

CHAPTER 2

Comparison of Ocean Models for the Carbon Cycle

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In this chapter, we compare simplified versions of models designed to estimate of the atmospheric CO_2 increase to be expected from continued combustion of fossil fuels. These models are global in extent and relate perturbations from an assumed preindustrial steady-state owing to the input of CO_2 derived from fossil fuel. The carbon cycle is very complex, but many aspects of it are not expected to change due to fossil fuel consumption, and consequently perturbation models are useful in estimating the response of the carbon cycle to fossil fuel consumption.

The emphasis here is on modelling the oceanic uptake of fossil fuel CO_2 . The models consist of an atmospheric reservoir of uniform CO_2 concentration interacting with a model ocean. The land biosphere is assumed to be passive, neither increasing nor decreasing in size; and thus it is omitted from the models.

The models under consideration all involve great simplifications of the physical ocean. They typically rely on calibration by tracers such as ^{14}C . Dynamic models, which do not require this type of calibration because they are based on the hydrodynamic equations, have not yet reached a state where they might be expected to be more reliable. The difficulty in developing dynamic ocean models is related to our ignorance of the turbulence properties of the ocean (Bryan and Sarmiento, 1979). It is consequently useful to compare more primitive oceanic models, each in as simple a form as possible, so that similarities and differences in their behavior may be most easily understood and related to aspects of ocean circulation.

Our goal is to find where the art of ocean modelling stands in depicting mathematically those aspects of the carbon cycle that are important to the oceanic uptake of fossil fuel CO_2 . We wish to note similarities and differences, the range of model parameters, and the responses permitted by the most important calibration data – steady-

state oceanic $^{14}\text{C}/\text{C}$ ratios. For validation, we principally compare the CO_2 airborne fraction predicted by the models with direct observations of this fraction.

We find two similarities among the models: (1) when parameters are given values consistent with our general understanding of ocean properties, the predicted airborne fractions are all much higher than the observed airborne fraction; this difference would imply that the biota in a complete model would have to be a net sink to achieve carbon balance: (2) for a particular scenario describing the combustion of the entire worldwide fossil fuel resource, the atmospheric responses of the models are similar, whether the ocean parameters are adjusted according to our best knowledge of ocean properties or are adjusted so that the observed airborne fraction is predicted.

2.1. OVERVIEW OF MODEL TYPES

The simplest ocean model that has some physical validity is probably the two-box model (2B model, Figure 1) first suggested by Craig (1957) and later applied to the fossil fuel problem by Bolin and Eriksson (1959), Cramer and Myers (1972, Machta (1973a and b), Keeling (1973), Bacastow and Keeling (1973), Zimen and Altenheim (1973), Hoffert (1974), Gowdy, Mulholland and Emanuel (1975), Keeling and Bacastow (1977), Revelle and Munk (1977), Bacastow and Keeling (1979), and Keeling (1979). This model is inspired by the observation that the oceans are highly stratified. Temperature profiles, in general, show a nearly constant value down to a thermocline depth which averages approximately 75 m. Below this wind-mixed layer, the profiles show a smooth transition to the cold 4°C deep ocean water. In the two-box ocean model, the surface ocean (or "mixed-layer") and the sub-surface ("deep") ocean are each represented by a well-mixed (randomly-mixed) box. The exchange of tracer between the two boxes is assumed to be by the transfer of water mass, either by advection or eddy diffusion, or both. The mixing time of the deep ocean is usually estimated from the observed average $^{14}\text{C}/\text{C}$ ratio in this reservoir relative to that of the surface layer. However, the so-called intermediate water in the temperature transition region (the main thermocline) has been particularly important to the uptake of CO_2 from fossil fuel combustion during the recent period of exponential fossil fuel production. This water is not well modelled by the two-box ocean because it has to be divided between the surface box and the deep ocean box. One does not know where to draw the line, except that the line should be deeper than the physical mixed-layer depth of approximately 75 m and less deep than the bottom of the thermocline, approximately 800 m.

The box diffusion model (Oeschger *et al.*, 1975; Siegenthaler and Oeschger, 1978) (BD or 2BD model, Figure 2) may be viewed as an attempt to model the intermediate water better. The surface ocean is given a thickness corresponding to the wind-mixed layer of approximately 75 m, and the deep ocean below is modeled by an eddy diffusion equation. The concentration of total dissolved inorganic carbon (DIC) is

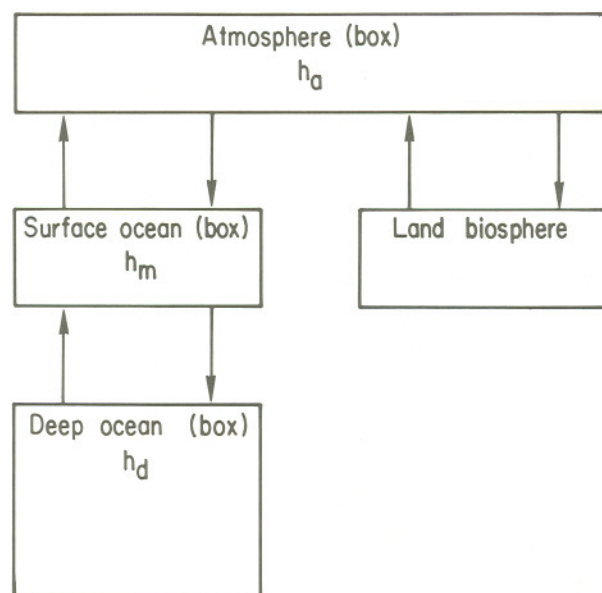


Figure 1: Two-box (2B) ocean model. The relative amounts of preindustrial carbon in the atmosphere, surface ocean, and deep ocean are given by ratios of h_a , h_m , and h_d . An undifferentiated land biosphere is shown to indicate how it would be incorporated in more complete models.

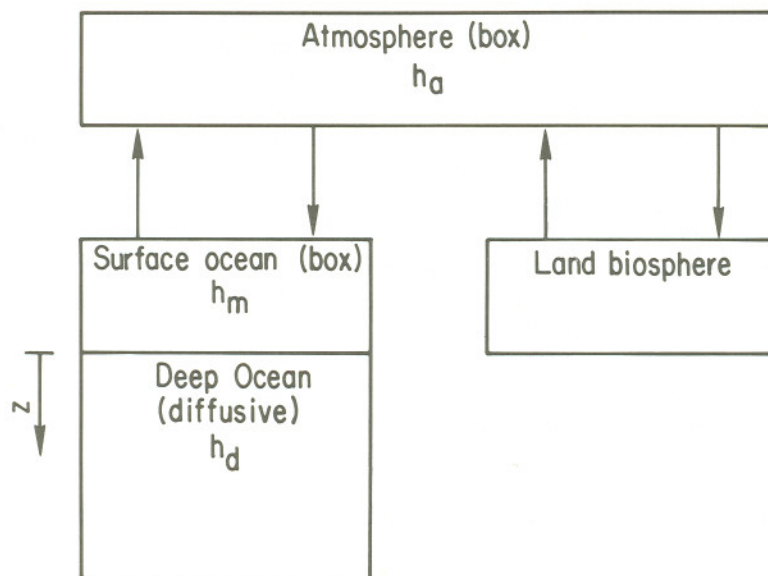


Figure 2: Box diffusion (BD or 2BD) model. A z axis is introduced with origin at the base of the surface ocean layer, increasing downward.

thus continuous at the surface ocean-to-intermediate water boundary. Diffusive transport allows that portion of the ocean which readily absorbs CO_2 from fossil fuel to be effectively "deeper" for slow phenomena than for fast phenomena. This is true also for the 2B model, but the variation is greater for the 2BD model (see Appendix A, Section (g)). The eddy-diffusivity, K , is typically estimated from the observed average $^{14}\text{C}/\text{C}$ ratio of the deep ocean relative to the surface ocean.

A question arises, however, concerning the box diffusion model which is similar to the question of how deep to set the base of the surface layer in the two-box ocean model. There are observations indicating that the diffusion constant that would best represent the upper part of the intermediate layer may be almost twice as large as the diffusion constant calculated from the average $^{14}\text{C}/\text{C}$ ratio in the deep water relative to surface water (Broecker, Peng and Engh, 1979). In order to represent a larger diffusion constant in the upper part of the intermediate water, and to still preserve a mathematically simple model, the surface ocean depth may be considered a parameter, and set deeper than the physical wind-mixed layer. One then returns to the problem of how deep to make the surface layer. The problem is similar if K is permitted to have different values in a top layer and bottom layer of the deep ocean.

Deep water formation is clearly dominated by penetrative convection in polar and subpolar regions rather than by eddy diffusion downward from the surface. Otherwise it would be difficult to explain why deep water is colder than surface water over most of the world oceans.

The advective-diffusive model (AD or 3AD model, Figure 3) is consequently an interesting extension of the box diffusion model. It is presented here for the first time, as a logical extension of the BD model and as a connection to the more complicated multi-box (MB) model described below. Downwelling in the Arctic and Antarctic is represented by a pipeline from a single surface ocean reservoir to the deep ocean, also represented by a single reservoir. Between the reservoirs is a box called the "intermediate ocean" with transport by vertical advection and diffusion. By adjusting the eddy diffusivity and the depth of the diffusive intermediate layer, this model can be made identical to either the 2B or 2BD models. The advective-diffusive model, consequently, has the interesting property that the two simpler models can be regarded as special cases, but being more flexible, it permits perhaps a more realistic description of the deep-sea circulation. In this study, we shall consider, as well, two other limiting cases of this model:

- (1) the bottom layer is set to a thickness of 1 m (i.e., made essentially to vanish) so that the model has the geometry of the 2BD model but includes advective upwelling as well as diffusive transport (2AD model).
- (2) the intermediate diffusive layer is set to 1000 m but there is no upwelling (3BD model).

As a specific example of the general case, the intermediate layer is set to 1000 m and there is advective upwelling (3AD model).

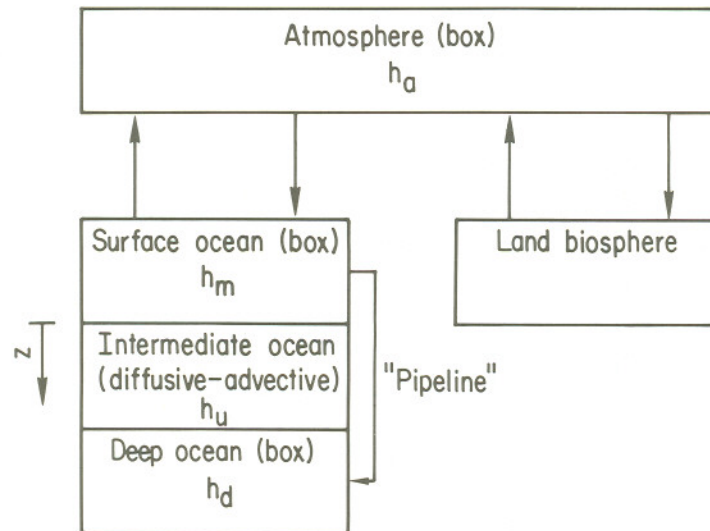


Figure 3: Advective-diffusive (AD) model. Flow down the pipeline from the surface ocean to the deep ocean is $wA \text{ m}^3/\text{yr}$, where w is the upwelling velocity and A the ocean area.

All the models discussed so far are horizontally uniform. Björkström (1979) has proposed a multi-box model (MB model, Figure 4) in which the surface ocean layer is horizontally divided into warm and cold water. Water below the surface is represented by ten horizontally uniform layers, or boxes: the intermediate water by two layers and the deep ocean by eight layers. Mixing into the intermediate water and deep water layers is directly from the cold surface layer. The model includes two aspects of ocean circulation that are averaged over in simpler models: cold surface water is somewhat richer than warm surface water in dissolved inorganic carbon (DIC), and deep water formation occurs principally by downwelling of cold surface or intermediate water.

The four ocean models just described are in some ways very similar. For example, the definition of a well delineated surface layer is common to all. So is the neglect of all horizontal inhomogeneities in below-surface water, and this simplification may make all these models deviate from reality in a serious way. In other ways, the models are clearly different. For example, the intermediate water (the main thermocline) is depicted in the multi-box (MB) model by two reservoirs, and can be indirectly represented by a proper choice of the eddy-diffusivity in the box diffusion (BD) model, but this water body can only be implicitly accounted for in the two-box (2B) model by making the surface layer depth much deeper than what the physical definition of this parameter admits. Furthermore, in the 2B model, the assumption is made that the outgoing flux of DIC from the deep ocean is always proportional to the average deep ocean DIC concentration. Incomplete vertical mixing is allowed for in both the box diffusion and multi-box models.

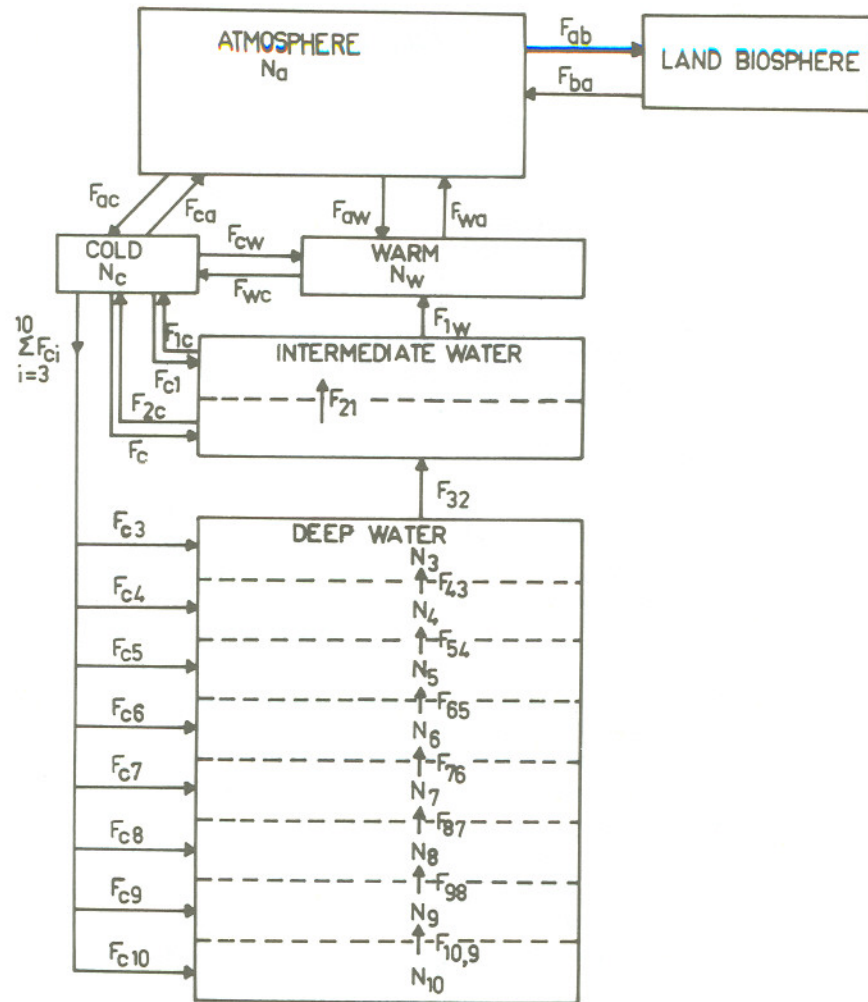


Figure 4: Multi-box (MB) model.

In ocean modelling there is long experience in representing vertical transport in restricted regions by an eddy diffusive process (see for example, Wyrski, 1962; Munk, 1966; Craig, 1969). The proportionality between “characteristic depth” and the square root of elapsed time, typical of diffusive transfer, is a dominant characteristic of the BD model, but it is lacking in the MB model. However, the MB model better describes the global scale vertical circulation pattern that is thought to exist in the oceans: polar downwelling and slow upward motion elsewhere. The advective-diffusive (AD) model depicts both diffusive and advective transport and tends to bridge the gap between the BD and MB models, but only in a highly simplified way.

2.2. METHOD OF COMPARISON

To expand our understanding of carbon cycle models, we need to determine systematically how specific behavioural features result from various model assumptions. Obviously, this is an undertaking that may be approached in several ways. Our philosophy here is to prepare simple versions of the principal existing models, and simple extensions to them, adjust each to the oceanic ^{14}C data in as consistent a way as possible, and examine their atmospheric response to identical fossil fuel inputs.

The implicit assumption is made that the pre-industrial ^{14}C distribution represents a steady state, i.e. that it is due to a natural atmospheric ^{14}C production which has remained constant for a time considerably longer than the turn-over time for the whole ocean, and that the steady-state carbon transfers in nature have also been unchanged for at least as long as the ^{14}C production has been constant. Since these assumptions may not be entirely correct, the model results must be interpreted with caution. At least with respect to the more limited aim of understanding the *differences* between the model structures, the steady state assumption, however, seems adequate.

Except for the MB model, the model oceans are assumed to be uniform in DIC concentration and constant in cross-sectional area to the bottom. The eight boxes of the deep ocean in the MB model could not be adjusted to an observed ^{14}C profile unless the ocean geometry were realistic and so the original geometry (Björkström, 1979) was retained.

Detrital flux from the surface to deeper water is neglected, consistent with the assumed constant concentration of dissolved inorganic carbon. Calculations based on the 2B model indicate that this flux is largely compensated for when the model is adjusted to ^{14}C measurements (Keeling, 1973, 1979).

Steady-state ^{14}C data are insufficient to set all of the model parameters. We consequently explore the effect on the models of variation of the parameters not so determined.

Much can be learned from linearized versions of the models and an assumed exponential input of CO_2 from fossil fuel. The principal linearization is the assumption of a constant surface ocean CO_2 evasion factor, ξ . The evasion factor has probably increased up to now by only about 7% relative to its preindustrial (steady-state) value, but will presumably increase much more in the future if fossil fuel consumption continues to grow.

Fossil fuel production since 1945 has increased nearly exponentially with a time constant of about 22.5 years. Rotty (1977) has pointed out that approximately this rate of growth has occurred since 1860, when good records are first available, except for hesitations associated with the two world wars and the depression of the 1930's. The entire fossil fuel record since 1860 best fits an exponential with a time constant of approximately 34 years, but the more recent rate is probably more appropriate since the airborne fraction calculated from the exponential input is to be compared with the airborne fraction observed at Mauna Loa, Hawaii, and the South Pole, be-

tween 1959 and 1978, and thus largely determined by the growth rate since 1945.

We examine two versions of each of the models depicted in Figure 1–4:

- (1) A linearized version with exponential fossil fuel production. We explore the sensitivity of the airborne fraction estimated by the model to variations in its principal parameters with no biospheric contribution.
- (2) A non-linear version with a numerical stepwise solution to the differential equations and with the fossil fuel production taken from either yearly data for the past or bell shaped “logistic curves” to represent future production scenarios. With these calculations we confirm conclusions drawn from the exponential fossil fuel versions above and we compare, for the various models, the response of the atmosphere to consumption of the entire fossil fuel resource.

2.3. COMMON MODEL FEATURES

To make model comparisons as meaningful as possible, all the models are adjusted, in so far as it is possible, to common geometry and identical initial conditions.

2.3.1. Ocean depth

All the ocean models are assumed to have uniform concentration of total dissolved inorganic carbon (DIC) and, except for the MB model, constant area to the bottom. The depth of this simplified ocean would be, except for the reason noted below, the ratio of the real ocean volume to area. Menard and Smith (1966) estimate that the ocean volume and area are $1.350 \times 10^{18} \text{ m}^3$ and $3.620 \times 10^{14} \text{ m}^2$, respectively. However, in the real ocean, the DIC concentration below the wind-mixed surface layer is about 10% higher than at the surface, owing to detrital flux. Because of the importance of ξ , the CO_2 evasion factor, to oceanic uptake, we choose to assign the correct average surface DIC concentration to all the ocean models and to adjust the ocean depth so that the models contain the same total amount of DIC as the real ocean. Takahashi and Broecker (this volume), report the concentration of DIC in the surface water (0–50 m) and the total ocean to be 2002 and 2254 $\mu\text{mol/kg}$, respectively, after adjustment to an average ocean salinity of 34.78‰. Our value for the total ocean depth, h_s , then becomes

$$h_s = \left(\frac{1.350 \times 10^{18}}{3.620 \times 10^{14}} \right) \left(\frac{2254}{2002} \right) = 4199 \text{ m} \quad (2.1)$$

2.3.2. Equivalent atmospheric depth

Since only ratios of reservoir pre-industrial carbon masses appear in the model equations, it is useful to define a depth of ocean water, h_a , that contains the same total

amount of DIC as that in the pre-industrial atmosphere. The pre-industrial atmospheric CO₂ concentration is uncertain within the range 275–295 ppm (parts per million by volume); we shall assume the value 290 ppm (Keeling, 1978). Fortunately, the models are relatively insensitive to this assumption. The mass of the dry atmosphere is approximately 5119×10^{18} g (Verniani, 1966), and the density of sea water is about 1025 kg/m³. Then

$$\begin{aligned} h_a &= \frac{615.6 \times 10^{15}}{(12.011) (2002 \times 10^{-6}) (1025) (3.620 \times 10^{14})} \\ &= 69.00 \text{ m} \end{aligned} \quad (2.2)$$

2.3.3. Surface ocean depth

The areal and seasonal average depth of the wind-mixed layer, h_m , in the North Pacific is reported by Bathen (1972) to be 75 m, but it is deeper in the winter than in the summer. Because the time constant for exponential growth in fossil fuel usage is much greater than one year, water that is mixed with surface water at any time during the year should probably be considered surface water when modelling fossil fuel uptake. Without formally averaging the winter maximum depths with respect to area, the value $h_m = 100$ m looks reasonable from Bathen's plot for the month of February. However, the difference between 100 m and the seasonally averaged value of 75 m is small (only a few percent difference in predicted airborne fraction in the models), so we use the value $h_m = 75$ m when a standard depth of surface layer is required.

2.4. DATA FOR MODEL CALIBRATION AND VALIDATION

2.4.1. Ocean ¹⁴C

Parameters to define the magnitudes of oceanic mixing and exchange are fixed or limited by being made consistent with pre-industrial ¹⁴C data. We represent these data by two quantities: $\rho'_{mo} = {}^{14}R'_{mo}/{}^{14}R'_{ao}$ and $\rho'_{so} = {}^{14}R'_{so}/{}^{14}R'_{ao}$, where ¹⁴R' is the fractionation corrected ¹⁴C to C ratio (see Appendix A, Section (f)), the subscripts m, s, and a refer to the surface ocean layer, total ocean, and atmosphere, respectively, and the second subscript o indicates a pre-industrial or steady-state value. We take as preferred values

$$\rho'_{mo} = 0.95 \quad (2.3)$$

$$\rho'_{so} = 0.84 \quad (2.4)$$

For ρ'_{mo} , we must rely on data collected before the nuclear bomb tests of the middle 1950's. The value of ρ'_{so} may be obtained from recent data because bomb ¹⁴C and fossil fuel CO₂ have not yet had much effect on the deep ocean water.

2.4.2. Atmospheric CO₂ Increase

Atmospheric CO₂ measurements at Mauna Loa, Hawaii, and the South Pole (Keeling *et al.*, this volume), for modelling purposes, can be reduced to an average global concentration at two dates, or alternatively, a concentration at one date and an airborne fraction between the two dates. The Mauna Loa and South Pole average concentrations on Jan. 1, 1959, and Jan. 1, 1978, were 315.60 ppm and 333.65 ppm, respectively, and the observed airborne fraction between them is 53%.

The utility of the airborne fraction is that it is a constant in a linear model with exponential atmospheric carbon input:

$$y_a = \bar{y}_a e^{\mu t} \quad (2.5)$$

where t denotes time and y_a and μ are constants. If the exponential input is begun with the model at steady state, the reservoir fractions become approximately constant after a few multiples of the exponential time constant, μ^{-1} ; it is not necessary to wait a time corresponding to the longest natural eigenfrequency of the model (Bacastow and Keeling, 1979).

Although the input of CO₂ from fossil fuel is reasonably well represented by an exponential function, there may have been an independent, non-exponential, biota source due to the so-called "pioneer effect", which refers to the large scale clearing of land for agriculture during the last century. Such a source, of 100 to 200 Gt, would cause the box diffusion (2BD) model to predict a 3% to 6% lower airborne fraction, as compared to the same model with only CO₂ input from fossil fuel production data (Bacastow and Keeling, this volume). Thus the observed airborne fraction may be 3% to 6% lower than the appropriate value for a model with no biota.

2.5. MODEL PARAMETERS

Each model includes at least one parameter that governs its response to short and medium time period disturbances ($< \approx 100$ years), such as the current fossil fuel input, and at least one other that mainly characterizes its behaviour in response to longer time disturbances. The most natural selection for the short and long time parameters for the two-box (2B) model are respectively, h_m , the surface layer depth, and k_{dm} , the inverse of the deep sea mixing time. For the box diffusion (2BD) model we choose h_m and K , the eddy-diffusivity of the deep ocean layer, but here the division is not quite so clear because K has more effect on short time disturbances than does k_{dm} . For the similar 3BD model, we also choose h_m and K . In the advective-diffusive models (2AD and 3AD), we again choose h_m for short time disturbances, and K , for long time disturbances, with w , the upwelling velocity, fixed at 1 m yr^{-1} .

In the multi-box (MB) model (Figure 4), the depth of the surface ocean layer is not a convenient short time parameter because, as already mentioned, a more realistic ocean geometry is required, and consequently, h_m is fixed at 75 m. The multi-box model has potentially many more degrees of freedom than the two-box model or the

various diffusive models with constant K . In order to produce model comparisons that can be interpreted in a meaningful way, it is necessary to investigate the effect of varying only a small number of parameters in each model, so that the range of possible values for the investigated parameters can be delimited.

The technique used here is to describe the exchange between the intermediate water and the cold surface water with a parameter T , and the deep advective circulation by a parameter P . The parameter T is defined as the total flux of water from the cold surface reservoir into the two boxes representing intermediate water. Seventy-five percent of this flux is assumed to go into the upper of the two intermediate boxes, and each of the two boxes returns the same amount of water to the cold surface water as it receives.

The parameter P is a measure of the amount of water sinking from the cold surface layer into the stratified layers below the intermediate water, i.e. below 1000 m. In these experiments, $P = 1$ corresponds to a penetration of $1320 \times 10^{12} \text{ m}^3/\text{yr}$, distributed among the MB model ocean reservoirs 3 to 10 so as to yield a prescribed ^{14}C -profile (cf "young ocean" case, Björkström, 1979). When P is smaller or greater than 1, each of these eight fluxes is assumed to be reduced or increased by this factor.

The parameters T and P , respectively, serve as the short and long time parameters for the MB model.

2.6. MODEL COMPARISON WITH EXPONENTIAL FOSSIL FUEL SOURCE

As already noted, the airborne fraction, within an adjustment time of the order of μ^{-1} , the e-fold time of the exponential input, closely approaches a constant. Consequently, the "ultimate airborne fraction", r_{af} , for a range of values of the model parameters, is useful for model comparison. We assume exponential growth with $\mu^{-1} = 22.5$ years. We have verified that this is a reasonable choice by comparing the airborne fraction calculated with the 2BD model ($K = 5020 \text{ m}^2/\text{yr}$, $h_m = 75 \text{ m}$) first with this exponential input and then, between 1959 and 1978, with fossil fuel production data input (see Appendix B). The airborne fractions so calculated are 66.4% and 65.9%, respectively; thus nearly the same.

The ultimate airborne fraction and oceanic steady-state $^{14}\text{C}/\text{C}$ depletion have been computed for a range of values of the short and long time model parameters by use of equations given in Appendix A. A constant value of the evasion factor, ξ , of 9.64 was used to linearize the models. Since the ^{14}C data, represented by ρ'_{mo} and ρ'_{so} , is corrected for fractionation, all fractionation coefficients $^{14}\alpha_{ij}$ in the ^{14}C equations were set to unity in these calculations (see Appendix A, Section (f)). Isopleths of r_{af} and ρ'_{so} are plotted in Figures 5–10 as functions of the model parameters at the constant value $\rho'_{\text{mo}} = 0.95$. In each model, the value of ρ'_{so} mainly determines the long time parameter, and the airborne fraction and short time parameter are closely related.

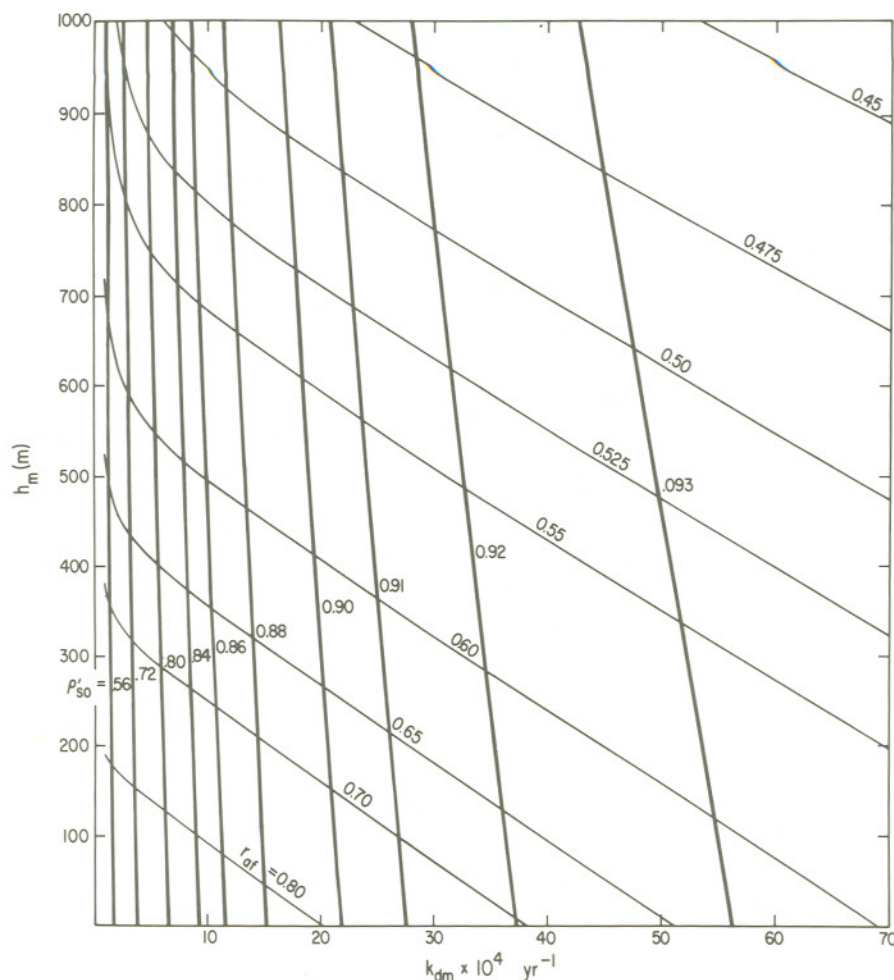


Figure 5: 2B model isopleths of ρ'_{so} , average $^{14}\text{C}/\text{C}$ ratio, adjusted for fractionation, in the preindustrial ocean relative to the atmosphere, and r_{af} , the airborne fraction after a long time of exponential fossil fuel growth, as functions of h_m and k_{dm} . The exponential time constant, μ , is $1/22.5 \text{ yr}^{-1}$. ρ'_{mo} , the $^{14}\text{C}/\text{C}$ ratio, adjusted for fractionation, in the preindustrial surface ocean relative to the atmosphere, is 0.95.

In model comparisons, ρ'_{so} has been varied rather than ρ'_{mo} for several reasons: (1) at the time of doing these calculations, a careful ocean average of ρ'_{so} had not yet been made (see Stuiver *et al.*, this volume), (2) a ^{14}C steady-state may not exist, and (3) airborne fractions are relatively insensitive to ρ'_{mo} , apart from a change in the ratio ρ'_{so}/ρ'_{mo} .

To depict observations, r_{af} must equal approximately 53% and ρ'_{so} must be about 0.84. If an unrealistically large value of the short time parameter (h_m or T) is required,

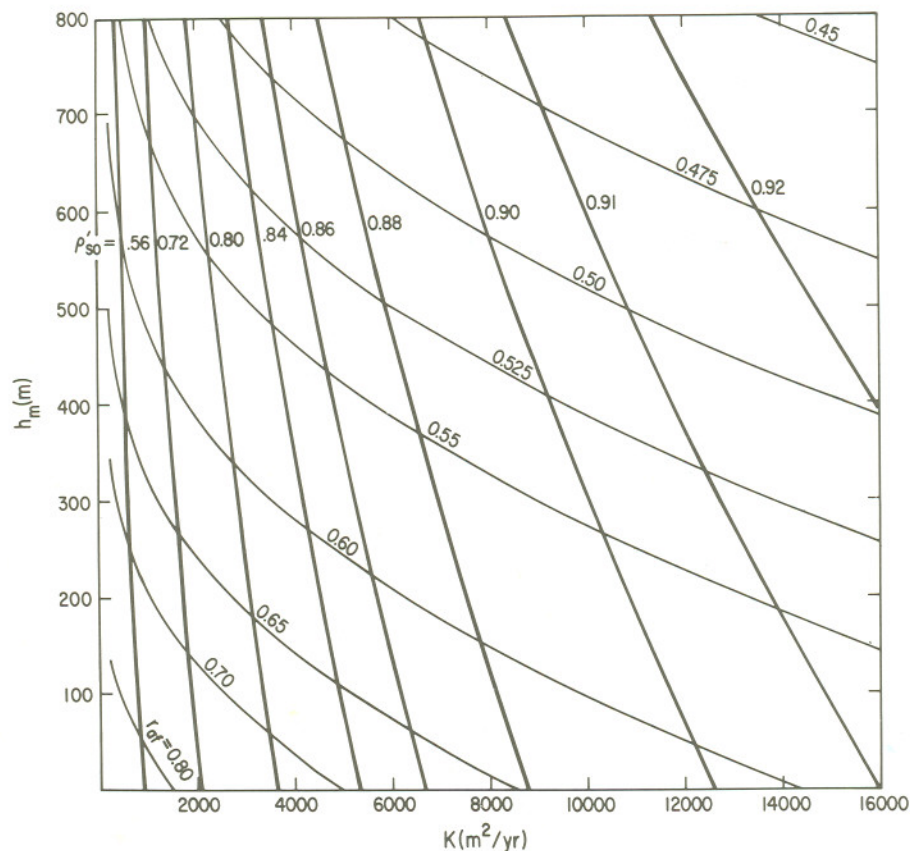


Figure 6: 2BD model isopleths of ρ'_{so} and r_{af} , as functions of h_m and K , with $\mu = 1/22.5 \text{ yr}^{-1}$ and $\rho'_{mo} = 0.95$.

it is an indication that the biota, in a complete model, would have to be a sink in order for the model as a whole to achieve carbon balance with a realistic value of the short time parameter. For the 2B model (Figure 5), isopleths of $r_{af} = 53\%$ and $\rho'_{so} = 0.84$ intersect at approximately $k_{dm} = 1370 \text{ yr}^{-1}$ and $h_m = 815 \text{ m}$ (more accurately calculated values are $k_{dm} = 1386 \text{ yr}^{-1}$ and $h_m = 812 \text{ m}$). Nowhere in the range $h_m = 0$ to 200 m is an adequate solution found. The 2BD model (Figure 6) requires a noticeably shallower surface layer than the 2B model to yield this same airborne fraction and ^{14}C depletion: $h_m = 595 \text{ m}$ and $K = 3250 \text{ m}^2/\text{yr}$ (more accurately calculated values are h_m unchanged and $K = 3255 \text{ m}^2/\text{yr}$). The picture is quite similar in the two models. The value of h_m required is many times the average depth of the mixed-layer of the real ocean (75 to 100 m).

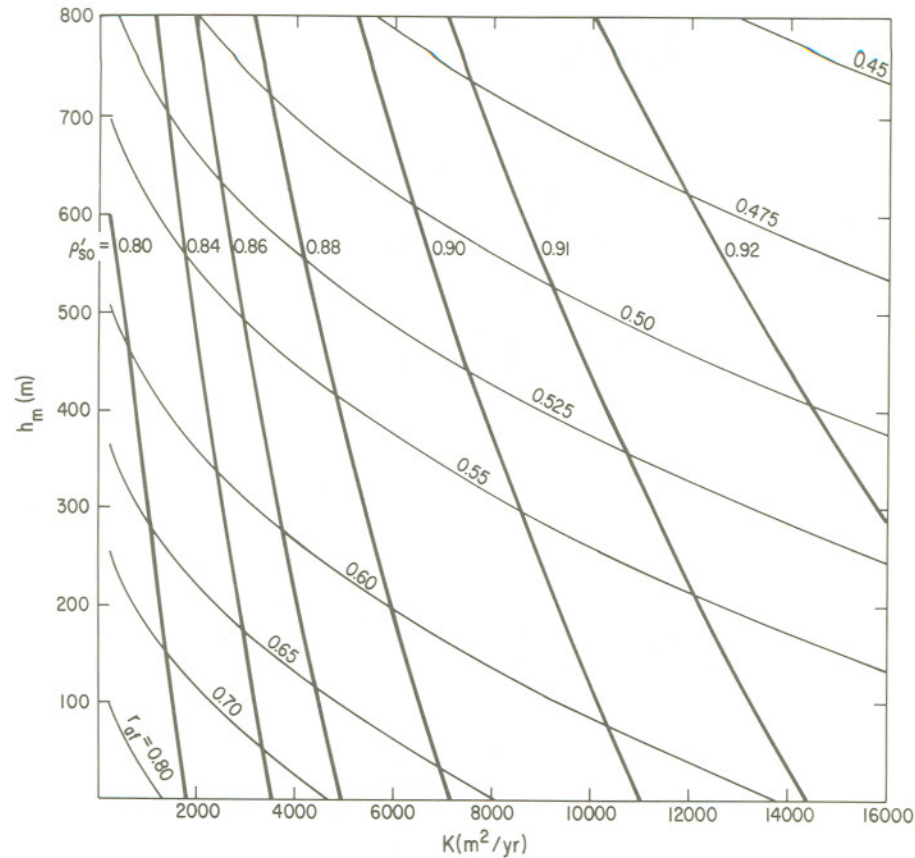


Figure 7: 2AD model isopleths of ρ'_{so} and r_{af} , as functions of h_m and K , with $\mu = 1/22.5 \text{ yr}^{-1}$, $\rho'_{mo} = 0.95$, and upwelling velocity $w = 1 \text{ m/yr}$.

The multi-box (MB) model also shows similar characteristics (Figure 10). The rate of exchange of water between the cold surface reservoir and the two intermediate ocean reservoirs has to be more than $80\,000 \times 10^{12} \text{ m}^3$ per year if r_{af} and ρ'_{so} are to take on realistic values. Figure 10 also shows that there needs to be upward advection of about $1000 \times 10^{12} \text{ m}^3/\text{year}$ through the intermediate water reservoirs. Since the volume of these reservoirs is about $630 \times 10^{15} \text{ m}^3$, the turn-over time of intermediate water due to downward mixing of cold surface water and upwelling of deep water, combined, is the order of 8 years ($630/(80+1)$).

The turnover time for a natural reservoir is strongly affected if extreme transit-times occur in some part of the reservoir, and we must not a priori dismiss the possibility that an appropriately weighted average transit time for this water might be considerably shorter than its average age. Our knowledge of mixing rates in the main

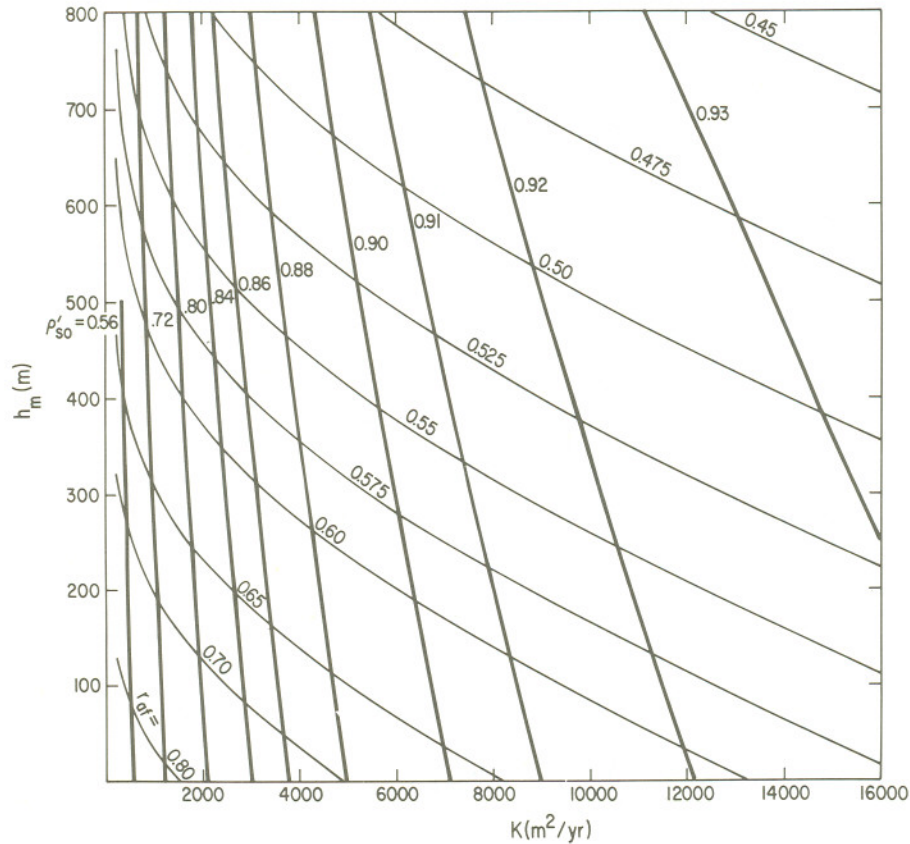


Figure 8: 3BD model isopleths of ρ'_{so} and r_{af} , as functions of h_m and K , with $\mu = 1/22.5 \text{ yr}^{-1}$ and $\rho'_{mo} = 0.95$.

oceanic thermocline is incomplete, but a model where the water between 75 and 1000 m in the ocean is on average assumed to be ventilated in less than twenty years is clearly incompatible with hydrological considerations (Reid, 1965), as well as the detailed ^{14}C distribution. Therefore the MB ocean model, when the parameters are given physically realistic values, also predicts an airborne fraction much higher than that which is observed. This feature corresponds with the larger than physical surface layer depths required by the 2B and 2BD models to fit both the ^{14}C content of the ocean and the observed airborne fraction.

It is interesting to compare the 2BD and 3BD models. The ultimate airborne fraction, with $\mu = 1/22.5 \text{ yr}^{-1}$, is insensitive to the size of the deep sea reservoir of the 3BD model until this layer becomes the order of, or larger than the diffusive layer. The airborne fraction is larger for the 3BD than for the 2BD model. With $h_m = 75 \text{ m}$, $\mu = 1/$

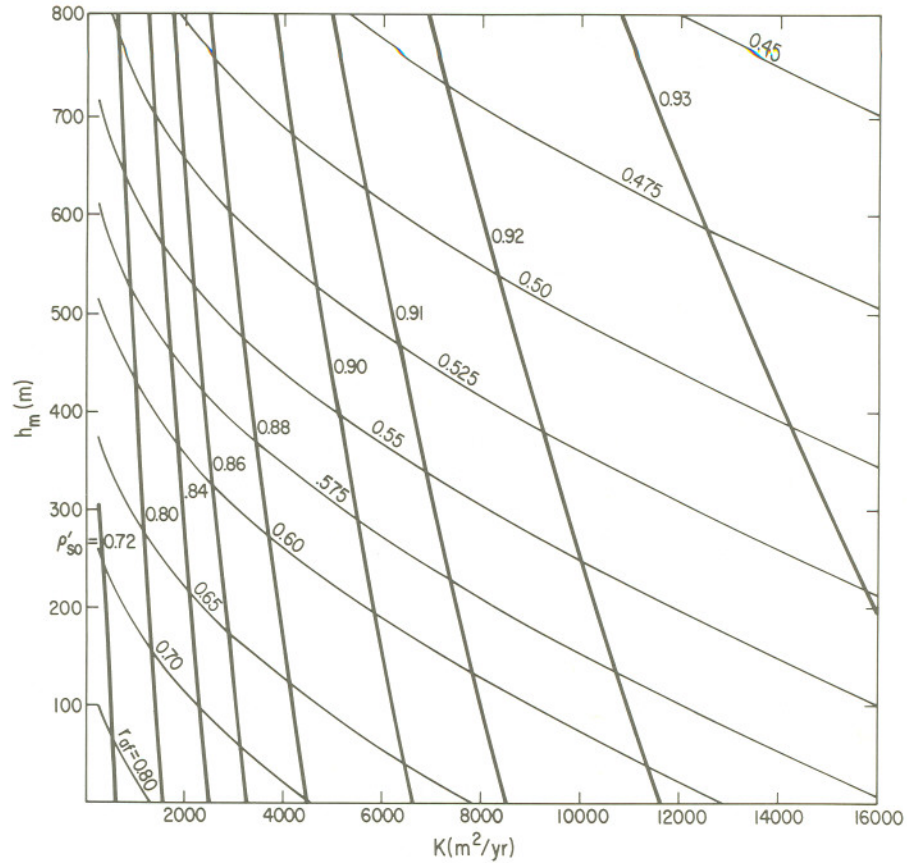


Figure 9: 3AD model isopleths of ρ'_{so} and r_{af} , as functions of h_m and K , with $\mu = 1/22.5 \text{ yr}^{-1}$, $\rho'_{mo} = 0.95$ and upwelling velocity $w = 1 \text{ m/yr}$.

22.5 yr^{-1} , and with h_u , the depth of the intermediate layer, equal to 1000 m, and K adjusted so that $\rho'_{mo} = 0.95$ and $\rho'_{so} = 0.84$, the airborne fraction is approximately 4% higher for the 3BD model than for the 2BD model. The airborne fraction for the 3BD model is always larger than or equal to the airborne fraction for the 2BD model for all reasonable μ (Figure 11) and h_m (Figure 12).

We may understand this behavior by recognizing that the lowest ultimate airborne fraction will be achieved by the model that has the most ocean water in the surface layer or closely coupled to it. In the 3BD model, the diffusive gradient just below the surface layer is steeper than the gradient in the 2BD model, with both models adjusted to the same ^{14}C parameters and surface layer depth. Consequently, the 2BD model will have more water closely coupled to the surface layer, and the lower air-

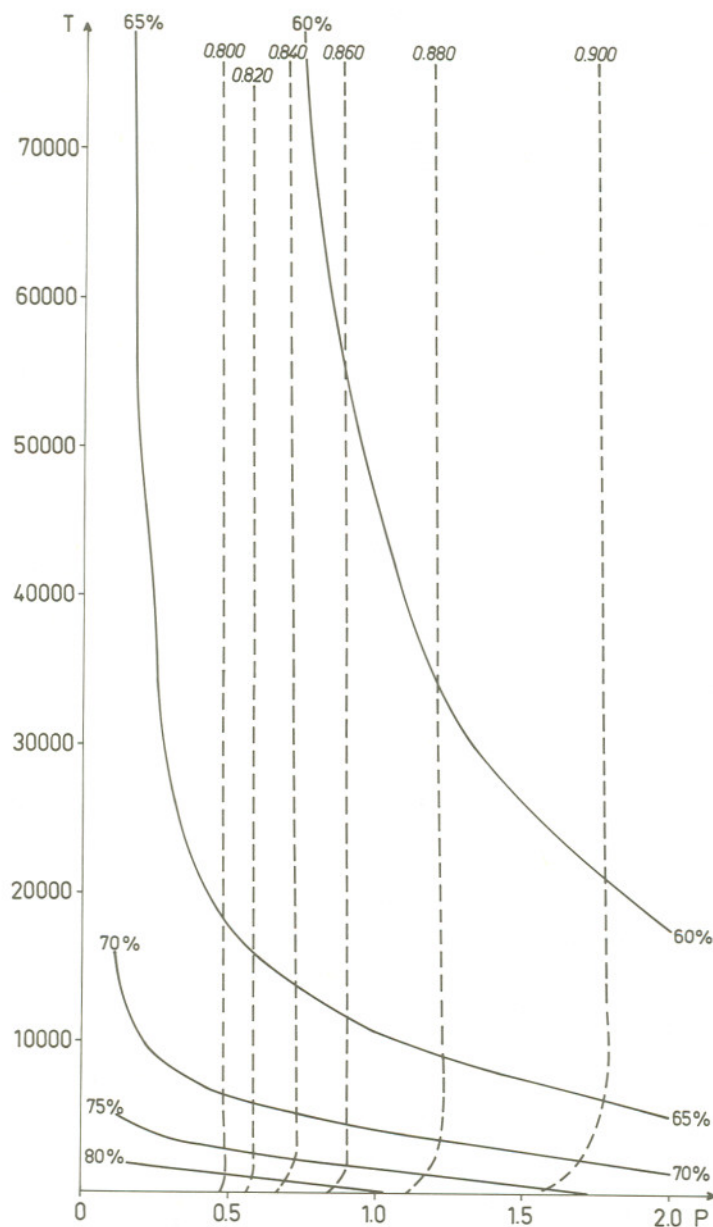


Figure 10: MB model isopleths of ρ'_{so} and r_{af} , as functions of T and P, with $\mu = 1/22.5 \text{ yr}^{-1}$ and $\rho'_{mo} = 0.95$. T is the total flux of water (m^3/yr) from the cold surface reservoir into the two intermediate water reservoirs. P is the total flux of water downwelling from the cold surface layer into the ocean layers below the two intermediate layers, divided by $1320 \text{ m}^3/\text{yr}$ (cf. Figure 4).

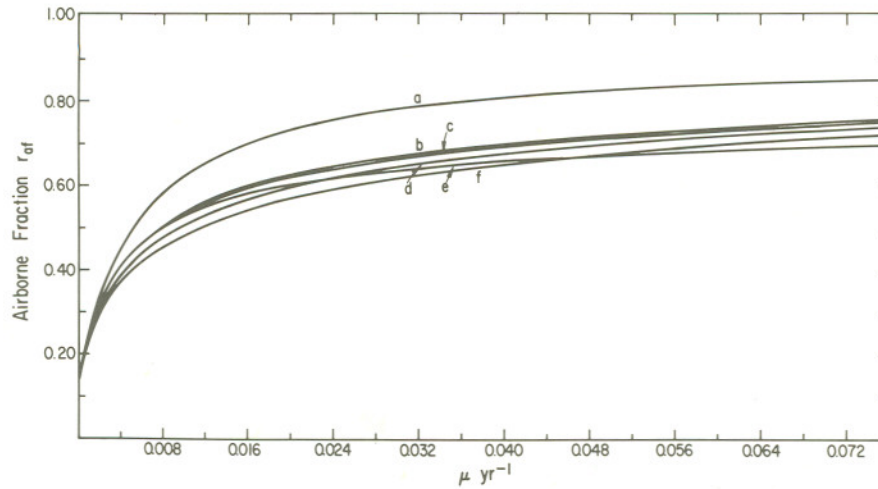


Figure 11: Variation of airborne fraction, r_{af} , of standard models with exponential time constant μ : (a) 2B model with $h_m = 75$ m, $k_{dm} = 1/1087$ yr $^{-1}$; (b) 3AD model with $h_m = 75$ m, $h_u = 1000$ m, $w = 1$ m/yr, $K = 2350$ m 2 /yr; (c) 3BD model with $h_m = 75$ m, $h_u = 1000$ m, $K = 2850$ m 2 /yr; (d) 2AD model with $h_m = 75$ m, $w = 1$ m/yr, $K = 3300$ m 2 /yr; (e) 2B model with $h_m = 340$ m, $k_{dm} = 1/1190$ yr $^{-1}$ (values chosen to produce approximately the same airborne fraction as the 2BD model at $\mu = 1/22.5$ yr $^{-1}$); (f) 2BD model with $h_m = 75$ m, $K = 5020$ m 2 /yr. The transport parameters k_{am} , k_{dm} , K , and w are all consistent with $\rho'_{mo} = 0.95$ and $\rho'_{so} = 0.84$ (see footnote to Figure 15 caption for more accurately calculated parameters; curves for more accurate values would not be significantly different from those plotted).

borne fraction. These qualitative arguments may be stated more analytically for simple models (see Section (g) of Appendix A).

The minimum ultimate airborne fraction for $\rho'_{mo} = 0.95$ and $\rho'_{so} = 0.84$ is thus expected to occur in the model with the maximum surface layer depth. This model would have no ^{14}C below a surface layer of depth

$$h_m = \left(\frac{.84}{.95} \right) (4199) = 3713 \text{ m} \quad (2.6)$$

and the airborne fraction would be 35%.

One might expect that if the inclusion of vertical upwelling lowers the airborne fraction this would also happen in the simplest advective models, such as the 2AD model. Isopleths of r_{af} and ρ'_{so} are given in Figure 7 for the 2AD model with upwelling velocity $w = 1$ m/yr. At the same value of K , the airborne fraction is reduced relative to that predicted by the 2BD model (Figure 6), but for fixed ρ'_{so} and with $\rho'_{mo} = 0.95$, it is increased. This model behavior is true also for the 3AD and 3BD models (see Figures 8 and 9). Airborne fractions for these models at $\rho'_{mo} = 0.95$ and $\rho'_{so} =$

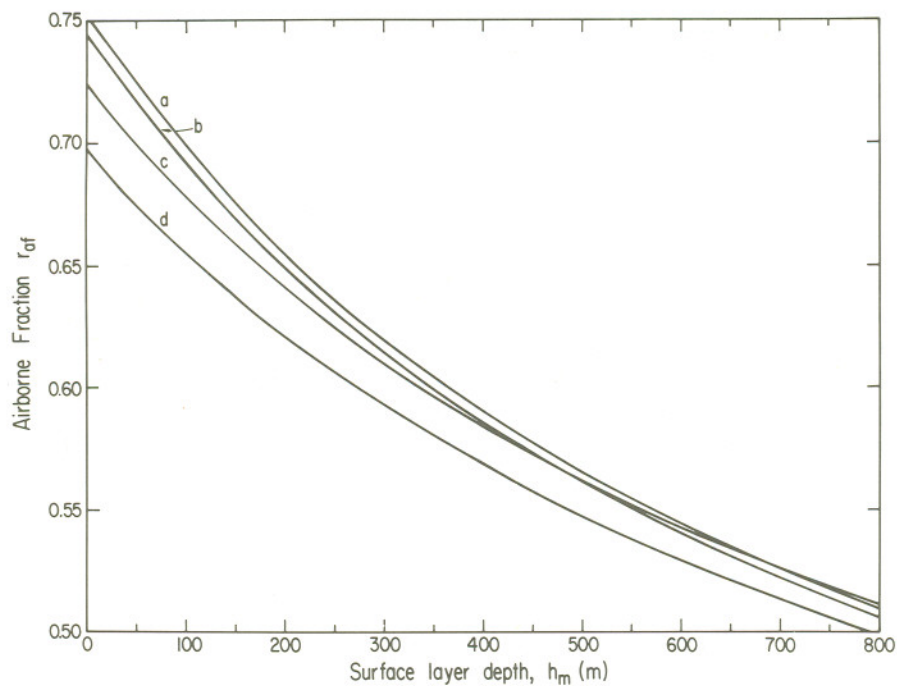


Figure 12: Variation of airborne fraction with surface ocean depth, h_m ; model consistent with $\rho'_{mo} = 0.95$, $\rho'_{so} = 0.84$ and $\mu = 1/22.5 \text{ yr}^{-1}$: (a) 3AD model, $h_u = 1000 \text{ m}$, $w = 1 \text{ m/yr}$; (b) 3BD model, $h_u = 1000 \text{ m}$; (c) 2AD model, $w = 1 \text{ m/yr}$; (d) 2BD model.

0.84 are given in Figures 11 and 12. Thus it appears unlikely that the neglect of vertical advection has produced predictions which underestimate oceanic uptake of fossil fuel CO_2 .

The extreme model with upwelling is one in which there is no diffusive transport ($K = 0$) and all the ventilation of the deep ocean is by upwelling. With $\rho'_{mo} = 0.95$, $\rho'_{so} = 0.84$, and $h_m = 75 \text{ m}$, the maximum upwelling velocity in the 2AD model is 1.95 m/yr and the ultimate airborne fraction of this "pipeline" model is 86%. This value is considerably higher than the value (66%) for a diffusive model with the same ^{14}C content of subsurface water.

The best estimate of K for the box diffusion model obtained from bomb ^3H and ^{14}C data is reported to be $2.2 \text{ cm}^2/\text{sec}$ (Broecker, Peng, and Engh, 1979), which in our formulation, with a deeper ocean, would be approximately $8800 \text{ m}^2/\text{yr}$. This value of K corresponds to an ultimate airborne fraction of 62% and a ρ'_{so} of 0.88 (see Figure 6). In order to predict the observed airborne fraction of 53%, it would be necessary to include the biota as a small sink, of approximately $(0.62 - 0.53) \times 5 = 0.5 \text{ Gt/yr}$ in size.

If it were believed that the airborne fraction should be corrected for a biota source during the last century (see 2.4.2), the size of this present sink would be further reduced.

For the near future, this 2BD model, with $K = 8800 \text{ m}^2/\text{yr}$, might be quite satisfactory for predictions of atmospheric CO_2 concentration because only the top part of the deep ocean (intermediate water) will be important for uptake of CO_2 , and this choice of K may be realistic for the upper part of the deep ocean. However, the deeper water will dominate as the fossil fuel input slows down relative to continued exponential growth, and the high value of ρ'_{so} predicted by this model (88%) indicates with a high degree of certainty that the deep water is not well modelled. For use during the entire fossil fuel era, it might be better to adjust the mixed layer depth so that the model will have the same response to short time disturbances, such as the present growth in fossil fuel combustion but to preserve the response to long time disturbances by setting K so that ρ'_{so} is 0.84. These responses would be achieved with $K = 4530 \text{ m}^2/\text{yr}$ and $h_m = 201 \text{ m}$.

2.7. MODEL COMPARISON WITH COMBUSTION OF THE TOTAL FOSSIL FUEL RESOURCE

Model predictions of the future behavior of the carbon cycle are of value for model validation in the sense that if substantially different but plausible models agree on a prediction more confidence may then be placed in it. An important reason for developing carbon cycle models is to calculate future atmospheric CO_2 levels, so it is of interest to compare the predictions of several different models with fossil fuel input corresponding to consumption of all of the resource.

We do not here consider the wide range of physical, economic, and socio-political factors that will govern future CO_2 release. Instead, we employ several simple scenarios, labeled by a parameter n , for the release of 10 times the carbon in the pre-industrial atmosphere ($10 \times 615.6 \text{ Gt}$) during the entire fossil fuel era (Figure 13, and Appendix B). We thus attempt to clarify the extent to which differences in predicted atmospheric CO_2 concentrations can be ascribed to differences in the formulation of the ocean models.

The atmospheric response, for the three scenarios of Figure 13, is shown in Figure 14a for the 2BD model and in Figure 14b for the MB model. These calculations have been done numerically with non-linear versions of the models (variable evasion factor).

The responses are relatively insensitive to the exact shape of the input pulse, for pulses short compared to the response time of the deep ocean. The ratio of input pulse height for the that for the $n = 1$ case relative to that for the $n = 0.25$ case is approximately 1.9, but the ratio in maximum response is only about 1.1. The maximum response for the $n = 0.25$ case is delayed about 130 years relative to that for the

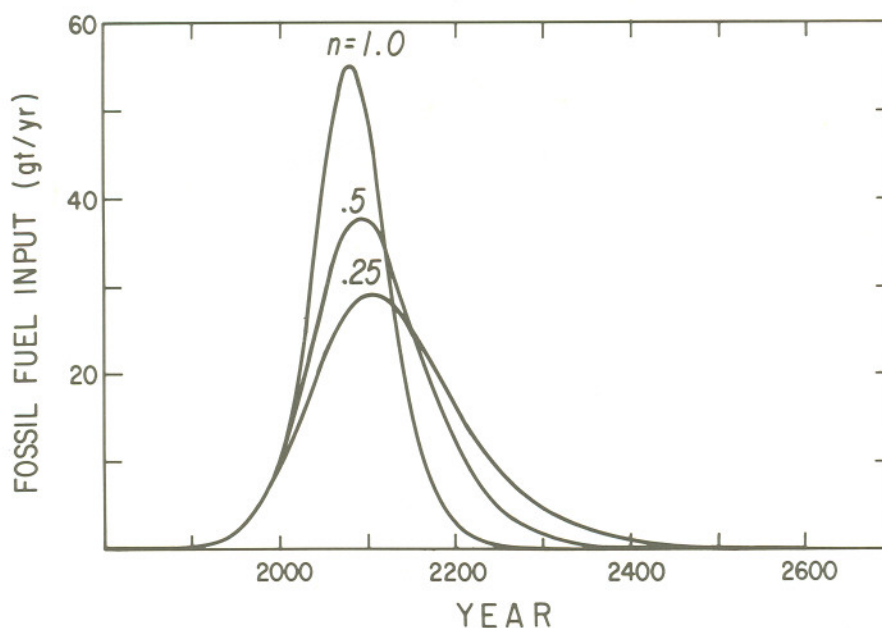


Figure 13: Fossil fuel input scenarios for consumption of all fossil fuel resources, assumed to be 10 times the carbon in the preindustrial atmosphere (10×615.6 Gt). The three scenarios correspond to $n = 1, 0.5$, and 0.25 of the “modified logistic function” described in Appendix B.

$n = 1$ case, but after that time, the atmospheric concentrations are very similar, and the decline to a new equilibrium value is slow, on a time scale determined by the mixing of surface ocean water into the deep ocean.

In Figure 15a–15f, the models compared in the previous section are further compared in their response to the fossil fuel scenario $n = 0.5$ case of Figure 13. For each model, two curves are plotted, the first corresponding to a physical surface ocean layer depth, 75 m (or, for the MB model, a physically realistic value of the parameter T), and the second to a surface layer depth (or T) that would produce the presently observed airborne fraction. All models are consistent with our standard values for ρ'_{mo} and ρ'_{so} .

The two curves in each of Figures 15a–15f are rather close. The difference between each pair is an indication of the uncertainty in prediction due to uncertainty in the amount of intermediate water that is closely coupled to the surface ocean in the corresponding model. The uncertainties are small for two reasons. As DIC increases in the surface ocean layer, the evasion factor increases and tends to exclude CO_2 from the ocean. Thus differences in ocean circulation become less important.

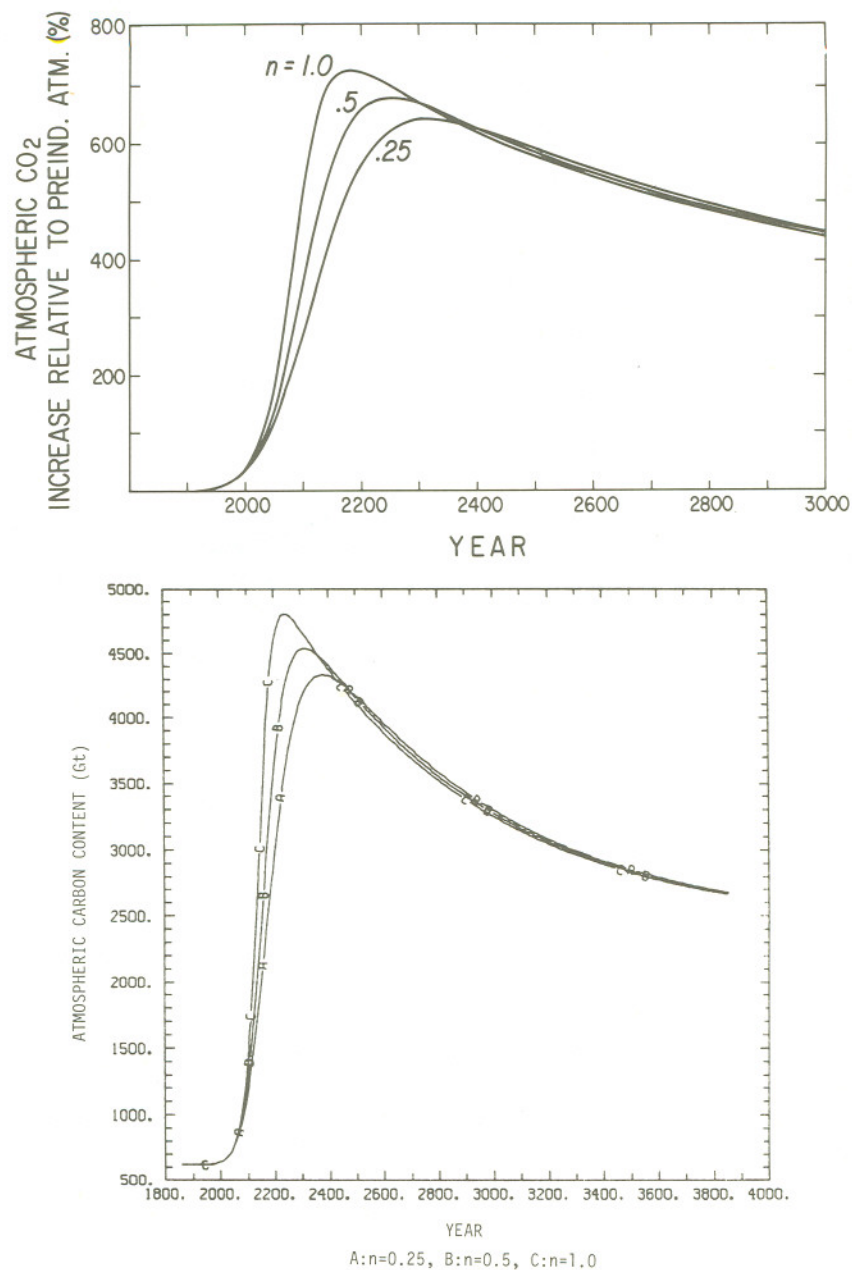


Figure 14: Model atmospheric response to combustion of all fossil fuel resources as indicated by the scenarios in figure 13:

14a. BD model, $h_m = 75$ m and $K = 5020$ m²/yr;

14b. MB model, $T = 10\,000 \cdot 10^{12}$ m³/yr, $P = 0.73$

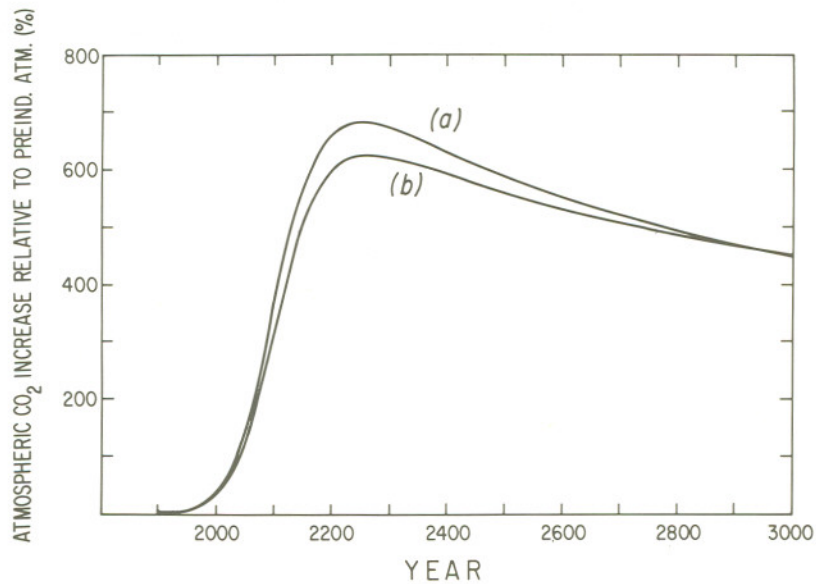
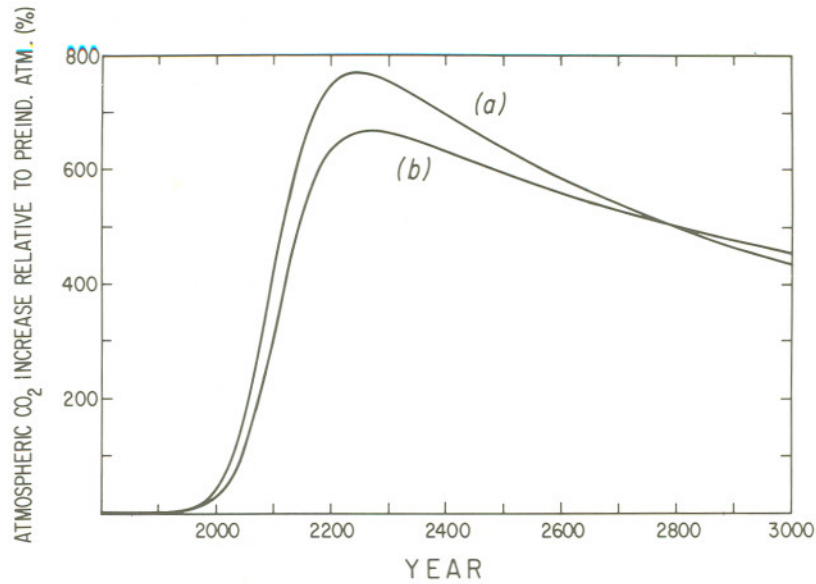
Both models are consistent with $\rho'_{m0} = 0.95$ and $\rho'_{s0} = 0.84$.

Also, when the input slows down relative to the present exponential increase in fossil fuel consumption, the near surface water comes close to equilibrium with the atmosphere, and model atmospheric response is determined largely by the slow turnover time of the deep water, which is better fixed by oceanic ^{14}C data than is the amount of water closely coupled to the surface layer.

The predictions, on the whole, are all quite similar. From the point of view of public policy decisions regarding the use of fossil fuel, the differences are probably not important.

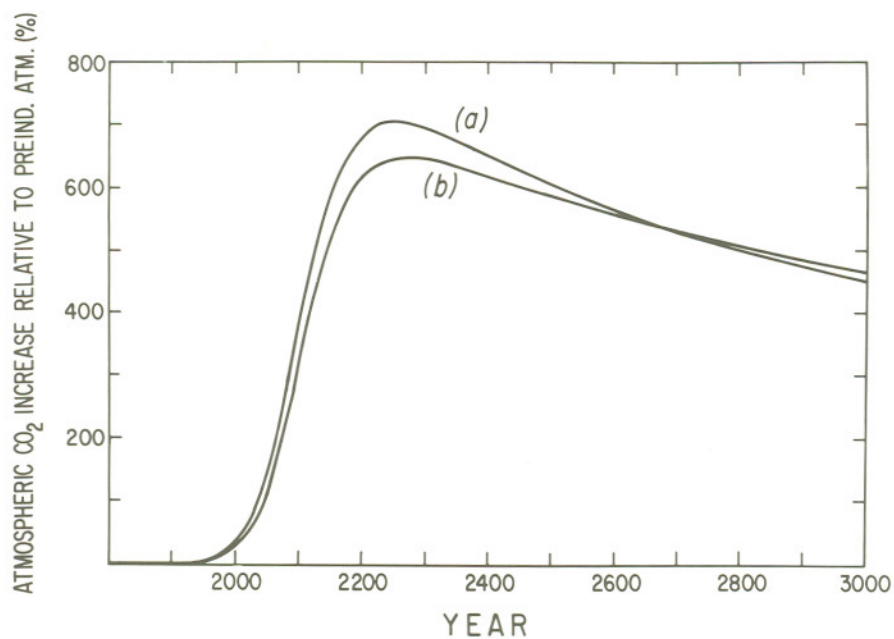
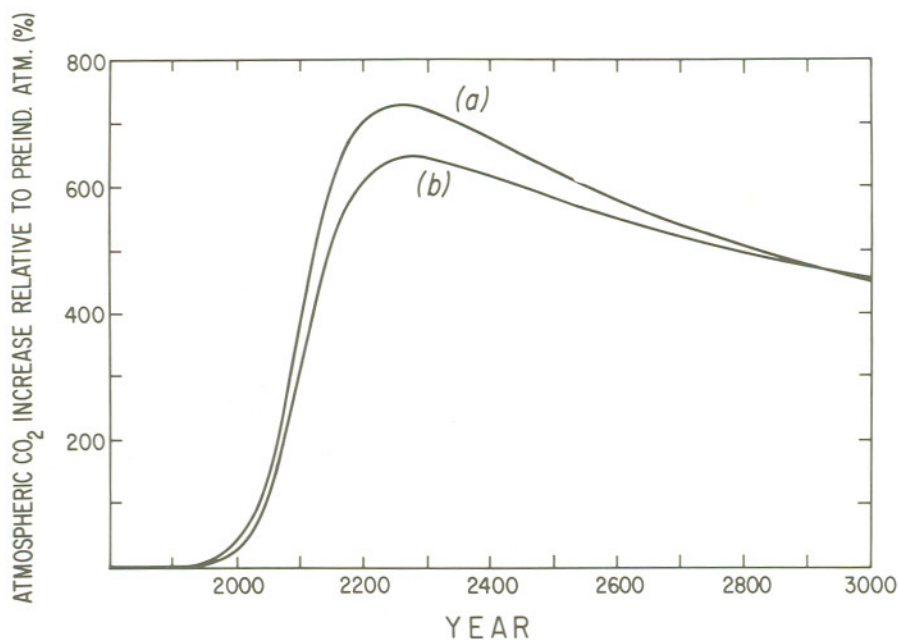
In calculating future CO_2 concentration, we are extrapolating our knowledge of the carbon cycle to a state very different from that presently observed. For example, Figure 16 illustrates that a large portion of the high predicted CO_2 concentration that occurs in future centuries is due to taking into consideration the large predicted increase in the CO_2 evasion factor, ξ , with increasing surface ocean DIC concentration. Although the variation of ξ with DIC is not in doubt for sea water having the chemical attributes assumed in the models, we cannot be sure that some neglected process, such as dissolution of carbonates, will not prove important and change the predicted relation. Also, there exist horizontal inhomogeneities, both between the Atlantic and Pacific, and between high and low latitudes, that are not incorporated in any of the model structures described here. Nevertheless, the similarity between model results is close enough to indicate that, in the absence of unexpected effects, the overall character of the future CO_2 development can be predicted with credibility for a given fossil fuel scenario.

Figures 15a–f: Model atmospheric response to combustion of all fossil fuel resources as in $n = 0.5$ scenario of Figure 13. The two curves in each drawing indicate uncertainty due to uncertainty in the rate of mixing in the upper part of the thermocline: the lower of the two curves is with the depth of the surface layer h_m , or T parameter of the MB model, set so that the model predicts the presently observed airborne fraction; the higher curve is for $h_m = 75$ m, approximately the physical value, or T parameter of the MB model set to a realistic value. The models are:

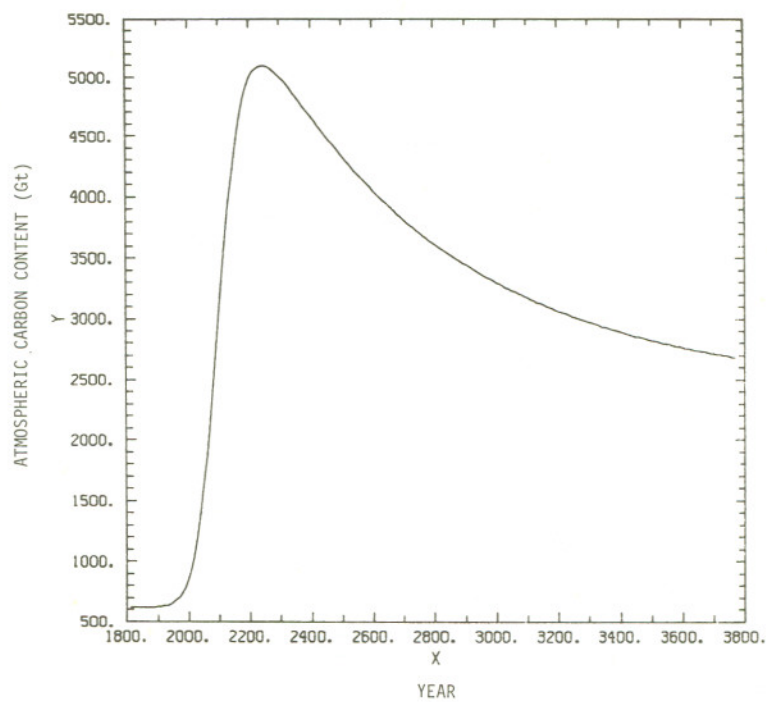
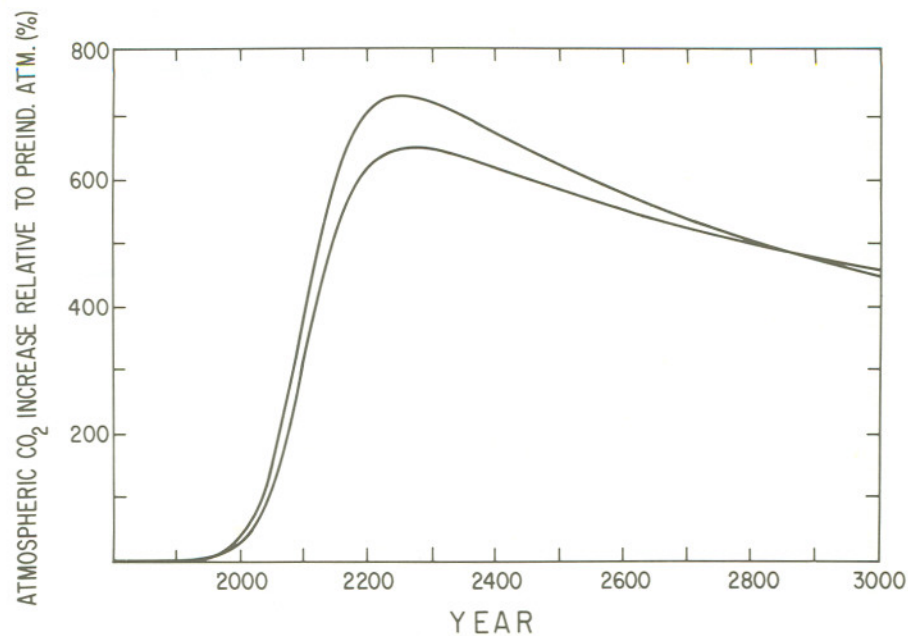


15a. 2B model, (1) $h_m = 75$ m, $k_{dm} = 1/1087$ ($1/1105$) yr^{-1} ; (b) $h_m = 815$ (812) m, $k_{dm} = 1/1370$ ($1/1386$) yr^{-1} ;
 15b. 2BD model, (a) $h_m = 75$ m, $K = 5020$ (4995) m^2/yr ; (b) $h_m = 595$ (595) m, $K = 3250$ (3255) m^2/yr ;

*The parameter values used to generate Figures 15a–15e were read from Figures 5–9 and are approximate; values given in parentheses are more accurately calculated. Curves drawn with the more accurate values would be essentially indistinguishable from those shown.



15c. 3BD model, (a) $h_m = 75$ m, $h_u = 1000$ m, $K = 2850$ (2870) m^2/yr ; (b) $h_m = 660$ (655) m, $h_u = 1000$ m, $K = 2000$ (1978) m^2/yr ;
 15d. 2AD model, (a) $h_m = 75$ m, $w = 1$ m/yr, $K = 3300$ (3288) m^2/yr ; (b) $h_m = 675$ (673) m, $w = 1$ m/yr, $K = 1450$ (1467) m^2/yr ;



15e. 3AD model, (a) $h_m = 75$ m, $h_u = 1000$ m, $w = 1$ m/yr, $K = 2350$ (2339) m^2/yr ; (b) $h_m = 675$ (677) m, $h_u = 1000$ m, $w = 1$ m/yr, $K = 1400$ (1396) m^2/yr ;
 15f. MB model, $T = 1000$ m^3/yr ;

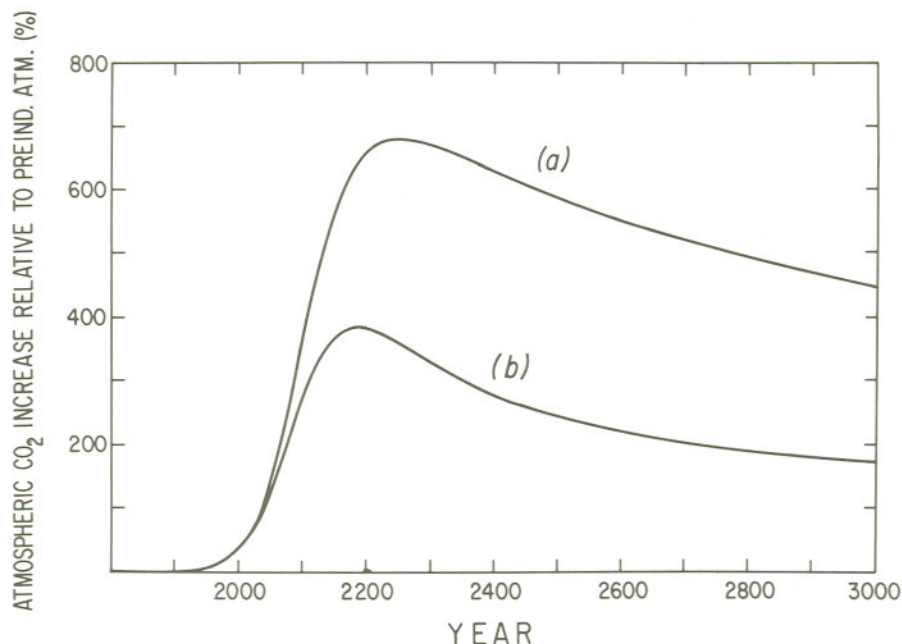


Figure 16 : BD model atmospheric response to combustion of all fossil fuel resources as in $n = 0.5$ scenario of Figure 13: (a) $h_m = 75$ m, $K = 5020$ m²/yr and evasion factor ξ varied with total CO₂ concentration in surface layer; (b) same as (a) but with evasion factor fixed at 9.64.

APPENDIX

A. MODEL EQUATIONS

Equations for carbon-total ($^{12}\text{C} + ^{13}\text{C} + ^{14}\text{C}$) and for ^{14}C in the steady-state in the two-box (2B) ocean model and the box diffusion (2BD) model are given in Sections (a) and (b) below; they are derived and extensively discussed elsewhere (Bolin and Eriksson, 1959; Keeling, 1973a; Oeschger *et al.*, 1975; Keeling, 1979). Equations for the two ocean layers beneath the surface layer in the advective-diffusive (3AD) model are given in Section (c); in Section (d), solutions are found for an exponential input and shown in Section (e) to reduce to simpler models as limiting cases. Use of fractionation corrected ^{14}C data ($\Delta^{14}\text{C}$ values) is discussed in Section (f). Relations are given in Section (g) for isopleths of r_{af} and ρ'_{so} for simple box and advective-diffusive models. In Section (h), equations are given for the multi-box (MB) model and the solution for an exponential input indicated. Since, in our model comparisons, we require that the land biosphere neither increase nor decrease, we have omitted this component of the carbon cycle from the models.

(a) Two-box ocean model

The three reservoirs that we consider in the two-box ocean model (Figure 1) are the atmosphere, the surface ocean, and the deep ocean. Subscripts referring to these reservoirs in the following equations are, respectively, a, m, and d. The symbol N represents the amount of carbon-total in a reservoir. Since ^{14}C is negligible in abundance compared to $^{12}\text{C} + ^{13}\text{C}$, carbon-total amounts are numerically equal to stable carbon amounts. In the atmosphere, N represents carbon-total in the form of CO_2 . In the oceans, several inorganic forms exist, but we consider only their sum, total dissolved inorganic carbon (DIC). Carbon in organic compounds (DOC and POC, see Chapter 3) is not considered. Small n denotes a perturbation in N . The subscript o indicates that the quantity is a preindustrial, steady-state value. The superscript 14 refers to the radioactive isotope ^{14}C . The transfer coefficient from reservoir i to j is k_{ij} , and the isotopic fractionation factor for transfer of ^{14}C from i to j is $^{14}\alpha_{ij}$.

Atmosphere. The rate of change of N_a is

$$\frac{dn_a}{dt} = -k_{am}(N_{ao} + n_a) + k_{ma}(N_{mo} + \xi n_m) + \gamma_a(t) \quad (\text{A.1})$$

The steady-state balance for ^{14}C is

$$0 = -^{14}\alpha_{am}k_{am}^{14}N_{ao} + ^{14}\alpha_{ma}k_{ma}^{14}N_{mo} - \lambda^{14}N_{ao} + ^{14}I_{ao} \quad (\text{A.2})$$

In the above equations, $\gamma_a(t)$ is the stable carbon source from combustion of fossil fuels, $^{14}I_{ao}$ is the natural steady-state ^{14}C source from atmospheric production, λ is the decay constant for ^{14}C ($1/8267 \text{ yr}^{-1}$), and ξ is the evasion factor:

$$\xi = \left(\frac{P_m - P_{mo}}{P_{mo}} \right) / \left(\frac{N_m - N_{mo}}{N_{mo}} \right) \quad (\text{A.3})$$

where P_m is the CO_2 pressure exerted by the surface ocean. The manner of writing (A.1) in terms of a steady-state part and a perturbation part is meant to imply both a steady-state equation and a perturbation equation. For example, the steady-state equation implied by (A.1) is

$$0 = -k_{am}N_{ao} + k_{ma}N_{mo} \quad (\text{A.4})$$

because all the perturbations are assumed to have been zero when γ_a , the fossil fuel stable carbon source, was zero. Equation (A.4) may then be subtracted from (A.1), to give the associated perturbation equation, and then used to eliminate k_{ma} :

$$\frac{dn_a}{dt} = -k_{am}n_a + k_{am}\frac{N_{ao}}{N_{mo}}\xi n_m + \gamma_a(t) \quad (\text{A.5})$$

Surface ocean. Carbon-total perturbation and ^{14}C steady-state equations are:

$$\begin{aligned} \frac{dn_m}{dt} = & k_{am} (N_{ao} + n_a) - k_{ma} (N_{mo} + \xi n_m) \\ & - k_{md} (N_{mo} + n_m) + k_{dm} (N_{do} + n_d) \end{aligned} \quad (\text{A.6})$$

$$\begin{aligned} 0 = & {}^{14}\alpha_{am} k_{am} {}^{14}N_{ao} - {}^{14}\alpha_{ma} k_{ma} {}^{14}N_{mo} \\ & - k_{md} {}^{14}N_{mo} + k_{dm} {}^{14}N_{do} - \lambda {}^{14}N_{mo} \end{aligned} \quad (\text{A.7})$$

Deep ocean. The equations are:

$$\frac{dn_d}{dt} = k_{md} (N_{mo} + n_m) - k_{dm} (N_{do} + n_d) \quad (\text{A.8})$$

$$0 = k_{md} {}^{14}N_{mo} - k_{dm} {}^{14}N_{do} - \lambda {}^{14}N_{mo} \quad (\text{A.9})$$

If the CO_2 evasion factor is assumed constant (a good approximation up to the present time), the response to an assumed exponential input, beginning a long time ago, is obtained by replacing the time derivative operators $\frac{d}{dt}$ by the exponen-

tial time constant μ (see Section (d)). The perturbation equations with an exponential input and the ^{14}C steady-state equations are summarized in Tables A.1 and A.2.

(b) Box diffusion model

The equation for the atmosphere in the box diffusion model is the same as for the atmosphere in the two-box ocean model. A z axis is taken downward with origin at the base of the surface layer. The steady-state concentration in the deep ocean is $C_{do}(z)$ and the perturbation in concentration is $c_d(z)$. The area of the ocean is considered constant and represented by A . The eddy-diffusivity is K . Equations for carbon-total and steady-state ^{14}C are:

Surface ocean

$$\begin{aligned} \frac{dn_m}{dt} = & k_{am} (N_{ao} + n_m) - k_{ma} (N_{mo} + \xi n_m) \\ & + KA \left. \frac{\partial}{\partial z} (C_{do} + c_d) \right|_{(z=0)} \end{aligned} \quad (\text{A.10})$$

$$\begin{aligned} 0 = & {}^{14}\alpha_{am} k_{am} {}^{14}N_{ao} - {}^{14}\alpha_{ma} k_{ma} {}^{14}N_{mo} \\ & + KA \left. \frac{\partial {}^{14}C_{do}}{\partial z} \right|_{(z=0)} - \lambda {}^{14}N_{mo} \end{aligned} \quad (\text{A.11})$$

Table A.1.

	Atmosphere a	Surface Ocean m	Deep Ocean d		Perturbation		Source
Atmo- sphere a	$U_1 + \mu$	$-U_2 \xi$			$\tilde{n}_a$		$\tilde{y}_a$
Surface Ocean m	$-U_1$	$U_2 \xi + U_3 + \mu$	$-U_4$	•	$\tilde{n}_m$	=	
Deep Ocean		$-U_3$	$U_4 + \mu$		$\tilde{n}_d$		

Table A.1. Total carbon perturbation equations for the two-box ocean model and the box diffusion model with exponential fossil fuel input. $y_a(t) = \tilde{y}_a e^{\mu t}$, $n_a(t) = \tilde{n}_a e^{\mu t}$ etc.

Two-box ocean model

$V_1 = \alpha_{am} k_{am}$
 $V_2 = \alpha_{ma} k_{ma}$
 $V_3 = k_{md}$
 $V_4 = k_{dm}$
 $k_{am} h_a = k_{ma} h_m$
 $k_{md} h_m = k_{dm} h_d$

Box-diffusion model

U's are same as two-box ocean model,
except $U_3 = \frac{K \nu}{h_m} \tanh(\nu h_d)$

$U_4 = 0$ where $\nu = \sqrt{\frac{\mu}{K}}$

$k_{am} h_a = k_{ma} h_m$

Table A.2.

	Atmosphere a	Surface Ocean m	Deep Ocean d		Steady State ^{14}C		Source
Atmo- sphere a	$V_1 + \lambda$	$-V_2$			$*N_{ao}$		$*Q_{ao}$
Surface Ocean m	$-V_1$	$V_2 + V_3 + \lambda$	$-V_4$	•	$*N_{ms}$	=	
Deep Ocean d		$-V_3$	$V_4 + \lambda$		$*N_{ds}$		

Table A.2. Steady-state ^{14}C equations for two-box ocean model and box diffusion model.

Two-box ocean model
 $V_1 = \alpha_{am} k_{am}$
 $V_2 = \alpha_{ma} k_{ma}$
 $V_3 = k_{md}$
 $V_4 = k_{dm}$
 $k_{am} h_a = k_{ma} h_m$
 $k_{md} h_m = k_{dm} h_d$

Box diffusion model
V's are same as for
two-box ocean model except
 $V_3 = \frac{K v'}{h_m} (\tanh v' h_d)$
 $V_4 = 0$
where $v' = \sqrt{\frac{\lambda}{K}}$
 $\lambda = 1/8267 \text{ yr}^{-1}$

Deep ocean

$$\frac{\partial c_d}{\partial z} = K \frac{\partial^2}{\partial z^2} (C_{do} + c_d) \quad (A.12)$$

$$0 = K \frac{\partial^2 {}^{14}C_{do}}{\partial z^2} - \lambda {}^{14}C_{do} \quad (A.13)$$

Boundary conditions are

$$(C_{do} + c_d) \Big|_{(z=0)} = \frac{N_{mo} + n_m}{h_m A} \quad (A.14)$$

$${}^{14}C_{do} \Big|_{(z=0)} = \frac{{}^{14}N_{mo}}{h_m A} \quad (A.15)$$

and

$$\frac{\partial (C_{do} + c_d)}{\partial z} \Big|_{(z=h_d)} = 0 \quad (A.16)$$

$$\frac{\partial {}^{14}C_{do}}{\partial z} \Big|_{(z=h_d)} = 0 \quad (A.17)$$

By the methods described below in connection with the advective-diffusive model, perturbation solutions are obtained for an exponential fossil fuel input and summarized in Table A.1. Steady state ${}^{14}C$ solutions are summarized in Table A.2.

(c) Advective-diffusive model

Equations for the atmosphere and surface ocean in the advective-diffusive model are as in the box diffusion model. The transfer of water from the surface ocean to the deep ocean via a “pipeline” does not directly appear in the equations for the surface ocean because water is replaced from the intermediate layer in the same quantity and DIC concentration as enters the pipeline.

Intermediate ocean. A z axis is taken increasing downward with origin at the base of the surface layer. The deep ocean layer then begins at $z = h_u$ (see figure 3). The equations for advective-diffusive transport are

$$\frac{\partial (C_{uo} + c_u)}{\partial t} = K \frac{\partial^2}{\partial z^2} (C_{uo} + c_u) - W \frac{\partial}{\partial z} (C_{uo} + c_u) \quad (A.18)$$

and

$$0 = K \frac{\partial^2}{\partial z^2} {}^{14}\text{C}_{\text{uo}} - W \frac{\partial}{\partial z} {}^{14}\text{C}_{\text{uo}} - \lambda {}^{14}\text{C}_{\text{uo}} \quad (\text{A.19})$$

where W is the water velocity in the positive z direction (downward). Boundary conditions are

$$(\text{C}_{\text{uo}} + \text{c}_u) \Big|_{(z=0)} = \frac{\text{N}_{\text{mo}} + \text{n}_m}{h_m A} \quad (\text{A.20})$$

$${}^{14}\text{C}_{\text{uo}} \Big|_{(z=0)} = \frac{{}^{14}\text{N}_{\text{mo}}}{h_m A} \quad (\text{A.21})$$

$$(\text{C}_{\text{uo}} + \text{c}_u) \Big|_{(z=h_u)} = \frac{\text{N}_{\text{do}} + \text{n}_d}{h_d A} \quad (\text{A.22})$$

$${}^{14}\text{C}_{\text{uo}} \Big|_{(z=h_u)} = \frac{{}^{14}\text{N}_{\text{do}}}{h_d A} \quad (\text{A.23})$$

Deep ocean. Water is assumed always to flow down the pipeline, never up, so

$$-W \geq 0 \quad (\text{A.24})$$

Then

$$\begin{aligned} \frac{dn_d}{dt} = & -KA \frac{\partial(\text{C}_{\text{uo}} + \text{c}_u)}{\partial z} \Big|_{(z=h_u)} + (-WA) \left(\frac{\text{N}_{\text{mo}} + \text{n}_m}{h_m A} \right) \\ & - (-WA) \left(\frac{\text{N}_{\text{do}} + \text{n}_d}{h_d A} \right) \end{aligned} \quad (\text{A.25})$$

$$\begin{aligned} 0 = & -KA \frac{\partial {}^{14}\text{C}_{\text{uo}}}{\partial z} \Big|_{(z=h_u)} + (-WA) \frac{{}^{14}\text{N}_{\text{mo}}}{h_m A} \\ & - (-WA) \frac{{}^{14}\text{N}_{\text{do}}}{h_d A} - \lambda {}^{14}\text{N}_{\text{do}} \end{aligned} \quad (\text{A.26})$$

(d) Advective-diffusive model with exponential input

Equation (A.18) separates into a steady-state equation and a perturbation equation:

$$\frac{\partial c_u}{\partial t} = K \frac{\partial^2 c_u}{\partial z^2} - W \frac{\partial c_u}{\partial z} - \lambda c_u \quad (\text{A.27})$$

With exponential growth in input of CO₂ from fossil fuel combustion, the atmospheric input term in the equations can be written:

$$y_a(t) = \tilde{y}_a e^{\mu t} \quad (\text{A.28})$$

The perturbations then also grow approximately exponentially after several e-fold times, μ^{-1} :

$$c_u(z, t) = \tilde{c}_u(z) e^{\mu t} \quad (\text{A.29})$$

$$n_m(t) = \tilde{n}_m e^{\mu t} \quad (\text{A.30})$$

$$n_d(t) = \tilde{n}_d e^{\mu t} \quad (\text{A.31})$$

In the equations above, $\tilde{y}_a$ and $\tilde{n}_i$ ($i = m$ or d) are constants, and $\tilde{c}_u$ is constant in time. Similar equations exist for $n_a(t)$, and $n_u(t)$ (see Table A.3). Then

$$\mu \tilde{c}_u = K \frac{\partial^2 \tilde{c}_u}{\partial z^2} - W \frac{\partial \tilde{c}_u}{\partial z} - \lambda \tilde{c}_u \quad (\text{A.32})$$

With boundary conditions implied by the perturbation parts of (A.20) and (A.22), the solution is

$$\begin{aligned} \tilde{c}_u = e^{\frac{Wz}{2K}} & [\cosh(vz) - \text{ctnh}(vh_u) \sinh(vz)] \frac{\tilde{n}_m}{h_m A} \\ & + e^{-\frac{W}{2K}(h_u - z)} \frac{\sinh(vz)}{\sinh(vh_u)} \frac{\tilde{n}_d}{h_d A} \end{aligned} \quad (\text{A.33})$$

where

$$v = \frac{\sqrt{W^2 + 4K\mu}}{2K} \quad (\text{A.34})$$

The perturbation in DIC in the intermediate layer is then obtained by the integration:

$$\tilde{n}_u = \int_0^{h_u} A \tilde{c}_u dz \quad (\text{A.35})$$

The result is

$$\begin{aligned} \tilde{n}_u = & \left\{ \nu e^{\frac{Wh_u}{2K}} [\sinh(\nu h_u) - \cosh(\nu h_u) \operatorname{ctnh}(\nu h_u)] \right. \\ & \left. + \frac{W}{2K} + \nu \operatorname{ctnh}(\nu h_u) \right\} \frac{K \tilde{n}_m}{\mu h_m} \\ & + \left\{ -\frac{W}{2K} + \nu \operatorname{ctnh}(\nu h_u) - \nu e^{-\frac{Wh_u}{2K}} \operatorname{csch}(\nu h) \right\} \frac{K \tilde{n}_d}{\mu h_d} \end{aligned} \quad (\text{A.36})$$

The flux from the surface layer to the intermediate ocean layer is required for the DIC balance in the surface layer:

$$\begin{aligned} -KA \left. \frac{\partial \tilde{c}_u}{\partial z} \right|_{(z=0)} &= \left[-\frac{W}{2} + K \nu \operatorname{ctnh}(\nu h_u) \right] \frac{\tilde{n}_m}{h_m} \\ &- K \nu e^{-\left(\frac{Wh_u}{2K}\right)} \operatorname{csch}(\nu h) \frac{\tilde{n}_d}{h_d} \end{aligned} \quad (\text{A.37})$$

Also, the flux from the intermediate layer to the deep ocean is needed for the deep ocean layer DIC balance:

$$\begin{aligned} -KA \left. \frac{\partial \tilde{c}_u}{\partial z} \right|_{(z=h_u)} &= K \nu e^{\left(\frac{Wh_u}{2K}\right)} \operatorname{csch}(\nu h) \frac{\tilde{n}_m}{h_m} \\ &- \left[\frac{W}{2} + K \nu \operatorname{ctnh}(\nu h_u) \right] \frac{\tilde{n}_d}{h_d} \end{aligned} \quad (\text{A.38})$$

The carbon-total perturbation equations are summarized in Table A.3, with $-W$ replaced by w , for convenience since W is always negative. The steady-state ^{14}C equations are of exactly the same form, with μ replaced by λ , and $\tilde{n}_i$ ($i = a, m, u, \text{ or } d$) replaced by $^{14}\text{N}_{i0}$ and γ_a replaced by $^{14}\Gamma_{a0}$. They are summarized in Table A.4.

Table A.3.

	Atmosphere a	Surface Ocean m	Intermediate Ocean u	Deep Ocean d	Perturbation	Source
Atmo- sphere a	$U_1 + \mu$	$-U_2 \xi$			$\tilde{n}_a$	$\tilde{y}_a$
Surface Ocean m	$-U_1$	$U_2 \xi + U_3 + \mu$		$-U_4$	$\tilde{n}_m$	
Inter- mediate Ocean u		$-U_3 + U_5$	μ	$U_4 - U_6$	$\tilde{n}_u$	
Deep Ocean d		$-U_5$		$U_6 + \mu$	$\tilde{n}_d$	

Table A.3. Total carbon perturbation equations for the advective-diffusive model with exponential fossil fuel input. $y_a(t) = \tilde{y}_a e^{\mu t}$, $n_a(t) = \tilde{n}_a e^{\mu t}$ etc.

$$U_5 = -\frac{W}{h_m} + \frac{K\nu}{h_m} e^{\left(\frac{W}{2K} h_u\right)} \operatorname{csch}(\nu h_u)$$

$$U_6 = -\frac{W}{2h_d} + \frac{K\nu}{h_d} \operatorname{ctnh}(\nu h_u)$$

$$\text{where } \nu = \frac{\sqrt{W^2 + 4K\mu}}{2K}$$

$$\begin{aligned} U_1 &= k_{am} \\ U_2 &= k_{ma} \\ k_{am} h_a &= k_{ma} h_m \end{aligned}$$

$$U_3 = -\frac{W}{2h_m} + \frac{K\nu}{h_m} \operatorname{ctnh}(\nu h_u)$$

$$U_4 = \frac{K\nu}{h_d} e^{\left(\frac{W}{2K} h_u\right)} \operatorname{csch}(\nu h_u)$$

Table A.4.

	Atmosphere a	Surface Ocean m	Intermediate Ocean u	Deep Ocean d	Steady State ^{14}C	Source
Atmo- sphere a	$V_1 + \lambda$	$-V_2$			$*N_{ao}$	$*Q_{ao}$
Surface Ocean m	V_1	$V_2 + V_3 + \lambda$		$-V_4$	$*N_{mo}$	
Inter- mediate Ocean u		$-V_3 + V_5$	λ	$V_4 - V_6$	$*N_{uo}$	
Deep Ocean d		$-V_5$		$V_6 + \lambda$	$*N_{do}$	

Table A.4. Steady-state ^{14}C equations for the advective-diffusive model.

$$\begin{aligned} V_1 &= \alpha_{am} k_{am} \\ V_2 &= \alpha_{ma} k_{ma} \\ k_{ma} h_a &= k_{ma} h_m \end{aligned}$$

Other V's are equal to corresponding U's (Table A.3) with $v(\mu)$ replaced by $v(\lambda)$:

$$v(\lambda) = \frac{\sqrt{W^2 + 4K\lambda}}{2K}$$

(e) Limiting cases of the advective-diffusive model

A useful check of the equations for the advective-diffusive model (Table A.3) is to show that they reduce, in appropriate limits, to the box diffusion model (Table A.1), pipeline model, and two-box ocean model (Figure A.1).

Box diffusion model limit: $w \rightarrow 0$ and $h_d \rightarrow 0$. The deep ocean has vanishing capacity as h_d approaches zero. Consequently, the deep ocean equation in Table A.3 becomes

$$-U_5 \tilde{n}_m + U_6 \tilde{n}_d = 0 \quad (\text{A.39})$$

The intermediate ocean equation

$$(-U_3 + U_5) + \mu \tilde{n}_u + (U_4 - U_6) \tilde{n}_d = 0 \quad (\text{A.40})$$

can then be combined with (A.39) so as to eliminate $\tilde{n}_d$:

$$(-U_3 + \frac{U_4 U_5}{U_6}) \tilde{n}_m + \mu \tilde{n}_u = 0 \quad (\text{A.41})$$

The above factor for $\tilde{n}_m$, with w set to zero, is:

$$\begin{aligned} -U_3 + \frac{U_4 U_5}{U_6} &= \frac{K v}{h_m} \left[-\text{ctnh}(v h_u) + \frac{\text{csch}^2(v h_u)}{\text{ctnh}(v h_u)} \right] \\ &= -\frac{K v}{h_m} \tanh(v h_u) \end{aligned} \quad (\text{A.42})$$

Equation (A.41) then becomes

$$-\frac{K v}{h_m} \tanh(v h_u) + \mu \tilde{n}_u = 0 \quad (\text{A.43})$$

in agreement with the box diffusion model, if we now identify the intermediate ocean of the advective-diffusive model with the deep ocean of the box diffusion model. Similarly, the surface ocean equation

$$-U_1 \tilde{n}_a + (U_2 \xi + U_3 + \mu) \tilde{n}_m - U_4 \tilde{n}_d = 0 \quad (\text{A.44})$$

involves the same combination of U 's as in (A.41), after $\tilde{n}_d$ has been eliminated by use of (A.39), and reduces to the corresponding box diffusion model equation in Table A.1.

Pipeline model limit: $K \rightarrow 0$. The limit as K vanishes is easily found for U_3 , U_5 , and U_6 :

$$U_3 \rightarrow \frac{w}{h_m} \quad (\text{A.45})$$

$$U_5 \rightarrow \frac{w}{h_m} \quad (\text{A.46})$$

$$U_6 \rightarrow \frac{w}{h_d} \quad (\text{A.47})$$

where $w = -W$ (see Section (d) above). However, to find the limit for U_4 requires more care because of the interaction between the exponential and hyperbolic cosecant factors. From the definition of U_4 :

$$U_4 = \frac{K}{h_d} e^{\frac{wh_u}{2K}} \left(\frac{2}{e^{\nu h_u} - e^{-\nu h_u}} \right) \quad (\text{A.48})$$

This becomes, after multiplication of numerator and denominator by $e^{-\nu h_u}$, and elimination of ν by substitution from (A.34):

$$U_4 = \frac{\frac{wh_u}{2K} (1 - \sqrt{1 + 4K\mu/w^2})}{h_d (1 - e^{-\sqrt{w^2 + 4K\mu} h_u/K})} e^{\frac{wh_u}{2K}} \quad (\text{A.49})$$

As K becomes small, the exponent in the numerator becomes

$$\frac{wh_u}{2K} \left(-\frac{2K\mu}{w^2} \right) = -\frac{h_u\mu}{w} \quad (\text{A.50})$$

and in the limit

$$U_4 \rightarrow \frac{w}{h_d} e^{-\frac{h_u\mu}{w}} \quad (\text{A.51})$$

The exponential factor in (A.51) represents the time delay as a change in n_d is carried by advection to the surface ocean.

Two-box ocean limit: $K \rightarrow 0$, $h_u \rightarrow 0$. The two-box ocean limit can be obtained from the pipeline model limit by making h_u vanish, and by identifying

$$k_{md} = \frac{w}{h_m} \quad (\text{A.52})$$

and

$$k_{dm} = \frac{w}{h_d} \quad (\text{A.53})$$

This limit corresponds to making both the “penetration depth”, $\sqrt{K/\mu}$, and h_u vanish, but the penetration depth must be required to vanish faster than h_u .

(f) Use of fractionation corrected ^{14}C data

Geochemical ^{14}C data are most often reported in terms of the fractionation corrected isotopic ratio $\Delta^{14}\text{C}$ (see Chapter 3 and references cited there). Fractionation corrections are made through the assumption that ^{14}C fractionation for all chemical processes occurs as the square of ^{13}C fractionation. As one might expect, a good approximation results if the fractionation coefficients $^{14}\alpha_{ij}$ are set to unity in the ^{14}C steady-state equations and ^{14}C quantities are replaced by fractionation corrected quantities. However, errors which could be avoided are introduced into the calculations by this procedure. The more straight forward approach to using $\Delta^{14}\text{C}$ data in modelling would be to convert the $\Delta^{14}\text{C}$ values to true $^{14}\text{C}/\text{C}$ ratios, relative to a standard ratio, but this entails difficulties since necessary data are often not available.

The $\Delta^{14}\text{C}$ value is related to concentration by

$$\Delta^{14}\text{C} = (1 + \delta^{14}\text{C}) \left(\frac{0.975}{1 + \delta^{13}\text{C}} \right)^2 - 1 \quad (\text{A.54})$$

where

$$\delta^{14}\text{C} = \frac{^{14}\text{R}}{^{14}\text{R}_\bullet} - 1 \quad (\text{A.55})$$

and

$$\delta^{13}\text{C} = \frac{^{13}\text{r}}{^{13}\text{r}_\bullet} - 1 \quad (\text{A.56})$$

In the above equations,

$$^{14}\text{R} = \frac{^{14}\text{N}}{\text{N}} \quad (\text{A.57})$$

and

$$^{13}\text{r} = \frac{^{13}\text{N}}{^{12}\text{N}} \quad (\text{A.58})$$

where ^{14}N , ^{13}N , ^{12}N , and N are amounts of ^{14}C , ^{13}C , ^{12}C , and C (carbon-total), respectively, and the subscript $\bullet$ refers to a standard. The ratio $(0.975/(1 + \delta^{13}\text{C}))^2$ is a correction for fractionation relative to a ^{13}C standard state unrelated to the ^{14}C standard. The fractionation correction is based on the assumption that for any two reservoirs that exchange carbon:

$$\frac{{}^{14}\alpha_{ij}}{{}^{14}\alpha_{ji}} = \frac{{}^{14}R_j}{{}^{14}R_i} = \left(\frac{{}^{13}R_j}{{}^{13}R_i}\right)^2 \approx \left(\frac{{}^{13}r_j}{{}^{13}r_i}\right)^2 \quad (\text{A.59})$$

where the difference between ${}^{14}R_j$ and ${}^{14}R_i$ is due only to isotopic fractionation and not, for example, to radioactive decay.

We now introduce fractionation corrected quantities into the ${}^{14}\text{C}$ steady-state equations. In the AD model, the sum of the ${}^{14}\text{C}$ equations in the surface layer and below is (Table A.4):

$$- {}^{14}\alpha_{am}k_{am} {}^{14}N_{ao} + {}^{14}\alpha_{ma}k_{ma} {}^{14}N_{mo} + \lambda({}^{14}N_{mo} + {}^{14}N_{uo} + {}^{14}N_{do}) = 0 \quad (\text{A.60})$$

We define the fractionation corrected ${}^{14}\text{C}$ amount, ${}^{14}N'_{io}$, by

$$(\Delta {}^{14}\text{C})_{io} = \frac{{}^{14}N'_{io}/N_{io}}{{}^{14}R_{\bullet}} - 1 \quad (\text{A.61})$$

in analogy with (A.55). It then follows from (A.54), (A.55), and (A.57) that

$${}^{14}N_{io} = \left[\frac{1 + (\delta^{13}\text{C})_{io}}{0.975} \right]^2 {}^{14}N'_{io} \quad (\text{A.62})$$

In practice, $\delta^{13}\text{C}$, as substituted into (A.54), is measured in a portion of the sample prepared for counting, and thus includes fractionation introduced by the preparation, but in (A.62), $(\delta^{13}\text{C})_{io}$ refers to the reservoir. This is permissible if (A.59) holds for laboratory procedures as well as natural processes, because the ratio $(1 + \delta^{14}\text{C})/(1 + \delta^{13}\text{C})^2$ is then fractionation invariant. Equation (A.60) becomes, after substitution from (A.62)

$$- {}^{14}\alpha_{am}k_{am} [1 + (\delta^{13}\text{C})_{ao}]^2 {}^{14}N'_{ao} + {}^{14}\alpha_{ma}k_{ma} [1 + (\delta^{13}\text{C})_{mo}]^2 {}^{14}N'_{mo} + \lambda \left\{ [1 + (\delta^{13}\text{C})_{mo}]^2 {}^{14}N'_{mo} + [1 + (\delta^{13}\text{C})_{uo}]^2 {}^{14}N'_{uo} + [1 + (\delta^{13}\text{C})_{do}]^2 {}^{14}N'_{do} \right\} = 0 \quad (\text{A.63})$$

Since $(\delta^{13}\text{C})_{uo} \approx (\delta^{13}\text{C})_{do}$, and the first term in braces is small compared to the sum of the second and third terms, the last term in (A.63) is very nearly equal to

$$\lambda [1 + (\delta^{13}\text{C})_{do}]^2 {}^{14}N'_{so}$$

where ${}^{14}N'_{so}$ refers to the ${}^{14}\text{C}$ in DIC in the ocean as a whole, corrected for fractionation:

$${}^{14}N'_{so} = {}^{14}N'_{mo} + {}^{14}N'_{uo} + {}^{14}N'_{do} \quad (\text{A.64})$$

After the introduction of

$$\frac{{}^{14}\alpha_{am}}{{}^{14}\alpha_{ma}} = \frac{[1 + (\delta^{13}C)_{mo}]^2}{[1 + (\delta^{13}C)_{ao}]^2} \quad (A.65)$$

which follows from (A.56) and (A.59), (A.63) simplifies considerably:

$$- {}^{14}\alpha_{ma}k_{am} {}^{14}N'_{ao} + {}^{14}\alpha_{ma}k_{ma} {}^{14}N'_{mo} + {}^{14}\alpha_{md}\lambda {}^{14}N'_{so} = 0 \quad (A.66)$$

where

$${}^{14}\alpha_{md} = [1 + (\delta^{13}C)_{do}]^2 / [1 + (\delta^{13}C)_{mo}]^2 \quad (A.67)$$

Then

$${}^{14}\alpha_{ma}k_{ma} = \frac{{}^{14}\alpha_{md}\lambda(h_s/h_m) \rho'_{so}}{1 - \rho'_{mo}} \quad (A.68)$$

where

$$\rho'_{io} = \frac{R'_{io}}{R'_{ao}} \quad (A.69)$$

$$R'_{io} = \frac{{}^{14}N'_{io}}{N_{io}}. \quad (A.70)$$

In the above two equations, *i* may be replaced by *s*, to represent a total ocean average quantity, in addition to the reservoir indices *a*, *m*, *u*, and *d*. Since the fractionation factor quotient ${}^{14}\alpha_{md}/{}^{14}\alpha_{ma}$ differs from unity by only a few percent, we have omitted it in calculating k_{am} :

$$k_{am} = \frac{\lambda(h_s/h_a)\rho'_{so}}{1 - \rho'_{mo}} \quad (A.71)$$

(g) Isopleths of r_{af} and ρ'_{so} for simple models

The ultimate airborne fraction of carbon-total, with exponential input, r_{af} , is obtained by the solutions to the equations implied by Tables A.1 or A.3 with $\bar{y}_a = 1$:

$$r_{af} = \frac{n_a(t)}{\int y_a(t)dt} = \frac{\bar{n}_a\mu}{\bar{y}_a} \quad (A.72)$$

Penetration depth h_p . For the simplest possible oceanic model, a single well-mixed reservoir ($k_{dm} = 0$ in Table A.1), the ultimate airborne fraction is:

$$r_{af} = \frac{1}{1 + 1/(\frac{\mu}{k_{am}} + \frac{h_a \xi}{h'_m})} \quad (\text{A.73})$$

The ultimate airborne fraction for the 2B model has the same form, but h_m is increased by the addition of a “penetration” depth, $(h_p)_{2B}$:

$$r_{af} = \frac{1}{1 + 1/(\frac{\mu}{k_{am}} + \frac{h_a \xi}{h_m})} \quad (\text{A.74})$$

where

$$h'_m = h_m + (h_p)_{2B} \quad (\text{A.75})$$

and

$$(h_p)_{2B} = \frac{\tilde{n}_d}{\tilde{n}_m} h_m = \left(\frac{k_{dm}}{\mu + k_{dm}} \right) h_d \quad (\text{A.76})$$

Similarly, the ultimate airborne fraction for the 2BD model is of the form (A.74) and (A.75), but with $(h_p)_{2B}$ replaced by $(h_p)_{2BD}$ and

$$(h_p)_{2BD} = \sqrt{\frac{K}{\mu}} \tanh \left(\sqrt{\frac{\mu}{K}} h_d \right) \quad (\text{A.77})$$

With $\mu > 1/100$, these last two expressions simplify to:

$$(h_p)_{2B} \approx \frac{k_{dm}}{\mu} h_d \quad (\text{A.78})$$

$$(h_p)_{2BD} \approx \sqrt{\frac{K}{\mu}} \quad (\text{A.79})$$

For realistic values of k_{dm} ($1/1200 \text{ yr}^{-1}$), h_d (4000 m), K ($5000 \text{ m}^2/\text{yr}$), and μ ($1/22.5 \text{ yr}^{-1}$), equation (A.78) predicts that $(h_p)_{2B} = 75 \text{ m}$, and equation (A.79) predicts that $(h_p)_{2BD} = 335 \text{ m}$. Consequently, for a realistic choice of parameters, the effective surface layer for fossil fuel CO_2 is much deeper in the 2BD model than in the 2B model. Also, the change in the effective surface layer depth, h'_m , with a small change in μ is larger for the 2BD model than for the 2B model. For example, equation (A.78) predicts for the 2B model a 7.5 m change in h_p for a 10% change in μ , while equation (A.79) predicts a change in h_p of approximately 17 m for the 2BD model with this same change in μ .

The ultimate airborne fraction of the advective-diffusive model also is of the form (A.74) and (A.75), but the expression for the penetration depth is more complicated:

$$\begin{aligned}
 (h_p)_{AD} &= \frac{\tilde{n}_u + \tilde{n}_d}{\tilde{n}_m} h_m \\
 &= \frac{w}{2\mu} + h_w \operatorname{ctnh}(vh_u) \\
 &\quad - \frac{h_w e^{\frac{wh_u}{2K}} \operatorname{csch}(vh_u) \left[\frac{w}{\mu} + h_w e^{-\frac{wh_u}{2K}} \operatorname{csch}(vh_u) \right]}{\frac{w}{2\mu} + h_w \operatorname{ctnh}(vh_u) + h_d}
 \end{aligned} \tag{A.80}$$

where

$$h_w \equiv \frac{Kv}{\mu} \tag{A.81}$$

w is the upwelling velocity (m/yr), and v is defined in equation (A.34).

In the limit of vanishing K , the advective-diffusive model becomes a “pipeline” model with penetration depth:

$$(h_p)_p = \frac{w}{\mu} \left(1 - \frac{\frac{w}{\mu} e^{-\frac{h_u \mu}{w}}}{\frac{w}{\mu} + h_d} \right) \tag{A.82}$$

For example, with $w = 1$ m/yr, $\mu = 1/22.5$ yr⁻¹, and $h_u = 1000$ m, equation (A.82) predicts $(h_p)_p \approx w/\mu = 22.5$ m.

Isopleths of ρ'_{so} . Isopleths of ρ'_{so} in figures 5–9 are lines of constant $h'_m(\lambda)/h_s$, where λ is the reciprocal of the mean life of ¹⁴C. This result, for the AD model, follows from

$$\begin{aligned}
 R'_{so} &= (^{14}N'_{mo} + ^{14}N'_{uo} + ^{14}N'_{do})/h_s \\
 &= R'_{mo} \left(h_m + \frac{^{14}N'_{uo} + ^{14}N'_{do}}{^{14}N'_{mo}} h_m \right)
 \end{aligned} \tag{A.83}$$

Because of the symmetry between the ¹⁴C equations and the carbon-total equations with exponential input,

$$\frac{(^{14}N'_{uo} + ^{14}N'_{do})}{^{14}N'_{mo}} h_m = h_p(\lambda) \tag{A.84}$$

Consequently

$$\rho'_{so} = \rho'_{mo} \frac{(h_m + h_p(\lambda))}{h_s} = \rho'_{mo} \frac{h'_m(\lambda)}{h_s} \quad (\text{A.85})$$

This equation applies also to the 2B and BD models.

Isopleths of r_{af} . Isopleths of ultimate airborne fraction in Figures 5–9 are not lines of constant $h'_m(\mu)/h_a$, because of variation of k_{am} (equation A.71)). Isopleths of k_{am} , at constant ρ'_{mo} , are identical to isopleths of ρ'_{so} . Along an isopleth of ρ'_{so} in Figure 5–9, the ultimate airborne fraction depends only on $h'_m(\mu)/h_a$. In general, isopleths of airborne fraction are lines of constant

$$\frac{\lambda}{\mu} \left(\frac{\rho'_{mo}}{1 - \rho'_{mo}} \right) \frac{h'_m(\lambda)}{h_a} + \frac{h'_m(\mu)}{\xi h_a}$$

The question of the surface layer depth for the 2B, BD or AD model which minimizes the airborne fraction while holding ρ'_{so} and ρ'_{mo} constant (see text leading to equation (2.6)) can now be formulated as follows: find h_m such that $h'_m(\mu)$ is as large as possible with $h'_m(\lambda)$ constant. The solution, for $\mu \geq \lambda$, is

$$h_p(\lambda) = h_p(\mu) = 0 \quad (\text{A.86})$$

and

$$h_m = \frac{\rho'_{so}}{\rho'_{mo}} h_s \quad (\text{A.87})$$

i.e. all the ^{14}C is in the surface layer and there is no exchange between this surface layer and deeper water.

(h) Multi-box model

This model consists of a coupled system of well-mixed reservoirs. In the linearized version, the transfer equations can be summarized in the form

$$\frac{d}{dt} \mathbf{N} = \mathbf{A} \mathbf{N} + \mathbf{B} \quad (\text{A.88})$$

where the 13×1 column vector $\mathbf{N}$ denotes the amount of carbon-total in reservoir i , and the 13×13 matrix $\mathbf{A}$ contains the time-constant transfer coefficients (see Table A.5). The constant column vector $\mathbf{B}$ contains non-zero components as a consequence of the buffer factor for sea-to-air transfer being different from unity. For the sake of illustration, if index 11 denotes cold surface water and index 13 denotes the atmosphere, the carbon-total flux $F_{11,13}$ is

$$F_{11,13} = k_{11,13} N_{11,0} + \xi k_{11,13} (N_{11} - N_{11,0}) \quad (\text{A.89})$$

where ξ denotes the time-constant buffer factor, and $N_{11,0}$ is the content of reservoir 11 at steady-state. After rearranging equation (A.89), we can write

$$F_{11,13} = \xi k_{11,13} N_{11} + k_{11,13} (1 - \xi) N_{11,0} \quad (\text{A.90})$$

which shows how the time-constant expression

$$k_{11,13} (1 - \xi) N_{11,0}$$

affects the component B_{13} of column vector $\mathbf{B}$, and, with opposite sign, the component B_{11} . The flux from warm surface water to the atmosphere similarly affects the components B_{12} and B_{13} . The components $B_i, i = 1 \dots, 10$ are zero in the present version of the model.

For the fluxes of ^{14}C we have

$$^{14}F_{ij} = ^{14}\alpha_{ij} \frac{^{14}N_i}{N_i} \quad F_{ij} = \frac{^{14}\alpha_{ij} F_{ij}}{N_i} \quad ^{14}N_i \quad (\text{A.91})$$

In the budget equations for ^{14}C , the transfer terms can therefore be written

$$^{14}\mathbf{A} \quad ^{14}\mathbf{N}$$

where all elements of $^{14}\mathbf{A}$ are equal to their corresponding elements in $\mathbf{A}$, except where the fractionation factor is different from one, or where the ratio F_{ij}/N_i is not a constant. The balance equations for ^{14}C can be written in vector form, analogously to (A.88)

$$\frac{d}{dt} ^{14}\mathbf{N} = ^{14}\mathbf{A} \quad ^{14}\mathbf{N} - \lambda \mathbf{E} \quad ^{14}\mathbf{N} + \mathbf{\Gamma} \quad (\text{A.92})$$

where $\mathbf{E}$ is the unit matrix, and the term $-\lambda \mathbf{E} \quad ^{14}\mathbf{N}$ is a diagonal matrix that denotes the radioactive decay. The atmospheric production of radiocarbon can be denoted symbolically by the column vector $\mathbf{\Gamma}$, which is nonzero only in the component Γ_{13} .

For given values of the parameters T , P and k_{am} (see Chapter 2) we solve the steady-state equation for carbon-total:

$$\mathbf{A} \mathbf{N} = -\mathbf{B} \quad (\text{A.93})$$

Since $\det \mathbf{A} = 0$, the system (A.93) has no unique solution. In the experiments, this was circumvented by replacing one of the 13 equations in (A.93) by the condition

$$N_{13} = 615.6 \text{ Gt} \quad (\text{A.94})$$

Given the matrix $\mathbf{A}$ and the steady-state solution $\mathbf{N}_0$, we determine $^{14}\mathbf{A}$ and solve the steady-state distribution of ^{14}C from Equation (A.92):

$$^{14}\mathbf{N}_0 = - (^{14}\mathbf{A} - \lambda \mathbf{E})^{-1} \mathbf{\Gamma} \quad (\text{A.95})$$

The solution $^{14}\mathbf{N}_0$ is unique except for the arbitrary value of Γ_{13} . The quantity we want to compute, however, is not affected by this:

$$\rho'_{so} = \frac{(\sum_{i=1}^{12} {}^{14}\text{N}'_{i,o})/(\sum_{i=1}^{12} \text{N}'_{i,o})}{{}^{14}\text{N}'_{13,0}/\text{N}'_{13,0}} \quad (\text{A.96})$$

Isopleths for this quantity as a function of T and P are shown in Figure 10.

If the system $\mathbf{N}$ is subjected to an exponentially growing external input into the atmosphere

$$\frac{d}{dt} \mathbf{N} = \mathbf{A} \mathbf{N} + \mathbf{B} + \mathbf{Y} \quad (\text{A.97})$$

where

$$y_{13} = \bar{y}_a e^{\mu t} \quad (\text{A.98})$$

the system will tend towards an asymptotic solution of the form

$$\mathbf{N}_i(t) = \mathbf{N}_{if} e^{\mu t} \quad (\text{A.99})$$

Since $\frac{d\mathbf{N}_i}{dt} = \mu \mathbf{N}_i$ for the asymptotic state, we obtain from (A.97)

$$(\mathbf{A} - \mu \mathbf{E}) \mathbf{N}_f = -\mathbf{B} - \mathbf{Y} \quad (\text{A.100})$$

which gives

$$\mathbf{N}_f = -(\mathbf{A} - \mu \mathbf{E})^{-1} (\mathbf{B} + \mathbf{Y}) \quad (\text{A.101})$$

where $\mathbf{N}_f$ is the column vector that consists of the relative amplitudes $\mathbf{N}_{if}$. Given T and P, we can solve (A.101) and compute the quantity

$$r_{af} = \frac{\text{N}_{13f}}{\sum_{i=1}^{13} \text{N}_{if}} \quad (\text{A.102})$$

Isopleths of this quantity are shown in Figure 10.

Table A.5.

Let the coefficient in row i and column j in matrix A of Equation (A.88) be denoted $A(i, j)$.

The following elements of matrix A are non-zero. (It is assumed that index 11 and 12 denote cold and warm surface water, respectively, and index 13 denotes the atmosphere.)

$$\begin{aligned}
 A(1,1) &= -4.808 * 10^{-6}T - 8.482 * 10^{-3} \\
 A(1,2) &= 9.001 * 10^{-3}P \\
 A(1,11) &= 8.333 * 10^{-5}T \\
 A(2,2) &= -9.001 * 10^{-3}P - 1.701 * 10^{-6}T \\
 A(2,3) &= 8.537 * 10^{-3}P \\
 A(2,11) &= 2.778 * 10^{-5}T \\
 A(3,3) &= -8.537 * 10^{-3}P \\
 A(3,4) &= 6.933 * 10^{-3}P \\
 A(3,11) &= 3.147 * 10^{-2}P \\
 A(4,4) &= -6.933 * 10^{-3}P \\
 A(4,5) &= 5.674 * 10^{-3}P \\
 A(4,11) &= 2.413 * 10^{-2}P \\
 A(5,5) &= -5.674 * 10^{-3}P \\
 A(5,6) &= 4.465 * 10^{-3}P \\
 A(5,11) &= 2.197 * 10^{-2}P \\
 A(6,6) &= -4.465 * 10^{-3}P \\
 A(6,7) &= 3.667 * 10^{-3}P \\
 A(6,11) &= 1.852 * 10^{-2}P \\
 A(7,7) &= -3.667 * 10^{-3}P \\
 A(7,8) &= 2.580 * 10^{-3}P \\
 A(7,11) &= 1.653 * 10^{-2}P \\
 A(8,8) &= -2.580 * 10^{-3}P \\
 A(8,9) &= 2.084 * 10^{-3}P \\
 A(8,11) &= 1.588 * 10^{-2}P \\
 A(9,9) &= -2.084 * 10^{-3}P \\
 A(9,10) &= 1.190 * 10^{-3}P \\
 A(9,11) &= 1.058 * 10^{-2}P \\
 A(10,10) &= -1.190 * 10^{-3}P \\
 A(10,11) &= 7.937 * 10^{-3}P \\
 A(11,1) &= 4.808 * 10^{-6}T \\
 A(11,2) &= 1.701 * 10^{-6}T \\
 A(11,11) &= -1.111 * 10^{-4}T - 0.294P - 7.884 k_{am} \\
 A(11,12) &= 1.47 * 10^{-2}P \\
 A(11,13) &= 0.3333 * k_{am}
 \end{aligned}$$

$$\begin{aligned}
A(12,1) &= 8.482 * 10^{-3}P \\
A(12,11) &= 1.47 * 10^{-1}P \\
A(12,12) &= -1.47 * 10^{-1}P - 7.884 * k_{am} \\
A(12,13) &= 0.6667 * k_{am} \\
A(13,11) &= 7.884 * k_{am} \\
A(13,12) &= 7.884 * k_{am} \\
A(13,13) &= -k_{am}
\end{aligned}$$

The elements in the vector B of Equation (A.88) are zero except for the last three:

$$\begin{aligned}
B(11) &= 1773 k_{am} \quad \text{Gt/yr} \\
B(12) &= 3546 k_{am} \quad \text{Gt/yr} \\
B(13) &= -5319 k_{am} \quad \text{Gt/yr}
\end{aligned}$$

B. NUMERICAL MODEL CALCULATIONS

Numerical models were started in the year A.D. 1800.0, and the input of CO₂ from fossil fuel combustion was either based on reported production (Section (a), below) or a so called "modified logistic function" (Section (b)). The evasion factor was obtained by spline interpolation from values given in Chapter 4. Standard numerical methods were employed: the Runge-Kutta method for box models and an explicit finite difference development for diffusive models.

(a) Production data

We used the production data given by Rotty (this volume), from 1860 to 1978, and the function

$$y_a = 0.092 e^{0.0435(t-1860)} \text{ Gt/yr} \quad (\text{B.1})$$

from 1800 through 1859 (see Keeling, 1973b, p 192), where β_a is the production rate of stable carbon and t is the decimal year (i.e., t is a continuous variable).

(b) Modified logistic function

For scenarios representing combustion of the entire fossil fuel resource, we used

$$y_a = \frac{dQ}{dt} = \mu \left[1 - \left(\frac{Q}{Q_T} \right)^n \right] Q \quad (\text{B.2})$$

where Q is the total amount of stable carbon added to the atmosphere prior to t , Q_T is the total resource, assumed to be 10×615.6 Gt of carbon, and n is a parameter that permits some variation in the scenarios. (See Figure 13).

A convenient feature of (B.2) is that it can be integrated analytically:

$$\int_{Q_0}^Q \frac{dQ}{Q[1 - (\frac{Q}{Q_T})^n]} = \mu \int_{t_0}^t dt \quad (B.3)$$

with the result

$$Q = \frac{Q_0 e^{\mu(t-t_0)}}{\left\{1 + \left(\frac{Q_0}{Q_T}\right)^n [e^{n\mu(t-t_0)} - 1]\right\}^{1/n}} \quad (B.4)$$

where $Q_0 = Q(t_0)$.

For simplicity, we employ (B.2) beginning with 1800.0. The adjustment of the parameters μ , and the initial value of $Q(t)$, $Q_0 = Q(1800.0)$, so that (B.2) approximates the observed production data, could be done in several ways. We have adjusted these parameters so that $Q(1977.0)$ represents an accumulation of 146.95 Gt, in agreement with calculations based on yearly data, and the production rate at the beginning of 1977, $dQ/dt(1977.0)$, equals 5.1505 Gt/yr, the average of the observed production rates for 1976 and 1977.

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