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GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 7, NO. 2, PAGES 353-368, JUNE 1993

OCEANIC $^{13}C/^{12}C$ OBSERVATIONS: A NEW WINDOW ON OCEAN CO_2 UPTAKE

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Abstract. Equations are developed describing the rate of change of carbon isotopic ratios in the atmosphere and oceans in terms of $\delta^{13}C$ quantities. The equations enable one to perform calculations directly with δ and ε quantities commonly reported in the literature. The main cause of the change occurring today is the combustion of fossil fuel carbon with lower $\delta^{13}C$ values. The course of this isotopic anomaly in atmosphere and oceans can provide new constraints on the carbon budgets of these reservoirs. Recently published $\delta^{13}C$ isotopic data of total inorganic carbon in the oceans [Quay et al., 1992] appear to lead to incompatible results with respect to the uptake of fossil fuel CO_2 by the oceans if two different approaches to the data are taken. Consideration of the air-sea isotopic disequilibrium leads to an uptake estimate of only a few tenths of a gigaton C (Gt, for 10^{15} g) per year, whereas the apparent change in the ocean $\delta^{13}C$ inventory leads to an estimate of more than 2 Gt C yr^{-1}. Both results are very uncertain with presently available data. The isotopic ratio has the advantage that the signal-to-noise ratio for the measurement of the uptake of the isotopic signal by the oceans is better than for the uptake of total carbon. The drawback is that isotopic exchange with carbon reservoirs that are difficult to characterize introduces uncertainty into the isotopic budget. The accuracy requirements for the measurements are high, demanding careful standardization at all stages.

INTRODUCTION

For accurate predictions of atmospheric CO_2 loadings well into the next century expected to result from continued fossil fuel combustion, the most important question to be answered at this time is what fraction of the current CO_2 input enters the oceans, and what fraction is taken up by the terrestrial biosphere. The answer matters because the nature of C storage in these two reservoirs is quite different. Once stored in the oceans, most of the carbon is not likely to reenter the atmosphere soon, while increased biomass or soil organic matter would appear to be very susceptible to continued human intervention and climate change.

Two recent studies of the global atmospheric CO_2 budget made use of the observed atmospheric latitudinal concentration gradient of CO_2, and both used a numerical three-dimensional atmospheric transport model to extract information about the latitudinal distribution of sources and sinks. They agreed that there has to be a strong CO_2 sink in the northern hemisphere. They came to somewhat different conclusions regarding the nature of that sink, however. Keeling et al. [1989], relying in addition on the observed latitudinal gradient of the $^{13}C/^{12}C$ isotopic ratio of CO_2, concluded that the oceans are the largest current net sink of CO_2. They call for considerable CO_2 uptake by the terrestrial biosphere as well, largely offsetting the loss of C due to deforestation. Tans et al. [1990], relying on a compilation of the difference of the partial pressure of CO_2 between ocean surface waters and the atmosphere (ΔpCO_2) concluded that terrestrial uptake has to be even larger, such that the largest net sink has to be found on the land.

Quay et al. [1992] have injected new data into this debate. They used measurements of the isotopic composition of total dissolved inorganic carbon (DIC) in seawater to infer that the net uptake of CO_2 by the oceans during the last two decades has been 2.1 ± 0.8 Gt C yr^{-1}. The natural abundance of ^{13}C

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Paper number 93GB00053.
0886-6236/93/93GB-00053$10.00

is 1.11% relative to $^{12}C + ^{13}C$, with small variations. CO_2 derived from fossil fuels and from plant organic matter contains a slightly lower proportion of ^{13}C to ^{12}C than atmospheric CO_2. Hence the $^{13}C/^{12}C$ ratio of atmospheric CO_2 is gradually being lowered as are the $^{13}C/^{12}C$ ratios, with some delay, of reservoirs in contact with the atmosphere, namely the oceans, the terrestrial biosphere, and the pool of organic matter and calcite in the oceans. Quay et al. used measurements to estimate the total amount of this isotopic anomaly accumulated by the oceans and the atmosphere between 1970 and 1990, from which, after making assumptions about the partial uptake of the isotopic anomaly by the terrestrial biota, they deduced the net amount of excess CO_2 absorbed by the oceans.

Their conclusions are premature, as will be shown in this paper. Two approaches are possible in using $^{13}C/^{12}C$ ratios to constrain the atmospheric and oceanic budgets. One approach sets up a mass balance for the atmosphere using observations of the isotopic disequilibrium across the air-sea interface to estimate how much of the isotopic anomaly has been absorbed by the oceans. The other method, employed by Quay et al., sets up a mass balance for the oceans and atmosphere combined, using measurements of $^{13}C/^{12}C$ of DIC as a function of depth to estimate the accumulated inventory of the anomaly. With currently available data there appears to be a substantial disagreement between the first and the second method.

Equations will be derived for both of these mass balance approaches in terms of δ and ε quantities (defined below in equations (14) and (15). The measurements are always reported in these quantities. The equations are then used to derive the oceanic uptake of fossil fuel CO_2 from the observations in both cases. The relative merits of both methods will be discussed and recommendations for further measurements will be made.

BASIC EQUATIONS — MASS CONSERVATION IN THE ATMOSPHERE AND OCEANS

The fluxes to be described by equations (1) - (8) are shown in Figure 1. Neglecting the weathering of carbonate rocks, the atmospheric mass balances for total CO_2 and its ^{13}C isotope are

$$\frac{d}{dt}C_a = F_f - F_{lph} + F_{lb} - F_{ao} + F_{oa} \tag{1}$$

$$\frac{d}{dt}{}^{13}C_a = F_f R_f - \alpha_{lph} F_{lph} R_a + F_{lb} R_{lb} - \alpha_{ao} F_{ao} R_a + \alpha_{oa} F_{oa} R_{os}. \tag{2}$$

Neglecting the carbonate sedimentation/weathering cycle again, the oceanic carbon balances are

$$A\int\left(\frac{d}{dt}C_o(z)\right)dz = -F_{oph} + F_{ob} - F_{sh} + F_{ca} + F_{ao} - F_{oa}, \tag{3}$$

$$A\int\left(\frac{d}{dt}{}^{13}C_o(z)\right)dz = -\alpha_{oph} F_{oph} R_{os} + F_{ob} R_{ob} - \alpha_{sh} F_{sh} R_{os} + F_{ca} R_{ca} + \alpha_{ao} F_{ao} R_a - \alpha_{oa} F_{oa} R_{os}. \tag{4}$$

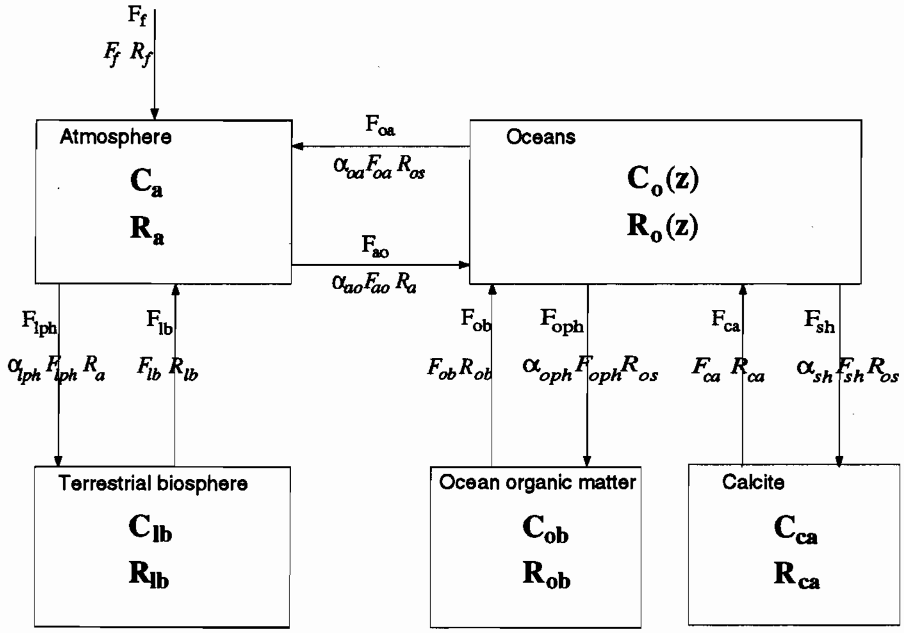

Fig. 1. Fluxes of total carbon (regular type) and ^{13}C (italics) between reservoirs. All ^{13}C fluxes are proportional to the corresponding fluxes of total carbon with the proportionality as the product of the isotopic ratio in the originating reservoir with an isotopic fractionation factor characteristic for each process. For explanation of symbols see main text and Table 1.

For the carbon contained in the terrestrial biosphere (standing wood and organic matter in soils) we have

$$\frac{d}{dt}C_{lb} = F_{lph} - F_{lb} \tag{5}$$

$$\frac{d}{dt}{}^{13}C_{lb} = \alpha_{lph}F_{lph}R_a - F_{lb}R_{lb}, \tag{6}$$

for dissolved and particulate organic matter in the oceans

$$\frac{d}{dt}C_{ob} = F_{oph} - F_{ob} \tag{7a}$$

$$\frac{d}{dt}{}^{13}C_{ob} = \alpha_{oph}F_{oph}R_{os} - F_{ob}R_{ob}, \tag{7b}$$

and for the formation and dissolution of calcite and aragonite shells

$$\frac{d}{dt}C_{ca} = F_{sh} - F_{ca} = 0 \tag{8a}$$

$$\frac{d}{dt}{}^{13}C_{ca} = \alpha_{sh}F_{sh}R_{os} - F_{ca}R_{ca}. \tag{8b}$$

In equations (1) - (8) the total inventories are designated by C, gross one-way fluxes by F, isotopic ratios by R, and isotopic fractionation factors (different from 1.0 by at most one or two percent) by α. A is the global ocean area, z is water depth, and $C_o(z)$ is the depth dependent concentration of total dissolved inorganic carbon (the sum of dissolved CO_2, bicarbonate ions and carbonate ions, abbreviated as DIC) in seawater. A global average $C_o(z)$ depth profile is assumed here. The subscripts a, os, lb, ob, lph, and oph stand for atmosphere, ocean surface, land biosphere, oceanic pool of organic matter, and photosynthesis on the land ("lph") and in the ocean ("oph") respectively. The subscript sh denotes calcium carbonate shell formation (both the calcite and aragonite forms) and ca denotes solid $CaCO_3$. F_f is the flux due to fossil fuel combustion, F_{lph} is net primary production through photosynthesis by terrestrial plants, F_{lb} is terrestrial respiration including destruction such as biomass burning, F_{oph} is oceanic new production, and F_{ob} is remineralization of organic C back into DIC. F_{ao} and F_{oa} denote one way air-to-ocean gas exchange and vice versa; the net gas exchange flux between the atmosphere and the oceans is given by the difference $F_{ao} - F_{oa}$. F_{sh} and F_{ca} are the fluxes of carbon associated with shell formation and dissolution respectively. In accordance with the neglect of the weathering/sedimentation cycle we have assumed that there is no net addition or removal of calcium from the oceans ($F_{sh} - F_{ca} = 0$). There may still be a change in the isotopic composition of the reservoir of solid $CaCO_3$, however. Also neglected in the equations above is the contribution of river runoff, which shifts a certain amount of C from the land to the oceans each year [Sarmiento and Sundquist, 1992].

All isotopic ratios R as used in the equations presented here, including that of the isotopic standard PDB (PeeDee bellemnite limestone), are defined relative to total carbon, i.e., $R = {}^{13}C/({}^{12}C + {}^{13}C)$, while the measured ratios are $^{13}C/^{12}C$. We will consistently substitute the measured ratios directly for R in our expressions. The errors introduced by this substitution are too small to be of interest; all $^{13}C/^{12}C$ ratios are larger than their corresponding $^{13}C/(^{12}C + {}^{13}C)$ ratios by very nearly the same amount.

Let us consider as our two unknown quantities $F_{lph} - F_{lb}$, the net accumulation of C by the terrestrial biosphere, and $F_{ao} - F_{oa}$, the net uptake of C by the oceans. The rate of increase in the atmosphere, dCa/dt, is being measured, and F_f is known from economic data. Equation (1) alone is not sufficient because it is one equation with two unknowns. Equation (2) is independent of equation (1) because the fractionation factors α differ sufficiently from each other. Combining equation (1) with equation (2) would provide the answer if all quantities other than $F_{lph} - F_{lb}$ and $F_{ao} - F_{oa}$ are known. The surface disequilibrium method follows this approach. The quantity $d^{13}C_a/dt$ is being measured (actually, changes in the isotopic ratio), and the fractionation factors α_{lph}, α_{ao}, α_{oa} and the isotopic ratios R_f, R_a, R_{os} have been or are being measured. We can make reasonable guesses for F_{lph}, the net primary productivity, and for F_{ao}, the air-sea transfer. A problem is R_{lb}, the isotopic composition of the terrestrial biosphere; it is very hard to measure directly due to its heterogeneous nature. It is almost certainly changing at this time due to the change in R_a. Plants are assimilating progressively "lighter" (lower $^{13}C/^{12}C$) CO_2 and storing the carbon in reservoirs with different lifetimes. We either have to make an assumption about it or we calculate R_{lb} with equations (5) and (6) or with a more sophisticated model of C storage in ecosystems.

The oceanic inventory method uses measurements of $d^{13}C_o(z)/dt$ (actually, the rate of change of $\delta^{13}C$) and equation (4) to eliminate the need to know R_{os}, the isotopic ratios in the surface ocean. Equation (3) is of no help because it has thus far not been possible to determine via direct measurements the increase in ocean carbon during the last decades. As equation (4) is written, we have the same practical problem with it as with equation (3). We do not know the change in total oceanic ^{13}C, which is increasing. We do know changes in the isotopic ratios $^{13}C/^{12}C$, however. The isotopic ratio is decreasing because the oceanic ^{12}C increase is proportionally more than the ^{13}C increase. Therefore we will recast the equations in terms of isotopic ratios.

There is a further and more fundamental problem with the use of equation (4), namely that the isotopic composition of organic matter in the oceans, R_{ob}, may be changing. Such a shift could be independent of any changes in C_{ob}, the total amount of organic matter. The same would be true for isotopic changes of the solid calcium carbonate reservoir. As in the case of the terrestrial biosphere, we have to calculate R_{ob} and R_{ca} with equations (7) and (8) or a better model of the turnover of organic matter and calcite, or we make an assumption about their composition.

Equations (1) - (8) suffice for setting up numerical computations. The approximate analytical solution we are going to derive will enable one to make fairly accurate estimates, and they will provide a certain amount of insight into the different processes that have an impact on the isotopic ratios.

AIR-SEA ISOTOPIC DISEQUILIBRIUM METHOD

We wish to find an expression for the change in the carbon isotopic ratio (R_a) of the atmosphere, rather than the change in the ^{13}C content itself because we have observations of the isotopic ratio, not of the total ^{13}C content. We start with the relation

$$\frac{d}{dt}{}^{13}C = \frac{d}{dt}(C_a R_a) = C_a \frac{d}{dt}R_a + R_a \frac{d}{dt}C_a. \tag{9}$$

Substituting the expressions equations (1) and (2) for dCa/dt and $d^{13}Ca/dt$ respectively, equation (9) can be rewritten as [Tans, 1980]

$$C_a \frac{d}{dt}R_a = F_f(R_f - R_a) - F_{lph}(\alpha_{lph} - 1)R_a + F_{lb}(R_{lb} - R_a)$$

$$-F_{ao}(\alpha_{ao} - 1)R_a + F_{oa}(\alpha_{oa}R_{os} - R_a). \tag{10}$$

Now let us define

$$R_a^e = (\alpha_{oa}/\alpha_{ao})R_{os} \tag{11}$$

and

$$R_{lb}^e = \alpha_{lph}R_a. \tag{12}$$

Here R_a^e is the isotopic composition of gaseous CO_2 that would be in thermodynamic equilibrium with the sea surface. R_a^e is completely determined by R of the surface water and the temperature of the water. The equilibrium fractionation factor is the quotient of the one-way kinetic fractionation factors: α_{oa}/α_{ao}. R_{lb}^e is the composition of the biosphere "in equilibrium" with the atmospheric ratio. There is assumed to be no fractionation associated with respiration. Combining equations (10), (11) and (12) yields

$$\begin{aligned} C_a \frac{d}{dt}R_a = {} & F_f(R_f - R_a) - (F_{lph} - F_{lb})(\alpha_{lph} - 1)R_a \\ & + F_{lb}(R_{lb} - R_{lb}^e) - (F_{ao} - F_{oa})(\alpha_{ao} - 1)R_a \\ & + F_{oa}\alpha_{ao}(R_a^e - R_a). \end{aligned} \tag{13}$$

We will now approximate equation (13) in a form using δ and ε symbols commonly reported in the literature. They are defined as

$$\delta_i = (R_i - R_{PDB})/R_{PDB} \tag{14}$$

$$\varepsilon_i = \alpha_i - 1 \tag{15}$$

permil respectively, where the subscript i stands for any C reservoir and R_{PDB} is the $^{13}C/(^{13}C+^{12}C)$ ratio of the generally adopted isotopic standard PDB limestone. After dividing all terms in equation (13) by R_{PDB} we obtain

$$\begin{aligned} C_a \frac{d}{dt}\delta_a = {} & F_f(\delta_f - \delta_a) - (F_{lph} - F_{lb})\varepsilon_{lph} + F_{lb}(\delta_{lb} - \delta_{lb}^e) \\ & -(F_{ao} - F_{oa})\varepsilon_{ao} + F_{oa}(\delta_a^e - \delta_a) \end{aligned} \tag{16}$$

where the approximation consisted of setting multiplicative factors of R_a/R_{PDB} and α_{ao} equal to one. These approximations are equivalent to decreasing ε_{lph} by less than 0.2‰ and F_{oa} by less than 0.2 Gt C yr^{-1} (see Table 1). The magnitude of the uncertainty of both of these quantities is much larger.

It should be pointed out that the sum $\sum_i C_i\delta_i$ is a conserved quantity. This is a very useful property when calculating isotopic budgets. In an analogy with paint, $\sum_i C_i\delta_i$ corresponds to the total amount of pigment in the system, and C_i, δ_i compare with the total amount of paint base and the color of each subsystem, respectively. It follows from equation (14) and our definition of isotopic ratios as $R_i = {}^{13}C_i/(^{13}C_i+^{12}C_i) = {}^{13}C_i/C_i$ that $\sum_i C_i\delta_i$ is equal to $(\sum_i {}^{13}C_i - R_{PDB}\sum_i C_i)/R_{PDB}$. The conservation of $\sum_i C_i\delta_i$ follows because both of the sums $\sum_i {}^{13}C_i$ and $\sum_i C_i$ are conserved and R_{PDB} is a defined constant. The units of $\sum_i C_i\delta_i$ are gigaton per mil of carbon.

An advantage of the formulation of equation (16) is to distinguish changes in the atmospheric isotopic ratio that are brought about by net fluxes between reservoirs from those caused by gross exchanges. The term $(F_{ao}-F_{oa})\varepsilon_{ao}$ represents net uptake of C by the oceans, which only leads to isotopic changes in the atmosphere if there is kinetic fractionation ($\varepsilon_{ao}\neq 0$) associated with the net transfer. The term $F_{oa}(\delta_a^e - \delta_a)$ represents the approach to isotopic equilibrium if the ocean surface and atmosphere are out of isotopic equilibrium ($\delta_a^e - \delta_a \neq 0$), which takes place independently of the direction of net transfer of C. In this process a $^{12}CO_2$ molecule enters the ocean for every $^{13}CO_2$ leaving, and vice versa. Similarly, $(F_{lph}-F_{lb})\varepsilon_{lph}$ represents net uptake of carbon by the land biosphere while $F_{lb}(\delta_{lb} - \delta_{lb}^e)$ represents the approach of the land biosphere to isotopic equilibrium with the atmosphere. A graphic representation of equation (16) is given in Figure 2, in which approximate magnitudes of the various terms are expressed in units of gigaton per mil per year.

It is difficult to determine by measurements how far the terrestrial biosphere is out of isotopic equilibrium with the current atmosphere. As the atmosphere becomes more depleted in ^{13}C due to the input of fossil fuel CO_2, the biosphere will follow with a certain time lag, if the globally averaged isotopic fractionation during photosynthesis does not change. The term $F_{lb}(\delta_{lb} - \delta_{lb}^e)$ would be positive in that case because currently the atmospheric δ values are decreasing, causing δ_{lb} to lag δ_{lb}^e. A rough estimate would be $\delta_{lb} - \delta_{lb}^e \approx -\frac{d}{dt}\delta_a * \tau$, where τ is the residence time of carbon in the biosphere which could be loosely defined as the total amount of biospheric carbon in standing wood and soils divided by F_{lb}. Although we treat it here as a globally averaged quantity, this time lag is very likely much larger at high latitudes than in the tropics. Raich and Schlesinger [1992] estimate soil residence times varying between 10 years for tropical grasslands and 500 years for tundra.

TABLE 1. Adopted Values for Quantities in the Equations

Quantity	Description	Value
C_a	average atmospheric CO_2 content 1970-1990	715 Gt C
$C_a(t_1) - C_a(t_0)$	atmospheric CO_2 increase 1970-1990	61 Gt C
$\int[\delta_o(t_1) - \delta_o(t_0)]dz$	integral oceanic DIC $\delta^{13}C$ change	-208‰ m
C_o	total oceanic dissolved inorganic carbon (DIC)	2.1 moles m^{-3}
A	surface area of the oceans	$350{*}10^{12} m^2$
F_f	average fossil fuel combustion 1970-1990	5.0 Gt C yr^{-1}
F_{ao}	global atmosphere-to-ocean gas transfer	85 Gt C yr^{-1}
F_{oa}	global ocean-to-atmosphere gas transfer	$\approx F_{ao}$
F_{lph}	terrestrial net primary production	60 Gt C yr^{-1}
F_{lb}	terrestrial ecosystem respiration plus destruction	$\approx F_{lph}$
F_{oph}	oceanic new production	15 Gt C yr^{-1}
$F_{oph} - F_{ob}$	net change in total amount of ocean organic matter	0 Gt C yr^{-1}
F_{sh}	rate of $CaCO_3$ shell formation in the oceans	4 Gt C yr^{-1}
F_{ca}	rate of $CaCO_3$ dissolution	$\approx F_{sh}$
$\delta_a(1970)$	$\delta^{13}C$ (w.r.t. to PDB) of atmospheric CO_2	−7.36‰
$\delta_a(1990)$		−7.76‰
δ_{os}	$\delta^{13}C$ of C_o of surface waters	1.8‰
δ_f	$\delta^{13}C$ of fossil fuel CO_2	−27.2‰
ε_{ao}	kinetic fractionation during air-sea transfer	−2.0‰
ε_{oa}	kinetic fractionation during sea-air transfer	−10.9‰
ε_{lph}	fractionation of terrestrial photosynthesis	−18.0‰
ε_{oph}	fractionation of oceanic photosynthesis	−22.0‰
$\delta_a^e - \delta_a$	disequilibrium ocean surface and atmosphere	0.43‰
$\delta_a^e - \delta_{os}$	isotopic equilibrium air and water (global average)	−8.9‰
$\delta_{lb} - \delta_{lb}^e$	disequilibrium terrestrial biosphere and atmosphere	0.2‰
$\delta_{ob} - \delta_{ob}^e$	disequilibrium ocean organic matter and surface DIC	0.35‰
$\delta_o(z_2)$	$\delta^{13}C$ of DIC at intermediate depth level	1.0‰

As plants respond to higher ambient CO_2 concentrations it is possible that the photosynthetic isotope fractionation (ε_{lph}) undergoes a shift. Current theory of the fractionation [Farquhar et al., 1982] and experiments on stomatal opening of plant leaves during photosynthesis under various conditions [Ball, 1988; Collatz et al., 1991] suggest that the fractionation would not change significantly.

OBSERVATIONS OF THE AIR-SEA ISOTOPIC DISEQUILIBRIUM

We have information about the isotopic disequilibrium between the atmosphere and surface waters in the Pacific Ocean in 1970 and in 1989-1991 [Kroopnick et al., 1977; Quay et al., 1992], as well as GEOSECS data obtained by Kroopnick for the Atlantic Ocean in 1972-1973 and the Indian Ocean in 1978 [GEOSECS, 1987]. The GEOSECS data are shown in Figure 3. Using climatological annual mean water temperatures and measured isotopic fractionation factors of the carbonate system, we can calculate the atmospheric $\delta^{13}C$ values that would be in isotopic equilibrium (δ_a^e) with the local water. The results are shown in Tables 2 and 3 as averages for 10-deg latitude bands. Our best estimate for the observed global average disequilibrium between the ocean surface and the atmosphere during the decade of the seventies is 0.41‰ (Table 3). Between 1970 and 1990 the disequilibrium appears to have increased by only 0.05‰ in the same area of the Pacific (Table 2).

We have some idea of the consistency of the disequilibrium values for the three separate ocean basins. The average standard deviation of those values for the same latitudes is 0.22‰ (Table 3). The statistical uncertainty for the global mean is surely smaller because all latitudes are averaged. A more important issue is potential systematic errors resulting from measurement techniques, gaps in data coverage, and from the uncertainty in the fractionation factors.

There is likely to be some seasonal bias in the surface oceanic $\delta^{13}C$ data if they are considered as annual mean values. The main influences on seasonality of $\delta^{13}C$ are marine biological productivity and respiration or decay. The $\delta^{13}C$ values of DIC in surface waters will tend to be higher in summer than in winter because ^{12}C is taken up preferentially by organisms, enriching ^{13}C in the DIC left behind in the

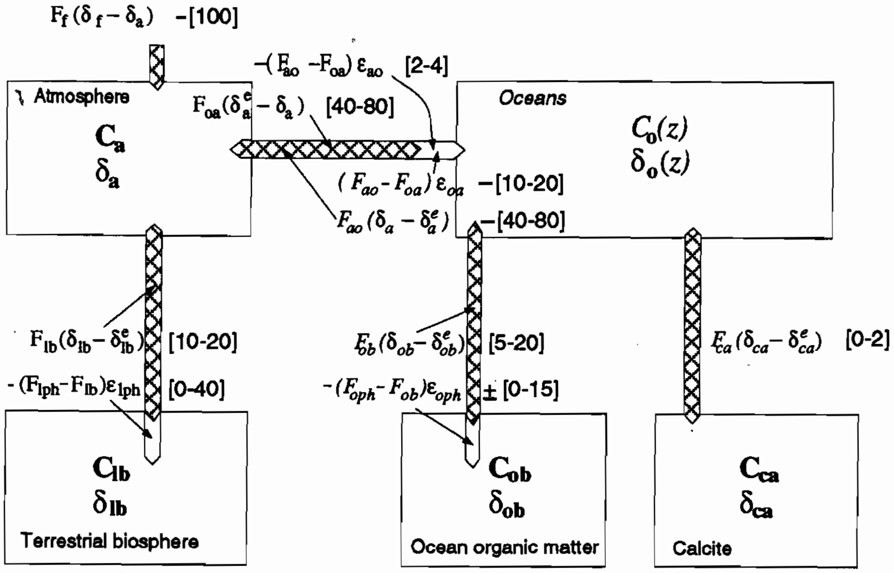

Fig. 2. Isotopic fluxes of Figure 1 expressed in units of δ and ε. There are two components to each exchange. There is pure isotopic exchange proportional to the isotopic disequilibrium between the reservoirs (hatched arrows), which takes place independent of any net exchange of C. Secondly there is net exchange of C (open arrows), which only changes the isotopic ratio of the reservoir if the kinetic isotopic fractionation factor (α) is different from 1 (or $\varepsilon \neq 0$). The same net air-sea flux has a slightly different effect on changes in δ in the ocean than in the atmosphere because the kinetic fractionation factors are different ($\varepsilon_{ao} \neq \varepsilon_{oa}$). Note that the contribution of the pure isotopic exchange fluxes between the oceans and the atmosphere is much larger than of the net exchange. All fluxes pertaining to changes in atmospheric δ are in regular type, those pertaining to oceanic δ are in italics. Estimated magnitudes are indicated in square brackets in units of Gt ‰ C yr^{-1}.

water. Most of the southern hemisphere $\delta^{13}C$ data considered in this paper were obtained in summer. A seasonal bias in those data would have made the sea surface values too "heavy," or the computed air-sea disequilibrium too large compared to the actual annual mean. The northern hemisphere data used in this study were obtained in spring, fall, and winter.

The estimate of the global mean disequilibrium depends on which values are adopted for the fractionation factors. Use of the values measured by Mook et al. [1974] for dissolved CO_2 and bicarbonate ions, and those of Lesniak and Sakai [1989] for carbonate ions leads to 0.41‰ as the global average disequilibrium during 1970-1980. If, instead, we use Lesniak's value for bicarbonate as well, the global mean disequilibrium would be 0.20‰. Emrich et al.'s [1970] value for bicarbonate would lead to 0.52‰, and Inoue and Sugimura's [1985] determination of the fractionation of gaseous CO_2 with respect to DIC (no speciation) results in 0.61‰ for the global mean. Inoue and Sugimura adjusted the pCO_2 of a seawater sample by adding acid or base at different temperatures. The other authors did not use seawater solutions. A careful experimental reevaluation of the fractionation factors in several actual seawater samples as a function of temperature would be useful. A this time we adopt the value of 0.41‰ as our best estimate for the decade 1970-1980 and 0.43‰ as the average for the entire period 1970-1990.

OCEANIC C UPTAKE DERIVED FROM THE SURFACE ISOTOPIC DISEQUILIBRIUM

The key to proceeding is to notice that the fractionation of fossil fuels with respect to atmospheric CO_2 is close to that of photosynthesis ($R_f - R_a \approx (\alpha_{lph}-1)R_a$). The first two right-hand terms of equation (13) can then be combined into $(F_f - F_{lph} + F_{lb})(R_f - R_a)$, which, in turn, can be simplified using equation (1). Equation (13) thus becomes

$$\begin{aligned}(F_{ao}-F_{oa})(R_f-\alpha_{ao}R_a) = {} & C_a\frac{d}{dt}R_a-\frac{d}{dt}C_a(R_f-R_a)\\ & -F_{lb}\left(R_{lb}-R_{lb}^e\right)\\ & -F_{oa}\alpha_{ao}\left(R_a^e-R_a\right).\end{aligned} \tag{17}$$

Integrated over a 20-year period and expressed in δ and ε notation, equation (17) is approximately equal to

TABLE 2. Air-Sea Disequilibrium for the Pacific Ocean

Latitude	T, °C	Area, $10^{12}m^2$	Transfer Velocity, cm hr^{-1}	1970 δ_o ‰	1970 δ_a^e ‰	1970 $\delta_a^e - \delta_a$ ‰	1990 δ_o ‰	1990 δ_a^e ‰	1990 $\delta_a^e - \delta_a$ ‰
70°S-60°S	-0.5	8.0	9	1.54	-9.21	-1.88			
60°S-50°S	5.6	11.0	26	1.97	-8.06	-0.73	1.79	-8.24	-0.51
50°S-40°S	11.4	13.1	27	2.33	-7.04	0.28	1.94	-7.43	0.29
40°S-30°S	17.5	13.9	17	2.06	-6.63	0.68	1.85	-6.84	0.87
30°S-20°S	22.6	15.3	13	2.05	-6.10	1.19	1.61	-6.54	1.15
20°S-10°S	25.7	17.5	13	2.25	-5.57	1.72	1.63	-6.19	1.50
10°S- 0°	27.0	18.9	10	2.12	-5.82	1.48	1.61	-6.08	1.62
0°-10°N	27.8	21.1	10	1.97	-5.64	1.68	1.60	-6.01	1.71
10°N-20°N	27.2	18.5	13	1.97	-5.70	1.64			
20°N-30°N	24.0	15.7	11	1.90	-6.10	1.28	1.42	-6.58	1.20
30°N-40°N	18.5	12.3	15	1.89	-6.67	0.75	1.37	-7.22	0.60
40°N-50°N	10.1	9.2	18	1.90	-7.61	-0.15	1.46	-8.05	-0.19
50°N-60°N	5.9	5.8	17	1.42	-8.58	-1.08	1.23	-8.77	-0.87

Sea surface $\delta^{13}C$ data in 1970 are from Kroopnick et al. [1977], and in 1989-1991 from Quay et al. [1992]. After averaging these data in 10° intervals, the $\delta^{13}C$ value of air in isotopic equilibrium with the average sea surface $\delta^{13}C$ at the local water temperature is calculated, using isotopic fractionation factors for dissolved CO_2 and HCO_3^- ions [Mook et al., 1974] and CO_3^{2-} ions [Lesniak and Sakai, 1989], and Pacific zonal annual mean sea surface temperatures 1950-1979 [Shea et al., 1990]. Weighting by ocean area in each zone and including the ≈0.2‰ latitudinal gradient of $\delta^{13}C$ in the atmosphere [Keeling et al., 1989; Francey et al., 1990], the ocean-atmosphere disequilibrium would be 0.85‰ in 1970 for the Pacific south of 60°N. Including as a weighting factor the latitudinal dependence of air-sea exchange (proportional to zonal annual mean transfer velocities for climatological winds as given by Etcheto and Merlivat, 1989) the average disequilibrium would be 0.68‰ for the same area in 1970. The last result is lower because higher wind speeds emphasize the high latitudes relative to the tropics. The disequilibrium appears to have increased by only 0.03‰ in the same area in 1990. Sea surface temperatures have increased by ≈0.2°C in the last 20 years [IPCC, Climate Change, 1990]. Including them would add another 0.02‰ to the disequilibrium in 1990.

$$
\begin{aligned}
\left(\overline{F_{ao}-F_{oa}}\right)\left(\bar{\delta}_f-\bar{\delta}_a-\varepsilon_{ao}\right)= \\
&\bar{C}_a\left[\delta_a(t_1)-\delta_a(t_0)\right]/\Delta t \\
&-\left(\bar{\delta}_f-\bar{\delta}_a\right)\left\{C_a(t_1)-C_a(t_0)\right\}/\Delta t \\
&-\bar{F}_{lb}\left(\overline{\delta_{lb}-\delta_{lb}^e}\right) \\
&-\bar{F}_{oa}\left(\delta_a^e-\delta_a\right), \qquad (18)
\end{aligned}
$$

where t_1 is the year 1990, t_0= 1970, Δt = 20 years, and the overbars (which will be dropped from here on) denote 20-year averages. At this point we have replaced the original equations (1) - (2) with equations (1) and (18). We do not need equations for the ocean isotopic budget because the oceans only enter the picture as a surface boundary condition with an accompanying flux. The first two right-hand terms of equation (18) are known through atmospheric measurements. In order to compare our results to those of Quay et al. we adopt their estimates of F_{lb} as 60 Gt C yr^{-1} and $\delta_{lb}-\delta_{lb}^e$ as 0.2‰ to yield $F_{lb}(\delta_{lb}-\delta_{lb}^e)$ = 12 Gt ‰ C yr^{-1}, and we assume the global annual mean value of 20 moles m^{-2} yr^{-1} for air-sea exchange based on ^{14}C data [Broecker et al., 1986] so that F_{ao} equals 85 Gt C yr^{-1}. Using the value of 0.43 ‰ for $\delta_a^e - \delta_a$ we can now solve for $F_{ao} - F_{oa}$. The solution is $F_{ao} - F_{oa}$ = 0.2 Gt C yr^{-1}.

A graphical representation of this solution is presented in Figure 4, in which equation (18) is shown as a linear relation between $F_{ao} - F_{oa}$ and $-F_{oa}(\delta_a^e - \delta_a)$. The latter term represents isotopic exchange due to the isotopic disequilibrium across the air-sea interface only. If F_{oa} equals 85 Gt C yr^{-1}, the exchange fluxes correspond to the amount of isotopic disequilibrium given in italics on the right hand side of the vertical axis. For different values of F_{oa} the right-hand vertical scale would shrink or expand accordingly. A disequilibrium of 0.43‰ corresponds to F_{ao}-F_{oa} = 0.2 Gt C yr^{-1}. The open double arrow denotes changes of 10 Gt ‰ C yr^{-1} in either direction in the first three right-hand terms of equation (18), which would shift the line horizontally parallel. Increasing $F_{lb}(\delta_{lb} - \delta_{lb}^e)$ from 12 to 22 Gt ‰ C yr^{-1} is seen to increase F_{ao}-F_{oa} from 0.2 to 0.7 Gt C yr^{-1} (dashed line, Figure 4). If Inoue and Sugimura's values for the fractionation factors are used the average 1970-1990 air-sea disequilibrium is estimated as 0.63‰ , and F_{ao}-F_{oa} would be 1.1 Gt C yr^{-1} (short dashed arrows, Figure 4).

Ocean uptake of 0.2 Gt C yr^{-1} is known to be too low. The partial pressure of CO_2 in surface waters has kept pace with the atmospheric increase during the last decades. A uniform increase of pCO_2 of 1.5 microatmospheres (μatm) per year (same as the atmospheric increase) in a surface layer of 80 m thickness over all of the oceans requires approxi-

TABLE 3. Global Air-Sea Disequilibrium During the Decade 1970-1980

	Pacific (1970)		Atlantic (1972)		Indian (1978)		Global (1970-1980)		
Latitude	Area, 10^{12} m^2	$\delta_a^o - \delta_a$, ‰	Area, 10^{12} m^2	$\delta_a^o - \delta_a$, ‰	Area, 10^{12} m^2	$\delta_a^o - \delta_a$, ‰	Area, 10^{12} m^2	$\delta_a^o - \delta_a$, ‰	Transfer Velocity cm hr^{-1}
70°S-60°S	8.0	−1.88	4.6	−2.14	4.5	−1.98	17.1	−1.98	9
60°S-50°S	11.0	−0.73	6.1	−1.75	8.4	−1.34	25.5	−1.17	26
50°S-40°S	13.1	0.28	7.2	−0.52	10.2	−0.04	30.5	−0.02	27
40°S-30°S	13.9	0.68	7.5	0.78	11.2	0.50	32.6	0.64	17
30°S-20°S	15.3	1.19	6.7	1.07	8.9	0.98	30.9	1.10	13
20°S-10°S	17.5	1.72	6.0	1.19	9.9	1.27	33.4	1.49	13
10°S- 0°	18.9	1.48	6.4	1.11	8.3	1.50	33.6	1.41	10
0°-10°N	21.1	1.68	6.7	1.67	6.1	1.55	33.9	1.65	10
10°N-20°N	18.5	1.64	8.2	1.52	4.8	1.45	31.5	1.58	13
20°N-30°N	15.7	1.28	9.4	1.05			25.1	1.19	11
30°N-40°N	12.3	0.75	8.5	0.93			20.8	0.82	15
40°N-50°N	9.2	−0.15	5.8	−0.33			15.0	−0.22	28
50°N-60°N	5.8	−1.08	5.1	−0.46			10.9	−0.79	17
60°N-70°N	1.4		7.0	−1.03			8.4	−1.03	9
70°N-80°N			8.2	−1.16			8.2	−1.16	3

The isotopic data for the Atlantic and the Indian Ocean are from the GEOSECS [1987]. The disequilibrium for 10° latitude intervals in the Atlantic and the Indian Oceans has been calculated in the same way as for the Pacific (see Table 2), using the annual zonal mean temperatures [Shea et al., 1990] for each ocean basin separately. The colder temperatures in the high southern latitudes of the Atlantic and Indian Ocean are the reason for the more negative disequilibrium values compared to the Pacific. For the disequilibrium calculation the atmospheric $\delta^{13}C$ value has been assumed to decrease by 0.02 ‰ yr^{-1}. The global values in this table are the area-weighted means of the three basins. The global area-weighted average is 0.55‰, and if the air-sea transfer velocities [Etcheto and Merlivat, 1989] are included in the weighting (last column), the global mean equals 0.44‰. We should take into account that the ocean's skin temperature is ≈0.3°C cooler than the bulk water [Robertson and Watson, 1992)]. The global mean disequilibrium value then drops from 0.44‰ to 0.40‰. When pCO_2 is also included in the weighting the global value equals 0.41‰.

mately 0.3 Gt C yr^{-1}, which is clearly a lower bound to the true oceanic CO_2 uptake.

THE OCEANIC INVENTORY METHOD

Following a strategy similar to what led us to equation (16) for the atmosphere, an isotopic mass balance equation can be derived for the oceans. We start with

$$A\int\left(\frac{d}{dt}{}^{13}C_o(z)\right)dz = A\int C_o(z)\left(\frac{d}{dt}R_o(z)\right)dz$$
$$+A\int R_o(z)\left(\frac{d}{dt}C_o(z)\right)dz, \qquad (19)$$

where A is the surface area of the oceans. Using the mean value theorem of calculus, equation (19) can be written as

$$A\int\left(\frac{d}{dt}{}^{13}C_o(z)\right)dz = AC_o(z_1)\int\left(\frac{d}{dt}R_o(z)\right)dz$$
$$+AR_o(z_2)\int\left(\frac{d}{dt}C_o(z)\right)dz \qquad (20)$$

where z_1 and z_2 are intermediate depth levels. Over most of the oceans C_o increases by about 10% and R_o decreases by 2‰ between the surface and deep waters due to falling organic particles that remineralize into DIC at depth. The shape of the resulting depth profiles of C_o and R_o does not change to a first order of approximation during the invasion of fossil fuel carbon into the oceans as long as biological processes and ocean circulation pretty much continue in the same way. Our argument in this paper does not depend on precise values for $C_o(z_1)$ and $R_o(z_2)$ because they enter only as multiplicative factors. Combining equation (20) with equations (3) and (4) yields

$$\begin{aligned}AC_o(z_1)\int\left(\frac{d}{dt}R_o(z)\right)dz = {}&\\ &(\alpha_{ao}R_a - R_o(z_2))F_{ao}\\ &-(\alpha_{oa}R_{os} - R_o(z_2))F_{oa}\\ &+(R_{ob} - R_o(z_2))F_{ob}\\ &-(\alpha_{oph}R_{os} - R_o(z_2))F_{oph}\\ &+(R_{ca} - R_o(z_2))F_{ca}\\ &-(\alpha_{sh}R_{os} - R_o(z_2))F_{sh}\end{aligned} \qquad (21)$$

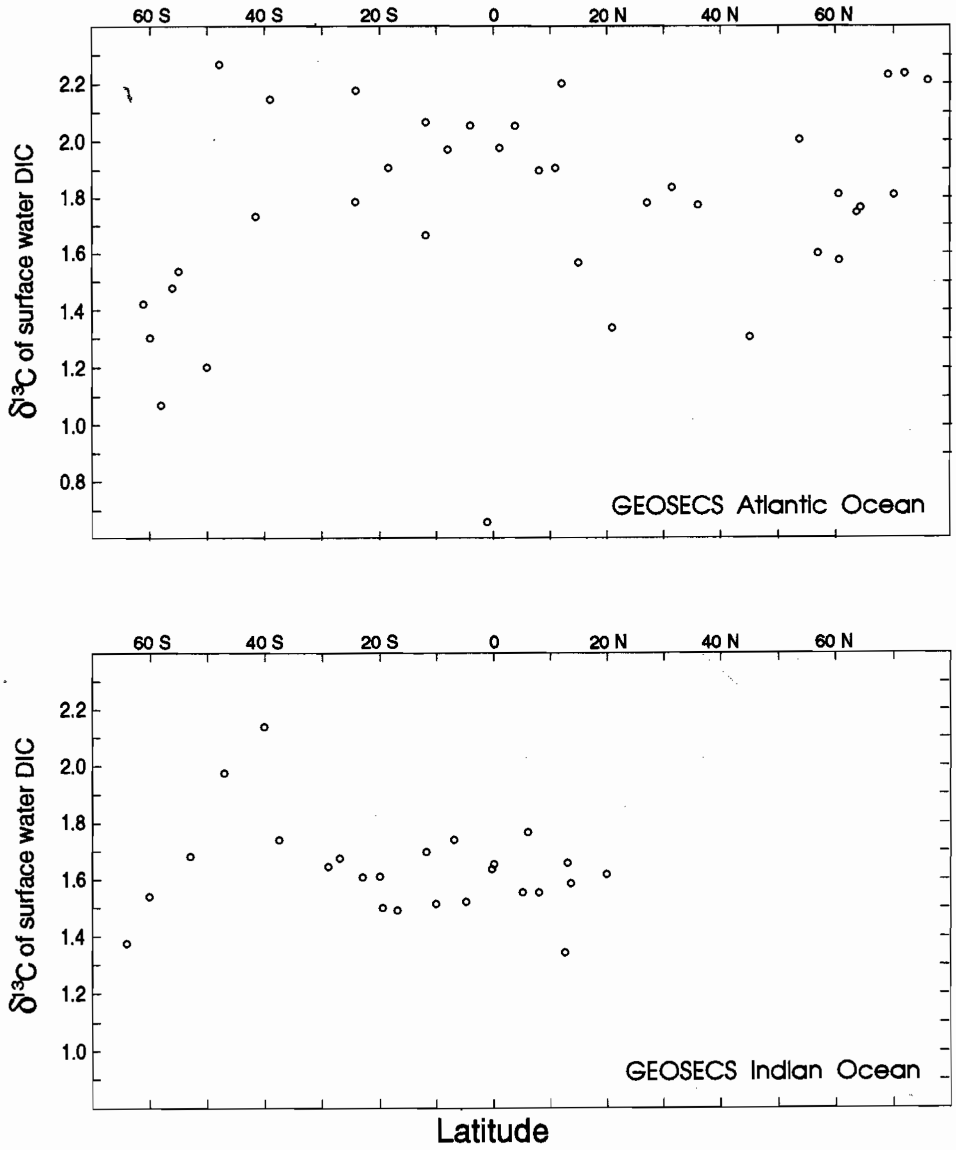

Fig. 3. Observed $\delta^{13}C$ values of total inorganic carbon in surface seawater during GEOSECS expeditions [GEOSECS Atlas, 1987].

We now define

$$R_{ob}^{e} = \alpha_{oph} R_{os}, \tag{22}$$

$$R_{ca}^{e} = \alpha_{sh} R_{os}, \tag{23}$$

where R_{ob}^{e} and R_{ca}^{e} are the isotopic ratio of marine organic matter and calcite "in equilibrium" with today's surface water. Combining equations (21), (11), (22), and (23) yields

$$\begin{aligned} AC_o(z_1)\int\left(\frac{d}{dt}R_o(z)\right)dz = {}&(F_{ao}-F_{oa})(\alpha_{oa}R_{os}-R_o(z_2)) \\ &+F_{oa}\alpha_{ao}\left(R_a-R_a^{e}\right) \\ &-\left(F_{oph}-F_{ob}\right)\left(\alpha_{oph}R_{os}-R_o(z_2)\right) \\ &+F_{ob}\left(R_{ob}-R_{ob}^{e}\right) \\ &+F_{ca}\left(R_{ca}-R_{ca}^{e}\right). \end{aligned} \tag{24}$$

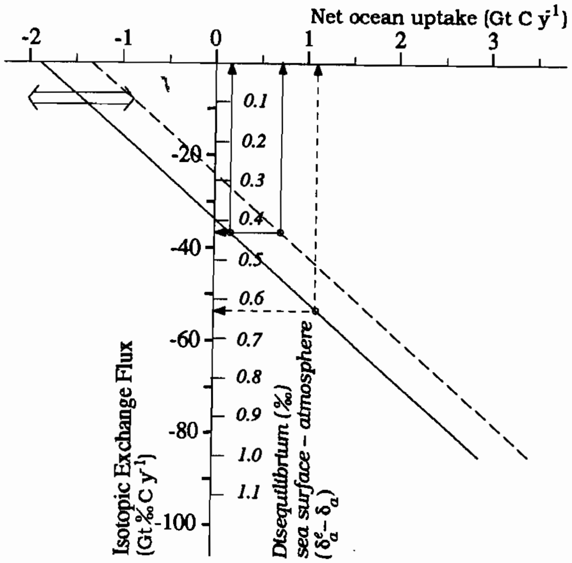

Fig. 4. Graphical representation of equation (18) as a relationship between net ocean uptake of carbon, $F_{ao}-F_{oa}$, and isotopic exchange between the atmosphere and the oceans, $-F_{oa}(\delta_a^e-\delta_a)$, due to the isotopic disequilibrium across the air-sea interface. The exchange flux is defined as negative when ocean δ values are lowered. See main text for discussion.

After dividing all isotopic ratios by R_{PDB}, we obtain

$$
\begin{aligned}
AC_o(z_1)\int\left(\frac{d}{dt}\delta_o(z)\right)dz = {}&\\
&(F_{ao}-F_{oa})(\varepsilon_{oa}+\delta_{os}-\delta_o(z_2))\\
&+F_{ao}(\delta_a-\delta_a^e)\\
&-(F_{oph}-F_{ob})(\varepsilon_{oph}+\delta_{os}-\delta_o(z_2))\\
&+F_{ob}(\delta_{ob}-\delta_{ob}^e)\\
&+F_{ca}(\delta_{ca}-\delta_{ca}^e), \qquad (25)
\end{aligned}
$$

where we have again made the approximation of setting the multiplicative factors of R_{os}/R_{PDB} and α_{ao} equal to one (compare equation (16)). Equation 25 can be simplified further if we neglect δ_{os}-$\delta_o(z_2)$ (about 1 permil) relative to ε_{oa} (10-12 permil) and ε_{oph} (20-24 permil). We then obtain

$$
\begin{aligned}
AC_o(z_1)\int\left(\frac{d}{dt}\delta_o(z)\right)dz = {}&\\
&(F_{ao}-F_{oa})\varepsilon_{oa}-F_{ao}(\delta_a-\delta_a^e)\\
&-(F_{oph}-F_{ob})\varepsilon_{oph}+F_{ob}(\delta_{ob}-\delta_{ob}^e)\\
&+F_{ca}(\delta_{ca}-\delta_{ca}^e). \qquad (26)
\end{aligned}
$$

These flux contributions are also depicted in Figure 2, with estimates of their magnitudes in units of gigaton per mil. Basically, we have replaced at this point equations (1) - (4) with equations (1), (16), (3), and (26).

It should be noted that in equation (26) the isotopic effect associated with the net air-sea transfer of C is obtained by multiplying $F_{ao}-F_{oa}$ by ε_{oa}, whereas in equation (16) multiplication is by ε_{ao}. Carbon entering the ocean with the atmospheric isotopic composition finds itself with too little ^{13}C compared to oceanic carbon. The difference $\varepsilon_{ao}-\varepsilon_{oa}$ corresponds to the equilibrium fractionation between the surface ocean and the atmosphere (see equation (11)). We can perform the following check on the correctness of equation (25) as an expression for isotopic exchange across the air-sea interface. We can calculate that

$$\frac{d}{dt}\left(\sum_i C_i\delta_i\right)=\sum_i\left(\delta_i\frac{d}{dt}C_i+C_i\frac{d}{dt}\delta_i\right)=F_f\delta_f$$

by setting all terms involving biological processes equal to zero, and by using equations (1), (3), (16), (25), and the (near-) equality $\delta_{os}=\delta_a^e+\varepsilon_{ao}-\varepsilon_{oa}$, which follows from equation (11). This confirms that the equations indeed conserve the quantity $\sum_i C_i\delta_i$.

The last three terms of equation (26) present a problem for the isotopic budget of the water column. We will discuss the third term on the right hand side of equation (26) first, which accounts for any changes in the total amount of dissolved organic carbon (DOC). Our knowledge of the amount of DOC and its rate of turnover is poor. The total amount is uncertain and is the subject of considerable debate [e.g., Sugimura and Suzuki, 1988; Martin and Fitzwater, 1992], but is comparable to the total amount of carbon in the terrestrial biosphere. It would be extremely difficult to detect changes of the order of 1 Gt C yr^{-1}, a magnitude which would have a relatively large impact on the isotopic budget. For now, we will assume $F_{oph}-F_{ob}=0$ due to our lack of knowledge.

Even in the case that $F_{oph}-F_{ob}=0$, we still have to contend with the term $F_{ob}(\delta_{ob}-\delta_{ob}^e)$. δ_{ob}^e may be changing for two reasons. First of all δ_{os} is becoming lower because of uptake of part of the fossil fuel isotopic signal by the ocean surface [Druffel and Benavides, 1986]. Second, the photosynthetic fractionation (α_{oph}) is likely to become more pronounced also, as Rau et al. [1989] and Jasper and Hayes [1990] found that α_{oph} depends on the concentration of dissolved CO_2 in the water. In the last 20 years the atmospheric CO_2 increase has been almost 10%, which has raised the dissolved CO_2 concentration of surface waters everywhere by roughly the same relative amount. This in turn should have lead, using Rau's data, to a lowering of $\delta^{13}C$ of newly formed organic matter (δ_{ob}^e) by about one per mil.

The magnitude of F_{ob} is closely related to oceanic "new production" [Dugdale and Goering, 1967] because it describes the amount of inorganic C and associated nutrients brought into the euphotic zone each year after having been remineralized at depth. A reasonable estimate would be 15 Gt C yr^{-1} [Jenkins and Goldman, 1985; Keeling and Shertz, 1992], which corresponds to a global average of 3.6 mol C m^{-2} yr^{-1}. This amount of material sinks below the 100 m depth level as particulate organic matter. The majority disintegrates before it reaches 500 m [Martin et al., 1987].

Most likely it enters the pool of dissolved organic matter before being fully oxidized ("remineralized") to CO_2 and nutrients. The magnitude of $\delta_{ob} - \delta^e_{ob}$ depends on the age of the remineralized material since it was last photosynthesized. A rough first estimate of the age might be obtained from the total amount of "excess" (i.e., relative to deeper waters) DOC in the upper 500 m of the water column, divided by an annual input of 15 Gt C. If the "excess" averages 50 μmol/kg over a depth range of 300 m, then the total global inventory would be 60 Gt C, with an average age of 4 years. $\delta_{ob} - \delta^e_{ob}$ would then be 0.3‰ due to both of the effects mentioned in the previous paragraph. With our choice of numbers, the contribution to the isotopic budget would be about 4.5 Gt‰ C yr^{-1}.

Whether this contribution to the isotopic budget is important depends heavily on the measurement of DOC in seawater which is still controversial. If the rate of change of δ^e_{ob} has been constant during the last two decades, the contribution of the term $F_{ob}(\delta_{ob} - \delta^e_{ob})$ to the 1970-1990 isotopic budget depends only on the total amount of "excess" DOC in the upper water column. Since $\delta_{ob} - \delta^e_{ob}$ is proportional to the lifetime of this DOC pool, and F_{ob} is the annual flux into the pool, $F_{ob}(\delta_{ob} - \delta^e_{ob})$ is proportional to the total amount.

There is also a component of very old DOC spread throughout the oceans. E. R. M. Druffel et al. (Cycling of dissolved and particulate organic matter in the open ocean, submitted to *Journal of Geophysical Research*, 1993) have measured its age as ≈5000 years and estimated the total amount as 1700 Gt C. Its annual turnover would then be about 0.34 Gt C yr^{-1}, and $\delta_{ob} - \delta^e_{ob}$ approximately 3‰, so that its effect on the budget would be about 1 Gt‰ C yr^{-1}. The total effect on the isotopic budget of exchange with young and old DOC is then estimated as 5 Gt‰ C yr^{-1}.

As long as we are not able to directly measure the oceanic and the terrestrial biospheric contributions to the isotopic budget they will have to be modeled. The statement by Quay et al. that their method yields model-independent values for the net oceanic CO_2 uptake rate is therefore incorrect.

We will now make an estimate for the last term of equation (26). The amount of C falling to the depths in the form of solid $CaCO_3$ is about one fourth of the amount of falling organic C [Broecker and Peng, 1982]. Therefore F_{sh} and F_{ca} are in the neighborhood of 4 Gt C yr^{-1}. If most of the redissolving calcite has been formed at least a few decades ago its isotopic composition should be heavier than what is formed today by about 0.5‰ because of the isotopic change of surface waters [Druffel and Benavides, 1986]. The expected isotopic flux contribution of this component is therefore about 2 Gt‰ C yr^{-1}. We will neglect it from here on.

OCEAN UPTAKE DERIVED FROM THE OCEANIC INVENTORY

Quay et al. eliminated the terms related to gross air-sea exchange of ^{13}C by measuring the column change in the $^{13}C/^{12}C$ ratio of DIC. Their analysis can easily be cast in terms of the above equations. The gross air-sea exchange terms are eliminated by adding equations (10) and (21), which yields

$$\begin{aligned} AC_o(z_1)\int\left(\frac{d}{dt}R_o(z)\right)dz = &\\ &+F_f(R_f - R_a)\\ &-(F_{lph} - F_{lb})(\alpha_{lph} - 1)R_a\\ &+F_{lb}(R_{lb} - R^e_{lb}) - C_a\frac{d}{dt}R_a\\ &+(F_{ao} - F_{oa})(R_a - R_o(z_2))\\ &-(F_{oph} - F_{ob})(\alpha_{oph}R_{os} - R_o(z_2))\\ &+F_{ob}(R_{ob} - R^e_{ob}), \end{aligned} \tag{27}$$

where we have again used equations (12) and (22) to separate net and gross exchange terms with the terrestrial and marine organic reservoirs, and where we have neglected the calcium carbonate reservoir.

Starting from equation (27) and using $R_f - R_a \approx (\alpha_{lph} - 1)R_a$ and equation (1) to combine the first two right-hand terms of equation (27), as we did in the surface disequilibrium approach, we have

$$\begin{aligned} (F_{ao} - F_{oa})(R_f - R_o(z_2)) = &\\ &-(R_f - R_a)\frac{d}{dt}C_a + C_a\frac{d}{dt}R_a\\ &-F_{lb}(R_{lb} - R^e_{lb})\\ &+AC_o(z_1)\int\left(\frac{d}{dt}R_o(z)\right)dz\\ &+(F_{oph} - F_{ob})(\alpha_{oph}R_{os} - R_o(z_2))\\ &-F_{ob}(R_{ob} - R^e_{ob}). \end{aligned} \tag{28}$$

Equation (28) can be described as follows. First the total amount of C is found, the sum of fossil fuel combustion and terrestrial biomass changes (with the isotopic ratio characteristic of fossil fuels) injected into the atmosphere by requiring it to balance the isotopic shift in all exchange reservoirs. Once $F_f - F_{lph} + F_{lb}$ has been established, equation (1) determines how much total carbon the oceans have absorbed during the last two decades.

Integrated over a 20-year period and expressed in δ and ε notation, Equation 28 is approximately equal to

$$\begin{aligned} \left(\overline{F_{ao} - F_{oa}}\right)(\bar{\delta}_f - \bar{\delta}_o(z_2)) = &\\ &-(\bar{\delta}_f - \bar{\delta}_a)\{C_a(t_1) - C_a(t_0)\}/\Delta t\\ &+\overline{C}_a[\delta_a(t_1) - \delta_a(t_0)]/\Delta t\\ &-\overline{F}_{lb}\left(\overline{\delta_{lb} - \delta^e_{lb}}\right)\\ &+\left\{A\overline{C}_o(z_1)\int[\delta_o(t_1) - \delta_o(t_0)]dz\right\}/\Delta t\\ &+\overline{(F_{oph} - F_{ob})\varepsilon_{oph}}\\ &-\overline{F_{ob}}\left(\overline{\delta_{ob} - \delta^e_{ob}}\right), \end{aligned} \tag{29}$$

where we again have neglected $\delta_{os} - \delta_o(z_2)$ relative to ε_{oph} (see equation (26)). From here on the overbars will be dropped again from the notation, but all quantities remain 20-year averages where appropriate.

The first and second right-hand terms of equation (29) are determined by atmospheric measurements. The fourth term, $A\,C_o(z_1)\int[\delta_o(t_1)-\delta_o(t_0)]dz$, has been estimated by Quay et al. to be -208‰ m for the global oceans, from a comparison of depth profiles of $\delta^{13}C$ in similar locations between 1989-1991 and 1970 and an analogy with bomb ^{14}C uptake. The product $A\,C_o(z_2)$ equals 8.8 Gt C m^{-1} (Table 1). Quay et al. do not take account of the last two terms in equation (29). If we again adopt their estimate of $F_{lb}(\delta_{lb}-\delta^e_{lb}) = 12$ Gt ‰ C yr^{-1}, the net uptake of carbon by the oceans, $F_{ao}-F_{oa}$, turns out to have been 2.2 Gt C yr^{-1}, when reasonable values for δ_f, δ_a etc. (Table 1) are entered.

For the purpose of subsequent discussions it is convenient to define the following quantity

$$R_{PDB}F_\delta = \frac{d}{dt}\left(\int {}^{13}C_o(z)dz + {}^{13}C_{ob} + {}^{13}C_a\right) \\ -R_o(z_2)\frac{d}{dt}\left(\int C_o(z)dz + C_{ob} + C_{ca}\right). \qquad (30)$$

F_δ is the driving force for changes in the isotopic composition of the oceanic carbon reservoirs because any changes in ^{13}C that are proportional, according to the existing isotopic ratio $R_o(z_2)$, to the change in total carbon are subtracted. Such proportional changes in ^{13}C would not produce a change in the isotopic ratio of ocean waters.

From equations (30), (3), (4), (7), and (8) it is easily shown that

$$R_{PDP}F_\delta = (\alpha_{ao}R_a - R_o(z_2))F_{ao} - (\alpha_{oa}R_{os} - R_o(z_2))F_{oa}. \qquad (31)$$

We see that $R_{PDB}F_\delta$ is, in effect, the total exchange flux of ^{13}C across the air-sea interface after subtracting the portion that would not produce any change in the isotopic ratio of the oceans. From equations (21), (22), and (23) it follows that

$$R_{PDP}F_\delta = AC_o(z_1)\int\frac{d}{dt}R_o(z)dz \\ +\left(F_{oph}-F_{ob}\right)\left(\alpha_{oph}R_{os}-R_o(z_2)\right) \\ -F_{ob}\left(R_{ob}-R^e_{ob}\right), \qquad (32)$$

where we have again neglected the term $F_{ca}(R_{ca}-R^e_{ca})$. As usual, we convert to the δ notation by dividing by R_{PDB}, obtaining

$$F_\delta = AC_o(z_1)\int\frac{d}{dt}\delta_o(z)dz \\ +\left(F_{oph}-F_{ob}\right)\left(\alpha_{oph}\delta_{os}-\delta_o(z_2)\right) \\ -F_{ob}\left(\delta_{ob}-\delta^e_{ob}\right), \qquad (33)$$

where F_δ is defined as the "total oceanic $\delta^{13}C$ uptake rate". In terms of F_δ, equation (29) can be written as

$$\left(F_{ao}-F_{oa}\right)\left(\delta_f-\delta_o(z_2)\right) = \\ F_\delta - \left(\delta_f-\delta_a\right)\left\{C_a(t_1)-C_a(t_0)\right\}/\Delta t \\ +C_a\left[\delta_a(t_1)-\delta_a(t_0)\right]/\Delta t - F_{lb}\left(\delta_{lb}-\delta^e_{lb}\right). \qquad (34)$$

The solution of equation (34) is presented in graphical form in Figure 5. The equation can be viewed as a linear relationship between $F_{ao}-F_{oa}$ (horizontal axis) and F_δ (vertical axis), which equals $A\,C_o(z_1)\int[\delta_o(t_1)-\delta_o(t_0)]dz$, the total column isotopic change of DIC, if the last two terms of equation (33) are ignored. The linear relationship represents the constraint on $F_{ao}-F_{oa}$ and F_δ imposed by our knowledge of the changes in atmospheric CO_2 and $\delta^{13}C$. Line "a" represents the independent constraint imposed on the isotopic change of DIC by the measurements of Quay et al. The solution is the (circled) intersection of the equation (at 45° angle) and line "a" corresponding to $F_{ao}-F_{oa} = 2.2$ Gt C yr^{-1}. The shaded area represents the uncertainty limits assigned by Quay et al. to their estimate of $\int[\delta_o(t_1)-\delta_o(t_0)]dz$. The horizontal open double arrows represent adjustments of ±10 Gt ‰ C yr^{-1} due to changes in the atmospheric terms and/or the amount of isotopic anomaly "hidden" in the terrestrial biosphere. In that case the line representing the equation is moved parallel and horizontally to the right if F_{lb} or $\delta_{lb}-\delta^e_{lb}$ become larger. The vertical open double arrows represent potential adjustments that need to be made to the total oceanic $\delta^{13}C$ uptake corresponding to the last two terms of equation (33). The scales of Figure 5 have been chosen such that adjustments of 10 Gt ‰ C yr^{-1} cause equal displacements horizontally or vertically. For instance, line "b" corresponds to $F_{ob}(R_{ob}-R^e_{ob}) = 5$ Gt‰ C yr^{-1} (see previous section) and $F_{oph}-F_{ob} = 0$. In that case the solution would be $F_{ao}-F_{oa} = 2.4$ Gt C yr^{-1}. The intersection with the horizontal axis represents the hypothetical case in which measurements would have shown that the isotopic composition of no oceanic reservoir had changed. That would have implied that the oceans lost 1.3 Gt C yr^{-1}, and consequently, that net uptake by the terrestrial biosphere was 3.25 Gt C yr^{-1}.

The above mass balance calculations have implications for how far the sea surface and the atmosphere are out of isotopic equilibrium. We can use equation (33) to express equation (26) as

$$F_\delta = \left(F_{ao}-F_{oa}\right)\varepsilon_{oa} + F_{ao}\left(\delta_a-\delta^e_a\right), \qquad (35)$$

which can be viewed as another independent linear relation between $F_{ao}-F_{oa}$ and F_δ in which the isotopic effects associated with the net transfer of C (first right-hand term) and with the pure isotopic disequilibrium (second right-hand term) combine to give the total oceanic isotopic change. At this point, we have in effect replaced the original equations (1) - (4) by equations (1), (3), (34), and (35). The original equations (2) and (4) are two independent expressions involving the isotopic ratios and we now have two new independent expressions in their place. Equation (35) is represented by the dashed lines in Figure 5. The intercept of this linear relationship with the y-axis depends on the value of $F_{ao}(\delta_a - \delta_a^e)$ so that we actually have a collection of lines, one for each value $F_{ao}(\delta_a - \delta_a^e)$, and with all slopes determined by ε_{oa}. If we assume a value for F_{ao} of 85 Gt C yr^{-1} (±20%) based on ^{14}C observations [Broecker et al., 1986], then each line can be labeled according to the value adopted for $\delta_a - \delta_a^e$. If a different value for F_{ao} is adopted then labeled values would change accordingly. For each line the value of $\delta_a - \delta_a^e$ can be read from its intersection with the vertical axis by dividing F_δ by F_{ao}.

The sea-air isotopic disequilibrium consistent with Quay et al.'s estimate of $\int[\delta_o(t_1) - \delta_o(t_0)]dz = -208‰$ m is $\delta_a - \delta_a^e = -0.79‰$ (Figure 5). Such a value appears to be incompatible with the surface ocean isotopic data.

In the hypothetical case where the oceans lose carbon at the rate of 1.3 Gt C yr^{-1} (see above) the net loss of carbon would cause an enrichment in the oceans via kinetic fractionation effects (ε_{oa}, mostly) which would be exactly balanced by a sea-air isotopic disequilibrium of $-0.17‰$.

DISCUSSION

The apparent inconsistency between the present ocean surface $\delta^{13}C$ data and the estimate of the depth-integrated $\delta^{13}C$ change could be due to a number of causes. First of all, both data sets are still very sparse. For the depth-integrated change an attempt was made to overcome the problem through an analogy with bomb ^{14}C uptake. The analogy is only partially valid. The time dependence of the ^{14}C and $\delta^{13}C$ inputs is quite different. The former peaked strongly in 1963 and decreased thereafter, while the latter kept gradually increasing until today.

Not all oceanic exchange reservoirs were taken into account properly, namely organic carbon in the oceans and solid $CaCO_3$. Taking those exchanges into account would make the disagreement between the two methods worse. The fluxes associated with these reservoirs redistribute DIC and $\delta^{13}C$ of DIC in the water column. The analogy with bomb ^{14}C uptake by the oceans largely fails to keep track of these effects. The change in ε_{oph} due to the increase in dissolved CO_2, which is likely the largest contributor to isotopic change in the organic pool, has no ^{14}C analogy. (Fractionation effects are not only of minor importance for ^{14}C data, but all ^{14}C data are also corrected for fractionation effects.) If the size of the total pool of DOC is changing it also could exert a substantial influence on $\delta^{13}C$ of DIC through the term $(F_{oph} - F_{ob})\varepsilon_{oph}$ for which there is no ^{14}C analogy. In this case the change could push the disagreement in both directions. If the organic pool is increasing the disagreement would worsen, whereas it would become smaller if the organic pool is shrinking.

The surface $\delta^{13}C$ values may be partially reconciled with the depth $\delta^{13}C$ values if the equilibrium fractionation factors are different from those adopted here. This is probably the largest contributing factor to the uncertainty of the surface disequilibrium method. A difference of 0.2‰ in the equilibrium fractionation leads to a change in the derived net uptake of C by the oceans of almost 1 Gt C yr^{-1} (Figure 4). The uncertainty of the large scale average sea surface temperatures is of the order of 0.1°K [Shea et al., 1992; Reynolds, 1988], too small to be important in this context. The ^{14}C calibration of the globally averaged gross air-sea exchange rate F_{ao} does not leave room for a major adjustment. A different local relationship between the velocity of air-sea transfer and wind speed (or other factors) would give a different weighting of the local disequilibria in building up the globally averaged disequilibrium. For instance, the global disequilibrium is increased by 0.11‰ if no weighting at all is applied (Table 3). In that case the tropical oceans receive relatively more emphasis in the global average.

The $\delta^{13}C$ values may also be partially reconciled if a uniform calibration offset is assumed to exist between the old and the modern $\delta^{13}C$ data. Quay et al.'s data would imply that the disequilibrium across the air-sea interface has changed little in 20 years while the atmospheric values fell by 0.4‰. Carbon cycle model calculations, on the other hand, tend to show that the change in $\delta^{13}C$ of DIC in the ocean surface is half as much as the change of $\delta^{13}C$ in the atmosphere (e.g., Table 12 in the work by Keeling et al. [1989]). Assuming, for the sake of argument, that the modern disequilibrium should be increased by 0.05‰ the 1970-1990 average net oceanic uptake would increase by 0.12 Gt C yr^{-1} as derived from the surface values. Consistent with the assumption of a calibration offset between the new and the old surface data we would now also have to assume that the true modern deep water values are heavier than Quay's by 0.05‰. Employing, as Quay et al. did, the correlation between the ocean uptake of ^{14}C and $\delta^{13}C$ the global estimate of the uptake of the isotopic anomaly would decrease by about 60‰ m. The reason is that some of the $\delta^{13}C$ profiles are very deep, in which case the assumed offset of 0.05‰ is integrated over thousands of meters. The sensitivity of the derived value of the net uptake of C by the oceans to such a change is high. A change of 60‰ m leads to a change in F_δ of 60*8.8/20 = 26.4 Gt ‰ C yr^{-1}, which in turn decreases $F_{ao} - F_{oa}$ by 0.9 Gt C yr^{-1} (Figure 5). If the calibration offset is as large as 0.1‰ the correlation between the accumulated ^{14}C and $\delta^{13}C$ uptakes would disappear altogether. This potential additional source of error in the estimates of the depth-integrated $\delta^{13}C$ uptake was not considered by Quay et al., who based their uncertainty estimate on the scatter of the values for seven depth profiles, although they omitted one pair of profiles from their comparison. Kroopnick estimates that the accuracy of his $\delta^{13}C$ data is ±0.1‰ [GEOSECS Atlas, 1987], but Quay et al. state that the uncertainty of those measurements is ±0.04‰, based on the reproducibility of replicate analyses.

A not very likely possibility to partially reconcile the surface and the deep $\delta^{13}C$ values is to assume that ε_{oa} for the real ocean is different from the kinetic fractionation measured in the laboratory by Schönleber [1976], O'Leary

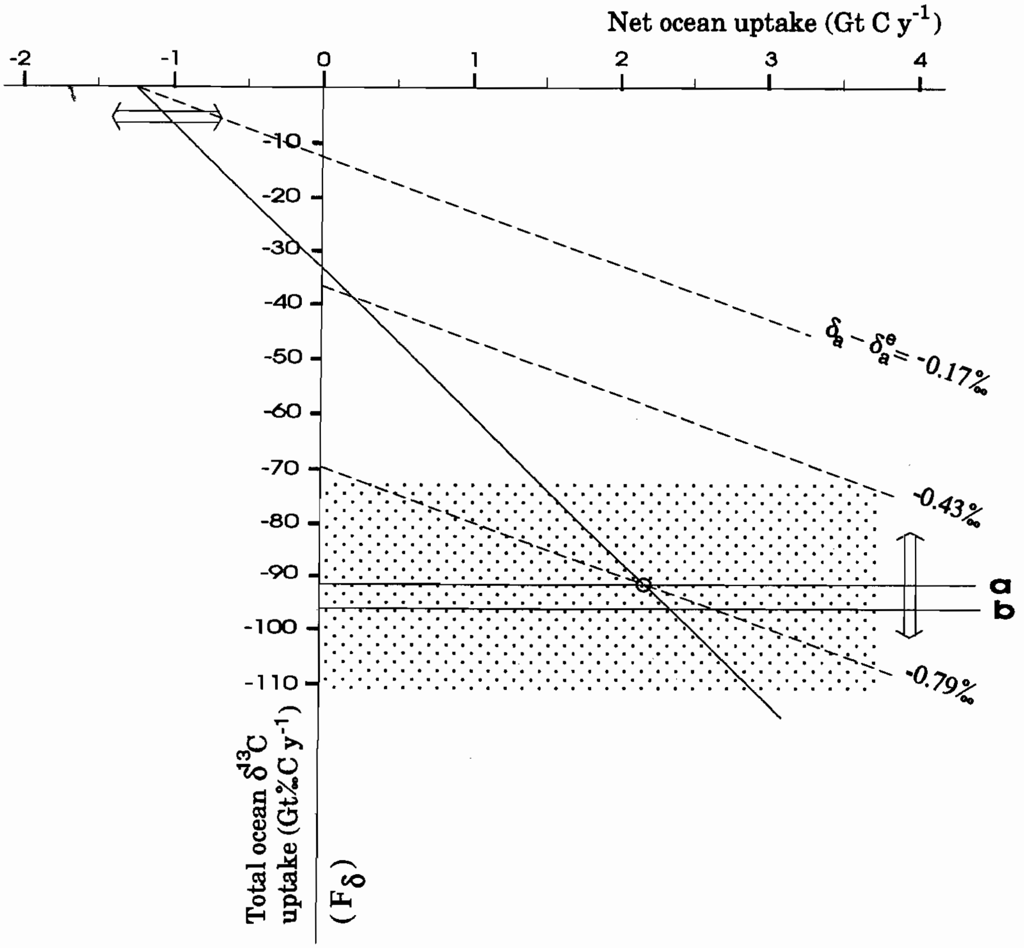

Fig. 5. Graphical representation of equations (34) and (35) as relationships between net ocean uptake of carbon ($F_{ao} - F_{oa}$) and depth-integrated total δ^{13}C change in the oceans ($F_δ$). See main text for discussion.

[1984], Inoue and Sugimura [1985], and Wanninkhof [1985]. This would cause the dashed lines in Figure 5, representing equation (35), to have a steeper slope. The value of $ε_{oa}$ is linked to $ε_{ao}$ because the observed equilibrium fractionation is the quotient of the two kinetic fractionation factors (equation (11)). Four experimental determinations of the kinetic fractionation obtained similar results, but the possibility can still not be entirely dismissed for the following reason. The ^{14}C calibrated global average air-sea exchange of CO_2 tends to be higher than many experiments based on inert gas behavior would suggest. There could be a process in the real ocean affecting the transfer of CO_2 that has thus far been overlooked or has not been properly quantified and/or simulated in the laboratory. If so, its contribution to isotopic fractionation would still have to be determined.

The implications of any revision of a globally averaged value of $ε_{ao}$ would be profound. The deconvolution of the historical δ^{13}C and CO_2 records which yielded a history of biomass loss [e.g., Peng et al., 1983] would have to be substantially revised. We might (partially) lose the isotopic signature distinguishing terrestrial photosynthetic uptake from ocean uptake. A revision of $ε_{ao}$ is not likely, however. First, the revision would have to be fairly large to have any impact. Secondly, a revised (more negative) value would make it almost impossible to explain the observed decrease of atmospheric δ^{13}C values toward high northern latitudes [Keeling et al., 1989; Francey et al., 1990]. Significant CO_2 uptake by any process at temperate northern latitudes would then be nearly ruled out because the fractionation during uptake would enrich the CO_2 left behind in the atmosphere. This would then be inconsistent with the atmospheric CO_2

data, which clearly imply that there has to be a substantial sink of CO$_2$ at high to temperate latitudes.

CONCLUSIONS

The apparent disagreement between the surface disequilibrium method and the oceanic inventory method as well as substantial uncertainties in the application of both methods themselves preclude at this time any firm conclusions on bounds set by the oceanic isotope data on the ocean uptake of CO$_2$.

The oceanic inventory method has difficulty to properly take account of biologically driven exchange reservoirs within the ocean. It will also be hard to remove lingering doubts about any calibration offsets of the old measurements with respect to the new measurements.

The surface disequilibrium method implicitly takes all internal ocean redistribution of C and ^{13}C into account. If, for example, the pool of organic matter is becoming more depleted ("lighter") in ^{13}C the surface ocean δ^{13}C of DIC will become heavier, thus increasing the disequilibrium between the air and the ocean surface. A further advantage is that today's measurements by themselves determine the disequilibrium. The disadvantage of this method is that it has to rely on estimates of air-sea gas exchange, and that there is too much uncertainty in the equilibrium fractionation factors. The latter problem can be solved through additional laboratory measurements of the fractionation, and the former through additional air-sea gas exchange measurements.

Both isotopic methods share the problem of the insufficiently known amount of isotopic exchange with the terrestrial biosphere. They both also are very demanding with respect to calibration and standardization, and the elimination of any systematic measurement artifacts. Accuracy to a few hundredths of a permil is required. The amount of δ^{13}C data available for our purpose is still very small for the application of either approach.

The ^{13}C methods have one important strength. The oceans absorb the δ^{13}C signal more readily than CO$_2$ itself. The reason is that the uptake of the isotopic signal is not "hampered", like CO$_2$ itself, by the quick adjustment of pCO$_2$ in the oceans in which a one percent increase in DIC causes a ten percent increase in pCO$_2$ (the "Revelle factor"; see, e.g., Broecker and Peng [1982]). Isotopic exchange takes place independently of any net change of total carbon.

The signal-to-noise (S/N) ratio for the detection of a δ^{13}C anomaly is better than for uptake of total carbon by the oceans. The δ^{13}C signal accumulated each year is of the order of 10‰ m (208‰ m in 20 years). The accumulated (integrated over depth) carbon increase is about 1.5 Gt C yr^{-1}, or 0.36 mmole kg^{-1} m yr^{-1}. Detection limits for these signals are approximately 0.02‰ and 0.002 mmole kg^{-1} respectively, taking into account only instrumental, not ocean variability. Dividing one by the other yields 500 m yr^{-1} and 180 m yr^{-1} respectively. We could call these depths the "resolution of the penetration depth", the depth over which the signal could be spread and still be detected. If the signal is to be found over a depth range of 500 m, then the comparative instrumental S/N in one year would be 1 for the isotopes and 0.36 for DIC.

The situation for the detection of the surface disequilibrium is much better for ^{13}C than for pCO2. With the ^{14}C-calibrated rate of air-sea transfer, the global average surface ΔpCO$_2$ required for the oceans to absorb 1.5 Gt C yr^{-1} is 5.3 μatm. The detection limit is in the neighborhood of 1 μatm. The isotopic disequilibrium is 0.46‰, with a detection limit of 0.02‰. The observed seasonal and spatial range of variation of ΔpCO$_2$ in ocean surface waters is up to 200 μatm, while for the isotopes it is about 1‰.

Acknowledgments. Chris Field had earlier pointed out to us the importance of isotopic exchange with the terrestrial biosphere in determining the latitudinal isotopic gradient of atmospheric CO$_2$. Rik Wanninkhof discussed experiments measuring isotopic fractionation during air-sea exchange. Martin Manning gave this paper a critical reading which resulted in many clarifications. Paul Quay discussed uncertainties associated with use of the surface isotopic data. This research has been supported in part by the Atmospheric Chemistry and the Ocean-Atmosphere Carbon Flux Projects of the Climate and Global Change Program of the National Oceanic and Atmospheric Administration.

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(Received July 27, 1992;
revised December 17, 1992;
accepted January 4, 1993.)