q_i$ and ${}^{C}q_i$ which are about the same as those given in Table 7, we assume the pH to be 8.19 or 8.20 for WSW; 8.15 or 8.16 for CSW. We obtain the concentration values shown in Table 11. (The original values for Case II′ are shown for comparison.)

As Table 11 shows, a change of 0.01 in pH produces shifts in the values of the ${}^{A}q_i$ larger than the difference in alkalinity between the two surface reservoirs. The ${}^{C}q_i$ also shift considerably. Table 10 shows the strong influence of pH on the values obtained for the source terms. Columns 3 to 6 give the solutions of the model for Δk, $k_{-1} = (2, 4)$ with the pH values of each reservoir, WSW and CSW, varied independently. The carbon source terms b_1 and b_2 shift by up to 25%, the carbon source terms a_1 and a_2 and the atmospheric flux of CO_2, f, by factors greater than 2. The transfer coefficients k_i and k_{-i} also change, but less noticeably. The uncertainty in measuring pH exceeds 0.01 pH units (Skirrow, 1965, p. 242). Thus, the present accuracy in determining inorganic carbon and alkalinity in the ocean, using observations of pH, is inadequate for any precise budget study of the carbon system in the ocean. This is even so if the ocean is divided into more than the three reservoirs used in the present study. We also notice that the tables of Harvey, originally intended for oceanographic studies but prepared only to the nearest 0.1 pH unit, do not approach the precision desirable.

8.5. *The atmospheric oxygen flux, g*

High values of the O_2 flux, g, are associated with high values for the atmospheric CO_2 flux, f, and the water vapor flux, F. If we favor f and F as large as possible (cf. subsections 7.5.2 and 7.5.3), we obtain (Table 10, column 10) $g = 3.5 \times 10^{17}$ mmol/yr.

Redfield *et al.* (1963, p. 55) have estimated

the O_2 flux into the Gulf of Maine as 12×10^4 ml O_2 m^{-2} $month^{-1}$ during the fall and winter, while Pytkowicz (1964) has estimated the O_2 flux out of the Pacific ocean near the coast of Oregon during the summer months as 1.2×10^4 ml O_2 m^{-2} $month^{-1}$. Converted to annual rates and multiplied by the area of WSW (cf. subsection 7.1) we obtain 4 to 40 times the largest value of g obtained by our model.

The data indicate that most of the O_2 flux in the Gulf of Maine and near the coast of Oregon is produced by varying temperature and by biological activity, and therefore is seasonal. The flux, g, however, ought to be considerably smaller since it represents only the yearly excess or deficit produced by large-scale horizontal and vertical transport processes after averaging over the seasons. Thus, the values we have obtained in the three-reservoir model are not unreasonably low.

Redfield estimated the exchange coefficient of O_2 during the winter as 2×10^7 ml m^{-2} $month^{-1}$ (1×10^3 mmol cm^{-2} yr^{-1} atm^{-1}), while Pytkowicz obtained a value 7 times smaller for the summer. The higher value agrees better with laboratory experiments (Richards, 1957, p. 190). Using equation (6.29) applied to O_2, the above values of $\varkappa$ applied to WSW, and our highest value for g, we calculate a net pressure excess in WSW of 1.5×10^{-4} to 1.0×10^{-3} atm.

It is doubtful whether such a low yearly pressure difference can be verified experimentally because much larger differences for short times and in restricted regions probably mask the net pressure difference.

8.6. *The carbon dioxide partial pressure*

Lack of direct measurements during winter in high latitudes discourages us from considering any estimate of p_2, the CO_2 partial pressure of CSW. Fairly representative data are available, however, to estimate p_1, the corresponding pressure for WSW. From two sets of direct measurements between 30° N and 30° S in the Pacific Ocean east of 150° E, Keeling *et al.* (1965) estimated average values of 336 and 343 for March and November, respectively. Between 40° N and 40° S near 180° where the other surface data in Table 7 were obtained, the annual average value may be lower but probably not less than 325 ppm. With $p_o = 315$ (cf. subsection 8.4) we expect $p_1 - p_o > 10$ ppm.

The values of $p_1 - p_o$ obtained from the three-reservoir model satisfy this limit only for preferred solutions near the lower limit of Δk and upper limit of k_{-1}, where relatively high values are obtained for the atmospheric CO_2 flux, f. When the salinity is adjusted to produce a satisfactory value for the atmospheric water vapor flux, F, the model predicts $(p_1 - p_o) =$ 22 ppm (cf. Table 10, column 10) in good agreement with the direct measurements in the East Pacific.

This agreement may be accidental, but it leads us to suspect that the ability of the model to yield satisfactory values for the variables describing the exchange of CO_2 at the ocean surface is closely linked to a satisfactory prediction of the water vapor flux, F. If so, the value of f given when $F = 0.67 \times 10^{17}$ l/yr (Table 10, column 10) may be close to the correct value, i.e., f is $\sim 1.3 \times 10^{17}$ mg-atoms/yr (0.6×10^{10} tons/yr), about one-fourth the estimate of Bolin & Keeling (1963).

8.7. *The radiocarbon balance*

How sensitive is the model to changes in the value of the radiocarbon content assigned to surface water? The results so far discussed are based on an assignment of a lower $^{14}C/^{12}C$ ratio in cold surface water than in warm surface water, in accordance with observations (cf. Fig. 11). If we assign the same ratio, ${}^{C}\mathcal{R}_i/\mathcal{R}_\bullet = 0.955$, to WSW and CSW, we obtain with Δk, $k_{-1} = (2, 4)$ the results of Table 10, column 2. Compared with Case II′ (shown in column 1) h_1 decreases, h_2 increases, $\varkappa_{2o}/\varkappa_{1o}$ increases drastically; but the other source terms and the reservoir transfer coefficients are only slightly changed.

The overall effect is best seen by comparing parametric plots of $b_1(b_1 + b_2)$, F, and $\varkappa_{2o}/\varkappa_{1o}$ versus Δk and k_{-1} with and without assigning the same radiocarbon ratio to WSW and CSW (cf. Figs. 15 and 16). If the surface water exchange is low ($k_{-1} \cong 0$), the two cases are very similar, but for higher values of k_{-1}, the limit $\varkappa_{2o}/\varkappa_{1o} = 6$, which lies parallel to lines of equal advection, Δk, in Fig. 16 exerts such a strong influence on the model that preferred solutions are cut off at $k_{-1} = 6 \times 10^{17}$ l/yr, in contrast to Case II′ with a cut-off for k_{-1} (owing to the restriction $k_3 \geqslant 0$) near 17×10^{17} l/yr (see Fig. 15). Furthermore, advection, Δk, less than 2×10^{17} l/yr is disallowed, and the highest value for atmospheric water vapor flux, F, within the range of preferred solutions is only

half the value for Case II′. The last result induces us to prefer the original Case II′ and leads us to conclude that a low radiocarbon content for surface waters in high latitudes of the South Pacific is an expected result of the vigorous exchange of cold surface water and deep water. This conclusion, to be sure, is coupled to an assumption that the rate of atmospheric CO_2 exchange at high latitudes is only moderately more rapid than at low latitudes. If we were to disregard an upper limit on $\varkappa_{2o}/\varkappa_{1o}$, the preferred solutions of the model would deliver values of the source terms for all tracers except radiocarbon indistinguishable from those for Case II′.

The experimental uncertainty of the radiocarbon measurements lies between 5 and 10‰ (Broecker, 1963*b*). Its effect on the isotopic ratio difference ${}^{C}\mathcal{R}_2 - {}^{C}\mathcal{R}_1$ can be seen to lead to some uncertainty in the results for the model, but far less than that produced by experimental error in the inorganic carbon concentrations and the alkalinity, described in subsection 8.4.

8.8. *The mass-flux ratio and radiocarbon age of deep water*

The age, ${}^{*}\tau_i$, of inorganic radiocarbon in reservoir i relative to atmospheric radiocarbon dioxide is prescribed by the law of radioactive decay:

$$ {}^{*}\tau_i = -\frac{1}{{}^{*}\lambda} \ln ({}^{C}\mathcal{R}_i/{}^{C}\mathcal{R}_o) \qquad (8.1) $$

The radiocarbon ratios of Table 7 imply average ages of 370 years for WSW, 630 for CSW, and 1690 for DW, irrespective of whether we consider Case I, II, or III. The increase in age of DW relative to cold surface water is 1060 years, in fairly close agreement with the mass-flux ratio for DW, τ_3, calculated by the three-reservoir model (cf. Table 8).

This agreement is related to the prediction by the model that over 90% of the radiocarbon in DW arrives there by water transport from CSW. For Case II′ the transfer rates (in mg-atoms of C* per year $\times 10^{17}$) are:

via water transport	${}^{*}q_2 k_2 = 23.2$ (92%)
via insoluble carbonate	${}^{*}\gamma_{A3} a_3 = 0.8$ (3%)
via organic (bio)carbon	${}^{*}\gamma_{B3} b_3 = 1.2$ (5%)

The agreement can also be seen to be a consequence of the close connection between the transport of isotopes of the same element (cf. Lal, 1962, p. 607) and of the small magnitude of the radiocarbon ages, ${}^{*}\tau_i$, relative to the radioactive decay time, ${}^{*}\lambda^{-1}$. The second and third terms of (7.7), which relate to the transport of biocarbon and insoluble carbonate, are small compared to the first term, are of opposite sign and of nearly equal magnitude. Therefore

$$ \tau_3 \cong \frac{1}{{}^{*}\lambda} ({}^{C}\mathcal{R}_2 - {}^{C}\mathcal{R}_3)/{}^{C}\mathcal{R}_3 \qquad (8.2) $$

Furthermore, the difference in radiocarbon age between CSW and DW (cf. 8.1) is:

$$ {}^{*}\tau_3 - {}^{*}\tau_2 = \frac{1}{{}^{*}\lambda} \ln ({}^{C}\mathcal{R}_2/{}^{C}\mathcal{R}_3) \cong \frac{1}{{}^{*}\lambda} ({}^{C}\mathcal{R}_2 - {}^{C}\mathcal{R}_3)/{}^{C}\mathcal{R}_3 \qquad (8.3) $$

and thus, nearly equal to τ_3.

The sum of the transfer coefficients into deep water, $k_2 + k_{-3}$ (inversely proportional to τ_3), is a measure of the rate of production of Pacific deep water. Since k_{-3} is found to be small for all cases considered, the model is consistent with a large body of evidence that this water is produced principally by the downwelling of polar waters (e.g., Stommel & Arons, 1960). We obtain by Case II′ a rate of about 12×10^{17} l/yr. This figure may be compared with estimates of the formation of deep water by Bolin & Stommel (1961) and by Munk (1966). The former authors obtain 5×10^{17} l/yr for the formation of common water (deep Pacific and Indian Ocean water) from other subsurface waters using salinity, temperature, and inorganic radiocarbon as tracers. Our model predicts approximately the same rate if we halve the size of each reservoir so that the volume of the deep water reservoir agrees with the volume of common water (6×10^{20} l). Munk, following a suggestion by Sverdrup *et al.* (1942, p. 217), estimated the rate of production of deep water of the world oceans as 9×10^{17} l/yr, based on evidence that one meter thick sea ice with a salinity of 5‰ forms each year over 2×10^{19} cm³ of the Antarctic Ocean, thereby increasing the salinity of the underlying water. He assumes that the salinity increases enough for the water to sink to the bottom, and he

OPTIMUM SOLUTIONS TO THE 3 RESERVOIR MODEL

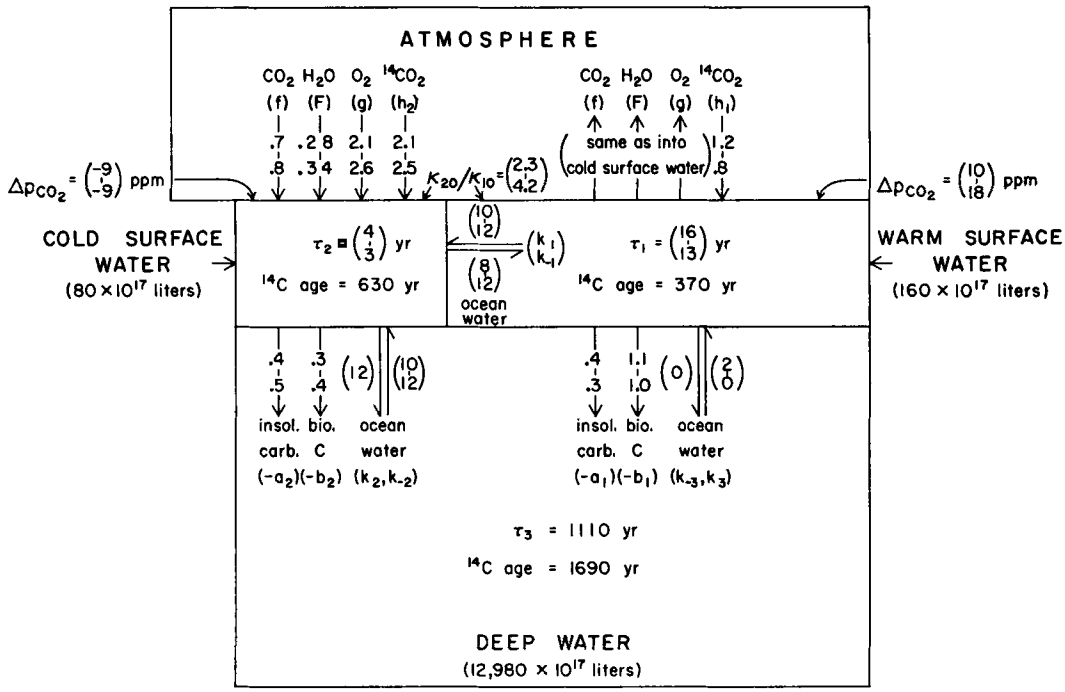


Fig. 17. Numerical solutions for the three-reservoir model (cf. Table 12): a_i, b_i, f, h_i, in units of 10^{17} mg-atoms/yr^{-1}; g in units of 10^{17} mmol/yr^{-1}; F, k_i, k_{-i}, in units of 10^{17} l/yr^{-1}. Upper figures denote advective solution; lower figures denote diffusive solution. Single figures denote invariants.

neglects the lesser contribution to deep water of surface water from the Northern Hemisphere.

Thus, the three-reservoir model produces values for the rate of production of deep water which are consistent with our present knowledge of the formation of deep Pacific waters.

8.9. *Oceanic circulation*

Some overall features of the circulation of the South Pacific Ocean emerge in qualitative agreement with previous knowledge. Most estimates based on the three-reservoir model are quantitatively very uncertain, but we may summarize our findings as follows:

(1) As discussed in subsection 7.2, deep water (DW) is produced largely by exchange with cold surface water (CSW), the exchange between warm surface water (WSW) and the deep water being relatively insignificant.

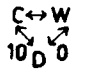
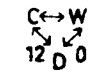
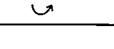
(2) The tracer data favor a general circulation WSW to CSW to DW to WSW over the reverse direction for the South Pacific Ocean, which agrees with the direct thermo-haline circulation of the ocean.

Both of these features are deduced by the model because the transfer coefficient from WSW to DW, k_{-3}, is found to be small (Case I) or approximately zero (Cases II or II′), and because we forbid negative values of the transfer coefficients consistent with the physical interpretation provided by (3.8). Actually (cf. subsection 3.3), we lack direct evidence that the transfer coefficients behave as physical constants independent of the tracers under investigation. Hence, all we can strictly say with regard to the ocean circulation is that the three-reservoir model gives results which are not in conflict with our general understanding of the ocean circulation.

8.10. *Search for an optimum solution to the three-reservoir model*

From the foregoing discussion it is clear that the three-reservoir model is beset by many

Table 12. *Optimum solutions to the three-reservoir model for the Pacific Ocean, 40° N–70° S*

Input data				Solutions		
Property	WSW	CSW	DW	Property	"Advective"	"Diffusive"
A_{i0} (10^{17} cm²)	2.4	1.2		$-a_1$ (10^{17} mg-at/l)	0.40	0.31
pH	8.20	8.08	7.98	$-a_2$ (10^{17} mg-at/l)	0.42	0.51
${}^{A}q_i$ (meq/l)	2.296	2.283	2.423	$-b_1$ (10^{17} mg-at/l)	1.10	1.03
${}^{B}q_i$ (mg-at/l)	0.08	0.08	0.08	$-b_2$ (10^{17} mg-at/l)	0.32	0.39
${}^{C}q_i$ (mg-at/l)	2.017	2.139	2.330	f (10^{17} mg-at/l)	0.68	0.81
${}^{IC}q_i$ (mg-at/l)	0.0	0.0	0.0	F (10^{17} l/yr)	0.28	0.34
${}^{O}q_i$ (mmol/l)	0.212	0.308	0.150	g (10^{17} mmol/yr)	2.14	2.56
${}^{P}q_i$ (μg-at/l)	0.18	1.17	2.58	h_1 (10^{17} mg-at/yr)	1.19	0.77
${}^{S}q_i$ (‰)	35.70	34.70	34.70	h_2 (10^{17} mg-at/yr)	2.06	2.49
${}^{C}R_i/R_\bullet$	0.955	0.925	0.810	k_1 (10^{17} l/yr)	9.7	11.7
T (°C)	25.27	6.89	1.50	k_{-1} (10^{17} l/yr)	8.0	12.0
W_i (10^{17} l)	160.0	80.0	12,980.0	k_2 (10^{17} l/yr)	11.7	11.7
α_{A3}			1.000	k_{-2} (10^{17} l/yr)	9.7	11.7
α_{B3}			1.000	k_3 (10^{17} l/yr)	2.0	0.0
${}^{O}\gamma$	−1.30 (invariant)			k_{-3} (10^{17} l/yr)	0.0	0.0
${}^{*}\gamma_{iA}$	0.955	0.925		p_1-p_o (ppm)	9.8	18.2
${}^{*}\gamma_{iB}$	0.936	0.906		p_2-p_o (ppm)	−8.6	−8.6
${}^{*}\gamma_{io}$	0.917	0.888		$\varkappa_{2o}/\varkappa_{1o}$	2.3	4.2
${}^{*}\lambda$	8.033 yr^{-1}	(invariant)		τ_1 (yr)	16.0	13.3
				τ_2 (yr)	4.1	3.4
				τ_3 (yr)	1110	1110
				${}^{IC}\tau_3$ (yr)	0	0
				${}^{B}\tau_3$ (yr)	760	760
				${}^{P}\gamma \times 10^3$	11.64	11.64
				Water exchanges[a]		
				Advection[a]		0

[a] Cf. footnote to Table 9.

uncertainties. Nevertheless, some readers may wish us to guess which of the array of possible solutions best fits present knowledge of the oceans.

Without attempting further to justify our choice of input data, we adopt Case II′ (see subsection 7.2), except for the surface salinity values, as best representing the tracer concentrations in the Pacific Ocean south of 40° N. We seek solutions to the model in approximate agreement with estimates from previous subsections: $b_1/(b_1+b_2)=0.7$ (net production of biocarbon per unit area the same for WSW and CSW, cf. subsection 7.4); $p_1-p_o=15$ ppm (cf. subsection 8.5). Direct observations in Tables 4 and 5 yield a surface salinity gradient, ${}^{S}\delta_1 = 35.20\,‰ - 34.30\,‰ = 0.90\,‰$, lower than that consistent with Wüst (1954) (see subsection 8.1). If we accept Wüst's model, but with this reduction in gradient, we expect $F \cong 0.40 \times 10^{17}$ l/yr.

Employing the data of Case II with ${}^{O}\gamma = -1.30$, we obtain as a reasonable compromise to our demands: ${}^{S}\delta_1 = 1.00\,‰$, Δk, $k_{-1} = (0, 12)$, $b_1/(b_1+b_2)=0.73$, $F = 34 \times 10^{17}$ l/yr, $p_1-p_o=18$ ppm. This result, which we may call the "diffusive solution", has the peculiarity that the four exchanges WSW⇌CSW⇌DW are approximately equal while those between DW and WSW are nearly zero.

If we introduce a moderate advection, $\Delta k = 2 \times 10^{17}$ l/yr, in qualitative accord with other evidence that upward advection of water occurs at low latitudes (e.g., see Stommel & Arons, 1961; Wyrtki, 1962) we obtain an "advective solution": Δk, $k_{-1} = (2, 8)$, $b_1/(b_1+b_2)=0.78$, $F = 0.28 \times 10^{17}$ l/yr, $p_1-p_o=10$ ppm. This result, which stretches rather far our guesses as to the magnitude of the latter three quantities, could be partially rectified by choosing a smaller, positive value of Δk, but considering the crudity of the model, to make a finer distinction in

Δk seems unwarranted. Between the advective and diffusive solutions we offer no preference. The full set of results appears in Table 12. The solutions are illustrated in Fig. 17.

9. Concluding remarks

The present study, though hardly conclusive, yields insight into the interplay between non-conservative chemical tracers in the oceans. Even with the very crude three-reservoir model of the ocean, we meet considerable difficulties and it hardly seems feasible to increase the spatial resolution by using a larger number of reservoirs without introducing the constraints on the motion of the ocean contained in the hydrodynamic and thermodynamic equations that govern the motion of the oceans. Moreover, the computations suggest that the introduction of *ad hoc* assumptions about the transfer process to reduce the number of unknowns can lead to widely varying results. When the distributions of only one or a few tracers are used, the possibility of inconsistencies increases rapidly. For example, models of Brœcker's, using radiocarbon alone as a tracer (Broecker, 1963*b*), do not successfully predict the distribution of other commonly measured tracers.

Our computations give reliable information on the experimental accuracies required for the tracers we have used. Particularly important is the need to increase drastically the accuracy of observations of inorganic carbon system. We conclude that present routine measurements of pH, not more accurate than ± 0.01, are of little value for general ocean circulation studies. Also, more information on organic carbon is needed.

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ОДНОВРЕМЕННОЕ ИСПОЛЬЗОВАНИЕ ХИМИЧЕСКИХ ТРАССЕРОВ В ИЗУЧЕНИИ ОКЕАНА II

Соленость, кислород, неорганический фосфор, органический и неорганический углерод, щелочи углерода и радиоактивный углерод были использованы одновременно в качестве трассеров для изучения циркуляции в океане, химических процессов внутри океана и химического обмена в пограничном слое океана. Были сделаны оценки скоростей этих процессов, используя уравнение для химического переноса в простейшей аппроксимации, которая прослеживает изменения пространственных переменных на границе океана и атмосферы, горичонтальный и вертикальный адвективный и турбулентный перенос и гравитационное оседание нерастворимых химических веществ в океане. Эта аппроксимация является циклической моделью с одним атмосферным и тремя океаническими резервуарами, между которыми трассеры обмениваются при помощи кинетических процессов первого порядка. Использовались данные для Тихого океана, усредненные по времени и по областям: теплая поверхностная вода, холодная поверхностная вода и глубокая вода. Северные и южные холодные поверхностные воды трактовались как альтернативные случаи.

Мы получим, что:

1) Величина массы глубокой воды в Тихом океане, деленной на скорость ее воссоздания, равна приблизительно 1100 годам; этот интервал времени находится в тесном согласии с ее средним радиоуглеродным возрастом по отношению к холодной поверхностной воде.

2) В южной части Тихого океана перенос воды между глубоким океаном и поверхностью происходит в основном за счет обмена с холодной поверхностной водой. Небольшая циркуляция от теплой поверхностной воды к холодной предусматривается моделью, но скорость ее нельзя вычислить с помощью имеющейся информации.

3) Трехрезервуарная модель не может, даже в первом приближении, объяснить циркуляцию северной части Тихого океана, потому что она не рассматривает поток глубокой воды в северную часть Тихого океана из южной части Тихого океана.

4) И кислород и углекислый газ извлекаются из поверхностных вод в низких широтах и поглощаются в высоких широтах. Скорости обмена теплой поверхностной воды с холодной поверхностной водой порядка 10^{17} ммоль/год.

5) Перенос радиоактивного углерода от поверхности и глубокой воде происходит в основном из-за биологических процессов, особенно гравитационного оседания органического углерода и нерастворимого карбоната. Только одна треть неорганического углерода в глубокой воде переносится туда самой водой.

6) Использование pH измерений для анализа растворенного неорганического углерода и щелочи сильно ограничивают достоверность углеродных данных в настоящей статье. Небольшие ошибки в измерении pH влекут за собой большие неопределенности в полученных скоростях гравитационного переноса органического углерода и нерастворимых карбонатов и в скорости обмена CO_2 с атмосферой.