

## The Suess Effect: <sup>13</sup>Carbon-<sup>14</sup>Carbon Interrelations

Charles D. Keeling

Scrpps Institution of Oceanography, University of California at San Diego, La Jolla, CA 92093, U.S.A.

The Suess Effect is a term which has come to signify the decrease in <sup>14</sup>C in atmospheric CO<sub>2</sub> owing to admixture of CO<sub>2</sub> produced by the combustion of fossil fuels. This term is here extended, as a concept, to the shifts in isotopic ratio of both <sup>13</sup>C and <sup>14</sup>C in any reservoir of the carbon cycle owing to anthropogenic activities. To explain this generalized Suess Effect a four reservoir global model of the natural carbon cycle is developed in which isotopic fractionation and radioactive decay are fully taken into account. The model includes the cases in which the deep ocean is treated either as a single undifferentiated box model reservoir or is vertically differentiated with eddy diffusion governing the transport of carbon. Also, the governing equations are expressed with sufficient generality to apply simultaneously to both rare isotopes. In so far as possible, the model is expressed without approximation of the isotopic processes even though this leads to non-linear differential equations to describe the rates of change of rare isotopic carbon within carbon reservoirs. Linear approximations are also developed and solved using the method of Laplace transforms. The sensitivity of the predicted Suess Effects to uncertainties in the assigned values of the model parameters is investigated in detail, including estimates of some of the effects of linearizing the governing equations.

The approximation of Stuiver, in which the atmospheric Suess Effect is assumed to be 0.018 times the corresponding effect for <sup>14</sup>C, is examined in detail and shown to arise when both isotopic fractionation and radioactive decay are left out of the model. This approximation, although correct as to order of magnitude, is found to be too imprecise to be recommended in modeling studies.

As found in previous work, the predicted atmospheric Suess Effect for <sup>13</sup>C for a given airborne fraction of industrial CO<sub>2</sub> is of similar magnitude whether the land biosphere has been a net source or sink of carbon during recent times. On the other hand, the corresponding effect for a surface ocean water is considerably smaller than otherwise if the land biosphere has been a source of CO<sub>2</sub> instead of a sink. The model is thus useful in indicating the need to consider isotopes in several reservoirs simultaneously.

Although the emphasis is on formulating models rather than surveying and interpreting data, observational data are summarized and compared with model predictions. The oceanic data are seen to be too meager as yet to help settle the question of biospheric responses to man's activities.

### List of symbols

The numbers in parentheses refer to the first equation in which the symbol appears. Symbols in parentheses denote steady state values. Symbols for chemical elements (e.g. C or Ca) are not listed.

The following algebraic symbols are used:

$A_i$ ,	average area of oceanic reservoir $i$	(8.50)
$A(z)$ ,	area of oceans at depth $z$	(8.49)
$a$ ,	subscript for atmospheric reservoir	(1.2)
$a_{Ca}$ , $a_{CO_3}$ , etc.,	chemical activity of subscripted chemical species	(10.49)
$b$ ,	subscript for land biospheric reser- voir or for an unspecified reservoir in contact with the atmosphere	(2.4)
$C_i$ ( $C_{i0}$ )	abundance of calcium, or calcium and magnesium, in reservoir $i$	(10.3)
$c$ ,	subscript for calcium or biogenic carbonate	(10.15)

$d$ ,	operator for differentiation	(2.4)
$d$ ,	subscript for subsurface ("deep") ocean reservoir	(8.1)
$e$ ,	natural logarithm base	(2.10)
$F$ , ( $F_0$ ),	flux of carbon-total emerging from an unspecified reservoir	(4.1)
$F_{ij}$ , ( $F_{i0}$ , $F_{ij0}$ ),	flux of carbon-total from reservoir $i$ to $j$	(3.2)
$F_{cij}$ ,	same for calcium from oceanic reservoir $i$ to $j$	(10.15)
$*F_{ij}$ , ( $*F_{i0}$ , $*F_{ij0}$ ),	same for <sup>13</sup> C or <sup>14</sup> C	(3.4)
$F_g$ , ( $F_{g0}$ ),	oceanic gravitational flux of carbon-total	(8.1)
$F_{cg}$ , ( $F_{cg0}$ ),	oceanic gravitational flux of carbon-total in the form of carbonate	(10.15)
$F_{pg}$ , ( $F_{pg0}$ ),	same for carbon-total in the form of particulate organic carbon	(10.33)

$f,$	general function with derivations, $f', f'', \dots$	(4.1)	$*n_{i0},$	same for $^{13}\text{C}$ or $^{14}\text{C}$	(2.30)
$g,$	subscript for oceanic gravitational flux	(8.1)	$o,$	subscript for preindustrial steady state	(1.7)
$\mathbf{g},$	special column vector	(9.21)	$P_{\text{CO}_2},$	partial pressure of $\text{CO}_2$	(7.13)
$h_a,$	depth of ocean water containing the same amount of inorganic carbon-total as the atmosphere in preindustrial times	(11.3)	$P_i, (P_{i0})$	partial pressure of $\text{CO}_2$ in reservoir $i$	(7.3)
$h_i,$	depth of oceanic layer $i$ below sea surface	(8.49)	$*P_i, (*P_{i0})$	same for $^{13}\text{C}$ or $^{14}\text{C}$	(7.26)
$i,$	general subscript	(1.1)	$p,$	subscript for particulate organic carbon	(10.33)
$J(z, t),$	rate of regeneration of inorganic carbonate-total from particulate organic carbon and biogenic carbonate at depth $z$ in subsurface ocean water per unit volume at time $t$	(8.49)	$Q,$	cumulative production of industrial $\text{CO}_2$ in units of carbon-total	(1.8)
$j,$	second general subscript	(1.6)	$q(z, t),$	concentration of carbon-total at depth $z$ in the oceans at time $t$	(8.51)
$k,$	steady state transfer coefficient for carbon-total for the flux emerging from an unspecified reservoir	(4.5)	$R,$	$^{13}\text{C}/\text{C}$ or $^{14}\text{C}/\text{C}$ ratio of an unspecified chemical	(11.27)
$\mathbf{k},$	matrix of perturbation transfer coefficients	(9.12)	$R_i,$	$^{13}\text{C}/\text{C}$ or $^{14}\text{C}/\text{C}$ ratio of carbon in reservoir $i$	(1.1)
$k_{i0}$	( $i = 1$ to 6) perturbation transfer coefficient for carbon-total for reservoir $i$	(5.6)	$R_f,$	$^{13}\text{C}/\text{C}$ or $^{14}\text{C}/\text{C}$ ratio of industrial $\text{CO}_2$ (zero for $^{14}\text{C}$ )	(1.12)
$*k_{i0}$	( $i = 1$ to 6) same for $^{13}\text{C}$ or $^{14}\text{C}$	(6.19)	$R_{\bullet},$	standard $^{13}\text{C}/\text{C}$ or $^{14}\text{C}/\text{C}$ ratio	(1.24)
$k_i',$	( $i = 7$ to 10) virtual source coefficient for reservoir $i$	(6.19)	$R_{\gamma i},$	average $^{13}\text{C}/\text{C}$ or $^{14}\text{C}/\text{C}$ ratio of the sum of all external sources of carbon-total to reservoir $i$	(6.18)
$k_{ij},$	steady state transfer coefficient for carbon-total from reservoir $i$ to $j$	(2.4)	$r_i,$	fraction of industrial $\text{CO}_2$ residing in reservoir $i$	(1.8)
$*k_{ij},$	same from $^{13}\text{C}$ or $^{14}\text{C}$	(6.2)	$\mathbf{r},$	column vector of $r_i$ and $*r_i R_{i0}/R_{a0}$	(9.24)
$K,$	oceanic vertical eddy diffusion coefficient	(8.51)	$*r_i,$	rate of change in abundance of rare isotopic carbon in reservoir $i$ relative to rate of industrial $\text{CO}_2$ input multiplied by preindustrial isotopic ratio of reservoir $i$ chemical	(1.14)
$K_{i0}$	( $i = 0, 1,$ or $2$ ) thermodynamic equilibrium quotients of carbonic acid in sea water	(7.11-13)	$\mu,$	standard $^{13}\text{C}/^{12}\text{C}$ or $^{14}\text{C}/^{12}\text{C}$ ratio	(11.33)
$K_{\text{CaCO}_3},$	same for solid $\text{CaCO}_3$ , respectively	(10.49,50)	$\mu_{\bullet},$	theoretical Suess Effect of reservoir $i$	(1.7)
$K_{\text{MgCO}_3},$	$\text{MgCO}_3$	(10.49,50)	$S_i,$	observed Suess Effect of reservoir $i$ at time $t_j$	(1.6)
$K_{sp},$	solubility product for calcium carbonate in sea water	(10.2)	$S_{ij},$	Laplace transform frequency	(2.9)
$K_{spC},$	same for $\text{CaCO}_3$ in a solid solution of calcium-magnesium carbonate	(10.51)	$s,$	subscript for ocean as a whole	(8.49)
$K_{spM},$	same for $\text{MgCO}_3$ in a solid solution of calcium-magnesium carbonate	(10.52)	$s,$	time	(2.4)
$\ell_i,$	isotopic label in reservoir $i$	(1.18)	$t,$	subscripts for subsurface oceanic reservoirs	(8.4)
$m,$	subscript for oceanic surface ("mixed") layer	(7.1)	$u \}$	volume of oceanic reservoir $i$	(8.3)
$N, (N_0)$	abundance of carbon-total in an unspecified reservoir	(4.1)	$v \}$	mole fraction of $\text{MgCO}_3$ in magnesium carbonate	(10.48)
$N_i, (N_{i0})$	abundance of carbon-total in reservoir $i$	(1.1)	$W_i,$	vertical coordinate in the oceans	(8.49)
$*N_i, (*N_{i0})$	same for $^{13}\text{C}$ or $^{14}\text{C}$	(1.1)	$x,$	isotopic fractionation factor for transfer of carbon from reservoir (or phase) $i$ to $j$	(6.08)
$\mathbf{n},$	column vector of $n_i$ and $*n_i$	(9.12)	$z,$	isotopic fractionation factor for transfer of $\text{CO}_2$ gas from reservoir $i$ to $j$ (applies only to air-sea exchange, expressed in terms of partial pressures $P_i$ and their rare isotopic equivalents)	(7.29)
$\mathbf{n}_0,$	column vector of $n_{i0}$ and $*n_{i0}$	(9.17)	$\alpha_{ij},$	equilibrium isotopic fractionation factor for surface ocean carbon-total relative to atmosphere $\text{CO}_2$	(11.73)
$n_i,$	departure of $N_i$ from its initial value $N_{i0}$	(1.9)	$\alpha_{ij}',$	perturbation factor relating a change in emerging flux to a change in carbon abundance for an unspecified reservoir	(4.4)
$*n_i,$	same for $*N_i$	(1.14)	$\beta,$		
$n_{i0},$	value of $n_i$ at time $t = 0$ assuming an exponential rate of increase in $n_i$ , (not a steady state value)	(2.19)			

$\beta_g$	factor for perturbation of the oceanic gravitational flux	(8.19)	$\delta^*C$ ,	relative variation in $^*C/^{12}C$ ratio from standard where $^*C$ denotes $^{13}C$ or $^{14}C$	(11.34)
$\beta_b$	perturbation factor for the dependence of the rate of transfer of carbon out of reservoir $i$ on the change in abundance of carbon-total in reservoir $i$	(3.1)	$\delta^{13}C_b$ ( $\delta^{13}C_{i0}$ )	same for $^{13}C$ in reservoir $i$	(11.39)
$\beta_i'$	same except related to a change in abundance of carbon-total in the reservoir to which carbon is being transferred	(4.9)	$\epsilon_{fi}$	relative variation in $^{13}C/C$ or $^{14}C/C$ ratio of industrial $CO_2$ from that of preindustrial carbon in reservoir $i$	(2.2)
$\beta_m$	factor for perturbation in flux from surface to deep ocean associated with the oceanic gravitational flux	(8.22)	$\zeta_i$	carbonate perturbation factor for reservoir $i$	(10.11)
$\beta_{m0}$	value of $\beta_m$ if gravitational flux is constant ( $\beta_g = 0$ ). (Factor is equal to ratio of concentration of carbon-total in surface ocean to that in deep ocean.)	(8.24)	$\zeta_{ij}$	terms in the Taylor's expansion of $\zeta_i$ ( $j = 0, 1, 2, \dots$ )	(10.10)
$\beta_{ci}, \beta_{cij}$	carbonate perturbation factors for oceanic reservoir $i$ corresponding to $\beta_i$ and $\beta_{ij}$	(10.16)	$\eta_i$	rate of dissolution of solid calcium carbonate in (oceanic) reservoir $i$ in same units as $\gamma_f$	(10.4)
$\beta_{pi}, \beta_{pij}$	same for particulate organic carbon	(10.34)	$\theta_g$	relative fraction of the change in gravitational flux of carbon-total in the oceans associated with particulate organic carbon (the remainder being associated with biogenic carbonate)	(10.27)
$\beta_{gj}$	terms in the Taylor's expansion of $\beta_g$ ( $j = 0, 1, 2, \dots$ )	(8.20)	$\theta_b$	relative fraction of change in abundance of carbon-total in reservoir $i$ owing to external sources (the remainder being due to carbonate dissolution)	(10.25), (10.26)
$\beta_{ij}$	terms in the Taylor's expansion of $\beta_i$ where the perturbation depends on the abundance of the donor reservoir $i$ only ( $j = 0, 1, 2, \dots$ )	(4.8)	$\xi$ ,	$CO_2$ evasion factor for carbon-total	(7.1)
$\beta_{ijk}, \beta_{ijk}'$	terms in the Taylor's expansion of $\beta_i$ , respectively $\beta_i'$ , where the perturbation depends on the abundances of both the donor reservoir and the receiver reservoir. (The first term is designated $\beta_{io}$ , respectively $\beta_{io}'$ . For the higher terms $j$ and $k$ take on values 1, 2, 3, ...)	(4.14)	$\xi_i$ ,	same for rare isotopic carbon	(7.28)
$\gamma$ ,	subscript to $R$ , an external source for the specified reservoir (e.g. $R_{\gamma a}$ denotes isotopic ratio of industrial $CO_2$ entering the atmosphere)	(6.18)	$\xi_i$ ,	terms in the Taylor's expansion of $\xi$ ( $i = 0, 1, 2$ )	(7.2)
$\gamma_i$	column vector of $\gamma_i$ and $^*\gamma_i/R_{ao}$	(9.12)	$\chi_{ij}$ ,	gas transfer coefficient for transfer of $CO_2$ gas from reservoir $i$ to $j$ (Applies only to air-sea exchange expressed in terms of partial pressures, $P_i$ and $P_j$ )	(7.3)
$\gamma_0$	column vector of $\gamma_{i0}$ and $^*\gamma_{i0}/R_{ao}$	(9.18)	$^*\Lambda_o$ ,	special function of $^*\lambda$	(6.24)
$^*\gamma_i$	combined external sources of carbon-total to reservoir $i$	(5.2)	$^*\lambda$ ,	radioactive decay constant for rare isotopic carbon (zero for $^{13}C$ )	(2.26)
$\gamma_f$	rate of production of industrial $CO_2$ in units of carbon-total	(2.4)	$\mu$ ,	reciprocal of $e$ -fold time for exponentially rising industrial $CO_2$ production	(2.16)
$\gamma_{f0}$	value of $\gamma_f$ at time $t = 0$ , assuming an exponential rate of increase in $\gamma_f$	(2.16)	$\Sigma C$ ,	total concentration of inorganic carbon-total dissolved in sea water	(7.14)
$^*\Gamma_o$	steady state (or average) rate of production of rare isotopic carbon by cosmic rays (zero for $^{13}C$ )	(2.26)	$\phi_b$	perturbation function for transfer of carbon from reservoir $i$ to another reservoir when the perturbation depends only on the abundance of carbon-total in the donor reservoir	(3.10)
$\Delta$ ,	change from preindustrial value for quantity preceded by $\Delta$	(1.27)	$\phi_{ij}$ ,	same except that the perturbation depends on abundances in both donor reservoir $i$ and receiving reservoir $j$	(6.15)
$\delta C$ ,	relative variation in $^{13}C/C$ or $^{14}C/C$ ratio from a standard value	(1.25)	$\phi_m$ ,	perturbation function for $CO_2$ evasion from surface ocean, defined as a function of thermodynamic quotients, $K_1$ and $K_2$ , and the hydrogen ion concentration, $[H^+]$	(7.17)
$^{13}\delta C$ ,	same specifically for $^{13}C$	(1.23)	$^*\phi_m$ ,	same for rare isotopic carbon	(7.27)
$^{14}\delta C$ ,	same specifically for $^{14}C$	(1.24)			
$(\delta C)_{ij}$ ,	same for reservoir $i$ at time $t_j$	(1.26)			

The following special symbols are used:

$*$ , left superscript, indicates that the

	main symbol refers to a rare isotope of carbon, either $^{13}\text{C}$ or $^{14}\text{C}$	(1.1)
13, 14,	left superscript, indicates that main symbol refers to $^{13}\text{C}$ , respectively $^{14}\text{C}$	(1.2, 1.3)
~ ,	over main symbol, Laplace transform defined by equation (2.10)	(2.9)
- ,	over main symbol, average over coordinate specified in parentheses after main symbol	(8.50)
[ ],	enclosing an algebraic symbol, a column vector (symbols used are $\bar{n}_i, *n_i, \bar{\gamma}_i, *\gamma_i, n_{i0}, *n_{i0}, \gamma_{i0}, *\gamma_{i0}, r_i, *r_i$ ) or square matrix (symbols used are $k_{ij}, *k_{ij}, k'_{ij}$ )	(9.6)
[ ],	( [ ] <sub>o</sub> ) enclosing a chemical symbol, such as $\text{H}^+$ or $\text{HCO}_3^-$ the concentration of the specified chemical species in sea water	(7.11)
$\partial$ ,	operator for partial differentiation	(8.51)
$\int$ ,	operator for integration	(2.17)
$\infty$ ,	infinity as a limit of integration	(2.17)
	<b>Bold type</b> for main symbol, indicates that the main symbol is a column vector or a square matrix	(9.12)

## Introduction

Atmospheric carbon dioxide ( $\text{CO}_2$ ) contains two rare carbon isotopes having atomic masses of 13 and 14. Their abundances relative to the dominant isotope of mass 12 have declined in recent years owing to dilution with  $\text{CO}_2$  depleted in both rare isotopes. A clearly documented component of this dilution is industrial  $\text{CO}_2$  added to the air as a by-product of the combustion of fossil fuels. This  $\text{CO}_2$  on average contains approximately 2% less  $^{13}\text{C}$  per mole than atmospheric  $\text{CO}_2$  and is virtually free of  $^{14}\text{C}$ .

A second less well defined component of the recent dilution of atmospheric  $\text{CO}_2$  stems from the large scale harvesting of timber and the clearing of forests and grasslands for agriculture. These activities have removed carbon not only from the terrestrial biota, i.e. the living organic material on land, but also from soils. The total amount of carbon removed, most of which is released to the air as  $\text{CO}_2$ , is believed by some investigators to approach in magnitude the  $\text{CO}_2$  produced from fossil fuels.

The rate of production of industrial  $\text{CO}_2$  during most of the industrial era is known to fair accuracy from historical data on fossil fuels. In addition, since A.D. 1956, direct measurements of atmospheric  $\text{CO}_2$  establish that the concentration of  $\text{CO}_2$  in air is rising at close to 50% of the rate of production.

This implies that somewhere there exists a sink for atmospheric  $\text{CO}_2$  which is accepting the remaining industrial  $\text{CO}_2$  and whatever additional  $\text{CO}_2$  is being released from the terrestrial biota and soils. The oceans account, beyond doubt, for part of the uptake, but it is

far from certain that they have taken up all of the industrial  $\text{CO}_2$  not remaining airborne. There is presently no direct evidence at all that they have taken up additional  $\text{CO}_2$  from the land biota and soils. Indeed, studies of chemical tracers suggest that the oceans are so limited in their ability to absorb atmospheric components that the land biota must be responding to increasing atmospheric  $\text{CO}_2$  and therefore with respect to the air is acting more as a sink than as a source of  $\text{CO}_2$ . This view is, however, not in good agreement with the expected behavior of terrestrial plants whose growth is generally limited by other environmental factors (Goudriaan, 79).

It is clear that either the oceans or the land biosphere are in truth accepting more  $\text{CO}_2$  than is currently believed possible. Unfortunately, existing direct measurements of carbon abundances are not accurate enough to detect possible changes which have occurred either in the ocean or in the biota and soils, and therefore the question as to which reservoir is being improperly assessed is not readily resolved.

Isotopic studies have been proposed as an indirect means of establishing where the "missing"  $\text{CO}_2$  has gone, but whether  $^{13}\text{C}$  and  $^{14}\text{C}$  are actually useful tracers of the redistribution of industrial and biospheric  $\text{CO}_2$  is not obvious either by examining existing isotopic data or from a consideration of published theoretical models of the carbon cycle.

It is the purpose of this article to make clearer than hitherto the advantages and shortcomings of these rare isotopes as tracers of industrial  $\text{CO}_2$ . The approach will be to predict, by means of generalized geochemical models, the expected shifts in isotopic ratio as  $\text{CO}_2$  from fossil fuel, or from plant communities disturbed by man, is redistributed throughout the carbon cycle.

Carbon-13 is stable. Its depletion in industrial  $\text{CO}_2$  is solely a result of isotopic fractionation. Most of this fractionation occurred long ago when the carbon was first removed from the atmosphere and incorporated by photosynthesis in marine and terrestrial plants, precursors of present day coal, petroleum, and natural gas. Subsequent diagenetic transformations to produce these fuels reduced the  $^{13}\text{C}$  abundance still further, especially in the case of natural gas. Very little further fractionation occurs during fuel consumption, since the carbon of fossil fuels is almost completely converted to  $\text{CO}_2$  by combustion (Keeling, 73a).

Carbon-14 is radioactive with a decay constant of about  $1/8000 \text{ yr}^{-1}$  (Olsson, 70). Long storage of fossil fuels in underground reservoir has caused the  $^{14}\text{C}$  originally present to disintegrate radioactively to form  $^{14}\text{N}$ , so that the carbon in these fuels contain only the stable isotopes.

Within all of the natural carbon reservoirs which exchange carbon with the atmosphere, the injection of industrial  $\text{CO}_2$  into the air has reduced  $^{13}\text{C}$  and  $^{14}\text{C}$  ratios relative to the abundance isotope  $^{12}\text{C}$ , and to the sum of isotopes which I will call *carbon-total* ( $C$ ). Especially affected are the  $^{13}\text{C}$  to carbon-total ( $^{13}\text{C}/C$ ) and  $^{14}\text{C}$  to carbon-total ( $^{14}\text{C}/C$ ) ratios of the pools in closest contact with the atmosphere: the inorganic carbon pool of the oceans and the organic carbon pool of the terrestrial biota and soils, which I will collectively call the *land biosphere*.

One might expect that the usefulness of  $^{13}\text{C}$  and  $^{14}\text{C}$  as tracers would be enhanced when both are measured. This is because the processes by which  $^{13}\text{C}/\text{C}$  ratios have changed in response to industrial  $\text{CO}_2$  production are known to be distinctly different from those which have changed  $^{14}\text{C}/\text{C}$  ratios. With respect to  $^{14}\text{C}$ , its total absence in fossil fuel is the major cause of depletion in the atmosphere and other carbon pools. The size of these carbon pools and the rates at which they exchange carbon-total are, therefore, the dominant factors which affect  $^{14}\text{C}/\text{C}$  variations. Of the pools that readily exchange carbon with the atmosphere, the oceanic is the largest. It follows that the magnitude of the shift in  $^{14}\text{C}/\text{C}$  ratio in all pools depends, in the main, on the rate of oceanic uptake and release of carbon and on the extent to which the large oceanic carbon pool in deep ocean water mixes with the lesser pool in surface water. Conversely,  $^{14}\text{C}/\text{C}$  ratios in all pools are insensitive to properties of the land biosphere.

With respect to  $^{13}\text{C}$ , isotopic fractionation during the redistribution of fossil fuel carbon from the air to other carbon pools is similar in magnitude to the original fractionation during formation of fossil fuel. Indeed, because fossil fuel was once plant carbon, industrial  $\text{CO}_2$  has nearly the same average  $^{13}\text{C}/\text{C}$  ratio as the carbon of living land plants. The  $^{13}\text{C}/\text{C}$  shift caused by biospheric transfer to the atmosphere therefore has nearly the same isotopic impact as a corresponding injection of industrial  $\text{CO}_2$ . Although the size of the biospheric pool is relatively unimportant for  $^{13}\text{C}$  for the same reason that it was unimportant for  $^{14}\text{C}$  (namely that it is overshadowed by the oceanic pool), nevertheless, in contrast to  $^{14}\text{C}$ ,  $^{13}\text{C}/\text{C}$  ratios are strongly influenced by *changes* in the size of the biospheric pool. This sensitivity to changing pool size is irrespective of whether the changes are natural or caused by human activities.

Such different isotopic tendencies guarantee that the simultaneous use of  $^{13}\text{C}$  and  $^{14}\text{C}$  will tell us more about the global response of the carbon cycle to industrial  $\text{CO}_2$  than either isotope alone. The advantage of two rare isotopes is lessened, however, because  $^{13}\text{C}$  and  $^{14}\text{C}$  ratios have only been measured for a few decades and because man-made, "bomb",  $^{14}\text{C}$  from nuclear weapons testing obliterated the industrial  $^{14}\text{C}$  effect after 1954.

Global average ratios for earlier times must be inferred from historic materials such as tree rings, vintage whiskies, coral rings and varved sediments. The overriding of global trends by local effects, a problem which probably can be overcome for  $^{14}\text{C}$  (Cain, 76), is more likely to confound  $^{13}\text{C}$  measurements, since the abundance of this isotope in natural materials is significantly effected by almost any extraneous isotopic fractionation process which occurs in the local environment of the plant. Thus  $^{14}\text{C}$  is not ideal but the preferred isotope for studying past industrial activity. Nevertheless,  $^{13}\text{C}$  is the only choice for recent times.

An isotopic effect attributed to industrial  $\text{CO}_2$ , was, in fact, first observed with respect to historical variations in  $^{14}\text{C}/\text{C}$  ratios. In A.D. 1953, Dr. Hans Suess, working for the U.S. Geological Survey, following a suggestion of G.E. Hutchinson (Hutchinson, 54; p. 590), investigated variations in the  $^{14}\text{C}$  content of wood of

known age. Suess detected a 3.4% decrease in  $^{14}\text{C}$  ratio of wood carbon during the preceding 50 yr for two trees from the eastern United States (Suess, 53). A tree from Alaska showed about half as much decrease. All ratios were corrected for radioactive decay back to the time of growth of the wood. Two years later Suess proposed that the decrease, and similar decreases which he found for several additional trees, were due to industrial coal production causing a decrease in the  $^{14}\text{C}/\text{C}$  of atmospheric  $\text{CO}_2$  which in turn caused proportional decrease in the carbon incorporated tree rings (Suess, 55). The isotopic decreases in trees of the eastern United States could be due to local industrial effects, but decreases in trees of remote areas such as Alaska suggested a global effect. After discounting local effects for each tree, he estimated the global effect to be 1% or less.

In A.D. 1957 Suess revised his opinion on the strength of the effect. In collaboration with Dr. Roger Revelle of the Scripps Institution of Oceanography he compared his tree ring data with  $^{14}\text{C}/\text{C}$  ratios in ocean water as a basis for determining how much industrial  $\text{CO}_2$  had been absorbed by the oceans during the period of  $^{14}\text{C}$  observation (Revelle, 57b). From the oceanic data he and Revelle predicted a global reduction in the  $^{14}\text{C}$  of atmospheric  $\text{CO}_2$  of about 1.7%. This value was not inconsistent with the tree ring data, and appears to be more reasonable than his previous estimate of about 1%. A 1.7% decrease was, however, still far less than the 10% decrease to be expected if all of the industrial  $\text{CO}_2$  had remained in the atmosphere in isolation from other carbon reservoirs. After considering the mechanism of  $\text{CO}_2$  exchange between the atmosphere and the oceans, including the influence of carbonate ion in sea water, Revelle and Suess concluded that a considerable part of the  $\text{CO}_2$  from combustion was exchanging with the carbon of sea water with between 40 and 70% being retained in the oceans. They declined to estimate the possible atmospheric increase because they lacked information on biospheric changes.

Their conclusions regarding oceanic uptake of  $\text{CO}_2$  were in contrast to the opinion of Callendar (38) that neither the oceans nor the biosphere had strongly modified the direct effect of industrial  $\text{CO}_2$  on the atmosphere. Callendar's conclusion, generally accepted at that time, soon appeared to be reinforced by new atmospheric  $\text{CO}_2$  measurements over Scandinavia carried out in connection with the International Geophysical Year. These data indicated an increase in  $\text{CO}_2$  nearly equal to the industrial  $\text{CO}_2$  input (Fonselius, 56; Callendar, 58). But in the next decade, additional new data from Hawaii and Antarctica established a considerably slower rate of rise in atmospheric  $\text{CO}_2$  and revived an interest in the role of the oceans in removing substantial amounts of industrial  $\text{CO}_2$  from the atmosphere (Bolin, 63; Pales, 65; Brown, 65). Suess and Revelle had, in effect, anticipated this result and thus had demonstrated how indirect isotopic measurements could yield insight into processes governing the redistribution of industrial  $\text{CO}_2$ .

From Suess's  $^{14}\text{C}$  data it soon became evident that a correct interpretation of  $^{14}\text{C}/\text{C}$  ratios for archeological and geochemical dating required that the industrial  $\text{CO}_2$  effect be properly allowed for in calibrating ancient

samples against modern materials. Suess's discovery received wide scientific attention and was soon referred to as the "Suess Effect". The term appeared shortly after in the scientific literature (Hayes, 56; Bolin, 59) and has been referred to widely since that time.

Extensive further measurements by Suess and his coworkers, and by others who have joined in these studies over the past two decades, confirm the existence of the Suess Effect. The data obtained from tree rings, oceanic materials, and direct measurements are summarized in Table 1. They indicate that the decrease in  $^{14}\text{C}/\text{C}$  from the middle of the nineteenth century to the early 1950s is close to the 1.7‰ estimate of Suess and Revelle. The data, in aggregate, however, are not consistent enough to establish an accurate global value. Local effects, such as local combustion of fossil fuels, have evidently influenced many of the reported measurements. Although Suess from the beginning of his studies was aware of the possibility of local effects, investigators regrettably have usually not furnished enough documentation to assess the magnitude of local interferences.

Table 1. The observed Suess Effect for  $^{13}\text{C}$  and  $^{14}\text{C}$

Investigator	Reported value (‰)	Date of most recent material measured	Hemisphere	Corrected for $^{13}\text{C}$ ?
Atmospheric $^{14}\text{C}$ Suess Effect inferred from tree rings				
Suess (1953, p. 55)	-3.4	1953	N	No
Suess (1955, p. 416)	-1.6	1953	N	Yes
	-3.0	1953	N	
	-1.6	1953	N	
	-0.4	1953	S	
Hayes <i>et al.</i> (1956, p. 191)	-4.0	1955	N	No
Brannon <i>et al.</i> (1957, p. 646)	-3.6	1955	N	No
	-3.3	1955	N	
	-2.8	1955	N	
	-1.7	1955	N	
Fergusson (1958, p. 564)	-2.01	1953	N	Yes
	-1.88	1953	S	
	-1.98	1953	S	
	-2.34	1953	S	
Münnich and Vogel (1958, p. 6)	-4.0	1953	N	Yes
	-2.8	1953	S	
de Vries (1958, p. 96)	-1.5	1935	N	Yes
Broecker and Walton (1959b, p. 311)	-3.2	1938	N	Yes
Suess (1965, p. 5941)	-2.4	1942	N	Yes
Houtermans <i>et al.</i> (1967, p. 58)	-2.3	1948	N	Yes
Lerman <i>et al.</i> <sup>(a)</sup> (1970, p. 287)	-2.34	1951	N	Yes
	-1.83	1950	N	
	-1.86	1952	N	
	-2.03	1952	N	
	-1.43	1951	N	
	-2.20	1951	S	
	-1.91	1952	S	
	-2.62	1947	N	
Damon <i>et al.</i> <sup>(b)</sup> (1973, p. 303)	-3.35	1948	N	Yes
	-3.91	1949	N	
	-3.15	1950	N	
	-2.55	1951	N	
	-3.05	1952	N	
	-3.05	1953	N	

Cain and Suess (1976, p. 3690)	-2.0	1940	N	Yes
Tans <sup>(c)</sup> (1978, p. 86)	-1.70	1945	N	Yes
	-2.40	1950	N	
Surface oceanic $^{14}\text{C}$ Suess Effect inferred from biogenic carbonates				
Brannon <i>et al.</i> (1957, p. 647)	-2.1	ca. 1950	N	No
	-3.2	1938	N	
Broecker <sup>(d)</sup> (1963, p. 140)	< -1.0	1957	N and S	Yes
Nozaki <i>et al.</i> <sup>(e)</sup> (1978, p. 826)	-2.2	1950	N	Yes
Druffel and Linick (1978, p. 915)	-1.1	1952	N	Yes
Atmospheric shift in $\delta^{13}\text{C}$				
Keeling <i>et al.</i> (1979, p. 122)			N	
Surface oceanic shift in $\delta^{13}\text{C}$				
Nozaki <i>et al.</i> <sup>(e)</sup> (1978, p. 826)	-0.24	1956-1978	N	
	-0.26	1850-1956		

#### Notes

- Preindustrial  $^{14}\text{C}/\text{C}$  ratio estimated from 3 samples, A.D. 1858-1866, with  $\Delta^{14}\text{C}$  of -0.04‰.
- Preindustrial  $^{14}\text{C}/\text{C}$  based on 0.950 of NBS oxalic acid standard. Additional data for A.D. 1940-1946 not shown.
- Preindustrial  $^{14}\text{C}/\text{C}$  estimated from six samples, A.D. 1862-1872, with  $\Delta^{14}\text{C}$  of -0.41‰.
- Upper limit deduced from data which range from -0.5 to +0.8‰. (See Table 2, p. 140 of original article).
- Estimated by reading from a graph.

A notable exception, however, is the study of William Cain, a student of Suess, who deliberately investigated the relative importance of local and global effects of industrial  $\text{CO}_2$  on  $^{14}\text{C}$  of tree rings (Cain, 76). Cain adopted the painstaking approach of measuring all possible individual rings (except perhaps the earliest which are locally affected by the low height of the tree) to obtain a complete time series for each tree. By carefully checking several series of rings for internal consistency, Cain discerned subtle interferences which, if he had not detected them, would have invalidated the use of these records to detect global changes in  $^{14}\text{C}/\text{C}$ . Most notably he found that "bomb"  $^{14}\text{C}$  had influenced the  $^{14}\text{C}/\text{C}$  or rings laid down as early as 1915 by its incorporation at the time of conversion from sapwood to heartwood. Cain did not attempt to establish the global Suess Effect accurately, but he demonstrated clearly that to do so will involve a large effort: complete series from a considerable number of trees are needed to be certain that local effects have been allowed for.

Very recently new data have been obtained by Stuiver and Quay (79) which suggest that sampling and experimental problems which have before hampered establishing of the global Suess Effect can be substantially reduced by adhering to very careful procedures. Stuiver's data indicate that the  $^{14}\text{C}/\text{C}$  ratio of atmospheric  $\text{CO}_2$  from 1850 to 1952 decreased by -2.4‰ (Stuiver, private communication). But so far Stuiver has described measurements of only one or two trees for any given time period. More trees from a variety of sites will be needed to establish that tree ring data unequivocally reflect the atmospheric Suess Effect.

Carbon-14 is produced in the atmosphere by the interaction of cosmic rays with nitrogen gas (Lingenfelter, 63; Light, 73). Unsteadiness in the rate of this production presents another problem in establishing the

industrial CO<sub>2</sub> influence on <sup>14</sup>C ratios. Variations in ratio of the order of 2‰ per century have been found in tree ring records as far back as ring counting extends: some 7000 years (Suess, 65, 70; Damon, 70; Eddy, 77; Damon, 78; Stuiver, 79). As suggested by Stuiver (65), these variations are likely to be due to variations in solar activity which in turn affects <sup>14</sup>C production. To test for this possibility an index of solar activity is needed, such as sunspot numbers. Suess and coworkers, however, found about 10 years ago that the direct statistical correlation of this existing <sup>14</sup>C/C data with sunspots was too poor to be a good predictor (Houtermans, 67).

Closely spaced and highly accurate tree rings analyses and more reliable sunspot data obtained recently by Stuiver and Quay (79) yield a better correlation between <sup>14</sup>C/C ratios and sunspots. If a causal connection exists, as seems likely from these new data, the correlation should be improved by giving careful attention to known aspects of the carbon cycle which may modify the correlation in predictable ways. This approach has not yet been very successful, however. Grey (69) and Grey and Damon (70) employed a one reservoir model which was clearly too simplistic, while Bacastow and Keeling (73), although they used an elaborate six-reservoir model, inadequately represented the <sup>14</sup>C production variation with sunspots and obtained almost no correlation at all.

It seems likely that the <sup>14</sup>C Suess Effect will continue to receive attention as new studies improve the data base. Recent suggestions that CO<sub>2</sub> from the land biosphere may actually exceed fossil fuel as a source of CO<sub>2</sub> to the atmosphere (Woodwell, 78; Stuiver, 78; Wilson, 78) also have stimulated new interest in the Suess Effect, because, if the Suess Effect were accurately known, it would establish within fairly narrow limits the capacity of the oceans to absorb industrial CO<sub>2</sub>, and hence, by difference, the change in biospheric carbon.

Possible variations in <sup>13</sup>C related to industrial CO<sub>2</sub>, have until recently not received the widespread interest accorded <sup>14</sup>C. In the past few years however a considerable body of data on tree rings has appeared (Freyer, 73, 74, 78a, 78b; Pearman, 76; Fraser, 78; Tans, 78; Wagener, 78; Wilson, 78), and one study of coral (Nozaki, 78). Also the isotopic shift in the atmosphere between A.D. 1956 and 1978 has very recently been reported from direct measurements (Keeling, 79a).

The tree ring data scatter badly, and for recent years do not agree very closely with the direct atmosphere observations. Until the causes of the scatter are better understood, it is difficult to decide whether these data will be of value to global studies.

The coral <sup>13</sup>C data show a more consistent trend, but it may be premature to generalize from a single example. The atmospheric <sup>13</sup>C data present the fewest complications, but are only available for two short periods, 22 yr apart. The coral and atmospheric data (Table 1) do suggest, however, that the <sup>13</sup>C/C ratios in atmospheric CO<sub>2</sub> and surface ocean water, at least qualitatively, have both shifted in the past 100 years as expected if industrial CO<sub>2</sub> or land biospheric CO<sub>2</sub> had entered the atmosphere.

Since nuclear weapons testing does not generate <sup>13</sup>C,

the industrial <sup>13</sup>CO<sub>2</sub> effect ought to be traceable for the entire industrial era and in the future. The advantage of possible future studies is considerable since the rate of industrial CO<sub>2</sub> production in A.D. 2000 is likely to be over twice that of A.D. 1978 and 6 times larger than in A.D. 1954 when the <sup>14</sup>C record was blocked out by weapons testing. Thus we may expect to see continued interest in <sup>13</sup>C measurements even if present data do not show unmistakable promise of success.

So far <sup>13</sup>C/C data have not received the detailed theoretical interpretation accorded <sup>14</sup>C data, but Stuiver (78), Oeschger and Siegenthaler (78) and Siegenthaler *et al.* (78) have presented evidence, based on models, that the shift in the tree ring data is considerably too large and begins too early to be owing solely to industrial CO<sub>2</sub> from the land biosphere from A.D. 1850 to 1950 comparable in magnitude to that of industrial CO<sub>2</sub>.

Although a biospheric release of carbon seems to follow unmistakably from the data, the geochemical calculations of Stuiver and Oeschger have not been presented in sufficient detail to assess directly the quantitative validity of their computations. Stuiver (78) indeed, avoided the direct use of a model for <sup>13</sup>C altogether by assuming that the decrease in <sup>13</sup>C/C owing to industrial CO<sub>2</sub> was proportional to the corresponding decrease in <sup>14</sup>C/C. Specifically he argued that since industrial CO<sub>2</sub> from A.D. 1850 to 1959 contained 18‰ less <sup>13</sup>C than atmospheric CO<sub>2</sub>, but 100‰ less <sup>14</sup>C, that therefore the shift in <sup>13</sup>C owing to industrial CO<sub>2</sub> should be 0.018 times the <sup>14</sup>C shift. To overcome the possible interference of variations in solar activity with the latter, he accepted a model prediction of the <sup>14</sup>C Suess Effect of Oeschger *et al.* (75). As shown below, his approximation, although correct as to order of magnitude, is substantially in error because it neglects isotopic fractionation associated with <sup>13</sup>C exchange between reservoirs.

To establish a correct prediction requires a detailed consideration of such fractionation. It is my purpose here to carry out this analysis giving equal consideration to both <sup>13</sup>C and <sup>14</sup>C. First I will precisely define the Suess Effect for <sup>14</sup>C, and its extension to <sup>13</sup>C. I will indicate how the effect relates to the fractions of industrial CO<sub>2</sub> which appear in the various reservoirs of the natural carbon system. The related fractions for <sup>13</sup>C and <sup>14</sup>C will also be considered. Next, I will show with a two reservoir geochemical model that the Stuiver approximation would prevail if isotopic fractionation and radioactive decay, as they affect the redistribution of industrial CO<sub>2</sub>, were negligible compared to the fractionation involved in the natural formation of fossil fuel. Then, for several pairs of reservoirs representing important segments of the natural carbon cycle, I will establish expressions for calculating the Suess Effect without neglecting fractionation and radioactive decay. The formulism of these two reservoir models will afterwards be employed to construct a four reservoir model involving simultaneously the land biosphere and a two layer ocean. Finally I will compare the experimental results for <sup>13</sup>C and <sup>14</sup>C with the predictions of this model for the important case of an exponentially growing industrial CO<sub>2</sub> source. To allow comparison with the vertical diffusive model of the oceans of Oesch-

ger *et al.* (75) the two layer ocean model will be so prescribed that it is equivalent to this diffusive model.

The emphasis of this article will be on formulating models rather than surveying or interpreting large amounts of observation data. Although the models to be described have simple geochemical properties, their formulation with isotopic fractionation included will be as complete as possible for possible application to more complicated (and presumably more realistic) models which may later on be derived when the observation data become more reliable.

Nevertheless, the usefulness of  $^{13}\text{C}$  and  $^{14}\text{C}$  as tracers of industrial  $\text{CO}_2$  will be reflected upon towards the end of the article. Indeed, for those readers who are not interested in the mathematical details, the article has been arranged so that sections 1 - 3 and subsection 11.1 form a sufficient background to allow readers to pass over the mathematical development (sections 4 - 10 and subsections 11.2 - 11.5) and still be able to comprehend the final section on interpretation.

## 1. Definition of the Suess Effect

### 1.1 General comments

The Suess Effect has generally been understood to denote the decrease in  $^{14}\text{C}/\text{C}$  ratio in atmospheric  $\text{CO}_2$  caused by the combustion of fossil fuel (Baxter, 70, p. 213). In no published study, however, has the Suess Effect been defined in precise mathematical terms.

For purposes of the present discussion, a broad definition is desirable. Therefore I will define the  $^{14}\text{C}$  Suess Effect as *the change in carbon-14 relative to carbon-total in any part of the carbon cycle caused by admixture of industrial  $\text{CO}_2$* . Also, I will introduce a corresponding  $^{13}\text{C}$  Suess Effect defined as the decrease in  $^{13}\text{C}$  brought about by industrial  $\text{CO}_2$ . The simple term "Suess Effect" will be used when the distinction between isotopes is not important. Industrial  $\text{CO}_2$  shall mean all of the  $\text{CO}_2$  produced by man commercially including the manufacture of cement (Baxter, 70; Keeling, 73a) but not  $\text{CO}_2$  from the combustion of wood or agricultural products. Carbon-total (symbol C), will refer to the sum of all the carbon isotopes, but practically speaking, to the sum of  $^{12}\text{C}$  and  $^{13}\text{C}$ , since the abundance of  $^{14}\text{C}$  is negligible in comparison.

Isotopic data are conventionally expressed relative to experimental laboratory standards, and in the case of  $^{14}\text{C}$  are usually corrected for variations in  $^{13}\text{C}$  (Broecker, 59a). I prefer not to make reference to these calibration procedures in the definition of the Suess Effect, although it is necessary to take them into account when comparing observational data with model predictions, as is done in section 12, below.

Carbon-13 variations are usually reported relative to carbon-12 rather than to carbon-total, because natural isotopic fractionation is directly expressed in terms of ratios of single isotopes. For natural carbon the rare isotopes are in such low abundance, however, that the slight inconstancy of fractionation factors, expressed relative to carbon-total, may be neglected (Keeling,

79b). Therefore, for uniformity with the definition of the  $^{14}\text{C}$  Suess Effect, the  $^{13}\text{C}$  Suess Effect will be defined in terms of  $^{13}\text{C}/\text{C}$  rather than  $^{13}\text{C}/^{12}\text{C}$  isotopes. The absolute abundance of  $^{13}\text{C}$  relative to  $^{12}\text{C}$  is well enough known to convert published data to  $^{13}\text{C}/\text{C}$  ratios without introducing appreciable errors (Mook, 73).

As just defined, the Suess Effect is essentially a theoretical concept. Observed variations in  $^{13}\text{C}$  and  $^{14}\text{C}$  in nature must in truth reflect a multiplicity of causes besides admixture of industrial  $\text{CO}_2$ . Indeed, as noted above, solar activity and other actions of man such as changing agricultural practices may cause greater isotopic variations than industrial  $\text{CO}_2$ . A related observable quantity to compare with the theoretical Suess Effect is thus useful. I will therefore define an "observable Suess Effect" as the change in  $^{13}\text{C}/\text{C}$  or  $^{14}\text{C}/\text{C}$  ratio of atmospheric  $\text{CO}_2$  (or the carbon in some other reservoir) owing to whatever causes were actually responsible for the change. To make the latter definition precise, the isotopic change will be measured from a prescribed year prior to which industrial  $\text{CO}_2$  had only a small influence. Since industrial  $\text{CO}_2$  production has been computed on a yearly basis only since A.D. 1860, that year might be a logical choice to mark the beginning of the observable Suess Effect, but earlier dates may be of interest as well. For such cases, assumption of an exponentially rising production rate prior to A.D. 1860, establishes accurately enough the  $\text{CO}_2$  production before 1860 (Keeling, 73a, p. 192). For  $^{14}\text{C}$  the observable Suess Effect effectively ends in A.D. 1954, but for  $^{13}\text{C}$  any recent or future ending date is appropriate.

### 1.2 Mathematical expressions for the Suess Effect

To formulate the above definitions mathematically requires that several other quantities first be defined.

The amount of carbon-total in a designated carbon pool or "reservoir" of the carbon cycle I will denote by  $N_i$  where  $i$  stands for a letter subscript denoting the reservoir. Following a widely used convention, "a" will denote the atmosphere, "b", the land biosphere, "m", the ocean surface "mixed" layer, "d", the ocean subsurface "deep" layer. This notation may obviously be extended to more reservoirs or to subdivisions of reservoirs.

In so far as possible, equations will be written which apply to both of the rare isotopes,  $^{13}\text{C}$  and  $^{14}\text{C}$ . A left superscript asterisk will be used to denote a rare isotopic quantity; e.g.  $*N_a$  will denote the  $^{13}\text{CO}_2$  or  $^{14}\text{CO}_2$  content of the atmosphere. (I will neglect other carbon species such as CO and  $\text{CH}_4$ , which exist in the atmosphere in quantities too small to be important here.)

Carbon isotopic ratios will in general be denoted by the symbol,  $R$ , subscripted to identify the carbon pool. Thus:

$$R_i = *N_i/N_i \quad (1.1)$$

refers to either the  $^{13}\text{C}/\text{C}$  or  $^{14}\text{C}/\text{C}$  ratio in reservoir  $i$ .



When it is necessary to distinguish isotopes, the atomic weight will be specified. Thus the ratios:

$$^{13}R_a = ^{13}N_a/N_a \quad (1.2)$$

$$^{14}R_a = ^{14}N_a/N_a \quad (1.3)$$

will refer, respectively, to the  $^{13}\text{C}/\text{C}$  and  $^{14}\text{C}/\text{C}$  ratios of atmospheric  $\text{CO}_2$ .

An optional additional subscript will denote a specific time. In particular, "o" will represent a preindustrial time in which the cumulative production of industrial  $\text{CO}_2$  is as yet essentially zero. Since some industrial  $\text{CO}_2$  was already present in A.D. 1860 or any other reasonable starting date for observations, this date will be called  $t_1$  rather than  $t_o$ , and the observable Suess Effect at time  $t_2$  will be defined by:

$$S_{a2} = (R_{a2} - R_{a1})/R_{a1} \quad (1.4)$$

or specifically for  $^{14}\text{C}$ :

$$^{14}S_{a2} = (^{14}R_{a2} - ^{14}R_{a1})/^{14}R_{a1} \quad (1.5)$$

where  $t_2$  is any suitable time after  $t_1$ .

Similarly, for any reservoir  $i$ , at time  $t_j$ , subsequent to  $t_1$ :

$$S_{ij} = (R_{ij} - R_{i1})/R_{i1} \quad (1.6)$$

where  $R_{i1}$  and  $R_{ij}$  denote the observed, i.e. actual, isotopic ratios for times  $t_1$  and  $t_j$ .

Consistent with the definition of the observable Suess Effect, the theoretical Suess Effect will be defined for reservoir  $i$  by the expression:

$$S_i = (R_i - R_{io})/R_{io} \quad (1.7)$$

where  $R_{io}$  denotes the preindustrial isotopic ratio, and  $S_i$  and  $R_i$  are regarded as continuous functions of time, determined by a geochemical model of the carbon cycle. To be completely consistent in defining the theoretical Suess Effect, the only independent disturbance considered in calculating  $S_i$  and  $R_i$  should be industrial  $\text{CO}_2$ . But because the interactions of the land biosphere and the atmosphere present a complex web of causes

and effects which are difficult to separate in terms of this single disturbance by man, the definition will be expanded to encompass changes in isotopic ratios related to biospheric perturbations stemming from human activities.

### 1.3 Relation of Suess Effect to industrial $\text{CO}_2$ production

The theoretical Suess Effect is, perforce, a function of the total amount of industrial  $\text{CO}_2$  production up to a given year. Since this latter quantity is not exactly known (e.g. Keeling (73a) estimates 13% uncertainty) the theoretical Suess Effect suffers numerical uncertainty quite apart from uncertainty related to an imperfect understanding of the natural carbon cycle. For the  $^{13}\text{C}$  Suess Effect, uncertainties in the  $^{13}\text{C}/\text{C}$  ratio of industrial  $\text{CO}_2$  of several per mil (see, e.g., Schwarz, 70) also influence the numerical evaluation. Moreover, to relate the theoretical Suess Effect to observable isotopic ratios requires a comparison of recent and preindustrial ratios. The latter are not clearly established, as discussed later on.

Keeping these limitations in mind, we shall now formulate the Suess Effect as a function of industrial  $\text{CO}_2$  production. Let  $Q$ , a function, of time, denote the cumulative input of industrial  $\text{CO}_2$  to the carbon cycle, and  $r_i$  the fraction of this industrial  $\text{CO}_2$  residing in reservoir  $i$  at the time  $Q$  is evaluated. Then:

$$r_i = (N_i - N_{io})/Q \quad (1.8)$$

$$= n_i/Q \quad (1.9)$$

where  $N_{io}$  denotes the preindustrial amount of  $\text{CO}_2$  in reservoir  $i$  and  $n_i$  the departure of  $N_i$  from this initial value. For example the airborne fraction:

$$r_a = n_a/Q \quad (1.10)$$

according to data for the period 1956 to 1978, has a value of approximately 54% (Keeling, 79a).

To relate the theoretical Suess Effect to  $Q$ , it is useful to define corresponding reservoir fractions for  $^{13}\text{C}$  and  $^{14}\text{C}$ . We encounter a problem for  $^{14}\text{C}$ , however. Industrial  $\text{CO}_2$  contains essentially no  $^{14}\text{C}$ , and thus a reservoir fraction for industrial  $^{14}\text{CO}_2$  cannot be defined.

It might appear at first glance that the amount of  $^{14}\text{C}$  in each reservoir would be unaffected by the input of other isotopes of carbon. But this would require not only that the isotopes exhibit identical chemical behavior, but that they also not interact mutually with other chemical species affected by industrial  $\text{CO}_2$ . This possibility is of some interest as a limiting case, and is

treated in section 2 below. In general, however, we expect that adding  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  to some part of the carbon cycle results in a redistribution of  $^{14}\text{C}$  within other interacting reservoirs, even though the total amount of  $^{14}\text{C}$  is not changed by the perturbation. Since this redistribution is a function of the industrial  $\text{CO}_2$  input,  $Q$ , it is useful to define dimensionless factors,  $^{14}r_i$  which are, in so far as possible, analogous to the carbon-total fractions,  $r_i$ .

Let us define these fractions by the expression:

$$^{14}r_i = \frac{^{14}n_i}{^{14}R_{io}Q} \quad (1.11)$$

The choice of  $^{14}R_{io}$  in the denominator is arbitrary, but turns out to be convenient in producing a simple expression relating the redistribution of  $^{14}\text{C}$  to the Suess Effect. By equation (1.11) we, in effect, compare the actual change in  $^{14}\text{C}$  in each reservoir,  $^{14}n_i$ , to the change which would have occurred if all of the industrial  $\text{CO}_2$  had accumulated in that reservoir, and (contrary to reality) had had the same  $^{14}\text{C}/\text{C}$  ratio as existed in the reservoir at the beginning of the industrial era.

A  $^{13}\text{C}$  airborne fraction could be defined in terms of the actual  $^{13}\text{CO}_2$  input:

$$^{13}Q = ^{13}R_f Q \quad (1.12)$$

where  $^{13}R_f$  denotes the  $^{13}\text{C}/\text{C}$  ratio of industrial  $\text{CO}_2$ . However, for consistency and later mathematical convenience, I will adopt a definition analogous to equation (1.11) i.e.:

$$^{13}r_i = \frac{^{13}n_i}{^{13}R_{io}Q} \quad (1.13)$$

Thus, for either isotope:

$$^*r_i = \frac{^*n_i}{R_{io}Q} \quad (1.14)$$

where  $^*n_i$  stands for  $^*N - ^*N_{io}$ .

For consistency in referring to the rare isotopic composition of industrial  $\text{CO}_2$ , the symbol  $R_f$  will be employed to denote either the  $^{13}\text{C}/\text{C}$  or  $^{14}\text{C}/\text{C}$  ratio with the understanding that in all cases

$$^{14}R_f = 0. \quad (1.15)$$

#### 1.4 Use of an isotopic label

Although the main body of this article proceeds from the definition already presented, it will prove convenient to carry out some model computations in section 3,

below, in terms of an isotopic "label" variable related to the isotopic perturbation  $R_i - R_{io}$ . Since an otherwise linear model for carbon-total and rare isotopic carbon becomes non-linear if isotopic ratios are treated as system variables, it is advantageous to define an isotopic label as a linear combination of the perturbations  $^*n_i$  and  $n_i$ . Since by definition (equation 1.1):

$$R_i - R_{io} = \frac{^*N_{io} + ^*n_i}{N_{io} + n_i} - \frac{^*N_{io}}{N_{io}} \quad (1.16)$$

it follows that:

$$R_i - R_{io} = (^*n_i - R_{io}n_i)/N_i \quad (1.17)$$

The label variable for any reservoir  $i$ , I will thus define by the expression:

$$\ell_i = (^*n_i - R_{io}n_i)/R_{ao} \quad (1.18)$$

which is equivalent to:

$$\ell_i = \frac{(R_i - R_{io})N_i}{R_{ao}} \quad (1.19)$$

This formulation gives us a quantity, which for small perturbations, is very nearly proportional to the isotopic ratio difference,  $R_i - R_{io}$ , but has the dimensions of carbon-total. I have normalized  $\ell_i$  to the preindustrial isotopic ratio of the carbon pool directly receiving the industrial  $\text{CO}_2$  source, i.e. to  $R_{ao}$ . This is an arbitrary, but convenient, choice.

Eliminating the  $^*n_i$  and  $n_i$  in equation (1.18) by means of equations (1.9) and (1.14):

$$\ell_i = (R_{io}/R_{ao})(^*r_i - r_i)Q \quad (1.20)$$

In terms of label the theoretical Suess Effect (cf. equations (1.7) and (1.19)) is therefore:

$$S_i = \frac{R_{ao}\ell_i}{R_{io}N_i} \quad (1.21)$$

whence, in accordance with equation (1.20):

$$S_i = (Q/N_i)(^*r_i - r_i) \quad (1.22)$$

This last formulation is especially useful in computing the theoretical Suess Effect because, as discussed later, the industrial  $\text{CO}_2$  input is approximated by an expo-

nential function of time. If the governing equations of carbon cycle model are linearized, which is appropriate for the small relative changes in  $N_i$  and  $R_i$  which have occurred up to the present, then the predicted values of  $r_i$  and  $r_i$  are invariant and readily evaluated.

### 1.5 Relating the Suess Effect to observational data

A minor complication occurs in comparing model predictions with observations because the preindustrial quantities,  $R_{io}$  and  $N_{io}$ , are not identical to the corresponding quantities for A.D. 1860 nor to any other year which might be selected as the starting year of the Suess Effect,  $t_1$ . Indeed, the carbon-total abundances,  $N_{io}$ , cannot be obtained from any historical data, such as tree rings, but must be assigned values inferred from the industrial period. Different approximations of the model equations, and of the functional form given to the input  $Q$ , therefore may lead to different assigned values. These assignments do not markedly hinder a comparison of theory and observation as parameters are varied for any given model, because of more serious uncertainties arising from the data and model assumptions. Choosing different initial values for different models makes comparison of models more difficult, however, because small differences in prediction may be of interest in deciding between models. Therefore it is worthwhile to pay close attention to the rational for assigning preindustrial values.

A more serious complication arises because a steady state between pools of the carbon cycle probably did not exist at the time when significant use of fossil fuel first began. Thus the perturbation of carbon and its isotopes must be superimposed on a time variable record of abundances and isotopic ratios. As noted in section 3, the models which we employ to determine the theoretical Suess Effect essentially do no more than predict those isotopic changes brought about by industrial  $\text{CO}_2$  which are large enough to overshadow the effects of other phenomena overlooked in the analysis.

For  $^{13}\text{C}$  it is customary to express isotopic ratios as the per mil variation from a standard ratio. The latter is typically that of the University of Chicago Standard, "PDB" (Craig, 57; Mook, 73). Since  $\delta^{13}\text{C}$ , the customary symbol for the per mil variation, typically refers to variations in  $^{13}\text{C}/^{12}\text{C}$ , I will adopt a different symbol,  $^{13}\delta\text{C}$ , for variations in  $^{13}\text{C}/\text{C}$ . Formally, I will define this quantity (in per mil or any other suitable unit) by:

$$^{13}\delta\text{C} = ^{13}R/^{13}R_{\bullet} - 1 \quad (1.23)$$

where  $^{13}R_{\bullet}$  denotes the  $^{13}\text{C}/\text{C}$  ratio of the standard.

For  $^{14}\text{C}$  the analogous formula is:

$$^{14}\delta\text{C} = ^{14}R/^{14}R_{\bullet} - 1 \quad (1.24)$$

where  $^{14}R_{\bullet}$  denotes the standard ratio. (This ratio is typically 0.95 of the ratio of an Oxalic Acid standard furnished by the U.S. National Bureau of Standards.) Hence for either isotope:

$$\delta\text{C} = R/R_{\bullet} - 1. \quad (1.25)$$

For reservoir  $i$  the observable change in  $\delta\text{C}$  from time  $t_1$  to  $t_2$  is related to the observable Suess Effect,  $S_{i2}$ , by:

$$(\delta\text{C})_{i2} - (\delta\text{C})_{i1} = (R_{i1}/R_{\bullet})S_{i2} \quad (1.26)$$

i.e., the isotopic change in terms of  $\delta\text{C}$  differs from  $S_{i2}$  merely in its referral to the standard ratio,  $R_{\bullet}$ , rather than to the ratio,  $R_{i1}$ .

The theoretical change in isotopic ratio for either rare isotope caused by admixture of industrial  $\text{CO}_2$  since preindustrial times, I will denote by  $\Delta\delta\text{C}_i$ . This quantity is related to the theoretical Suess Effect by the relation:

$$\Delta\delta\text{C}_i = (R_{io}/R_{\bullet})S_i \quad (1.27)$$

or in terms of label (cf. equation (1.21)):

$$\Delta\delta\text{C}_i = (R_{ao}/R_{\bullet})(\ell_i/N_i). \quad (1.28)$$

## 2. The Stuiver Approximation

### 2.1 Mathematical expression for the approximation

The Suess Effects for  $^{13}\text{C}$  and  $^{14}\text{C}$  are obviously closely related. Thus the proposal of Stuiver (78) to estimate the atmospheric Suess Effect for  $^{13}\text{C}$  by multiplying the  $^{14}\text{C}$  Suess Effect by the  $^{13}\text{C}/^{12}\text{C}$  ratio of fossil fuel relative to atmospheric  $\text{CO}_2$  is not an unreasonable first approximation. It will help in understanding how the Suess Effect arises to investigate two relatively simple examples in which his approximation holds. The first example will be considered in this section, the second in the following section.

Let us express the Stuiver approximation using the symbols of the previous section. We identify  $t_1$  with A.D. 1850 and  $t_2$  with A.D. 1950, the inclusive years considered by Stuiver. His approximation is:

$$^{13}S_{a2} = -^{13}\epsilon_{fa} \ ^{14}S_{a2} \quad (2.1)$$

where:

$$^{13}\epsilon_{fi} = \frac{^{13}R_f - ^{13}R_{io}}{^{13}R_{io}} \quad (2.2)$$

denotes the relative variation in  $^{13}\text{C}/\text{C}$  ratio of industrial  $\text{CO}_2$  from that of preindustrial carbon of reservoir  $i$ . A similar expression will apply to  $^{14}\text{C}$  (see equation 2.41). The theoretical Suess Effect corresponding to equation (2.1) is:

$$^{13}S_a = -^{13}\epsilon_{fa} \ ^{14}S_a. \quad (2.3)$$

According to Stuiver,  $^{13}\epsilon_f$  is equal to 0.018 (often written 18‰) for A.D. 1850-1950.

## 2.2 A simple model to illustrate the approximation

Let us consider a simple geochemical model in which a perturbation by industrial  $\text{CO}_2$  is imposed on two interacting carbon pools which would otherwise be in a steady state (Fig. 1). We will assume that the two reservoirs exchange carbon of all isotopic forms according to a first order kinetic law in which the flux of a given isotope from one reservoir to the other is proportional to the amount of that isotope in the reservoir from which the flux emanates. Therefore, the proportionality constants are the same for carbon-total and both rare isotopes, i.e. isotopic fractionation does not occur.

One pool, reservoir *a*, represents the atmosphere; the other, reservoir *b*, represents a second carbon pool which exchanges carbon directly with the atmosphere. It might, for example, be either biospheric or oceanic. Let us restrict our concern to reservoir exchanges which appreciably influence the atmospheric carbon distribution on time scales of 100 yr or less. Thus we assume that changes in the fluxes are not appreciably influenced by radioactive decay for which the time constant is the order of 8000 yr.

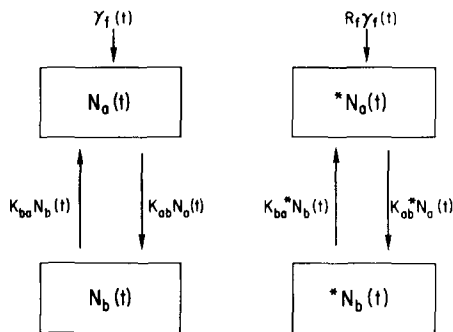


Fig. 1. Two-reservoir model in which exchange of carbon-total is proportional to the amount in the donor reservoir for all isotopes.

## 2.3 Basic equations for carbon-total

The time dependent amounts of carbon-total,  $N_a$  and  $N_b$ , in the above described model, are influenced by the instantaneous industrial source,  $\gamma_f$ , according to the pair of first order differential equations:

$$\left. \begin{aligned} dN_a/dt &= k_{ba}N_b - k_{ab}N_a + \gamma_f \\ dN_b/dt &= -k_{ba}N_b + k_{ab}N_a \end{aligned} \right\} \quad (2.4)$$

where  $k_{ba}$  and  $k_{ab}$  denote constant (i.e. steady state) transfer coefficients and  $t$  denotes time. The source term,  $\gamma_f$ , is related to the cumulative industrial  $\text{CO}_2$  production,  $Q$ , according to:

$$Q = \int_{t_0}^t \gamma_f dt. \quad (2.5)$$

To solve equation (2.4) we decompose each carbon mass,  $N_i$ , into a steady state term,  $N_{i0}$ , and a perturbation,  $n_i$ , yielding the steady state equations:

$$dN_{a0}/dt = -dN_{b0}/dt = k_{ba}N_{b0} - k_{ab}N_{a0} = 0 \quad (2.6)$$

and the perturbation equations:

$$dn_a/dt = k_{ba}n_b - k_{ab}n_a + \gamma_f \quad (2.7)$$

$$dn_b/dt = -k_{ba}n_b + k_{ab}n_a. \quad (2.8)$$

The mathematical solution to these equations is conveniently obtained using Laplace transforms. Each term is multiplied by  $e^{-st}$  where  $s$  is a generalized frequency appearing in the transforms but not in the final solution. Integrating from  $t = 0$  to  $\infty$ :

$$\left. \begin{aligned} (s + k_{ab})\tilde{n}_a - k_{ba}\tilde{n}_b &= \tilde{\gamma}_f \\ (s + k_{ba})\tilde{n}_b - k_{ab}\tilde{n}_a &= 0 \end{aligned} \right\} \quad (2.9)$$

where:

$$\tilde{n}_i = \int_0^{\infty} e^{-st} n_i dt \quad (2.10)$$

$$\tilde{\gamma}_f = \int_0^{\infty} e^{-st} \gamma_f dt \quad (2.11)$$

$$\int_0^{\infty} e^{-st} (d n_i / dt) dt = - (n_i)_{t=0} + s n_i \quad (2.12)$$

$$= s n_i \quad (2.13)$$

where:

$$i = a, b.$$

In matrix notation and with  $\tilde{n}_b$  preceding  $\tilde{n}_a$  (as a convenience to check with section 9, below):

$$\begin{bmatrix} s + k_{ba} & -k_{ab} \\ -k_{ba} & s + k_{ab} \end{bmatrix} \begin{bmatrix} \tilde{n}_b \\ \tilde{n}_a \end{bmatrix} = \begin{bmatrix} 0 \\ \tilde{\gamma}_f \end{bmatrix} \quad (2.14)$$

Since the  $\tilde{n}_i$  are related by a set of linear algebraic equations, they are readily solved for by the use of determinants (see for example, Bronson, 69). Thus:

$$\left. \begin{aligned} \bar{n}_a &= \frac{\tilde{\gamma}_f(s + k_{ba})}{s(s + k_{ba} + k_{ab})} \\ \bar{n}_b &= \frac{\tilde{\gamma}_f k_{ab}}{s(s + k_{ba} + k_{ab})} \end{aligned} \right\} \quad (2.15)$$

The general solution for  $n_a$  and  $n_b$  will not be discussed (see for example, Keeling, 73b). Considerable insight into the properties of this model can be obtained, however, by considering the case of an industrial CO<sub>2</sub> source which obeys the exponential relationship:

$$\gamma_f = \gamma_{fo} e^{\mu t} \quad (2.16)$$

where  $\gamma_{fo}$  and  $\mu$  are constants.

As shown in Fig. 2, the production of industrial CO<sub>2</sub> is actually approximated by an exponential function of the form of equation (2.16) except for the period A.D. 1914 to 1945 when two world wars and a great economic depression interfered with industrial growth. The value of  $\mu$  for a fit of the production data both before and after this period is close to 1/22 yr<sup>-1</sup>. It is likely that a somewhat slower but also nearly exponential growth prevailed for many years before 1860 (Hubbert, 74).

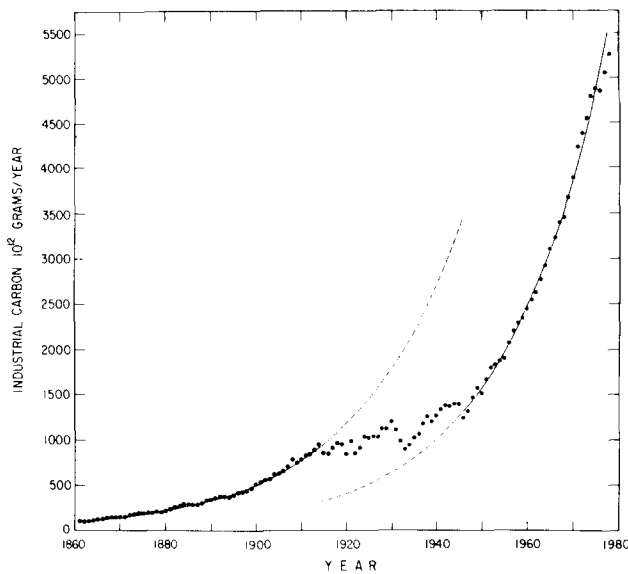


Fig. 2. The rate of production of industrial CO<sub>2</sub> plotted in units of 10<sup>12</sup> g of carbon per year. Dots: annual values based on fuel production data of the United Nations as interpreted by Keeling (73a) for A.D. 1860 to 1969, thereafter as computed by Rotty (77, and private communication). Solid curves: exponential fits to the intervals A.D. 1860 to 1914 and 1945 to 1978. The respective  $e$ -fold times,  $\mu^{-1}$ , are approximately 24.0 and 22.5 yr. Dashed curves: extensions of the solid curves beyond the interval of fitting.

With such a rapid rise in production (a doubling time of the order of 20 yr) the precise rate of growth is in any case unimportant before A.D. 1860. We may therefore

assume to good approximation that the cumulative production up to 1914 is:

$$Q = \int_{-\infty}^t \gamma_f dt \quad (2.17)$$

$$= (\gamma_{fo}/\mu) e^{\mu t} \quad (2.18)$$

It also turns out that the equation (2.18) leads to quite realistic predictions over the recent interval A.D. 1945 to 1978, since the period is greater than one  $e$ -fold time (Bacastow, 79).

It can be demonstrated that, if equation (2.18) holds, the solutions to equations (2.7) and (2.8) are of the form:

$$n_i = n_{io} e^{\mu t} \quad (2.19)$$

where the  $n_{io}$  are constants. If the exponential relationships (2.16) and (2.19) are introduced into the perturbation equations (2.7) and (2.8), the factor,  $e^{\mu t}$ , appears in all of the terms and factors out. The result in matrix notation is:

$$\begin{bmatrix} \mu + k_{ba} & -k_{ab} \\ -k_{ba} & \mu + k_{ab} \end{bmatrix} \begin{bmatrix} n_{bo} \\ n_{ao} \end{bmatrix} = \begin{bmatrix} 0 \\ \gamma_{fo} \end{bmatrix} \quad (2.20)$$

with the solution:

$$\begin{aligned} n_{ao} &= \frac{\gamma_{fo}(\mu + k_{ba})}{\mu(\mu + k_{ba} + k_{ab})} \\ n_{bo} &= \frac{\gamma_{fo} k_{ab}}{\mu(\mu + k_{ba} + k_{ab})} \end{aligned} \quad (2.21)$$

Thus the general solution for the transforms,  $\bar{n}_i$ , can be further transformed into a solution for the  $n_{io}$  by making the replacements:

$$\left. \begin{aligned} n_{io}/(s - \mu) &= \bar{n}_i \\ \gamma_{fo}/(s - \mu) &= \tilde{\gamma}_f \\ \mu &= s \end{aligned} \right\} \quad (2.22)$$

The first two replacements proceed directly from the Laplace transforms of equations (2.16) and (2.19), while the third is readily established by inspection after the first two replacements have been made. The corre-

sponding reservoir fractions are of the form (cf. equations (1.9), (2.18), (2.19)):

$$r_i = \frac{n_{io}\mu}{\gamma_{fo}} \quad (2.23)$$

Hence:

$$\left. \begin{aligned} r_a &= \frac{\mu + k_{ba}}{\mu + k_{ba} + k_{ab}} \\ r_b &= \frac{k_{ab}}{\mu + k_{ba} + k_{ab}} \end{aligned} \right\} \quad (2.24)$$

Since  $\mu$ ,  $k_{ab}$  and  $k_{ba}$  are constant,  $r_a$  and  $r_b$  are invariant.

#### 2.4 Basic equations for rare isotopic carbon

Let us next consider the corresponding equations for the rare isotopes. For  $^{14}\text{C}$ , the industrial perturbation is superimposed on a steady state in which radioactive decay is continually removing  $^{14}\text{C}$  while cosmic rays are continually producing it. If time variations in  $^{14}\text{C}$  production are neglected, the  $^{14}\text{C}$  production rate,  $^{14}\Gamma_o$ , is a constant related to preindustrial decay in both reservoirs by:

$$^{14}\Gamma_o = ^{14}\lambda (^{14}N_{ao} + ^{14}N_{bo}) \quad (2.25)$$

where  $^{14}\lambda$  denotes the radiocarbon decay constant.

Generalizing to both rare isotopes:

$$^*\Gamma_o = *\lambda (*N_{ao} + *N_{bo}) \quad (2.26)$$

where, since  $^{13}\text{C}$  is nonradioactive:

$$\left. \begin{aligned} ^{13}\lambda &= 0 \\ ^{13}\Gamma_o &= 0 \end{aligned} \right\} \quad (2.27)$$

The steady state equations for  $^{13}\text{C}$  and  $^{14}\text{C}$  are therefore:

$$\left. \begin{aligned} \frac{d *N_{ao}}{dt} &= k_{ba} *N_{bo} - k_{ab} *N_{ao} + ^*\Gamma_o - *\lambda *N_{ao} = 0 \\ \frac{d *N_{bo}}{dt} &= -k_{ba} *N_{bo} + k_{ab} *N_{ao} - *\lambda *N_{bo} = 0 \end{aligned} \right\} \quad (2.28)$$

and the perturbation equations:

$$\left. \begin{aligned} \frac{d *n_a}{dt} &= k_{ba} *n_b - k_{ab} *n_a - *\lambda *n_a + R_f \gamma_f \\ \frac{d *n_b}{dt} &= -k_{ba} *n_b + k_{ab} *n_a - *\lambda *n_b \end{aligned} \right\} \quad (2.29)$$

We will, for simplicity, assume that  $R_f$ , the  $^{13}\text{C}/\text{C}$  or  $^{14}\text{C}/\text{C}$  ratio of industrial  $\text{CO}_2$ , is constant.

Since our concern is restricted to processes which appreciably influence carbon distributions on the time scale of 100 yr or less, we are justified in neglecting the perturbation terms,  $*\lambda n_i$ , for radioactive decay, in comparison to the transfer fluxes  $k_{ba} *n_b$  and  $k_{ab} *n_a$ .

With the terms  $*\lambda n_i$  omitted, equations (2.29) are identical to those for carbon-total except that  $*n_i$  replaces  $n_i$  and  $R_f \gamma_f$  replaces  $\gamma_f$ . For the case where  $\gamma_f$  is an exponential function of time (equation (2.16)), it follows that the  $*n_i$  are also exponential time functions of the form:

$$*n_i = *n_{io} e^{\mu t} \quad (2.30)$$

analogous to equation (2.19). Carrying out a calculation similar to that for carbon-total, we find that:

$$\left. \begin{aligned} *n_{ao} &= \frac{R_f \gamma_{fo} (\mu + k_{ba})}{\mu (\mu + k_{ba} + k_{ab})} \\ *n_{bo} &= \frac{R_f \gamma_{fo} k_{ab}}{\mu (\mu + k_{ba} + k_{ab})} \end{aligned} \right\} \quad (2.31)$$

#### 2.5 Derivation of the Suess Effect and the Stuiver approximation

Comparing the above results for rare isotopic carbon with equations (2.21) for carbon-total, we find for the exponential case that:

$$*n_{io} = R_f n_{io} \quad (2.32)$$

Also, it follows from the definition of the reservoir fractions for carbon-total and the rare isotopes (see equations (1.9) and (1.14)) that:

$$*r_i = \frac{*n_i r_i}{R_{io} n_i} \quad (2.33)$$

Therefore, for the exponential case (equation (2.32)):

$$*r_i = \frac{R_f}{R_{io}} r_i \quad (2.34)$$

The corresponding theoretical Suess Effect is obtained by substituting this expression for  $*r_i$  in equation (1.22):

$$S_i = \frac{(R_f - R_{io})Qr_i}{R_{io}N_i} \quad (2.35)$$

or, in terms of the industrial CO<sub>2</sub> isotopic variation factors,  $\epsilon_{fi}$ , defined by equation (2.2):

$$S_i = \epsilon_{fi} \frac{Q}{N_i} r_i \quad (2.36)$$

This expression is readily evaluated numerically for either reservoir. First, the  $r_i$  are found in terms of the transfer coefficients,  $k_{ab}$  and  $k_{ba}$  by equations (2.24). Then the  $N_i$  are computed from the  $r_i$  using equation (1.8), i.e.:

$$N_i = N_{io} (1 + r_i Q) \quad (2.37)$$

For <sup>13</sup>C, which does not decay radioactively, the steady state equations (2.28) simplify to:

$$k_{ab} {}^{13}N_{ao} = k_{ba} {}^{13}N_{bo} \quad (2.38)$$

whence (cf. equation (2.6)) the isotopic ratios at steady state are equal, i.e.:

$${}^{13}R_{ao} = {}^{13}R_{bo} \quad (2.39)$$

Thus for <sup>13</sup>C (cf. equation (2.2)):

$${}^{13}\epsilon_{fa} = {}^{13}\epsilon_{fb} \quad (2.40)$$

For <sup>14</sup>C, since  $R_f$  is zero (see equation (1.15)):

$${}^{14}\epsilon_{fi} = -1 \quad (2.41)$$

Therefore it follows from equation (2.36) that:

$${}^{13}S_i = -{}^{13}\epsilon_{fa} {}^{14}S_i \quad (2.42)$$

and thus the Stuiver approximation holds for both reservoirs.

### 3. Another look at the Stuiver Approximation

#### 3.1 A more general perturbation model

The foregoing two reservoir model, although useful as an introductory attempt to derive the Suess Effect for <sup>13</sup>C and <sup>14</sup>C, is an inadequate representation of atmospheric CO<sub>2</sub> exchange with either the land biosphere or the oceans, because not even approximately do either of these reservoirs exchange carbon with the atmosphere in accordance with a first order kinetic law of the kind depicted by equations (2.4).

With respect to carbon-total, a far more realistic model can be devised based on the assumption that the *change* in flux of carbon emanating from a reservoir is proportional to the *change* in amount of carbon in the reservoir. The perturbation equations for this model take the form:

$$\left. \begin{aligned} \frac{dn_a}{dt} &= k_{ba} \beta_b n_b - k_{ab} \beta_a n_a + \gamma_f \\ \frac{dn_b}{dt} &= -k_{ba} \beta_b n_b - k_{ab} \beta_a n_a \end{aligned} \right\} \quad (3.1)$$

where, as before,  $k_{ba}$  and  $k_{ab}$  denote exchange coefficients appropriate to the steady state, represented by equations (2.6), (2.28), and (2.39). The former perturbation fluxes,  $k_{ba}n_b$  and  $k_{ab}n_a$ , are now modified, however, by new constant factors  $\beta_b$  and  $\beta_a$ . The latter, which I will call ‘‘perturbation factors’’, may differ from unity by any finite amount. This model is illustrated in Fig. 3.

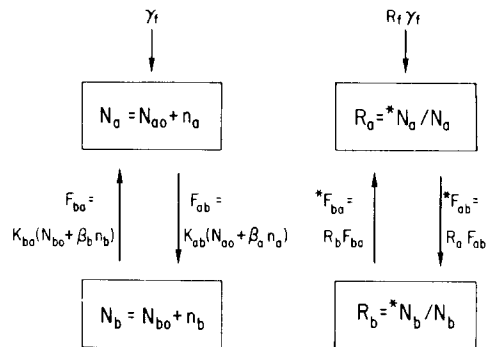


Fig. 3. Two-reservoir model in which exchange of carbon-total is proportional to the change in amount in the donor reservoir. Rare isotopic carbon exchange is proportional to the isotopic ratio of the donor reservoir without isotopic fractionation.

#### 3.2 Exchange fluxes of carbon-total and rare isotopic carbon

Although the model described in Section 2 was solved by direct consideration of the differential equations (2.4) and (2.29) governing carbon perturbations in each separate reservoir, it is convenient for the understanding of this more complicated model to consider first the relationships for the fluxes of carbon transferred

between reservoirs. For carbon-total it follows from equations (2.6) and (3.1) that:

$$\left. \begin{aligned} F_{ab} &= k_{ab}N_{ao} + \beta_a k_{ab} n_a \\ &= F_{bo}(1 + \beta_a n_a/N_{ao}) \\ F_{ba} &= k_{ba}N_{bo} + \beta_b k_{ba} n_b \\ &= F_{bo}(1 + \beta_b n_b/N_{bo}) \end{aligned} \right\} \quad (3.2)$$

where  $F_{ij}$  denotes the flux of carbon-total from reservoir  $i$  to  $j$ , with steady state value,  $F_{io} = F_{jo}$ , i.e.:

$$\left. \begin{aligned} F_{bo} &= k_{ab}N_{ao} \\ &= k_{ba}N_{bo} \end{aligned} \right\} \quad (3.3)$$

There is no compelling reason that the above flux equations (3.2) should apply to rare isotopic carbon since the physical, chemical and biological processes which determine  $\beta_a$  and  $\beta_b$  are only slightly influenced by the presence of rare isotopes. If we assume that reservoir exchange involves no preference for one isotope over another, i.e. that isotopic fractionation again does not occur, the flux of carbon-total at any given moment will carry with it the same mix of isotopes as exists at the moment in the emitting reservoir. Hence the rare isotopic fluxes will obey the relationships:

$$\left. \begin{aligned} *F_{ab} &= R_a F_{ab} \\ *F_{ba} &= R_b F_{ba} \end{aligned} \right\} \quad (3.4)$$

where  $*F_{ij}$  denotes, the flux of rare isotope from reservoir  $i$  to  $j$ . Substituting for  $F_{ab}$  and  $F_{ba}$  from equations (3.2) we obtain for rare isotopic carbon:

$$\left. \begin{aligned} *F_{ab} &= R_a F_{bo}(1 + \beta_a n_a/N_{ao}) \\ *F_{ba} &= R_b F_{bo}(1 + \beta_b n_b/N_{bo}) \end{aligned} \right\} \quad (3.5)$$

### 3.3 Perturbations of the exchange fluxes

The time dependent rare isotopic flux from reservoir  $a$  to  $b$ ,  $*F_{ab}$ , departs from its steady state value by the perturbation:

$$\left. \begin{aligned} \Delta *F_{ab} &= R_a F_{ab} - R_{ao} F_{bo} \\ &= F_{bo} \left[ R_a(1 + \beta_a n_a/N_{ao}) - R_{ao} \right] \end{aligned} \right\} \quad (3.6)$$

or, in terms of the isotopic label,  $\ell_a$ , (see equation (1.19)):

$$\Delta *F_{ab} = F_{bo} \left[ \frac{\ell_a R_{ao}}{N_{ao}} \frac{(1 + \beta_a n_a/N_{ao})}{(1 + n_a/N_{ao})} + \frac{R_{ao} \beta_a n_a}{N_{ao}} \right] \quad (3.7)$$

Similarly for the rare isotopic flux in the reverse direction:

$$\left. \begin{aligned} \Delta *F_{ba} &= R_b F_{ba} - R_{bo} F_{bo} \\ &= F_{bo} \left[ R_b(1 + \beta_b n_b/N_{bo}) - R_{bo} \right] \end{aligned} \right\} \quad (3.8)$$

In terms of label,  $\ell_b$ :

$$\Delta *F_{ba} = F_{bo} \left[ \frac{\ell_b R_{ao}}{N_{bo}} \frac{(1 + \beta_b n_b/N_{bo})}{(1 + n_b/N_{bo})} + \frac{R_{bo} \beta_b n_b}{N_{bo}} \right] \quad (3.9)$$

These expressions are non-linear owing to the perturbation factors:

$$\phi_i = \frac{1 + \beta_i n_i/N_{io}}{1 + n_i/N_{io}} \quad (3.10)$$

which multiply the label variables,  $\ell_i$ . For the case where the perturbation factors  $\beta_i$  are equal to unity, these perturbation functions are also equal to unity, and we obtain fluxes appropriate to the earlier model. For the general case, where the  $\beta_i$  depart from unity let us re-write equations (3.7) and (3.9) in terms of the  $\phi_i$  and steady state exchange coefficients  $k_{ba}$  and  $k_{ab}$ . We then obtain the expressions:

$$\left. \begin{aligned} \Delta *F_{ab} &= k_{ab} (R_{ao} \phi_a \ell_a + R_{ao} \beta_a n_a) \\ \Delta *F_{ba} &= k_{ba} (R_{ao} \phi_b \ell_b + R_{bo} \beta_b n_b) \end{aligned} \right\} \quad (3.11)$$

### 3.4 Solving the model equations

The perturbation equations for carbon-total may be solved in the same manner as for the previous models since they differ only in that the former constant factors  $k_{ab}$  and  $k_{ba}$  of equation (2.7) and (2.8) are replaced by new constant factors,  $\beta_a k_{ab}$  and  $\beta_b k_{ba}$ . Thus, the Laplace transforms,  $\tilde{n}_i$ , (cf. equation (2.15)) are given by:



$$\left. \begin{aligned} \tilde{n}_a &= \frac{\tilde{\gamma}_f(s + \beta_b k_{ba})}{s(s + \beta_b k_{ba} + \beta_a k_{ab})} \\ \tilde{n}_b &= \frac{\tilde{\gamma}_f \beta_a k_{ab}}{s(s + \beta_b k_{ba} + \beta_a k_{ab})} \end{aligned} \right\} \quad (3.12)$$

The perturbation equations for the rare isotopic abundance,  $*n_i$ , take the general form:

$$\left. \begin{aligned} d*n_a/dt &= \Delta*F_{ba} - \Delta*F_{ab} + R_f \gamma_f \\ d*n_b/dt &= \Delta*F_{ab} - \Delta*F_{ba} \end{aligned} \right\} \quad (3.13)$$

From the definition of the label variables,  $\ell_i$  (equation (1.18)), it follows that the time rates of change of the  $\ell_i$  are related to those of the  $*n_i$  according to:

$$\left. \begin{aligned} R_{ao} d\ell_a/dt &= d*n_a/dt - R_{ao} d n_a/dt \\ R_{bo} d\ell_b/dt &= d*n_b/dt - R_{bo} d n_b/dt \end{aligned} \right\} \quad (3.14)$$

Substituting for the  $d*n_i/dt$  via equation (3.13), for the  $dn_i/dt$  via equation (3.1), and subsequently for the  $\Delta*F_{ij}$  via equations (3.11):

$$\left. \begin{aligned} R_{ao} d\ell_a/dt &= R_{ao}(k_{ba}\phi_b \ell_b - k_{ab}\phi_a \ell_a) \\ &+ (R_f - R_{ao})\gamma_f + (R_{bo} - R_{ao})k_{ba}\beta_b n_b \\ R_{bo} d\ell_b/dt &= R_{ao}(-k_{ba}\phi_b \ell_b + k_{ab}\phi_a \ell_a) \\ &- (R_{bo} - R_{ao})k_{ab}\beta_a n_a \end{aligned} \right\} \quad (3.15)$$

For  $^{13}\text{C}$ , since the isotopic ratios at steady state are equal (cf. equation (2.39)), the final terms in both equations (3.15) vanish.

For  $^{14}\text{C}$  the isotopic ratios of the carbon reservoirs differ at steady state owing to radioactive decay even in the absence of isotopic fractionation. For reservoirs or portions of reservoirs which are in contact with the atmosphere and which exchange carbon so as effectively to turn over their inventories of carbon in a 100 yr or less, the average ratios differ from that of atmospheric  $\text{CO}_2$  by a few percent. In this case, although the terms in  $(R_{bo} - R_{ao})$  do not vanish for  $^{14}\text{C}$  even for small perturbations, they may be ignored with only a small loss of accuracy.

Let us therefore neglect these terms for both rare isotopes and further restrict ourselves to small perturbations so that the non-linear quotients,  $\phi_i$ , approach unity. Equations (3.15) then simplify to:

$$d\ell_a/dt = k_{ba}\ell_b - k_{ab}\ell_a + \epsilon_{fa} \gamma_f \quad (3.16)$$

$$d\ell_b/dt = -k_{ba}\ell_b + k_{ab}\ell_a \quad (3.17)$$

where  $\epsilon_{fa}$  is as defined by equation (2.2) extended to both rare isotopes.

These equations are of the form of equations (3.1) for carbon-total, except for the factor,  $\epsilon_{fa}$ , which multiplies the industrial  $\text{CO}_2$  source term,  $\gamma_f$ , and the absence of the  $\beta_i$  which appear in equation (3.1). Therefore, the Laplace transforms of the  $\ell_i$  are given by:

$$\tilde{\ell}_i = \epsilon_{fa} \tilde{n}_i' \quad (3.18)$$

where  $\tilde{n}_i'$  denote the  $\tilde{n}_i$  of equations (3.12) evaluated for  $\beta_i = 1$ , i.e.:

$$\left. \begin{aligned} \tilde{n}_a' &= \frac{\tilde{\gamma}_f(s + k_{ba})}{s(s + k_{ba} + k_{ab})} \\ \tilde{n}_b' &= \frac{\tilde{\gamma}_f k_{ab}}{s(s + k_{ba} + k_{ab})} \end{aligned} \right\} \quad (3.19)$$

From the definition of the Laplace transform (cf. equation (2.10)) it follows that:

$$\ell_i = \epsilon_{fa} n_i' \quad (3.20)$$

### 3.5 Derivation of the Suess Effect and Stuiver approximation

For the model under consideration, the Suess Effect is obtained by substituting the above result in equation (1.21):

$$S_i = \epsilon_{fa} \frac{R_{ao} n_i'}{R_{io} N_i} \quad (3.21)$$

For  $^{13}\text{C}$ , since  $R_{ao}$  and  $R_{bo}$  are equal (see equation (2.39)):

$$^{13}S_i = ^{13}\epsilon_{fa} \frac{n_i'}{N_i} \quad (3.22)$$

For  $^{14}\text{C}$ ,  $R_{ao}$  and  $R_{bo}$  differ by a few percent owing to radioactive decay, but since this inequality was disre-

garded in the derivation of equations (3.16) through (8.20), and since it can produce only a few percent error in  $^{14}S_b$ , and none in  $^{14}S_a$ , let us ignore it again. As in the previous model,  $^{14}\epsilon_{fa}$  is equal to negative one (equation (2.41)), and hence, assuming  $^{14}R_{ao}/^{14}R_{bo}$  is equal to unity:

$$^{14}S_i = -\frac{n_i'}{N_i} \quad (3.23)$$

Eliminating  $n_i'$  between equations (3.22) and (3.23) we again obtain equation (2.42). Thus the Stuiver approximation again holds. Furthermore, the derivation, in this case, does not assume any special exponential form for the input function,  $\gamma_f$ . The Stuiver approximation thus applies irrespective of the form of input. Finally, the methodology is easily extended to any number of reservoirs exchanging with the atmosphere, so that a model including both an oceanic and land biospheric reservoir will also obey the Stuiver approximation if, again, all isotopic fractionation effects are neglected except for the difference in ratio between industrial and atmospheric  $\text{CO}_2$  and if the approximations that led to equations (3.16) and (3.17) are made again.

On the other hand, it would seem unlikely that the Stuiver approximation would hold if the non-linear or the final terms in equations (3.15) were important contributors to the time variations of the  $\ell_i$ . These terms involve the carbon-total perturbation factors,  $\beta_i$ , which, depending on their magnitudes, will have more or less influence on the computed Suess Effect independent of the isotopic industrial  $\text{CO}_2$  factor,  $\epsilon_{fa}$ . Also, it would be unlikely that the influence of the  $\beta_i$  would almost cancel out when relating  $^{13}S_i$  to  $^{14}S_i$ .

Still more seriously, the assumption that the flux of carbon-total carries with it the same mix of isotopes as the emitting reservoir (equation (3.4)) neglects known isotopic fractionation effects of the order of magnitude of the isotopic industrial  $\text{CO}_2$  factor,  $^{13}\epsilon_{fa}$ . Therefore, it is important to consider a model of the carbon cycle in which fractionation is included, in order to determine precisely how large are the influences of fractionation, as well as of the perturbation terms,  $\beta_i$ , on the Suess Effect.

In regard to the land biosphere, it is also important to improve on the formulation for carbon-total because the perturbed uptake of  $\text{CO}_2$  may depend not only on the change in the amount of atmospheric  $\text{CO}_2$ , as considered above, but also on the amount of plants photosynthesizing  $\text{CO}_2$ .

Because much of the needed formulism is already revealed by considering more general versions of the two reservoir model just discussed, I will postpone consideration of models with more than two reservoirs until the general isotopic properties of the two reservoir model are examined in detail for several pairs of reservoirs of interest to the industrial  $\text{CO}_2$  problem. But before undertaking even this examination, it will be useful to make a few general remarks about the application of reservoir models to the carbon cycle.

#### 4. General remarks concerning two reservoir models

##### 4.1 Donor reservoir model

A reservoir or "box" model typically describes a system of reservoirs or compartments in which the behavior of a trace substance is prescribed principally or solely in terms of its rate of entering and escaping from each reservoir. A reservoir boundary may be a clearly defined physical surface, such as an air-sea boundary, or it may merely divide regions into convenient subregions, such as shallow and deep ocean water. Within the volumes described by these boundaries only averages or total of the properties of the reservoir are considered.

If time variable aspects of some geochemical cycle are under investigation, the flux of chemical tracer passing from one reservoir to another is most often assumed to vary in a prescribed way with the total amount, or mass, of tracer contained within the "donor" reservoir, i.e. within the reservoir from which the flux emerges. This time variable behavior of the model is often compared with a time invariant condition called a "steady state", in which the mass of tracer is everywhere conserved, in spite of gains and losses between individual reservoirs.

To express such a model in mathematical terms, let flux,  $F$ , be a function of the mass of tracer,  $N$ , in the donor reservoir:

$$F = f(N) \quad (4.1)$$

where both  $F$  and  $N$  may vary with time,  $t$ . Assume that  $F$  possesses derivatives  $f'$ ,  $f''$ , ..., with respect to  $N$ . Expanding  $f$  is a Taylor's series in the neighborhood of  $F_o = f(N_o)$ :

$$F = F_o + f'(N_o)(N - N_o) + 1/2 f''(N_o)(N - N_o)^2 + \dots \quad (4.2)$$

If the fractional increase in tracer in the reservoir is only a few percent (as is the case for additions of industrial  $\text{CO}_2$  to the carbon cycle up to the present time) it is likely that equation (4.1) can be approximated by retaining only the constant and first order terms in the expansion, i.e.:

$$F - F_o = f'(N_o)(N - N_o). \quad (4.3)$$

This expression I will rewrite:

$$\Delta F = (F_o/N_o) \beta n \quad (4.4)$$

$$= k \beta n \quad (4.5)$$

where  $\Delta F$  and  $n$  denote, respectively, the departures of  $F$  and  $N$  from the unperturbed values  $F_o$  and  $N_o$ , and  $\beta$  is a constant such that  $(F_o/N_o) \beta$  is equal to  $f'(N_o)$ . The

constant  $k$  (equal to  $F_o/N_o$ ) is often called a "transfer coefficient". In a steady state the perturbation factor  $\beta$  is not established; with respect to an emerging flux only the transfer coefficient,  $k$ , is relevant. The reciprocal of  $k$  is sometimes called a "turn over" or "residence" time. This time factor is a property of the steady state. It is not a governing property of the perturbation unless  $\beta$  is unity so that:

$$F = kN. \tag{4.6}$$

4.2 Coupled reservoir model

For transfer of carbon from the atmosphere to the land biosphere, equation (4.1), in spite of its generality, is still an inadequate representation. Rather, the transfer rate in general depends on changes in amount of carbon in the receiving biospheric pool as well as in the atmospheric donor pool. This is because the rate of photosynthesis depends on the amount of plants assimilating carbon.

To allow for a dependency of flux on the receiving reservoir mass let us postulate that the flux from reservoir "a" (say, the atmosphere) to "b" (say, the land biosphere) is given, not by equation (4.1), but by the differentiable function:

$$F_{ab} = f(N_a, N_b). \tag{4.7}$$

Expanding  $f$  in a Taylor's Series, the departures of  $F_{ab}$  from its steady state value  $F_{abo}$  is given by:

$$\Delta F_{ab} = F_{abo} \left\{ \beta_a \frac{n_a}{N_{ao}} + \beta_b \frac{n_b}{N_{bo}} + \beta_{aa} \left( \frac{n_a}{N_{ao}} \right)^2 + \beta_{bb} \left( \frac{n_b}{N_{bo}} \right)^2 + \beta_{ab} \left( \frac{n_a n_b}{N_{ao} N_{bo}} \right) + \dots \right\} \tag{4.8}$$

where the  $\beta_i$  and  $\beta_{ij}$  are constants, and as in previous sections,  $N_{ao}$  and  $N_{bo}$  denote steady state amounts of carbon-total, and  $n_i$  is written for  $N_i - N_{io}$ . To first order the perturbation flux,  $\Delta F_{ab}$ , is given by the expression:

$$\Delta F_{ab} = F_{bo} \left\{ \beta_a \frac{n_a}{N_{ao}} + \beta_b' \frac{n_b}{N_{bo}} \right\} \tag{4.9}$$

where a prime indicates a factor related to an entering reservoir, and where  $F_{bo}$  denotes the steady state flux of carbon-total.

Although the perturbation factors  $\beta_a$  and  $\beta_b'$  arise from mathematical considerations, they have an easily grasped practical significance. Suppose that is established that a small, say 1%, increase in the concentration of atmospheric CO<sub>2</sub> produces an x% change in

the growth of individual plants. Then, in the absence of precise information on the growth behavior and if x is not more than a few percent, it is probably reasonable to assume that a 2% increase in atmospheric CO<sub>2</sub> will produce a 2x% change in growth. The factor x is expressed in the model by  $\beta_a$ . A similar argument applies to the factor  $\beta_b'$ .

If the flux from reservoir  $b$  to reservoir  $a$  is also assumed to have a dual dependency on  $N_a$  and  $N_b$ , and if again only first order terms are retained in a Taylor's expansion, the returning perturbation flux  $\Delta F_{ba}$  is given by:

$$\Delta F_{ba} = F_{bo} \left\{ \beta_b \frac{n_b}{N_{bo}} + \beta_a' \frac{n_a}{N_{ao}} \right\}. \tag{4.10}$$

It follows that the net flux between reservoirs  $a$  and  $b$  is given by:

$$\Delta F_{ab} - \Delta F_{ba} = F_{bo} \left\{ (\beta_a - \beta_a') \frac{n_a}{N_{ao}} - (\beta_b - \beta_b') \frac{n_b}{N_{bo}} \right\}. \tag{4.11}$$

In terms of the steady state transfer coefficients defined by:

$$\left. \begin{aligned} k_{ba} &= F_{bo}/N_{bo} \\ k_{ab} &= F_{bo}/N_{ao} \end{aligned} \right\} \tag{4.12}$$

equation (4.11) may be rewritten:

$$\Delta F_{ab} - \Delta F_{ba} = k_{ab} (\beta_a - \beta_a') n_a - k_{ba} (\beta_b - \beta_b') n_b. \tag{4.13}$$

4.3 Higher order perturbation models and their simplification

In solving reservoir models by numerical approximation it may be preferable to retain higher order terms of the Taylor's expansion to allow for known or postulated non-linear effects (Kohlmaier, 78). For this purpose the equations just derived may be reinterpreted by including higher orders within the definition of the perturbation factors,  $\beta_a, \beta_b'$ , etc. Thus, for the flux from reservoir  $a$  to  $b$  let:

$$\left. \begin{aligned} \beta_a &= \beta_{a0} + \beta_{a10} \frac{n_a}{N_{ao}} + \beta_{a01} \frac{n_b}{N_{bo}} + \beta_{a20} \left( \frac{n_a}{N_{ao}} \right)^2 + \dots \\ \beta_b' &= \beta_{b0}' + \beta_{b10}' \frac{n_b}{N_{bo}} + \beta_{a01}' \frac{n_b}{N_{bo}} + \beta_{b20}' \left( \frac{n_b}{N_{bo}} \right)^2 + \dots \end{aligned} \right\} \tag{4.14}$$

where the factors  $\beta_{ijk}$  ( $i = a$ ) and  $\beta_{ijk}'$  ( $i = b$ ) are constants, and cross terms of the original expansion are included in either  $\beta_a$  or  $\beta_b'$  depending on convenience in the computations.

Although equations (4.9), (4.10) and (4.11) are a useful starting point in setting up a model, in practice they may be simplified for the carbon cycle. For the land biosphere it is reasonable to assume, *a priori*, that the release of CO<sub>2</sub> by plants is not influenced by changes in atmospheric CO<sub>2</sub>, i.e. that  $\beta_a'$  is zero. Also, it is possible that whatever the manner in which the uptake and release of CO<sub>2</sub> is perturbed by industrial CO<sub>2</sub> both fluxes will depend on the size of the biospheric pool to nearly the same extent, so that  $\beta_b$  and  $\beta_b'$  will be nearly the same magnitude. Thus it may suffice to assume:

$$\beta_a = \beta_b - \beta_b' = 0 \quad (4.15)$$

as was done by Bacastow and Keeling (73).

In the case of exchange between the atmosphere and the oceans and within the oceans, the expressions involving the perturbation factors may also be considerably simplified as discussed in sections 7 and 8.

#### 4.4 External factors in atmospheric-biospheric carbon exchange

In addition to interreservoir transfers of tracer which result from mechanisms intrinsic to the model, further tracer transfers are allowed in the formulation of box models provided that they arise from causes external to the reservoir system and thus are not functions of the  $N_i$ .

In modeling the carbon cycle the addition of industrial CO<sub>2</sub> to the atmosphere is such an external process. Other external processes may also be important, however. Considerable evidence has been presented recently (Adams, 77; Bolin, 77; Revelle, 77; Woodwell, 78; Wong, 78) that man has significantly reduced the carbon content of the land biosphere by land clearing, soil cultivation, and man-made forest fires. Also by reforestation, fire prevention, and fertilization of soils, man has promoted plant growth which to some degree may have counteracted man induced losses. These biospheric changes are reflected in changes in atmospheric CO<sub>2</sub> since, on a global basis, the atmosphere is the principal source and sink of land biospheric carbon.

That man's activities may have directly resulted in losses of carbon from the biosphere does not mean that the biospheric pool has necessarily lost more carbon to the atmosphere than it has gained back by internal mechanisms. For example, forest fires temporarily remove large amounts of carbon from the areas affected, but the forests, if not further disturbed by man after a fire, will usually grow back. Unless the frequency and severity of forest fires varies widely with time, the net global effect is small. But even if extended areas of land are irreversibly degraded with a significant loss of carbon and consequent increase in the atmospheric concentration, this increase may in turn accelerate uptake

of carbon in undisturbed areas of forest or grass land so that the net global loss of carbon from human activities is not as great as would appear from the direct impact. Reservoir models allow us to examine the interplay of such external and internal disturbances to the preindustrial carbon cycle.

The properties of carbon reservoirs provide no direct basis for estimating the strengths of external processes. In the direct solution of the modeling equations, the external sources are specified in the model as functions of time. But once this specification is made, the rates of change in the masses,  $N_i$  and  $*N_i$ , can be calculated on the basis of the internal responses specified by the exchange coefficients,  $k_{ij}$ , and perturbation factors,  $\beta_i$  and  $\beta_i'$ . To estimate one or more external sources by means of model calculations requires an inverse solution of the model, in which these external sources are deduced from a knowledge of the time variations in one or more of the masses,  $N_i$  or  $*N_i$ . Almost all calculations until now have employed direct solutions of the equations, but inverse solutions may become increasingly useful if reliable time series become established for <sup>13</sup>C and <sup>14</sup>C (Siegenthaler, 78).

In most cases, the fluxes between reservoirs cannot be determined from direct observations with the accuracy and on the large scale basis required for modeling the global carbon cycle, and thus they are not an aid in inferring external sources.

As noted in section 2, we cannot be sure that the carbon cycle was in balance before the industrial era, but in the absence of definite information it is perhaps better to assume a steady state than to guess at some other preindustrial condition. But if information is adequate, further external sources may be added to the model to reduce the errors arising from having assumed a preindustrial steady state.

#### 5. A detailed two reservoir model for carbon-total

Let us return to a discussion of the Suess Effect by examining one at a time the reservoir exchanges which result in significant readjustments of <sup>13</sup>C/C and <sup>14</sup>C/C ratios when industrial CO<sub>2</sub> is added to the atmosphere. To begin, let us consider a general case which is most directly applicable to the land biosphere but is sufficiently general to be adaptable to other reservoirs as well. Afterwards we will give specific attention to air-sea and subsurface oceanic exchanges.

The general two reservoir model is depicted by Fig. 4. As an initial steady state condition, let us postulate that the internally controlled fluxes of carbon-total between reservoirs "a" and "b" are in balance, and that no external processes are present. In terms of the symbols of section 4:

$$F_{bo} = k_{ba} N_{bo} = k_{ab} N_{ao}. \quad (5.1)$$

Subsequent to the time of steady state the time changes in carbon-total abundance in reservoirs *a* and *b* are given by the differential equations:

$$\left. \begin{aligned} dN_a/dt &= F_{ba} - F_{ab} + \gamma_a \\ dN_b/dt &= F_{ab} - F_{ba} + \gamma_b \end{aligned} \right\} \quad (5.2)$$

where  $F_{ab}$  and  $F_{ba}$ , as before, denote the total fluxes of carbon-total from  $a$  to  $b$  and return, and where the  $\gamma_i$  ( $i = a, b$ ) denote the sum of the external sources of carbon-total for reservoirs  $a$  and  $b$  respectively (external losses from reservoirs  $a$  and  $b$  are expressed as negative values of  $\gamma_a$  and  $\gamma_b$ ).

The corresponding equations for the perturbations in  $N_a$  and  $N_b$  from steady state are:

$$\left. \begin{aligned} dn_a/dt &= \Delta F_{ba} - \Delta F_{ab} + \gamma_a \\ dn_b/dt &= \Delta F_{ab} - \Delta F_{ba} + \gamma_b \end{aligned} \right\} \quad (5.3)$$

If the difference,  $\Delta F_{ab} - \Delta F_{ba}$ , is as specified by equation (4.13):

$$\left. \begin{aligned} [d/dt + k_{ab}(\beta_a - \beta_a')] n_a - k_{ba}(\beta_b - \beta_b') n_b &= \gamma_a \\ [d/dt + k_{ba}(\beta_b - \beta_b')] n_b - k_{ab}(\beta_a - \beta_a') n_a &= \gamma_b \end{aligned} \right\} \quad (5.4)$$

where the equations are arranged with internal processes represented on the left and external processes on the right side of the equality sign.

Since in general the perturbation factors,  $\beta_i$  and  $\beta_i'$ , are functions of the  $n_i$  according to equations (4.14), the differential equations (5.4) are non-linear and cannot be solved by exact analytical methods. If, on the other hand, variations in the factors  $\beta_i$  and  $\beta_i'$  can be neglected, then the mathematical solution to equations (5.4) is

conveniently obtained using Laplace transforms as described in section 2. Multiplying each term by  $e^{-st}$  and integrating from  $t = 0$  to  $\infty$ :

$$\left. \begin{aligned} (s + k_2) \tilde{n}_a - k_1 \tilde{n}_b &= \tilde{\gamma}_a \\ (s + k_1) \tilde{n}_b - k_2 \tilde{n}_a &= \tilde{\gamma}_b \end{aligned} \right\} \quad (5.5)$$

where to save in writing (Keeling, 73b) I introduce the perturbation transfer coefficients:

$$\left. \begin{aligned} k_1 &= k_{ba}(\beta_b - \beta_b') \\ k_2 &= k_{ab}(\beta_a - \beta_a') \end{aligned} \right\} \quad (5.6)$$

The subscripts will be numbered serially as an aid to formulating a four reservoir model in section 9. (Higher numbers will be used for air-sea and oceanic exchanges and certain special isotopic factors.)

In matrix notation and with  $\tilde{n}_b$  preceding  $\tilde{n}_a$ :

$$\begin{bmatrix} s + k_1 & -k_2 \\ -k_1 & s + k_2 \end{bmatrix} \begin{bmatrix} \tilde{n}_b \\ \tilde{n}_a \end{bmatrix} = \begin{bmatrix} \tilde{\gamma}_b \\ \tilde{\gamma}_a \end{bmatrix} \quad (5.7)$$

Solving for the  $\tilde{n}_i$  as in the case of equation (2.14):

$$\left. \begin{aligned} \tilde{n}_b &= \frac{\tilde{\gamma}_a(k_2) + \tilde{\gamma}_b(s + k_2)}{s(s + k_1 + k_2)} \\ \tilde{n}_a &= \frac{\tilde{\gamma}_a(s + k_1) + \tilde{\gamma}_b(k_1)}{s(s + k_1 + k_2)} \end{aligned} \right\} \quad (5.8)$$

We shall not consider here the general analytic solution to equation (5.4), although it presents no particular difficulties if the  $\beta_i$  and  $\beta_i'$  are constants. For cases where the  $\beta_i$  and  $\beta_i'$  are not constant, approximate numerical methods usually must be resorted to.

For the previously considered case where the only external source is industrial  $\text{CO}_2$ , and if this source is exponential in form according to equation (2.16), then the reservoir fractions (cf. equations (2.24)) are:

$$\left. \begin{aligned} r_b &= \frac{k_2}{\mu + k_1 + k_2} \\ r_a &= \frac{\mu + k_1}{\mu + k_1 + k_2} \end{aligned} \right\} \quad (5.9)$$

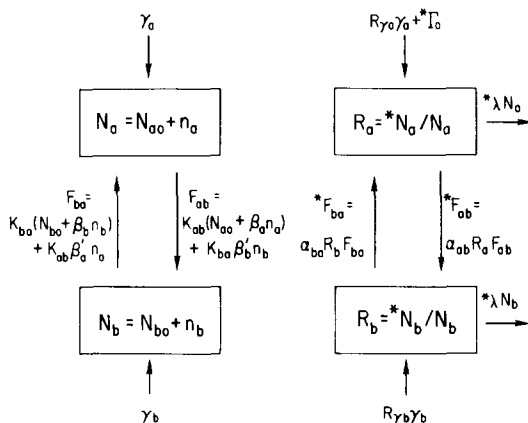


Fig. 4. Two-reservoir model in which exchange of carbon-total depends on the change in amount in both the donor and receiver reservoirs. Rare isotopic carbon exchange is proportional to the isotopic ratio of the donor reservoir modified by isotopic fractionation.

provided that the  $\beta_i$  and  $\beta_i'$ , and hence  $k_1$  and  $k_2$ , are constant.

6. The same two-reservoir model for rare isotopic carbon

6.1 Steady-state relationships

The two reservoir exchange model just considered for carbon-total will now be adapted to predict isotopic variations. Since  $^{14}\text{C}$  is produced naturally only in the atmosphere, it is now worthwhile to specify unequivocally which carbon reservoir represents the atmosphere. I shall choose reservoir  $a$ , so that reservoir  $b$  represents either the land biosphere or some other reservoir in contact with the atmosphere, such as the surface layer of the oceans. For convenience, a constant rate of  $^{14}\text{C}$  production will be assumed, although it is not necessary to do so (Bacastow, 73).

Estimates of the actual production of  $^{14}\text{C}$  during recent years have been made from direct stratospheric observations (Lingenfelter, 63), but the long term mean rate over time periods comparable to the turn-over times of the reservoirs of the carbon cycle is better established from calculations of the decay of  $^{14}\text{C}$  in these reservoirs. This is because the amount of carbon and the  $^{14}\text{C}/\text{C}$  ratio are sufficiently well known for each reservoir, that a more precise estimate can be obtained by multiplying the average amount of  $^{14}\text{C}$  for each reservoir by the  $^{14}\text{C}$  decay constant,  $^{14}\lambda$ , and summing over the reservoirs.

Since a two reservoir model does not consider all of the reservoirs of the carbon cycle which contain  $^{14}\text{C}$ , the steady state of radiocarbon for this model is correctly described only if the assumed natural production is reduced, as by equation (2.25), to match the decay occurring in the two reservoirs considered in the model. For the atmosphere the  $^{14}\text{C}$  steady state may be expressed as a balance between production and transfer from reservoir  $b$  which add  $^{14}\text{C}$  to the atmosphere and radioactive decay and transfer to reservoir  $b$  which remove  $^{14}\text{C}$  from the atmosphere, i.e.:

$$^{14}\Gamma_o + ^{14}k_{ba} ^{14}N_{bo} = (^{14}k_{ab} + ^{14}\lambda) ^{14}N_{ao} \quad (6.1)$$

where  $^{14}\Gamma_o$  denotes the steady state rate of production of  $^{14}\text{C}$  and  $^{14}k_{ba}$  and  $^{14}k_{ab}$  are the steady state transfer coefficients for  $^{14}\text{C}$ .

These latter coefficients, and similar coefficients,  $^{13}k_{ij}$ , for  $^{13}\text{C}$ , in general differ a few percent from those of carbon-total,  $k_{ij}$ , owing to differing chemical properties of the isotopes. To allow for the resulting isotopic fractionation, I introduce factors,  $\alpha_{ij}$ , such that in general:

$$^*k_{ij} = \alpha_{ij} k_{ij} \quad (6.2)$$

where  $^*k_{ij}$  and  $\alpha_{ij}$  refer to either rare isotope.

Specifically for the two reservoir model:

$$\left. \begin{aligned} ^*k_{ba} &= \alpha_{ba} k_{ba} \\ ^*k_{ab} &= \alpha_{ab} k_{ab} \end{aligned} \right\} \quad (6.3)$$

where  $\alpha_{ab}$  and  $\alpha_{ba}$  are identified, respectively, with the uptake and release of  $\text{CO}_2$  by reservoir  $b$ . In general the  $\alpha_{ij}$  are constants which are established from laboratory or field experiments in advance of formulating any geochemical model.

Eliminating  $^{14}\Gamma_o$  from equation (6.1) via equation (2.25):

$$(^{14}k_{ba} + ^{14}\lambda) ^{14}N_{bo} = ^{14}k_{ab} ^{14}N_{ao} \quad (6.4)$$

This last equation may be generalized to include the stable isotope,  $^{13}\text{C}$ , by writing:

$$(^*k_{ba} + ^*\lambda) ^*N_{bo} = ^*k_{ab} ^*N_{ao} \quad (6.5)$$

where it is understood that  $^{13}\lambda$  is equal to zero (cf. equation (2.27)).

If the  $^*k_{ij}$  in equation (6.5) are replaced by  $\alpha_{ij}k_{ij}$  according to equation (6.2), and the resulting equation is divided by the second equality of equation (5.1), we obtain as the steady state relationship between the isotopic ratios:

$$(\alpha_{ba} + ^*\lambda/k_{ba}) (^*N_{bo}/N_{bo}) = \alpha_{ab} (^*N_{ao}/N_{ao}) \quad (6.6)$$

whence, writing  $R_{io}$  for  $^*N_{io}/N_{io}$ , and rearranging:

$$\left. \begin{aligned} \alpha_{ab} R_{ao} - \alpha_{ba} R_{bo} &= ^*\lambda R_{bo}/k_{ba} \\ &= ^*\lambda \alpha_{ab} R_{ao}/(\alpha_{ba} k_{ba} + ^*\lambda) \end{aligned} \right\} \quad (6.7)$$

For  $^{13}\text{C}$  since  $^{13}\lambda$  is zero (see equation (2.27)) these expressions establish  $^{13}R_{bo}/^{13}R_{ao}$  to be equal to the quotient of the fractionation factors,  $^{13}\alpha_{ab}/^{13}\alpha_{ba}$ . For both the land biosphere and the oceans the  $^{13}\text{C}/^{12}\text{C}$  ratios are well enough known to establish the ratio,  $^{13}\alpha_{ba}/^{13}\alpha_{ab}$ , within one or two per mil through this relationship.

The fractionation factors for  $^{14}\text{C}$  are expected to be the squares of those for  $^{13}\text{C}$  (Skirrow, 65) and therefore  $^{14}\alpha_{ba}/^{14}\alpha_{ab}$  is also known once  $^{13}\alpha_{ba}/^{13}\alpha_{ab}$  is established. If the  $^{14}\text{C}$  isotopic ratio,  $^{14}R_{bo}$ , is known along with  $^{14}\alpha_{ba}/^{14}\alpha_{ab}$ , this fact is a basis for establishing  $k_{ba}$  through the first equality of equations (6.7) since  $^*\lambda$  is non-zero and known for  $^{14}\text{C}$ . This equality has been used extensively to establish steady state exchange coefficients for oceanic reservoirs. (For example, equation (11.6), below, is a variant of equation (6.7) so employed.) Alternatively, if  $^{14}R_{bo}$  is not known, but the exchange rate can be established from other data as is the case for the land biosphere, then  $^{14}R_{bo}$  can be eliminated from consideration in terms of  $k_{ba}$  using the second

equality of equation (6.7). This is done, for example, in deriving equations (6.23) below.

## 6.2 Perturbation relationships

Because of their low concentrations relative to  $^{12}\text{C}$ , both  $^{13}\text{C}$  and  $^{14}\text{C}$  act essentially as passive tracers in the carbon cycle. It is thus reasonable to postulate that their rates of transfer vary directly with their isotopic ratios in the respective emitting reservoirs. In terms of the fluxes of carbon-total,  $F_{ij}$ :

$${}^*F_{ab} = \alpha_{ab} R_a F_{ab} \quad (6.8)$$

$${}^*F_{ba} = \alpha_{ba} R_b F_{ba} \quad (6.9)$$

where isotopic fractionation is prescribed by the same factors,  $\alpha_{ij}$ , which govern steady state exchange of rare isotopic carbon (equation (6.5)). The corresponding perturbation fluxes are:

$$\Delta {}^*F_{ab} = \alpha_{ab} [R_a (F_{bo} + \Delta F_{ab}) - R_{ao} F_{bo}] \quad (6.10)$$

$$\Delta {}^*F_{ba} = \alpha_{ba} [R_b (F_{bo} + \Delta F_{ba}) - R_{bo} F_{bo}]. \quad (6.11)$$

Substituting for  $\Delta F_{ab}$  and  $\Delta F_{ba}$  according to equations (4.9) and (4.10):

$$\Delta {}^*F_{ab} = \alpha_{ab} F_{bo} \left[ R_a \left( 1 + \beta_a \frac{n_a}{N_{ao}} + \beta_b' \frac{n_b}{N_{bo}} \right) - R_{ao} \right]. \quad (6.12)$$

$$\Delta {}^*F_{ba} = \alpha_{ba} F_{bo} \left[ R_b \left( 1 + \beta_a' \frac{n_a}{N_{ao}} + \beta_b \frac{n_b}{N_{bo}} \right) - R_{ao} \right]. \quad (6.13)$$

To express these relations in terms of the perturbations of the rare isotope and of carbon-total, let us replace the  $R_i$  according to:

$$R_i = \frac{{}^*n_i}{N_i} + \frac{R_{io} N_{io}}{N_i} \quad (6.14)$$

consistent with the definition of  $R_i$  (equation (1.1)). Also, to simplify the writing let us introduce perturbation functions:

$$\phi_{ij} = \frac{1 + \beta_i (n_i/N_{io}) + \beta_j' (n_j/N_{jo})}{1 + n_i/N_{io}} \quad (6.15)$$

analogous to  $\phi_i$  of equation (3.10), but allowing for dependency on the abundances of both the donor reservoir,  $i$ , and the receiver reservoir,  $j$ .

Substituting these relations in equations (6.12) and (6.13):

$$\Delta {}^*F_{ab} = \alpha_{ab} F_{bo} \left\{ \phi_{ab} ({}^*n_a/N_{ao}) + R_{ao} \left[ \frac{(\beta_a - 1)(n_a/N_{ao})}{1 + n_a/N_{ao}} + \frac{\beta_b' (n_b/N_{bo})}{1 + n_a/N_{ao}} \right] \right\}, \quad (6.16)$$

$$\Delta {}^*F_{ba} = \alpha_{ba} F_{bo} \left\{ \phi_{ba} ({}^*n_b/N_{bo}) + R_{bo} \left[ \frac{(\beta_b - 1)(n_b/N_{bo})}{1 + n_b/N_{bo}} + \frac{\beta_a' (n_a/N_{ao})}{1 + n_b/N_{bo}} \right] \right\}. \quad (6.17)$$

The general perturbation equations for  $^{13}\text{C}$  and  $^{14}\text{C}$  are analogous to those for carbon-total (equations (5.3)) except that the external carbon-total sources  $\gamma_a$  and  $\gamma_b$  are modified by multiplication respectively by the (generally time dependent) isotopic ratios,  $R_{\gamma_i}$  ( $i = a, b$ ), which are weighted means of the isotopic ratios for the various individual sources. Also, although no radioactive source appears in the perturbation equations because the production rate,  ${}^*\Gamma_o$ , has been assumed constant, radioactive decay terms appear as perturbations of the general terms,  ${}^*\lambda {}^*N_i$ . Thus:

$$\left. \begin{aligned} d {}^*n_a/dt &= \Delta {}^*F_{ba} - \Delta {}^*F_{ab} + R_{\gamma_a} \gamma_a - {}^*\lambda {}^*n_a \\ d {}^*n_b/dt &= \Delta {}^*F_{ab} - \Delta {}^*F_{ba} + R_{\gamma_b} \gamma_b - {}^*\lambda {}^*n_b \end{aligned} \right\} \quad (6.18)$$

Substitution of the expression for  $\Delta {}^*F_{ab}$  and  $\Delta {}^*F_{ba}$  (equations (6.16) and (6.17)) leads to equations which contain terms in both the  $n_i$  and  ${}^*n_i$ . These equations are quite complicated, and as an aid in identifying terms in the  $n_i$  and  ${}^*n_i$ , I will again introduce perturbation transfer coefficients,  $k_i$ , as was done for carbon-total. The expressions for the  $d {}^*n_i/dt$  then take the general form (Keeling, 73b):

$$\left. \begin{aligned} (d/dt + {}^*\lambda + {}^*k_2) {}^*n_a - {}^*k_1 {}^*n_b &= R_{\gamma_a} \gamma_a + k_{10}' n_a - k_9' n_b \\ (d/dt + {}^*\lambda + {}^*k_1) {}^*n_b - {}^*k_2 {}^*n_a &= R_{\gamma_b} \gamma_b - k_{10}' n_a + k_9' n_b \end{aligned} \right\} \quad (6.19)$$

where the internal isotopic processes are represented on the left side of the equality sign, and the external source terms in  $\gamma_i$  and the terms in carbon-total,  $n_i$ , are on the right side. The terms,  ${}^*k_i$ , are perturbation transfer co-

efficients for rare isotopic carbon analogous to the terms,  $k_i$ , of equation (5.5) for carbon-total. The factors  $k_9'$  and  $k_{10}'$  are special functions of steady state parameters and the perturbation factors,  $\beta_i$  and  $\beta_i'$  as explained below. Since solution for the  $n_i$  in terms of the  $\gamma_i$  are obtained by solving the carbon-total equations (5.4), the terms,  $k_9'n_b$  and  $k_{10}'n_a$ , may be regarded as representing external sources with respect to isotopic exchange. Since they are not true sources, I will call them "virtual sources". The proportionality factors,  $k_9'$  and  $k_{10}'$  (or  $k_i'$  in general), are designated with primes to indicate that they have a different significance than the transfer coefficients,  $k_{ij}$ , and the related perturbation coefficients,  $k_i$  and  $*k_i$ .

Comparing equations (6.18) with (6.19) after  $\Delta^*F_{ab}$  and  $\Delta^*F_{ba}$  in equations (6.18) have been replaced according to equations (6.16) and (6.17), we obtain:

$$\left. \begin{aligned} *k_1 &= \frac{\alpha_{ba} F_{bo} \phi_{ba}}{N_{bo}} \\ *k_2 &= \frac{\alpha_{ab} F_{bo} \phi_{ab}}{N_{ao}} \end{aligned} \right\}, \quad (6.20)$$

$$\left. \begin{aligned} k_9' &= \frac{F_{bo}}{N_{bo}} \left\{ \frac{\alpha_{ba} R_{bo} (1 - \beta_b)}{1 + n_b/N_{bo}} + \frac{\alpha_{ab} R_{ao} \beta_b'}{1 + n_a/N_{ao}} \right\} \\ k_{10}' &= \frac{F_{bo}}{N_{ao}} \left\{ \frac{\alpha_{ab} R_{ao} (1 - \beta_a)}{1 + n_a/N_{ao}} + \frac{\alpha_{ba} R_{bo} \beta_a'}{1 + n_b/N_{bo}} \right\} \end{aligned} \right\} \quad (6.21)$$

where:

$$\left. \begin{aligned} \phi_{ab} &= \frac{1 + \beta_a (n_a/N_{ao}) + \beta_b' (n_b/N_{bo})}{1 + (n_a/N_{ao})} \\ \phi_{ba} &= \frac{1 + \beta_a' (n_a/N_{ao}) + \beta_b (n_b/N_{bo})}{1 + (n_b/N_{bo})} \end{aligned} \right\} \quad (6.22)$$

The expressions for the virtual source coefficients,  $k_9'$  and  $k_{10}'$  may be alternately written with explicit recognition of radioactive decay by eliminating  $\alpha_{ba}R_{bo}$  via equation (6.7):

$$\left. \begin{aligned} k_9' &= \frac{\alpha_{ab} R_{ao} F_{bo}}{N_{bo}} \left\{ \frac{\beta_b'}{1 + n_a/N_{ao}} + \frac{1 - \beta_b}{1 + n_b/N_{bo}} (1 - *\Lambda_o) \right\} \\ k_{10}' &= \frac{\alpha_{ab} R_{ao} F_{bo}}{N_{ao}} \left\{ \frac{1 - \beta_a}{1 + n_a/N_{ao}} + \frac{\beta_a'}{1 + n_b/N_{bo}} (1 - *\Lambda_o) \right\} \end{aligned} \right\} \quad (6.23)$$

where I introduce the special function:

$$*\Lambda_o = *\lambda / (\alpha_{ba} F_{bo} / N_{bo} + *\lambda). \quad (6.24)$$

The existence of the factors  $(1 + n_i/N_{io})$  in the expressions for  $*k_1$ ,  $*k_2$ ,  $k_9'$  and  $k_{10}'$  and the possibility that any or all of the  $\beta_i$  and  $\beta_i'$  are functions of the  $n_i$ , signify that these equations are non-linear and cannot be solved by the use of Laplace transforms or any other exact analytical method.

For small perturbations in which second and higher order terms in  $n_i$  can be neglected, the  $k_i$ ,  $\beta_i$ ,  $\beta_i'$ , and  $R_{\gamma i}$  become constants and the  $\phi_{io}$  are unity. In this case equations (6.20) and (6.21) simplify to:

$$*k_1 = \alpha_{ba} k_{ba} \quad (6.25)$$

$$*k_2 = \alpha_{ab} k_{ab}$$

$$k_9' = \alpha_{ab} k_{ba} R_{ao} [\beta_{bo}' + (1 - \beta_{bo}) (1 - *\Lambda_o)]$$

$$k_{10}' = \alpha_{ab} k_{ab} R_{ao} [(1 - \beta_{ao}) + \beta_{ao}' (1 - *\Lambda_o)] \quad (6.26)$$

where  $\beta_{io}$  and  $\beta_{io}'$  denote the first terms in the expansion (4.14). Substitution of these simplified expressions for the  $*k_i$  and  $k_i'$  into equations (6.19) leads to linear differential equations. From these equations Laplace transforms can be derived analogous to equations (5.5) for carbon-total.

For this linear case, in matrix notation, and with  $*n_b$  preceding  $*n_a$ , the transforms of equation (6.19) take the form:

$$\begin{bmatrix} s + *\lambda + *k_1 & -*k_2 \\ -*k_1 & s + *\lambda + *k_2 \end{bmatrix} \begin{bmatrix} *\tilde{n}_b \\ *\tilde{n}_a \end{bmatrix} = \begin{bmatrix} R_{\gamma b} \tilde{\gamma}_b \\ R_{\gamma a} \tilde{\gamma}_a \end{bmatrix} +$$

$$\begin{bmatrix} k_9' & -k_{10}' \\ -k_9' & k_{10}' \end{bmatrix} \begin{bmatrix} \tilde{n}_b \\ \tilde{n}_a \end{bmatrix}. \quad (6.27)$$



The solutions for the  $*n_i$  (cf. equation (5.8)) are:

$$\left. \begin{aligned} *n_b &= \frac{R_{\gamma_a} \tilde{\gamma}_a (*k_2) + R_{\gamma_b} \tilde{\gamma}_b (s + *\lambda + *k_2)}{(s + *\lambda) (s + *\lambda + *k_1 + *k_2)} + \frac{-k_{10}' \tilde{n}_a + k_9' \tilde{n}_b}{s + *\lambda + *k_1 + *k_2} \\ *n_a &= \frac{R_{\gamma_a} \tilde{\gamma}_a (s + *\lambda + *k_1) + R_{\gamma_b} \tilde{\gamma}_b (*k_1)}{(s + *\lambda) (s + *\lambda + *k_1 + *k_2)} + \frac{k_{10}' \tilde{n}_a - k_9' \tilde{n}_b}{s + *\lambda + *k_1 + *k_2} \end{aligned} \right\} (6.28)$$

where terms related to external rare isotopic sources,  $R_{\gamma_b}$  are for clarity separated from terms which arise from the virtual sources  $k_{10}'n_a$  and  $k_9'n_b$ .

### 6.3 Derivation of the Suess Effect and Stuiver approximation

For the linear case just considered, the solutions for the  $n_i$  and  $*n_i$  may be obtained for arbitrary inputs,  $\gamma_a$  and  $\gamma_b$ , by the use of partial fractions and convolution integrals as described by Keeling (73b). The theoretical Suess Effects for each reservoir and rare isotope are obtained by substituting into the expression:

$$S_i = \frac{1}{N_i} \left( \frac{*n_i}{R_{i_o}} - n_i \right) \quad (6.29)$$

which derives from equations (1.7) and (1.17).

To investigate how this general linear case can be simplified to yield the Stuiver approximation, let us first make the simplification that the only external source is industrial CO<sub>2</sub>, so that:

$$\left. \begin{aligned} \gamma_a &= \gamma_f \\ R_{\gamma_a} &= R_f \\ \gamma_b &= 0 \end{aligned} \right\} (6.30)$$

Also, let us obtain an expression for isotopic perturbations in terms of the isotopic label,  $\ell_i$ . Taking Laplace transforms of equation (1.18):

$$R_{a_o} \tilde{\ell}_i = *n_i - R_{i_o} \tilde{n}_i. \quad (6.31)$$

For the atmosphere, if we substitute for  $*n_a$  via the second equation of (6.28), for  $\tilde{n}_a$  and  $\tilde{n}_b$  in the resulting expression via equations (5.8), and then we make the

substitutions indicated by equations (6.30) and finally we multiply both sides of the resulting equation by the Laplace transform frequency,  $s$ , we obtain:

$$sR_{a_o} \tilde{\ell}_a = \frac{R_f \gamma_f s (s + *\lambda + *k_1)}{(s + *\lambda) (s + *\lambda + *k_1 + *k_2)} + \frac{\tilde{\gamma}_f [k_{10}' (s + k_1) - k_9' k_2]}{(s + *\lambda + *k_1 + *k_2) (s + k_1 + k_2)} - \frac{R_{a_o} \tilde{\gamma}_f (s + k_1)}{s + k_1 + k_2}. \quad (6.32)$$

The Stuiver approximation is a more restrictive case; it is expected to hold only if we further assume that isotopic fractionation and radioactive decay are negligible, i.e.:

$$\left. \begin{aligned} R_{a_o} &= R_{b_o} \\ \alpha_{a_b} &= \alpha_{b_a} = 1 \\ *\lambda &= 0 \end{aligned} \right\} (6.33)$$

If we now substitute in equation (6.32) for  $k_9'$  and  $k_{10}'$  by equations (6.26) and then make the simplifications indicated by equations (6.33), we obtain, after considerable algebraic rearrangement and use of equations (5.6) and (6.25):

$$R_{a_o} \tilde{\ell}_a = \frac{(R_f - R_{a_o}) \tilde{\gamma}_f (s + k_{b_a})}{s (s + k_{b_a} + k_{a_b})}. \quad (6.34)$$

Hence, simplifying by means of the first of equations (3.19):

$$R_{a_o} \tilde{\ell}_a = (R_f - R_{a_o}) \tilde{n}_a'. \quad (6.35)$$

This equation is equivalent in all respects to equation (3.18) applied to the atmospheric reservoir and thus leads to the Stuiver approximation.

But we are now able to compare this simplified result with the alternative linear case in which isotopic fractionation and radioactive decay are not neglected, since these phenomena are taken fully into consideration in equation (6.32). It is even possible for us to examine the influence of non-linear features neglected in the linear model because of the relative ease in obtaining numerical approximations for the  $n_i$  and  $*n_i$ , using equations (6.19) through (6.22), and then solving equation (6.29).

On the other hand, the model just considered, even without approximation, does not produce realistic predictions of the Suess Effect, because the carbon cycle

cannot be successfully simplified to two reservoirs. Therefore, further examination of the Stuiver approximation will be postponed until a model has been developed which couples the atmosphere with both the land biosphere and the oceans. This is done in Sections 7 through 9, below.

## 7. Atmosphere-ocean exchange model

### 7.1 Relationships for carbon-total

The general formulation developed in section 6, above, may be applied to any pair of reservoirs in which the interreservoir exchange of carbon-total depends principally on the abundance of carbon in one or both of the reservoirs. In the case of atmosphere-surface ocean exchange, the correct functional form of the dependence is known because the fluxes between reservoirs respond to known laws of gas exchange and chemical thermodynamics. In this section I will show that at the air-sea surface the perturbation equations (5.4) for carbon-total simplify to:

$$\left. \begin{aligned} (d/dt + k_{am}) n_a - k_{ma} \xi n_m &= \gamma_a \\ (d/dt + k_{ma} \xi) n_m - k_{am} n_a &= \gamma_m \end{aligned} \right\} \quad (7.1)$$

where "m", for the ocean surface "mixed" layer, replaces the general symbol "b". Perturbation equations will subsequently be derived for rare isotopic carbon, based on the same principals by which equations (7.1) were obtained.

The factor,  $\xi$ , which I will call the "CO<sub>2</sub> evasion factor" is analogous to the perturbation factor,  $\beta_b$ , of equation (5.4). But unlike the case of the land biosphere in which the mechanism of response to a CO<sub>2</sub> increase is highly uncertain and the magnitudes of the  $\beta_i$  are not known beforehand, the factor,  $\xi$ , is a known function of the chemical properties of sea water (Bacastow, 73, 79). As was assumed for the  $\beta$ s of the previous section,  $\xi$  can be represented by a power series in the perturbation,  $n_m$ , i.e.:

$$\xi = \xi_0 + \xi_1 \left( \frac{n_m}{N_{mo}} \right) + \xi_2 \left( \frac{n_m}{N_{mo}} \right)^2 + \dots \quad (7.2)$$

where the  $\xi_i$  are known constants.

The flux of CO<sub>2</sub> gas across the air-sea interface is a turbulent phenomenon in which processes within a thin oceanic boundary layer are believed to be rate determining (Broecker, 78). At equilibrium, the laws of thermodynamics require that the partial pressures of CO<sub>2</sub> gas in the two phases be equal, while, for departures from equilibrium, kinetic considerations strongly suggest that the net flux is proportional to the difference in partial pressure (Skirrow, 75, p.135). These relations are equivalent to assuming that the one-way flux in each direction is proportional to the CO<sub>2</sub> pressure in the phase from which that flux originates.

The rate of CO<sub>2</sub> gas exchange cannot be predicted by any existing theory, and it is not even known with certainty how the rate constant varies with wind, wave conditions, or temperature. Nevertheless it seems reasonable to assume that the global averages of these physical properties have not varied markedly during the industrial era. Therefore I will postulate that the global average flux,  $F_{am}$ , from the atmosphere to the ocean and the return flux,  $F_{ma}$ , are given by the simple proportionalities:

$$\left. \begin{aligned} F_{am} &= \kappa_{am} P_a \\ F_{ma} &= \kappa_{ma} P_m \end{aligned} \right\} \quad (7.3)$$

where  $\kappa_{am}$  and  $\kappa_{ma}$  denote time-independent gas transfer coefficients, and  $P_i$  (with steady state value  $P_{io}$ ) denotes the average partial pressure of CO<sub>2</sub> as the boundary of reservoir  $i$  where gas exchange occurs.

For compatibility with the previously derived exchange equations, let us define steady state exchange coefficients,  $k_{am}$  and  $k_{ma}$ , by the expressions:

$$\left. \begin{aligned} F_{mo} &= k_{am} N_{ao} \\ F_{mo} &= k_{ma} N_{mo} \end{aligned} \right\} \quad (7.4)$$

where  $F_{mo}$  is the value of  $F_{am}$  and  $F_{ma}$  (which must be the same) at steady state. It follows that:

$$F_{am} = k_{am} N_{ao} (P_a/P_{ao}) \quad (7.5)$$

$$F_{ma} = k_{ma} N_{mo} (P_m/P_{mo}) \quad (7.6)$$

### 7.2 Chemical relationships of carbonic acid and their influence on the air-sea exchange of carbon-total

In the atmosphere since the laws of gas mixtures apply, and since the atmosphere is well mixed over time scales of interest, the average CO<sub>2</sub> partial pressure,  $P_a$ , is proportional to the global CO<sub>2</sub> abundance,  $N_a$ , so that:

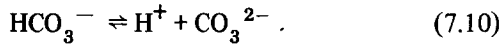
$$P_a/P_{ao} = N_a/N_{ao} \quad (7.7)$$

Therefore:

$$F_{am} = k_{am} N_a \quad (7.8)$$

For surface ocean water, even if spacial variations are neglected, the concentration of carbon-total is not in general proportional to the partial pressure of CO<sub>2</sub>. To relate the partial pressure,  $P_m$ , to the abundance,  $N_m$ , it is necessary to consider explicitly the chemical reactions which occur between dissolved CO<sub>2</sub> gas and its principal dissociation products. The chemical species in solution are related by the chemical reaction equations:





If CO<sub>2</sub> is added or removed from sea water, the amount in solution almost instantaneously readjusts with the ions of bicarbonate, HCO<sub>3</sub><sup>-</sup>, and carbonate, CO<sub>3</sub><sup>2-</sup>, to preserve constant the ratios:

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (7.11)$$

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (7.12)$$

where brackets denote concentrations in any convenient units, say, moles per 1000 g of sea water; and [H<sup>+</sup>] stands for the concentration of hydrogen ions.

In addition, the partial pressure, denoted in general by *p*<sub>CO<sub>2</sub></sub>, remains proportional to the concentration of dissolved CO<sub>2</sub> so that:

$$K_0 = \frac{[\text{CO}_2]}{P_{\text{CO}_2}} \quad (7.13)$$

where *K*<sub>0</sub> is the gas solubility coefficient.

The quantities *K*<sub>0</sub>, *K*<sub>1</sub>, and *K*<sub>2</sub> are thermodynamic equilibrium quotients which are invariant to CO<sub>2</sub> exchange at the sea surface, but which vary with temperature and the total salt content (salinity) of sea water. Because the equations involving these factors will be put to use only in connection with CO<sub>2</sub> exchange over a moderate range in [H<sup>+</sup>], it is not necessary to consider other dissolved inorganic species such as H<sub>2</sub>CO<sub>3</sub>, or ion pairs of the dissociation products of H<sub>2</sub>CO<sub>3</sub> with sea salts such as NaCO<sub>3</sub><sup>-</sup> or MgHCO<sub>3</sub><sup>+</sup>. To avoid specifying these and yet to allow for their influence on the conservation of mass, the symbol [CO<sub>2</sub>] will be understood to represent the concentration of H<sub>2</sub>CO<sub>3</sub> as well as CO<sub>2</sub>, and [HCO<sub>3</sub><sup>-</sup>] and [CO<sub>3</sub><sup>2-</sup>] will include the contributions of all ion pairs of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, respectively. The equilibrium quotients in general vary with barometric pressure, but since the pressure at the sea surface is very nearly constant, this dependency need not be considered. The total concentration of inorganic carbon dissolved in sea water is then the sum:

$$\Sigma C = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (7.14)$$

Using equations (7.11), (7.12), and (7.13) to eliminate [HCO<sub>3</sub><sup>-</sup>] and [CO<sub>3</sub><sup>2-</sup>] from equation (7.14), we obtain the relation:

$$P_{\text{CO}_2} = \left[ K_0 + \frac{K_0 K_1}{[\text{H}^+]} + \frac{K_0 K_1 K_2}{[\text{H}^+]^2} \right]^{-1} \Sigma C \quad (7.15)$$

In applying this equation to reservoir models, we shall assume that spacial variability in chemical parameters can be neglected, an assumption which has not been tested, but appears reasonable as long as we are dealing only with perturbations. Let [H<sup>+</sup>]<sub>o</sub> refer to the hydrogen ion concentration for average preindustrial surface sea water. We obtain then the relationship:

$$\frac{P_m}{P_{m_o}} = \phi_m \frac{N_m}{N_{m_o}} \quad (7.16)$$

where *N<sub>m</sub>* (with steady state value *N<sub>m</sub>o*) denotes the amount of dissolved inorganic carbon in surface ocean water and:

$$\phi_m = \frac{1 + K_1/[\text{H}^+]_o + K_1 K_2/[\text{H}^+]_o^2}{1 + K_1/[\text{H}^+] + K_1 K_2/[\text{H}^+]^2} \quad (7.17)$$

Since [H<sup>+</sup>] varies with Σ*C*, φ<sub>*m*</sub> is a function of *N<sub>m</sub>*. Equation (7.16) can therefore be expanded in a Taylor's Series in the neighborhood of *N<sub>m</sub>o*:

$$\frac{P_m}{P_{m_o}} = 1 + \xi_o \frac{n_m}{N_{m_o}} + \xi_1 \left( \frac{n_m}{N_{m_o}} \right)^2 + \dots \quad (7.18)$$

Or, according to equation (7.2):

$$\frac{P_m}{P_{m_o}} = 1 + \xi \frac{n_m}{N_{m_o}}$$

It follows directly that:

$$\phi_m = \frac{1 + \xi n_m/N_{m_o}}{1 + n_m/N_{m_o}} \quad (7.20)$$

Thus φ<sub>*m*</sub> has the same functional form as the general perturbation function, φ<sub>*ij*</sub>, of equation (6.15) for the case where the transfer rate is dependent only in the abundance of carbon in the donor reservoir (β<sub>*j*</sub>' = 0).

Before equations (7.15) and (7.17) are useful to evaluate the CO<sub>2</sub> evasion factor, ξ, the hydrogen ion concentration, [H<sup>+</sup>] must be determined as a function of Σ*C*. Several methods for doing so have been described. Bolin and Eriksson (59) and Broecker *et al.* (71) developed equations which essentially found the term, ξ<sub>o</sub>, of equation (7.18) for any given fixed set of values for all of the relevant chemical parameters of sea water including Σ*C*. By dropping small terms in their equations, they were

able to obtain expressions which could be solved directly for  $[H^+]$  and  $\xi_o$ . Keeling (73b) Bacastow and Keeling (73) using iterative procedures without approximation, and Revelle and Suess (77) by graphic methods, explicitly considered the variation in  $\xi$  with  $\Sigma C$ , equivalent to determining all significant terms in the power series of equation (7.18). For the present discussion, it is sufficient to assume that the coefficients  $\xi_o, \xi_1, \xi_2, \dots$ , are known so that  $\xi$  can be evaluated as needed during a step-wise numerical computation of the model equations, or can be declared a constant if a linear approximation is used.

### 7.3 Perturbations of the exchange fluxes for carbon-total

If we eliminate  $P_m$  between equations (7.6) and (7.16) we find that the flux of carbon-total from the surface ocean layer to the atmosphere is given in terms of  $\phi_m$  by the expression:

$$F_{ma} = k_{ma} \phi_m N_m. \quad (7.21)$$

The departures in the transfer rates,  $F_{am}$  and  $F_{ma}$ , from their preindustrial steady state value,  $F_{mo}$ , are found directly from equations (7.8) and (7.21):

$$\Delta F_{am} = k_{am} (N_a - N_{ao}) \quad (7.22)$$

whence:

$$\Delta F_{am} = k_{am} n_a, \quad (7.23)$$

similarly:

$$\Delta F_{ma} = k_{ma} (\phi_m N_m - N_{mo}). \quad (7.24)$$

In terms of the  $CO_2$  evasion factor,  $\xi$ , (cf. equation (7.20)) this latter equation simplifies to:

$$\Delta F_{ma} = k_{ma} \xi n_m. \quad (7.25)$$

Substituting for  $\Delta F_{am}$  and  $\Delta F_{ma}$  in the general two reservoir equations (5.3) with "m" replacing "b", we obtain the carbon-total perturbation equations (7.1).

### 7.4 Relationships for rare isotopic carbon

For the rare isotopes the relations between  $CO_2$  partial pressure and total dissolved inorganic carbon depend on the dissociation constants of carbonic acid, as in the case of carbon-total. With due regard to isotopic fractionation (cf. equation (7.16)):

$$\frac{*P_m}{*P_{mo}} = * \phi_m \frac{*N_m}{*N_{mo}} \quad (7.26)$$

where (cf. equations (7.17)):

$$* \phi_m = \frac{1 + *K_1/[H^+]_o + *K_1 *K_2/[H^+]_o^2}{1 + *K_1/[H^+] + *K_1 *K_2/[H^+]^2}. \quad (7.27)$$

The dissociation quotients  $*K_1$  and  $*K_2$  differ up to several per mil from  $K_1$  and  $K_2$  (Emrich, 70; Mook, 74) but the quotient:  $* \phi_m$ , is equal to  $\phi_m$  within one part in  $10^5$  for the most extreme changes possible from industrial  $CO_2$  uptake in the next few centuries (Keeling, 77). The distinction between  $* \phi_m$  and  $\phi_m$  will therefore be maintained in the derivation of exchange equations only for analytical clarity.

Let us define an isotopic  $CO_2$  evasion factor,  $* \xi$ , by the relation:

$$* \phi_m = \frac{1 + * \xi n_m/N_{mo}}{1 + n_m/N_{mo}}. \quad (7.28)$$

For applications of interest,  $* \xi$  differs from its carbon-total counterpart,  $\xi$ , by no more than 1 in  $10^4$ , and thus is also numerically indistinguishable from its counterpart,  $\xi$ , as was  $* \phi_m$  from  $\phi_m$ .

The dependence of  $* \phi_m$  on  $n_m$  rather than on  $*n_m$  arises because the hydrogen ion concentration,  $[H^+]$ , depends on carbon-total. The concentration is independent of isotopic composition except for a very small effect arising from the variable contribution of  $^{13}C$  to carbon-total.

The transfers of rare isotopic carbon involve additional kinetic fractionations which modify the gas transfer coefficients,  $\chi_{am}$  and  $\chi_{ma}$ , by factors which I will denote by  $\alpha_{am}'$  and  $\alpha_{ma}'$ . Thus:

$$*F_{am} = \alpha_{am}' \chi_{am} *P_a, \quad (7.29)$$

$$*F_{ma} = \alpha_{ma}' \chi_{ma} *P_m. \quad (7.30)$$

In terms of the corresponding fluxes of carbon-total (equation (7.3)):

$$*F_{am} = \alpha_{am}' (*P_a/P_a) F_{am}, \quad (7.31)$$

$$*F_{ma} = \alpha_{ma}' (*P_m/P_m) F_{ma}. \quad (7.32)$$

Since the partial pressure and abundance of atmospheric  $CO_2$  are proportional for all isotopic species:

$$*P_a/P_a = *N_a/N_a \quad (7.33)$$

so that:

$$*F_{am} = \alpha_{am}' (*N_a/N_a) F_{am} \quad (7.34)$$

and since equation (7.8) holds:

$$*F_{am} = \alpha_{am} k_{am} *N_a \quad (7.35)$$

where the prime on  $\alpha_{am}'$  is dropped because the fractionation factor is the same whether defined with respect to partial pressure or carbon abundance.

For surface ocean water, the relationships are more complicated. We shall make use of the factors,  $^*\phi_m$  and  $^*\xi$ , to establish the correct functional dependence of isotopic flux on the perturbation masses,  $^*n_i$  and  $n_i$ .

Eliminating  $^*P_m$  between equations (7.26) and (7.32):

$$^*F_{ma} = \alpha_{ma}' \cdot ^*\phi_m \left( \frac{^*N_m \cdot ^*P_{mo}}{^*N_{mo} \cdot P_m} \right) F_{ma} \quad (7.36)$$

Let us introduce the factor  $\alpha_{ma}$  to denote the overall isotopic fractionation between atmospheric CO<sub>2</sub> and total dissolved inorganic carbon in surface ocean water at steady state. Thus, by definition

$$\alpha_{ma} \frac{^*N_{mo}}{N_{mo}} = \alpha_{ma}' \frac{^*P_{mo}}{P_{mo}} \quad (7.37)$$

Eliminating  $\alpha_{ma}'$  between the last two equations:

$$^*F_{ma} = \alpha_{ma} \cdot ^*\phi_m \left( \frac{^*N_m \cdot P_{mo}}{N_{mo} \cdot P_m} \right) F_{ma} \quad (7.38)$$

and hence eliminating  $P_{mo}F_{ma}/(N_{mo}P_m)$  via equation (7.6):

$$^*F_{ma} = \alpha_{ma} k_{ma} \cdot ^*\phi_m \cdot ^*N_m \quad (7.39)$$

analogous to equation (7.21) for carbon-total.

The departures of the transfer rates,  $^*F_{am}$  and  $^*F_{ma}$ , from their preindustrial steady state values are obtained directly from equations (7.35) and (7.39):

$$\Delta^*F_{am} = \alpha_{am} k_{am} (^*N_a - ^*N_{ao}) \quad (7.40)$$

$$= \alpha_{am} k_{am} \cdot ^*n_a, \quad (7.41)$$

$$\Delta^*F_{ma} = \alpha_{ma} k_{ma} (^*\phi_m \cdot ^*N_m - ^*N_{mo}) \quad (7.42)$$

$$= \alpha_{ma} k_{ma} [^*\phi_m \cdot ^*n_m + ^*N_{mo} (^*\phi_m - 1)]. \quad (7.43)$$

But from equation (7.28) it follows that:

$$^*\phi_m - 1 = \frac{(^*\xi - 1) n_m / N_{mo}}{1 + n_m / N_{mo}} \quad (7.44)$$

Therefore:

$$\Delta^*F_{ma} = \alpha_{ma} k_{ma} \left\{ ^*\phi_m \cdot ^*n_m + \frac{R_{mo} (^*\xi - 1) n_m}{1 + n_m / N_{mo}} \right\} \quad (7.45)$$

In terms of the steady state carbon-total flux,  $F_{mo}$  (cf. equations (7.4):

$$\Delta^*F_{ma} = \alpha_{ma} F_{mo} \left\{ ^*\phi_m (^*n_m / N_{mo}) + \frac{R_{mo} (^*\xi - 1) (n_m / N_{mo})}{1 + n_m / N_{mo}} \right\} \quad (7.46)$$

This expression corresponds to the general two reservoir expression (equation (6.17) except that subscript  $m$  replaces  $b$ ,  $^*\xi$  replaces  $\xi$ , the direct analogue of  $\beta_b$ , and  $^*\phi_m$  replaces  $\phi_m$ , the direct analogue of  $\phi_b$ . Also  $\beta_a'$  is zero since the evasion of CO<sub>2</sub> from sea water is independent of the amount of CO<sub>2</sub> in the atmosphere.

The substitutions of  $^*\xi$  for  $\xi$  and  $^*\phi_m$  for  $\phi_m$  arise because the general isotopic postulate, analogous to equation (6.9):

$$^*F_{ma} = \alpha_{ma} R_m F_{ma} \quad (7.48)$$

is not exactly fulfilled by equation (7.39). Instead, consistent with equations (7.21) and (7.39):

$$^*F_{ma} = \alpha_{ma} R_m (^*\phi_m / \phi_m) F_{ma} \quad (7.49)$$

Since  $^*\phi_m / \phi_m$  differs very slightly from unity, as noted earlier, this quotient can be neglected without introducing noticeable error into the calculations. Thus the general formulism of section 6 is adequate for practical applications.

By subtracting  $^*\xi - 1$  from both sides of equation (7.44) it can be shown that:

$$\frac{(^*\xi - 1)}{1 + n_m / N_{mo}} = (^*\xi - ^*\phi_m) \quad (7.50)$$

Hence the perturbation flux  $^*F_{ma}$  may also be written:

$$\Delta^*F_{ma} = \frac{\alpha_{ma} k_{am} N_{ao}}{N_{mo}} [R_{mo} (^*\xi - ^*\phi_m) n_m + ^*\phi_m \cdot ^*n_m] \quad (7.51)$$

where  $F_{mo}$  is replaced according to the first of equations (7.4). Equation (7.51) is equivalent to equation (6.49) of Keeling (73b) if dissolved organic carbon, allowed for in

his expression, is neglected, and we note that  $*\phi_m$  is equivalent to the quotient,  $\phi/\phi_0$ , in his equation.

7.5 Solving the model equations

In terms of the perturbation fluxes,  $F_{am}$ , and  $F_{ma}$ , the equations for the perturbations in  $N_a$  and  $N_m$  are given in general by equations (5.3) with "m" replacing "b", i.e.:

$$\left. \begin{aligned} d n_a / dt &= \Delta F_{ma} - \Delta F_{am} + \gamma_a \\ d n_m / dt &= \Delta F_{am} - \Delta F_{ma} + \gamma_m \end{aligned} \right\} \quad (7.52)$$

where  $\gamma_a$  and  $\gamma_m$  denote the combined external sources of carbon-total for the two reservoirs. A source term for the ocean surface layer,  $\gamma_m$ , is included for completeness. For example, if we were to investigate the proposal of Marchetti (76) to inject industrial CO<sub>2</sub> into the oceans this might require a calculation in which  $\gamma_m$  was non-zero.

In later applications of these equations, it will prove convenient to introduce perturbation terms for coefficients similar to those of sections 5 and 6. Thus (cf. Keeling, 73b) equations (7.52) will now be rewritten:

$$\begin{aligned} (d/dt + k_3) n_a - k_4 n_m &= \gamma_a, \\ (d/dt + k_4) n_m - k_3 n_a &= \gamma_m. \end{aligned} \quad (7.53)$$

Similarly for rare isotopic carbon:

$$\begin{aligned} d*n_a / dt &= \Delta*F_{am} - \Delta*F_{ma} + R_{\gamma_a} \gamma_a - *\lambda n_a, \\ d*n_m / dt &= \Delta*F_{ma} - \Delta*F_{am} + R_{\gamma_m} \gamma_m - *\lambda n_m \end{aligned} \quad (7.54)$$

whereas, consistent with the notation of equation (6.19):

$$\begin{aligned} (d/dt + *\lambda + *k_3) *n_a - *k_4 *n_m &= R_{\gamma_a} \gamma_a + k_7' n_m, \\ (d/dt + *\lambda + *k_4) *n_m - *k_3 *n_a &= R_{\gamma_m} \gamma_m - k_7' n_m. \end{aligned} \quad (7.55)$$

In this last expression a virtual source coefficient  $k_7'$  has been introduced analogous to the use of  $k_9'$  and  $k_{10}'$  in equations (6.19). Matching terms after substituting for the perturbation fluxes according to equations (7.23), (7.25), (7.41) and (7.51) it follows that:

$$k_3 = k_{am} \quad (7.56)$$

$$k_4 = \xi k_{ma} \quad (7.57)$$

$$*k_3 = \alpha_{am} k_{am} \quad (7.58)$$

$$*k_4 = \alpha_{ma} k_{ma} *\phi_m \quad (7.59)$$

$$k_7' = \alpha_{ma} k_{ma} R_{m_0} (*\xi - *\phi_m). \quad (7.60)$$

The solutions for the  $n_i$  (cf. equation (5.8)) are:

$$\left. \begin{aligned} \tilde{n}_a &= \frac{\tilde{\gamma}_a (s + k_4) + \tilde{\gamma}_m (k_4)}{s (s + k_3 + k_4)} \\ \tilde{n}_m &= \frac{\tilde{\gamma}_a (k_3) + \tilde{\gamma}_m (s + k_3)}{s (s + k_3 + k_4)} \end{aligned} \right\} \quad (7.61)$$

while for rare isotopic carbon (cf. equation (6.28)):

$$\left. \begin{aligned} \tilde{n}_a &= \frac{R_{\gamma_a} \tilde{\gamma}_a (s + *\lambda + *k_4) + R_{\gamma_m} \tilde{\gamma}_m (*k_4)}{(s + *\lambda) (s + *\lambda + *k_3 + *k_4)} \\ &+ \frac{-k_7' n_m}{s + *\lambda + *k_3 + *k_4} \\ \tilde{n}_m &= \frac{R_{\gamma_a} \tilde{\gamma}_a (*k_3) + R_{\gamma_m} \tilde{\gamma}_m (s + *\lambda + *k_3)}{(s + *\lambda) (s + *\lambda + *k_3 + *k_4)} \\ &+ \frac{k_7' n_m}{s + *\lambda + *k_3 + *k_4} \end{aligned} \right\} \quad (7.62)$$

The theoretical Suess Effect for the atmosphere and surface ocean can be derived from the  $n_i$  and  $*n_i$  by the procedures discussed in section 6.

But since neither this model nor that of section 6 adequately portrays the perturbed carbon cycle as a whole, it is not worthwhile deriving these expressions. Rather, we shall, in the next section, take up the problem of modeling transport of carbon within the oceans. Then in section 9 we will consider a composite model with four reservoirs, as the basis for computing the Suess Effect realistically.

8. Vertical exchange of carbon within the oceans

8.1 General remarks

The vertical transport of carbon within the oceans proceeds by both water motion (advection and eddy diffusion) and by gravitational settling of particles,

principally of biological origin (Menzel, 74; Parsons, 75). Although the former mechanism is clearly dominant, approximately 10% of the carbon arrives in deep water via the second mechanism (Keeling, 68; Mopper, 79, p. 293). Both organic (reduced) carbon and biogenic carbonate are involved with organic carbon providing about two-thirds of the total flux (Broecker, 74, p. 11). Up to the present time the existence of this gravitational flux can have had only a minor influence globally on the transient adjustment of carbon-total between the atmosphere and oceans because the flux does not respond appreciably to small changes in CO<sub>2</sub> partial pressure. For rare isotopic carbon, however, the gravitational transport responds to changes in isotopic ratio in the ocean surface layer and therefore enters into the relationships for transient adjustment arising from CO<sub>2</sub> exchange at the air-sea boundary.

Within the published literature the gravitational transport of rare isotopic carbon in response to industrial CO<sub>2</sub> has been considered only in terms of a two reservoir model of the oceans consisting of surface and deep ocean layers (Bacastow, 73; Keeling, 73b). Because the influence of gravitational flux is found in these models to be a small effect, it does not seem worthwhile here to carry out a detailed analysis for more complex models of subsurface oceanic transport. Nevertheless, in so far as practicable, I will develop the formalism in a manner which can be extended to such models in case this proves to be desirable in the future.

To express water transport and the gravitational flux of carbon in the framework of a two reservoir model, let  $F_g$  denote the time-dependent gravitational flux of carbon-total transported downward from the surface layer into the water immediately below, and let  $k_{md}N_m$  denote the corresponding downward flux transported by sea water, where  $k_{md}$  is a time-invariant transfer coefficient. The latter flux is thus assumed to be proportional to the mass of carbon-total in the ocean surface layer. An assumption of proportionality is reasonable when the mechanism of transport is conveyance of a chemical solution of uniform composition within the surface layer. The dependence of the gravitational flux on properties of ocean water will not, at this point, be specified. It will be understood, however, that the bottom of the surface layer is deep enough that all of the gravitational flux originates in this layer.

Let  $F_{md}$  denote the time-dependent downward flux of carbon-total at the boundary between surface and subsurface water by both transport mechanisms. Then:

$$F_{md} = k_{md} N_m + F_g \tag{8.1}$$

where subscript,  $d$ , denotes the subsurface ("deep") ocean reservoir. In the absence of any external sources of carbon, the downward flux must be balanced by a return from the subsurface ocean, and since gravity carries carbon only downward, this flux is properly assumed to result solely from motion of the sea water. Thus, in a two reservoir approximation of oceanic transport we may write for the return flux of carbon-total:

$$F_{dm} = k_{dm} N_d \tag{8.2}$$

where  $N_d$  denotes all of the oceanic carbon-total below the surface layer, and where  $k_{dm}$ , like  $k_{md}$  is a time-invariant transfer coefficient. In contrast to  $k_{md}$ , however, there is little physical basis to justify constancy of  $k_{dm}$  during a perturbation in carbon abundance. The plausibility of equation (8.2) needs, therefore, to be examined.

### 8.2 The two reservoir vertical exchange model in perspective

Let  $W_m$  denote the mass of water in the ocean surface layer and  $W_d$  the entire mass of water laying below that layer. In a two reservoir model the products,  $k_{md}W_m$  and  $k_{dm}W_d$ , express respectively the downward and upward flux of water across the boundary dividing surface and subsurface waters. To preserve continuity of water within the two layers:

$$k_{md} W_m = k_{dm} W_d \tag{8.3}$$

This equation essentially defines the transfer coefficient,  $k_{dm}$ , in terms of  $k_{md}$ , and the ratio of water volumes.

To obtain some impression of the shortcoming of this approach, let us briefly consider an alternative model in which the water below a surface ocean layer having always the same dimensions is further differentiated vertically by subdivision into any number of layers,  $u$ ,  $v$ , and so on, in the descending direction (Fig. 5). In the limit of a large number of such layers, such a subdivided model approaches the vertical diffusion model of Oeschger *et al.* (75). A small number of reservoirs may, however, also be of interest. For example, Broecker (66) divided the upper 750 meters of the non-polar ocean into five equally spaced layers overlying a single deep ocean reservoir in order to portray the diffusive character of the main oceanic thermocline.

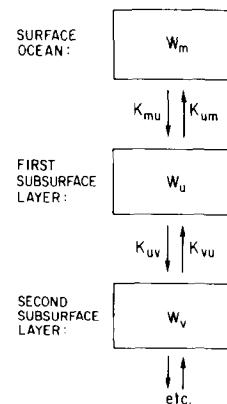


Fig. 5. Multiple reservoir model of the vertical exchange of tracers in the oceans. Relationships are shown only for exchange of water. Tracers are assumed to be carried by the water in proportion to their concentrations in the donor reservoirs.

Let  $N_u, N_v, \dots$ , denote the amount of carbon-total and  $W_u, W_v, \dots$ , the masses of water, in each subsurface layer. These quantities are related to the deep water variables previously defined by:

$$N_d = N_u + N_v + \dots \quad (8.4)$$

$$W_d = W_u + W_v + \dots \quad (8.5)$$

where the sums are over all subsurface layers.

Let  $k_{ij}W_i$  and  $k_{ji}W_j$  denote, respectively, the downward and upward fluxes of water between any pair of adjacent oceanic reservoirs  $i$  and  $j$ . The fluxes of water at the base of the surface layer in the two reservoir and multiple reservoir models are the same if we assume:

$$k_{md} W_m = k_{mu} W_u, \quad (8.6)$$

$$k_{dm} W_d = k_{um} W_u. \quad (8.7)$$

Since the surface layer has been defined to include the entire zone in which the gravitational flux,  $F_g$ , originates, the former expression for  $F_{md}$ , (equation (8.1)) holds, irrespective of the number of subsurface layers designated in the model.

On the other hand, it is unlikely that the two-reservoir upward flux,  $F_{dm}$ , as given by equation (8.2) will be equal to the upward flux,  $F_{um}$ , in the multiple reservoir model since this would require that:

$$k_{dm} N_d = k_{um} N_u \quad (8.8)$$

which, in view of equation (8.7) is equivalent to:

$$N_u/W_u = N_d/W_d \quad (8.9)$$

i.e. the average concentration of carbon-total would have to be the same in reservoir  $u$  as in the entire subsurface ocean.

The presence of a gravitational flux requires, however, that the concentration of carbon-total increase with depth, and therefore equation (8.9) is not a reasonable condition to impose on a comparison between models. Furthermore, the gravitational flux is a physical quantity capable of direct measurements, and therefore its steady-state value,  $F_{go}$ , should be approximately the same for all models having the same surface layer conditions. In order that the steady-state distribution of carbon-total be satisfied under these circumstances, the upward and downward fluxes of water at the base of the surface layer must generally increase in the model if the number of subsurface reservoirs increases. Therefore, models with different numbers of subsurface reservoirs cannot be perfectly matched at the lower boundary of the surface layer.

Matching is likely to be still less perfect if the surface layers of the models are made dissimilar. For example,

if the surface layer is made several hundred meters deep, as in the two reservoir models of Keeling (73) and Keeling and Bacastow (77), part of the gravitational flux,  $F_g$ , is lost within that layer. Both terms of the right side of equation (8.1) then differ in magnitude from corresponding terms for a multiple reservoir model with a shallow surface layer.

Discrepancies between global carbon cycle models having differently subdivided oceanic reservoirs may not be serious, however, if the magnitudes of the transfer coefficients are based on the same assumed pre-industrial spacial distributions of chemical concentrations. In particular, the predictions of industrial  $\text{CO}_2$  perturbations for surface ocean water and the land biosphere, are likely to be nearly the same, because the industrial perturbation originates in a reservoir remote from subsurface ocean waters while the surface ocean and biospheric reservoirs of interest are in close contact with the atmosphere. This point was investigated by Keeling and Bacastow (77) for the carbon-total fractions,  $r_i$  by comparing the predictions of the two reservoir model with the vertical diffusion model of Oeschger *et al.* (75) ignoring transport by the gravitational flux. Indeed, if the only carbon-total perturbation under consideration is an exponentially increasing input of industrial  $\text{CO}_2$  to the atmosphere, a two reservoir model can be constructed which gives identical predictions of atmospheric, biospheric and total oceanic change to that of the vertical diffusion model, after meeting the above requirements regarding steady-state conditions. Thus, provided that details of the transport and storage of carbon within the oceans are not under investigation, a two reservoir oceanic model is a useful starting point for studies of the Suess Effect.

### 8.3 Exchange fluxes of carbon-total and rare isotopic carbon in relation to steady state

With the above concepts in mind we shall proceed to develop the equations for the two-reservoir model.

By analogy, with equations (8.1) and (8.2) the time-dependent isotopic fluxes are given by the expressions:

$$*F_{md} = k_{md} *N_m + \alpha_{mg} R_m F_g \quad (8.10)$$

$$*F_{dm} = k_{dm} *N_d \quad (8.11)$$

where the factor  $\alpha_{mg}$  allows for isotopic fractionation associated with the gravitational flux. Approximately 70% of the carbon in this flux is derived from sea water bicarbonate by the photosynthesis of marine plants (Broecker, 74, p. 11) which preferentially assimilate  $^{12}\text{C}$  by the order of 20‰. The remaining 30%, also derived from sea water bicarbonate, is calcareous and aragonitic carbonate which is enriched in  $^{12}\text{C}$  only to a very small degree (ca. 1‰) (Craig, 70; Kroopnick, 74, p. 213). The overall factor,  $\alpha_{mg}$ , (see equation (10.36) and Table 2, below) is obtained as a weighted average of these two fractionations. No isotopic fractionation is to be expected in the transport of carbon by water motion since turbulence in this motion prevents the influence of



molecular scale forces which could affect one isotope differently than another.

At steady state the upward and downward fluxes for carbon-total are equal, i.e.:

$$\left. \begin{aligned} F_{do} &= k_{md} N_{mo} + F_{go} \\ &= k_{dm} N_{do} \end{aligned} \right\} \quad (8.12)$$

where  $F_{do}$  denotes the preindustrial (steady-state) value of  $F_{md}$  (or  $F_{dm}$ ). For rare isotopic carbon at steady state:

$$k_{md} *N_{mo} + \alpha_{mg} R_{mo} F_{go} = k_{dm} *N_{do} + * \lambda *N_{do} \quad (8.13)$$

where the term in  $* \lambda$  provides for radiocarbon decay in the subsurface ocean layer, "d".

Consistent with equations (8.12) and (8.13), the magnitudes of the flux constants and of  $F_{go}$  may be expressed in terms of concentrations  $N_{mo}/W_m$ ,  $N_{do}/W_d$ , and the isotopic ratios. Solving (8.12) for  $F_{go}$ , we find:

$$F_{go} = k_{dm} W_d \left( \frac{N_{do}}{W_d} - \frac{N_{mo}}{W_m} \right) \quad (8.14)$$

where the factor in parentheses is obtained by making use of equation (8.3). Equation (8.14) shows that the gravitational flux is balanced by a net transport proportional to the product of the water flux and the concentration difference between reservoirs.

Similarly, for rare isotopic carbon:

$$\alpha_{mg} R_{mo} F_{go} = k_{dm} W_d \left( \frac{*N_{do}}{W_d} - \frac{*N_{mo}}{W_m} \right) + * \lambda *N_{do} \quad (8.15)$$

where due regard is given to isotopic fractionation and radioactive decay.

By eliminating  $F_{go}$  between equations (8.14) and (8.15), we obtain a relation similar to the general expressions (6.7):

$$\left. \begin{aligned} \alpha_{md} R_{mo} - R_{do} &= * \lambda R_{do} / k_{dm} \\ &= * \lambda \alpha_{md} R_{mo} / (k_{dm} + * \lambda) \end{aligned} \right\} \quad (8.16)$$

where:

$$\alpha_{md} = \alpha_{mg} + \frac{N_{mo}}{W_m} \frac{W_d}{N_{do}} (1 - \alpha_{mg}) \quad (8.17)$$

is the apparent isotopic fractionation factor of deep water carbon relative to surface water owing to the downward flux of carbon by gravitational settling. (This term is the same as  $\alpha_{dm}$  of Keeling (73b).) Equations (8.16) are useful to establish  $^{13}R_{do}/^{13}R_{mo}$  or  $k_{dm}$  in the manner discussed after equation (6.7).

#### 8.4 Perturbations of the exchange fluxes

Although there is as yet no direct evidence that the gravitational flux is perturbed by industrial CO<sub>2</sub>, this possibility will be considered in deriving perturbation equations to be prepared if such evidence is found in the future. Including such a provision also permits a check to be made on the sensitivity of the calculations to an assumption of constant flux.

Let us therefore assume that the gravitational flux, including both organic particles and biogenic carbonate, departs from its steady state value in a manner that can be expressed as a function of the amount of carbon-total in the ocean surface layer, i.e.:

$$F_g = f(n_m). \quad (8.18)$$

If  $F_g$  is expanded in a Taylor's series (cf. equation (4.2) in the neighborhood of  $F_{go}$ :

$$\Delta F_g = \beta_g F_{go} n_m / N_{mo} \quad (8.19)$$

where:

$$\beta_g = \beta_{go} + \beta_{g1} \left( \frac{n_m}{N_{mo}} \right) + \beta_{g2} \left( \frac{n_m}{N_{mo}} \right)^2 + \dots \quad (8.20)$$

The coefficients,  $\beta_{gi}$ , are constants derived from the expansion. The departure of the total downward flux,  $F_{md}$ , from its steady state value (cf. equation (8.1)) is:

$$\Delta F_{md} = k_{md} n_m + \Delta F_g. \quad (8.21)$$

Since  $F_{md}$  is a function of  $n_m$  we may write, analogous to equation (4.9):

$$\Delta F_{md} = \beta_m F_{do} n_m / N_{mo} \quad (8.22)$$

where the perturbation factor,  $\beta_m$ , is a function of  $n_m$ . If we replace  $\Delta F_g$  in equation (8.21) according to equation (8.19), eliminate  $\Delta F_{md}$  via equations (8.22), and solve the resulting expression for  $\beta_m$ , we obtain:

$$\beta_m = \frac{k_{md} N_{mo}}{F_{do}} + \frac{F_{go} \beta_g}{F_{do}}. \quad (8.23)$$

Next, we let  $\beta_{mo}$  denote the first term of this expression, i.e.:

$$\beta_{m_o} = \frac{k_{md} N_{m_o}}{F_{d_o}}. \quad (8.24)$$

Since  $\beta_g$  is zero for a constant gravitational flux,  $\beta_{m_o}$  represents the value of  $\beta_m$  in the absence of a perturbation in  $F_g$ . Also,  $\beta_{m_o}$  is equal to the fraction of the total downward flux of carbon-total at steady state transported by water motion. The overall perturbation factor,  $\beta_m$  exceeds  $\beta_{m_o}$  by the gravitational perturbation factor,  $\beta_g$ , multiplied by the fraction of steady state downward flux of carbon-total carried by gravity.

Next let us eliminate  $F_{d_o}$  and  $F_{g_o}$  between the first of equations (8.12), and equations (8.23) and (8.24) to arrive at the compact expression:

$$\beta_m = \beta_{m_o} + \beta_g (1 - \beta_{m_o}). \quad (8.25)$$

Also, by eliminating  $F_{d_o}$  between equations (8.22) and (8.24) we arrive at a compact expression for the downward perturbation flux in terms of the ratio of  $\beta_m$  and  $\beta_{m_o}$ :

$$\Delta F_{md} = (\beta_m / \beta_{m_o}) k_{md} n_m. \quad (8.26)$$

The upward perturbation flux is a result of water transport alone and thus is given by the simple expression (cf. equation (8.2)):

$$\Delta F_{dm} = k_{dm} n_d. \quad (8.27)$$

The steady-state perturbation factor,  $\beta_{m_o}$ , is also useful in obtaining an alternative expression for the apparent fractionation factor  $\alpha_{md}$  of equation (8.17). Substituting in equation (8.24) the expression for  $F_{d_o}$  given by the second of equations (8.12) we find with the aid of equation (8.3) that:

$$\beta_{m_o} = \frac{N_{m_o} W_d}{N_{d_o} W_m} \quad (8.28)$$

and hence:

$$\alpha_{md} = \beta_{m_o} + \alpha_{mg} (1 - \beta_{m_o}). \quad (8.29)$$

Since  $\beta_{m_o}$  is equal to the fraction of the total downward flux of carbon-total transported by water motion at steady-state, the factor,  $\alpha_{md}$ , is evidently the weighted average of the fractionation factor,  $\alpha_{mg}$ , associated with the downward flux of rare isotopic carbon by gravitational settling, and the fractionation factor for water transport, which is unity.

For the rare isotopes we obtain directly from equations (8.10) and (8.11) the perturbation fluxes:

$$\Delta^* F_{md} = k_{md} n_m + \alpha_{mg} [R_m (F_{g_o} + \Delta F_g) - R_{m_o} F_{g_o}], \quad (8.30)$$

$$\Delta^* F_{dm} = k_{dm} n_d. \quad (8.31)$$

Substituting for  $R_m$  in equation (8.30) the expression (cf. equation (6.14)):

$$R_m = \frac{n_m}{N_m} + \frac{R_{m_o} N_{m_o}}{N_m} \quad (8.32)$$

and for  $\Delta F_g$  according to equation (8.19), we obtain (cf. equation (6.16)):

$$\Delta^* F_{md} = k_{md} n_m + \alpha_{mg} F_{g_o} \left\{ \left( \frac{1 + \beta_g n_m / N_{m_o}}{1 + n_m / N_{m_o}} \right) n_m / N_{m_o} + \left( \frac{R_{m_o} (\beta_g - 1)}{1 + n_m / N_{m_o}} \right) n_m / N_{m_o} \right\}. \quad (8.33)$$

As shown in subsection 10.4 the expression for  $^*F_{md}$  is slightly modified if the organic and biogenic carbon fluxes are considered separately and if their perturbation by external sources (i.e.  $\beta_g$  non-zero) produce changes in the fluxes which are different functions of the respective steady-state fluxes.

### 8.5 Solving the model equations

In terms of the perturbation fluxes,  $\Delta F_{md}$  and  $\Delta F_{dm}$ , the equations for the perturbations in  $N_m$  and  $N_d$  are given in general by equations (5.3) with "m" replacing "a" and "d" replacing "b", i.e.:

$$\left. \begin{aligned} d n_m / dt &= \Delta F_{dm} - \Delta F_{md} + \gamma_m \\ d n_d / dt &= \Delta F_{md} - \Delta F_{dm} + \gamma_d \end{aligned} \right\} \quad (8.34)$$

where  $\gamma_m$  and  $\gamma_d$  denote the combined external sources of carbon-total for reservoirs,  $m$  and  $d$ , respectively.

In terms of perturbation transfer coefficients similar to those of previous sections (Keeling, 73b) these equations may be rewritten:

$$\left. \begin{aligned} (d/dt + k_5) n_m - k_6 n_d &= \gamma_m \\ (d/dt + k_6) n_d - k_5 n_m &= \gamma_d \end{aligned} \right\} \quad (8.35)$$

Similarly for rare isotopic carbon (cf. equation (6.18)):

$$\left. \begin{aligned} d^*n_m/dt &= \Delta^*F_{dm} - \Delta^*F_{md} + R_{\gamma_m} \gamma_m - * \lambda^* n_m \\ d^*n_d/dt &= \Delta^*F_{md} - \Delta^*F_{dm} + R_{\gamma_d} \gamma_d - * \lambda^* n_d \end{aligned} \right\} \quad (8.36)$$

or in terms of perturbation transfer and virtual source coefficients:

$$\left. \begin{aligned} (d/dt + * \lambda + * k_5) * n_m - * k_6 * n_d &= R_{\gamma_m} \gamma_m + k_8' n_m \\ (d/dt + * \lambda + * k_6) * n_d - * k_5 * n_m &= R_{\gamma_d} \gamma_d - k_8' n_m \end{aligned} \right\} \quad (8.37)$$

Matching terms after substituting for the perturbation fluxes according to equations (8.22), (8.27), (8.31) and (8.33) it follows that:

$$\left. \begin{aligned} k_5 &= k_{md} + \frac{\beta_g F_{go}}{N_{mo}} \\ &= (\beta_m / \beta_{mo}) k_{md} \end{aligned} \right\} \quad (8.38)$$

where the second equality makes use of equations (8.23) and (8.24),

$$k_6 = k_{dm} \quad (8.39)$$

$$*k_5 = k_{md} + \frac{\alpha_{mg} F_{go}}{N_{mo}} \left( \frac{1 + \beta_g n_m / N_{mo}}{1 + n_m / N_{mo}} \right) \quad (8.40)$$

$$*k_6 = k_{dm} \quad (8.41)$$

$$k_8' = \frac{\alpha_{mg} R_{mo} F_{go} (1 - \beta_g)}{N_{mo} (1 + n_m / N_{mo})} \quad (8.42)$$

Making use of equations (8.3) and (8.14) we may alternatively write for  $k_5$ :

$$k_5 = k_{dm} \left\{ \frac{W_d}{W_m} + \left( \frac{N_{do}}{N_{mo}} - \frac{W_d}{W_m} \right) \beta_g \right\} \quad (8.43)$$

Making use of equations (8.3), (8.14), (8.17), (8.28) and (8.29) we may write from  $*k_5$ :

$$*k_5 = \alpha_{md} k_{dm} (N_{do} / N_{mo}) * \phi_{md} \quad (8.44)$$

where:

$$*\beta_m = [\beta_{mo} + \alpha_{mg} (1 - \beta_{mo}) \beta_g] / \alpha_{md}, \quad (8.45)$$

$$*\phi_{md} = \frac{1 + *\beta_m n_m / N_{mo}}{1 + n_m / N_{mo}} \quad (8.46)$$

Equations (8.43) and (8.44) agree with equations (7.23) and (7.25) of Keeling (73b p. 296) if higher order terms are ignored by setting  $*\phi_{md}$  equal to unity, and if  $\beta_g$  is set equal to zero on the assumption that the gravitational flux,  $F_g$ , is constant (the symbol  $\alpha_{md}$  replaces  $\alpha_{dm}$  of Keeling (73b)).

Making use of equations (8.14), and (8.28) we may write alternatively for  $k_8'$ :

$$k_8' = \frac{\alpha_{mg} R_{mo} k_{dm} N_{do} (1 - \beta_{mo}) (1 - \beta_g)}{N_{mo} (1 + n_m / N_{mo})} \quad (8.47)$$

or:

$$k_8' = \alpha_{mg} R_{mo} k_{dm} \left( \frac{N_{do}}{N_{mo}} - \frac{W_d}{W_m} \right) \left( \frac{1 - \beta_g}{1 + n_m / N_{mo}} \right) \quad (8.48)$$

This last equation agrees with equation (7.27) of Keeling (73b, p. 200), if the perturbation factor,  $\beta_g$ , and the second order term,  $n_m / N_{mo}$ , are set equal to zero.

The solution for the reservoir perturbations,  $n_i$  and  $*n_i$ , and the Suess Effect are obtained in a manner similar to that described in section 6 and 7.

### 8.6 Adaptation of the two reservoir model to portray continuous vertical diffusion

In their investigation of industrial CO<sub>2</sub> uptake by the oceans and land biota, Oeschger *et al.* (75) approached the problem of modeling the ocean beneath the surface mixed layer using a "box diffusion" model in which the vertical distribution of carbon-14 aids in establishing the response of the oceans to the atmospheric CO<sub>2</sub> input. The input of carbon-14 to the oceans is known from tree-ring studies to have been more or less constant for thousands of years, and therefore its distribution is

likely to have reflected an oceanic steady state prior to recent artificial creation of carbon-14 from nuclear bombs. Since an oceanic steady-state reflects a wide range of characteristic response times, this distribution in principal should be a valuable aid in devising a model valid for predictions of industrial CO<sub>2</sub> uptake by the oceans. But because few observations of oceanic <sup>14</sup>C were made prior to introduction of bomb <sup>14</sup>C into the oceans, the steady-state distribution is well established only in the deep waters of the oceans where bomb <sup>14</sup>C has still not penetrated appreciably. In the surface and intermediate waters above a depth of one thousand meters, where the oceanic response to industrial CO<sub>2</sub> is important, the addition of bomb <sup>14</sup>C has made difficult or impossible the determination of the preindustrial <sup>14</sup>C distribution needed for modeling industrial CO<sub>2</sub>.

The authors have avoided the difficult problem of trying to correct the observational data for bomb <sup>14</sup>C by constraining their model to fit only the most obvious undisturbed features of the <sup>14</sup>C distribution: <sup>14</sup>C/C ratio in surface water, measured in the early 1950s before bomb <sup>14</sup>C had appreciably affected the oceans, and the <sup>14</sup>C/C ratio below 1000 meters. Furthermore, only the <sup>14</sup>C/C ratio at 4000 meters depth and the average ratio below 1000 meters were considered quantitatively. Regional differences were disregarded by taking areal weighted averages of the main ocean basins. The authors forced a constant eddy diffusion coefficient, *K*, to predict the observed <sup>14</sup>C/C ratios at the surface and 4000 meters. The value of *K* found in this way, was of the order of 4000 m<sup>2</sup> yr<sup>-1</sup>. This value led to a predicted average <sup>14</sup>C/C ratio below 1000 meters in satisfactory agreement with observations, thus confirming that an assumption of constancy for *K* was not unreasonable.

As noted by Veronis (75) and others, salinity and temperature data indicate that it is unlikely that the ocean circulation obeys a constant vertical diffusive principle, and, therefore, the box diffusion model, like the two reservoir model of the carbon cycle, is a highly simplified parameterization of the transfer and storage of oceanic carbon. It too must be justified on the grounds, that it accords with data for time-dependent phenomena.

With respect to such phenomena the authors have noted that the box diffusion model satisfactorily predicts both the uptake of "bomb" carbon-14 produced since A.D. 1954 and the atmospheric <sup>14</sup>C Suess Effect resulting from industrial CO<sub>2</sub> production before A.D. 1954. The prediction of the latter is also compatible with the expected airborne fraction of carbon-total. Bomb carbon-14 as a tracer has the advantage that it was injected into the atmosphere over a short time period and like a single spike allows the free response of the oceans to be revealed. Although the source to the atmosphere is not so well established as that for industrial CO<sub>2</sub>, the amount in the atmosphere as a function of time is known quite precisely. Thus the uptake by the oceans can be estimated from a knowledge of the rate coefficient, *k<sub>am</sub>*, and the distribution of <sup>14</sup>C in surface water as a function of time. But neither *k<sub>am</sub>* nor the <sup>14</sup>C distribution in surface water are well enough known to calculate the uptake of <sup>14</sup>C by the

oceans very precisely. Furthermore, the observing period since the end of major weapons testing is too short to yield information on characteristic response times longer than a few years. Thus bomb carbon-14 as yet is of limited value in evaluating models to be used for predictions of industrial CO<sub>2</sub> uptake. Additional time dependent tracer data, such as tritium from bomb tests, have been investigated to test both models, and more complicated models as well, but neither the distributions nor the source strengths of these tracers are yet well enough known to provide a convincing demonstration in favor of any particular model.

With respect to the atmospheric <sup>14</sup>C Suess Effect, it turns out that the box diffusion model for different intensities of vertical diffusion predicts a relationship to the airborne fraction which is indistinguishable from that for a linear two reservoir ocean model when the assumed depth of the surface layer is varied (Keeling, 77, pp. 88-91). A finding that the box diffusion model successfully predicts both of these effects is therefore not a compelling argument for preferring that model over the two reservoir model with adjustable surface layer. A more convincing argument is that the box diffusion model predicts the Suess Effect, given the steady state distribution of <sup>14</sup>C, whereas the two reservoir model typically uses the Suess Effect to establish the effective depth of the surface layer. Although it appears reasonable to choose the surface layer depth near the middle of the main thermocline, say between 200 and 600 m depth (Bacastow, 79), the physical basis for this choice is less secure than the choice of parameters of the box diffusion model. But even this advantage of the box diffusion model is weakened because the diffusion coefficient, *K*, was obtained from a fit of the <sup>14</sup>C/C distribution at only two depths and therefore is also insecurely established. In balance, the box diffusion model appears to be physically more realistic than the two reservoir model but not strikingly so.

Let us now derive expressions for the box diffusion model corresponding to the detailed expressions developed above in subsection 8.3. This model was solved approximately by Oeschger *et al.* (75) by subdividing the subsurface ocean into forty-six reservoirs, where each adjacent pair is governed by exchange equations similar to the multiple reservoir model discussed in subsection 8.2. The authors ignored the gravitational flux, assuming for simplicity that the steady state distribution of carbon-total was constant with depth. Let us now consider how the gravitational flux might be included in the formulation. This flux is not necessarily uniform with depth, and we may therefore appropriately assume that it varies as a function of the vertical coordinate, *z*, or from reservoir to reservoir if the vertical column is subdivided.

Let *J(z, t)* denote the (possibly time dependent) rate of regeneration of inorganic carbon-total particulate organic carbon and biogenic carbonate per unit volume in subsurface water at depth *z*. Then the total gravitational flux, originating in surface water, is given by the integral:

$$F_g(t) = \int_{h_m}^{h_s} J(z, t) A(z) dz \quad (8.49)$$

where  $h_m$  and  $h_s$  denote the average depth of the surface layer and ocean bottom, respectively, and  $A(z)$  denotes the area at depth,  $z$ . Thus for layers,  $u, v, \dots$ , of the multiple layer model, there appears corresponding sources of carbon-total,  $F_u, F_v$ , where, for say layer  $v$ :

$$F_v = A_v \overline{J_v(z, t)} (h_u - h_v) \quad (8.50)$$

where  $\overline{J_v(z, t)}$  denotes the average of  $J(z, t)$  at time  $t$  over layer  $v$ ,  $h_i$  denotes the depth of the top ( $i = u$ ) and bottom ( $i = v$ ) of the layer, and  $A_i$  ( $i = v$ ) denotes its horizontal area.

Although the introduction of a vertically varying gravitational flux is in principal straightforward, so few data exist to establish it that only very approximate formulations have been attempted (Björkström, 79) and only for carbon-total, not for isotopic distributions. It lies beyond the scope of this discussion to explore the implications of industrial CO<sub>2</sub> to the detailed distribution of isotopes in the subsurface oceans, and therefore, I will limit the discussion to a consideration of average differences in isotopic ratios between surface and deep water, similar to the approach of Oeschger *et al.* (75) to establish the diffusion coefficient,  $K$ . This approach permits use of a simplified analytic solution of the box diffusion model for which present data, and the assumption of a constant diffusion coefficient, are more or less adequate to cope with the gravitational flux term.

The box diffusion model is equivalent to increasing the number of layers of a multiple reservoir model without limit. The rate of change in concentration as a function of depth of carbon-total below the surface layer of depth,  $h_m$ , is given by Fick's diffusion equation with an added local source term,  $J(z, t)$ :

$$\frac{\partial q(z, t)}{\partial t} = K \frac{\partial^2 q(z, t)}{\partial z^2} + J(z, t) \quad (8.51)$$

where  $q(z, t)$  denotes the concentration of carbon-total at depth,  $z$ , and time,  $t$ , and where  $K$ , the eddy diffusion coefficient, is assumed to be constant. A similar equation applies to rare isotopic carbon, with a radioactive decay  $\lambda q(z, t)$  added in the case of carbon-14.

For steady-state distributions of chemical tracers this equation has been solved where the rate of regeneration,  $J$ , is assumed to be constant or to vary exponentially with depth (Wyrki, 62; Munk, 77; Craig, 69). Equation (8.51) has not been employed to predict time variable tracer concentrations.

Without a gravitational flux, the time dependent solution of equation (8.51) for carbon-total and carbon-14 was derived by Oeschger *et al.* (75) for an exponentially rising industrial CO<sub>2</sub> source. In further simplification they neglected radioactive decay because the time spans of interest were short compared to radioactive

decay time,  $\lambda^{-1}$ , and they neglected isotopic fractionation, since transport was assumed to be only by water motion.

For purposes of comparing surface and deep water averages, we need consider exchange only at the base of the surface layer, but we shall want to include consideration of gravitational flux and isotopic fractionation. Nevertheless, let us initially neglect the gravitational flux to establish the basic relationships between the models with only isotopic fractionation as an added complication. For the comparison and surface and deep water, the two reservoir oceanic model will be shown to provide most of the formulism needed to solve the box diffusion model, for an exponential CO<sub>2</sub> source.

With  $F_g = 0$  the net flux of carbon-total from a homogeneous surface ocean layer to a diffusive layer immediately below is given by:

$$\Delta F_{md} - \Delta F_{dm} = -KA \left( \frac{\partial q}{\partial z} \right)_{z=h_m} \quad (8.52)$$

which leads to the result (Oeschger, 75):

$$\Delta F_{md} - \Delta F_{dm} = \frac{n_{m_o} e^{\mu t} \mu \sqrt{K/\mu} \tanh(h_d \sqrt{\mu/K})}{h_m} \quad (8.53)$$

where, in accordance with equation (2.19) the perturbation,  $n_m$ , in the surface layer is assumed to increase exponentially, i.e.:

$$n_m = n_{m_o} e^{\mu t} \quad (8.54)$$

throughout the time period of interest. Similarly, below the surface layer, if an exponential increase is again assumed:

$$q = q_o(z) e^{\mu t} \quad (8.55)$$

For the two reservoir model, the same equation (8.54) applies for surface water while for deep water:

$$n_d = n_{d_o} e^{\mu t} \quad (8.56)$$

Equations (8.55) and (8.56) are not serious further constraints over assuming equation (8.54) to hold, since, as shown by Bacastow and Keeling (79) all the reservoirs of a linearly coupled system increase nearly exponentially within about one  $e$ -fold time of the commencement of an exponentially increasing external source.

To obtain an expression for the two reservoir model corresponding to equation (8.53) we eliminate  $n_m$  and  $n_d$  in the second of equations (8.35) by means of the

exponential functions (8.54) and (8.56). With  $\gamma_d$  equal to zero (since industrial CO<sub>2</sub> is the only external source considered) this leads to:

$$n_d = \frac{k_5 n_{m0} e^{\mu t}}{\mu + k_6} \tag{8.57}$$

Substituting the first derivative of this expression for  $n_d$  in the second of equations (8.34) (again with  $\gamma_d$  equal to zero):

$$\Delta F_{md} - \Delta F_{dm} = \frac{n_{m0} e^{\mu t} \mu k_5}{\mu + k_6} \tag{8.58}$$

Equations (8.53) and (8.58) indicate that the two models will predict the same net perturbation in the flux of carbon-total from surface to deep ocean water, if the perturbation transfer coefficients  $k_5$  and  $k_6$  are so related to the diffusion coefficient  $K$  that both equations are satisfied for a given value of the  $e$ -fold time  $\mu^{-1}$ , i.e.:

$$\frac{\mu k_5}{\mu + k_6} = \frac{\sqrt{K\mu} \tanh(h_d \sqrt{\mu/K})}{h_m} \tag{8.59}$$

where the depth of the surface layer, and thus the perturbation  $n_m$ , are assumed to be the same for both models.

For the two reservoir model (cf. equations (8.38) and (8.39)):

$$\frac{\mu k_5}{\mu + k_6} = \frac{\mu (\beta_m / \beta_{m0}) k_{md}}{\mu + k_{dm}} \tag{8.60}$$

Eliminating  $k_{md}$  via steady state equation (8.3):

$$\frac{\mu k_5}{\mu + k_6} = \frac{\mu (\beta_m / \beta_{m0}) k_{dm} (W_d / W_m)}{\mu + k_{dm}} \tag{8.61}$$

For realistic values of  $\mu$ , and with  $\beta_m$  equal to  $\beta_{m0}$  (i.e. assuming a constant gravitational flux),  $k_{dm}$ , to be compatible with equations (8.59) and (8.61), is found to be approximately 4 times larger than predicted by the first equality of equation (8.16) using the steady state carbon-14 distribution from which  $K$  was derived by Oeschger *et al.* (75). The same result holds if the gravitational flux is ignored, since then both  $\beta_m$  and  $\beta_{m0}$  are equal to unity.

As noted by Keeling and Balastow (77) this inconsistency can be remedied by increasing the assumed surface layer depth,  $h_m$ , for the two reservoir model to

approximately 4 times the 75 m chosen by Oeschger *et al.* (75) as the actual thickness of the homogeneous surface layer. This approach indeed leads to exactly the same prediction of the airborne fraction and atmospheric <sup>14</sup>C Suess Effect with both models for a certain unique value of the two reservoir model surface layer thickness,  $h_m$ . But increasing  $h_m$  is not the most direct way to adapt the two reservoir model to the diffusive case, and it cannot give exact correspondence between models for the oceanic Suess Effect even at the air-sea boundary.

An alternative approach is to regard  $k_5$  and  $k_6$  for the two reservoir model as perturbation coefficients and to disregard the steady state equations in their evaluation. For example, the reciprocal,  $k_5^{-1}$ , may be postulated to represent the characteristic time for a surface contaminant to be diffused into the bulk of the ocean. Since diffusion into the surface layer of a contaminant injected into deep water is not under investigation,  $k_6$  can be set equal to zero. As a further basis for setting  $k_6$  equal to zero, the steady state equations for <sup>14</sup>C indicate that  $k_{dm}$ , to which  $k_6$  corresponds in the two reservoir model, is of the order of 1/(1000 yr) or less, and thus negligible in comparison to  $\mu$  for typical  $e$ -fold times of industrial CO<sub>2</sub> of 20 to 50 yr (see section 11 below).

The two reservoir and box diffusion models lead to the same predictions for a given choice of the  $e$ -fold time,  $\mu$ , if:

$$\left. \begin{aligned} k_5 &= \frac{\sqrt{K\mu}}{h_m} \\ k_6 &= 0 \end{aligned} \right\} \tag{8.62}$$

The factor  $\tanh(h_d/\sqrt{\mu/K})$  is indistinguishable from unity for  $\mu^{-1}$  less than several hundred years and hence has been dropped from the expression for  $k_5$ .

Using equation (8.62), the vertical diffusion model is solved only at the base of the surface layer. But since the net flux across this boundary is fully prescribed, the integrated build-up of carbon-total in the subsurface ocean as a whole is also exactly prescribed. This is obviously as much as can be expected in adapting the two reservoir model to a computation of vertical diffusion.

Let us next consider the perturbation equations for rare isotopic carbon with the gravitational flux still neglected. In this case the perturbation coefficients,  $k_5$  and  $k_6$ , for the two reservoir model are the same for carbon-total and rare isotopic carbon. Since the radioactive decay terms in equations (8.36) can be shown to contribute negligibly, the differential equations (8.35) and (8.37) for carbon-total and rare isotopic carbon reduce to expressions of identical form. Hence solutions compatible with the box diffusion model for rare isotopic abundances,  $*n_i$ , are obtained by evaluating  $*k_5$  and  $*k_6$  by the expressions:

$$\left. \begin{aligned} *k_5 &= \frac{\sqrt{K\mu}}{h_m} \\ *k_6 &= 0 \end{aligned} \right\} \quad (8.63)$$

Let us now consider the case where a gravitational flux is included in both models. The correspondence between models cannot be made perfect, and in the absence of a direct simultaneous solution of the diffusion equation (8.51) for both carbon-total and rare isotopic carbon, we are obliged to seek some approximate relation connecting the steady state coefficients,  $k_{md}$  and  $k_{dm}$ , which appear in equations (8.38) through (8.41) with the perturbation coefficients,  $k_5$  and  $k_6$ . There is no difficulty in again setting  $k_6$  and  $*k_6$  equal to zero since they are still both associated with a nearly negligible return perturbation flux of tracer, for  $e$ -fold times,  $\mu^{-1}$  of interest. With respect to  $k_5$  and  $*k_5$  it would appear reasonable to assume that the steady state gravitational flux,  $F_{go}$ , is held constant (see subsection 8.2). Thus, the models ought to give nearly the same predictions for rare isotopic carbon if we assume that:

$$k_5 = \frac{\sqrt{K\mu}}{h_m} + \frac{\beta_g F_{go}}{N_{mo}}, \quad (8.64)$$

$$*k_5 = \frac{\sqrt{K\mu}}{h_m} + \frac{\alpha_{mg} F_{go}}{N_{mo}} \left( \frac{1 + \beta_g n_m / N_{mo}}{1 + n_m / N_{mo}} \right) \quad (8.65)$$

Although these equations cannot yield entirely correct solutions to the diffusion equation, they have been tested by comparing predictions based on them with predictions of a two reservoir model with an enlarged surface layer (Keeling, 77). The two models produce almost the same change in predicted atmospheric Suess Effect when a steady state gravitational flux of the same magnitude is alternately included and excluded from both calculations.

As it happens, since the gravitational flux cannot be established reliably by direct measurements, probably the best estimates of  $F_{go}$  are those derived by considering the difference in concentration of carbon-total between surface and deep water in which the rate of turn-over of the deep water is estimated by carbon-14 data (Broecker, 74).

In other words, the two reservoir model is probably at present the best model available to calculate the gravitational flux. The box diffusion model with the gravitational flux included is then solved via equations (8.64) and (8.65), with the value of  $F_{go}$  established from a

separate two reservoir model calculation via equation (8.14). The value of  $k_{dm}$  in the latter equation is made consistent with the steady state carbon-14 distribution assuming no gravitational flux by solving the first equality of equation (8.16) for  $k_{dm}$  with  $^{14}R_{mo}/^{14}R_{do}$ , evaluated as described in section 11 (see equation 11.11) and with  $\alpha_{md}$  set equal to unity. Since  $\alpha_{md}$  is found to be very close to unity when the gravitational flux is included, this approach cannot lead to significant distortion of the evaluation of  $k_{dm}$ .

Similarly, the neglect of gravitation flux by Oeschger *et al.* (75) probably has not contributed significant error in the determination of  $K$ . In principal the diffusion equation should have been separately solved for  $^{14}C$  and  $C$  with the gravitational flux included, as Craig (69, 71) has forcibly pointed out. But in practice the use of  $^{14}C/C$  ratios (especially ratios normalized to the variation in  $^{13}C/C$ ) appear very nearly to cancel out the influence of local sources of carbon in the tracer in the vertical column (Lal, 62). This problem deserves additional study which cannot be pursued here.

## 9. Four reservoir model

The simplest geochemical model which describes the main features of the industrial  $CO_2$  perturbation of the carbon cycle consists of a combination of the four reservoirs already considered pairwise. Such a model is depicted in Fig. 6. Its adequacy is discussed by Oeschger *et al.* (75) and Keeling and Bacastow (77). As these authors point out, a single undifferentiated land biosphere is a reasonable first approximation to the global biospheric model. Very long cycled biospheric carbon, excluded in the single reservoir approximation, interacts only weakly with the industrial  $CO_2$  perturbation while the short cycled carbon, also excluded, is in too small abundance to matter. The oceans, because of layering of warm water over cold, cannot be effectively modeled by a single undifferentiated ocean, however. A single reservoir model produces unrealistic responses to perturbations occurring in the range from 10 to 100 yr, the range of greatest interest to studies of industrial  $CO_2$ .

Nevertheless, as discussed above in section 8, a simple extension of the one reservoir ocean model appears to produce a realistic response to perturbations over a wide range of characteristic times. In this extended model the ocean beneath a homogeneously mixed surface layer is assumed to mix vertically by eddy diffusion. Even when the diffusion coefficient is assumed to be constant the response characteristics appear to be realistic. Furthermore, as Keeling and Bacastow (77) demonstrate, if the subsurface ocean is assumed to be randomly mixed, for example, by assuming two homogeneous reservoirs which exchange water, the response to perturbations in the range from 10 to 100 yr is similar to the diffusive model, provided that the ocean is divided well within the transition zone between the relatively homogenous surface and deep layers.

Obviously, more complex models both of the ocean and of land biosphere will be helpful in refining our understanding of the Suess Effect. But we have already

encountered considerable complexity with respect to isotopic relationships with the biosphere and oceans simplified to single and paired reservoirs, respectively, and it therefore seems preferable to limit the present discussion to the coupling of these three reservoirs to the atmosphere, in other words to restrict further discussion to what is implied by the rare isotopic and carbon-total equations already developed in sections 5 to 8, above.

Such a four reservoir perturbation model is readily constructed using the flux expressions already derived. The only new consideration is that, in contrast to the previously considered models, the atmosphere and ocean surface layer each exchange with two reservoirs. For carbon-total this is according to the general equations (cf. Fig. 6):

$$d n_j/dt = \Delta F_{ij} + \Delta F_{kj} - \Delta F_{ji} - \Delta F_{jk} + \gamma_j \quad (9.1)$$

where reservoirs  $i$  and  $k$  exchange carbon with reservoir  $j$ . A similar equation applies to rare isotopic carbon. In terms of the perturbation exchange coefficients,  $k_1 \dots k_6$ , we arrive, for carbon-total, at the set of differential equations:

$$\left. \begin{aligned} (d/dt + k_1) n_b - k_2 n_a &= \gamma_b \\ -k_1 n_b + (d/dt + k_2 + k_3) n_a - k_4 n_m &= \gamma_a \\ -k_3 n_a + (d/dt + k_4 + k_5) n_m - k_6 n_d &= \gamma_m \\ -k_5 n_m + (d/dt + k_6) n_d &= \gamma_d \end{aligned} \right\} (9.2)$$

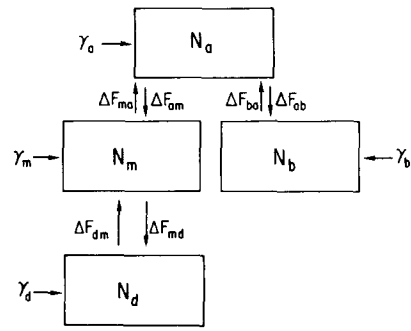


Fig. 6. Four-reservoir model of the exchange of carbon-total between the atmosphere (carbon abundance,  $N_a$ ), land biosphere ( $N_b$ ), surface ocean ( $N_m$ ) and deep ocean ( $N_d$ ). External sources of carbon-total,  $\gamma_i$ , are assumed to exist for all reservoirs. The change in rates of exchange,  $\Delta F_{ij}$ , as the external sources operate, are as described in sections 6 through 8.

equations are made linear by requiring all the coefficients,  $k_i, *k_i, k_i'$  to be constants, additional numerical methods, for example, involving the computation of the eigenvectors of the matrix of coefficients,  $k_{ij}$  (Bacastow, unpublished) are available. These linear methods, however, offer little advantage over more direct numerical methods applied directly to the original equations.

The analytic solutions for  $n_i$  and  $*n_i$  are greatly simplified for the case where the equations are linear, and in addition, the only external sources of carbon-total are exponential functions of time, i.e. (cf. equation (2.16)):

$$\gamma_i = \gamma_{i0} e^{\mu t} \quad (9.4)$$

For rare isotopic carbon, the corresponding equations are:

$$\left. \begin{aligned} (d/dt + * \lambda + * k_1) * n_b - * k_2 * n_a &= R_{\gamma_b} \gamma_b + k_9' n_b - k_{10}' n_a \\ -* k_1 * n_b + (d/dt + * \lambda + * k_2 + * k_3) * n_a - * k_4 * n_m &= R_{\gamma_a} \gamma_a - k_9' n_b + k_{10}' n_a + k_7' n_m \\ -* k_3 * n_a + (d/dt + * \lambda + * k_4 + * k_5) * n_m - * k_6 * n_d &= R_{\gamma_m} \gamma_m + (-k_7' + k_8') n_m \\ -* k_5 * n_m + (d/dt + * \lambda + * k_6) * n_d &= R_{\gamma_d} \gamma_d - k_8' n_m \end{aligned} \right\} (9.3)$$

Since in general these differential equations are non-linear, approximate numerical methods are required to solve for the perturbations,  $n_i$  and  $*n_i$ . Several methods of solution exist, for example, as described by Bacastow and Keeling (73), and by Oeschger *et al.* (75). If the

and for rare isotopic carbon, the isotopic ratios  $R_{\gamma_i}$  are constants so that the isotopic sources,  $*\gamma_i$ , are also exponential functions of time, i.e.:

$$*\gamma_i = R_{\gamma_i} \gamma_{i0} e^{\mu t} \quad (9.5)$$



A solution using these exponential functions, may be obtained using the Laplace transformed counterparts of the governing differential equations. From equations (9.2) we obtain in matrix notation:

$$\begin{bmatrix} s+k_1 & -k_2 & 0 & 0 \\ -k_1 & s+k_2+k_3 & -k_4 & 0 \\ 0 & -k_3 & s+k_4+k_5 & -k_6 \\ 0 & 0 & -k_5 & s+k_6 \end{bmatrix} \begin{bmatrix} \tilde{n}_b \\ \tilde{n}_a \\ \tilde{n}_m \\ \tilde{n}_d \end{bmatrix} = \begin{bmatrix} \tilde{\gamma}_b \\ \tilde{\gamma}_a \\ \tilde{\gamma}_m \\ \tilde{\gamma}_d \end{bmatrix} \quad (9.6)$$

which I will abbreviate by:

$$[k_{ij}] [\tilde{n}_i] = [\tilde{\gamma}_i]. \quad (9.7)$$

Similarly the Laplace transformed equations of equations (9.3) are:

$$\begin{bmatrix} s+*\lambda+*k_1 & -*k_2 & 0 & 0 \\ -*k_1 & s+*\lambda+*k_2+*k_3 & -*k_4 & 0 \\ 0 & -*k_3 & s+*\lambda+*k_4+*k_5 & -*k_6 \\ 0 & 0 & -*k_5 & s+*\lambda+*k_6 \end{bmatrix} \begin{bmatrix} *\tilde{n}_b \\ *\tilde{n}_a \\ *\tilde{n}_m \\ *\tilde{n}_d \end{bmatrix} = \quad (9.8)$$

$$\begin{bmatrix} R_{\gamma_b} \tilde{\gamma}_b \\ R_{\gamma_a} \tilde{\gamma}_a \\ R_{\gamma_m} \tilde{\gamma}_m \\ R_{\gamma_d} \tilde{\gamma}_d \end{bmatrix} + \begin{bmatrix} k_9' & -k_{10}' & 0 & 0 \\ -k_9' & k_{10}' & k_7' & 0 \\ 0 & 0 & -k_7'+k_8' & 0 \\ 0 & 0 & -k_8' & 0 \end{bmatrix} \begin{bmatrix} \tilde{n}_b \\ \tilde{n}_a \\ \tilde{n}_m \\ \tilde{n}_d \end{bmatrix}$$

which I will abbreviate by:

$$[*k_{ij}] [*n_i] = [*\tilde{\gamma}_i] - [k_{ij}'] [\tilde{n}_i]. \quad (9.9)$$

$$n_i = n_{io} e^{\mu t}, \quad (9.14)$$

$$*n_i = *n_{io} e^{\mu t}, \quad (9.15)$$

To avoid the computation of absolute isotopic abundances, which are less well known than isotopic ratios relative to a standard ratio, it is convenient to divide this last equation by the isotopic ratio of atmospheric CO<sub>2</sub>, R<sub>ao</sub>. Thus:

$$[*k_{ij}] [*n_i/R_{ao}] = [*\tilde{\gamma}_i/R_{ao}] - [k_{ij}'/R_{ao}] [\tilde{n}_i] \quad (9.10)$$

$$n_o = \tilde{k}^{-1} \underline{\gamma}_o \quad (9.16)$$

The analytic solutions of equations (9.7) and (9.10) with  $\gamma_b, \gamma_m$  and  $\gamma_d$  equal to zero (e.g. when industrial CO<sub>2</sub> is the only external source) are given by Keeling and Bacastow (73b). These solutions permit, with certain restrictions, an arbitrary functional form of  $\gamma_a$  with respect to time; provided that a convolution integral is evaluated. The method may be extended to provide solutions where all of the  $\gamma_i$  are arbitrary functions of time, but in this general case considerable numerical computation is required.

If the sources  $\gamma_i$  are exponential functions of time, a direct analytic solution is possible. Although this latter approach uses a minimum amount of computation, a still simpler approach, if a high speed computer is available, is to solve equations (9.6) and (9.8) directly. Indeed these may be first combined into the single matrix equation:

$$\begin{bmatrix} [k_{ij}] & [0] \\ [k_{ij}'/R_{ao}] & [*k_{ij}] \end{bmatrix} \begin{bmatrix} [\tilde{n}_i] \\ [*n_i/R_{ao}] \end{bmatrix} = \begin{bmatrix} [\tilde{\gamma}_i] \\ [*\tilde{\gamma}_i/R_{ao}] \end{bmatrix} \quad (9.11)$$

which I will abbreviate by:

$$kn = \underline{\tilde{\gamma}} \quad (9.12)$$

The direct solution for  $n$  is obtained as:

$$\tilde{n} = k^{-1} \underline{\gamma} \quad (9.13)$$

where  $k^{-1}$  is the inversion of  $k$ , obtained numerically (Bronson, 69, p. 60).

Since the external sources are assumed to be exponential according to equations (9.4) and (9.5), the solutions of equations (9.2) and (9.3) for the  $n_i$  and  $*n_i$  take the form:

as was the case for the two reservoir model discussed in section 2 (equation (2.19) and (2.30)).

Corresponding to these equations, there exists a matrix solution of equations (9.13) in terms of the perturbation coefficients,  $n_{io}$ , and  $*n_{io}$ , i.e.:

where  $n_o$  and  $\underline{\gamma}_o$  denote the column vectors:

$$n_o = [n_{io}], [*n_{io}/R_{ao}] \quad (9.17)$$

$$\underline{\gamma}_o = [\gamma_{io}], [*\gamma_{io}/R_{ao}]. \quad (9.18)$$

Equations (9.16) thus permits a complete solution for the  $n_i$  and  $*n_i$  by little more than a single matrix inversion.

If industrial CO<sub>2</sub> is the only external source, i.e. if:

$$\left. \begin{aligned} \gamma_a &= \gamma_{fo} e^{\mu t} \\ \gamma_i &= 0, \quad i \neq a \end{aligned} \right\} \quad (9.19)$$

the solution can be written in the more specific form:

$$n_o = k^{-1} g \gamma_{fo} \quad (9.20)$$

where  $g$  denotes the column vector:

$$g = [0, 1, 0, 0, 0, R_f, 0, 0] \quad (9.21)$$

As in the more general linear case (equation (9.5)), the rare isotopic ratio of industrial CO<sub>2</sub>, R<sub>f</sub>, is assumed to be constant.

The reservoir fractions needed to compute the Suess Effect are related to the  $n_{io}$ , and  $*n_{io}$  (cf. equations (1.9), (1.14), (2.18) and (2.23)) by:

$$r_i = \frac{n_{io} \mu}{\gamma_{fo}}, \quad (9.22)$$

$$*r_i = \frac{*n_{io} \mu}{R_{io} \gamma_{fo}}. \quad (9.23)$$

Since these fractions differ from the  $n_{io}$  and  $*n_{io}$  only by constant factors, it follows that:

$$r = k^{-1} g \mu \quad (9.24)$$

where  $r$  denotes the column vector:

$$r = [r_i], [*r_i R_{io} / R_{ao}] \quad (9.25)$$

Thus a matrix solution for the factors,  $r_i$  and  $*r_i R_{io} / R_{ao}$ , can be obtained directly.

After the solution for  $r$  is found, the Suess Effect is computed (cf. equations (1.22), (2.37)) by:

$$S_i = \frac{Q (*r_i - r_i)}{N_{io} (1 + r_i Q)} \quad (9.26)$$

where (cf. equation (2.18)):

$$Q = (\gamma_{fo} / \mu) e^{\mu t} \quad (9.27)$$

and where the  $*r_i$  are obtained from the 5th to 8th elements of vector  $r$  by multiplication by  $R_{ao} / R_{io}$ .

## 10. Carbonate dissolution within the oceans

### 10.1 General remarks

The predicted relationships between rare isotopic carbon and carbon-total in the carbon cycle are altered considerably if appreciable amounts of sedimentary carbon on the sea floor are assumed to dissolve and furnish additional carbonate ion to the sea water.

In deep ocean water, marine carbonates are likely to dissolve as soon as industrial  $\text{CO}_2$  reaches these waters (Peng, 78). Even under normal conditions, most solid carbonate particles entering the oceans from rivers, and most biogenic carbonate shell material produced in surface water, dissolve on reaching the deeper ocean basins. The carbonate ions produced by dissolution are returned to shallower waters above by the deep water circulation. During the industrial  $\text{CO}_2$  era, an accelerated dissolution is likely to occur and perturb this otherwise nearly steady-state condition. This tendency will have little effect on the oceanic uptake of industrial  $\text{CO}_2$

for several hundred years, however, because of the slowness with which deep water exchanges with the ocean surface.

If dissolution of shallow marine carbonates should also occur, the oceanic uptake of industrial  $\text{CO}_2$  from the air would increase considerably even in early stages of the industrial era because of the proximity of the overlying waters to the air-sea boundary. Arguing against this possibility is the generally high degree of supersaturation of surface water with respect to carbonates (Revelle, 57a; Edmond, 70; Ingle, 73). Pure calcite will probably not dissolve appreciably in near-surface sea water even at the time of highest atmospheric  $\text{CO}_2$  when the pH of the water might drop as low as 7.6 (Bacastow, 73 and unpublished). The more soluble carbonate mineral, aragonite, is abundant in shallow tropical seas, and some aragonite is likely to dissolve during the next century. It is doubtful, however, whether there is enough of this mineral available to reduce atmospheric  $\text{CO}_2$  levels more than a few percent.

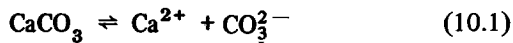
Perhaps the most likely shallow water carbonates to dissolve under the influence of industrial  $\text{CO}_2$  are deposits of high magnesian calcite, which according to Wollast and Reinhard-Derie (77), may attach to calcitic sediments. Such deposits, which essentially consist of a solid solution of  $\text{MgCO}_3$ , may be sufficiently soluble to be already dissolving as a result of industrial  $\text{CO}_2$  entering shallow water. Thus an analysis of the processes affecting the Suess Effect is not complete until the influence of carbonate dissolution is considered.

The problem of predicting carbonate dissolution from industrial  $\text{CO}_2$  is complicated by uncertainties as to the amount of soluble carbonates at shallow depths and by kinetic factors involving the rate at which solid carbonates dissolve when the acidity of sea water changes (Berner, 74, 76). As a first step in solving the general problem, I will disregard the possible exhaustion of material and the time delays attending dissolution by assuming that the carbonate ion in sea water remains in equilibrium with an inexhaustible supply of solid carbonate. Calculations based on this assumption will establish upper limits for the magnitude of the carbonate effect for given values of other model parameters.

It is not immediately evident how to incorporate carbonate dissolution into the formulism developed in previous sections, because dissolution not only provides sources of carbonate to the oceanic reservoirs where it dissolves, but afterwards this carbonate is redistributed by water motion between oceanic reservoirs. The transport relationships of carbonate ion are made complicated by the chemical dependence of dissolved carbonate on the concentrations of bicarbonate ion and carbonic acid (see equations (7.9) and (7.10)) and other weak acids in sea water such as boric acid (Edmond, 70). There is a way around this difficulty, however, because carbonate dissolution releases calcium and magnesium ions which can be traced as they are transported from one region to another. The degree to which calcium and magnesium is complexed with carbonate and bicarbonate ion (Whitfield, 75) is not important in this regard because only the total amount of dissolved calcium and magnesium is relevant in keeping track of the dissolved carbonate.

## 10.2 Chemical relationships of carbonate dissolution and their influence on the gravitational flux of carbon-total

To explain the use of calcium as a tracer, let us first disregard the influence of dissolved magnesium and postulate that equilibrium is maintained between pure solid calcium carbonate and sea water by the chemical reaction:



At equilibrium:

$$[\text{Ca}^{2+}] [\text{CO}_3^{2-}] = K_{sp} \quad (10.2)$$

where brackets denote concentrations. The solubility product,  $K_{sp}$ , as in the case of the dissociation constants,  $K_1$  and  $K_2$ , is invariant to reaction (10.1) but varies with temperature, salinity and hydrostatic pressure.

To apply this equation to the two reservoir model, let  $C_i$  denote the amount of dissolved calcium ( $\text{Ca}^{2+}$  and its ion complexes) in oceanic reservoir  $i$  in units of moles multiplied by the molecular weight of carbon. Let  $\Delta C_i$  denote perturbations from an assumed initial steady state value  $C_{io}$ , i.e.:

$$\Delta C_i = C_i - C_{io} \quad (10.3)$$

Let  $\eta_i$  denote the rate of dissolution of solid calcium carbonate,  $\text{CaCO}_3$ , in reservoir  $i$  in the same units as used for the carbon-total of industrial  $\text{CO}_2$  source,  $\gamma_f$ . Then:

$$\partial n_i / dt = \partial \Delta C_i / dt = \eta_i \quad (10.4)$$

for the changes in  $N_i$  and  $C_i$  owing solely to dissolution. This simple relation results because the amounts of dissolved calcium and carbonate are defined in the same mass units (g of C). Because the carbonate equilibrium equation (10.2) establishes a direct functional relationship between dissolved calcium and carbon-total concentrations, the total change in  $N_i$  and  $C_i$ , i.e. the change owing all processes including transport also obeys equation (10.4).

To establish how carbonate equilibrium affects the exchange processes in the reservoir model we make use of equation (10.4) to compare perturbed and steady states. Neglecting spacial variability in chemical parameters within reservoir  $i$  we obtain directly:

$$\frac{[\text{Ca}^{2+}]}{[\text{Ca}^{2+}]_o} = \frac{[\text{CO}_3^{2-}]_o}{[\text{CO}_3^{2-}]} \quad (10.5)$$

where subscript "o" denotes a preindustrial steady state. Next, we relate this equation to the equilibrium of the other dissolved species of carbon-total, namely  $\text{CO}_2$ , and  $\text{HCO}_3^-$ . The product of equations (7.11), (7.12), and (7.13) is:

$$K_0 K_1 K_2 = \frac{[\text{H}^+]^2 [\text{CO}_3^{2-}]}{P_{\text{CO}_2}} \quad (10.6)$$

whence:

$$\frac{[\text{Ca}^{2+}]}{[\text{Ca}^{2+}]_o} = \frac{\left( P_{\text{CO}_2} \right)_o [\text{H}^+]^2}{P_{\text{CO}_2} [\text{H}^+]_o^2} \quad (10.7)$$

Thus, for the oceanic surface layer:

$$\frac{C_m}{C_{mo}} = \frac{P_{mo}}{P_m} \frac{[\text{H}^+]^2}{[\text{H}^+]_o^2} \quad (10.8)$$

or, in view of equation (7.16):

$$\frac{C_m}{C_{mo}} = \frac{N_{mo}}{\phi_m N_m} \frac{[\text{H}^+]^2}{[\text{H}^+]_o^2} \quad (10.9)$$

Since  $[\text{H}^+]$  and  $\phi_m$  are functions of  $N_m$ , we can expand in a Taylor's series (cf. equation (4.8)) in the neighborhood of  $N_{mo}$ :

$$\frac{C_m}{C_{mo}} = 1 + \zeta_{mo} \left( \frac{n_m}{N_{mo}} \right) + \zeta_{m1} \left( \frac{n_m}{N_{mo}} \right)^2 + \dots \quad (10.10)$$

whence:

$$\frac{\Delta C_m}{C_{mo}} = \zeta_m \frac{n_m}{N_{mo}} \quad (10.11)$$

where:

$$\zeta_m = \zeta_{mo} + \zeta_{m1} \left( \frac{n_m}{N_{mo}} \right) + \dots \quad (10.12)$$

As in the case of the CO<sub>2</sub> evasion factor,  $\xi$ , the hydrogen ion concentration,  $[H^+]$ , must be determined or eliminated as an intermediate step in finding the carbonate factor,  $\zeta_m$ . Bolin and Eriksson (59) developed approximate equations which essentially found the term,  $\zeta_{mo}$ , of equation (10.12), while Bacastow and Keeling (79) used an iterative procedure without approximating the chemical equations, equivalent to determining all significant terms in equation (10.12). As in the case of  $\xi$ , it is sufficient in our consideration of the problem merely to assume that the coefficients,  $\zeta_{mo}$ ,  $\zeta_{ml}$ , ..., are known. The corresponding factors,  $\zeta_{io}$ ,  $\zeta_{ib}$ , ..., of any subsurface reservoir, can similarly be assumed to be known.

### 10.3 Model equations for carbon-total

To establish relationships for the two reservoir model adapted to include carbonate dissolution, the perturbation equations of carbon-total (equations (8.35)) are revised by the inclusion of carbonate sources,  $\eta_m$  and  $\eta_d$  defined by equation (10.4):

$$(d/dt + k_5) n_m - k_6 n_d - \eta_m = \gamma_m, \quad (10.13)$$

$$(d/dt + k_6) n_d - k_5 n_m - \eta_d = \gamma_d \quad (10.14)$$

where  $k_5$  and  $k_6$  are related by equations (8.38) and (8.39) to the steady state coefficients,  $k_{md}$  and  $k_{dm}$ . Since the carbonate sources,  $\eta_i$  are dependent upon the external sources,  $\gamma_i$ , they are here written on the left side of the equality sign (cf. equation (5.4)).

To establish corresponding equations for dissolved calcium it is first necessary to determine the influence of the gravitational flux of particulate carbonate which accounts for about 30% of the total gravitational flux between surface and subsurface waters at steady state (Broecker, 74, p. 11), as noted in subsection 8.3.

The new terms for this derivation will be designated by addition a subscript "c" before the subscripts of the corresponding terms for carbon-total. The fluxes of calcium between reservoirs  $m$  and  $d$ , including both particulate and dissolved forms, are then given by:

$$\left. \begin{aligned} F_{cmd} &= k_{md} C_m + F_{cg} \\ F_{cdm} &= k_{dm} C_d \end{aligned} \right\} \quad (10.15)$$

as the counterparts of equations (8.1) and (8.2).

The gravitational fluxes of both organic particles and biogenic particulate carbonate were postulated by equation (8.18) to vary in response to changes in the amount of carbon-total in the ocean surface layer. Thus for the particulate carbonate flux by itself we write as the counterpart of equation (8.19):

$$\Delta F_{cg} = \beta_{cg} F_{go} n_m / N_{mo} \quad (10.16)$$

Since this flux consists of particles of CaCO<sub>3</sub>, it may be regarded both as a flux of carbon-total and of calcium.

Similarly for the perturbation in flux of calcium to subsurface water by both water transport and gravitational flux, as the counterpart of equation (8.22):

$$\Delta F_{cmd} = \beta_{cm} F_{do} n_m / N_{mo} \quad (10.17)$$

or, alternatively, as the counterpart of equation (8.26):

$$\Delta F_{cmd} = (\beta_{cm} / \beta_{mo}) k_{md} n_m \quad (10.18)$$

where  $\beta_{cg}$  and  $\beta_{cm}$  are power series in  $n_m/N_{mo}$  defined in a manner similar to equation (8.20).

Corresponding to equation (8.23):

$$\beta_{cm} = \frac{k_{md} \zeta_m C_{mo}}{F_{do}} + \frac{F_{go} \beta_{cg}}{F_{do}} \quad (10.19)$$

The return perturbation flux of calcium is obtained directly from the second of equations (10.15) since only water motion is involved (cf. equation (8.27)):

$$F_{cdm} = k_{dm} \Delta C_d \quad (10.20)$$

In terms of the perturbation in carbon-total,  $n_d$ :

$$\Delta F_{cdm} = \frac{k_{dm} \zeta_d C_{do} n_d}{N_{do}} \quad (10.21)$$

where, analogous to equation (10.11)  $\zeta_d$  is defined by the expression:

$$\frac{\Delta C_d}{C_{do}} = \zeta_d \frac{n_d}{N_{do}} \quad (10.22)$$

The perturbation equations for dissolved calcium are (cf. equations 8.34):

$$\left. \begin{aligned} d C_m / dt (= d \Delta C_m / dt) &= \Delta F_{cdm} - \Delta F_{cmd} + \eta_m \\ d C_d / dt (= d \Delta C_d / dt) &= \Delta F_{cmd} - \Delta F_{cdm} + \eta_d \end{aligned} \right\} \quad (10.23)$$

where we assume that no external sources of carbonate are present. Substitution for  $\Delta F_{cmd}$  and  $\Delta F_{cdm}$  according to equations (10.18) and (10.21):

$$\left. \begin{aligned} d \Delta C_m / dt + [(\beta_{cm} / \beta_{mo}) k_{md}] n_m - \\ (\zeta_d C_{do} / N_{do}) k_{dm} n_d - \eta_m = 0 \\ d \Delta C_d / dt + [(\zeta_d C_{do} / N_{do}) k_{dm}] n_d - \\ (\beta_{cm} / \beta_{mo}) k_{md} n_m - \eta_d = 0 \end{aligned} \right\} \cdot (10.24)$$

These equations may be expressed as perturbations in carbon-total by eliminating  $d \Delta C_m / dt$  and  $d \Delta C_d / dt$  via equations (10.11) and (10.22), respectively. Introducing the symbols,  $\theta_i$ , to express the fractions of the change in reservoir abundances,  $n_i$ , and in gravitational flux perturbation,  $\Delta F_{md}$ , which are *not* due to carbonate dissolution, i.e.:

$$\theta_m = 1 - \zeta_m C_{mo} / N_{mo} \quad (10.25)$$

$$\theta_d = 1 - \zeta_d C_{do} / N_{do} \quad (10.26)$$

$$\theta_g = 1 - \beta_{cm} / \beta_m \quad (10.27)$$

we obtain:

$$\left. \begin{aligned} (1 - \theta_m) dn_m / dt + (1 - \theta_g) (\beta_m / \beta_{mo}) k_{md} n_m - \\ (1 - \theta_d) k_{dm} n_d - \eta_m = 0 \\ (1 - \theta_d) (d/dt + k_{dm}) n_d - \\ (1 - \theta_g) (\beta_m / \beta_{mo}) k_{md} n_m - \eta_d = 0 \end{aligned} \right\} \cdot (10.28)$$

Eliminating  $k_{md}$  and  $k_{dm}$  via equations (8.38) and (8.39), we obtain:

$$\left. \begin{aligned} (1 - \theta_m) dn_m / dt + (1 - \theta_g) k_5 n_m - \\ (1 - \theta_d) k_6 n_d = \eta_m \\ (1 - \theta_d) (d/dt + k_6) n_d - (1 - \theta_g) k_5 n_m = \eta_d \end{aligned} \right\} \cdot (10.29)$$

We obtain the desired equations for the carbon-total perturbations,  $n_i$ , by substituting the above expressions for the calcium carbonate dissolution sources,  $\eta_i$ , in equations (10.13) and (10.14):

$$\left. \begin{aligned} \theta_m (dn_m / dt) + \theta_g k_5 n_m - \theta_d k_6 n_d = \gamma_m \\ \theta_d (d/dt + k_6) n_d - \theta_g k_5 n_m = \gamma_d \end{aligned} \right\} \cdot (10.30)$$

From the definitions of the functions,  $\theta_i$ , it can be seen that equations (10.30) account for the transport of carbon owing to the external sources,  $\gamma_i$ , after subtracting the transport owing to carbonate dissolution.

The fractions,  $\theta_m$  and  $\theta_d$ , are evaluated in terms of the non-linear factors,  $\zeta_m$  and  $\zeta_d$ , defined by equation (10.11) and (10.22). The latter, as may be recalled, express how the concentrations of calcium and carbon in surface and deep oceans vary in response to the external sources,  $\gamma_i$ . The function,  $\theta_g$ , depends not only on one of these factors,  $\zeta_m$ , but also on the parameters,  $\beta_g$  and  $\beta_{cg}$  which express how the total gravitational flux,  $F_g$ , and the biogenic carbonate portion of that flux,  $F_{cg}$ , respond to these external sources. To evaluate  $\theta_g$  we proceed via equation (8.23) and (10.19) which define  $\beta_m$  and  $\beta_{cm}$ , respectively.

The factor,  $\beta_{cm}$ , given by equation (10.19), is conveniently reexpressed by an equation derived in the manner of equation (8.25) with  $\zeta_m C_{mo} / N_{mo}$  replaced in accordance with equation (10.25), i.e.:

$$\beta_{cm} = \beta_{mo} (1 - \theta_m) + \beta_{cg} (1 - \beta_{mo}). \quad (10.31)$$

Substituting this expression for  $\beta_{cm}$  and the expression for  $\beta_m$  of equation (8.25) into equations (10.27) we obtain after some rearrangement:

$$\theta_g = \theta_m + \frac{(1 - \beta_{mo}) [\beta_g (1 - \theta_m) - \beta_{cg}]}{\beta_{mo} + (1 - \beta_{mo}) \beta_g}. \quad (10.32)$$

As can be seen,  $\theta_m$  and  $\theta_g$  are equal unless the gravitational flux varies with external sources (i.e.  $\beta_g$  and  $\beta_{cg}$  are nonzero).

#### 10.4 Model equations for rare isotopic carbon

For the rare isotopes we are obliged to consider separately the two gravitational fluxes which were combined in section 8 as the single global flux,  $F_g$ . With properties of the organic flux distinguished by the

subscript  $p$  (for ‘‘particulate organic carbon’’) we redefine  $F_g$  as the sum:

$$F_g = F_{cg} + F_{pg} \tag{10.33}$$

The perturbation factor,  $\beta_g$ , is likewise composed of a sum:

$$\beta_g = \beta_{cg} + \beta_{pg} \tag{10.34}$$

where  $\beta_{pg}$  is defined (cf. equation (10.16)) by:

$$\Delta F_{pg} = \beta_{pg} F_{go} n_m / N_{mo} \tag{10.35}$$

The fractionation factor,  $\alpha_{mg}$ , associated with the steady-state gravitational flux,  $F_{go}$ , is now defined as a weighted mean of the factors for organic carbon and biogenic carbonate:

$$\alpha_{mg} = (\alpha_{cmg} F_{cgo} + \alpha_{pmg} F_{pgo}) / F_{go} \tag{10.36}$$

Consistent with these definitions the perturbation flux,  $\Delta F_{md}$ , given by equation (8.30) is now reexpressed with two separate terms associated respectively with fractionation of biogenic carbon and particulate organic carbon:

$$\begin{aligned} \Delta F_{md} = & k_{md} n_m + \alpha_{cmg} [R_m (F_{cgo} + \Delta F_{cg}) - R_{mo} F_{cgo}] \\ & + \alpha_{pmg} [R_m (F_{pgo} + \Delta F_{pg}) - R_{mo} F_{pgo}] \end{aligned} \tag{10.37}$$

Proceeding as in subsection 8.5, we obtain for the perturbation exchange coefficient,  $*k_5$ , and the virtual source coefficient,  $k_8'$ :

$$\begin{aligned} *k_5 = & k_{md} + \frac{F_{go}}{N_{mo}} \left( \frac{\alpha_{mg} + (\alpha_{cmg} \beta_{cg} + \alpha_{pmg} \beta_{pg}) n_m / N_{mo}}{1 + n_m / N_{mo}} \right) \\ k_8' = & \frac{R_{mo} F_{go} (\alpha_{mg} - \alpha_{cmg} \beta_{cg} - \alpha_{pmg} \beta_{pg})}{N_{mo} (1 + n_m / N_{mo})} \end{aligned} \tag{10.38}$$

If the perturbations in the gravitational flux for particulate organic carbon and biogenic carbonate grow in proportion to their relative magnitude at steady-state, i.e. if:

$$\left. \begin{aligned} \beta_{cg} &= \beta_g F_{cgo} / F_{go} \\ \beta_{pg} &= \beta_g F_{pgo} / F_{go} \end{aligned} \right\} \tag{10.39}$$

then:

$$\alpha_{mg} \beta_g = \alpha_{cmg} \beta_{cg} + \alpha_{pmg} \beta_{pg} \tag{10.40}$$

and the expressions for  $*k_5$  and  $k_8'$  simplify to the former equations (8.40), and (8.42) respectively.

The former equations (8.37) for the perturbations of rare isotopic carbon are rewritten with isotopic carbonate sources:

$$\left. \begin{aligned} (d/dt + *\lambda + *k_5) *n_m - *k_6 *n_d &= R_{cm} \eta_m \\ &+ R_{\gamma m} \gamma_m + k_8' n_m \\ (d/dt + *\lambda + *k_6) *n_d - *k_5 *n_m &= R_{cd} \eta_d \\ &+ R_{\gamma d} \gamma_d - k_8' n_m \end{aligned} \right\} \tag{10.41}$$

where  $R_{cm}$  and  $R_{dm}$  denote, respectively, the isotopic ratios of previously solid carbonate which is dissolving in surface and subsurface reservoirs. Eliminating the  $\eta$ , via equations (10.13) and (10.14):

$$\left. \begin{aligned} (d/dt + *\lambda + *k_6) *n_m - *k_6 *n_d &= k_8' n_m + R_{\gamma m} \gamma_m \\ &+ R_{cm} [(d/dt + k_5) n_m - k_6 n_d - \gamma_m] \\ (d/dt + *\lambda + *k_5) *n_d - *k_5 *n_m &= -k_8' n_m + R_{\gamma d} \gamma_d \\ &+ R_{cd} [(d/dt + k_6) n_d - k_5 n_m - \gamma_d] \end{aligned} \right\} \tag{10.42}$$

10.5 Solving the model equations

In the four reservoir model the changes in formulation to allow for carbonate dissolution are now readily incorporated. In matrix notation the submatrices of equation (9.11) are:

$$[k_{ij}] = \begin{bmatrix} s + k_1 & -k_2 & 0 & 0 \\ -k_1 & s + k_2 + k_3 & -k_4 & 0 \\ 0 & -k_3 & \theta_m s + k_4 + \theta_g k_5 & -\theta_d k_6 \\ 0 & 0 & -\theta_g k_5 & \theta_d (s + k_6) \end{bmatrix} \tag{10.43}$$

$$[k'_{ij}/R_{ao}] = \frac{-1}{R_{ao}} \begin{bmatrix} k'_9 & -k'_{10} & 0 & 0 \\ -k'_9 & k'_{10} & k'_7 & 0 \\ 0 & -R_{cm} k_3 & -k'_7 + k'_8 + R_{cm} (s + k_4 + k_5) & -R_{cm} k_6 \\ 0 & 0 & -k'_8 - R_{cd} k_5 & R_{cd} (s + k_6) \end{bmatrix} \tag{10.44}$$

$$[*k_{ij}] = \begin{bmatrix} s + *\lambda + *k_1 & -*k_2 & 0 & 0 \\ -*k_1 & s + *\lambda + *k_2 + *k_3 & -*k_4 & 0 \\ 0 & -*k_3 & s + *\lambda + *k_4 + *k_5 & -*k_6 \\ 0 & 0 & -*k_5 & s + *\lambda + *k_6 \end{bmatrix} \tag{10.45}$$

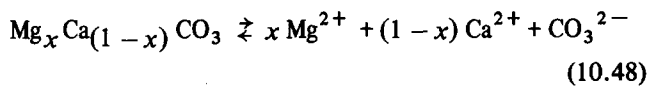
$$[\tilde{\gamma}_i] = \begin{bmatrix} \tilde{\gamma}_b \\ \tilde{\gamma}_a \\ \tilde{\gamma}_m \\ \tilde{\gamma}_d \end{bmatrix}, \quad [* \tilde{\gamma}_i / R_{ao}] = \frac{1}{R_{ao}} \begin{bmatrix} R_{\gamma b} \tilde{\gamma}_b \\ R_{\gamma a} \tilde{\gamma}_a \\ (R_{\gamma m} - R_{cm}) \tilde{\gamma}_m \\ (R_{\gamma d} - R_{cd}) \tilde{\gamma}_d \end{bmatrix} \tag{10.46}, \tag{10.47}$$



The matrix [ $*k_{ij}$ ] is unchanged from the case without carbonate dissolution (equation (9.8)). Additional terms  $R_{cm}k_3$  and  $R_{cm}k_4$  arise in matrix [ $k_{ij}'/R_{ao}$ ] as a result of including transfer terms between the atmosphere and surface layer in the equation for the ocean surface layer (cf. equations (9.2) and (10.13)).

### 10.6 Influence of magnesium on equilibrium carbonate dissolution

Let us now consider briefly how the above relationships are modified if magnesium calcite rather than pure calcium carbonate remains in equilibrium with sea water during the industrial era. According to Wollast and Reinhard-Derie (77) this equilibrium involves a solid solution of  $MgCO_3$  and  $CaCO_3$  for which the instantaneous chemical reaction is:



where  $x$  is the mole fraction of  $MgCO_3$  in the solid solution. For a finite extent of reaction the mass balance relationship between dissolved and solid species is complicated owing to the tendency for the solid solution to change composition so as to maintain constant the quotients:

$$K_{CaCO_3} = \frac{a_{Ca} a_{CO_3}}{a_{CaCO_3}} \quad (10.49)$$

$$K_{MgCO_3} = \frac{a_{Mg} a_{CO_3}}{a_{MgCO_3}} \quad (10.50)$$

where  $a_{Ca}$ ,  $a_{Mg}$  and  $a_{CO_3}$  are the chemical activities, respectively, of  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $CO_3^{2-}$  in sea water, and  $a_{CaCO_3}$  and  $a_{MgCO_3}$  are the activities in the solid phase. For a perturbation owing to industrial  $CO_2$ , it is probably justified to assume that the chemical activities in the solid phase as well as in sea water are proportional to concentration since the ranges in concentration will be small. With this simplification:

$$[Ca^{2+}] [CO_3^{2-}] = K_{spC} (1-x) \quad (10.51)$$

$$[Mg^{2+}] [CO_3^{2-}] = K_{spM} x \quad (10.52)$$

where  $K_{spC}$  and  $K_{spM}$  are constants for any given water mass.

Since both magnesium and calcium ions are released by dissolution, let us redefine  $C_i$  as the sum of the concentrations of  $Ca^{2+}$  and  $Mg^{2+}$  (including ion com-

plexes) in oceanic reservoir  $i$  in moles times molecular weight of carbon. Then, comparing perturbed and steady states (cf. equation (10.5)):

$$\frac{C_i}{C_{io}} = \frac{[Ca^{2+}] + [Mg^{2+}]}{[Ca^{2+}]_o + [Mg^{2+}]_o} \quad (10.53)$$

where the concentrations denoted by the brackets apply to reservoir  $i$ . Eliminating  $[Ca^{2+}]$  and  $[Mg^{2+}]$  and their steady state values by means of equations (10.51) and (10.52), we find that:

$$\frac{C_i}{C_{io}} = \frac{[CO_3^{2-}]_o^2}{[CO_3^{2-}]} \left\{ \frac{K_{spC} (1-x) + K_{spM} x}{K_{spC} (1-x_o) + K_{spM} x_o} \right\} \quad (10.54)$$

where  $x_o$  is the mole fraction of  $MgCO_3$  in the solid solution at steady state.

Since the mole fraction,  $x$ , is a function of the total dissolved carbon in reservoir  $i$  it is again possible to obtain a Taylor's series expansion as in the case of dissolution of  $CaCO_3$ . Thus the previous formulation of the two reservoir model with calcium carbonate dissolution still applies. The perturbation parameters  $\xi_i$  and  $\theta_i$  take on different values, but the differences are expected to be slight.

If we assume an unlimited supply of magnesian calcite then the mole fraction  $x$  is constant and equation (10.42) simplifies to:

$$\frac{C_i}{C_{io}} = \frac{[CO_3^{2-}]_o}{[CO_3^{2-}]} \quad (10.55)$$

An assumption of unlimited magnesium calcite is probably not realistic, but in view of the lack of data on the solubility and occurrence of magnesium carbonates, and lack of assurance that equilibrium will be maintained during a perturbation by industrial  $CO_2$ , it is not justified to attempt to evaluate  $x$  from the general mass balance and equilibrium relationships given by Wollast and Reinhard-Derie (77). We may therefore consider the equilibrium case as a somewhat dubious upper limit on the influence of dissolution of oceanic  $CO_2$  uptake.

Because the molar concentration of magnesium in sea water greatly exceeds that of dissolved inorganic carbon, dissolution of carbonate sediments in response to industrial  $CO_2$  could not appreciably change the sum of the concentrations of calcium and magnesium up to the present time. It follows from equations (10.55) that the carbonate ion concentration,  $[CO_3^{2-}]$  in sea water remains essentially constant if equilibrium with magnesium calcite is maintained. In this case, it can be shown that the  $CO_2$  evasion factor,  $\xi$ , tends to a limiting value of 2. Since  $\xi$  is found to be approx-

imately 2.5 if magnesium is assumed to play no part in carbonate dissolution controlled by equilibrium with sea water (see section 11), the inclusion of magnesium in the equilibrium will not produce marked changes in prediction. The possibility is so remote that calcium carbonate dissolution has occurred to the extent predicted by  $\xi$  equal to 2.5, that the more extreme case of magnesium carbonate dissolution will not be further considered.

## 11. Preparing the four reservoir model for calculations

### 11.1 *Strategy for testing the model*

A limited analysis of the capabilities of the foregoing four reservoir isotopic carbon cycle model will be undertaken now to identify which factors in the global carbon cycle appear to be the most important in predicting the Suess Effect and, by extension, what is likely to be learned about the carbon cycle from new isotopic time series. Existing information is adequate, or nearly so, to investigate the sensitivity of the model to estimated uncertainties in the observational data from which the model parameters are derived. Such an investigation is relatively straightforward because most of the model parameters behave as nearly independent variables, at least for small perturbations. A sensitivity analysis, for example, will indicate the order of magnitude of error in isotopic predictions when fractionation is neglected as in the Stuiver approximation.

The best strategy for carrying out a sensitivity analysis is not immediately obvious, however. The degree of numerical uncertainty in model parameters varies considerably. Also, some parameters are closely related to observational data of known accuracy, but others depend on indirect calculations. Some are difficult to trace back to observational data and some even rely on assumptions inconsistent with the model under examination. Ideally, such indirect numerical inputs would be avoided altogether, but this would unduly complicate the analysis.

A large and valuable part of the observational data is closely related to the *output* produced by solving the differential equations of the model under study. Direct use of these data would require an inverse solution of the model equations, a task which is not only more complicated than the direct solution, but may lead to subtle mathematical instabilities (Twomey, 77). This problem is lessened, however, if we restrict our attention to intervals of the time record when the abundances of both carbon-total and rare isotopic carbon were changing nearly exponentially. Stated more correctly, we may steer around the inverse problem by concerning ourselves only with hypothetical cases of exponential perturbations similar, but not identical, to the perturbations which have actually occurred in the carbon cycle.

As a major simplification of the real problem, the only time varying source of carbon to be considered will be industrial CO<sub>2</sub>. Any man-induced CO<sub>2</sub> exchanges with the biosphere will be portrayed indirectly by an adjustment of the biosphere pertur-

bation factor,  $\beta_a$ . This is equivalent to assuming that man's effect on biospheric exchange, whatever its magnitude and direction, has risen proportionally with increased consumption of fossil fuel. Actually this is not an unreasonable first approximation, since fossil fuel has provided most of the world's commercial energy since the late 1800s, and man's agricultural activities have grown roughly in proportion to energy consumption. Whether this is a good assumption or not, existing data on land clearing and forest practices are of little help in finding a better relationship. It is difficult enough just to estimate the cumulative amount of land cleared and forests harvested, and the resultant release of CO<sub>2</sub> to the atmosphere over the industrial era as a whole (Revelle, 77; Schlesinger, 77). Nevertheless, a sensitivity analysis involving less restricted biospheric sources would be valuable, and should be undertaken.

As a further simplification, the sensitivities of parameters will be tested only for small perturbations such that a linearized model is adequate. This is an important first step, since it is necessary to establish which parameters are critical to all perturbations whether large or small.

Also, a concern about future levels of atmospheric CO<sub>2</sub> applies mainly to carbon as a chemical and not as a tracer, and thus perfecting isotopic models applicable to the next century is not of great interest at this time. Conversely, because existing isotopic data are only useful to test models of the carbon cycle during the recent period of small perturbations, these data are not of much help in establishing nonlinear relationships which are likely to appear later on. This is especially the case for the <sup>14</sup>C Suess Effect which extends only to about A.D. 1954. The principal benefits of isotopic studies are to validate steady-state parameters and to indicate the relative importance of oceanic and biospheric uptake of industrial CO<sub>2</sub> over the past 100 yr.

Because the average change in atmospheric CO<sub>2</sub> concentration since A.D. 1958 is known from direct observations, it is important to establish parametric sensitivities in a manner which does not contradict this record. This is especially necessary in connection with the atmospheric Suess Effect, since the predicted isotopic ratios for both <sup>13</sup>C and <sup>14</sup>C closely follow the predicted rise in carbon-total, irrespective of the parameter being varied.

Those parameters which influence the prediction of the airborne fraction,  $r_a$ , will therefore be covaried such that  $r_a$  remains constant from case to case. Since the magnitude of the biospheric perturbation parameter,  $\beta_a$ , is unknown at present even as to its sign, this parameter will be given the reduced status of a dependent variable; it will be adjusted each time some other parameter affecting carbon-total is varied. This approach leads to some surprising relationships for different parametric choices, but as far as I can tell, leads to a more revealing analysis than if parameters are varied without regard for their effect on  $r_a$ . As proposed in section 1, the theoretical Suess Effect, although considered primarily a function of industrial CO<sub>2</sub> input to the carbon cycle, will be regarded also to be a function of biospheric changes such as are implied by an adjustable  $\beta_a$ .

For an exponentially rising CO<sub>2</sub> input, a sensitivity analysis is essentially an examination of how the reservoir fractions,  $r_i$  and  $r_{i0}$ , or more explicitly, their differences:

$$\Delta r_i = r_i - r_{i0} \quad (11.1)$$

vary as functions of the model parameters. These fractions, which are constant for a given exponential source, will therefore be tabulated for representative choices of the model parameters. The theoretical Suess Effect,  $S_i$ , for reservoir  $i$ , is readily derived from  $\Delta r_i$ , since (cf. equation (1.22)):

$$S_i = (Q/N_i) \Delta r_i. \quad (11.2)$$

For <sup>13</sup>C the function  $\Delta\delta C_i$  (cf. equation (1.27)) will be tabulated instead of the Suess Effect since this quantity, expressed in terms of <sup>13</sup>C/<sup>12</sup>C ratios instead of <sup>13</sup>C/C ratios, is more readily compared to published observational data. It is likely that a comprehensive set of standardized input data to test carbon cycle models will soon be established elsewhere (Bolin, private communication) and, therefore, I have made only a minor attempt here to update or refine existing observational data. I have relied principally on my own previous investigations and those of Oeschger *et al.* (75) to form a set of parameters adequate for a sensitivity analysis.

All calculations discussed below were performed using a version of the four-reservoir which, for the oceans, closely resembles the box-diffusion model of Oeschger *et al.* (75), as described in subsection 8.6, above.

Because of the complexities of including an oceanic gravitational flux in the formulation for the box diffusion model, and the relatively minor influence this flux has on isotopic ratios as demonstrated below, this feature of the oceanic carbon cycle will be examined as a separate aspect of the sensitivity analysis.

## 11.2 Standardized model parameters

As a basis for testing the sensitivity of the four-reservoir model to changes in model parameters, a standard case has been chosen which resembles the actual carbon cycle in as many respects as practicable. The essential inputs to the model for this standard case are listed in Table 2. Choices which are not obvious from the table and its footnotes will now be explained; first, in this subsection, for the case in which the gravitational flux,  $F_{g0}$ , is set equal to zero; then, in the following subsection, for the case where  $F_{g0}$  is not zero.

The lack of observational data prior to the industrial era makes difficult the assigning of standard values, either to the steady-state abundances,  $N_{i0}$ , or to the steady-state exchange coefficients,  $k_{ij}$ . Some of the choices must inevitably be based on computations which, strictly speaking, are themselves model dependent since, as noted in section 1, the available observational data are only for times when industrial CO<sub>2</sub> has already begun to perturb the carbon cycle. The

precise standard values used are, however, not critical to a sensitivity analysis, and therefore in most instances do not justify refining previous calculations to yield values fully consistent with the model under investigation.

In the case of CO<sub>2</sub> exchange with the land biosphere, the variables selected as model inputs are the abundances  $N_{a0}$ ,  $N_{b0}$ , and the steady-state flux,  $F_{b0}$ . For purpose of establishing the steady-state coefficient,  $k_{ab}$ , (equal to the quotient  $F_{b0}/N_{a0}$ ) the value of  $N_{a0}$  will be assumed to be equivalent to a mixing ratio of 290 ppm. In calculating the atmospheric Suess Effect via equation (11.2) the value of  $N_{a0}$  will depend, however, on the choice of the time period being considered. To make this clear, the symbol  $N_{a\bullet}$  will henceforth be used to denote the amount of atmospheric CO<sub>2</sub> corresponding to 290 ppm. This value is close to the value believed to have prevailed in the late 19th century, as discussed below. In contrast,  $N_{a0}$  will refer to the initial value of  $N_a$  used in solving the model equations.

In the case of air-sea exchange, the chosen input parameters, in addition to  $N_{a0}$ , will be the steady-state coefficient,  $k_{am}$ , and the depth of water,  $h_a$ , containing the same amount of inorganic carbon-total as the atmosphere in preindustrial times, i.e.:

$$h_a = \frac{N_{a\bullet} W_m}{N_{m0} A} \quad (11.3)$$

where  $A$  is the area of the oceans including adjacent seas. In terms of the depth of the surface layer defined by:

$$h_m = W_m / A \quad (11.4)$$

the abundance of carbon-total in surface ocean water is given by the expression:

$$N_{m0} = N_{a\bullet} (h_m / h_a) \quad (11.5)$$

For convenience in comparing results with those of Oeschger *et al.* (75),  $h_a$  will be set equal to 58 meters. For an oceanic area of  $3.61 \times 10^{14}$  (Sverdrup, 42) and  $N_{a\bullet}$  of  $6.156 \times 10^{17}$  g (see Table 2), this choice leads to a concentration of carbon-total in surface sea water,  $N_{a\bullet} / (Ah_a)$ , of  $29.50 \text{ g m}^{-3}$  or  $2.45 \text{ mmol l}^{-1}$ . This concentration is an extreme value for deep ocean water and thus nearly 20% too high for surface water, as noted below in subsection 11.3. If the surface waters of adjacent seas, especially of the Arctic ocean, are excluded, the implied deep ocean concentration is still higher. Because of the insensitivity of predictions of the Suess Effect parameters (as found below) the choice of standard value is not important enough to warrant re-adjustment.

The air to sea exchange coefficient,  $k_{am}$ , was calculated to be consistent with the steady-state vertical distribution of <sup>14</sup>C/C implied by the box-diffusion model. Numerical values for the parameters,  $^{14}R_{m0} / ^{14}R_{a0}$ ,  $h_m$ , and  $K$  were chosen to agree with those of

Table 2. Model parameters for the standard case

Steady-state factors		Notes	Value			
$N_{bo}$	carbon in land biosphere	(1)	$1560 \times 10^{15}$ g of C	$\beta_a$	gravitational flux dependence of concentration of carbon-total in surface ocean	(11) 0 0
$F_{bo}$	flux of CO <sub>2</sub> between atmosphere and land biosphere	(1)	$26 \times 10^{15}$ g of C yr <sup>-1</sup>	$\phi_{ms}$	perturbation function for evasion of CO <sub>2</sub> from surface ocean	(12) 1.0 1.0
$N_a \bullet$	CO <sub>2</sub> in atmosphere, for mixing ratio of 290 ppm	(1)	$615.6 \times 10^{15}$ g of C	$\phi_{ab}$	perturbation function for land biospheric uptake of CO <sub>2</sub>	(12) 1.0 1.0
$h_a$	depth of hypothetical surface ocean layer containing $N_a \bullet$ g of carbon	(2)	58 m	$\phi_{ba}$	same for biospheric release	(12) 1.0 1.0
$h_m$	depth of surface ocean layer	(2)	75 m	$\theta_{ms}$	carbonate dissolution factor for surface ocean	(9) 1.0 0.53653
$h_s$	average depth of ocean (including adjacent seas)	(2)	3800 m	$\theta_a$	same for deep ocean	(9) 1.0 0.53036
$k_{am}$	transfer coefficient for uptake of CO <sub>2</sub> by surface ocean	(3)	1/(7.53 yr)	Other factors		
$K$	vertical eddy diffusion coefficient	(2)	$3987 \text{ m}^2 \text{ yr}^{-1}$		Notes	Value
$k_{dm}$	transfer coefficient for carbon-total from deep ocean to surface ocean	(4)	1/(1129 yr)	$^{14}\lambda$	radioactive decay constant for <sup>14</sup> C	(1) 1/(8267 yr)
$m_o$	ratio of concentration of carbon-total in surface ocean water to that in deep ocean water	(4)	$2.09 \text{ mmol } \ell^{-1} / 2.33 \text{ mmol } \ell^{-1}$	$^{13}\lambda \bullet$	<sup>13</sup> C/ <sup>12</sup> C ratio of standard, P.D.B.	(13) 0.0112372
$F_{go}$	gravitational flux of particulate organic carbon and biogenic carbonate from surface to deep ocean	(4)	$3.5 \times 10^{15}$ g of C yr <sup>-1</sup>	$^{13}R \bullet$	<sup>13</sup> C/ <sup>12</sup> C ratio of same	(14) 0.0111123
$F_{cgo}/F_{go}$	fraction of gravitational flux which is biogenic carbonate	(5)	0.3	$A$	area of oceans	(15) $3.61 \times 10^{14} \text{ cm}^2$
Carbon isotopic fractionation factors						
		Notes	<sup>13</sup> C	<sup>14</sup> C		
$\alpha_{ab}$	uptake of CO <sub>2</sub> by land biosphere	(6)	0.982	(0.982) <sup>2</sup>		
$\alpha_{ba}$	release of CO <sub>2</sub> by land biosphere	(6)	1.0	1.0		
$\alpha_{am}$	uptake of CO <sub>2</sub> by surface ocean	(6)	0.986	(0.986) <sup>2</sup>		
$\alpha_{eq}$	equilibrium between atmospheric CO <sub>2</sub> and surface oceanic bicarbonate	(6)	1.009	(1.009) <sup>2</sup>		
$\alpha_{mg}$	transfer in surface ocean from bicarbonate to carbon of the gravitational flux (particulate organic carbon and biogenic carbonate combined)	(7)	0.983	(0.983) <sup>2</sup>		
$\alpha_{mc}$	transfer in surface ocean from bicarbonate to particulate (biogenic) carbonate	(8)	0.999	(0.999) <sup>2</sup>		
Perturbation factors and functions						
		Notes	Carbon-absent dissolution	Carbon-included dissolution		
$\xi$	surface ocean CO <sub>2</sub> ("evasion factor")	(9)	8.8957	2.4282		
$\xi$	same for rare isotopic carbon	(9)	= $\xi$	= $\xi$		
$\beta_a$	atmospheric dependence of land biospheric uptake of CO <sub>2</sub> , ("biospheric growth factor") A.D. 1956-1978	(10)	0.290549	-0.113678		
$\beta_a'$	Same for A.D. 1886-1956	(10)	-0.325097	-0.656475		
$\beta_a''$	atmospheric dependence of land biospheric release of CO <sub>2</sub>	(11)	0	0		
$\beta_b - \beta_a'$	land biospheric dependence of net release of CO <sub>2</sub>	(11)	0	0		

- (1) Keeling (1973b) p. 301.
- (2) Oeschger *et al.* (1975) p. 184.
- (3) Calculated by equation (11.6).
- (4) Applicable only if gravitational flux is included in model. Concentration ratio,  $\beta_{mo}$ : from deep ocean data of Eriksson (1959) p. 151 and surface ocean data of Keeling (1973b) p. 298 as explained in subsection 11.3. Flux,  $F_{go}$ : calculated by equation (11.41). Coefficient,  $k_{dm}$ : by equation (11.42) as explained in subsection 11.3. (This non-zero value of  $k_{dm}$  applies only to the calculation of  $N_{do}$  with non-zero  $F_{go}$ , see Table 4 and subsection 8.6.)
- (5) Broecker (1974) p. 11. Applicable only if  $F_{go}$  is non-zero. See note (4), above.
- (6) Keeling (1973b) p. 302. The fractionation factors from <sup>14</sup>C are the square of the corresponding <sup>13</sup>C factors (Skirrow, 1965, p. 288).
- (7) From direct measurements of <sup>13</sup>C/<sup>12</sup>C ratios and the concentration of carbon-total in sea water Craig (1970) p. 693 estimated the following  $\delta^{13}\text{C}$  values: for the gravitational flux irrespective of its chemical form: -15‰ for carbon-total in surface water + 2‰; hence  $^{13}\alpha_{mg} = 0.983$ .  $^{14}\alpha_{mg}$  is obtained as the square. (This computation does not require separate consideration of the particular organic carbon and biogenic carbonate as discussed in section 8.3 and expressed by equation (10.36). Assuming that 30% of the flux is carbonate with a  $\delta^{13}\text{C}$  of +1‰ consistent with recent nannofossils (see note (8) below), Craig's value implies  $\delta^{13}\text{C}$  of particular organic carbon of -22‰ and thus  $^{13}\alpha_{pmg} = 0.976$ ).
- (8) Kroopnick *et al.* (1977) p. 304 indicate in their figure 5 an average  $\delta^{13}\text{C}$  for  $\Sigma\text{C}$  in ocean surface water of +2.0‰. Also, they state (p. 318) that recent nannofossils exhibit  $\delta^{13}\text{C}$  of 0.6 to 0.8‰; hence a fractionation factor of 0.999. Laboratory experiments of Rubinson and Clayton quoted by Kroopnick *et al.* (1977) p. 318 confirm this value.
- (9) Bacastow and Keeling (1979). Factor of rare isotopic carbon assumed to be same as for carbon-total.
- (10) Adjusted such that the model reproduces the observed cumulative airborne fraction for the prescribed time interval.
- (11) Assumed to be zero as described in subsection 4.3 of the text.
- (12) Assumed to be unity, consistent with small perturbations.
- (13) Mook and Grootes (1973). See also Craig (1957).
- (14) By equation (11.27).
- (15) Sverdrup *et al.* (1942) p. 15. Area includes adjacent seas. Used only in the determination of the gravitational flux,  $F_{go}$ . See subsection 11.3 and note (4), above.

Oeschger *et al.* (75). Since these authors calibrated their model using  $^{14}\text{C}/\text{C}$  ratios corrected for isotopic fractionation, a special procedure was followed in applying their calibration to the present model which includes fractionation in its formulation.

Specifically, the steady-state relationship for  $^{14}\text{C}/\text{C}$  of Keeling and Bacastow (73b, p. 288; equation (6.30)) leads to the relationship:

$$^{14}\overline{R}_{do} / ^{14}R_{mo} = \frac{\tanh \sqrt{*}\lambda / K h_d}{\sqrt{*}\lambda / K h_d} \quad (11.11)$$

Adopting the values of  $*\lambda$ ,  $K$ ,  $h_m$  and  $h_d$  of Oeschger *et al.* (see Table 2) we obtain:

$$^{14}\overline{R}_{do} / ^{14}R_{mo} = 0.879864.$$

$$k_{am} = *\lambda \frac{[(^{14}R_{mo} / ^{14}R_{ao}) / (h_m / h_a) + (^{14}\overline{R}_{do} / ^{14}R_{ao}) / (h_d / h_a)]}{1 - ^{14}R_{mo} / ^{14}R_{ao}} \quad (11.6)$$

where the fractionation factors,  $\alpha_{am}$  and  $\alpha_{ma}$ , have been set equal to unity in accordance with the use of corrected ratios, and  $^{14}R_{do}$  denotes the average  $^{14}\text{C}/\text{C}$  ratio of the subsurface ocean. Since the gravitational flux is assumed to be zero, the concentration of carbon is everywhere the same, i.e.:

$$\frac{N_{do}}{W_d} = \frac{N_{mo}}{W_m} \quad (11.7)$$

In terms of the depths,  $h_m$  and  $h_d$ , as defined by equations (11.3) and (11.4) and the areal average depth of the deep ocean,  $h_d$ , defined by:

$$h_d = W_d / A \quad (11.8)$$

the oceanic abundances,  $N_{mo}$  and  $N_{do}$ , are related to each other and to the atmospheric abundance,  $N_a$  by:

$$\frac{N_{do}}{h_d} = \frac{N_{mo}}{h_m} = \frac{N_a}{h_a} \quad (11.9)$$

Consistent with the above equations the mass ratios,  $N_{mo}/N_{ao}$  and  $N_{do}/N_{ao}$ , in equation (6.30) of Keeling and Bacastow (73b) have been replaced by corresponding depth ratios,  $h_m/h_a$  and  $h_d/h_a$ .

The box diffusion model (Oeschger, 75) predicts that the corrected  $^{14}\text{C}/\text{C}$  ratio of subsurface water at steady-state varies with depth according to:

$$\frac{^{14}R_{do}(z)}{^{14}R_{mo}} = \frac{\cosh[\sqrt{*}\lambda / K (h_d - z)]}{\cosh[\sqrt{*}\lambda / K h_d]} \quad (11.10)$$

where  $z$  denotes the vertical coordinate, positive downward. The vertically averaged value of  $R_{do}$  is obtained by integrating equation (11.10) from  $z = h_m$  to  $z = h_m + h_d$ . Hence:

For the ratio,  $^{14}R_{mo}/^{14}R_{ao}$ , Oeschger *et al.* (75) adopted the value 0.950 based on direct observations of  $^{14}\text{C}/\text{C}$  ratio of surface water obtained from A.D. 1955 to mid-1977. These are the earliest observations of  $^{14}\text{C}$  in surface water and are the closest to preindustrial conditions ever obtained.

To assume that these data are representative of preindustrial values is in contrast to the approach of Bacastow and Keeling (73) who assumed that surface water as late as A.D. 1955 was influenced by industrial  $\text{CO}_2$  and forced their model to predict the observed values of  $^{14}R_m/^{14}R_a$  on this assumption. They unavoidably obtained slightly different values of the preindustrial ratio,  $^{14}R_{mo}/^{14}R_{ao}$ , as a function of various choices of other model parameters.

It may be argued that  $^{14}\text{C}$  from weapons testing in 1954 had already entered surface waters so as to very nearly compensate for the local Suess Effect at the time of the early surface water measurements. This view is supported by the coral records of Nozaki *et al.* (78), and Druffel and Linick (78), but additional proxy records of surface water  $^{14}\text{C}/\text{C}$  would be valuable as further verification. In any case the uncertainty in the significance of the observed values of surface water  $^{14}\text{C}/\text{C}$  in the 1950s suggests that the refinements in the calculation of Bacastow and Keeling (73) are not justified here. Therefore the value 0.950 will be adopted; whence, we obtain via equation (11.4):

$$k_{am}^{-1} = 7.53 \text{ yr.}$$

This value was not changed when  $h_d$  or  $K$  were afterwards varied in the sensitivity analysis, because fundamentally  $k_{am}$  is an expression of gas exchange which does not depend on either  $h_d$  or  $K$ .

On the other hand, the steady state relationships between  $k_{am}$  and  $^{14}R_{mo}$  should be made internally consistent in model calculations where fractionation is included. Accordingly, after the value of  $k_{am}$  was established, the value of  $^{14}R_{mo}$  was redetermined making full use of the steady state relationship with

fractionation (but not the gravitational flux) included (Keeling, 73b, p. 388; equation (6.31)) i.e.:

$$\frac{{}^{14}R_{mo}}{{}^{14}R_{ao}} = \frac{{}^{14}\alpha_{am}}{{}^{14}\alpha_{ma} + (*\lambda/k_{am}) [(h_m/h_a) + ({}^{14}\bar{R}_{do} / {}^{14}R_{mo}) (h_d/h_a)]} \quad (11.12)$$

For <sup>13</sup>C, the steady state isotopic ratio for surface water was calculated on the assumption of equilibrium with the atmosphere, i.e.:

$${}^{13}R_{mo} / {}^{13}R_{ao} = {}^{13}\alpha_{eq} \quad (11.13)$$

where <sup>13</sup>α<sub>eq</sub>, the equilibrium fractionation factor (equal to α<sub>am</sub>/α<sub>ma</sub>), is known from laboratory data (Deuser, 67; Mook, 74).

For deep water in the absence of a gravitational flux, since transport by water is without fractionation:

$${}^{13}R_{mo} = {}^{13}R_{do} \quad (11.14)$$

With respect to carbonate dissolution, chemical equilibrium was assumed for both isotopes between solid carbonate and total dissolved inorganic carbon in the sea water of the reservoir involved, i.e.:

$$\begin{aligned} R_{cio}/R_{io} &= \alpha_{ic} \\ i &= m, d \end{aligned} \quad (11.15)$$

where α<sub>ic</sub> denotes the equilibrium fractionation factor between dissolved bicarbonate and solid carbonate for reservoir *i*. Since the assumption of equilibrium for carbon-total is an extreme case chosen essentially as an upper limit of the extent of dissolution, it seems logical to adopt an upper limit for the <sup>14</sup>C concentration in carbonates by leaving out of consideration the possible radioactive decay of <sup>14</sup>C of the carbonate undergoing dissolution.

With respect to the land biosphere, the ratio <sup>14</sup>R<sub>bo</sub>/<sup>14</sup>R<sub>ao</sub> for carbon-14 was calculated by the expression:

$$\frac{{}^{14}R_{bo}}{{}^{14}R_{ao}} = \frac{{}^{14}\alpha_{ab}}{{}^{14}\alpha_{ba} + *\lambda N_{bo}/F_{bo}} \quad (11.16)$$

This equation is derived by solving the first of equations (6.7) for R<sub>bo</sub>/R<sub>ao</sub> after replacing k<sub>ba</sub> by its equivalent F<sub>bo</sub>/N<sub>bo</sub> according to the first of equations (4.12).

For the land biosphere, in accordance with equations (6.7) applied to <sup>13</sup>C, with <sup>13</sup>λ set equal to zero (cf. equations (2.27)):

$${}^{13}R_{bo} / {}^{13}R_{ao} = {}^{13}\alpha_{ab} / {}^{13}\alpha_{ba} \quad (11.17)$$

The theoretical Suess Effect for <sup>13</sup>C will be compared with observations for the period A.D. 1956 to 1978. For all but the first three years of this period the concentration of CO<sub>2</sub> in the atmosphere is established from nearly continuous measurements at Mauna Loa Observatory, Hawaii and twice monthly data from the South Pole (Keeling, 76a, 76b and unpublished) but even for the earlier years, A.D. 1956 to 1959, enough direct measurements were made elsewhere to establish monthly average concentrations reasonably representative of the northern hemisphere (Keeling, 78). For A.D. 1955, 1956 and 1978 <sup>13</sup>C/<sup>12</sup>C ratios of atmospheric CO<sub>2</sub> were also measured concurrently with concentration measurements.

From these data, Keeling *et al.* (79) computed best estimates of the concentration of carbon-total and of the <sup>13</sup>C/<sup>12</sup>C ratio of atmospheric CO<sub>2</sub> in the northern hemisphere for January 1 of 1956 and 1978, as listed in Table 3. For atmospheric CO<sub>2</sub> (Fig. 7) the concentration has risen in a manner consistent with an exponentially rising input of industrial CO<sub>2</sub>. The *e*-fold time of rise for

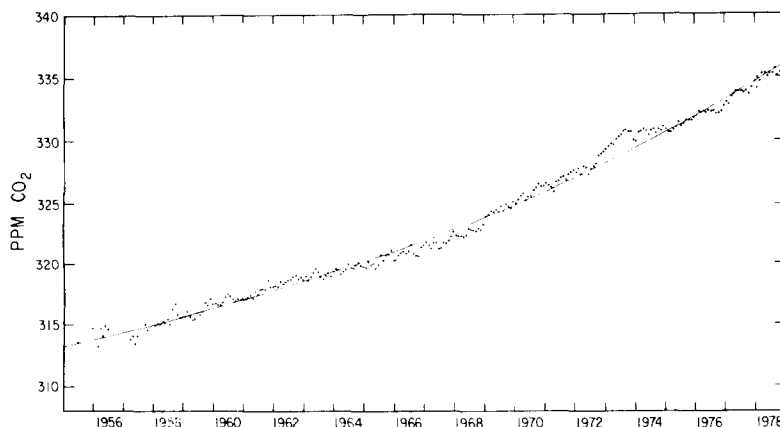


Fig. 7. Trend in concentration of atmospheric CO<sub>2</sub> at Mauna Loa Observatory, Hawaii (19°N, 156°W). Dots: Monthly average concentrations in parts per million (ppm) by volume of dry air. Curve: exponential fit of the monthly averages after seasonal adjustment as described by Bacastow and Keeling (73). Points before March 1958 refer to proxy data (Keeling, 78) which are not included in determining the exponential fit.

Table 3. Additional model parameters related to industrial and atmospheric CO<sub>2</sub> for the standard case

Time interval ( $t_1 - t_2$ ):		1886-1956	1956-1978
Industrial CO <sub>2</sub> production rate for A.D. 1860		Notes	
		(1) 0.1963 Gt/yr	0.08346 Gt/yr
$\mu$ ,	exponential factor	(1) 0.0241/yr	0.0433/yr
$\mu^{-1}$ ,	$e$ -fold time	(2) 41 yr	22 yr
$Q_2 - Q_1$ ,	cumulative production from $t_1$ to $t_2$	(3) 67.13713 Gt	78.81615 Gt
$\gamma_{ro}/\mu$ ,	cumulative production coefficient which multiplies exponential factor, $e^{\mu t}$ (equal to $Q_1$ )	(4) 14.87260 Gt	45.86916 Gt
Atmospheric CO <sub>2</sub>			
atmospheric CO <sub>2</sub> concentration at $t_1$ same at $t_2$		(5) 288.4 ppm	314.1 ppm
$N_{a1}$ ,	atmospheric CO <sub>2</sub> abundance at $t_1$	(6) 612.20359 Gt	666.75848 Gt
$N_{a2}$ ,	same at $t_2$	(6) 666.75848 Gt	709.42593 Gt
$n_{a0}$ ,	coefficient which multiplies exponential factor, $e^{\mu t}$	(7) 12.08531 Gt	24.83146 Gt
$N_{a0}$ ,	preindustrial abundance, assuming an exponential rate of increase during the industrial era	(8) 600.11827 Gt	641.92702 Gt
Isotopic Ratios			
$^{13}R_{af}/R_{a0}$ ,	$^{13}C/C$ ratio of industrial CO <sub>2</sub> relative to preindustrial atmospheric CO <sub>2</sub>	(9) —	0.980
$^{13}C_{a1}$ ,	$^{13}C/^{12}C$ ratio relative to standard P.D.B. of atmospheric CO <sub>2</sub> at $t_1$	(10) —	-6.69 ‰
$^{13}C_{a2}$ ,	same at $t_2$	(10) —	-7.24 ‰

## Notes

- (1) Based on least squares fit to industrial CO<sub>2</sub> production data (Keeling *et al.*, 1979b) using equation (11.18) with  $t = 0$  on January 1, 1860. Gt = 10<sup>15</sup> g of C.
- (2) For A.D. 1886 - 1956 reciprocal of above values of  $\mu$ , rounded to nearest year. For A.D. 1956 - 1978 22 yr was adopted (instead of 23 yr as given from above value of  $\mu$ ) to conform to the value used earlier by Keeling and Bacastow (1977) p. 93.
- (3) Based directly on production data of Keeling *et al.* (1979b).
- (4) Computed by equation (11.20) using above values of  $Q_2 - Q_1$  and  $\mu^{-1}$ ;  $t = 0$  for yr  $t_1$ .
- (5) For A.D. 1886 from Callendar (1958) as described in subsection 11.2. For A.D. 1956 and 1978 from Keeling *et al.* (1979a).
- (6) Computed from above assuming that 290 ppm corresponds to 615.6 Gt (see  $N_a$  of Table 2). Abundances are expressed to nearest 10<sup>-5</sup> Gt to avoid rounding errors as isotopic parameters are varied.
- (7) Computed by equation (11.22) with above values for  $N_{a1}$ ,  $N_{a2}$ , and  $\mu^{-1}$ ;  $t = 0$  for yr  $t_1$ .
- (8) Computed from equation (11.21) with  $t = 0$ ,  $N_a = N_{a1}$ , and above value of  $n_{a0}$ .
- (9) From Schwarz (1970) the following approximate averages are deduced for  $\delta^{13}C$ : coal, -24 ‰; crude oil, -27 ‰; natural gas, -40 ‰; cement (limestone), 0 ‰. The proportions of these fuels and of cement in 1956 (Keeling, 1973a) p. 193 were 0.599, 0.307, 0.079, 0.015. In 1977 they were 0.304, 0.493, 0.188, and 0.015 according to Table 1 of United Nations (1978) p. 2, assuming the same proportion from cement. Hence the  $\delta^{13}C$  of industrial CO<sub>2</sub> was -25.8 ‰ in 1956; -28.1 ‰ in 1977. The weighted average (total of 2.96 × 10<sup>15</sup> g C in 1956, 5.25 × 10<sup>15</sup> g C in 1977 (Keeling *et al.*, 1979b)) is -27.4 ‰. The  $\delta^{13}C$  of preindustrial CO<sub>2</sub> is found by the model to be -6.4 ‰ (see Table 4), hence  $R_f/R_{a0}$  is approximately 0.9791. This value was rounded to 0.980 in the calculations.
- (10) Keeling *et al.* (1979a).

atmospheric CO<sub>2</sub> found as the best fit to the data is 23 yr, in agreement with that of industrial CO<sub>2</sub> for the same time interval as indicated in Table 3.

For <sup>13</sup>CO<sub>2</sub> a corresponding exponential trend cannot be ascertained from observations. Indeed, it would be difficult to establish such a trend even if a complete series of observations were available, because the shift in <sup>13</sup>C/<sup>12</sup>C ratio is too small. Thus the only practical means of comparing atmospheric <sup>13</sup>CO<sub>2</sub> observation with prediction is in terms of the shift in <sup>13</sup>C/<sup>12</sup>C ratio from the beginning to the end of the interval assuming the shift to be consistent with the trend in atmospheric CO<sub>2</sub>.

To calculate the theoretical Suess Effect for <sup>14</sup>C, I have chosen the period A.D. 1886 to 1956 on the basis of meager, but perhaps relevant, atmospheric CO<sub>2</sub> concentration data of western Europe for the late nineteenth century. These data were examined in detail by Callendar (38, 40) who sought to establish which measurements were most representative of the "free air of the North Atlantic region." He selected only those observations at rural sites near the Atlantic sea coast for which he could establish from local meteorological data and weather maps that the air flux had come from the Atlantic ocean at the time of sampling. From the five sets of most precise observation he established "preferred" values of 291, 289, 287, 289, and 286 ppm for approximately the years 1872, 1880, 1881, 1897, and 1900, respectively (Callendar, 58). These values show no trend. The unweighted mean is 288.4 ppm, and the average year is 1886.

Of special interest is that Callendar also deduced from these five sets of selected observations what we now know to be approximately the correct seasonal variation in CO<sub>2</sub> for the latitude of the observations (Fig. 8). To my knowledge, no other study for the 19th century ever made this discovery. For example, the exhaustive statistical analysis of Bray (59) yields an amplitude which is too high and a maximum in January when it should appear in late spring. To what degree can Callendar's selected data be biased by local contamination and still reproduce the correct seasonal amplitude? One cannot be certain, especially since the variation is deduced from the data for all wind directions with an annual mean of 295 ppm. Nevertheless, bias with respect to the preferred mean greater than the amplitude itself would seem unlikely. Therefore the mean concentration near A.D. 1890 might be expected to lie between 280 and 296 ppm. I would judge that a bias from the chemical analysis would be less important than that from sampling errors, because several methods were used, and the investigators typically claimed accuracies of the order of 1 ppm.

The choice of A.D. 1956 is dictated by the necessity to terminate the calculation close to the time when the <sup>14</sup>C Suess Effect was obliterated by nuclear weapons testing. The advent of accurate data in A.D. 1956, is only a short time after A.D. 1953, the first year in which large amounts of <sup>14</sup>C were released into the air. Thus only the predictions for the last few years of the interval need to be discarded.

The model calculations, based on the intervals A.D. 1886 to 1956 and 1956 to 1978, were carried out as

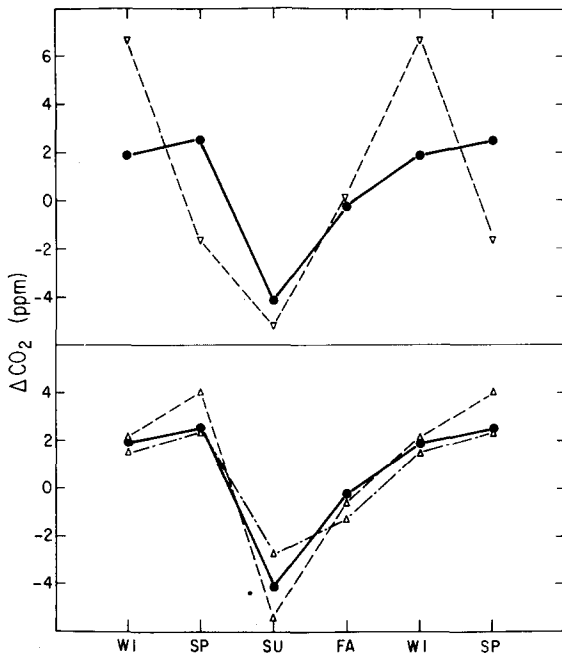


Fig. 8. Seasonal variation in atmospheric CO<sub>2</sub> for western Europe in the late nineteenth century as deduced by Callendar (40) compared with data from other sources. *Upper and lower solid lines:* Callendar's values. *Upper dashed lines:* nineteenth century European means of Bray (59, p. 222) assuming same annual average as Callendar. *Lower dashed lines:* Weather Ship 'P' at 50°N, 145°W from A.D. 1969-1978 (Keeling *et al.*, unpublished). *Lower dot-dashed curve:* aircraft data for 50°N as summarized by Bolin (63, p. 3911). WI = winter, SP = spring, SU = summer, FA = fall. Winter and spring are plotted twice to reveal the seasonal patterns more fully.

follows. First, as indicated in Table 3, data for the annual production of industrial CO<sub>2</sub> were fitted by the method of least squares to the function (cf. equation (2.16)):

$$\gamma_f = \gamma_{fo} e^{\mu t} \tag{11.18}$$

over the time interval in question,  $t_1$  to  $t_2$ , to obtain a value for the  $e$ -fold time,  $\mu^{-1}$ . The cumulative production of CO<sub>2</sub> was assumed to obey the relationship (cf. equation (2.18) and Figs 8 and 9):

$$Q = (\gamma_{fo} / \mu) e^{\mu t} \tag{11.19}$$

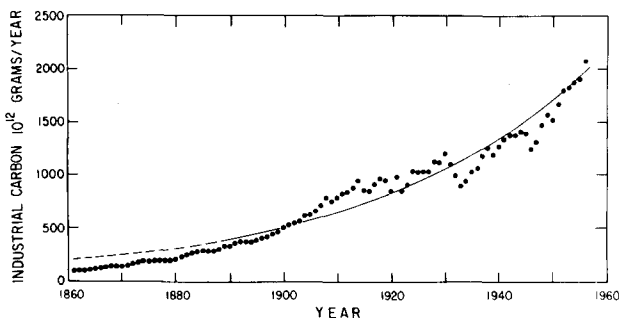


Fig. 9. The rate of production of industrial CO<sub>2</sub> as in Fig. 1 except that the curve is an exponential fit to the interval A.D. 1886 - 1956. The  $e$ -fold time is approximately 41.4 yr.

where  $\mu^{-1}$  was given by the above curve fit, except rounded to the nearest year. The value of  $\gamma_{fo}/\mu$  was then determined such that equation (11.18) exactly predicted the observed cumulative production from  $t_1$  to  $t_2$ , i.e.:

$$\gamma_{fo}/\mu = (Q_2 - Q_1)/(e^{\mu t_2} - e^{\mu t_1}). \tag{11.20}$$

The increase in atmospheric CO<sub>2</sub> was assumed to obey the relationship (cf. equation (2.19)):

$$N_a = N_{ao} + n_{ao} e^{\mu t}. \tag{11.21}$$

The constant,  $n_{ao}$ , was determined such that equation (11.21) exactly predicted the observed amount of atmospheric CO<sub>2</sub> at  $t_1$  and  $t_2$ , i.e.:

$$n_{ao} = (N_{a2} - N_{a1})/(e^{\mu t_2} - e^{\mu t_1}). \tag{11.22}$$

The airborne fraction over the interval was then calculated by the expression:

$$r_a = (N_{a2} - N_{a1})/(Q_2 - Q_1). \tag{11.23}$$

Finally,  $N_{ao}$  was calculated to be consistent with equation (11.21), i.e.:

$$N_{ao} = N_{a1} - n_{ao} e^{\mu t_1}. \tag{11.24}$$

Next, the biospheric perturbation factor,  $\beta_a$ , was adjusted by trial so that the model predicted  $r_a$ , as determined above, within 1 part in 10<sup>8</sup>. Since the total amount of carbon in any reservoir for an exponential source (cf. equation (2.19)), is given by:

$$N_i = N_{io} + n_{io} e^{\mu t} \tag{11.25}$$

at any time,  $t$ , it follows (cf. equations (2.23) and (11.18)) that:

$$N_i = N_{io} + r_i Q \tag{11.26}$$

where  $r_i$  is given by the model prediction.

The theoretical Suess Effect in reservoir  $i$  for either isotope was computed by equation (11.2), where  $Q$  was obtained according to equation (11.19),  $N_i$  was obtained via equation (11.26) and  $\Delta r_i$  was computed by the model.

For <sup>13</sup>C the shift in <sup>13</sup>C/<sup>12</sup>C isotope was also calculated to facilitate comparison with observational data.

The isotopic abundance of <sup>13</sup>C in natural materials is almost always expressed in terms of its ratio to <sup>12</sup>C. Conversion to this mode of expression from the <sup>13</sup>C/C ratios of the model and vice versa is accomplished by the formulas:

$$R = \eta / (1 + \eta) \tag{11.27}$$

$$\eta = R / (1 - R) \tag{11.28}$$



where  $\kappa$  and  $R$  denote, respectively the  $^{13}\text{C}/^{12}\text{C}$  and  $^{13}\text{C}/^{13}\text{C}$  ratios of the substance under investigation, and  $^{13}\text{C}$  denotes a rare isotope of carbon. For a carbon pool containing an amount of carbon-total,  $N$ , with corresponding amount of rare carbon isotope  $^*N$ :

$$\kappa = ^*N / ^{12}N \quad (11.29)$$

$$= ^*N / (N - ^*N) \quad (11.30)$$

while, consistent with equation (1.1):

$$R = ^*N / N. \quad (11.31)$$

The corresponding expressions for the relative variation from a standard ratio (cf. equation (1.25)) in the two modes are:

$$\delta C = R / R_{\bullet} - 1 \quad (11.32)$$

$$= \frac{\kappa(1 + \kappa_{\bullet})}{\kappa(1 + \kappa)} - 1 \quad (11.33)$$

$$\delta ^*C = \kappa / \kappa_{\bullet} - 1 \quad (11.34)$$

$$= \frac{R(1 - R_{\bullet})}{R_{\bullet}(1 - R)} - 1 \quad (11.35)$$

where subscript,  $\bullet$ , denotes a standard ratio and where the symbol,  $\delta ^*C$ , denotes a  $^{13}\text{C}/^{12}\text{C}$  ratio, relative to a standard.

To calculate the shift in  $\delta^{13}\text{C}$  the first step was to compute the theoretical atmospheric  $^{13}\text{C}$  Suess Effect at time,  $t_1$ , by the model. Then the preindustrial  $^{13}\text{C}/^{12}\text{C}$  ratio for atmospheric  $\text{CO}_2$  was computed as a function of the shift in  $^{13}\text{C}/^{12}\text{C}$  ratio indicated by this Suess Effect (now regarded as an estimate of the observable Suess Effect,  $S_{a1}$ ) and the observed  $\delta^{13}\text{C}$  value for atmospheric  $\text{CO}_2$  in A.D. 1956. Specifically, the relative ratio,  $^{13}R_{a1}/^{13}R_{\bullet}$ , was first evaluated from the observations by the formula:

$$^{13}R_{a1} / ^{13}R_{\bullet} = \frac{(\delta^{13}C_{a1} + 1)(1 + ^{13}\kappa_{\bullet})}{1 + (\delta^{13}C_{a1} + 1)^{13}\kappa_{\bullet}} \quad (11.36)$$

which follows from equations (11.32), (11.33) and (11.34). Then in accordance with the definition of the theoretical Suess Effect (equation (1.7)) the preindustrial ratio relative to standard was found by the formula:

$$^{13}R_{ao} / ^{13}R_{\bullet} = (^{13}R_{a1} / ^{13}R_{\bullet}) / (^{13}S_{a1} + 1). \quad (11.37)$$

The isotopic shifts for all reservoirs at any time,  $t$ , were computed by essentially reversing the above procedure. First, from the  $^{13}\text{C}$  Suess Effect,  $^{13}S_i$ , as computed by the model, the  $^{13}\text{C}/^{12}\text{C}$  isotopic ratio relative to standard was found by the formula:

$$^{13}R_i / ^{13}R_{\bullet} = \left( \frac{^{13}R_{io}}{^{13}R_{ao}} \right) \left( \frac{^{13}R_{ao}}{^{13}R_{\bullet}} \right) (^{13}S_i + 1) \quad (11.38)$$

where the  $^{13}R_{io}/^{13}R_{ao}$  were established from the equilibrium fractionation factors listed in Table 2. From the ratios,  $^{13}R_i/^{13}R_{\bullet}$ , the corresponding  $\delta^{13}\text{C}$  values were computed by:

$$\delta^{13}C_i = \frac{(^{13}R_i / ^{13}R_{\bullet})(1 - ^{13}R_{\bullet})}{1 - (^{13}R_i / ^{13}R_{\bullet})^{13}R_{\bullet}} - 1. \quad (11.39)$$

The preindustrial  $^{13}\text{C}$  value of reservoir  $i$  was calculated by the same procedure but with  $S_i$  equal to zero in equation (11.38). Specifically:

$$\delta^{13}C_{io} = \frac{(^{13}R_{io} / ^{13}R_{ao})(^{13}R_{ao} / ^{13}R_{\bullet})(1 - ^{13}R_{\bullet})}{1 - (^{13}R_{io} / ^{13}R_{ao})(^{13}R_{ao} / ^{13}R_{\bullet})^{13}R_{\bullet}} - 1. \quad (11.40)$$

### 11.3 Inclusion of an oceanic gravitational flux

To determine the theoretical Suess Effect using the four-reservoir model with an oceanic gravitational flux,  $F_g$ , included in the formulation, the approach will be to modify the calculations just described by explicitly including terms proportional to  $F_g$ . These terms will be evaluated in such a way that the steady-state parameters for the deep ocean are modified but not those for the surface ocean, on the grounds that the latter are better known from observational data than are the former. Specifically, equation (8.65), which relates to the exchange of rare isotopic carbon between surface and deep water for nonzero  $F_g$ , will be employed to evaluate the perturbation coefficient,  $^*k_5$ , in place of equation (8.63). To reduce the complexity of the calculation, and since little evidence exists to support a time variable flux, only a constant gravitational flux,  $F_{go}$ , will be considered in the calculations at this point (i.e.  $\beta_g$  will be set equal to zero). It follows that equations (8.62) and (8.64) which relate to the exchange of carbon-total with zero and nonzero  $F_{go}$ , respectively, lead to the same value for  $k_5$ . This is to be expected since a constant gravitational flux cannot perturb the distribution of carbon-total.

A separate calculation will now be made to estimate the magnitude of the flux,  $F_{go}$ . Since, as discussed in

subsection 8.6, neither data nor methodology are available to calculate this flux using the box diffusion model, the two reservoir model will serve as a substitute. Specifically, the perturbation coefficients for the return fluxes from the deep ocean,  $k_6$  and  $*k_6$ , for the purpose of calculating  $F_{go}$ , are made compatible with the steady-state equation (8.3) rather than being set equal to zero. In this way equation (8.14) can be employed in the calculation. Rewritten in terms of the deep water depth,  $h_d$ , and the area of the oceans,  $A$ , this expression is:

$$F_{go} = k_{dm} h_d A \left( \frac{N_{do}}{W_d} - \frac{N_{mo}}{W_m} \right) \quad (11.41)$$

i.e. the steady-state gravitational flux, in the two reservoir oceanic model, is proportional to the steady-state coefficient,  $k_{dm}$ , and to the concentration in carbon-total different between surface and deep water ( $N_{do}/W_d - N_{mo}/W_m$ ). In computing  $k_{dm}$  we preserve a reasonable degree of correspondence at steady-state with the box diffusion model of Oeschger *et al.* (75) by solving the first equality of equation (8.16) for  $k_{dm}^{-1}$  with isotopic fractionation ignored, i.e.:

$$k_{dm}^{-1} = [(^{14}R_{mo}/^{14}R_{do}) - 1] ^{14}\lambda^{-1} \quad (11.42)$$

where  $^{14}R_{mo}/^{14}R_{do}$  is set equal to the value derived in subsection 11.2. The result, rounded to the nearest year, is:

$$k_{dm} = 1/(1129 \text{ yr}).$$

The global average vertical concentration gradient in carbon-total in sea water may be roughly established from several sets of published data, but no accurate gradient can be derived from these sets because of the necessity to consider data of questionable reliability to obtain results for all of the major oceans. Even the best of the published data are somewhat questionable. The chemical studies of the GEOSECS expeditions (Craig, 74) have produced an extensive set of new observations, but these data are still being evaluated and have not yet been brought out in suitable summary form.

The best known summary data for deep water are by Eriksson (59, p. 151), based on the Swedish Deep Sea Expedition (A.D. 1945 to 1948), by Postma (64, p. 274; Fig. 10) based on Russian Expeditions of the International Geophysical Year (I.G.Y.) (A.D. 1957 - 1958), and by Li (69, p. 5519; Fig. 5) based on expeditions of the Vema and Conrad (A.D. 1956 - 1966). These sources suggest that the world average is between 2.30 and 2.40 mmol  $\ell^{-1}$ . These data may be regarded as preindustrial because of the very small admixture of industrial  $\text{CO}_2$  which could occur in deep water up to now. Since the estimate of Eriksson was derived specifically for global model studies and is not inconsistent with the other sources, I shall adopt his value of 2.33 mmol  $\ell^{-1}$  (28.0 g  $\text{m}^{-3}$ ) as the average for all waters below 75 m depth.

For total dissolved inorganic carbon in surface water

I will accept the estimate of Keeling (73b, p. 298) of 2.09 mmol  $\ell^{-1}$  (25.1 mg  $\text{m}^{-3}$ ) based on alkalinity and pH data of the same Russian I.G.Y. (Expeditions considered by Postma.) Carbon-total concentrations were originally calculated by Keeling (73b) using the dissociation constants of both Buch (51) and Lyman (57). Recent evidence (Mehrbach, 73; Takahashi, 76; Sundquist, 79) indicate that Lyman's constant is more nearly correct than Buch's, and I therefore choose this value over 2.06 mmol  $\ell^{-1}$ , based on Buch's constants. These data have been corrected for industrial  $\text{CO}_2$  assuming a preindustrial atmospheric concentration of 290 ppm. With  $h_m$  and  $A$  evaluated according to Table 2, the gravitational flux is thus computed to be:

$$F_{go} = 3.454 \times 10^{15} \text{ g of C yr}^{-1}.$$

In Table 2 this flux is rounded to  $3.5 \times 10^{15}$ . The steady-state abundance of carbon-total in the deep oceans,  $N_{do}$ , to be compatible with the above calculation, is computed as a function of the concentration,  $N_{mo}/W_m$ , of surface water and of its ratio to that of deep water which is given by the factor  $\beta_{mo}$  (see equation (8.28)), i.e.:

$$N_{do} = (h_d/h_m) (N_{mo}/\beta_{mo}) \quad (11.43)$$

where  $W_d/W_m$  is replaced by  $h_d/h_m$  in accordance with equations (11.4) and (11.8) and where  $\beta_{mo}$  is equal to the concentration ratio:

$$\beta_{mo} = 2.09/2.33.$$

The steady state  $^{14}\text{C}/\text{C}$  ratio of deep water relative to surface water, to be compatible with the assumption of isotopic fractionation in the gravitational flux, is computed by solving the first equality of equation (8.16) for  $R_{do}/R_{mo}$ , i.e.:

$$^{14}R_{do}/^{14}R_{mo} = \frac{^{14}\alpha_{md}}{1 + ^{14}\lambda/k_{dm}} \quad (11.44)$$

(This equation is analogous to equation (11.16) for the atmosphere biosphere exchange.) For  $^{13}\text{C}$ , since  $^{13}\lambda$  is equal to zero (cf. equation (2.27)):

$$^{13}R_{do}/^{13}R_{mo} = ^{13}\alpha_{md} \quad (11.45)$$

The isotopic fractionation factor,  $\alpha_{md}$ , is computed by the expression:

$$\alpha_{md} = \alpha_{mg} + \left( \frac{N_{mo}}{N_{do}} - \frac{h_d}{h_m} \right) (1 - \alpha_{mg}) \quad (11.46)$$

where  $W_d/W_m$  is replaced by  $h_d/h_m$  in equation (8.17) as in the derivation of equation (11.43). The quantities  $N_{mo}$ ,  $N_{do}$ , and  $h_d/h_m$  are computed with the same values used to compute  $F_{go}$  by equation (11.41).

The isotopic ratios of deep water relative the atmosphere,  $R_{do}/R_{ao}$ , for both isotopes, are computed by the relationship:

$$R_{do}/R_{ao} = (R_{do}/R_{mo})(R_{mo}/R_{ao}) \quad (11.47)$$

where  $R_{mo}/R_{ao}$  is assigned the value computed previously for the case without gravitational flux, i.e. by use of equations (11.12) and (11.13).

### 11.4 Determination of preindustrial conditions

The four-reservoir model predicts perturbations of the carbon cycle against a background steady-state which ideally would be established without reference to that perturbation. But all but a few features of the carbon cycle when first observed were already affected by industrial CO<sub>2</sub>. Indeed, the only chemical data used in the formulation of the present model which are practically free of influence of the industrial CO<sub>2</sub> perturbation are the measurements of deep ocean carbon. In a few other cases, notably respecting the land biosphere, the perturbations, although not negligible, are so small relative to the uncertainty in the estimated contemporary values that it would be unjustified to adjust the latter to reflect preindustrial conditions. But in other cases, such adjustments were attempted. If possible these were done without recourse to the model itself. For example, the concentration of carbon-total in surface ocean water was estimated from the presumed change in CO<sub>2</sub> partial pressure between the late nineteenth century and recent times (Keeling, 73b). In other cases the preindustrial values were calculated by the model itself to avoid inconsistency in calculating perturbations. A few of these parameters, for example the rare isotopic ratios of carbon in surface ocean water, provide inputs to the model which affect the values of the Suess Effect calculated for all of the reservoirs, i.e. they influence one or more of the values assigned to the perturbation coefficients,  $k_i$ ,  $*k_i$  or  $k_i'$ , and hence influence the calculation of the elements of the matrix,  $r$  (equation (9.25)). In the remaining cases, the steady-state values are used only to establish the Suess Effect for the particular reservoir involved.

In subsection 11.2 and 11.3, above, all of the steady-state calculations are explained. But since the methodology is somewhat complex and difficult to trace back to the original data base, I have summarized in Table 4 the full set of preindustrial value for the standard case with the sources of data indicated by footnotes. If the inclusion of a gravitational flux leads to different values than otherwise, these values are included in the table below the corresponding values. They are enclosed in parentheses.

For the interested reader, the following additional comments are offered to aid in explaining the results listed in Table 4.

None of the assigned reservoir abundances,  $N_{io}$ , are dependent on results of the perturbation model. The preindustrial atmospheric abundance,  $N_{ao}$ , depends,

Table 4. Preindustrial reservoir abundances and isotopic ratios for the standard case (If gravitational flux is included, figures are enclosed in parentheses)

Carbon total		Notes	carbonate dissolution either absent or included	
$N_{bo}$	land biosphere	(1)	1560 Gt	
$N_{ao}$	atmosphere			
	for A.D. 1886-1956:	(2)	600	
	for A.D. 1956-1978:	(2)	642	
$N_{mo}$	surface ocean	(3)	796	
$N_{do}$	deep ocean	(4)	39536	
		(5)	(44076)	

Isotopic ratios and factors		<sup>13</sup> C		<sup>14</sup> C	
	Notes	carbonate dissolution		carbonate dissolution	
		absent	included	absent	included
$R_{bo}/R_{ao}$	(6)	0.9820	0.9820	0.9574	0.9574
$R_{mo}/R_{ao}$	(7)	1.0090	1.0090	0.9649	0.9649
$R_{do}/R_{ao}$	(8)	1.0090	1.0090	0.8490	0.8490
	(9)	(1.0072)	(1.0072)	(0.8460)	(0.8460)
$R_{cmo}/R_{ao}$	(10)	—	1.0080	—	0.9630
$R_{cdo}/R_{ao}$	(10)	—	1.0080	—	0.8473
	(10)	—	(1.0062)	—	(0.8443)
$R_{ao}/R_{\bullet}$	(11)	0.99367	0.99371	—	—
$\alpha_{md}$	(12)	1.0	1.0	1.0	1.0
	(12)	0.9982	0.9982	0.9965	0.9965
$\delta^{13}C$ (‰)					
$\delta^{13}C_b$	land biosphere		(13)	-24.48	-24.44
$\delta^{13}C_a$	atmosphere		(13)	-6.40	-6.36
$\delta^{13}C_m$	surface ocean		(13)	2.64	2.69
$\delta^{13}C_d$	deep ocean		(13)	2.64	2.69
			(13)	(0.86)	(0.90)

Notes

- (1) Rounded from Table 2. Gt = 10<sup>15</sup> g of C.
- (2) Rounded from Table 3.
- (3) By equation (11.5) using data from Table 2.
- (4) Based on equation (11.9) using data from Table 2.
- (5) Based on equation (11.43)
- (6) For <sup>14</sup>C, by equation (11.16); for <sup>13</sup>C by equation (11.17) using data from Table 2.
- (7) For <sup>14</sup>C by equation (11.12); for <sup>13</sup>C by equation (11.13) using data from Table 2.
- (8) For <sup>14</sup>C, computed as the product of <sup>14</sup>R<sub>do</sub>/<sup>14</sup>R<sub>mo</sub>, taken from Table 2, and <sup>14</sup>R<sub>mo</sub>/<sup>14</sup>R<sub>ao</sub> as given above. For <sup>13</sup>C, set equal to <sup>13</sup>R<sub>mo</sub>/<sup>13</sup>R<sub>ao</sub>, above, in accordance with equation (11.14).
- (9) Same as above except that <sup>13</sup>R<sub>do</sub>/<sup>14</sup>R<sub>mo</sub> by equation (11.44) using data from Table 2.
- (10) For both <sup>13</sup>C and <sup>14</sup>C computed in accordance with equation (11.15) as the product of  $\alpha_{ic}$  as quoted in Table 2, and  $R_{io}/R_{ao}$  as given above.
- (11) Calculated by combining equations (11.36) and (11.37) to eliminate  $R_{ai}/R_{\bullet}$ , and then evaluating the resulting expression with  $\delta^{13}C_a$ , taken from Table 3,  $R_{\bullet}$  from Table 2, and <sup>13</sup>S<sub>ai</sub>, calculated by the model for the standard case. The ratios are expressed to five decimal places to reveal small differences between cases.
- (12) By equation (11.46) as described in the text following that equation. Set equal to unity if gravitational flux is zero.
- (13) By equation (11.40) with <sup>13</sup>R<sub>io</sub>/<sup>13</sup>R<sub>ao</sub> as above, <sup>13</sup>R<sub>ao</sub>/<sup>13</sup>R<sub>●</sub> as in this table, and <sup>13</sup>R<sub>●</sub> from Table 2.

however, upon the CO<sub>2</sub> concentrations for the beginning and end of the time interval in which exponential growth in industrial CO<sub>2</sub> is assumed to have occurred, as discussed in the text accompanying equations (11.18) to (11.24), above.

The deep ocean abundance,  $N_{do}$ , by means of equation (11.43) was assigned a value consistent with the steady-state equation (11.41) used to establish the gravitational flux,  $F_{go}$ . If  $F_{go}$  is assumed to be zero, the

concentration of surface and deep water is required to be equal (consistent with equation (11.7)). Since it was desirable that the surface ocean concentration be the same in all cases (except when the parameter,  $h_a$ , was varied) the deep water concentration,  $N_{do}/W_d$ , varies from case to case.

The isotopic ratio,  $R_{do}/R_{mo}$ , determined by equations (11.44) and (11.45) and hence the ratio  $R_{do}/R_{ao}$  established via equation (11.47) likewise varies with  $F_{go}$  for both rare isotopes. If  $F_{go}$  is zero, then, similar to the case for  $N_{do}$ , the deep water value is made to agree with that for surface water. The related ratio,  $R_{cdo}/R_{ao}$ , varies in a similar way with  $F_{go}$  (see equation (11.15)).

Because of the ambiguities associated with adapting the box diffusion model of Oeschger *et al.* (75) to the ocean with a gravitational flux, care was taken that none of the perturbation coefficients,  $k_i$ ,  $*k_i$ , or  $k_i'$  be expressed in terms of  $N_{do}$ , or  $R_{do}$ . Indeed, if the gravitational flux,  $F_{go}$  is equal to zero, the only time dependent predictions affected by the assignment of deep water steady-state values are the isotopic ratios,  $R_d/R_{ao}$  and the shift in  $^{13}C$  for deep water. The resulting variations in these latter ratios are so slight as to be of little interest.

The steady-state isotopic ratios relative to atmospheric  $CO_2$  both for reservoirs,  $R_{io}/R_{ao}$ , and for solid carbonates,  $R_{cio}/R_{ao}$ , were established solely in terms of fractionation factors and the steady-state exchange coefficients,  $k_{ij}$ . In all instances these assigned values were obtained independent of a consideration of perturbations. The calculated preindustrial  $^{13}C/^{12}C$  variations, from standard PDB, on the other hand, depend on knowing  $R_{ao}R_{\bullet}$ , the preindustrial  $^{13}C/C$  ratio of atmospheric  $CO_2$  relative to PDB. Therefore, as indicated by equation (11.37), these quantities,  $\delta^{13}C_{io}$ , differ from case to case as the predicted  $^{13}C$  atmospheric Suess Effect,  $^{13}S_{at}$ , varies. The differences are slight however: approximately 0.04‰ lower  $\delta^{13}C_{io}$  values are calculated when carbonate dissolution is included in the model, approximately 0.002‰ lower values when the gravitational flux is included. The latter differences do not appear in the table, since the  $\delta^{13}C$  values are shown rounded to the nearest 0.01‰.

If  $F_{go}$  is not zero, the time dependent isotopic ratio for deep water carbonate,  $R_{cd}$ , enters into the vertical source matrix,  $[k_{ij}'/R_{ao}]$  (see equation (10.44)) and the source vector  $[*\gamma_i/R_{ao}]$  (see equation (10.47)); it thus influences the predicted isotopic effects for all reservoirs. But the effect is far less than that which arises, because radioactive decay of biogenic carbonate has been neglected (see equation (11.15)).

11.5 Computational results for the four reservoir model

The four-reservoir model, with its parameters set according to the standard case listings in Table 2 and the industrial  $CO_2$  source factors in Table 3, produces the results shown in Table 5. As an aid in explaining the significance of the equations of Sections 9 and 10 some of the intermediate computations are displayed as well as the desired reservoir fractions and isotopic effects. The results are arranged in matrices identified by the symbols of equations (9.7) to (9.26) and (11.1). The

order of rows and columns is: land biosphere, atmosphere, surface ocean, and deep ocean.

Table 5. Matrices used in the solution of the standard case without gravitational flux

Carbonate dissolution absent			
For carbon-13 <sup>(a)</sup>			
$[k_{ij}] =$	$\begin{bmatrix} 0.0454545 & -0.0122714 & 0 & 0 \\ 0 & 0.190528 & -0.913591 & 0 \\ 0 & -0.132802 & 1.138540 & 0 \\ 0 & 0 & 0.179494 & 0.0454545 \end{bmatrix}$		
$[^{13}k_{ij}] =$	$\begin{bmatrix} 0.0621212 & -0.041475 & 0 & 0 \\ -0.0166667 & 0.217872 & -0.100359 & 0 \\ 0 & -0.130943 & 0.325308 & 0 \\ 0 & 0 & -0.179494 & 0.0454545 \end{bmatrix}$		
$\frac{^{13}k_{ij}'}{R_{ao}}$	$\begin{bmatrix} -0.0163667 & 0.029424 & 0 & 0 \\ 0.0163667 & -0.029424 & -0.799538 & 0 \\ 0 & 0 & 0.799538 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$		
$^{13}g =$	$\begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0.980 \\ 0 \\ 0 \\ 0 \end{bmatrix}$	$^{13}r =$	$\begin{bmatrix} 0.146150 \\ 0.541354 \\ 0.063145 \\ 0.249351 \\ 0.140744 \\ 0.537198 \\ 0.061036 \\ 0.241023 \end{bmatrix}$
		$[r_i] =$	$\begin{bmatrix} 0.146150 \\ 0.541354 \\ 0.063145 \\ 0.249351 \\ 0.143324 \\ 0.537198 \\ 0.060491 \\ 0.238873 \end{bmatrix}$
		$[^{13}r_i] =$	$\begin{bmatrix} 0.146150 \\ 0.541354 \\ 0.063145 \\ 0.249351 \\ 0.143324 \\ 0.537198 \\ 0.060491 \\ 0.238873 \end{bmatrix}$
	$[\Delta^{13}r_i] =$	$[^{13}S_i] =$	$\begin{bmatrix} -0.002826 \\ -0.004157 \\ -0.002654 \\ -0.010478 \end{bmatrix}$
			$\begin{bmatrix} -0.022326 \\ -0.073054 \\ -0.041156 \\ -0.003302 \end{bmatrix}$
		$[\delta^{13}C_{i2} - \delta^{13}C_{i1}] =$	$\begin{bmatrix} -0.000139 \\ -0.000447 \\ -0.000263 \\ -0.000021 \end{bmatrix}$
For carbon-14			
$^{14}g =$	$\begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$	$^{14}r =$	$\begin{bmatrix} -0.457449 \\ 0.812589 \\ 0.100904 \\ 0.543956 \\ -0.650457 \\ 0.599641 \\ 0.007985 \\ 0.042831 \end{bmatrix}$
		$[r_i] =$	$\begin{bmatrix} -0.457449 \\ 0.812589 \\ 0.100904 \\ 0.543956 \\ -0.679417 \\ 0.599641 \\ 0.008275 \\ 0.050451 \end{bmatrix}$
		$[^{14}r_i] =$	$\begin{bmatrix} -0.457449 \\ 0.812589 \\ 0.100904 \\ 0.543956 \\ -0.679417 \\ 0.599641 \\ 0.008275 \\ 0.050451 \end{bmatrix}$
	$[\Delta^{14}r_i] =$	$[^{14}S_i] =$	$\begin{bmatrix} -0.221968 \\ -0.212948 \\ -0.092629 \\ -0.493504 \end{bmatrix}$
			$\begin{bmatrix} -0.011374 \\ -0.025064 \\ -0.008999 \\ -0.000974 \end{bmatrix}$
Carbonate dissolution included			
For carbon-13			
$[r_i] =$	$\begin{bmatrix} -0.057182 \\ 0.541354 \\ 0.194269 \\ 0.776069 \end{bmatrix}$	$[^{13}r_i] =$	$\begin{bmatrix} -0.060453 \\ 0.536543 \\ 0.190645 \\ 0.761748 \end{bmatrix}$
$[\Delta^{13}r_i] =$	$\begin{bmatrix} -0.003271 \\ -0.004811 \\ -0.003624 \\ -0.014321 \end{bmatrix}$	$[\delta^{13}C_{i2} - \delta^{13}C_{i1}] =$	$\begin{bmatrix} -0.000164 \\ -0.000517 \\ -0.000349 \\ -0.000029 \end{bmatrix}$
For carbon-14			
$[r_i] =$	$\begin{bmatrix} -0.923736 \\ 0.812589 \\ 0.324057 \\ 1.767254 \end{bmatrix}$	$[^{14}r_i] =$	$\begin{bmatrix} -1.145354 \\ 0.601920 \\ 0.230321 \\ 1.424363 \end{bmatrix}$
$[\Delta^{13}r_i] =$	$\begin{bmatrix} -0.221617 \\ -0.210669 \\ -0.093736 \\ -0.342890 \end{bmatrix}$	$[^{14}S_i] =$	$\begin{bmatrix} -0.011634 \\ -0.024796 \\ -0.008914 \\ -0.000675 \end{bmatrix}$

Note  
 (a) ( $^{13}S_i$ ) is for A.D. 1978; ( $\delta^{13}C_{i2} - \delta^{13}C_{i1}$ ) is for A.D. 1956 to 1978; ( $^{14}S_i$ ) is for A.D. 1954.

## 12. Numerical predictions using the four-reservoir model

### 12.1 Results for carbon-total

For the choice of parameters designated in section 11 as a “standard case”, the four reservoir model predicts that industrial CO<sub>2</sub> after entering the air, is redistributed between the atmosphere, land biosphere, and a two layer vertically diffusive ocean as shown in Table 6.

Table 6. Predictions for carbon-total for the standard case without gravitational flux

Time interval:	1886 – 1956		1956 – 1978	
Carbonate dissolution:	Absent	Included	Absent	Included
<b>Reservoir fractions (%)</b>				
$r_b$ , land biosphere	-45.74	-92.37	14.61	-5.72
$r_a$ , atmosphere	81.26	81.26	54.14	54.14
$r_m$ , surface ocean	10.09	32.41	6.31	19.43
$r_d$ , deep ocean	54.40	176.73	24.94	77.61
<b>Rates of change (Gt/yr)</b>				
$\gamma_i$ , industrial CO <sub>2</sub> input	2.00	2.00	5.67	5.67
$\eta_m$ , surface ocean carbonate dissolution	0	1.92	0	2.52
$\eta_d$ , deep ocean carbonate dissolution	0	0.04	0	0.05
$N_b$ , land biospheric C	-0.92	-1.85	0.83	-0.32
$N_a$ , atmospheric C	1.63	1.63	3.07	3.07
$N_m$ , surface oceanic C	0.20	0.65	0.36	1.10
$N_d$ , deep oceanic C	1.09	3.53	1.41	4.40
$\dot{C}_m$ , surface oceanic carbonate	0	0.30	0	0.51
$\dot{C}_d$ , deep oceanic carbonate	0	1.66	0	2.07

If carbonate dissolution does not occur in the oceans, the model predicts that 14% of the industrial CO<sub>2</sub> produced between A.D. 1956 to 1978 has entered the land biosphere. The biospheric growth factor,  $\beta_a$ , for this case is equal to 0.29, i.e. for every 1% increase in atmospheric CO<sub>2</sub> from its preindustrial value, plant growth is assumed by the model to increase by 0.29%. This biospheric uptake is considerably smaller than predicted by Keeling (73a) and Bacastow and Keeling (73) because their two layer ocean models predicted a less effective oceanic uptake of industrial CO<sub>2</sub> than the present model and hence, by difference, a greater biospheric uptake. The predictions of the present model, for all reservoirs, are close to those of Oeschger *et al.* (75) for an exponentially increasing industrial CO<sub>2</sub> source with an  $e$ -fold time,  $\mu^{-1}$ , of 35 yr. In particular, these authors derived the relative fractions:

$$r_b : r_a : r_m : r_d = 12.1\% : 52.8\% : 5.9\% : 29.2\%$$

while the present model predicts:

$$r_b : r_a : r_m : r_d = 14.6\% : 54.1\% : 6.3\% : 24.9\%$$

This good agreement arises, of course, because the present model and its standard case were chosen to be compatible in most respects with the vertical diffusion model of Oeschger *et al.* (75).

If carbonate dissolution is assumed to occur, the present model predicts that the oceans have absorbed all of the non-airborne industrial CO<sub>2</sub> produced between A.D. 1956 and 1978, and in addition have taken up a small increment from the land biosphere ( $r_b$  equal to -5.7%). The growth factor,  $\beta_a$ , in this case is equal to -0.11. A negative value for  $\beta_a$  is not consistent with any reasonable mechanism for photosynthetic uptake of CO<sub>2</sub>, but reflects the parametric use of this perturbation factor to mimic the sum of all of man impacts on the land biosphere for an exponentially rising energy consumption.

For the period A.D. 1886 to 1956 the predicted partitioning of industrial CO<sub>2</sub> is strikingly different than as just discussed for more recent years. This circumstance is a result of adopting the late nineteenth century average concentration of atmospheric CO<sub>2</sub> deduced by Callendar (58) from contemporary observations. His value of 288 ppm (see subsection 11.2, above), is far below the 302 ppm found by extrapolating an exponentially rising concentration for A.D. 1956 to 1978 backwards to A.D. 1886. Even if the actual yearly production of industrial CO<sub>2</sub> is used in a time stepped version of the present model in place of an exponentially growing source, the model predicts about 297 ppm for A.D. 1886, still well above Callendar’s value (Bacastow and Keeling, unpublished).

In order for the present model to predict the change in atmospheric CO<sub>2</sub> demanded by Callendar’s nineteenth century atmospheric CO<sub>2</sub> value, the airborne fraction,  $r_a$ , from A.D. 1886 to 1956 must be 81%. This fraction implies a substantial loss of carbon from the land biosphere. If carbonate dissolution is absent, the loss is equal to 46% of the industrial CO<sub>2</sub> input; it is 92% if dissolution occurs. Such a large biospheric loss is roughly what Stuiver (78) predicted from a consideration of <sup>13</sup>C/<sup>12</sup>C variations in tree rings. Specifically, Stuiver estimated that the land biosphere from A.D. 1850 to 1950 gave up 120 Gt of carbon while fossil fuel produced 280 Gt; hence a biospheric fraction,  $r_b$ , of -67%. By adopting Callendar’s value we thus test the present model for presumed historical changes in terms qualitatively similar to Stuiver’s.

Table 6 lists, in addition to the predicted fractions,  $r_i$ , the rates of reservoir increase:

$$\dot{N}_i \equiv d n_i / dt \tag{12.1}$$

for the last year of each exponential period considered in the computations. These predictions aid in sorting out the perturbation fluxes predicted by the model, especially the relative importance of surface and deep water as the location of carbonate dissolution and the subsequent redistribution of this dissolved carbonate by oceanic transport. These redistributions are also illustrated in Fig. 10. Since they are reasonably self-explanatory, I shall not comment on them further.

The results listed in Table 6 are the same whether a constant gravitational flux is assumed to be present or not. If a variable gravitational flux is assumed, the results are slightly different. The latter are presented in Section 12.4 as part of the sensitivity analysis of the four-reservoir model.

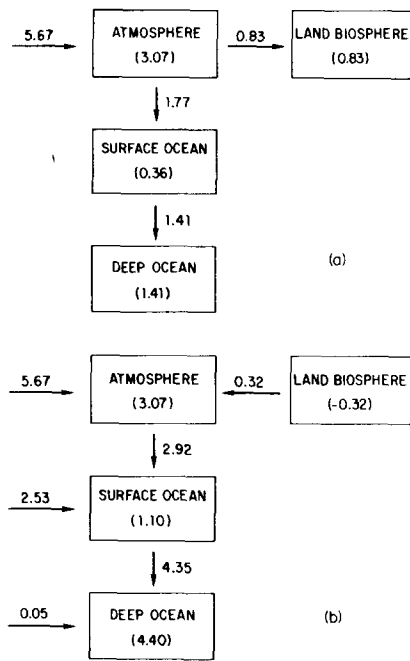


Fig. 10. Redistribution of industrial  $\text{CO}_2$  in Gt/yr of carbon-total predicted by the four reservoir model for the standard case of Table 2. *Plot a*: carbonate dissolution absent; *Plot b*: carbonate dissolution included. *Arrow from left to atmosphere*: industrial  $\text{CO}_2$  source. *Arrows from left to oceanic reservoirs*: dissolution of biogenic carbonate. *Arrows between reservoirs*: net exchanges of carbon-total. Figures in parentheses are net increases of carbon-total within reservoirs. All figures are for A.D. 1978.

This model provides a test of the proposal advanced by Woodwell *et al.* (78) that the land biosphere has in recent years released to the atmosphere much larger amounts of  $\text{CO}_2$  than indicated by models in which the oceanic  $\text{CO}_2$  transport is prescribed by the steady-state radiocarbon distribution. According to Woodwell *et al.* the probable range in release of carbon from the biosphere owing to man's activities is 4 to 8 Gt/yr. They believe that the release may be as high as 18 Gt/yr. The authors are aware that such large releases pose a problem for carbon cycle modelers. The authors state (*loc cit.* p. 245):

"If the current appraisals are correct, the contemporary biotic release of carbon is approximately equal to the fossil fuel release. The total for both sources exceed 10 [Gt] annually. Of this about 2.3 [Gt] accumulates in the atmosphere. The remainder probably enters the oceans, but the mechanism for this remains puzzling. The apparently erroneous assumption that the biota is a contemporary sink for  $\text{CO}_2$  arose because the data on oceanic mixing seem to show that the oceans have a limited capacity for absorbing  $\text{CO}_2$  in the short run of years or decades ... and other sinks have seemed necessary. The problem is still more puzzling if the biota not only is not a sink for fossil fuel carbon but is an additional source of  $\text{CO}_2$ . The validity and appropriateness of the models of oceanic mixing are obviously in question ..."

An extreme "upper limit" for the oceanic uptake of  $\text{CO}_2$  from all sources may be obtained for each of the

four cases just considered repeating the calculations with the eddy diffusion coefficient,  $K$ , raised to such a high value that the oceans below the surface layer are in essence mixed instantaneously. Results of such a calculation are listed in Table 7, in which the value for  $K$  has been increased 100 fold with the biospheric growth factor,  $\beta_a$ , adjusted so that the predictable airborne fraction is the same as for the standard case. The exchanges of carbon for A.D. 1978 are displayed in Fig. 11. Without carbonate dissolution the upper limit for biospheric release of carbon to the air as  $\text{CO}_2$  in 1978 is about 3.4 Gt; with dissolution it is about 4.6 Gt.

Table 7. Predictions for carbon-total with the eddy diffusion coefficient  $K$  of the standard case raised by a factor of 100

Time interval:		1886 - 1956		1956 - 1978	
Carbonate dissolution:		Absent	Included	Absent	Included
Reservoir fractions (%)					
$r_b$	land biosphere	-244.28	-309.71	-59.83	-80.41
$r_a$	atmosphere	81.26	81.26	54.14	54.14
$r_m$	surface ocean	4.79	11.15	2.61	5.81
$r_d$	deep ocean	258.23	608.02	103.09	232.21
Rates of change (Gt/yr)					
$\gamma_i$	industrial $\text{CO}_2$ input	2.00	2.00	5.67	5.67
$\eta_m$	surface ocean	0	5.68	0	6.18
$\eta_a$	carbonate dissolution				
	deep ocean	0	0.14	0	0.15
$\dot{N}_b$	land biospheric C	-4.89	-6.19	-3.39	-4.56
	atmospheric C	1.62	1.62	3.07	3.07
$\dot{N}_m$	surface oceanic C	0.10	0.22	0.15	0.33
	deep oceanic C	5.17	12.16	5.84	13.16
$\dot{C}_m$	surface oceanic carbonate	0	0.10	0	0.15
	deep oceanic carbonate	0	5.71	0	6.18

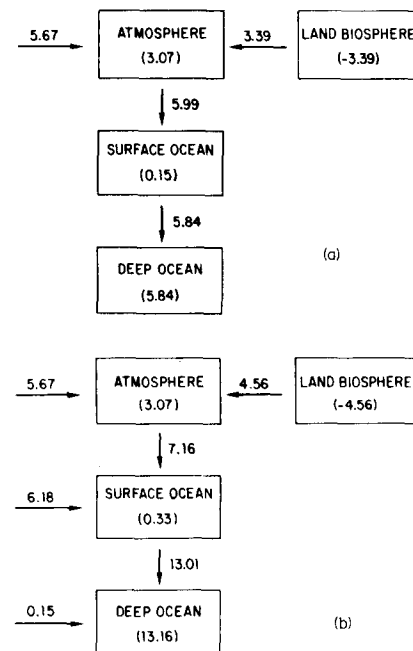


Fig. 11. Redistribution of industrial  $\text{CO}_2$  as in Fig. 10 except that eddy diffusion coefficient,  $K$ , for vertical transport in the oceans is increased 100 fold from standard case.

The release is still higher if, also, the coefficient for CO<sub>2</sub> uptake by the oceans,  $k_{am}$ , is increased by 50% as in the sensitivity analysis of subsection 12.4, below. This increase in  $k_{am}$  leads to a predicted biospheric release of 5.1 Gt of carbon in A.D. 1978 without dissolution, 7.2 Gt with dissolution. The rates of release could be raised still further by arbitrarily increasing the gravitational flux of carbon,  $F_{go}$ , as a function of the concentration of carbon in surface water, i.e. by setting the perturbation parameter,  $\beta_g$  above zero. An increase in  $F_g$  turns out, however, to have very little effect on the predicted biospheric release of CO<sub>2</sub> unless values far in excess of unity are prescribed for  $\beta_g$ . In any case the rates of biospheric release with  $\beta_g$  equal to zero are already large enough, when  $K$  alone is increased, to test the isotopic consequences of large biospheric releases compensated by large oceanic uptake, the main reason for my introducing this calculation.

An eddy diffusion coefficient,  $K$ , 100 times the value calculated from the radiocarbon distribution is ridiculously high as a parameter of oceanic circulation. Such a value implies that <sup>14</sup>C/C ratios for deep water are virtually the same as for pre-bomb surface water, whereas observed ratios (10 to 20% lower) indicate circulation times of the order of 1000 yr. An abundance by other oceanic evidence also argues against a diffusion rate substantially larger than the value of  $K$  chosen for the standard case. If carbonate dissolution is included in the model, this dissolution is assumed to keep pace with the rapid circulation so that every part of the oceans remains in equilibrium with calcium carbonate sediments.

A more reasonable upper limit for biospheric release must remove from the presumed rapidly circulating oceanic reservoir most of the waters below 1000 meters, i.e. about three fourths of the ocean's volume. It follows that a reasonable upper limit for biospheric CO<sub>2</sub> release probably lies near 1 Gt/yr, perhaps 2 Gt/yr if the standard case value for  $k_{am}$  is significantly less than the true value. The calculation with high  $K$  is useful, however, to test how sensitive rare isotopic carbon is as a possible indicator of large net biospheric releases of CO<sub>2</sub>. This topic will be discussed further in subsection 12.4, below.

Predicted changes in reservoir fractions of carbon-total, as other model parameters take on non-standard values, are indicated in Table 8. For the ranges chosen (see subsection 12.4), the reservoir fractions vary little from the standard case. Although changes in fractions are shown only for A.D. 1956 to 1978 with carbonate dissolution absent, relative insensitivity is also found with carbonate dissolution included and for the earlier period, A.D. 1886 to 1956.

### 12.2 Results for rare isotopic carbon

The isotopic predictions for the standard case appear in Table 9. They are recopied in more recognizable per mil and per cent notation from the matrix listings of Table 5 and are supplemented by listings for additional time periods and intervals. To gain a perspective as to the reasonableness of these predictions it is worthwhile to compare them to available observational data. The

Table 8. Reservoir fractions for carbon-total with various choices of input parameters for A.D. 1956 – 1978

Parameter varied	$\beta_a$	$r_b$	$r_a$	$r_m$	$r_d$
Carbonate dissolution absent					
Standard case	0.2905	14.61	54.14	6.31	24.94
$F_{bo}$ (increased 20%)	0.2421	14.61	54.14	6.31	24.94
$h_a$ (increased 20%)	0.3765	18.94	54.14	5.44	21.49
$k_{am}$ (increased 50%)	0.2468	12.41	54.14	6.76	26.70
$\xi$ (increased to 9.445)	0.3199	16.09	54.14	6.02	23.76
$K$ (increased 100 fold)	-1.1895	-59.83	54.14	2.61	103.09
$\beta_s$ (increased to 1)	0.2808	14.13	54.14	6.29	25.45
Carbon dissolution included					
Standard case	-0.1137	-5.72	54.14	19.43	77.61
$F_{bo}$ (increased 20%)	-0.0947	-5.72	54.14	19.43	77.61
$h_a$ (increased 20%)	0.0081	0.41	54.14	17.12	68.39
$k_{am}$ (increased 50%)	-0.2384	-12.01	54.14	21.80	87.07
$\xi$ (increased to 9.445)	-0.0727	-3.66	54.14	18.65	74.51
$K$ (increased 100 fold)	-1.5986	-80.41	54.14	5.81	232.21
$\beta_s$ (increased to 1)	-0.1445	-7.27	54.14	19.14	80.81

Table 9. Isotopic predictions for the standard case without gravitational flux

Time:	1956	1978	1956-1978	1956	1978	1956-1978
carbonate dissolution:	Absent			Included		
$\delta^{13}C$ (‰)						
land biosphere	-24.57	-24.71	-0.14	-24.53	-24.70	-0.16
atmosphere	-6.69	-7.14	-0.45	-6.69	-7.21	-0.52
surface ocean	2.49	2.22	-0.26	2.48	2.13	-0.35
deep ocean	2.63	2.61	-0.02	2.67	2.64	-0.03
Time:	1950	1954	1950	1954		
carbonate dissolution	Absent		Included			
<sup>14</sup> C Suess Effect (‰)						
land biosphere	-1.03	-1.14	-1.05	-1.16		
atmosphere	-2.29	-2.51	-2.27	-2.48		
surface ocean	-0.82	-0.90	-0.81	-0.89		
deep ocean	-0.09	-0.10	-0.06	-0.07		

predicted shifts in  $\delta^{13}C$  for atmospheric CO<sub>2</sub> from A.D. 1956 to 1978 are:

$$\delta^{13}C_{a2} - \delta^{13}C_{a1} = \begin{cases} - .45\text{‰} , \text{ carbonate dissolution absent} \\ - .52\text{‰} , \text{ carbonate dissolution included} \end{cases}$$

Both predictions agree within stated accuracy with the direct measurements reported for Keeling (79a):

$$\delta^{13}C_{a2} - \delta^{13}C_{a1} = -0.55 \pm 0.14\text{‰}$$

The predicted <sup>13</sup>C shift is closer to the observed value, if carbonate dissolution is included in the model, but the uncertainty in observations is so large compared with the shift, that this prediction is not particularly favored.

For the atmospheric <sup>14</sup>C Suess Effect the predicted values for A.D. 1954 are:

$$^{14}S_a = \begin{cases} -2.51\% , \text{ carbonate dissolution absent} \\ -2.48\% , \text{ carbonate dissolution included.} \end{cases}$$

The best estimate of the observed  $^{14}\text{C}$  Suess Effect for A.D. 1954 is difficult to obtain from the literature values listed in Table 1, because the effect was probably increasing rapidly after A.D. 1940, and because some of the data are for samples involving several years of tree growth. To obtain a best estimate for A.D. 1954 based on these data, Bacastow and Keeling (73) used a six reservoir model which they forced to reproduce as closely as possible the data of Lerman *et al.* (70) for the 1860s and the data of these same investigators and of Suess and his coworkers for observations after A.D. 1940. They deduced for A.D. 1954:

$$^{14}S_a = \begin{cases} -2.8\%, \text{ relative to preindustrial conditions} \\ -2.5\%, \text{ relative to the } \Delta^{14}\text{C scale (Broecker 59).} \end{cases}$$

The same calculation indicates a Suess Effect of about 0.3‰ in the 1860s, consistent with the observations of Lerman *et al.* (70) that tree rings during that decade exhibit  $^{14}\text{C}/\text{C}$  ratios close to zero on the  $\Delta^{14}\text{C}$  scale. A model similar to the present one, but with the actual industrial  $\text{CO}_2$  source used instead of an exponential approximation (Bacastow and Keeling, unpublished), leads to predicted values near -2.3‰, thus -0.5‰ less negative than the observations of Lerman, Suess and their coworkers.

This lack of agreement is not a strong basis for rejecting the model, however, because, as indicated by the scatter of values in Table 1, the observations are probably not reliable to much better than 0.5‰. But a more serious problem, discussed above in the introduction, is the lack of evidence for a steady-state for  $^{14}\text{C}$  prior to the industrial era. Variations in solar activity may produce variations in  $^{14}\text{C}$  production which lead to observed values less negative than predicted on the assumption of steady  $^{14}\text{C}$  production. But until more is known about the solar phenomenon (see for example, Stuiver and Quay (79)), it is not possible to obtain a good time varying function for the natural  $^{14}\text{C}$  production. The model produces one definite result, however: the predictions are about the same whether carbonate dissolution occurs or not. Thus the  $^{14}\text{C}$  atmospheric Suess Effect cannot be used to distinguish these two possibilities.

For surface ocean water, observational data are meager, as indicated in Table 1. For  $^{13}\text{C}$  the results of a single coral from Bermuda are available for comparison with prediction. For A.D. 1956 to 1978 the observations of this coral indicate:

$$\delta^{13}\text{C}_{m2} - \delta^{13}\text{C}_{m1} = -0.24\text{‰}$$

whereas the model predicts:

$$\delta^{13}\text{C}_{m2} - \delta^{13}\text{C}_{m1} = \begin{cases} -0.26\text{‰}, \text{ carbonate dissolution} \\ \text{absent} \\ -0.35\text{‰}, \text{ carbonate dissolution} \\ \text{included.} \end{cases}$$

With respect to preindustrial times the observations indicate a shift or -0.50‰, whereas the model predicts -0.42‰ if dissolution is absent, -0.56‰, if present. Predictions and observations agree within experimental precision (which is the order of 0.1‰). But the shifts are so small that it is not possible to decide whether the observations actually support either prediction.

For  $^{14}\text{C}$ , data are available for two corals but the nineteenth century coral values of Nozaki *et al.* (78) are too scattered to estimate a Suess Effect. For the Florida coral of Druffel and Linick (78), which yielded steady nineteenth century values, these authors themselves estimated that:

$$^{14}S_m = -1.2\text{‰}$$

whereas the model predicts:

$$^{14}S_m = \begin{cases} -.90\% \text{ with carbonate dissolution absent} \\ -.89\% \text{ with carbonate dissolution included} \end{cases}$$

The agreement is good, but the variations again are too small to gain much support for the model. As in the case of the atmospheric effect,  $^{14}S_a$ , the predictions are about the same whether carbonate dissolution occurs or not.

For the land biosphere and deep oceans no observational data are available to estimate isotopic shifts on a global scale. Thus the above comparisons for the atmosphere and the surface oceans are the only controls available to test the standard case. About all that can be stated positively about these is that, for both isotopes, the agreement is sufficiently good to justify using the standard case for a further examination of isotopic effects.

### 12.3 The Stuiver approximation

Stuiver (78) estimated the shift in  $^{13}\text{C}$  of atmospheric  $\text{CO}_2$  on the basis of predicted values of the  $^{14}\text{C}$  Suess Effect. As shown in Sections 2 and 3, his approximation is consistent with a model which neglects isotopic fractionation during the redistribution of industrial  $\text{CO}_2$ , but preserves the isotopic ratio difference between industrial and atmospheric  $\text{CO}_2$ . In Table 10 predictions for the standard case of the four reservoir model are shown for A.D. 1956 to 1978 for both rare isotopes, with and without fractionation.

Since the Suess Effect for either isotope is proportional to the reservoir fraction difference,  $\Delta r_i$ , the Stuiver approximation can be checked through the relation:

$$\Delta^{13}r_i = -^{13}\epsilon_{fa} \Delta^{14}r_i \quad (12.1)$$



which follows from equations (2.42) and (11.2). As can be determined from Table 10, the approximation holds for all reservoirs of the four reservoir model. It also holds if the perturbation exchange coefficient,  $k_6$ , and gravitational flux,  $F_{go}$ , are non-zero although these cases are not shown in the table. (Also the approximation was found to hold to the maximum number of 8 decimal places printed in the computer printouts.) A remarkable feature of the approximation is that the predictions are the same for  $\Delta r_i$  whether carbonate dissolution is present or absent. Thus the differences in prediction which occur for these two cases, when fractionation is included, are not closely dependent on the different fractions of  $CO_2$  entering the various reservoirs, but are associated directly with different degrees of isotopic fractionation for the two cases.

Table 10. Isotopic predictions with and without fractionation for the standard case without gravitational flux, A.D. 1956-1978

Reservoir	$\Delta^{13}r_i$ (‰)	$\delta^{13}C_2 - \delta^{13}C_1^{(a)}$ (‰)	$\Delta^{14}r_i$ (‰)	$^{14}S_p^{(a)}$ (‰)		
		carbonate dissolution in-			carbonate dissolution in-	
		absent			absent	cluded
<b>0600</b>						
no fractionation						
land biosphere	-0.3689	-0.18	-0.19	-18.47	-1.46	-1.48
atmosphere	-0.5426	-0.58	-0.58	-27.13	-4.77	-4.77
surface ocean	-0.2199	-0.22	-0.21	-11.00	-1.71	-1.67
deep ocean	-0.8685	-0.07	-0.02	-43.53	-0.14	-0.14
with fractionation and carbonate dissolution						
land biosphere	-0.3271	—	-0.16	-19.31	—	-1.55
atmosphere	-0.4811	—	-0.52	-28.21	—	-4.96
surface ocean	-0.3624	—	-0.35	-10.86	—	-1.65
deep ocean	-1.4321	—	-0.03	-38.36	—	-0.12
with fractionation but carbonate dissolution absent						
land biosphere	-0.2826	-0.14	—	-19.31	-1.53	—
atmosphere	-0.4157	-0.45	—	-28.37	-4.99	—
surface ocean	-0.2654	-0.26	—	-10.78	-1.67	—
deep ocean	1.0478	-0.02	—	-44.91	-0.14	—

(a) Change in  $\delta^{13}C$  is from A.D. 1956-1978;  $^{14}C$  Suess Effect,  $^{14}S_p$ , is for A.D. 1978.

For  $^{13}C$  when fractionation is neglected, the predictions for the atmospheric and biosphere are about 31% too high with carbonate dissolution absent, about 13% too high with dissolution included. For the other two reservoirs the predictions for dissolution absent and included are, respectively, 17% and 39% too low. In either case the errors are so large as to rule out use of the approximation except for very coarse estimates. With respect to the  $^{14}C$  Suess Effect the relative errors range from 1 to 4% except for the deep oceans with carbonate dissolution included, for which the prediction is 13% too large. This latter case is of little interest, however, because the Suess Effect is so nearly negligible for this reservoir. The errors for  $^{13}C$  and  $^{14}C$ , for all reservoirs except the deep ocean, turn out to be of opposite sign so that the Stuiver approximations, in which the  $^{14}C$  Suess Effect is used to estimate the  $^{13}C$  effect, is even in somewhat greater error than the model predictions without fractionation for  $^{13}C$  taken separately.

If the fractionation factor for  $CO_2$  uptake by the oceans is close to unity, rather than equal to 0.986 as assumed in the standard case (see subsection 12.4 below), the Stuiver approximation is closer to being correct than otherwise, but the improvement in prediction is still not sufficient to render the method reliable.

### 12.4 Sensitivity tests for $^{13}C$ and $^{14}C$

To determine the degree to which the predicted Suess Effects of the four-reservoir model are sensitive to likely uncertainties in the model abundances and coefficients, fourteen model parameters were varied over ranges chosen to reflect these uncertainties. The results for the atmosphere and surface ocean are summarized in Figs 12 and 13. For the case where carbonate dissolution is absent, they are also listed in Table 11. For  $^{13}C$  the shifts in  $\delta^{13}C$  are displayed as being more convenient to study than the related  $^{13}C$  Suess Effect.

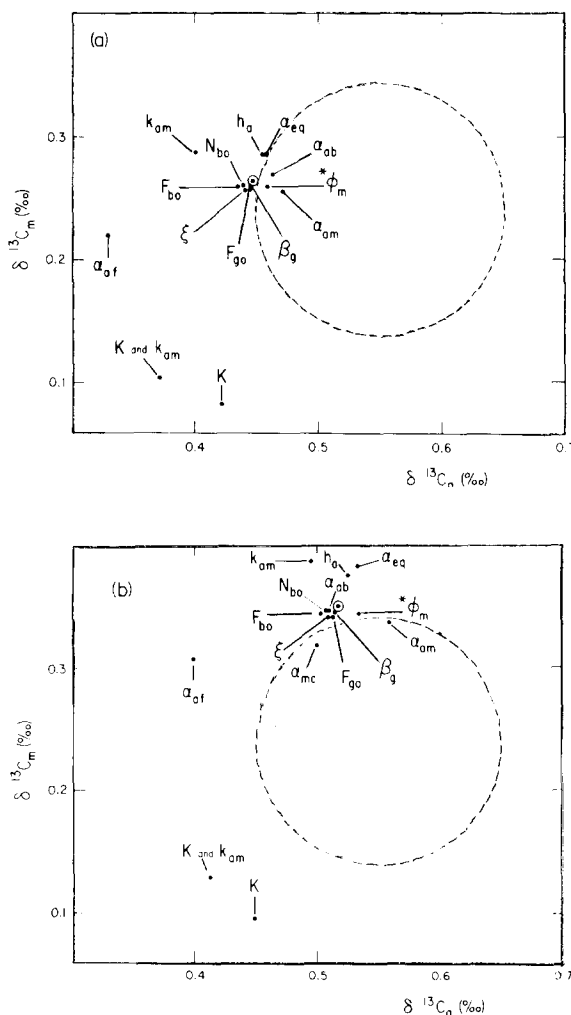


Fig. 12. Shift in  $\delta^{13}C$  of surface oceans ( $\delta^{13}C_m$ ) versus atmosphere ( $\delta^{13}C_a$ ) from A.D. 1956 to 1978 predicted by the four reservoir model of Fig. 6 for various choices of input parameters as defined in Tables 2 and 3.  $\alpha_{of}$  is an abbreviation for  $^{13}R_{of}/^{13}R_{atm}$ . Dashed circles enclose observed values as discussed in the text. Upper plot: carbonate dissolution absent. Lower plot: carbonate dissolution included.

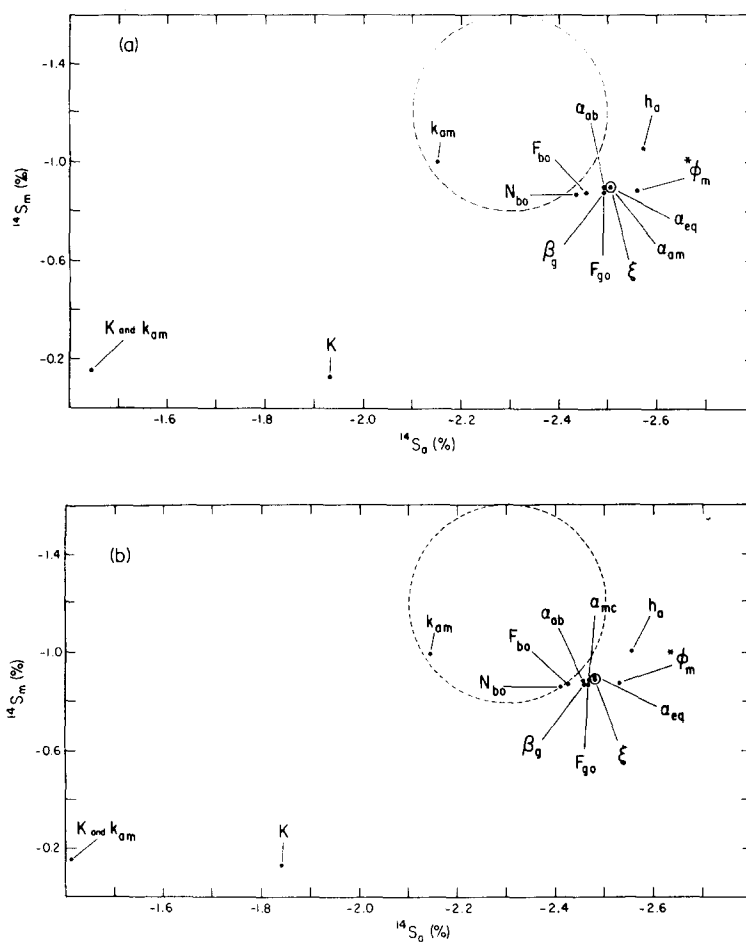


Fig. 13. Theoretical  $^{14}\text{C}$  Suess Effect of surface ocean ( $^{14}S_m$ ) versus atmosphere ( $^{14}S_a$ ) in A.D. 1954 predicted by the four-reservoir model of Fig. 6 for various choices of input parameters as defined in Tables 2 and 3. Dashed circles enclose probable true values as discussed in the text. *Upper plot*: carbonate dissolution absent, *Lower plot*: carbonate dissolution included.

Since the choices of ranges are not critical to a sensitivity analysis, they will be only briefly explained.

The most uncertain parameters for carbon-total are probably the land biospheric abundance,  $N_{bo}$ , and the air-to-sea exchange coefficient,  $k_{am}$ . I have raised the values of both by 50% in the sensitivity tests. For  $h_a$ , which represented the depth of oceans having the same amount of carbon-total as the atmosphere, and for  $F_{bo}$ , the rate of uptake of carbon-total by the land biosphere, the values were raised by 20%. Regarding  $h_a$ , this increase essentially overcomes the bias introduced because a typical deep water concentration of carbon was used to establish its value. For  $F_{bo}$  the choice is arbitrary: the likely error depends not only on uncertain knowledge of photosynthesis uptake of carbon by land plants but also on what fraction of the total to exclude from the model as pertaining to short cycled carbon. For all of these parameters except  $h_a$  the values could just as well have been proportionally lowered. The isotopic shifts for these cases were calculated and found to be very nearly equal in magnitude but opposite in sign.

For the oceanic  $\text{CO}_2$  evasion factor,  $\xi$ , and the surface ocean perturbation function,  $^*\phi_m$ , the values were raised to those found for A.D. 1978 by a non-linear model with similar parameterization (Bacastow, 79). These choices thus exaggerate somewhat the shortcomings of the present model, since the average effect of variable  $\xi$  and  $^*\phi_m$  will be less than the extreme changes from preindustrial times to the latest year considered in the model. For calculations involving carbonate dissolution, the change in  $\xi$  was made proportionally the same as for the case of no dissolution.

To test the possibility that the gravitational flux may have increased in response to human activities, the perturbation factor,  $\beta_g$  was raised from zero to unity. This was a logical but arbitrary choice since there is no evidence that the gravitational flux has varied.

With respect to isotopic fractionation, the factors,  $^{13}\alpha_{ij}$ , were all arbitrarily raised by 4 per mil. For  $^{14}\text{C}$  the factors,  $^{14}\alpha_{ij}$ , as in the standard case, were determined as the squares of the  $^{13}\text{C}$  factors.

Table 11. Shift in  $\delta^{13}\text{C}$  from A.D. 1956 to 1978 for various choices of input parameters without carbonate dissolution

Parameters varied	$\delta^{13}\text{C}_{i2} - \delta^{13}\text{C}_{i1} (\text{‰})$			
	bio-sphere	atmos-phere	surface ocean	deep ocean
Standard case	-0.1386	-0.4467	-0.2628	-0.0212
Variations within the range of uncertainty				
$N_{bo}$ (increased by 50%)	-0.1002	-0.4388	-0.2599	-0.0209
$F_{bo}$ (increased by 20%)	-0.1539	-0.4356	-0.2588	-0.0208
$h_a$ (increased by 20%)	-0.1403	-0.4543	-0.2847	-0.0229
$k_{am}$ (increased by 50%)	-0.1269	-0.4082	-0.2862	-0.0231
$\alpha_{ab}$ (increased by .004)	-0.1444	-0.4635	-0.2690	-0.0216
$\alpha_{am}$ (increased by .004)	-0.1463	-0.4715	-0.2552	-0.0205
$\alpha_{eq}$ (increased by .004)	-0.1419	-0.4575	-0.2843	-0.0229
$\alpha_{mc}\xi$ (increased by .004)	-0.1386	-0.4467	-0.2628	-0.0212
$\xi$ (increased to 9.445)	-0.1369	-0.4419	-0.2566	-0.0206
$^*\phi_m$ (increased to 1.107)	-0.1425	-0.4593	-0.2589	-0.0208
$^{13}R_{af}/^{13}R_{ao}$ (increased by 0.004)	-0.1021	-0.3292	-0.2196	-0.0177
Gravitational flux included				
$F_{go}$ (increased from 0 to 3.5 Gt yr <sup>-1</sup> )	-0.1379	-0.4444	-0.2586	-0.0183
$\beta_g$ (increased from 0 to 1)	-0.1382	-0.4450	-0.2589	-0.0185
Large variations				
$K$ (increased 100 fold)	-0.1418	-0.4208	-0.0825	-0.0656
$K$ (increased 100 fold) and $k_{am}$ (increased 50%)	-0.1295	-0.3710	-0.1042	-0.0830
$\alpha_{am}$ (increased to 1)	-0.1653	-0.5329	-0.2363	-0.0190

For the air to sea uptake factor,  $\alpha_{am}$ , the value is not known even within 4 ‰. Laboratory experiments involving the absorption of CO<sub>2</sub> in an alkaline solution (Craig, 53), suggest a preference for <sup>12</sup>C over <sup>13</sup>C of about 14‰. This value was therefore chosen for the standard case. Recently the fractionation effect for CO<sub>2</sub> gas in water has been found to be approximately 1‰ (Schönleber, 76). If the rate determining step in CO<sub>2</sub> uptake is diffusion in a liquid boundary layer, as is often supposed (Broecker, 74, p. 125; Skirrow, 75, p. 134; Kester, 75, p. 511), then the fractionation may be close to the equilibrium value (about + 1‰) as pointed out by Tans (78, p. 34). Given the large uncertainty in  $\alpha_{am}$ , all sensitivity calculations were repeated with an alternative standard case in which  $\alpha_{am}$  was set equal to unity. For the atmosphere and surface the results are shown in Figs 14 and 15.

The predicted Suess Effect for the land biosphere is of little interest because large inhomogeneities in plant materials prevent any reliable direct estimate of changes in global average isotopic ratios. For the deep ocean the Suess Effect for either isotope is too small to be worth examining.

For the atmosphere and surface oceans, on the other hand, model predictions are worth comparing with the observational data discussed in subsection 12.2. Hence it is the results of the sensitivity calculations for these two reservoirs that are displayed in Figs 12 - 15. For <sup>13</sup>C and <sup>14</sup>C dashed circles have been drawn to enclose

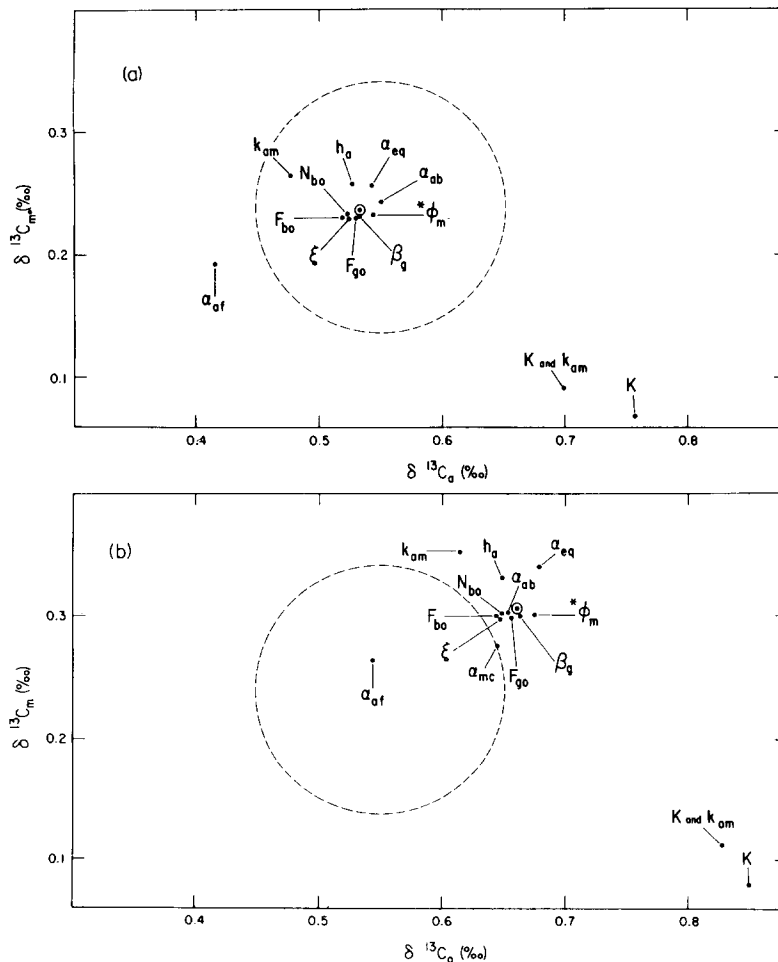


Fig. 14. Same as Fig. 12 except that  $^{13}\alpha_{am} = 1$ .

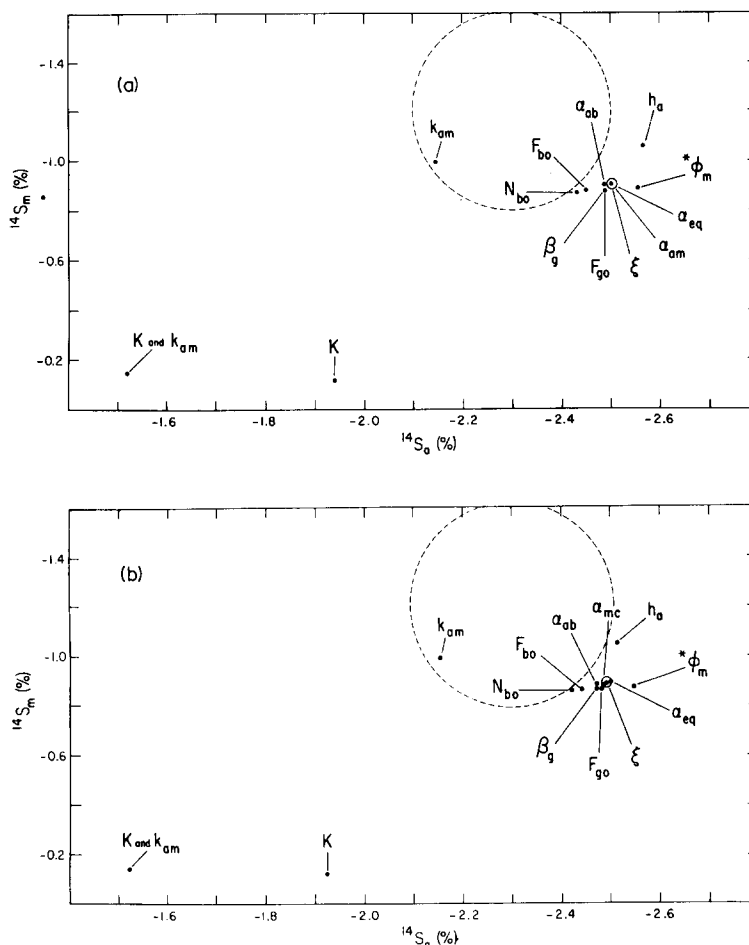


Fig. 15. Same as Fig. 13 except that  $^{14}\alpha_{am} = 1$ .

all predictions which lie, respectively, within 0.1‰ and 0.2‰ of the observed values discussed in subsection 12.2. For the atmospheric Suess Effect, since the observations do not take into account a modulation in the  $^{14}\text{C}$  source owing to variable solar activity, I have tried to allow for this very approximately using the results of a stepped model with the actual  $\text{CO}_2$  production data as input, similar to the procedure of Bacastow and Keeling (73). I have not attempted, however, to adjust similarly the surface ocean Suess Effect because such an adjustment would be small relative to the uncertainty in the observed value. These circles very roughly display the probable true values assuming that the errors in the observations data are a result only of analytical uncertainties, not of sampling bias.

In all but a very few cases the predictions cluster relatively close to the standard case values. The only parameters which produce significantly different predictions are the  $^{13}\text{C}/\text{C}$  ratio of industrial  $\text{CO}_2$ ,  $^{13}R_f$ , (only for  $^{13}\text{C}$ ), the air-to-sea steady-state exchange coefficient,  $K_{am}$  (mainly for  $^{14}\text{C}$ ), and large eddy diffusion coefficient,  $K$  (for both isotopes). The small influence of variations in the other parameters is not without interest, however. For example, the minor effect of leaving out the gravitational flux might not have been anticipated from reading the recent literature on the importance of this flux to isotopic calculations (Craig, 71).

Table 12.  $^{14}\text{C}$  Suess Effect in A.D. 1954 for various choices of input parameters without carbonate dissolution

Parameters varied	Suess Effect (%)			
	bio-sphere	atmos-phere	surface ocean	deep ocean
Standard case	-1.137	-2.506	-0.900	-0.097
Variations within the range of uncertainty				
$N_{bo}$ (increased by 50%)	-0.852	-2.435	-0.969	-0.094
$F_{bo}$ (increased by 20%)	-1.232	-2.455	-0.878	-0.095
$h_a$ (increased by 20%)	-1.159	-2.571	-1.059	-0.117
$k_{am}$ (increased by 50%)	-0.979	-2.149	-0.996	-0.109
$\alpha_{ab}$ (increased by 0.004)	-1.132	-2.494	-0.895	-0.097
$\alpha_{am}$ (increased by 0.004)	-1.137	-2.505	-0.900	-0.097
$\alpha_{eq}$ (increased by 0.004)	-1.138	-2.508	-0.900	-0.097
$\alpha_{mc}$ (increased by 0.004)	-1.137	-2.506	-0.900	-0.097
$\xi$ (increased to 9.445)	-1.136	-2.508	-0.900	-0.098
$*\phi_m$ (increased to 1.107)	-1.161	-2.558	-0.886	-0.096
Gravitational flux included				
$F_{go}$ (increased from 0 to 3.5 Gt/yr)	-1.131	-2.493	-0.880	-0.088
$\beta_g$ (increased from 0 to 1)	-1.132	-2.492	-0.879	-0.088
Large variations				
$K$ (increased 100 fold)	-0.993	-1.863	-0.125	-0.087
$K$ (increased 100 fold and $k_{am}$ (increased 50%))	-0.831	-1.446	-0.145	-0.096
$\alpha_{am}$ (increased to 1)	-1.135	-2.502	-0.901	-0.098

When  $\alpha_{am}$  is changed to unity and new sensitivity calculations made for the other parameters previously varied (Figs 14 and 15), the results for  $^{14}\text{C}$  are almost unchanged, reflecting the small influence of isotopic fractionation on the redistribution of  $^{14}\text{C}$  from industrial  $\text{CO}_2$  injections. But for  $^{13}\text{C}$  the results are considerably different. All of the atmospheric values are considerably higher, while the surface ocean values are slightly lower. Of particular interest is that the results with large  $K$  are distinctly different from standard  $K$  for both atmospheric and oceanic  $\delta^{13}\text{C}$ . This is in sharp contrast to the prediction with  $^{13}\alpha_{am}$  set equal to 0.986. In the latter case the atmospheric  $^{13}\text{C}$  ratio with high  $K$  is indistinguishable from the standard case.

Given the present state of knowledge of isotopic distributions in the carbon cycle, what can we expect to learn from observations of the Suess Effect? If nuclear bomb tests had not profoundly altered the relationships for  $^{14}\text{C}$  after A.D. 1954, this isotope would almost surely be the more valuable isotopic tracer to establish partitioning of industrial  $\text{CO}_2$  between the biosphere and oceans. The  $^{14}\text{C}/\text{C}$  ratio of surface ocean water would not be in doubt, and thus  $k_{am}$  would be securely established. One would be able to choose easily between the standard case and that for rapid oceanic mixing, parameterized by large  $K$ . Even with our limited ability to establish the small shifts in  $^{14}\text{C}$  up to A.D. 1954 this isotope appears to be as likely as  $^{13}\text{C}$  to increase our understanding of the industrial  $\text{CO}_2$  partitioning up to the present time. If reliable  $^{14}\text{C}$  data from tree rings before A.D. 1954 become available, it may be possible to draw conclusions as to whether the oceans are capable of absorbing large amounts of industrial  $\text{CO}_2$  as demanded by Woodwell *et al.* (78).

For  $^{13}\text{C}$ , there are serious difficulties in interpreting the observations even if they are reliable reflections of global perturbations. Several crucial global factors remain uncertain. In the first place, the predicted values of  $\delta^{13}\text{C}$ , especially for the atmosphere, are closely tied to the  $^{13}\text{C}/\text{C}$  ratio of industrial  $\text{CO}_2$ ,  $^{13}R_f$ . This means that we need to know how that ratio has varied as a function of time from one fuel to another and from one source region to another. For natural gas, because its isotopic content is so variable (Schwarz, 70), this information is especially important. As long as natural gas contributes such a large fraction to fossil fuel as it does today, the average  $^{13}\text{C}/\text{C}$  for industrial  $\text{CO}_2$  may remain uncertain by as much as 2‰. Even if the  $^{13}\text{C}/\text{C}$  ratio of each major fuel has remained nearly constant over the time intervals of interest (which may not be true), the shift from coal to petroleum, and more recently to natural gas means that accurate predictions of  $^{13}\text{C}$  changes will require that  $^{13}R_f$  be treated as a time dependent parameter in models after approximately A.D. 1945.

The marked dependence of predictions on the fossil fuel isotopic ratio,  $^{13}R_f$ , has not previously emphasized, but illustrates a characteristic weakness in using stable isotopes to elucidate geochemical processes: isotopic ratios of natural substances often furnish not much more than better data on hitherto poorly known fractionation factors. Thus even if  $^{13}R_f$  becomes well established, observations are likely to tell us more about the

correct value of the air-sea fractionation factor,  $\alpha_{am}$ , than about partitioning of industrial  $\text{CO}_2$ , until the global average and regional variation of  $\alpha_{am}$  are independently determined to high precision.

In spite of these problems,  $^{13}\text{C}$  as a tracer has the distinct advantage that it will continue to reflect man-induced distributions of the carbon cycle in the decades to come. If fuel use continues to grow even at a moderate pace of, say, only 2‰ per year, the average  $^{13}\text{C}/\text{C}$  ratios for the atmosphere and surface ocean water in 35 yr will shift as much as during the past 100 yr. By carefully measuring these shifts and also by improving our knowledge of fractionation factors by deliberate experiments, it may be possible from  $^{13}\text{C}$  studies to learn useful details about the fate of industrial  $\text{CO}_2$ .

*Acknowledgements* — The present article is an outgrowth of discussions with Dr. Pieter Tans, who spent the past year as a postdoctoral fellow with my group. I owe largely to him and to his former professor, Dr. Wilhelm Mook, of Groningen University, the motivation to carry out the present analysis. Also, I appreciate very much Dr. Tans' reading of the completed manuscript with a critical eye to the equations. I also thank Drs. Robert Bacastow, Tim Linick, Yoschiyuki Nozaki, Minze Stuijver, Hans Suess, Karl Turekian, and Ms. Ellen Druffel for insight into theory and practice of isotopes and modeling which they shared with me. Thanks are also due to Mr. David Moss for advice on use and maintenance of the Interdata mini-computer used to carry out the calculations, to Mr. William Bollenbacher for reviewing the first sections of the article from the point of view of an undergraduate student, and to Mrs. Alane Herron for help with the very considerable task of running the computer calculations and assembling the data. The cost of computations and preparing the article for publication were borne by the Climate Dynamic Program of the National Science Foundation under Grant NSF ATM-77-25141.

## References

- J.A.S. Adams, M.S.M. Mantovani and L.L. Lundell. (1977) Wood versus fossil fuel as a source of excess carbon dioxide in the atmosphere: a preliminary report. *Science* **196**, 54-56.
- R. Bacastow and C.D. Keeling. (1973) Atmospheric carbon dioxide and radiocarbon in the natural carbon cycle: II. Changes from A.D. 1700 to 2070 as deduced from a geochemical model. In: *Carbon and the Biosphere*, G.M. Woodwell and E.V. Pecan, Eds, pp. 86-135, United States Atomic Energy Commission.
- R.B. Bacastow and C.D. Keeling. (1979) Models to predict future atmospheric  $\text{CO}_2$  concentrations. In: *Environmental Effects of Carbon Dioxide*, W.P. Elliott, Ed., in press.
- M.S. Baxter and A. Walton. (1970) A theoretical approach to the Suess Effect. *Proc. R. Soc. Lond.* **318** A, 213-230.
- R.A. Berner. (1976) The solubility of calcite and aragonite in seawater at atmospheric pressure and 34.5‰ salinity. *Am. J. Sci.* **276**, 713-730.
- R.A. Berner and J.W. Morse. (1974) Dissolution kinetics of calcium carbonate in sea water. IV. Theory of calcite dissolution. *Am. J. Sci.* **274**, 108-134.
- A. Björkström. (1979) A model of  $\text{CO}_2$  interaction between atmosphere, oceans, and land biota. In: *The Global Carbon Cycle*, B. Bolin, E.T. Degens, S. Kempe and P. Ketner, Eds, pp. 403-457, Wiley, New York.
- B. Bolin. (1977) Changes of land biota and their importance for the carbon cycle. *Science* **196**, 613-615.
- B. Bolin and E. Eriksson. (1959) Changes in the carbon dioxide content of the atmosphere and sea due to fossil fuel combustion. In: *The Rossby Memorial Volume*, pp. 130-142, Rockefeller Institute Press, New York.
- B. Bolin and C.D. Keeling. (1963) Large-scale atmospheric mixing as deduced from the seasonal and meridional variations of carbon dioxide. *J. geophys. Res.* **68**, 3899-3920.

- H.R. Brannon Jr., A.C. Daughtry, D. Perry, W.W. Whitaker and M. Williams. (1957) Radiocarbon evidence on the dilution of atmospheric and oceanic carbon by carbon from fossil fuels. *Trans. Am. geophys. Union* **38**, 643-650.
- J.R. Bray. (1959) An analysis of the possible recent change in atmospheric carbon dioxide concentration. *Tellus* **11**, 220-230.
- H.C. Broecker, J. Petermann and W. Siems. (1978) The influence of wind on CO<sub>2</sub>-exchange in a wind-wave tunnel, including the effects of monolayers. *J. marine Res.* **36**, 595-610.
- W.S. Broecker. (1963) C<sup>14</sup>/C<sup>12</sup> ratios in surface ocean water. *Nucl. Geophys.* pp. 138-149, National Academy of Sciences — National Research Council, Washington, D.C.
- W.S. Broecker (1966) Radio isotopes and the ratios mixing across the main thermoclines of the ocean. *J. geophys. Res.* **71**, 5827-5836.
- W.S. Broecker. (1974) *Chemical Oceanography*. Harcourt Brace Jovanovich, New York.
- W.S. Broecker and E.A. Olson. (1959a) Lamont radiocarbon measurements VI. *Am. J. Sci. Radiocarbon Suppl.* **1**, 111-132.
- W.S. Broecker and A. Walton. (1959b) Radiocarbon from nuclear tests. *Science* **130**, 309-314.
- W.S. Broecker, Y.H. Li and T.H. Peng. (1971) Carbon dioxide — man's unseen artifact. In: *Impingement of Man on the Oceans*, D.H. Hood, Ed., pp. 287-324, Wiley-Interscience, New York.
- R. Bronson. (1969) *Matrix Methods*. Academic Press, New York.
- C.W. Brown and C.D. Keeling. (1965) The concentration of atmospheric carbon dioxide in Antarctica. *J. geophys. Res.* **70**, 6077-6085.
- K. Buch. (1951) Das Kohlensäure Gleichgewichtssystem im Meerwasser. *Havsforskningsinstitutets Skrift*, **151**, Helsinki.
- W.F. Cain and H.E. Suess. (1976) Carbon-14 in tree rings. *J. geophys. Res.* **81**, 3688-3694.
- G.S. Callendar. (1938) The artificial production of carbon dioxide and its influence on temperature. *Q. Jl. R. meteorol. Soc.* **64**, 223-240.
- G.S. Callendar. (1940) Variations of the amount of carbon dioxide in different air currents. *Q. Jl. R. meteorol. Soc.* **66**, 395-400.
- G.S. Callendar. (1958) On the amount of carbon dioxide in the atmosphere. *Tellus* **10**, 243-248.
- H. Craig. (1953) The geochemistry of the stable carbon isotopes. *Geochim. Cosmochim. Acta* **3**, 53-92.
- H. Craig. (1957) Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochim. Cosmochim. Acta* **12**, 133-149.
- H. Craig. (1969) Abyssal carbon and radiocarbon in the Pacific. *J. geophys. Res.* **74**, 5491-5506.
- H. Craig. (1970) Abyssal carbon-13 in the South Pacific. *J. geophys. Res.* **75**, 691-695.
- H. Craig. (1971) Son of abyssal carbon. *J. geophys. Res.* **76**, 5133-5139.
- H. Craig. (1974) The GEOSECS Program: 1972-1973. *Earth planet. Sci. Lett.* **23**, 63-64.
- P.E. Damon. (1970) Climatic versus magnetic perturbation of the atmospheric C<sup>14</sup> reservoir. In: *Radiocarbon Variations and Absolute Chronology*, Proceedings of the Twelfth Nobel Symposium, I.U. Olsson, Ed., pp. 571-593, Wiley-Interscience Division, New York.
- P.E. Damon, A. Long and E.I. Wallick. (1973) On the magnitude of the 11-yr radiocarbon cycle. *Earth planet. Sci. Lett.* **20**, 300-306.
- P.E. Damon, J.C. Lerman and A. Long. (1978) Temporal fluctuations of atmospheric <sup>14</sup>C: Causal factors and implications. *Ann. Rev. Earth planet. Sci.* **6**, 457-494.
- W.G. Deuser and E.T. Degens. (1967) Carbon isotope fractionation in the system CO<sub>2</sub> (gas)-CO<sub>2</sub>(aqueous). *Nature* **215**, 1033-1035.
- E.M. Druffel and T.W. Linick. (1978) Radiocarbon in annual coral rings of Florida. *Geophys. Res. Lett.* **5**, 913-916.
- J.A. Eddy. (1977) Climate and the changing sun. *Climatic Change* **1**, 173-190.
- J.M. Edmond and J.M.T.M. Gieskes. (1970) On the calculation of the degree of saturation of sea water with respect to calcium carbonate under *in situ* conditions. *Geochim. Cosmochim. Acta* **34**, 1261-1291.
- K. Emrich, D.H. Ehhalt and J.C. Vogel. (1970) Carbon isotope fractionation during the precipitation of calcium carbonate. *Earth planet. Sci. Lett.* **8**, 363-371.
- E. Eriksson. (1959) The circulation of some atmospheric constituents in the sea. *The Rossby Memorial Volume*, pp. 147-157, Rockefeller Institute Press, New York.
- G.J. Fergusson. (1958) Reduction of atmospheric radiocarbon concentration by fossil fuel carbon dioxide and the mean life of carbon dioxide in the atmosphere. *Proc. R. Soc. Lond.* **243 A**, 561-574.
- S. Fonselius, F. Koroleff and K.E. Wärme. (1956) Carbon dioxide variations in the atmosphere. *Tellus* **8**, 176-183.
- P.J.B. Fraser, R.J. Francey and G.I. Pearman. (1978) Stable carbon isotopes in tree rings as climatic indicators. *DSIR Bulletin* **220** pp. 67-73, New Zealand Department of Scientific and industrial Research, Wellington.
- H.D. Freyer. (1978a) On the <sup>13</sup>C record in tree rings. 1. <sup>13</sup>C variations in northern hemispheric trees during the last 150 yr. Submitted to *Tellus*.
- H.D. Freyer. (1978b) Preliminary evaluation of past CO<sub>2</sub> increase as derived from <sup>13</sup>C measurements in tree rings. In: *Carbon Dioxide, Climate and Society*, J. Williams, Ed., pp. 69-77, Pergamon Press, New York.
- H.D. Freyer and L. Wiesberg. (1973) <sup>13</sup>C decrease in modern wood due to the large scale combustion of fossil fuels, *Naturwissenschaften* **60**, 517-518.
- H.D. Freyer and L. Wiesberg. (1974) Anthropogenic carbon-13 decrease in atmospheric carbon dioxide as recorded in modern wood. Proceedings FAO/IAEA Symposium, *Isotope ratios as pollutant source and behavior indicators*, pp. 49-62. International Atomic Energy Agency, Vienna.
- J. Goudriaan and G.L. Ajtay. (1979) The possible effects of increased CO<sub>2</sub> on photosynthesis. *The Global Carbon Cycle*, B. Bolin, E.T. Degens, S. Kempe and P. Ketner, Eds, pp. 237-249, New York.
- D.C. Grey. (1969) Geophysical mechanisms for C<sup>14</sup> variations. *J. geophys. Res. Space Phys.* **74**, 6333-6340.
- D.C. Grey and P.E. Damon. (1970) Sunspots and radiocarbon dating in the middle ages. In: *Scientific Methods in Medieval Archaeology*, R. Berger, Ed., pp. 167-182, University of California Press, Berkeley.
- F.N. Hayes, E.C. Anderson and J.R. Arnold. (1956) Liquid scintillation counting of natural radiocarbon. *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, **14**, pp. 187-192, United Nations, New York.
- J. Houtermans, H.E. Suess and W. Munk. (1967) Effect of industrial fuel combustion on the carbon-14 level of atmospheric CO<sub>2</sub>. International Atomic Energy Agency, Vienna, Publication No. SM-87/53, pp. 57-68.
- M.K. Hubbert. (1974) *U.S. Energy Resources, A Review as of 1972*, Background paper prepared for the Committee on Interior and Insular Affairs, United States Senate, U.S. Government Printing Office, Washington, Serial No. 93-40 (92-75).
- G.E. Hutchinson. (1954) The biochemistry of the terrestrial atmosphere. In: *The Earth as a Planet*, G.P. Kuiper, Ed., pp. 371-433, The University of Chicago Press, Chicago.
- S.E. Ingle, C.H. Culberson, J.E. Hawley and R.M. Pytkowicz. (1973) The solubility of calcite in seawater at atmospheric pressure and 35 salinity. *Marine Chem.* **1**, 295-307.
- C.D. Keeling. (1973a) Industrial production of carbon dioxide from fossil fuels and limestone. *Tellus* **25**, 174-198.
- C.D. Keeling. (1973b) The carbon dioxide cycle: Reservoir models to depict the exchange of atmospheric carbon dioxide with the oceans and land plants. In: *Chemistry of the Lower Atmosphere*, S.I. Rasool, Ed., pp. 251-329, Plenum Press, New York.
- C.D. Keeling. (1978) The influence of Mauna Loa Observatory on the development of atmospheric CO<sub>2</sub> research. *Mauna Loa Observatory, a 20th Anniversary Report*, John Miller, Ed., pp. 36-54, U.S. Department of Commerce, Washington, D.C.
- C.D. Keeling and B. Bolin. (1968) The simultaneous use of chemical tracers in oceanic studies II. A three-reservoir model of the North and South Pacific Oceans. *Tellus* **20**, 17-54.
- C.D. Keeling, J.A. Adams Jr., C.A. Ekdahl Jr. and P.R. Guenther. (1976a) Atmospheric carbon dioxide variations at the South Pole. *Tellus* **28**, 552-563.
- C.D. Keeling, R.B. Bacastow, A.E. Bainbridge, C.A. Ekdahl Jr., P.R. Guenther and L.S. Waterman. (1976b) Atmospheric carbon dioxide variations at Mauna Loa Observatory, Hawaii. *Tellus* **28**, 538-551.
- C.D. Keeling and R.B. Bacastow. (1977) Impact of industrial gases on climate. In: *Study of Energy and Climate: Outer Limits to Growth?* pp. 72-95, U.S. National Academy of Sciences, Washington, D.C.
- C.D. Keeling, W.G. Mook and P.P. Tans. (1979a) Recent trend in the <sup>13</sup>C/<sup>12</sup>C ratio of atmospheric carbon dioxide. *Nature* **277**, 121-123.
- C.D. Keeling, R.B. Bacastow and P.P. Tans. (1979b) Predicted shift in the <sup>13</sup>C/<sup>12</sup>C ratio of atmospheric carbon dioxide, *Geophys. Res. Lett.* (In press).
- D.R. Kester. (1975) Dissolved gases other than CO<sub>2</sub>. In: *Chemical Oceanography*, 2nd ed., Vol. 1, J.P. Riley and G. Skirrow, Eds, pp. 497-556, Academic Press, New York.
- G.H. Kohlmaier, E.O. Siré, G. Kratz and U. Fischbach. (1978) Stabi-

- litätsanalyse kinetischer Modelle des globalen C-Zyklus: Austausch von Kohlenstoff zwischen Landbiota und Atmosphäre unter dem Einfluss des Menschen. *Ber. Bunsen Gesellschaft*, In press.
- P. Kroopnick. (1974) The dissolved  $O_2$ - $CO_2$ - $^{13}C$  system in the eastern equatorial Pacific. *Deep-Sea Res.* **21**, 211-277.
- P. Kroopnick, S.V. Margolis and C.S. Wong. (1977)  $\delta^{13}C$  Variations in marine carbonate sediments as indicators of the  $CO_2$  balance between the atmosphere and oceans. *The Fate of Fossil Fuel  $CO_2$  in the Oceans*. N.R. Anderson, Ed. pp. 295-321, Plenum Press, New York.
- D. Lal. (1962) Cosmic ray produced radionuclides in the sea. *J. Oceanogr. Soc. Japan*. 20th Anniversary Volume, 600-614.
- D. Lal. (1969) Characteristics of large-scale oceanic circulation as derived from the distribution of radioactive elements. "Morning Review Lectures" Second International Oceanographic Congress, Moscow. Unesco, pp. 29-48, Imprimerie Berger-Levrault.
- J.C. Lerman, W.G. Mook and J.C. Vogel. (1970) C-14 in tree rings from different localities. Proceedings, Twelfth Nobel Symposium, *Radiocarbon Variations and Absolute Chronology*, I.O. Olsson, Ed., pp. 275-301, Wiley-Interscience, New York.
- Y.-H. Li, T. Takahashi and W.S. Broecker. (1969) Degree of saturation of  $CaCO_3$  in the oceans. *J. geophys. Res.* **74**, 5507-5525.
- E.S. Light, M. Merker, H.J. Verschell, R.B. Mendell and S.A. Korff. (1973) Time dependent worldwide distribution of atmospheric neutrons and of their products. *J. geophys. Res.* **78**, 2741-2762.
- R.E. Lingenfelter. (1963) Production of carbon-14 by cosmic-ray neutrons. *Rev. geophys.* **1**, 35-55.
- J. Lyman. (1957) Buffer mechanism of sea water. Ph.D. Thesis, University of California at Los Angeles.
- C. Marchetti. (1976) On geoengineering and the  $CO_2$  problem. Research Memorandum RM 76-17. International Institute for Applied Systems Analysis, Laxenburg, Austria.
- C. Mehrbach, C.H. Culberson, J.E. Hawley and R.M. Pytkowicz. (1973) Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.* **18**, 897-907.
- D.W. Menzel. (1974) Primary productivity, dissolved and particulate organic matter, and the sites of oxidation of organic matter. In: *The Sea*, Vol. 5, Marine Chemistry, E.D. Goldberg, Ed., pp. 659-678, Wiley, New York.
- W.G. Mook and P.M. Grootes. (1973) The measuring procedure and corrections for the high-precision mass-spectrometric analysis of isotopic abundance ratios, especially referring to carbon, oxygen and nitrogen. *Inter. J. Mass Spectrometry Ion Phys.* **12**, 273-298.
- W.G. Mook, J.C. Bommerson and W.H. Staverman. (1974) Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth planet. Sci. Lett.* **22**, 169-176.
- K. Mopper and E.T. Degens. (1979) Organic carbon in the ocean: nature and cycling. In: *The Global Carbon Cycle*, B. Bolin, E.T. Degens, S. Kempe and P. Ketner, Ed., pp. 293-316, Wiley, New York.
- K.O. Münnich and J.C. Vogel. (1958) Durch Atomexplosionen erzeugter Radiokohlenstoff in der Atmosphäre. *Naturwissenschaften* **14**, 327-329.
- W.H. Munk. (1966) Abyssal recipes. *Deep-Sea Res.* **13**, 707-730.
- Y. Nozaki, D.M. Rye, K.K. Turekian and R.E. Dodge. (1978) A 200 yr record of carbon-13 and carbon-14 variations in a Bermuda coral. *Geophys. Res. Lett.* **5**, 825-828.
- H. Oeschger, U. Siegenthaler, U. Schotterer and A. Gugelmann. (1975) A box diffusion model to study the carbon dioxide exchange in nature. *Tellus* **27**, 168-192.
- H. Oeschger and U. Siegenthaler. (1978) The dynamics of the carbon cycle as revealed by isotope studies. *Carbon Dioxide, Climate and Society*, J. Williams, Ed., pp. 45-61, Pergamon Press, New York.
- I.U. Olsson. (1970) Proceeding, Twelfth Nobel Symposium, *Radiocarbon Variations and Absolute Chronology*, 607-612, Wiley-Interscience, New York.
- J.C. Pales and C.D. Keeling. (1965) The concentration of atmospheric carbon dioxide in Hawaii. *J. geophys. Res.* **70**, 6053-6076.
- T.R. Parsons. (1975) Particulate organic carbon in the sea. In: *Chemical Oceanography 2*, J.P. Riley and G. Skirrow, Ed., pp. 365-383, Academic Press, New York.
- G.I. Pearman, R.J. Francey and P.J.B. Fraser. (1976) Climatic implications of stable carbon isotopes in tree rings. *Nature* **260**, 771-773.
- T.-H. Peng and W.S. Broecker. (1978) Effect of sediment mixing on the rate of calcite dissolution by fossil fuel  $CO_2$ . *Geophys. Res. Lett.* **5**, 349-352.
- H. Postma. (1964) The exchange of oxygen and carbon dioxide between the ocean and the atmosphere. *Neth. J. Sea Res.* **2**, 258-283.
- R. Revelle and R. Fairbridge. (1957a) Carbonates and carbon dioxide. *Treatise on Marine Ecology and Paleocology, Vol. 1, Geol. Soc. America, Memoir* **67**, 239-296.
- R. Revelle and H.E. Suess. (1957b) Carbon dioxide exchange between atmosphere and ocean, and the question of an increase of atmospheric  $CO_2$  during the past decades. *Tellus* **9**, 18-27.
- R. Revelle and W. Munk. (1977) The carbon dioxide cycle and the biosphere. In: *Study of Energy and Climate, Outer Limits of Growth*, pp. 140-158, National Academy of Sciences, Washington, D.C.
- R.M. Rotty. (1977) Global carbon dioxide production from fossil fuels and cement, A.D. 1950-2000. *The Fate of Fossil Fuel  $CO_2$  in the Oceans*, N.R. Anderson, Ed. pp. 167-181, Plenum Press, New York.
- W.H. Schlesinger. (1977) Carbon balance in terrestrial detritus. *Ann. Rev. Ecol. Syst.* **8**, 51-81.
- G. Schönleber. (1976) Messung der Isotopentrennung bei der Diffusion von  $^{13}CO_2$  und  $^{12}CO_2$  in Wasser. Institut für Umweltphysik, Universität Heidelberg.
- H.P. Schwarz. (1970) I. The stable isotopes of carbon. From isotopes in Nature, Chap. 6B. In: *Handbook of Geochemistry*, K.H. Wedepohl, Ed., Springer-Verlag, New York.
- U. Siegenthaler, M. Heimann and H. Oeschger. (1978) Model responses of the atmospheric  $CO_2$  level and  $^{13}C/^{12}C$  ratio to biogenic  $CO_2$  input. *Carbon Dioxide, Climate and Society*, J. Williams, Ed., pp. 79-87, Pergamon Press, New York.
- G. Skirrow. (1965) The dissolved gases — carbon dioxide. In: *Chemical Oceanography 1*, J.P. Riley and G. Skirrow, Eds, pp. 227-322, Academic Press, New York.
- G. Skirrow. (1975) The dissolved gases — carbon dioxide. In: *Chemical Oceanography 2*, J.P. Riley and G. Skirrow, Eds, pp. 1-192, Academic Press, New York.
- M. Stuiver. (1965) Carbon-14 content of 18th- and 19th-century wood: variations correlated with sunspot activity. *Science* **149**, 533-535.
- M. Stuiver. (1978) Atmospheric carbon dioxide and carbon reservoir changes. *Science* **199**, 253-258.
- M. Stuiver and P.D. Quay. (1980) Changes in atmospheric  $^{14}C$  caused by a variable sun. *Science* **207**, 11-19.
- H.E. Suess. (1953) Natural radiocarbon and the rate of exchange of carbon dioxide between the atmosphere and the sea. Proceedings of the Conference on Nuclear Processes in Geologic Settings, pp. 52-56. National Academy of Sciences, National Research Council, Washington, D.C.
- H.E. Suess. (1955) Radiocarbon concentration in modern wood. *Science* **122**, 415-417.
- H.E. Suess. (1965) Secular variations of the cosmic-ray-produced carbon-14 in the atmosphere and their interpretations. *J. geophys. Res.* **70**, 5937-5932.
- H.E. Suess. (1970) The three causes of the secular C-14 fluctuations, their amplitudes and time constants. Proceeding of the Twelfth Nobel Symposium, *Radiocarbon Variations and Absolute Chronology*, I.U. Olsson, Ed., pp. 595-605, Wiley-Interscience, New York.
- E.T. Sundquist, L.N. Plummer and T.M.L. Wigley. (1979) Carbon dioxide in the ocean surface: The homogeneous buffer factor. *Science* **204**, 1203-1205.
- H.U. Sverdrup, M.W. Johnson and R.H. Fleming. (1942) *The Oceans — Their Physics, Chemistry, and General Biology*. Prentice-Hall, Inc., New Jersey.
- T. Takahashi, P. Kaiteris, W.S. Broecker and A.E. Bainbridge. (1976) An evaluation of the apparent dissociation constants of carbonic acid in seawater. *Earth planet. Sci. Lett.* **32**, 458-467.
- P.P. Tans. (1978) Carbon-13 and carbon-14 in trees and the atmospheric  $CO_2$  increase. Proefschrift, Rijksuniversiteit Groningen.
- S. Twomey. (1977) *Introduction to the Mathematics of Inversion in Remote Sensing and Indirect Measurements*, Developments in Geomathematics 3. Elsevier Scientific Publishing Company, New York.
- United Nations. (1978) *World Energy Supplies 1972-1976*, Statistical Papers Series J. No. 21 Dept. of International Economic and Social Affairs of the United Nations, New York.
- G. Veronis. (1975) The Role of Models in Tracer Studies. Special Studies using Numerical Models. In: *Numerical Models of Ocean Circulation*, pp. 133-146, National Academy of Sciences, Washington, D.C.
- H.L. de Vries. (1958) Variation in concentration of radiocarbon with time and location on earth. *Proc. Koninkl. Nederl. Akad. Wetensch.* **B61**, 94-102.

- K. Wagener. (1978) Total anthropogenic CO<sub>2</sub> production during the period 1800-1935 from carbon-13 measurements in tree rings. *Rad. envir. Biophys.* **15**, 101-111.
- M. Whitfield. (1975) Sea water as an electrolytic solution. In: *Chemical Oceanography* **1**, J.P. Riley and G. Skirrow, Ed., pp. 44-172, Academic Press, New York.
- A.T. Wilson. (1978) Pioneer agriculture explosion and CO<sub>2</sub> levels in the atmosphere. *Nature* **273**, 40-41.
- R. Wollast and D. Reinhard-Derie. (1977) Equilibrium and mechanism of dissolution of Mg-calcites. *The Fate of Fossil Fuel in the Oceans*, N.R. Anderson, Ed., pp. 479-493, Plenum Press, New York.
- C.S. Wong. (1978) Atmospheric input of carbon dioxide from burning wood. *Science* **200**, 197-200.
- G.M. Woodwell, R.H. Whittaker, W.A. Reiners, G.E. Likens, C.C. Delwiche and D.B. Botkin. (1978) The biota and the world carbon budget. *Science* **199**, 141-146.
- K. Wyrski. (1962) The oxygen minima in relation to ocean circulation. *Deep-Sea Res.* **9**, 11-23.