

A Box-Diffusion Carbon Cycle Model with Upwelling, Polar Bottom Water Formation and a Marine Biosphere

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ABSTRACT

A Global Carbon Cycle Model is described. It is based on an extension of Oeschger's box-diffusion approach insofar as the atmosphere and oceanic surface mixed layer are treated as discrete well-mixed reservoirs and the deep ocean as a one-(vertical) dimensional zone with a continuous distribution of inorganic carbon (ΣC). The model includes upwelling in the deep ocean inorganic carbon conservation-of-mass equation, with a concomitant downwelling of polar water to balance water and carbon mass in the deep ocean, allowing polar water to equilibrate with P_{CO_2} at the cooler polar mixed layer temperature which brings water relatively enriched in ΣC to the sea floor. The model also includes a carbon sink term in the mixed layer associated with CO_2 removal by particulate outfall and photosynthesis which is balanced by deep sea regeneration processes. The model has been run under steady-state conditions and gives reasonably good agreement with observed ΣC profiles. It has also been run under unsteady conditions to predict the build-up of atmospheric carbon dioxide using the fossil fuel burning source function of Siegenthaler and Oeschger.

1. INTRODUCTION

The current generation of carbon cycle models focus on addressing a number of questions which are being asked with regard to the well-documented build-up of atmospheric carbon dioxide from fossil fuel burning, and on the climatological implications of this build-up by the CO_2 "greenhouse effect". To understand the increase in atmospheric carbon dioxide observed worldwide thus far, and to attempt to forecast the future changes associated with different scenarios of fuel utilization, it is necessary to understand and model first the natural distribution of carbon in the environment under unperturbed conditions.

Carbon is, of course, variously distributed in reservoirs of the atmosphere-biosphere-oceanic-lithosphere-system. The approximate amounts in gigatons estimated from various sources in the literature (see below) are: atmosphere (700), terrestrial and marine biosphere, living (800), soils (3 000), oceanic mixed layer (600), deep oceans (40 000), fossil fuels (7 000), oxidized sediments (50×10^6), reduced sedi-

ments (20×10^6) and igneous rocks (3×10^6). This carbon cycles continuously through these reservoirs at rates which determine the distribution in the steady state, and the general problem in carbon cycle modeling is to establish the internal and external rate processes by calibration or mechanistic sub-models. A current picture of the details of carbon exchange in the principal reservoirs can be found in the recent reviews by Bolin *et al.* (1979) and Broecker *et al.* (1979). In general one must keep track of carbon atoms as they are shuffled through various chemical transformations in the different reservoirs, from gaseous CO_2 in the atmosphere, to organic carbohydrates formed by photosynthesis in the biosphere and calcium carbonate shells in the marine biosphere, to dissolved CO_2 , carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions in seawater, to sedimentary CaCO_3 in layers on the sea floor, etc.

The traditional approach toward modeling the carbon cycle is the multi-box mass exchange method (Revelle and Suess, 1957; Bolin and Eriksson, 1959; Broecker *et al.*, 1971; Machta, 1973; Hoffert, 1974; Keeling 1973, 1977; Bacastow and Keeling, 1973, 1977), where one seeks the mass of carbon or radiocarbon N_i or *N_i , in each of a number of well-mixed boxes or reservoirs. The number of reservoirs considered, and the disaggregation of reservoirs into subreservoirs is a matter of judgement on the part of the modeler, but most box model carbon cycles include at least atmospheric ($i = a$), oceanic mixed layer ($i = m$) and deep sea ($i = d$) boxes. These models generally incorporate first-order kinetics insofar as the outflux of carbon mass from reservoir i to adjacent reservoir l is $k_{il}N_i$, where k_{il} is an empirical and time-invariant exchange coefficient, and the equations governing the distribution of carbon in the presence of an internal source y_i , say, from fossil fuel burning, added to the i th reservoir are

$$\frac{dN_i}{dt} = \sum_{\substack{l=1 \\ l \neq i}}^n (k_{li}N_l - k_{il}N_i) + y_i - \lambda N_i$$

where n is the number of reservoirs, and the decay term $-\lambda N_i$ applies to radio-carbon, $\lambda = (\ln 2)/(5730) \cong 1.21 \times 10^{-4} \text{ yr}^{-1}$ being the decay constant for radiocarbon decay ($^{14}\text{C} \rightarrow ^{14}\text{N} + \beta^- + \nu$).

A potential problem with this classical approach is that the reservoirs must truly be well-mixed, or uniform in concentration, for the approximation to hold. This is certainly not the case for the oceans as a whole which mix internally on a timescale of 1000 years, much longer than the timescale for CO_2 build-up in the atmosphere from fossil fuel burning. This has led some investigators to disaggregate the world ocean reservoir according to current oceanographic ideas of internal circulation. Perhaps the most articulated scheme in the box model genre is that of Björkström (1979) who uses ten boxes at different depths in the world ocean; the upper two representing intermediate water, or perhaps the oceanic thermocline, exchange material with a "cold" surface ocean, a high-latitude oceanic reservoir which is distinguished in this model from the warm surface ocean associated with the traditional mid-latitude mixed layer. The lower eight ocean boxes are each fed individually by the cold

surface, whereas the warm surface interacts only with the uppermost intermediate water box.

Our approach to modeling the carbon transport in the deep sea is based on the assumption of a continuous distribution of total carbon in a one-(vertical) dimensional world ocean in which the lower boundary of the ocean is fed by seawater from the polar bottom-water forming regions, essentially the Weddel and Norwegian Seas. It belongs to a family of such models (Craig, 1969; Fiadeiro, 1975; Munk, 1966, 1979; Oeschger *et al.*, 1975, and Siegenthaler and Oeschger, 1978) which have been applied to various tracer studies, but is the first we are aware of which attempts to represent the steady-state and transient oceanic profiles of total inorganic carbon, total alkalinity and dissolved oxygen during the fossil fuel era using an upwelling-diffusion approximation for the world ocean. It might be noted that models with continuous distributions of concentration in the oceanic reservoir lend themselves more readily to incorporation of steady-state and transient tracer data (Hoffert and Broecker, 1978; Broecker *et al.*, 1979) than box models. Extensions of the continuous concentration distribution models to multiple spatial dimension also admit the possibility of preferred mixing surfaces such as pycnoclines in the modeling formalism. Of course, the multi-box and continuum approaches are not entirely independent, as discussed by Oeschger *et al.* (1975) and Bolin (1977). However, the continuous distribution has some distinct advantages when one is considering internal oceanic sources. For example, in a recent study (Hoffert *et al.* 1979) we sought the impact on the atmospheric CO₂ history of a scheme proposed by Marchetti (1977) to alleviate the build-up in the atmosphere of carbon dioxide by direct injections of fossil fuel emissions into the deep ocean, thereby short-circuiting the slow exchange rates in the oceanic thermocline. Clearly, a box model with a single deep-sea reservoir would not have distinguished between different injection depths in the deep sea whereas we find a significant difference in the atmospheric response to injections of the same amount of CO₂ at different depths.

The idea of an upwelling-diffusing world ocean is not new, and was proposed in substantially the form treated here almost 20 years ago (Wyrтки, 1961, 1962). In what follows, we simply develop this idea in the context of a world ocean carbon cycle reservoir, including separate continuity equations for total carbon, total alkalinity and dissolved oxygen.

2. FORMULATION OF GOVERNING EQUATIONS

In formulating the ordinary differential equations for the mass of carbon in the atmospheric reservoir N_a and the mass of carbon in the oceanic mixed layer N_m , a major assumption is that the flux of carbon (in the form of gaseous CO₂) across the air/sea interface depends on the difference between the partial pressure of CO₂ on the air side P_a and the partial pressure of CO₂ gas dissolved in the well-mixed layer P_m immediately beneath the sea surface. Thus, the net flux into the mixed layer may be written.

$$F = k_{am}' (P_a - P_m) = k_{am}' P_a - k_{ma}' P_m,$$

where $k_{am}' = k_{ma}'$ is an air/sea exchange coefficient averaged over all the world's oceans incorporating the influence of wind stress, turbulence, surface capillary waves and all other phenomena influencing gas exchange across the air/sea interface in a lumped parameter sense.

Consider now the relationship between CO₂ partial pressure in the adjacent atmosphere and mixed layer reservoirs to the carbon masses in these reservoirs. In the atmosphere, the carbon in the form of gaseous CO₂ exerts a downward force at the earth's surface equal to $g \times (M_{CO_2}/M_C) \times N_a \times (M_{air}/M_{CO_2}) = g N_a M_{air}/M_C$, where g is the gravitational acceleration (9.81 m/s²), M_C is the molecular weight of carbon (12 kg/kmole), M_{CO_2} is the molecular weight of CO₂ (44 kg/kmole), and M_{air} is the molecular weight of air (29 kg/kmole). This force is distributed uniformly over the earth's surface area $4\pi a^2$, where $a = 6.37 \times 10^6$ m is the earth's radius, so the partial pressure of CO₂ in the atmosphere at the surface can be written $P_a = (M_{air}/M_C) g N_a / (4\pi a^2)$. For example, an atmospheric carbon mass of $N_{ao} = 63 \times 10^{15}$ g corresponds to a CO₂ partial pressure in the atmosphere at sea level of $P_{ao} = 29.38 \text{ N/m}^2 = 2.90 \times 10^{-4} \text{ atm}$, i.e., to a volumetric CO₂ concentration level of 290 ppmv in the atmosphere.

Accordingly, it is convenient to define a new air/mixed layer exchange coefficient $k_{am} = (M_{air}/M_C) g k_{am}' / (4\pi a^2)$ so that we may write the air/sea carbon flux in the form,

$$F = k_{am} N_a - k_{ma}' P_m,$$

where k_{am} and k_{ma}' are constant coefficients (with different units) which are independent of time. The relationship between carbon dioxide partial pressure in the mixed layer P_m and the mixed layer carbon mass N_m is affected by the fact that dissolved CO₂ reacts rapidly in seawater to form a dilute carbonic acid (H₂CO₃) solution composed of CO₂ and carbonate (CO₃²⁻), bicarbonate (HCO₃⁻) and hydrogen (H⁺) ions whose equilibrium concentrations are governed by $[CO_2] = K_0 P_m$, $[HCO_3^-] = K_1 [CO_2] / [H^+]$ and $[CO_3^{2-}] = K_2 [HCO_3^-] / [H^+]$, where K_0 , K_1 and K_2 are temperature and salinity-dependent equilibrium constants for the system. Since the carbon dissolved in the sea is redistributed amongst the CO₂, HCO₃⁻ and CO₃²⁻ species, it is convenient to work with the pseudospecies for total inorganic carbon in seawater,

$$\Sigma C = [CO_2] + [HCO_3^-] + [CO_3^{2-}] = P_m / \Phi,$$

where $\Phi^{-1} = K_0 (1 + K_1/[H^+] + K_1 K_2/[H^+]^2)$ is a factor of proportionality between ΣC in the mixed layer and the mixed layer partial pressure of CO₂ which depends on water temperature, salinity and the hydrogen ion concentration or, equivalently, the $\text{pH} = -\log_{10}[H^+]$. As described by Bacastow and Keeling (1973) and Hoffert *et al.* (1979), the hydrogen ion concentration depends on titration alkalinity, concentration of total borate, temperature, salinity, and the ΣC concentration itself. Typical values for the preindustrial steady state are a titration alkalinity of 2.435 equivalent moles/m³, total borate concentration of 0.409 mole/m³, seawater temperature of

292.8 °K (19.6 °C) and a salinity of 34.76 ‰. For the mixed layer total carbon level of $\Sigma C_o = 2.057 \text{ mole/m}^3$ cited by Keeling (1973, Table 2), the corresponding pH is 8.271 and the hydrogen ion level is $[H^+] = 5.36 \times 10^{-9} \text{ kmole/m}^3$. The corresponding P_{CO_2} factor is $\Phi_o = 0.1411 \text{ atm-m}^3/\text{kmole}$, so the initial partial pressure of $P_{mo} = \Phi_o \Sigma C_o = 2.90 \times 10^{-4} \text{ atm}$ is recovered, i.e., $P_{ao} = P_{mo}$. The mixed-layer initial carbon concentration on a mass basis is simply $M_C \Sigma C_o = 0.0247 \text{ kg/m}^3$. Taking the world ocean volume at $1.37 \times 10^{18} \text{ m}^3$ with a surface area equal to $A = 3.34 \times 10^{14} \text{ m}^2$ gives a mean depth of 4100 m, of which we assume the first 100 m are the well-mixed layer; $h_m = 100 \text{ m}$ and $h_d = 4000 \text{ m}$. Accordingly, the total carbon mass in the mixed layer preindustrially is $N_{mo} = C_{mo} h_m A = 825 \times 10^{15} \text{ g}$, or about 1.3 times an assumed preindustrial carbon mass in the atmosphere, $N_{ao} = 631 \times 10^{15} \text{ g}$ (equivalent to 290 ppmv).

Returning now to the air/sea flux expression, it is convenient to define a new mixed layer/air exchange coefficient $k_{ma} = k_{ma}' P_{mo} / N_{mo}$ so that

$$F = k_{am} N_a - k_{ma} N_{mo} \frac{P_m}{P_{mo}}$$

Since the flux goes to zero when $P_m = P_{mo}$, the exchange coefficients are inversely proportional to the initial reservoir sizes, $k_{am} N_{ao} = k_{ma} N_{mo}$. To express the variation of P_m/P_{mo} in terms of N_m , Keeling (Bacastow and Keeling, 1973) has introduced the *buffer factor*

$$\zeta = \frac{(P_m - P_{mo})/P_{mo}}{(N_m - N_{mo})/N_{mo}},$$

which can be set constant, or evaluated stepwise from $P_m = \Phi N_m / (M_C h_m A)$, where $\Phi = \Phi(N_m, T)$, T being the local water temperature. Thus, the ratio of P_{CO_2} in the mixed layer at any time to that at the initial preindustrial state can be written in terms of the buffer factor as follows,

$$\frac{P_m}{P_{mo}} = \frac{1}{N_{mo}} (N_{mo} + (N_m - N_{mo})\zeta),$$

and the net flux of carbon from the atmospheric reservoir into the mixed layer across the air/sea interface is

$$F = k_{am} N_a - k_{ma} (N_{mo} + (N_m - N_{mo})\zeta).$$

Now, introducing the perturbed carbon masses in the atmospheric and mixed layer reservoirs,

$$n_a \equiv N_a - N_{ao}, \quad n_m \equiv N_m - N_{mo}, \quad (1)$$

the rate equation for carbon mass in the atmospheric reservoir can be written

$$\frac{dN_a}{dt} = k_{ma} (N_{mo} + \zeta n_m) - k_{am} (N_{ao} + n_a) + y_a, \quad (2)$$

where $y_a = y_f - y_b$ is composed of carbon dioxide generated per unit time by fossil fuel burning (y_f) less the net flux of carbon into the land biosphere (y_b). Equation (2) was used by Keeling (1973) and Oeschger *et al.* (1975) for the atmospheric reservoir. Recently, Revelle and Munk (1977) have formulated a new submodel for the land biosphere sink (or source) term which includes a lid (or maximum size) on the land biosphere, a reasonable relationship between atmospheric CO_2 and the amount of organic carbon in the land biosphere, and an explicit relationship for the influence of land clearing on the rate at which CO_2 in the biomass is released to the atmosphere by deforestation, etc. However, in view of the controversial nature of the land biosphere term, and in order to focus on the role of the oceans on anthropogenic CO_2 uptake, we have taken $y_b = 0$ in the numerical results to be discussed later. Also assumed in the calculations is an air/mixed layer exchange time of $\tau_{am} = 7.7$ yr, so that

$$k_{am} = \tau_{am}^{-1} = 0.13 \text{ yr}^{-1},$$

$$k_{ma} = k_{am} (N_{ao}/N_{mo}) = k_{am}/(1.3) = 0.10 \text{ yr}^{-1}.$$

In formulating the rate equation for carbon mass in the oceanic mixed layer we include the effect of mixed layer/atmosphere carbon flux, exchange with the deep ocean and a sink term associated with the removal of mixed layer CO_2 by mixed layer phytoplankton photosynthetically fixing a fraction of the carbon dioxide in surface water to an organic carbon form via $h\nu + n\text{CO}_2 + n\text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})_n + n\text{O}_2$, where $(\text{CH}_2\text{O})_n$ represents a plant carbohydrate. It is assumed that this organic material falls to the deep ocean where it is oxidized back to CO_2 by the inverse of photosynthesis (respiration and decay), consuming a fraction of dissolved oxygen in the process. The exchange with the deep ocean is based on a physical model of the deep ocean which is one-dimensional in the vertical coordinate z (representing a horizontal average over the world's oceans) with $0 \leq z \leq h_d$, where $z = 0$ is at the bottom of the mixed layer and $z = h_d = 4000$ m is the bottom of the deep ocean. It is assumed that the deep ocean has a continuous distribution of total (inorganic) carbon concentration $C_d(z, t)$ described by one-dimensional conservation-of-mass equation with a constant turbulent eddy diffusivity $K = 2000 \text{ m}^2/\text{yr}$ and constant upwelling velocity $w = 4 \text{ m}/\text{yr}$. The eddy diffusivity mechanism introduces a diffusive influx term in the mixed layer rate equation equal to $AK \partial C_d / \partial z \big|_{z=0}$ in kg/yr when C_d is the concentration of ΣC in kg/m^3 . The fact that the oceans of area A are upwelling water at an inorganic carbon concentration $C_d(0, t)$ into the mixed layer implies a mixed layer influx term of $AwC_d(0, t)$, where w is the upwelling velocity. Clearly, to balance the water mass, the volumetric flow $wA \approx 1.34 \times 10^{15} \text{ m}^3/\text{yr}$ must be brought to the sea floor. Physically, this process corresponds to the formation of bottom water in polar regions, e.g., the Norwegian Sea in the North Polar waters and the Weddell Sea in the South Polar waters. In the model it is assumed that a volumetric flow of water equal to wA leaves the lateral boundaries of the oceanic mixed layer, with a carbon total concentration $C_c(t)$, where index c denotes polar "cold" water. This water is assumed to be "instantly" inserted back into the water column at the sea floor. Since

the polar waters are assumed to have a vanishingly small area, the local downwelling velocity is consistently infinite and the flux leaving the mixed layer at the sides wAC_c must appear in the lower boundary condition on the deep ocean. Under these assumptions, the rate equation for the mixed layer is written,

$$\frac{dN_m}{dt} = k_{am}(N_{ao} + n_a) - k_{ma}(N_{mo} + \zeta n_m) + AK \cdot \left. \frac{\partial C_d}{\partial z} \right|_{z=0} + Aw [C_d(0,t) - C_c] - F_{mb} \quad (3)$$

where F_{mb} is the flux of carbon into the mixed layer marine biosphere due to photosynthesis by surface-layer phytoplankton.

Again, under the present set of assumptions, the continuity equation governing ΣC concentration in the deep ocean may be written,

$$\frac{\partial C_d}{\partial t} = \frac{\partial}{\partial z} K \cdot \frac{\partial C_d}{\partial z} + w \cdot \frac{\partial C_d}{\partial z} + J(z), \quad (4)$$

where the signs in this expression correspond to z positive downward and w positive upward. the term $J(z)$ is an inorganic source per unit time in $\text{kg/m}^3\text{-yr}$ associated with oxidation of the organic debris containing the carbon removed in the mixed layer by photosynthesis. Accordingly, it has the integral property

$$F_{mb} = A \int_0^h J(z) dz$$

Equation (4) is solved numerically along with (2) and (3) in the present model. However, it is important in this connection to specify the initial conditions $C_d(z,0)$ and the two boundary conditions for concentrations needed to solve this parabolic partial differential equation. The first condition, following Oeschger *et al.* (1975), is simply continuity of concentration at the boundary between the bottom of the mixed layer and the top of the deep ocean:

$$C_d(0,t) = C_m(t) = \frac{N_m(t)}{h_m A} \quad (5)$$

Notice the implication from this boundary condition that if water leaving the lateral boundaries of the mixed layer in polar waters has the mean ΣC concentration, i.e., if $C_c = C_m$, then the term $Aw[C_d(0,t) - C_c]$ drops out of the mixed layer rate equation, equation (3), because $C_c = C_d(0,t)$, for this case. In general, we expect $C_c > C_m$ because surface water in equilibrium with a given P_m and alkalinity but at the cooler sea surface temperatures prevalent at the poles will be relatively enriched in ΣC (see Broecker, 1974, p. 124, Fig. 5-4(c)).

In formulating a lower boundary condition for the system, it is worth briefly reviewing the interaction between inorganic carbon in solution, $\Sigma C = \text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-}$, and the calcium carbonate in sediments at the sea floor. The sediments have been accumulated over geologic time because many microscopic plants (i.e., coccolithophorida) and animals (i.e., foraminifera and pteropods) form CaCO_3

skeletal parts which are continuously raining down on the sea floor. It is usually assumed that a steady state exists between the rate at which this particulate matter falls on the sea floor, the rate at which CaCO_3 in the sediments dissolves into solution at the sea floor, and the sediment accumulation rate. Takahashi and Broecker (1977) have discussed a number of models for the dissolution of calcite at the sea floor and conclude that the dissolution flux, equal to the flux rate of the CO_3^{2-} ion out of the sediment, can be satisfactorily represented by a term proportional to the difference between the critical CO_3^{2-} concentration for calcite and the CO_3^{2-} concentration at the sea floor. Recall that the pH of the carbon dioxide carbonate-bicarbonate system under consideration can be written in terms of the equilibrium constants discussed earlier in the form

$$\text{pH} = -\log_{10} [\text{H}^+] = -(1/2) [\log_{10} (K_1 K_2) + \log_{10} ([\text{CO}_2]/[\text{CO}_3^{2-}])].$$

As anthropogenic carbon added at the sea surface penetrates to the sea floor and $C_d(h_d, t)$ increases above its preindustrial value, the concentration of CO_3^{2-} decreases, and the pH at the sea floor decreases (i.e., the sea floor acidity *increases*). Presently, the calcite sediments at the sea floor are exposed to water which is saturated or supersaturated with CaCO_3 . But as fossil fuel carbon is transported to the ocean bottom the acidity will rise, and the CO_3^{2-} concentration will drop to the level where CaCO_3 is undersaturated, at this point the calcium carbonate in sediments will begin to dissolve at some rate F_{sed} , the excess above the steady-state, with the units of, say, $\text{kmole/m}^2\text{-yr}$, which could be evaluated in terms of the sea-floor $[\text{CO}_3^{2-}]$ concentration using, for example, the method of Takahashi and Broecker (1977). In turn, this would bring into play the following reaction between dissolved CO_2 and dissolved CaCO_3 :



The point to be stressed in formulating the lower boundary condition on the inorganic carbon conservation equation (4) is that each mole of ΣC combining with a mole of dissolved calcium carbonate on the left-hand-side of this reaction produces two moles of ΣC in the form of HCO_3^- ions. Accordingly, one mole of ΣC is *produced* for each mole of CaCO_3 dissolved. We may therefore write the mass flux of carbon into the deep ocean at the sea floor per unit area in terms of the sediment dissolution rate $F_s = M_C F(\text{CaCO}_3)$, where $M_C = 12 \text{ kg/kmole}$ is the molecular weight of carbon.

The lower boundary condition on (4) consistent with the physical picture developed thus far, namely, that the net upward carbon flux at the sea floor (diffusive plus upwelling) must equal the sum of the flux AwC_c brought to the bottom from surface polar waters and the carbon input associated with sediment dissolution, is

$$AK \cdot \left. \frac{\partial C_d}{\partial z} \right|_{z=h_d} + AwC_d(h_d, t) = AwC_c(t) + AM_C F(\text{CaCO}_3). \quad (6)$$

This is a linear combination of the concentration and the concentration gradient at the lower boundary of the model, and is readily incorporated in finite-difference numerical solutions of equation (4). In the numerical solutions presented here, the sediment dissolution term is neglected ($F_{\text{sed}} = 0$), the numerical study of this important effect being deferred to a subsequent paper.

In considering the implications of boundary condition (6) on the rate equation for total inorganic carbon in the deep sea reservoir,

$$N_d = A \int_0^{h_d} C_d(z) dz,$$

it is instructive to begin by multiplying equation (4) by the differential volume $A dz$, and integrating between $z = 0$ and $z = h_d$ to get

$$\frac{dN_d}{dt} = AK \cdot \left. \frac{\partial C_d}{\partial z} \right|_{z=h_d} - AK \cdot \left. \frac{\partial C_d}{\partial z} \right|_{z=0} + Aw [C_d(h_d, t) - C_d(0, t)] + F_{mb}$$

Now, using the lower boundary condition (6) to eliminate the diffusive and upwelling flux at the $z = h_d$ boundary gives the deep ocean carbon integral rate equation in the form,

$$\frac{dN_d}{dt} = -AK \cdot \left. \frac{\partial C_d}{\partial z} \right|_{z=0} + Aw [C_p(t) - C_d(0, t)] + F_{mb} + AM_c F(\text{CaCO}_3) \quad (7)$$

where the first term on the right-hand-side is the upward diffusion of inorganic carbon to the mixed layer, and the second term is the net influx to the deep sea. (The concentration of inorganic carbon injected at the sea floor from cool polar waters is higher than that upwelling into the mixed layer based on horizontally averaged conditions.) The third term is an internal deep sea carbon source associated with oxidation of organic detritus, and the fourth is the carbon source at the sea floor from calcium carbonate sediment dissolution. Notice that the first three terms of equation (7) are identical, but opposite in sign, to the last three terms of the mixed layer carbon rate equation (3), and correspond physically to fluxes exchanged between the mixed layer and the deep ocean. It has been proposed by some authors, for example, Keeling and Bacastow (1977), that the continuously distributed concentration model for the deep ocean may be effectively replaced by a single reservoir, single ordinary differential equation model. But we see from equation (7) that the rate of change of the total deep ocean carbon mass depends on the concentration and concentration gradient history at the mixed layer/deep sea interface. Since these depend on the detailed history of $C_d(z, t)$ in general, it is unlikely that a single equation for a deep sea model could reproduce the influence of different combinations of diffusivity, upwelling, injection concentration, etc.

3. STEADY STATE PROFILES

As a preliminary test of the formulation, and for purposes of initializing the unsteady problem, we have carried out a series of calibrations of the steady profiles of inorganic carbon, total alkalinity and dissolved oxygen based on world ocean profiles supplied by T. Takahashi (personal communication). Note first that in the constant eddy diffusivity approximation, equation (4) can be applied to the steady-state concentration distribution $C_\lambda(z)$ of a λ , stable (nonradioactive) tracer

$$z^* d^2c_\lambda/dz^2 + dc_\lambda/dz = -J_\lambda/w \quad (8)$$

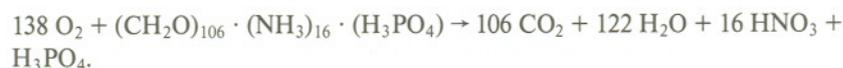
where $z^* = K/w$ is a characteristic depth scale. From prior calibrations based on matching the depth distribution of potential temperature in the world ocean we set $K = 2000 \text{ m}^2/\text{yr}$, $w = 4 \text{ m/yr}$ so that $z^* = 500 \text{ m}$.

To proceed, it is helpful to review the factors influencing the internal source terms J_λ for the carbon, alkalinity and oxygen species and in particular the relationships that exist between these source or sink terms. In this way, it should be possible to crosscheck the consistency of the model profiles. Consider first the vertical profile of total inorganic carbon ΣC . In a purely diffusive model with no flux at the sea floor and no internal sources the only admissible solution in the steady state is ΣC equal to a constant, independent of depth (Oeschger *et al.*, 1975). But observations clearly show the natural concentration of ΣC increases from its surface ocean value with increasing depth, reaching a peak in the vicinity of 1500 m, and then perhaps decreasing again as the floor is approached. This happens as a result of two distinct sinks for ΣC in the surface ocean or mixed layer. There is firstly a sink for dissolved CO_2 associated with photosynthesizing plankton inhabiting the euphotic zone (the upper thirty meters or so of ocean) which transfer CO_2 to organic compounds in their own tissues or those of predators. A second mechanism for removing ΣC involves the formation of calcium carbonate (CaCO_3), or "hard", parts by surface marine organisms using calcium and carbonate ions which are ordinarily supplied by river runoff. Broecker (1974) has estimated the CaCO_3 sink in surface waters as about half that due to organic carbon fixation. Both types of particles fall through the water column where they are regenerated as $\Sigma C = \text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-}$ by distinct processes. Although the depth-dependence of the regeneration of these different types of particles is different, it may be noted for reference purposes that if the sources of ΣC were completely regenerated and uniformly distributed in the water column, we might expect

$$J_{\text{CO}_3^{2-}} \cong 1/2 J_{\text{org}} \quad (9)$$

In the simplest model, we might expect that the soft organic detritus (represented by the "carbohydrate" CH_2O) is simply reoxidized to CO_2 via an "inverse photosynthesis" reaction, $\text{O}_2 + \text{CH}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$. However, it has been known for some time that there is additional utilization of dissolved oxygen by organic matter associated with oxidation of NH_3 . It has been found experimentally (Redfield *et al.*, 1963) that nitrogen in NH_3 and phosphorous in H_3PO_4 occur in fairly fixed ratios in organic

detritus relative to carbon in CH_2O . The effective oxidation reaction may be written (Bolin, 1977)



This reaction is actually reversible which is why phosphates and nitrates are biolimiting factors in plant carbohydrate production by photosynthesis. For our present purposes we simply note that the internal sink term for the dissolved oxygen profile is related to the organic component of the source term for carbon by the stoichiometry of this reaction:

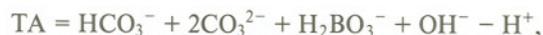
$$J_{\text{O}_2} = - (138/106)J_{\text{org}} \cong - 1.3J_{\text{org}}. \quad (10)$$

The regeneration of ΣC tied up in CaCO_3 particles works differently. These do not become part of total inorganic carbon unless they first dissolve to form calcium and carbonate ions, $\text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$, which is immediately followed by the reaction $\text{CO}_3^{2-} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^-$. Adding these gives the effective reaction for removing calcium carbonate



But this will happen only if the local water environment is undersaturated with respect to dissolved CaCO_3 . Biomineralized calcium carbonate occurs in the mineral forms of both calcite and aragonite, and while the aragonite is more soluble the surface waters of the world ocean are superaturated relative to both forms. This is fortunate, of course, for the organisms with calcareous shells inhabiting these waters. However, the solubility properties of these minerals as a function of temperature and pressure are such that seawater becomes undersaturated at some oceanic depth where CaCO_3 starts to dissolve. The initial transition level is termed the *lysocline*. At still greater depths, all calcareous remains exposed to sea water completely dissolve (all forms of CaCO_3 are undersaturated). This depth is the *carbonate compensation depth*. Typically, it occurs at about 3700 m, although there is considerable local variability with the transition levels lying lower in the Atlantic than the Pacific. The result is that about 80% of the sea floor is bathed in CaCO_3 -undersaturated water (Broecker, 1974), where the hard parts falling from surface waters dissolve and re-enter the aqueous phase. The remaining 20% is supersaturated and CaCO_3 sediments are still accumulating. This discussion suggests that representing the dissolution of CaCO_3 particles as a uniform source in the water column is a poor approximation (because dissolution happens near the bottom), a thesis we shall test shortly.

The final property of seawater which plays a key role in establishing the surface buffer factor, and in determining whether fossil fuel carbon penetrating to the sea floor will dissolve existing CaCO_3 sediments, is the total (or titration) alkalinity. This alkalinity may be defined formally as the sum of excess anionic charges carried by weak acids in seawater, $\text{TA} \equiv [\text{Na}^+ + \text{K}^+ + 2(\text{Mg}^{2+}) + 2(\text{Ca}^{2+})] - [\text{Cl}^- + \text{Br}^- + 2(\text{SO}_4^{2-})]$, and can be shown to equal



where the concentration of TA is generally cited in equivalent moles per unit volume or per unit mass of seawater. Notice that for each mole of CaCO_3 that dissolves, one mole of carbonate ion CO_3^{2-} is produced in the aqueous phase, one mole of ΣC is produced, and two equivalent moles of TA are produced. By this logic the source term for TA is

$$J_{\text{TA}} = 2J_{\text{CO}_3^{2-}} \quad (11)$$

Since total alkalinity is fed by dissolving CaCO_3 pellets close to the sea floor, we would expect an increase in TA with increasing depth, but with peak values closer to the sea floor than the profiles of ΣC (which has an organic source higher up) and O_2 .

We have tested the realism of these source models by comparison of the implied profiles with the data on ΣC and TA given by Takahashi *et al.* (1980) and on O_2 by T. Takahashi (personal communication). The vertical profiles for the world ocean were generated from the GEOSECS data base by first averaging over all data in each basin to obtain profiles for seven "ocean basins": the North and South Atlantic, North and South Pacific, North and South Indian Ocean and the Antarctic Ocean. The mean and standard deviations based on the seven ocean profiles were then found. The world ocean profiles \pm one standard deviation for ΣC , TA and O_2 are shown in figure 1, where TA is corrected to constant salinity by scaling with the Cl^- ionic concentration, and the data supplied by Takahashi *et al.* (1980) in mole/kg was converted to a volumetric concentration by multiplying by a characteristic seawater density, 1030 kg/m^3 .

For a constant J_λ , the solution to equation (8) is simply

$$c_\lambda(z) = c_1 e^{-z/z^*} + c_2 - (J_\lambda/w)z \quad (12)$$

where the constants are evaluated from the surface boundary condition $c_\lambda(0) = c_{\lambda m}$ and an integral boundary condition on the mean deep sea concentration,

$$\bar{c}_\lambda = \frac{N_{\lambda d}}{M_\lambda h_d A_d} = \frac{1}{h_d} \int_0^{h_d} c_\lambda(z) dz$$

where M_λ is the molecular weight of species λ . Solving for the constants gives

$$\begin{aligned} c_1 &\approx [c_{\lambda m} - \bar{c}_\lambda - J_\lambda h_d / (2w)] / [1 - (z^*/h_d)], \\ c_2 &= c_{\lambda m} - c_1. \end{aligned} \quad (13)$$

The total inorganic carbon profile in Figure 1 (a) was first computed by fixing the surface ocean and mean deep sea concentrations at the values used by Bacastow and Keeling (1973) in their carbon cycle model and the internal source term was set at $J_{\Sigma\text{C}} = J_{\text{org}} = 2 \times 10^{-4} \text{ mole/m}^3 \cdot \text{yr}$ (solid line). For comparison, the profile was also computed for the same surface and mean value with the source term increased by 3/2 corresponding to dissolution of CaCO_3 particles formed in the mixed layer at 1/2 the rate organic detritus is manufactured by net photosynthesis. As indicated earlier,

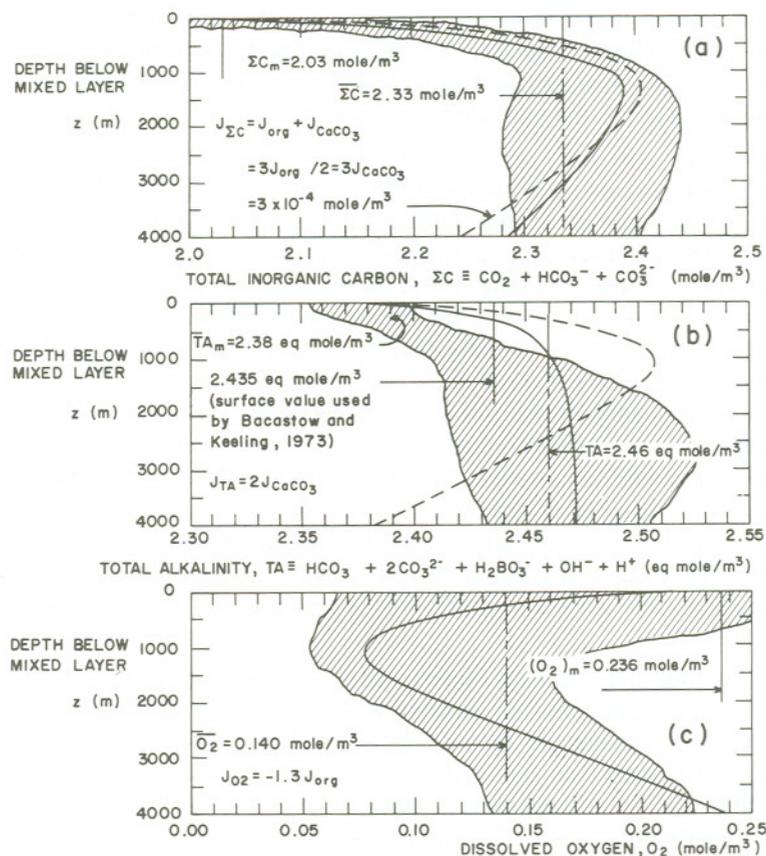


Figure 1: Steady state world ocean profiles of ΣC , TA and O_2 ; comparison of GEOSECS data (shaded areas) with one-dimensional upwelling-diffusion model: (a) inorganic carbon distribution where the dashed curve is for an internal carbon source composed of both oxidizing organic detritus and calcium carbonate particulates dissolving in the water column, the solid curve for the organic oxidation only, with the CaCO_3 falling to the sediments and presumably redissolving there; (b) the total alkalinity for internal and sea floor dissolution of biomineralized CaCO_3 . The internal source is twice $J_{\text{CO}_3^{2-}}$ of (a) because for each mole of dissolved CaCO_3 removed by $\text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{Ca}^{2+}$, two moles of bicarbonate ion, and therefore two equivalent moles of total alkalinity, are produced; (d) dissolved oxygen based on internal sink for oxidation of planktonic detritus plus additional utilization of O_2 for oxidation of NH_3 (Redfield *et al.*, 1963).

the uniform source component for CaCO_3 is unlikely in view of the supersaturation of the upper ocean, and the solid curve does appear to give a slightly better representation. Notice that this steady state profile reproduces the increase in ΣC as one descends from the surface, and then decreases again toward the bottom. This contrasts with the constant steady-state ΣC profile one obtains with a purely diffusive

model (Oeschger *et al.*, 1975). The concentration peak at about 1500 meters implies that carbon in the steady state is actually being transported upward between this peak and the surface because diffusion always brings material from high to low concentration zones. Likewise, the upwelling is pushing the carbon upwards.

The steady state total carbon profile is therefore established by the balance between this upward oceanic transport and the calcium carbonate and soft tissue particles falling down by gravitational settling. The first effect of an increase in fossil fuel carbon at the ocean surface is to decrease the gradient $\Sigma C / z$ in the upper ocean, but because ΣC changes relatively little for observed changes in atmospheric CO_2 , the net diffusion is still *upwards*. This contrasts somewhat with the conventional wisdom that fossil fuel CO_2 is diffusing *downwards* in the upper ocean [see, for example, the discussions of this point by Keeling (1973) and Björkström (1979)]. In fact, what is very likely happening is that it is diffusing toward the surface less rapidly than in preindustrial times while the outfall of particles falling from the surface has remained constant (or possibly increased under the stimulus of biolimiting nutrients like phosphates which have been released by man into the environment in significant amounts of late – see Broecker *et al.*, 1979, for a discussion of phosphorous matching, etc.). The result is an uptake of fossil fuel by the oceans, although the mechanism clarifies, we believe, the possible role of particulates at the surface as a carbon sink (or source).

The total alkalinity and dissolved oxygen profiles shown in Figure 1 (b) and 1 (c) also show reasonable good agreement with the GEOSECS world ocean data, with the TA profile for alkalinity fed by CaCO_3 dissolution at the sea floor (solid line) looking much better than that for uniform dissolution in the water column (dashed line). The dissolved oxygen curve exhibits a minimum near the 1500 meter depth corresponding to the peak in total carbon associated with the organic carbon source term. Overall, the three profiles exhibit a reasonably consistent picture. However, a slight problem exists with regard to consistent evaluation of atmospheric carbon dioxide and the surface buffer factor. In particular, the the surface concentration of total alkalinity derived from the GEOSECS world ocean data is somewhat less than that used by Bacastow and Keeling (1973) which we have been using in our carbonate chemistry calculations. This value, as well as the surface ocean total carbon concentration at preindustrial conditions will have to be recalibrated in order to recover the proper value of the preindustrial atmospheric CO_2 level (about 290 ppm). Furthermore, the assumption that all cold surface water enters at the bottom of the deep sea reservoir should be re-examined as well. Björkström (1979), for example lets the injection of cold water into the deep water reservoir also be a function of depth.

It is also interesting to reexamine the effect of an upwelling-diffusion model on the computed profile of radiocarbon for fixed surface and depth-averaged values, in comparison with the purely diffusive model of Oeschger *et al.* (1975). Because of the small absolute concentration of radiocarbon (^{14}C), it is customary to work with the specific activity $\delta^{14}\text{C} \equiv [(^{14}\text{C}/^{12}\text{C})/R - 1]$, where R is the $^{14}\text{C}/^{12}\text{C}$ ratio of an oxalic

acid standard at the National Bureau of Standards, USA ($\cong 1.2 \times 10^{-12}$). Because the $^{14}\text{C}/^{12}\text{C}$ fraction in the atmospheric reservoir has been greatly enriched by nuclear weapons tests, Oeschger *et al.* (1975), who were interested in the evolution of radiocarbon in the oceans as well as the prebomb distribution, worked with the vertical profile of the *fractionation factor*,

$$A \equiv \frac{{}^{14}\text{C}/{}^{12}\text{C}}{({}^{14}\text{C}/{}^{12}\text{C})_a} = \frac{1 + \delta^{14}\text{C}}{1 + (\delta^{14}\text{C})_a}, \quad (14)$$

where subscript a denotes the atmospheric reservoir. Since data presented by Machta (1973) show an atmospheric $^{14}\text{C}/^{12}\text{C}$ ratio of about 1.2×10^{-12} in 1954 prior to a significant build-up of radiocarbon from weapons tests, a pre-bomb level of $(\delta^{14}\text{C}) = 0\text{‰}$ is assumed here. The steady-state upwelling-diffusion model applied to the distribution of fractionation factor gives the differential equation,

$$z^* d^2 A/dz^2 + dA/dz - (\lambda/A) \cong 0, \quad (15a)$$

subject to the boundary conditions

$$\text{at } z = 0: A = A_m \quad \text{and} \quad \text{at } z = h_d: z^* dA/dz + A = A_p. \quad (15b)$$

where we use the same ocean transport properties as before ($K = 2000 \text{ m}^2/\text{yr}$, $w = 4 \text{ m/yr}$, $z^* = K/w = 500 \text{ m}$ and $\lambda = 1.21 \times 10^{-4} \text{ yr}^{-1}$).

For the case considered by Oeschger *et al.* (1975) in which radioactive decay in the deep sea is balanced by pure diffusion ($w = 0$) and the diffusive flux at the sea floor is set equal to zero, the distribution of radiocarbon is

$$A(z) = A_m \cdot \frac{\cosh [(\lambda/K)^{1/2}(h_d - z)]}{\cosh [(\lambda/K)^{1/2}h_d]}$$

which implies the depth-averaged value

$$A = \frac{1}{h_d} \cdot \int_0^{h_d} A(z) dz = A_m \cdot \frac{\tanh [(\lambda/K)^{1/2}h_d]}{(\lambda/K)^{1/2}h_d}.$$

Using the radiocarbon measurements of Broecker *et al.* (1960), Bien *et al.* (1960) and Fairhall *et al.* (1972) to estimate a surface prebomb level of $A_m = 0.95$ ($\delta^{14}\text{C} = -50\text{‰}$) and mean deep sea value of $A = 0.82$ ($\delta^{14}\text{C} = -180\text{‰}$), Oeschger *et al.* (1975) calibrate the ocean's effective eddy diffusivity at $K = 4000 \text{ m}^2/\text{yr}$, about twice the value of our upwelling-diffusion model. It is interesting that we can impose the same conditions for A_m and A whilst maintaining the values of eddy diffusivity and upwelling cited earlier because we have an additional degree of freedom in our model; namely, the specific activity in the polar sea. By calculating the polar sea value in the context of our model and comparing it with observations we can carry out another crosscheck on the model's consistency. The general solution to (15a) is simply

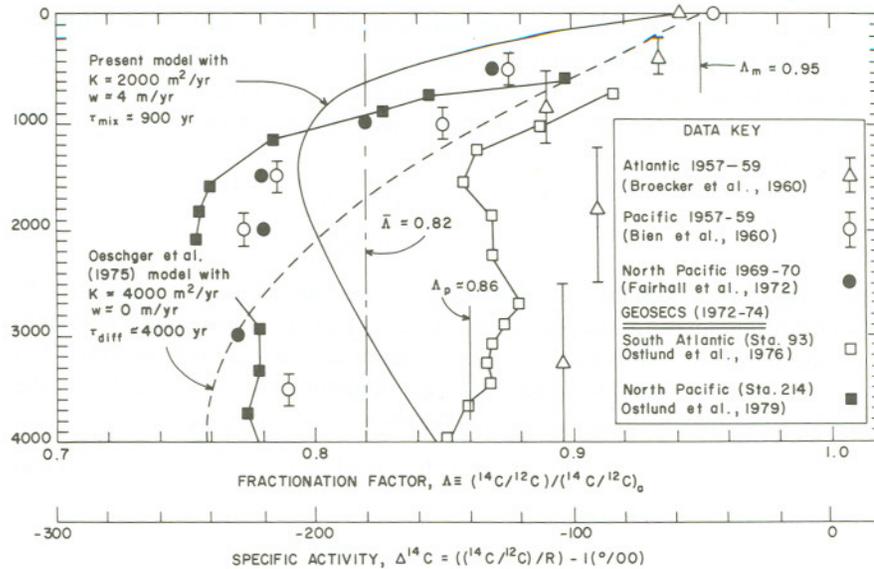


Figure 2: Prebomb radiocarbon distribution in the world ocean. The upwelling-diffusion model proposed here is compared with a diffusion-only (Oeschger) profile having the same fractionation factor in the mixed layer and the same vertical mean. Also shown are the pre-bomb data points in the Atlantic and Pacific basins used by Oeschger *et al.* to calibrate the vertical eddy diffusivity in their model and some of the more recent GEOSECS data which displays the minimum predicted by the upwelling-diffusion model.

$$A(z) = c_1 e^{z/z_1} + c_2 e^{-z/z_2},$$

where the scaling depths are

$$z_{1,2} = 2z^*/[\sqrt{1 + 4z^*(\lambda/w)} \pm 1] = 33,600 \text{ m}, 493 \text{ m}.$$

Now, applying the same conditions as before, that is, $A_m = 0.95$ and $A = 0.82$, we can evaluate the constants at $c_1 \cong 0.75$ and $c_2 \cong 0.25$. The fractionation factor in the polar sea is then calculable from the lower boundary condition of (15b)

$$A_p = c_1 (1 + z^*/z_1) \exp(h_d/z_1) + c_2 (1 - z^*/z_2) \exp(-h_d/z_2) \cong 0.86$$

($\delta^{14}\text{C} = -140\text{‰}$).

This value compares favorably with the bomb-corrected specific activities of $-141 \pm 12\text{‰}$ for Antarctic surface waters below 3°C cited by Broecker (1963).

The radiocarbon profiles themselves are compared in Figure 2 which shows the purely diffusive (dashed line) and upwelling-diffusion model (solid line) compared to the original data used by Oeschger *et al.* (1975) and to more recent radiocarbon profiles in the South Atlantic and North Pacific Basins obtained during the GEOSECS

program by Östlund *et al.* (1975, 1979). Although both theoretical profiles have the same mean and surface values, the shapes are quite different, with the purely diffusive model showing a monotonically decreasing radiocarbon activity, whereas the upwelling-diffusion profile exhibits a minimum in specific activity at about 1500 meters. This latter feature is associated with the enrichment of radiocarbon at the sea floor fed by the polar sea. It may be noted that the GEOSECS profiles presented also display such minimums in the 1000–2000 meter depth range. There is a final point of some interest in relation to the comparison of the purely diffusive and upwelling-diffusive ocean transport models. If we recognize that diffusive transport is augmented by direct ventilation of the deep sea by the polar sea route, the characteristic timescale for these processes *in parallel* is

$$\tau_{\text{mix}} = (K/h_d^2 + w/h_d)^{-1}. \quad (16)$$

It follows that the oceanic mixing times for the pure-diffusion model and the upwelling-diffusion model are 4000 and 900 years, respectively, for the same radiocarbon calibration data. The suggestion here that deep sea mixing rates inferred from tracer data may be model-dependent will be interesting to investigate further using the time-dependent version of this model.

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