GLOBAL DISTRIBUTIONS OF ATMOSPHERIC CARBON DIOXIDE IN THE FOSSIL-FUEL ERA: A PROJECTION

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Abstract—A model describing latitudinal mixing and accumulation of carbon dioxide in the atmosphere over the entire (projected) fossil-fuel era of human history but in the absence of climatic feedback is developed, including a new formulation of the oceanic sink term based on the tendency of atmospheric concentrations toward chemical and phase equilibrium with carbonic acid reactions in the deep oceans. For a "Gaussian" fuel consumption cycle wherein all potentially recoverable fossil reserves are eventually burned, the model predicts a doubling in global CO₂—above a pre-industrial level of approximately 300 ppm—by the year 2025, and a five-fold increase about 200 y from now. Some latitudinal asymmetry in ambient concentration was found to be generated by anthropogenic sources which predominate in the northern hemisphere at peak emission rates. At most, a difference of some 20 ppm was predicted between the hemispheres, much less than the changes which can be induced in global-mean concentrations by fossil fuel burning over the coming century. While projected increases in CO₂ levels were found to be largely reversible within the next 10 y, they become increasingly less so as the carbonic acid equilibrium of the oceans is shifted. The qualitative effects of climatic feedbacks and the relationship of the present work to a more general model for climatic change are also discussed.

1. INTRODUCTION

It is presently accepted that the burning of carbonaceous fossil fuels since the 19th century industrial revolution has resulted in measurable increases in atmospheric carbon dioxide on a global scale (SCEP, 1970; SMIC, 1971). Moreover, given the present state of energy technology and energy policy in the industrially developed nations this trend is likely to continue for some time, at least, and a growing concern has developed as to its potential consequences for the environment.

This current interest in anthropogenically-generated CO₂ centers on its relationship to the climate. As a strong absorber in the infra-red, the carbon dioxide molecule plays a major role in determining the amount of long-wave radiation from earth reflected back into space and the amount which is retained as heat in the lower atmosphere (the greenhouse effect). The idea that CO₂ levels regulate atmospheric temperatures is not new, having been proposed independently by Chamberlin (1899) and Arrhenius (1903) over 70 y ago. But since then the status of the "climate modification" problem has become much more involved. It is now recognized that the radiative-convective energy balance over (say) a latitude zone is determined by a number of optically active constituents of the atmosphere including water vapor, clouds and aerosols as well as the reflectivity of the underlying surface; and that feedback mechanisms couple temperature and circulation changes induced by variations in these constituents back to the levels and distributions of the constituents themselves (SMIC, 1971). Furthermore, in order to adequately describe these feedbacks it is necessary to account for the exchange of mass and energy between the atmosphere and oceans.
Let us see how this might work in the case of a carbon dioxide increase. It has been estimated that (neglecting a possible compensatory cooling trend by anthropogenic aero-
sol scattering) a doubling of atmospheric CO$_2$ levels would result in a climatologically sig-
nificant increase of a few degrees centigrade in the mean temperature of the troposphere
(Manabe and Wetherald, 1967; Rasool and Schneider, 1971). If this happens, then over a
timescale of hundreds of years—the characteristic time for thermal adjustment of the
joint atmosphere–ocean system (Manabe, 1971)—the oceans too would become somewhat
warmer, tending to drive some of their dissolved carbon dioxide out of solution and also
to raise the absolute humidity of the atmosphere in a globally-averaged sense by increased
evaporation at the air–sea interface. [According to Moller (1963) the atmosphere tends to
maintain a constant relative humidity but absolute humidity goes up with increasing tem-
perature because of the increased saturation vapor pressure of water.] Since both CO$_2$ and
H$_2$O are infra-red absorbers, the mean tropospheric temperature should go up still more,
and so on, until a stable condition obtains.

Now, current estimates indicate a projected lifetime for the fossil-fuel era which is also
of the order of hundreds of years (Hubbert, 1969). Accordingly, the first point to be made
here is that anthropogenically-enhanced CO$_2$ levels are likely to vary over timescales com-
parable to those over which this type of climatic feedback operates. Also, since climate
is governed by atmosphere–ocean dynamics driven by latitudinal imbalances in radiative
absorption, a second point is that latitude variations of optically active constituents like
CO$_2$ might be important in unravelling certain subtleties of climatic feedbacks—see, e.g.
Schneider’s (1972) discussion of the cloudiness feedback. As of about 10 y ago, measure-
ments indicated that atmospheric CO$_2$ concentrations were a few parts per million higher
in the northern hemisphere than in the southern hemisphere (Bolin and Keeling, 1963).
These relatively small perturbations are probably not climatologically significant at pres-
cent, but it can be anticipated that the asymmetry will become more pronounced if the pres-
ent globally lopsided pattern of industrial development persists and emission rates con-
tinue to rise.

The fact is that climatological models capable of predicting the influence of changes in
levels and distributions of CO$_2$ over hundreds of years in a coupled—as opposed to para-
meterized—way do not yet exist. The most ambitious proposals in this direction involve
numerical time-integration in three dimensions of the joint atmosphere–ocean system over
these hundreds of (simulated) years (Manabe, 1971). Because of prohibitive costs, and for
other reasons, it is more likely that climate models will evolve initially along two-dimen-
sional lines, retaining the vertical and latitude variability of the atmosphere and oceans
in a zonally-averaged approximation. This approach has been used with some success to
evaluate various theories of the Ice Ages (MacCracken, 1968). In any event, it seems clear
that long-range projections of CO$_2$ levels and latitude distributions are a key ingredient
of a comprehensive climate model—presumably, to be developed—and it is this aspect of
the larger question which is addressed in this paper.

To first order, such projections do not require an energetically-coupled model but can
be derived from a simpler (no feedback) mass-conservation model for the dispersion and
accumulation of CO$_2$ in the earth’s atmosphere subject to projected emission rates from
fossil fuel burning and incorporating the physically active sinks for this effluent. Nonethe-
less, the conservation of atmospheric CO$_2$ problem is still not entirely straightforward: Car-
bon dioxide is exchanged between reservoirs in the atmosphere, the land and water bios-
pheres, and the oceans; and, while air chemistry is not a factor, there are a number of out-
standing questions relating to the proper formulation of source and sink terms in the conservation equation for atmospheric CO$_2$ because exchange rates across interfaces with other reservoirs, particularly the oceans, can be dominated by nonlinear chemistry within these other reservoirs. A number of prior studies have addressed various aspects of the problem of anthropogenic perturbations of the natural carbon cycle including the work of Bolin and Eriksson (1959), Bolin and Keeling (1963), Machta (1971), Broecker et al. (1971) and Cramer and Meyers (1972). Recently, Keeling (1973) has provided a very detailed review of linear multi-reservoir carbon cycle models. On the other hand, none of the existing perturbed carbon cycle models are entirely satisfactory in the present context for several reasons: (i) they do not extend far enough forward in time; or (ii) they do not include latitude variations; or (iii) they do not include non-linear inter-reservoir effects.

While the model to be developed here is to some extent based on all of the cited prior work we shall endeavor to remove these limitations, proposing in the process a new formulation for the oceanic CO$_2$ sink appropriate to long-range projections. In this regard we shall make use of certain recent thermochemical calculations by Plass (1972) expressing the partial pressure of atmospheric CO$_2$ as a non-linear function of the total amount of carbon dioxide in the atmosphere-ocean system. More generally our modelling efforts will be guided by the currently accepted picture of the terrestrial carbon cycle as described by Rubey (1951), Bolin (1970), Johnson (1970), MacIntyre (1970), Robinson and Robbins (1971) and Butcher and Charlson (1972). We wish to emphasize at the outset that because of the many uncertainties inherent in long-range forecasts of fossil fuel consumption, and other unknowns, the projections of atmospheric CO$_2$ developed here are not intended as predictions per se, but rather as illustrations of the potential effects associated with plausible perturbations of the natural carbon cycle.

2. CONSERVATION OF ATMOSPHERIC CO$_2$

In formulating the model, it is convenient to introduce various definitions and simplifying assumptions, and to consider certain relevant properties of the governing equation, prior to a more detailed discussion of sources and sinks.

Let $X$ be the concentration of atmospheric carbon dioxide expressed as a volumetric mixing ratio in ppm units. It is assumed that $X$, hereafter denoted the zonally-averaged concentration, depends on latitude $\phi$ and time $t$ only, variations with altitude and longitude being subsumed by averages over these directions. Some time-averaging is also implied in our model since no attempt is made to resolve seasonal variations in $X$. These, apparently, are systematic periodic oscillations associated with the biosphere which are superposed on but essentially extraneous to the secular changes we are after here (Junge and Czeplak, 1968; Bolin and Bishof, 1970).

We want to determine how $X(\phi,t)$ develops under the influence of atmospheric transports and an atmospheric CO$_2$ source function $X(\phi,t)$, to be discussed later, as described by the conservation of mass equation for carbon dioxide in the earth's atmosphere. In principle, this equation contains both advective and turbulent diffusive transport terms, but order-of-magnitude arguments can be invoked to show the advective terms are negligible. These follow from the observation that the relevant advective velocity is the net meridional drift velocity of atmospheric mass across latitude lines (since $X$ is uniform in altitude). Because of the virtual cancellation of vertically-integrated mean motion associated with cellular general circulation patterns in the meridional plane, this velocity is only of the order of $v \sim 10^{-1} \text{ cm s}^{-1}$ (Oort and Rasmusson, 1971), much less than the values attained.
locally by meridional winds. In contrast, the latitudinal turbulent diffusion coefficient always has a positive sign, and its zonal and global averages do not generally differ in order-of-magnitude from local values. Furthermore, Junge and Czeplak (1968) in their investigation of seasonal variations found little difference in computed meridional distributions of CO$_2$ when they replaced a variable diffusivity with its (constant) globally-averaged value. We therefore adopt a constant eddy diffusion coefficient here, using the value $K = 3 \times 10^{14}$ cm$^2$ s$^{-1}$ suggested by Bolin and Keeling (1963) in subsequent calculations. The relative importance of advection and turbulent diffusion can now be assessed by comparing their characteristic times for global-scale transport, $\tau_{ad} = a/v$ and $\tau_{diff} = a^2/K$, respectively, where $a = 6.37 \times 10^6$ cm is the earth’s radius. If $\tau_{diff}/\tau_{ad} \ll 1$, then advection is too slow to be important; but with $v = 10^{-1}$ cm s$^{-1}$ and $K = 3 \times 10^{10}$ cm$^2$ s$^{-1}$ we find $\tau_{diff}/\tau_{ad} \simeq 2 \times 10^{-3}$ which clearly satisfies this requirement. Advection can therefore be safely neglected, in which case $X(\phi,t)$ is governed by

$$\frac{\partial X}{\partial t} = \frac{K \cos \phi}{a^2 \cos \phi} \frac{\partial^2 X}{\partial \phi^2} + \dot{X}^A + \dot{X}^N,$$

(1)

where the source function $\dot{X}$ has been resolved into a component $\dot{X}^A$ associated with anthropogenic sources and sinks, and a component $\dot{X}^N$ associated with natural sources and sinks. To solve equation (1) it is necessary to specify the latitudinal distribution of $X$ at some initial time $t_0$, $\int_{\phi} X = X_0(\phi)$, and the boundary conditions for $t > t_0$ at the north and south poles. Because the zonally-averaged latitudinal distributions are axially-symmetric, the boundary conditions are available from the requirement that $\phi$-gradients vanish at the poles: $\mid a \phi = \pm \pi/2; \frac{\partial X}{\partial \phi} = 0$. (2a)

It will prove useful to work with the globally-averaged carbon dioxide concentration denoted here by $\langle X(t) \rangle$, as well as the zonally-averaged (latitude-dependent) concentration $X(\phi,t)$. To compute $\langle X \rangle$ from $X = X(\phi,t)$ it is necessary to account for the fact that the differential mass of CO$_2$ in any latitude zone is proportional to the differential air mass in that zone, as well as the mixing ratio. Suppose $m_{air}$ is the mass of the atmosphere. At any latitude $\phi$ the differential air mass is given very nearly by $\mathrm{dm}_{air} \simeq \int_0^\infty \rho(z)dz \times dS$, where $\rho$ is the altitude ($z$)-dependent air density and $dS = 2\pi a \times \alpha \cos \phi d\phi$ is the differential surface area of the earth at that latitude. Accordingly, the mass-weighted, global-mean concentration can be expressed as $\langle X \rangle = \int X \mathrm{dm}_{air}/m_{air} = \int X dS/S$ where $S = 4\pi a^2$ is the earth’s surface area; therefore:

$$\langle X(t) \rangle = (1/2) \int_{-\pi/2}^{\pi/2} X(\phi,t) \cos \phi \, d\phi.$$

(3)

Similar definitions apply for the globally-averaged source terms $\langle \dot{X}^A(t) \rangle$ and $\langle \dot{X}^N(t) \rangle$.

Variations of $\langle X \rangle$ with time are governed by an ordinary differential equation easily obtained from equation (1) by multiplying it by $\cos \phi$ and integrating the result over $d\phi$ between $+\pi/2$ and $-\pi/2$:

$$\frac{d\langle X \rangle}{dt} = \langle \dot{X}^A \rangle + \langle \dot{X}^N \rangle.$$


Note the cancellation of transportive effects with respect to the global averages. The natural sources and sinks of CO₂, particularly those associated with the reservoir in the ocean surface layer, are generally nonuniformly distributed in latitude but we shall assume, following Bolin and Keeling (1963), that they balance each other out in a globally-averaged sense so that the natural source function vanishes (see also the later discussion in Section 3):

\[
\langle \dot{X}^N \rangle = 0. \tag{4}
\]

This means that changes in \( \langle X \rangle \) are driven by the net globally-averaged anthropogenic source function \( \langle \dot{X}^A \rangle \) only. This term is resolvable further into influx and outflux components,

\[
\langle \dot{X}^A(t) \rangle = \langle \dot{X}_{\text{in}}^A(t) \rangle - \langle \dot{X}_{\text{out}}^A(t) \rangle,
\]

where \( \langle \dot{X}_{\text{in}}^A \rangle \) is the globally-averaged emission rate of carbon dioxide from fossil fuel burning and \( \langle \dot{X}_{\text{out}}^A \rangle \) is the removal rate from the atmosphere, globally-averaged, of anthropogenically-generated CO₂; accordingly,

\[
\frac{d\langle X \rangle}{dt} = \langle \dot{X}_{\text{in}}^A \rangle - \langle \dot{X}_{\text{out}}^A \rangle. \tag{5}
\]

To proceed further it is necessary to consider the space and time variations of the source functions appearing in equations (1 and 5).

3. SOURCES AND SINKS

**Carbon cycle reservoirs**

The terrestrial carbon cycle is characterized by a continuous interchange of carbon atoms in various compounds between four primary reservoirs: the atmosphere, the oceans, the biosphere and the lithosphere. Before man's introduction of fossil fuel burning on a massive scale, the exchange of carbon between these reservoirs was in a state of dynamic equilibrium. In developing our model for perturbations from this state it is useful now to review the properties of these reservoirs affecting sources and sinks of atmospheric CO₂.

In the *atmosphere*, gaseous carbon dioxide is the principal carbon-bearing substance. Here CO₂ is chemically inert and very well mixed in the vertical below the stratosphere at least. As mentioned in section 1 some latitudinal nonuniformities in concentration can be generated by nonsuniform sources at the surface which are not entirely smoothed out by atmospheric transports. The indications are that the preindustrial global-mean CO₂ concentration was 300 ppm or less compared with the present value of about 325 ppm. (Much higher concentrations are likely during the early evolutionary phase of the earth's atmosphere, but analysis of these is beyond the scope of this paper.)

In the *oceans*, carbon dioxide dissolved in seawater reacts rapidly to form a dilute solution of carbonic acid (H₂CO₃) in the form of carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) ions and hydrogen ions (H⁺) according to:

\[
\text{CO}_2(\text{gas}) + \text{H}_2\text{O}(\text{liquid}) \leftrightarrow \text{H}^+ + \text{HCO}_3^-, \tag{6a}
\]

\[
\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}. \tag{6b}
\]
Because a large fraction of dissolved CO$_2$ is transformed into carbonic acid, the oceans absorb much more atmospheric CO$_2$ than they would were the gas nonreactive. The spatial distribution of inorganic carbon—carbon dioxide plus the carbonate and bicarbonate ions—in the sea is controlled primarily by oceanic transport processes, while the partitioning of this inorganic carbon into CO$_2$, CO$_3^-$ and HCO$_3^-$ at any "point" is governed by the temperature-dependent equilibrium constants of equations (6a and b) and the solubility of CO$_2$. Natural oceanic transports tend to distribute inorganic carbon into more or less distinct layers associated with different depth and latitude regimes, a feature which is approximated in multi-reservoir carbon cycle models by assigning these layers to two or three discrete subreservoirs of the ocean. The uppermost subreservoir, in contact with the atmosphere, is a shallow, relatively warm, surface mixed layer some 50–100 m deep. (say) 1/50th the mean depth of the oceans as a whole $h \approx 3800$ m (Sverdrup et al., 1942, p. 15). Broecker et al. (1971) treat the main oceanic thermocline some 1000 m deep as a distinct subreservoir through which inorganic carbon must pass to reach the largest subreservoir in the deep ocean (Fig. 1a), but most authors (Bolin and Eriksson, 1959; Machta, 1971; Cramer and Myers, 1972; Keeling, 1973) have preferred to subsume this intermediate regime into the mixed layer and/or the deep ocean (Fig. 1b). These subreservoirs are viewed as exchanging carbon amongst themselves and with the atmospheric and marine biosphere reservoirs; however each one is treated as internally homogeneous, essentially an instantaneously mixed "box" characterized by a single (average) level of inorganic carbon (see later discussion).

The reaction of calcium ions (Ca$^{2+}$) with CO$_3^-$ to form calcium carbonate at the sea floor via

$$\text{Ca}^{2+} + \text{CO}_3^- \rightleftharpoons \text{CaCO}_3 \quad (7)$$

is an important sink of inorganic carbon over the long (millenia) timescales required for dissolved carbonate ions to come into contact with sedimentary CaCO$_3$ by oceanic circulations. It appears also to play a role as a natural buffering mechanism through which perturbations in the pH of the ocean owing to changes in inorganic carbon are restored to the fairly narrow limits required by marine organisms. However, in assessing the oceanic response to anthropogenic perturbations over the 100-yr timescales of interest here it is appropriate to neglect equation (7) the oceanic carbonate equilibrium of equations (6a and b) (Plass, 1972).

![Fig. 1. Multi-reservoir models of carbon dioxide exchange in the atmosphere-ocean system. (a) Three-layer ocean model of Broecker et al. (1971). (b) Two-layer ocean model assumed here.](image)
The biosphere, which broadly speaking includes all the plants and animals, living and dead, excepting their fossilized remains and organic debris too deeply buried to be susceptible to oxidative attack, is the reservoir of circulating organic carbon. It is conveniently separable into land (or terrestrial) and marine biospheres, each of which is treated somewhat differently in carbon cycle models. Chemically, the key CO$_2$–organic carbon transformation is photosynthesis and its reverse reaction:

$$hv + n\text{CO}_2 + n\text{H}_2\text{O} \Leftrightarrow [\text{CH}_2\text{O}]_n + n\text{O}_2.$$  

(8)

During the lifetime of green plants carbohydrates ($[\text{CH}_2\text{O}]_n$) and molecular oxygen (O$_2$) are formed from sunlight ($hv$), water (H$_2$O) and carbon dioxide (CO$_2$); some fraction of these plant carbohydrates are later ingested by animals along the food chain; but eventually, virtually all of this organically-fixed carbon is reconverted to CO$_2$ by natural oxidation processes: organic decay, respiration and (naturally occurring) combustion—essentially the reverse reaction in equation (8). The “throughput” of the biospheres is relatively large [for the land biosphere alone Keeling (1973) estimates an exchange rate with the atmosphere some 10 times current anthropogenic CO$_2$ emission rates], but because of the steady state the effect of this exchange on perturbations in secular atmospheric carbon dioxide levels is relatively small, and altogether negligible if the reservoir size (or its total biomass) remains constant.

Some authors have speculated that the steady-state biospheric reservoirs would change in size if the availability of different levels of atmospheric CO$_2$ affected photosynthesis rates, or if the amount of vegetation was altered by a shift in the ecological balance. Because the major factors limiting photosynthesis in terrestrial plants are light, water and nutrients, it is unlikely that a greater CO$_2$ concentration in air would cause a substantial rise of photosynthesis rates on land (Broecker et al., 1971). In the marine biosphere photosynthesis takes place primarily in phytoplankton, some of which are eaten by marine animals—primarily zooplankton, but including (eventually) various predator fishes. Again, almost all of this organic carbon gets converted back to CO$_2$ by dissolved oxygen in seawater, but before this happens some unoxidized organic debris settles to the deep ocean regime. As the plankton inhabit the euphotic zone—the zone of sunlight penetration, roughly coincident with the mixed layer—Cramer and Myers (1972), following Bolin (1970), argue that an organic carbon transfer path from the shallow to the deep ocean exists and ought to be accounted for in carbon cycle models. Accordingly, their marine biosphere includes three organic carbon subreservoirs in the mixed layer, one each for phytoplankton, zooplankton and dead organic carbon. Treating mixed-layer plankton as discrete reservoirs of variable size, Cramer and Myers estimated the effect of large decreases in phytoplankton—arising from (say) increased oceanic pollution by pesticides and mercury—on atmospheric CO$_2$ removal rates. In the present model, for simplicity, and because we want to focus on the role of the deep-ocean carbonate equilibrium, carbon transfer from the mixed layer to the deep ocean is treated as a single process which is understood to include both inorganic and organic paths, at constant biomass.

The lithosphere is the carbon reservoir in the earth’s crust gradually accrued from the other reservoirs over geologic time. Ordinarily, the exchange rates with the lithosphere are too slow to include in dynamic carbon cycle models over time-scales of less than millenia. But because these mechanisms have operated for hundreds of millions of years and more, the lithosphere is presently the largest reservoir in the carbon cycle; it contains both inorganic carbon—in the form of sedimentary carbonates created for example by equation
and buried organic debris. The small fraction of organically-fixed carbon leaked from the biosphere, roughly 1 carbon atom in 10000, has accumulated in sedimentary mud and peat bogs in an oxygen-free environment to the point where some $6.8 \times 10^{21}$ g of carbon is presently buried in sedimentary rocks (Rubey, 1951). The part of this lithospheric organic carbon which has taken the form of the fossil fuels—coal, crude oil and natural gas—is the source of the historical and potential carbon cycle perturbations of interest here. Current estimates of fossil fuel reserves vary by a factor of 2 at least, depending on assumptions relating to undiscovered reserves and the economic feasibility of recovering marginal ones. For coal, Hubbert (1969) projects a reserve in the range of $4.3$ to $7.6 \times 10^{12}$ tonnes (1 tonne = 1 metric ton = $10^6$ g). Although crude oil, natural gas and natural gas liquids are more difficult to estimate, Darmstader et al. (1971) quote values ranging from 0.6 to $2.1 \times 10^{12}$ tonnes of coal equivalent for this category, but this does not include their estimates of the world reserve of undiscovered and/or marginal shale oil and oil in bituminous rock, some $3.0 \times 10^{12}$ tonnes equivalent of coal.

For computational purposes we assign the total global fossil fuel reserve at $8.4 \times 10^{12}$ tonnes equivalent of coal, a reasonable value in light of present estimates, particularly if we assume that some of the shale oil is economically recoverable. This fuel, an aggregate of all types, is taken to have an average carbon content of 81 per cent by mass; again, a reasonable average of the 75 per cent for coal and 86 per cent for refined oil used by the authors of SCEP (1970). This gives a total mass of fossil fuel carbon potentially available for burning of $6.8 \times 10^{18}$ g. Since the $\text{CO}_2/\text{C}$ molecular weight ratio is 44/12, if this were actually burned to completion, the anthropogenically-liberated carbon dioxide mass over the entire fossil-fuel era would be

$$m^A_{\text{tot}} \approx 2.5 \times 10^{19} \text{ g.}$$

*Carbon dioxide exchange model for the atmosphere–ocean system*

The conservation equations of Section 2 for atmospheric $\text{CO}_2$ require expressions for the source functions $\dot{X}^N$ and $\dot{X}^A$ which are physically consistent with the reservoir exchanges described above. Assuming the simplest physically plausible case, the land and marine biospheres are taken of constant steady-state size with sources and sinks in balance at all latitudes. The oceanic reservoir is then the critical one governing anthropogenic perturbations of the carbon cycle. Excepting fossil fuel burning itself, exchanges with the lithosphere are too slow to effect the results.

For the oceans a two-layer model (Fig. 1b) is adopted where subscript $m$ denotes properties of the mixed layer and subscript $d$ those of the deep ocean. Thus, including the atmosphere, our carbon cycle has three reservoirs; each of which exchanges $\text{CO}_2$ with its neighbor(s) at finite rates and each of which is generally permitted (zonally-averaged) latitude variations. Vertical distributions are taken as uniform and “instantaneously” attained by vertical mixing; a good approximation in the atmosphere and oceanic mixed layer; and for the deep oceans, simply the most convenient approximation consistent with the fact that the distribution of deep ocean carbon with respect to the time of its entry—that is, its “age” since it was transferred from the atmosphere—has never been deduced from hydrographic or chemical tracer information (Keeling, 1973).

In each of the oceanic reservoirs, denoted generically by subscript $j (j = m,d)$, the partial pressure of $\text{CO}_2$ and the level of inorganic carbon can be related to carbon dioxide concentrations expressed in the same (ppm) units as $X$ in the atmosphere. Since air behaves
very nearly as a perfect gas mixture, the volumetric concentration of CO$_2$ in a parcel of seawater brought to pressure equilibrium at sea level is simply

$$X_j = p(CO_2)_j/p_0 \times 10^b, \quad (ppm)$$

(10)

where $p(CO_2)_j$ is the partial pressure of carbon dioxide in solution and $p_0 = 1$ atm is the sea level air pressure. Also, by Henry's Law the molar concentration of carbon dioxide in each reservoir $[CO_2]_j$ in moles $l^{-1}$ is also related to this partial pressure by

$$[CO_2]_j = \alpha(T_j) \times p(CO_2)_j,$$

(11)

where $\alpha(T_j)$ is the absorption coefficient of CO$_2$ in seawater in moles $l^{-1}$ atm$^{-1}$, a function of the absolute temperature $T_j$ in each layer. The total inorganic carbon level is expressible either as the molar concentration of carbon dioxide plus carbonate and bicarbonate ions,

$$\sum[CO_2]_j \equiv [CO_2]_j + [CO_3^-]_j + [HCO_3^-]_j,$$

(12)

or as a (fictitious) mass density $\rho_j$ potentially available were all the inorganic carbon moles converted to carbon dioxide,

$$\rho_j \equiv M(CO_2) \times \sum[CO_2]_j,$$

(13)

where $M(CO_2) \sim 44$ g mole$^{-1}$ is carbon dioxide's molecular weight.

Because of the rapidity of the carbonic acid reactions it is usual to assume equations (6a and b) in chemical equilibrium at some temperature $T_j$. From chemical thermodynamics it is then possible using the equilibrium constants of these reactions and equations (10–13) to express the carbon dioxide concentrations in terms of the water temperature and inorganic carbon mass (or density) in each layer

$$X_j = X(T_j, \rho_j);$$

(14)

or alternately, the rate of change of $X_j$ with respect to $\rho_j$ for isothermal reactions (Keeling, 1973),

$$\left(\frac{\partial X}{\partial \rho_j}\right)_T = \zeta(T_j, \rho_j) \frac{X_j}{\rho_j},$$

(15)

where $\zeta(T, \rho)$ is the buffer factor. Ordinarily, $\zeta$ increases with increasing temperature and increasing inorganic carbon, both tending toward a saturated solution driving more potential carbon dioxide mass ($\rho_j$) into actual CO$_2$ gas. This is an important consideration for large changes in the oceanic carbon content because the ocean's capacity to assimilate excess carbon dioxide from air as carbonate and bicarbonate ions diminishes as more CO$_2$ is added to the atmosphere–ocean system. However, infinitesimal changes in CO$_2$ for example in the mixed layer ($i = m$) are linearly related to infinitesimal changes in total inorganic carbon by

$$dX_m = \left(\frac{\partial X_m}{\partial \rho_m}\right)_T \rho_m = \zeta X_m \rho_m/d\rho_m.$$

(16)

Here, we will assume this linearity extends to small but finite changes between the mixed layer and the deep oceans when their thermodynamic states are not too different—strictly speaking, when $|X_m - X_m|/X_m, |T_m - T|m|/T_m \ll 1$ (absolute temperatures); that is

$$X_m - X_d \approx \zeta X_m (\rho_m - \rho_d)/\rho_m,$$

(17)
with the buffer factor taken constant. The mixed layer and deep ocean are presumed always to be in near equilibrium in the foregoing sense, but the carbonate equilibrium of each is permitted to shift in the non-linear way symbolized by equation (14) as the inorganic carbon content increases by absorption of anthropogenic CO₂.

Now consider the case when global-mean carbon dioxide levels of all three reservoirs are in equilibrium at the same concentration: \( \langle X_{aq} \rangle = \langle X \rangle = \langle X_m \rangle = \langle X_d \rangle \). Plass (1972) has computed the function (Fig. 2)

\[
\langle X_{aq} \rangle = \langle X \rangle \left( \frac{m_{kO}}{m_k} \right)
\]

where \( \langle T_d \rangle \) is the global-mean deep ocean temperature and

\[
m_{kO} = m_a + \rho d v_m + \rho d v_d.
\]

is the total potential CO₂ mass in the atmosphere ocean system, \( v_m \) being the volume of the mixed layer reservoir, \( v_d \) the volume of the deep ocean and \( m_a \) the mass of carbon dioxide in the atmospheric reservoir. Note from Fig. 1 that \( v_d/v_m \approx 50 \); note also that \( m_a \) is related to the global-mean concentration in air \( \langle X \rangle \) by

\[
m_a = \left( \frac{M(CO_2)m_{air} \times 10^0}{M(air)} \right) \times \langle X \rangle,
\]

where \( M(air) \approx 29 \text{ g mole}^{-1} \) is the molecular weight of air and \( m_{air} \approx 5.136 \times 10^{21} \text{ g} \).
Atmospheric CO₂ in fossil-fuel era (Verniani, 1966) is the mass of the entire atmosphere—the entire mass is used as CO₂ is well-mixed below altitudes containing over 99 per cent of the atmosphere; numerically,

\[ m_a \approx 7.79 \times 10^{15} \times \langle X \rangle, \tag{20} \]

when \( m_a \) is in g and \( \langle X \rangle \) is in ppm.

During the pre-industrial equilibrium, (say) at some initial time \( t = t_0 \), the total potential carbon dioxide mass in the atmosphere–ocean system was about \( m_{CO_2}(t_0) \approx 1.40 \times 10^{20} \) g (Plass, 1972). Assuming a global-mean deep ocean temperature of \( \langle T_d \rangle = 4^\circ C (277^\circ K) \), this corresponds in Plass’ carbonate equilibrium calculations to a pre-industrial CO₂ concentration of \( \langle X_{eq}(t_0) \rangle = \langle X_0 \rangle \approx 300 \) ppm denoted as state (0) in the thermodynamic diagram of Fig. 2. If the oceanic reservoir were altogether absent (or completely saturated, \( \zeta \to \infty \)) and the fossil fuels completely burned, then the effluent would remain in the atmosphere and CO₂ levels would, from equations (9 and 20), increase by

\[ \langle X_{tot}^A \rangle \approx \frac{2.5 \times 10^{19} \text{ g}}{7.79 \times 10^{15} \text{ g/ppm}} \approx 3210 \text{ ppm} \tag{21} \]

giving a total CO₂ level in air of \( \langle X_0 \rangle + \langle X_{tot}^A \rangle \approx 3510 \) ppm, more than 10 times the current value. But because \( \zeta \) is finite the oceans would have to absorb some of this. Post-industrial atmospheric CO₂ levels consistent with the oceanic carbonate equilibrium can be estimated from Plass’ curves by assuming the average deep-ocean temperature remains constant at 4°C (no climatic feedback) while anthropogenic emissions raise the total potential carbon dioxide mass in the system to \( m_{CO_2} = m_{CO_2}(t_0) + m_{tot}^A \approx 1.65 \times 10^{20} \) g over the fossil fuel era. In Fig. 2 it is seen that this corresponds to a concentration of roughly \( \langle X_1 \rangle \approx 1500 \) ppm at the post-industrial state (1), still a large increase from the standpoint of potential climate fluctuations. [If sufficient time is allowed for carbonates formed by equation (7) to come to equilibrium with ocean floor sediments, these anthropogenically-enhanced CO₂ concentrations would drop to about \( \langle X_2 \rangle \approx 700 \) ppm—state (2) of Fig. 2—but this should happen slowly, over thousands of years.]

To describe the time-dependent approach of the air–sea system to carbonate equilibrium we need to model inorganic carbon transfers between oceanic subreservoirs as finite-rate processes. The usual assumption is made here that atmosphere-mixed layer exchanges are sufficiently rapid compared with mixed layer-deep ocean exchanges to justify taking the latter as rate-controlling in CO₂ exchanges between the air and sea as a whole (Bolin and Eriksson, 1959; Machta, 1971; Cramer and Myers, 1972). Also carried over from these multi-reservoir models is the linear transfer rate assumption: that mixed layer-to-deep ocean inorganic carbon transfer rates are directly proportional to mixed layer inorganic carbon mass (say) \( \rho_{ml}v_m \) and inversely proportional to a transfer time \( \tau_{md} \); deep ocean-to-mixed layer transfers being directly proportional to deep ocean inorganic carbon mass \( \rho_d v_d \) and inversely proportional to a (different) transfer time \( \tau_{dm} \). Both \( \tau_{md} \) and \( \tau_{dm} \) are presumed time-invariant and governed physically by oceanic circulations in the mixed layer and deep oceans respectively. The net inorganic carbon mass flux from the mixed layer to the deep oceans \( d(\rho_m v_m)/dT \)—accounting for flow in both directions—is therefore \( \rho_m v_m/\tau_{md} \) less \( \rho_d v_d/\tau_{dm} \); accordingly:

\[ \dot{\rho}_{md} = \frac{d\rho_m}{dt} = \frac{\rho_m}{\tau_{md}} - \frac{\rho_d}{\tau_{dm}} \left( \frac{v_d}{v_m} \right). \tag{22} \]
(Note that our assumption of a constant steady-state size for the marine biosphere means that mixed layer-to-deep ocean organic carbon transfers are exactly cancelled by upwelling CO₂ formed in the deep ocean by oxidation of settled organic debris.)

Being time-invariant \( \tau_{md} \) and \( \tau_{dm} \) can be evaluated at any state for which \( \dot{\rho}_{md} \), \( \rho_{m} \) and \( \rho_d \) are known. In particular, when the oceanic subreservoirs are in equilibrium: \( \dot{\rho}_{md} = 0 \), \( \rho_{m} = \rho_d \) and equation (22) yields

\[
\tau_{md} = (\nu_m/\nu_d)\tau_{dm};
\]

so that in the more general nonequilibrium case equation (25) is expressible as:

\[
\dot{\rho}_{md} = \frac{d\rho_m}{dt} = \frac{\rho_m - \rho_d}{\tau_{md}}.
\]

We can now use the constant inter-reservoir buffer factor approximation, namely equations (16 and 17), in the above to get the net mixed layer-to-deep ocean CO₂ concentration flux:

\[
\dot{X}_{md} \approx \frac{X_m - X_d}{\tau_{md}}.
\]

Note the cancellation of the buffer factor.

It is worth recalling our earlier assumption (common to all multi-reservoir models) that \( X_d \) is depth-averaged and presumed instantaneously to adjust to the depth-averaged values of \( \rho_d \) and \( T_d \) to satisfy the deep ocean carbonate equilibrium, again, in some depth-averaged sense. Vertical stratifications of the deep ocean are conceivably amenable to treatment by a more dimensionally sophisticated model but are excluded here because experimental uncertainties in deep ocean carbon age distributions and intra-reservoir mixing processes appear, at least in the present context, not to warrant this sizable computational task. Because the deep oceans contain almost all the oceanic carbon—over 98 per cent by mass—we assume \( X_d \) is interchangeable with \( X_{eq} \), a depth-averaged CO₂ concentration for carbonate equilibrium in the atmosphere/mixed layer/deep ocean system as a whole whose global mean is given, for example, in Fig. 2. Furthermore, since the mixed layer-to-deep ocean flux \( \dot{X}_{md} \) controls, in other words approximately equals, the net air-to-sea flux \( \dot{X}_{as} \), we can replace the difference \( X_m - X_d \) in equation (24) by \( X - X_{eq} \) to get

\[
\dot{X}_{as} = \frac{X - X_{eq}}{\tau}.
\]

where \( \tau = \tau_{md} = (\nu_m/\nu_d)\tau_{md} \) [see equation (23)] now has the significance of the average lifetime in the atmosphere of a CO₂ molecule prior to its dissolution in the sea. The mixed layer/deep ocean volume ratio \( \nu_m/\nu_d \) cannot be specified too precisely, but values in the range 0.01–0.02 are reasonable (Fig. 1). Together with Bolin and Eriksson’s (1959) estimates of \( \tau_{dm} \approx 500 \) y, this indicates atmospheric CO₂ lifetimes of order \( \tau \approx 5-10 \) y, consistent with independent estimates by Craig (1957; \( \tau \approx 4-10 \) y) and Revelle and Suess (1957; \( \tau \approx 10 \) y) based on the relative abundance of the carbon isotopes C₁₂, C₁₃ and C₁₄ in the atmosphere, biosphere and oceans. Equation (25) provides a physical basis for interpreting the natural source function \( \dot{X}^N \) and the atmospheric outflux component \( \dot{X}_{out}^A \) of the anthropogenic source function.

The natural source function is defined here as the net \( \phi \)-dependent CO₂ emission rate at a global-mean, steady-state (\( \dot{c}/\dot{c}t = 0 \)) concentration \( \langle X^N \rangle \) resulting in some latitude
distribution $X^N(\phi)$ in the absence of anthropogenic emissions ($\dot{X}^A = 0$). From equation (1) $X^N$ is related to $\dot{X}^N$ by

$$\frac{1}{\cos \phi} \frac{d}{d\phi} \left( \cos \phi \frac{dX^N(\phi)}{d\phi} \right) = -\tau_{\text{diff}} \dot{X}^N(\phi),$$

where $\tau_{\text{diff}} = a^2/K \approx 0.43$ y is a characteristic latitudinal diffusion time in the atmosphere. The natural source function in this case can be expressed using equation (25) by recognizing that when $X = X^N$, $\chi_{as} = -X^N$ so that

$$X^N(\phi) = -\frac{X^N(\phi) - X_{eq}(\phi)}{\tau},$$

where $X_{eq}(\phi)$ here is understood to reflect latitude nonuniformities in oceanic CO$_2$ concentration. These have been measured primarily near the surface. For example, Keeling et al. (1965) found latitude variations of more than 100 ppm in the mixed layer of the Pacific Ocean with peak values in tropical waters. This is consistent with the carbonate equilibrium which tends to drive more inorganic carbon into CO$_2$ gas at higher water temperatures. Another factor mitigating toward equatorially high levels of CO$_2$ in water is the relative scarcity of phytoplankton—Sverdrup et al. (1942, p. 941) plot low-latitude total plankton organism measurements in the South Atlantic mixed layer some ten times lower than those at high latitudes—tending, in turn, toward locally diminished CO$_2$ uptake rates by photosynthesis.

Since atmospheric mixing is much faster than air–sea mixing ($\tau/\tau_{\text{diff}} \approx 23 \gg 1$), carbon dioxide concentrations in air $X^N(\phi)$ are much more uniform than those in the water $X_{eq}(\phi)$. The effect of these different distributions with the same global mean driving toward local equilibrium with each other is to create natural sources ($\dot{X}^N > 0$ when $X_{eq} > X^N$) over low latitudes and compensating natural sinks ($\dot{X}^N < 0$ when $X_{eq} < X_{eq} < X^N$) over middle latitudes. It is usually assumed (Bolin and Keeling, 1963) that $\dot{X}^N \rightarrow 0$ at the poles. The intensity of the equatorial natural source can be estimated, for example, by letting: $\Delta X(0) = X_{eq}(0) - X^N(0) \approx 100$ ppm; then with $\tau \approx 5$–10 y equation (26) gives $X^N \approx \Delta X(0)/\tau \approx 10$–20 ppm y$^{-1}$; this must be balanced by the mid-latitude sinks to insure $\langle X^N \rangle = 0$.

Generally, both $\dot{X}^A$ and $\dot{X}^N$ are present; each contributes to the zonal-mean distribution $X = X^A + X^N$, but only $\langle \dot{X}^A \rangle$ can change the global-mean level $\langle X(t) \rangle$. On the other hand, higher global-mean CO$_2$ levels will result in more intense air–sea transfers (in both directions) because of the linear inter-reservoir transfer rate law discussed earlier so $\dot{X}^N$, which reflects the local (latitudinal) imbalance of these more intense transfers, should be affected accordingly. Suppose $\dot{X}^N(\phi,t^*)$ is known at time $t^*$ when $\langle X \rangle = \langle X \rangle^*$. To extrapolate the natural source function to different CO$_2$ levels $\langle X(t) \rangle$ in the presence of $\dot{X}^A$, we assume, plausibly, that the global-mean-normalized concentration deficit $[X^N(\phi,t) - X_{eq}(\phi,t)]/\langle X(t) \rangle$ is a function of the latitude only, equation (26) then implying the scaling law

$$\dot{X}^N(\phi, t) = \frac{\langle X(t) \rangle}{\langle X \rangle^*} \times \dot{X}^N(\phi, t^*).$$

While the natural CO$_2$ source function has never actually been measured, it has been deduced (approximately) from measurements of the latitude distribution of carbon dioxide.

* Note that $\langle X^N \rangle = \langle X_{eq} \rangle$ to insure $\dot{X}^N = 0$ in equation (26) [see equation (4)].
in air \(X(\phi, t^*)\) during the 1957–1963 period, here assigned to the "instant" \(t^* = 1960\) y, by Bolin and Keeling who used equation (1) together with a number of simplifying assumptions to separate out the contributions from fossil fuel burning. Their main assumptions were: (i) a solution to equation (1) at time \(t^*\) for \(X(\phi, t^*)\) exists in the form of a Legendre polynomial \(P_\mu(\mu)\) series expansion in the variable \(\mu = \sin\phi\); (ii) \(\dot{X}^A = 0\) in the southern hemisphere \((-\pi/2 \leq \phi < 0)\); and (iii) \(X^N\) is symmetric about the equator: \(\dot{X}^N(\phi, t^*) = \dot{X}^N(-\phi, t^*)\). In our model, the natural source function at any time \(t\) is described by equation (27) where \(\dot{X}^N(\phi, t^*)\) is obtained from the values plotted in Bolin and Keeling (1963).

Suppose now that owing to anthropogenic perturbations the air–sea system is temporarily disturbed from CO2 equilibrium in a global-mean sense: \(\dot{X} = \dot{X}_{eq}\). Given historical patterns of industrialization and the global distribution of land masses, it is likely that fossil fuel burning will continue to predominate in the northern hemisphere. But because atmospheric mixing is much faster than air–sea mixing it is also plausible to assume the oceanic sink of anthropogenic emissions is and will remain much more spread out than the source (Bolin and Keeling, 1963). Taking the anthropogenic outflux term as uniform in \(\phi\), we have \(X^A_{out}(\phi, t) = \langle \dot{X}^A_{eq} \rangle\), and equation (25) yields

\[
\dot{X}^A_{out}(\phi, t) = \langle \dot{X}^A_{out}(t) \rangle = \frac{\langle X(t) \rangle - \langle X_{eq} \rangle \langle T_d \cdot m_{CO_2}(t) \rangle}{T}.
\]  

(28)

Note that \(\langle \dot{X}^A_{out} \rangle\) is nonzero only when \(\langle X \rangle \neq \langle X_{eq} \rangle\). In our model we estimate \(\langle X_{eq} \rangle\) in terms of the deep-sea mean temperature \(\langle T_d \rangle\) and the potential mass of CO2 in the air–sea system \(m_{CO_2}\), using the carbonate equilibrium graphs of Plass (1972; Fig. 2) but allowing the total carbon dioxide in the system to vary as a function of time according to

\[
m_{CO_2}(t) = n_{CO_2}(t_0) + m^A(t),
\]  

(29)

where \(n_{CO_2}(t_0) \approx 1.4 \times 10^{20}\) g is the pre-industrial value and \(m^A(t)\) is the carbon dioxide mass added to the system up to time \(t\) as described below.

**Anthropogenic source function**

The quantity \(\langle X^A_{tot} \rangle\) is the total amount of carbon dioxide in ppm potentially available by burning all the fossil fuel reserves. Because timescales of interest here are comparable to those projected for producing most of this (see Section 1), it is necessary to specify the anthropogenic influx term \(\dot{X}^A_{in}(\phi, t)\) over the entire fossil fuel era, bearing in mind that the finite fossil reserves impose an integral constraint on this function of the form:

\[
\int \dot{X}^A_{in}(t) \, dt = \langle X^A_{tot} \rangle.
\]  

(30)

The prior behavior of \(\dot{X}^A_{in}(\phi, t)\) can be estimated from historical fossil fuel consumption data, but future trends must be projected according to some scheme which is consistent with equation (30) and plausible in terms of the economics of fuel extraction and consumption.

For example, simple extrapolations of present exponential energy consumption growth rates commonly used in linear carbon cycle models (Bolin and Eriksson, 1959; Keeling, 1973) — i.e. \(\dot{X}^A_{in}(t) \propto \exp(t/\tau_A)\) where \(\tau_A^{-1}\) is the fractional annual growth rate — are inappropriate in the present context since the integral of a growing exponential over all time is infinite while the fossil fuel reserve is clearly bounded.
More likely over the long run is that fossil fuel consumption rates—and therefore anthropogenic carbon dioxide emissions—will follow a "Gaussian" cycle as proposed, for example, by Hubbert (1969). According to this model, present exponential growth rates are only the initial phase of a long-term fossil energy cycle in which consumption rates must eventually level-off as fuel extraction and processing costs go up, decreasing finally to zero as reserves are depleted. This general trend is plausible even accepting the likelihood of cost-competitive energy alternatives some time in the future—nuclear, thermonuclear, solar, etc.—because of the time-lags inherent in the diffusion of these new technologies. But regardless of the actual course of events, the Gaussian cycle projected to fossil-fuel depletion provides a useful limit for exploring “worst case” effects in the anthropogenically-perturbed terrestrial carbon cycle. In this spirit, the time-dependent, global-mean CO₂ influx rate from fossil fuel burning is represented here by the Gaussian function

\[
\langle \dot{X}^A_{\text{in}}(t) \rangle = \frac{\langle X^A_{\text{tot}} \rangle}{\sqrt{2 \pi \sigma}} \exp \left( -\frac{(t - t_m)^2}{2\sigma^2} \right),
\]

where \( \langle X^A_{\text{tot}} \rangle \approx 3210 \text{ ppm} \) from equation (21) and where \( \sigma \) and \( t_m \) are parameters chosen to match CO₂ emission rates over the early part of the fossil fuel cycle where they can be estimated or projected with some realism. Note that \( \langle \dot{X}^A_{\text{in}}(t) \rangle \) as given by equation (31) identically satisfies the integral constraint of equation (30).

Using equation (31) we found the parameter values \( \sigma = 45.7 \text{ y} \) and \( t_m = 2069 \text{ y} \) yielded a rather good fit to anthropogenic CO₂ emission rates in the 1950–1965 period and the rates projected to 1980, where these emission rates were derived in turn from corresponding global fossil fuel consumption rates quoted in Darmstader et al. (1971) by assuming an aggregate 81 per cent carbon mass fraction as before, a CO₂/C molecular weight ratio of 44/12, and the conversion factor: 1 ppm y⁻¹ = 7.79 \times 10^{15} \text{ g(CO₂) y}⁻¹ [see equation (20)]. The resulting curve for \( \langle \dot{X}^A_{\text{in}}(t) \rangle \) is plotted in Fig. 3. It is noteworthy that most of the fuel in this projection (≈ 68 per cent) is burned over a period of \( 2\sigma \approx 91.4 \text{ y} \) centered at the year 2069, consistent with our earlier estimates of a fossil fuel era of the order of 100 y long.

In carbon dioxide mass units, the anthropogenic emission rate is expressible as

\[
\dot{m}^A(t) = \frac{m^A_{\text{tot}}}{\sqrt{2 \pi \sigma}} \exp \left( -\frac{(t - t_m)^2}{2\sigma^2} \right),
\]

where from equation (9) \( m^A_{\text{tot}} \approx 2.5 \times 10^{19} \text{ g} \). Since the CO₂ mass anthropogenically added to the air–sea system up to time \( t \) is

\[
m^A(t) = \int_{-\infty}^{t} \dot{m}^A(\tilde{t}) d\tilde{t},
\]

\( \tilde{t} \) being a dummy variable of integration, the potential carbon dioxide mass in the air–sea system at any time during the fossil fuel era is derivable from the above relations and equation (29) in the form

\[
m_{\text{CO}_2}(t) = m_{\text{CO}_2}(t_0) + \frac{m^A_{\text{tot}}}{2} \left[ 1 + \text{erf} \left( \frac{t - t_m}{\sqrt{2 \sigma}} \right) \right].
\]

Equation (32) is used in our model to determine the carbonate equilibrium concentration \( \langle X_{\text{eq}} \rangle \) in equation (28) as a function of time for those cases where the sea is treated as a finite (nonlinear) reservoir.
The latitude-dependence of the anthropogenic influx term is parameterized here by representing the zonal-mean as the product of its global-mean and a "universal" latitudinal distribution function $\Phi(\phi)$:

$$\dot{X}_{\text{in}}(\phi,t) = \langle \dot{X}_{\text{in}}(t) \rangle \cdot \Phi(\phi);$$

(33)

where from equation (3) $\Phi(\phi)$ satisfies the normalization:

$$\int_{-\pi/2}^{\pi/2} \Phi(\phi) \cos\phi \, d\phi = 2.$$  

(34)

At any latitude, the function $\Phi(\phi)$ is directly proportional to the local (differential) fossil fuel emission rate in CO$_2$ mass units and inversely proportional to the local (differential) air mass

$$dm_{\text{air}} = m_{\text{air}} \times (1/2) \cos\phi \, d\phi$$

which dilutes it (see Section 2). Of course locally, as well as globally, we can take CO$_2$ emissions in mass units proportional to fossil fuel consumption rates, here making use of fuel
consumption data broken down into geographic regions (or latitude zones). For example, if $\frac{d\dot{e}}{d\phi}$ is the fossil fuel consumption rate per unit latitude, $\dot{e} = \int_{-\pi/2}^{\pi/2} (d\dot{e}/d\phi) d\phi$ being the global fuel consumption rate, then

$$\Phi(\phi) = \frac{d\dot{e}/\dot{e}}{dm_{air}/m_{air}};$$

and if, furthermore, the fraction of fossil fuel consumed in a latitude band of width $d\phi$ centered at $\phi$ is defined by

$$f(\phi) \equiv \frac{1}{\dot{e}} \frac{d\dot{e}}{d\phi} \approx \frac{1}{\dot{e}} \frac{\Delta \dot{e}}{\Delta \phi};$$

with the normalization

$$\int_{-\pi/2}^{\pi/2} f(\phi) d\phi = 1, \tag{35}$$

then $\Phi(\phi)$ can be related directly to the latitude distribution of fossil fuel consumption $f(\phi)$ by

$$\Phi(\phi) = \frac{2f(\phi)}{\cos \phi}. \tag{36}$$

Note the recovery of equation (34) when (36) is substituted back into (35).

Implied by equation (33) is that latitude distributions of anthropogenic CO$_2$ emissions are not likely to depart appreciably from historical patterns, the intensity at any latitude then scaling essentially with the global-mean anthropogenic emission rate. Accordingly, contemporary geographic patterns of fossil fuel consumption can be used to estimate $f(\phi)$ and therefore $\Phi(\phi)$. In Fig. 4 we plot the quantity $\Delta \dot{e}/(\dot{e} \Delta \phi)$ as a histogram derived from 1965 fossil fuel consumption figures quoted by Darmstader et al. (1971) for different coun-

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**Fig. 4.** Fraction of global energy consumption per unit latitude versus latitude. The histogram derived from 1965 energy consumption data (Darmstader et al., 1971) is compared with the continuous analytical function $f(\phi)$ used in the present model.
tries by distributing the regional data over discrete $\Delta \phi = 10$-latitude-wide zones. Evidently, consumption rates peak at the middle latitudes of the heavily-industrialized northern hemisphere, but the southern hemisphere contribution is small enough to neglect altogether. Also shown in Fig. 4 is the continuous analytical function $f(\phi)$ used in our model to approximate this distribution for purposes of computing $\Phi(\phi)$ from equation (36). Note that this $f(\phi)$ satisfies the normalization of equation (35).

The relations derived thus far from our model of the sources and sinks of atmospheric carbon dioxide can be summarized as follows: The net, latitudinally-varying, zonal-mean anthropogenic source function $\dot{X}_A(\phi, t) = \dot{X}_A^a(\phi, t) - \dot{X}_A^u(\phi, t)$ is given [from equations (28 and 33)] by

$$\dot{X}_A(\phi, t) = \langle \dot{X}_A^a(\phi, t) \rangle \cdot \Phi(\phi) - \langle \dot{X}_A^u(\phi, t) \rangle$$

with $\Phi(\phi)$ defined above; the net, latitudinally-varying, zonal-mean natural source function $\dot{X}_N(\phi, t)$ by equation (27)—the latter augmented by a tabulation of the Bolin–Keeling function $\dot{X}_N^r(\phi, t^*)$; the global-mean anthropogenic source $\langle \dot{X}_A^a(t) \rangle$ by equation (31) and the global-mean anthropogenic sink $\langle \dot{X}_A^u(t) \rangle$ by equation (28)—the latter (generally) augmented by equation (32) and a tabulation of the carbonate equilibrium curves in Fig. 2 to compute $\langle X_{eq}(t) \rangle$. Having prescribed all the functions appearing in Section 2, we now proceed with the solution of equations (5 and 1) for the globally- and zonally-averaged atmospheric carbon dioxide concentrations in the fossil fuel era.

4. FOSSIL FUEL BURNING EFFECTS ON ATMOSPHERIC CO$_2$: MODEL PROJECTIONS AND DISCUSSION

Globally-averaged concentrations

The time-derivative of global-mean carbon dioxide levels in air given in general terms by equation (5) is now expressible more explicitly with the help of the anthropogenic source and sink functions of equations (31 and 28) as

$$\frac{d\langle X \rangle}{dt} = \langle X_{tot} \rangle \cdot \exp \left( \frac{(t - t_m)^2}{2\sigma^2} \right) + \frac{\langle X_{eq}(t) \rangle - \langle X \rangle}{\tau}.$$  

(38)

As stated in the Introduction, we have neglected the possible feedback of CO$_2$-induced atmospheric temperature changes on the mean temperature of the deep-ocean reservoir, taking this now at a constant, pre-industrial value $\langle T_d \rangle = 4 \, ^\circ C$ over the whole fossil fuel burning era. A general solution of the above differential equation for $\langle X(t) \rangle$ starting from some initial value $\langle X(0) \rangle = \langle X_0 \rangle$ can then be obtained by numerical integration, using equation (32) to find $n_{CO_2}(t)$ and Plass’ carbonate equilibrium curves to find $\langle X_{eq}[\langle T_d \rangle, n_{CO_2}(t)] \rangle$. This approach to the calculation of $\langle X_{eq}(t) \rangle$ allows for the ocean’s finite capacity to assimilate anthropogenic CO$_2$ over the fossil fuel era taking into account its nonlinear buffer properties, and is hereafter called the finite ocean model.

Before discussing the finite-ocean-model solutions, it is instructive to consider the case where the oceans can be treated as “infinite” in their capacity to assimilate CO$_2$ from air. This could, for example, approximate the situation during the early part of the fossil fuel era when the CO$_2$ mass added—$m^4$ in equation (29)—was still sufficiently small compared with the pre-industrial mass in the system $n_{CO_2}(t_0)$ to justify taking $\langle X_{eq} \rangle \approx \langle X_0 \rangle$. Alternatively, we can imagine (fictitious) oceans wherein all the carbon dioxide absorbed at concentration $\langle X_0 \rangle$ is reversibly converted into carbonic acid: $\zeta(\langle X_0 \rangle, \rho) = 0$—such nonbuffered oceans should be distinguished from linearly-buffered oceans where $\zeta$ is constant.
Atmospheric CO$_2$ in fossil-fuel era (Keeling, 1973). But regardless of the physical model, the mathematical approximation $\langle X_{eq} \rangle = \langle X_0 \rangle$ is hereafter called the *infinite ocean* model. With the infinite ocean model, an analytical solution to equation (38) exists, subject to the pre-industrial initial condition $\langle X \rangle = \langle X_0 \rangle$ of the form:

$$
\langle X(t) \rangle = \langle X_0 \rangle + \frac{X_{eq}}{2} \exp \left( -\frac{t + t_m + \sigma^2/(2\tau)}{\tau} \right) \times \left[ 1 + \text{erf} \left( \frac{t - t_m - \sigma^2/\tau}{\sqrt{2\sigma}} \right) \right].
$$

(39)

Because the present atmospheric carbon dioxide levels are still only some 10 per cent above the pre-industrial equilibrium, equation (34) is a useful approximation for calibrating the parameters $\langle X_0 \rangle$ and $\tau$—recall from section 3 their nominal values $\langle X_0 \rangle \sim 300$ ppm, $\tau \sim 5-10$ y, and the anthropogenic source function parameters $X_{eq} = 3210$ ppm, $\sigma = 45.7$ y and $t_m = 2069$ y—from the increase in secular concentrations observed in the recent past. Measurements of atmospheric CO$_2$ have been taken sporadically as far back as the 19th Century (see e.g. the historical data summarized by Callendar, 1958); but the most systematic and accurate data are available after the inauguration of a worldwide monitoring program in the International Geophysical Year of 1957/1958. Figure 5 shows the annually-averaged (secular) carbon dioxide concentrations measured during the 1958–1970 period at various latitudes over the globe by a number of different investigators: Brown and Keeling (1965), Pales and Keeling (1965), Kelly (1969), Bainbridge (1970) and Bolin and Bishof (1970). Also displayed is the increase in global-mean concentration over this period computed with equation (39) by adjusting the parameter values to $\langle X_0 \rangle = 303.8$ ppm, $\tau = 9.5$ y. These serve to pass the concentration curve rather closely through the Mauna Loa, Hawaii, data points believed indicative of global-mean trends. Also, being time-independent, these values are used in the *finite ocean* model calculations as well. Note the systematically higher concentrations by a few parts per million at Barrow, Alaska, compared with the Antarctic data, suggesting that even at present-day
emission rates the northern hemisphere anthropogenic sources are not entirely smoothed out by atmospheric transports.

Evidently, equation (39) gives a reasonably good description of global-mean CO₂ increases measured thus far, but it must become increasingly unrealistic for long-range projections as the equilibrium concentration \( \langle X_{eq}(t) \rangle \) is shifted to many times \( \langle X_0 \rangle \) over the fossil fuel era (Fig. 2). It is nonetheless worth extending the infinite-ocean-model solution over the longer timescales to show the degree-of-irreversibility of variations projected by the more realistic finite ocean model. For this purpose the infinite ocean represents a hypothetical non-buffered deep-sea reservoir which tends always to reversibly restore the anthropogenically-perturbed atmospheric reservoir to its pre-industrial level, \( \langle X_0 \rangle \). The projections of both models over the entire fossil fuel era are compared in Fig. 6, where the solid curve denotes the finite ocean model solution obtained by numerical integration of equation (38), and the dashed curve the infinite ocean model solution of equation (39). The circled area in Fig. 6 covers the period spanned in Figure 5 wherein the projections of the two models are still fairly close; but shortly thereafter they begin to diverge markedly, the difference being almost 30 ppm by the year 2000—367 ppm for the infinite ocean and 395 ppm for the finite ocean model. These values can also be compared with the short-range (in the present context) year 2000 global-mean CO₂ projections of 379 ppm by Machta (1971) and 350 ppm by Cramer and Myers (1972).

In the long run, the difference between the two projections is critical: By definition, the infinite ocean concentration seeks always to equilibrate with \( \langle X_0 \rangle \), the finite ocean concentration with the continuously-shifting \( \langle X_{eq}(t) \rangle \); the latter eventually reaching some 1500 ppm (state 1 of Fig. 2) by the end of the 22nd Century; the difference between the
curves is therefore an indication of the "permanent" or irreversible effect of fossil fuel burning beyond the few hundred year timescales of interest here. But even if sufficient additional time (millenia) were allowed for the calcium carbonates formed in equation (7) to come to equilibrium with sediments at the sea floor, at \( T_a = 4^\circ C \) the anthropogenically-perturbed global-mean concentration would still not return to \( \langle X_n \rangle \simeq 300 \text{ ppm} \) but to \( \langle X_2 \rangle \simeq 700 \text{ ppm} \) (state 2 of Fig. 2).

A number of salient inferences can be drawn from the *finite ocean* model projections which are worth stressing here: (i) Five-fold increases over pre-industrial atmospheric CO\(_2\) levels—larger than any contemporary projections we are aware of—are plausible if all the fossil fuels are burned; (ii) should increases of this magnitude actually occur, their (greenhouse) effect on atmospheric heating would, because of "irreversible" shifts in the carbonate equilibrium, predominate in the long run over climatic changes induced by sunlight-scattering anthropogenic aerosols which typically exist in air over short (~1–10 y) lifetimes before they are reversibly scavenged; (iii) the effect of such atmospheric heating feeding back to higher mean ocean temperatures would be to generate even higher CO\(_2\) levels than those quoted here. Again, the reader is cautioned that these observations are necessarily model-dependent and are offered in a tentative rather than deterministic spirit.

### Zonally-averaged concentrations

Suppose for a moment that the latitude distribution of the *zonally-mean* atmospheric CO\(_2\) concentration at some initial time \( X_0(\phi) \) is known [equation (2a)]. Having specified the net, zonal-mean source functions \( \dot{X}^N(\phi,t) \) and \( \dot{X}^A(\phi,t) \) in Section 3 we have in effect determined all the inputs needed to solve the partial differential for the zonal-mean concentration \( X(\phi,t) \) [equation (1)] subject to the polar symmetry boundary conditions of equation (2b). For example, the latitude distributions of these source functions computed as described in Section 3 and evaluated at \( t^* = 1960 \text{ y} \) are displayed in Fig. 7. Because these are the net natural and anthropogenic source functions we can have \( \dot{X}^N \) and \( \dot{X}^A \) either positive or negative at a given latitude depending on whether the local CO\(_2\) flux is into or out of the atmosphere; but recall that on a global-mean basis these local fluxes cancel out for the natural source function only; the global-mean of the anthropogenic source function being the driving factor behind changes in the global-mean concentration.

To solve equation (1), an explicit (forward-time, centered-space) finite-difference integration scheme was coded for the GISS IBM 360/95 computer, with latitude-increments \( \Delta \phi = 5^\circ \) and time-increments \( \Delta t \) chosen for stability. The preindustrial zonal-mean distribution was found by running the program with the preindustrial natural source function, given by equation (27) as

\[
\dot{X}^N(\phi, t_0) = \frac{\langle X_0 \rangle}{\langle X \rangle^*} \times \langle \dot{X}^N(\phi, t^*) \rangle,
\]

but without anthropogenic sources (\( \dot{X}^A = 0 \)), starting from an arbitrarily-shaped concentration distribution having the pre-industrial global-mean value \( \langle X_0 \rangle = 303.8 \text{ ppm} \) until the solution converged to a steady state, that is, \( X_0(\phi) \). (With anthropogenic sources absent, the global mean concentration necessarily remained constant.) In subsequent runs, the program was always started from this \( X_0(\phi) \) which was assigned to the nominal initial time \( t_0 = 1960 \text{ y} \) when anthropogenic emissions were still negligibly small.

To check mass conservation in the computer program, zonal-mean concentrations \( X(\phi,t) \) were first computed for the *infinite ocean* model where an analytical solution for
Fig. 7. Latitude distributions of the net, zonal-mean natural and anthropogenic source functions, \( X^N(\phi, t^*) \) and \( X^A(\phi, t^*) \), evaluated at \( t^* = 1960 \) y. Numerical values of \( \dot{X}^N(\phi, t^*) \) obtained from the plots in Bolin and Keeling (1963) were adjusted slightly to satisfy \( \dot{X}^N \bigg|_{t^* = 0} = 0 \).

\[ \langle X(t) \rangle \text{ exists. In these tests, the global-mean was computed from } X(\phi, t) \text{ using equation (3), and the results compared with the exact solution of equation (39). Since the two methods of computing } 
\langle X(t) \rangle \text{ were in agreement to four significant figures over the whole fossil fuel era, the finite-difference integration scheme was deemed mass-conservative in an integral sense.}

Finally, we computed the zonal-mean CO₂ latitude distributions over the fossil fuel era with the finite ocean model, the more physically realistic case of interest here. As the computed latitude variations were generally small compared with global-mean values, we have plotted our results as the difference between the zonal- and global-mean concentrations, \( X(\phi, t) - \langle X(t) \rangle \), vs latitude at various times. Fig. 8(a) showing the projections prior to the year 2080 and Fig. 8(b) afterwards. Evidently, this concentration deficit starts symmetrically distributed at the pre-industrial state with an equatorial maximum, becomes progressively more asymmetric as anthropogenic sources build up in the northern hemisphere and reaches a peak in the vicinity of 55° N sometime near the year 2080. As fossil fuel burning diminishes, the local concentrations relax toward a post-fossil-fuel distribution which is symmetrical as before but more intense because of the higher overall level of atmospheric CO₂ (see Fig. 6). Excepting a possibly spurious dip in the Bolin and Keeling (1973) data in Fig. 8(a) at about 18° N: the distributions computed at \( t^* = 1960 \) y are in reasonably good agreement with measurements made during the 1957-1963 period. This is to some extent to be expected because the Bolin–Keeling natural source function was inferred from these measurements in the first place, but it does furnish another check on the internal consistency of the model.
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Fig. 8. Latitude distributions of the concentration deficit $X(\phi,t) - \langle X(t) \rangle$ between zonal- and global-mean values showing the evolution. (a) From the pre-industrial state to $t = 2080$ y. (b) From $t = 2080$ y to the post-fossil-fuel state.

At most, the difference between CO₂ concentrations in the northern and southern hemispheres is some 20 ppm, much less than the variations in global-mean concentration projected over comparable timescales. This is to be expected from the relatively fast latitudinal mixing rates in the atmosphere.

Concluding remarks

In the present work, we have attempted to provide a framework for extrapolation of global- and zonal-mean CO₂ concns in air over the fossil fuel era, a key step in assessing carbon dioxide effects on climate. To this end, an anthropogenic source function was projected corresponding to a time-dependent "Gaussian" fuel consumption cycle where potential reserves are burned to completion and where the present latitudinal source distribution is maintained. The bulk of the paper is taken up with the formulation of expressions for the time and latitude dependence of natural and anthropogenic sources and sinks of atmospheric CO₂, based on the concept that carbonic acid reactions in the deep sea establish the local equilibrium state toward which CO₂ concentrations in air are constantly relaxing.

Our model differs generally from prior work on this problem insofar as we include latitude variations and the recent nonlinear air–sea equilibrium relationships of Plass (1972). Over the long timescales, only the global-mean, perturbed carbon cycle model of Cramer and Myers (1972) offers some basis for comparison. These authors, using a more elaborate sub-reservoir model for intra-ocean transfer, project a peak CO₂ level in air of only 750 ppm by the year 2450, with subsequent decay. The time of their peak can probably be explained by their assumed anthropogenic source function which is much more spread out than our equation (31). But the discrepancy in maximum levels, ours being twice as large, is more serious; arising very likely from certain fundamental differences in the dynamics.
Our model differs specifically from Cramer and Myers' in two basic ways: First, we have taken the marine biosphere at constant steady-state size with its sources and sinks of CO₂ cancelling (on the average) everywhere, while they break this down into a number of organic carbon sub-reservoirs in the mixed layer and deep ocean. Secondly, we have neglected exchange rates with the ocean-floor lithosphere as too slow to affect atmospheric CO₂ over the fossil fuel era, taking the deep-ocean CO₂ level from the carbonic acid equilibrium in terms of the total inorganic carbon (CO₂ + CO₃²⁻ + HCO₃⁻) level in the air-sea system; Cramer and Myers treat CO₂ and ionic carbon (CO₃²⁻ + HCO₃⁻) in the deep oceans as separate species whose concentration (on the average) is governed by separate differential equations driven by transfer rates with the mixed layer and ocean floor, interconversion rates between CO₂ and ionic carbon and (for CO₂) an influx term from deep-ocean oxidation of organic debris. But because the CO₂-ionic carbon conversion rate cancels out in their analysis, so does the deep-ocean carbonate equilibrium, so furthermore, there is no constraint on deep-ocean CO₂ to satisfy the relationship of (say) Fig. 2. We believe it is physically inconsistent to eliminate the carbonate equilibrium between the equations for [CO₂] and [CO₃²⁻ + HCO₃⁻] because this equilibrium is sufficiently "fast" compared with other terms to effectively determine the relative concentrations of these species. Finally, since the equilibrium calculations of Plass (1972) indicate a post-fossil-fuel concentration of about 1500 ppm at Tₐ = 4°C independent of thermodynamic path and therefore the details of intra-ocean carbon transfers, we must differ with Cramer and Myers as to the potential peak levels of atmospheric CO₂.

As we have repeatedly stressed, the present effort is a tentative early phase of a more comprehensive model for climatic change. To address the climatology problem, it is necessary to consider interactions of solar and terrestrial radiation with CO₂ and other optically active constituents, and the feedback from these energy transfers to the dynamics of the atmosphere and oceans. Despite the tentative nature of our projections, the prospect of large, irreversible increases in atmospheric carbon dioxide appears sufficiently plausible to warrant additional study of the climatological implications of man's intervention in the terrestrial carbon cycle.

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REFERENCES
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Chamberlin T. C. (1899) An attempt to frame a working hypothesis of the cause of glacial periods on an atmospheric basis. J. Geology 7, 575, 667, 751.


Chamberlin T. C. (1899) An attempt to frame a working hypothesis of the cause of glacial periods on an atmospheric basis. J. Geology 7, 575, 667, 751.


