

On calculating the transfer of carbon-13 in reservoir models of the carbon cycle

By PIETER P. TANS,¹ *Scripps Institution of Oceanography, University of California at San Diego, 2314 Ritter Hall, A-020, La Jolla, CA 92093 U.S.A.*

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ABSTRACT

An approach to calculating the transfer of isotopic tracers in reservoir models is outlined that takes into account the effects of isotopic fractionation at phase boundaries without any significant approximations. Simultaneous variations in both the rare isotopic tracer and the total elemental (the sum of its isotopes) concentration are considered. The proposed procedure is applicable to most models of the carbon cycle and a four-box model example is discussed. Although the exact differential equations are non-linear, a simple linear approximation exists that gives insight into the nature of the solution. The treatment will be in terms of isotopic ratios which are the directly measured quantities.

1. Introduction

Recent measurements of the $^{13}\text{C}/^{12}\text{C}$ ratios in tree rings make it desirable to take a close look at isotopic exchange and fractionation processes in global carbon models. These measurements (for example, Stuiver, 1978; Freyer, 1979; Tans and Mook, 1980) are aimed at establishing the history of global biomass increases and shrinkages from the atmospheric $^{13}\text{C}/^{12}\text{C}$ ratios.

Models that explain in a satisfactory way the behavior of transient ^{14}C signals do not necessarily also explain ^{13}C variations. The reason is that the isotopic labeling of the CO_2 added to (or subtracted from) the atmosphere is only about 18‰ in $\delta^{13}\text{C}$, due to fractionation during photosynthesis. Fractionation effects at the air-sea boundary are of the same order of magnitude. On the other hand, the ^{14}C labeling of the CO_2 from fossil fuels is –1000‰ in $\delta^{14}\text{C}$ (corresponding to zero ^{14}C) which is very large compared to fractionations taking place in the global carbon cycle. As a result approximations are allowed in ^{14}C calculations that may not work for ^{13}C in the same models.

We present here an approach to calculating the transfer of tracers that is formulated in terms of isotopic ratios. The formulation will be close to our

intuitive understanding of isotopic exchange. The effect of various approximations will be investigated. An important feature is that the “inverse problem”, the historic reconstruction of the isotopic source function (e.g. deforestation and fossil fuel burning) from a time series of observed isotopic ratios, can be more readily solved when the equations are given directly in terms of isotopic ratios.

2. The isotopic ratio equation

A useful expression for the change with time of an isotopic ratio of an element, R , can be obtained by differentiating the product NR , where N is the total elemental abundance:

$$\frac{d}{dt}(NR) = N \frac{d}{dt}R + R \frac{d}{dt}N$$

After rearrangement we obtain:

$$N \frac{d}{dt}R = \frac{d}{dt}(NR) - R \frac{d}{dt}N \quad (1)$$

By choosing R to be the ratio of one isotope, say ^{13}C , to the sum of the other isotopes, $^{12}\text{C} + ^{13}\text{C}$ (+ ^{14}C), the right-hand terms in eq. (1) can easily be found for particular models. The first right-hand term is the change in time of the isotope in question and the second is the change of the elemental

¹ Present address Lawrence Berkeley Laboratory 50/232, University of California, Berkeley, CA 94720 U.S.A.

abundance (the sum of its isotopes) multiplied by the instantaneous ratio R . No assumptions have been made in eq. (1) and it is therefore valid for continuous models, box models and for different elements.

A very minor approximation comes in as soon as rate constants are entered into the isotopic flux term of eq. (1). In general a particular isotope can be assumed to be carried along with the elemental flux except for a kinetic fractionation factor that may occur at phase boundaries. The isotopic flux, then, is given by the elemental flux times the isotopic ratio R as defined above times a kinetic fractionation factor. This fractionation factor cannot properly be defined as a constant because we consider the flux of one isotope versus the flux of the sum of all the isotopes of that element. The sum will not remain constant in composition as minor changes in isotopic composition occur. However, deviations of the fractionation factor from a true constant (at a given temperature and pressure) will in almost all cases be negligible because, in general, the isotopic composition changes very little and often one isotope dominates in the elemental abundance. For instance, for ^{13}C the range of the dependence of the fractionation factor as here defined on the isotopic composition in natural environments is only about 1 part in 10^6 .

3. Perturbation equations for a two-box model

We will derive an equation for a most simple two-box model in which we can separate out different terms corresponding to pure isotopic exchange and chemical changes. If we have two well-mixed boxes, a and b , between which an element is exchanged with the transfer constants k_1 and k_2 , the changes in one box are given by

$$\frac{d}{dt} N_a = -k_1 N_a + k_2 N_b$$

$$\frac{d}{dt} {}^*N_a = -{}^*k_1 {}^*N_a + {}^*k_2 N_b \quad (2)$$

N_i is the total amount of the element in reservoir i , *N_i the corresponding amount of the isotopic tracer and R_i will be the isotopic ratio ${}^*N_i/N_i$. Asterisks are placed on the transfer constants of the tracer to

allow for isotopic fractionation. It follows that the equilibrium isotopic ratios in reservoir a and b , R_{a0} and R_{b0} , are related by:

$$\alpha_1 R_{a0} = \alpha_2 R_{b0} \quad (3)$$

The α 's are the kinetic fractionation factors defined as $\alpha_i = {}^*k_i/k_i$. The equilibrium isotopic fractionation factor (R_{a0}/R_{b0}) is thus seen to be the quotient of the kinetic fractionation factors.

In writing eq. (1) for this model in a perturbation form we will append a suffix 0 to denote the steady state values of the variables in the unperturbed system, write $r_i = R_i - R_{i0}$ and $n_i = N_i - N_{i0}$ for the perturbations and express *N_i as:

$${}^*N_{i0} + {}^*n_i = {}^*N_{i0} + N_i r_i + R_{i0} n_i \quad (4)$$

After the introduction of elemental source functions γ_i (positive or negative) with respective tracer isotopic ratios $R_{\gamma i}$ we find:

$$\frac{d}{dt} n_a = -k_1 n_a + k_2 n_b + \gamma_a$$

$$\frac{d}{dt} n_b = k_1 n_a - k_2 n_b + \gamma_b \quad (5)$$

For the isotopic ratio the combination of eq. (1), (2) and (4) yields:

$$\begin{aligned} N_a \frac{d}{dt} R_a &= -\alpha_1 k_1 N_a r_a + \alpha_2 k_2 N_b r_b \\ &+ \left(\alpha_1 - \frac{R_a}{R_{a0}} \right) R_{a0} (-k_1 n_a + k_2 n_b) \\ &+ (R_{\gamma a} - R_a) \gamma_a \\ N_b \frac{d}{dt} R_b &= \alpha_1 k_1 N_a r_a - \alpha_2 k_2 N_b r_b \\ &+ \left(\alpha_2 - \frac{R_b}{R_{b0}} \right) R_{b0} (k_1 n_a - k_2 n_b) \\ &+ (R_{\gamma b} - R_b) \gamma_b \end{aligned} \quad (6)$$

The first two right-hand terms describe a pure isotopic exchange process in which isotopic atoms or molecules are substituted for one another in the two reservoirs. The third terms represent the adjustment of the isotopes to a changing chemical situation (n_a and $n_b \neq 0$). The isotopes have to do this adjustment in their striving for thermo-

dynamic equilibrium which in this case requires $R_a/R_b = \alpha_2/\alpha_1$. The last terms give the source functions in terms of the strength of the isotopic signal they carry.

The numerical integration of a non-linear equation like eq. (6) is not difficult to perform on a computer. However, here will make a linearizing approximation to discuss some common approximations. For R_a we then have:

$$N_{a0} \frac{d}{dt} R_a = -\alpha_1 k_1 N_{a0} r_a + \alpha_a k_2 N_{b0} r_b + \left(\alpha_1 - \frac{R_a}{R_{a0}} \right) R_{a0} (-k_1 n_a + k_a n_b) + (R_{ya} - R_a) \gamma_a \quad (7)$$

By introducing the ε and δ notation familiar in isotopic work:

$$\delta_a = \frac{R_a - R_s}{R_s}$$

$$\varepsilon_1 = \alpha_1 - 1 \simeq \alpha_1 - \frac{R_a}{R_{a0}}$$

where R_s is the isotopic ratio of a standard, eq. (7) and its equivalent for R_b are transformed into:

$$N_{a0} \frac{d}{dt} \delta_a = -\alpha_1 k_1 N_{a0} \Delta \delta_a + \alpha_2 k_2 N_{b0} \Delta \delta_b + \varepsilon_1 (-k_1 n_a + k_2 n_b) + (\delta_{ya} - \delta_{a0}) \gamma_a$$

$$N_{b0} \frac{d}{dt} \delta_b = \alpha_1 k_1 N_{a0} \Delta \delta_a - \alpha_2 k_2 N_{b0} \Delta \delta_b + \varepsilon_2 (k_1 n_a - k_2 n_b) + (\delta_{yb} - \delta_{b0}) \gamma_b \quad (8)$$

The solution to eq. (8) when $\gamma_b \equiv 0$ and γ_a is a delta function or spike, denoted as γ_{sp} , with a $\delta^{13}\text{C}$ value of δ_{sp} , is:

$$N_{a0} \Delta \delta_a = \frac{1}{r'} (\alpha_2 k_2 + \alpha_1 k_1 e^{-r't}) \gamma_{sp} (\delta_{sp} - \delta_{a0}) + \frac{k_1}{r} \frac{\alpha_2 k_2}{r'} (1 - e^{-rt}) \gamma_{sp} (\delta_{a0} - \delta_{b0}) - C(e^{-r't} - e^{-rt}) \gamma_{sp}$$

$$N_{b0} \Delta \delta_b = \frac{\alpha_1 k_1}{r'} (1 - e^{-r't}) \gamma_{sp} (\delta_{sp} - \delta_{a0})$$

$$+ \frac{k_1}{r} \frac{\alpha_1 k_1}{r'} (1 - e^{-rt}) \gamma_{sp} (\delta_{a0} - \delta_{b0}) + C(e^{-r't} - e^{-rt}) \gamma_{sp} \quad (9)$$

where we have employed the following definitions:

$$r = k_1 + k_2$$

$$r' = \alpha_1 k_1 + \alpha_2 k_2$$

$$C = \frac{k_1}{\alpha_1 k_1 + \alpha_2 k_2} \frac{\alpha_1 k_1 \varepsilon_1 + \alpha_2 k_2 \varepsilon_2}{k_1 + k_2 - \alpha_1 k_1 - \alpha_2 k_2}$$

Also $-\varepsilon_1 + \varepsilon_2$ has been replaced by $\delta_{a0} - \delta_{b0}$ which is a very good approximation.

The solution clearly brings out the separate features discussed with eq. (6): ordinary isotopic exchange with an e -fold time $(\alpha_1 k_1 + \alpha_2 k_2)^{-1}$ and the signal proportional to $\delta_{sp} - \delta_{a0}$, the adjustment of the isotopes to a new chemical equilibrium with an e -fold time $(k_1 + k_2)^{-1}$ and kinetic terms that will disappear at equilibrium.

We will now verify that the solution meets two basic requirements: thermodynamic equilibrium at $t = \text{infinity}$ and mass conservation of the tracer. Thermodynamic equilibrium means in our case $\alpha_1 R_a = \alpha_2 R_b$ and therefore also $\alpha_1 \Delta \delta_a = \alpha_2 \Delta \delta_b$, a condition that is met by eq. (9) at $t = \text{infinity}$. Mass conservation of the tracer is in our case rigorously expressed as:

$$\Delta(\sum_i N_i \delta_i) = \gamma_{sp} \delta_{sp}$$

"conservation of label", as follows from our definition of δ . Evaluating $\Delta(\sum_i N_i \delta_i) = n_a \delta_{a0} + n_b \delta_{b0} + N_{a0} \Delta \delta_a + N_{b0} \Delta \delta_b$ by using eq. (9) indeed leads to $\gamma_{sp} \delta_{sp}$.

An often used approximation of the tracer equations that only takes into account the first terms that describe the pure isotopic exchange process (the " ^{14}C approximation", see for instance Stuiver, 1978) thus not only neglects transient kinetic effects but also violates conservation of tracer. The amount of label that is lost in this approximation is expressed by:

$$\frac{k_1}{r} (\delta_{a0} - \delta_{b0}) (1 - e^{-rt}) \gamma_{sp}$$

The rate of loss is $k_1 e^{-rt} (\delta_{a0} - \delta_{b0}) \gamma_{sp}$ for our spike input. This amount does not depend on the isotopic signal of the input and will be larger than the total

input of label for certain combinations of δ_{a0} , δ_{b0} , δ_p .

4. A simple global carbon model

In order to see the relative magnitudes of the effects discussed in the previous section for ^{13}C in a "realistic" global model, we will present the results of some actual numerical calculations. The model for which the calculations have been made is given in Fig. 1 and Table 1. It comprises a biosphere,

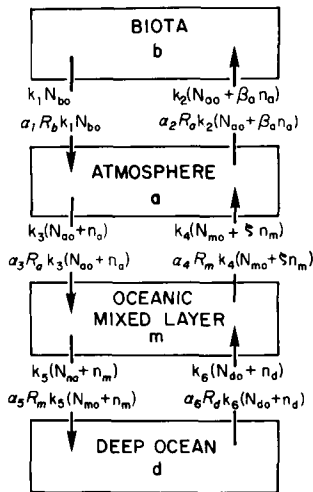


Fig. 1. Four box model for which isotopic equations are developed.

and atmosphere and the oceans divided in two parts: a wind-mixed layer and the deep seas. It is basically a simplified version of C. D. Keeling's six-box model (Keeling, 1973). The parameters have been chosen (see caption Fig. 2) very similar to the values in the six-box model and also similar to those of Oeschger et al. (1975). The tracer fluxes are given according to the prescription of section 2. An expression for the change in isotopic ratio in each reservoir can be found by entering the isotopic and elemental fluxes from Fig. 1 into eq. (1). Assuming that interoceanic exchange and also the decay of plant matter proceed without fractionation, we will set $\alpha_1 = \alpha_3 = \alpha_6 = 1$. After adding an elemental source γ with an isotopic delta δ_p to the atmosphere, we then find in the linear approximation for small perturbations:

$$N_{b0} \frac{d}{dt} \Delta \delta_b = -k_1 N_{b0} \Delta \delta_b + *k_2 N_{a0} \Delta \delta_a$$

$$N_{a0} \frac{d}{dt} \Delta \delta_a = k_1 N_{b0} \Delta \delta_b - *k_2 N_{a0} \Delta \delta_a - \varepsilon_2 k_2 \beta_a n_a + \gamma(\delta_p - \delta_{a0}) - *k_3 N_{a0} \Delta \delta_a + *k_4 N_{m0} \Delta \delta_m + \varepsilon_3(-k_3 n_a + k_4 \zeta n_m)$$

$$N_{m0} \frac{d}{dt} \Delta \delta_m = *k_3 N_{a0} \Delta \delta_a - *k_4 N_{m0} \Delta \delta_m + \varepsilon_4(k_3 n_a - k_4 \zeta n_m) - k_5 N_{m0} \Delta \delta_m + k_6 N_{d0} \Delta \delta_d$$

$$N_{d0} \frac{d}{dt} \Delta \delta_d = k_5 N_{m0} \Delta \delta_m - k_6 N_{d0} \Delta \delta_d \quad (10)$$

Table 1. Explanation of symbols in a four-box model

b, a, m, d	in order: biota, atmosphere, mixed layer, deep oceans
N_{i0}	steady state total carbon inventory of reservoir i
n_i	perturbation from that steady state value
N_i	$N_{i0} + n_i$
k_1, k_2	resp. transfer constants biota-atmosphere and vice versa
k_3, k_4	resp. transfer constants atmos.-mixed layer and vice versa
k_5, k_6	resp. transfer constants mixed l-deep seas and vice versa
β_a	biota growth factor
ζ	oceanic buffer factor
*	(asterisk) denotes tracer isotope
R_{i0}	$*N_{i0}/N_{i0}$, steady state isotopic ratio
r_i	perturbation from steady state ratio
α_j	$*k_j/k_j$, kinetic isotope fractionation factor
R_s	isotopic ratio of a standard such as PBD
δ_j	$(R_j - R_s)/R_s$
ε_j	$\alpha_j - 1$

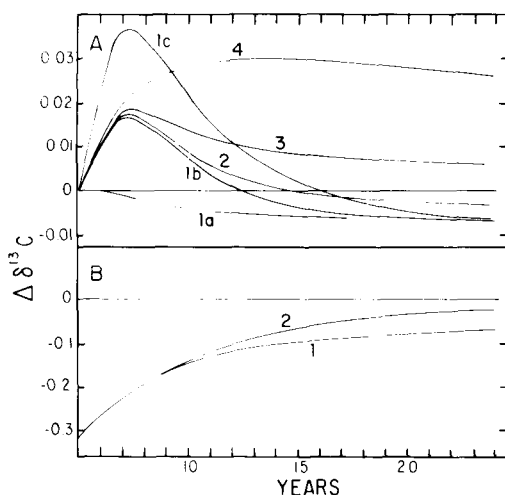


Fig. 2. $\delta^{13}\text{C}$ of the atmosphere after a spike input of CO_2 to the atmosphere. The total effect is the sum of Fig. 2A and 2B. Note the change in scale from Fig. 2A to Fig. 2B. The absolute magnitudes of the calculated effects are not important as they depend entirely on how large the spike has been chosen to be. However, the relative magnitudes are determined by the amount of isotopic labeling (-18‰ in this case) as compared to the kinetic isotope fractionation effects (-14‰ and -23‰ in all but one case). Choice of parameters (Table 1), if not mentioned otherwise: $k_1 = \frac{1}{60} \text{ yr}^{-1}$, $k_3 = \frac{1}{2} \text{ yr}^{-1}$, $N_{b0}/N_{a0} = 2.5$, $N_{m0}/N_{a0} = 1.5$, $N_{d0}/N_{a0} = 60$, $\beta_a = 0$, $\zeta = 10$, $\epsilon_2 = -18\text{‰}$, $\epsilon_3 = -14\text{‰}$, $\epsilon_3 - \epsilon_4 = 9\text{‰}$, $\delta_v - \delta_{a0} = -18\text{‰}$, $\Delta\delta_d = 0$.

Fig. 2A. Behavior of the isotopic adjustment terms. Curve 1a: $k_3 = 0$; $\epsilon_1 = 0$; 1b: $k_3 = 0$, $\epsilon_3 = -14\text{‰}$; 1c: $k_3 = 0$, $\epsilon_3 = -28\text{‰}$; curves 2, 3, 4; $k_3 = \frac{1}{2}, \frac{1}{6}, \frac{1}{2} \text{ yr}^{-1}$ respectively, $\epsilon_3 = -14\text{‰}$.

Fig. 2B. Behavior of the isotopic exchange terms. Curve 1: $k_3 = \frac{1}{2} \text{ yr}^{-1}$; curve 2: $k_3 = \frac{1}{2} \text{ yr}^{-1}$.

Solutions for the case in which γ is a spike are plotted in Fig. 2A,B for various parameters. The complete solutions always are the sum of the external forcing, displayed in Fig. 2B and corresponding to $\gamma(\delta_v - \delta_{a0})$ and to the first two right-hand terms of eq. (10), and the internal isotopic fractionation effects displayed in Fig. 2A. The magnitude of the transient effect is almost linearly related (Fig. 2A, curve 1a, 1b, 1c) to the choice of ϵ_3 (ϵ_4 is then determined $\epsilon_3 - \epsilon_4 = \delta_{m0} - \delta_{a0}$) which is an as yet unknown quantity in global models. We chose $\epsilon_1 = -14\text{‰}$ as our preferred value as that is the value commonly found when absorbing CO_2 into alkaline solutions. However, in that case we are dealing with the movement of

CO_3^{2-} ions through the boundary layer, while in the real ocean-atmosphere system this is not the dominating process.

The relative importance of the transient effects also increases when the mixed layer to deep sea transfer (k_3) is enhanced (Fig. 2A). The larger k_3 is, the more the mixed layer and the atmosphere are prevented from equilibrating with each other. As a result the transient effects will become more pronounced.

In the case of ^{14}C the external isotopic forcing (Fig. 2B) would be 50 times higher ($\delta_v^{14} - \delta_{a0}^{14} \cong 1000\text{‰}$) than for ^{13}C ($\delta_v^{13} - \delta_{a0}^{13} \cong -18\text{‰}$) while the internal fractionation effects (Fig. 2A) are only twice those for ^{13}C ($\epsilon_i^{14} = 2\epsilon_i^{13}$). Therefore, it is a very good approximation in model calculations of the ^{14}C Suess effect, the dilution of the atmospheric ^{14}C level by the combustion of ^{14}C -free fossil fuels, to set the ϵ 's equal to zero (see for instance Oeschger et al., 1975).

Table 2. $\delta^{13}\text{C}$ Suess effect in 1978

The parameters of the four-box model that are held fixed are: $k_1 = \frac{1}{60} \text{ yr}^{-1}$, $k_3 = \frac{1}{2} \text{ yr}^{-1}$, $N_{b0}/N_{a0} = 2.5$, $N_{m0}/N_{a0} = 1.5$, $N_{d0}/N_{a0} = 60$, $\beta_a = 0$, $\zeta = 10$, $\epsilon_2 = -18\text{‰}$, $\epsilon_3 - \epsilon_4 = 9\text{‰}$, $\delta_v - \delta_{a0} = -18\text{‰}$, $\Delta\delta_d = 0$.

$k_3 =$	$\frac{1}{2} \text{ yr}^{-1}$	$\frac{1}{6} \text{ yr}^{-1}$	$\frac{1}{2} \text{ yr}^{-1}$
$\epsilon_3 = -14\text{‰}$	-1.42	-1.04	-0.69
$\epsilon_3 = 0$	-1.51	-1.24	-1.01

For ^{13}C the situation is more complicated. A calculation of the Suess effect for ^{13}C is shown in table 2 for various parameters of the four-box model of eq. (10). Also we see how the transient kinetic effects can be important when the atmosphere and the mixed layer are prevented from equilibrating with each other (higher values of k_3). A "realistic" value for k_3 in our four-box model would be $\frac{1}{2} \text{ yr}^{-1}$ which is obtained from Oeschger's box-diffusion model when the e -fold time of the fossil fuel combustion is taken as 25 yr.

5. Summary

We have shown a way to formulate equations that describe the behavior of a tracer isotope in reservoir models when both the tracer and the abundant isotope undergo change. The correct equations are essentially non-linear.

In all cases the equations consist of two parts. First, the familiar isotopic exchange terms that we would find in the absence of changes in the total chemistry of the situation. This part responds to the isotopic signal that is carried by the input. In other words, it responds to the external isotopic forcing. Second, we find an adjustment of the isotopic ratios to a changing chemistry. This part depends on the internal isotopic fractionation existing within the system multiplied by the response of the

system forcing. The latter part has to be taken into account in global carbon model calculations for ^{13}C .

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О ВЫЧИСЛЕНИИ ПЕРЕНОСА УГЛЕРОДА 13 В БОКСОВЫХ МОДЕЛЯХ УГЛЕРОДНОГО ЦИКЛА

Описан подход для вычисления переноса углеродных трассеров в боксовых моделях, который учитывает эффекты изотопного фракционирования на границах раздела фаз без каких-либо существенных приближений. Рассматриваются одновременные изменения как с трассерах, так и в полном количестве углерода. Предлагаемая процедура применима к большинству моделей углеродного

цикла; обсуждается пример четырехблочной модели. Хотя точные дифференциальные уравнения нелинейны, существует простое линейное приближение, которое проясняет природу решения. Рассмотрение ведется в терминах изотопных отношений, которые являются непосредственно измеряемыми величинами.