Effect of the nonlinearity of the carbonate system on partial pressure of carbon dioxide in the oceans

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Abstract. Partial pressure of CO_2 is a nonlinear function of several seawater properties. Due to the nonlinearity in this relationship, the partial pressure of a uniform ocean would be different from that of a nonuniform ocean with the same bulk seawater properties. Assuming uniformity of seawater properties at some temporal and spatial scales in carbon models leads to systematic errors in partial pressure of CO_2. In this paper we evaluate the magnitude of these errors. We partition the Geochemical Ocean Sections Study and Transient Tracers in the Oceans data according to the horizontal structure of several box models from the literature. Our results suggest that assumption of uniformity at large scales leads to underestimation of global surface ocean partial pressure of CO_2 by at least 3-12 μatm. Nonlinear effects also introduce systematic errors in the buffer factor estimated from bulk seawater properties. We find the standard deviation of partial pressure of CO_2 to be an indicator of the magnitude of the nonlinear effects. We discuss the implications of these errors for some conclusions drawn from carbon models. Biogeochemical processes, such as mixing, gas exchange, or biological activity, influence the distribution of the seawater properties. A shift in spatial or temporal patterns of these processes can modify the nonuniformity of the seawater properties and thus alter the partial pressure of the surface waters, even if the mean intensities of the processes remain constant.

1. Introduction

The role of the oceans in the global carbon cycle has attracted much interest in recent years. Some aspects of this problem have still received little attention. In this paper we examine, theoretically and through data analysis, how the nonlinearity of the carbonate system may modify the partial pressure of CO_2 of the surface ocean and the flux of carbon between the ocean and the atmosphere.

The partial pressure of CO_2 in the oceans is controlled by several seawater properties: temperature, salinity, total alkalinity, dissolved inorganic carbon, and, to a smaller extent, by other components such as concentration of silicate and phosphate. A decrease in alkalinity or an increase in temperature or dissolved inorganic carbon tends to raise the partial pressure quasi-exponentially. An increase in salinity, silicate or phosphate concentration has a similar effect, albeit much less pronounced.

Due to the nonlinearities in these relationships, the average partial pressure of a set of seawater samples is usually different from the partial pressure calculated from the average values of the controlling seawater properties. For example, if we consider two water masses with distinct temperatures, the average partial pressure of the two water masses would be different from that associated with their average temperature. The nonlinearity of the carbonate system implies that the partial pressure of a uniform ocean would be different from that of a nonuniform ocean with the same bulk properties as the uniform ocean. As the transfer of CO_2 through the ocean-atmosphere interface is driven by the difference in partial pressure of CO_2 across this interface, an alteration of partial pressure in surface waters would affect the net flux of carbon between the ocean and the atmosphere.

Various biogeochemical processes affect the properties of the surface layer and, through them, the uptake of atmospheric carbon. Usually, the role of a given process in this uptake is evaluated based on area-average or time-average properties of seawater. In such conditions, only the mean intensity of the process affects the results. Our work underscores the importance of the spatial and temporal patterns of a biogeochemical process. Changes in these patterns, such as an alteration of timing and location of phytoplankton blooms, may increase or decrease the nonuniformity in the distribution of seawater properties. As a result, the overall partial

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pressure of CO_2 of the ocean may be altered. Therefore a change in the temporal or spatial pattern of a geochemical process, even without any change in the mean intensity of this process, could alter the potential of the ocean to act as a sink or a source of atmospheric CO_2.

The nonlinearity of the carbonate system also affects the results of the carbon models. These models usually represent the ocean by a small number of boxes, and it is assumed that the seawater properties are horizontally uniform within each box. This implies that the nonlinearity of the carbonate system is ignored within each box, and consequently the partial pressures estimated from the average properties of each box are biased with respect to the real ocean.

In this paper we try to assess the magnitude of the error incurred when the nonlinearities of the carbonate system are ignored. We concentrate on the surface waters which are in direct contact with the atmosphere. We use the horizontal structure of existing carbon models to partition the data into one or more boxes and to compare the results of simple models with those of more complex models. Our results show that incorporation of nonlinear effects leads to an increase in the estimated partial pressure of CO_2. We examine some implications of these results for carbon cycle models.

Accounting for the nonlinearity of the carbonate system may modify the estimates of oceanic uptake rate of anthropogenic CO_2. When air-sea CO_2 flux is estimated directly from the difference in partial pressure between the atmosphere and the surface ocean, errors incurred in neglecting the nonlinear effects translate into errors in the estimate of the flux. If the ice-free area of the ocean is on average $340 \times 10^{12} \, m^2$, and the global average gas-transfer coefficient is $0.067 \, mol \, CO_2 \, m^{-2} \, yr^{-1} \, \mu atm^{-1}$ [*Tans et al.*, 1990], then a difference of 1 μatm in the partial pressure, at the global scale, would lead to a change in the estimated carbon flux of about $0.27 \, Gt \, C \, yr^{-1}$. This value is equivalent to 6% of the anthropogenic emission in the mid-1970s (the period from which most of the data used in this work originates).

In box models of the transient response of the ocean to the anthropogenic emissions of CO_2, the consequences of neglecting the nonlinear effect are more difficult to quantify. In these models the final results are influenced by dynamic interactions between carbon reservoirs in the atmosphere, the mixed layer and the deep ocean; hence the consequences of nonlinearity would depend on the assumptions used in the model and the structure of the model. We compute the error caused by neglecting nonlinear effects in some simplified models and examine the possible consequences of these effects for more realistic models.

The nonlinear effect may also modify results of diagnostic box models. These models try to deduce the rates of mixing and of biochemical processes using a set of physical and biochemical constraints [*Rintoul*, 1992]. Partial pressure of CO_2 is one such constraint; hence accounting for the nonlinear effects may modify conclusions drawn from these models as well.

2. Data

2.1. Geochemical Ocean Sections Study Data

To estimate the nonlinear effects we used mainly the Geochemical Ocean Sections Study (GEOSECS) data [*Bainbridge*, 1981; *Broecker et al.*, 1982; *Weiss et al.*, 1983]. This is the only global carbon data set available to date, and it has been widely used in studies of the global carbon cycle.

The GEOSECS data do not cover the whole ocean and represent mostly the summer seasons in both hemispheres [*Takahashi et al.*, 1981a], thus our estimates of the nonlinear effects refer to the idealized "GEOSECS ocean" and, as discussed later, probably represent a lower bound for the nonlinear effects in the real ocean.

We are interested in the nonlinear effects in the mixed layer, as the waters in this layer are in direct contact with the atmosphere. To evaluate the properties of these waters we used the GEOSECS data from the top 49 m of the water column, corresponding to the depth ranges 0-24 m and 24-49 m in the GEOSECS carbonate data summary of *Takahashi et al.* [1981b].

We chose the 0-49 m depth range as a compromise between minimizing the influence of the deep waters and retaining a large number of observations. Using data from a greater depth range (for instance, one corresponding to a mixed layer of 75 m used in the majority of carbon models) would introduce the risk of admitting, in areas where the mixed layer is shallow, observations that are strongly influenced by the properties of deep waters, thus being unrepresentative of waters in direct contact with the atmosphere. Using a smaller depth range in our analysis, on the other hand, would reduce the already sparse coverage of some oceanic regions. For instance, in the North Indian Ocean, samples from depths 50-74 m had an average partial pressure of CO_2 higher by 124 μatm than the samples from 0-49 m. Incorporation of the samples from the 50-74 m layer would strongly affect both the average and the variance in seawater properties within this region. Restriction of the analysis to observations from the depth range of 0-24 m, on the other hand, would leave only three samples in the whole region.

Following *Takahashi et al.* [1981b], we partitioned the GEOSECS data into 10 regions: each ocean was divided into a northern section (north of 10°N), an equatorial section (10°N-10°S), and a southern section (10-50°S); all waters south of 50°S were pooled into the Antarctic region (Table 1). The regional averages of variables controlling partial pressure of CO_2 calculated here may differ, however, from those of *Takahashi et al.* [1981b], as we admitted only those observations in which the complete set of the controlling variables was measured, while Takahashi et al. used all the available data.

The area weights for the regions (Table 1) are based on *Moiseev* [1971]. The area of the waters south of 50°S was decreased by $4 \times 10^{12} \, m^2$, corresponding to the minimum range of the Antarctic sea ice [*Zwally et*

Table 1. Partial Pressure of CO_2 Above 300 μatm and the Nonlinear Contribution at the Regional Scale

Regions	Number of Samples N_r	Area Weight a_r	Partial Pressure of CO_2		Nonlinear Contribution c_r
			Nonuniform Case $\overline{p}_r$	Uniform Case $p(\overline{T}_r, \overline{S}_r, ..)$	
GEOSECS, Atlantic:					
I, 10°N-36°N	25	0.067	32.5	30.9	1.6
II, 10°S-10°N	18	0.040	57.4	57.0	0.4
III, 10°S-50°S	34	0.087	28.5	21.5	7.0
GEOSECS, Pacific:					
IV, 10°N-53°N	48	0.179	24.8	13.9	10.9
V, 10°S-10°N	15	0.127	79.0	76.6	2.4
VI, 10°S-50°S	38	0.183	19.6	16.3	3.3
GEOSECS, Indian:					
VII, North of 10°N	6	0.016	69.0	68.8	0.2
VIII, 10°S-10°N	26	0.044	60.5	60.5	0.0
IX, 10°S-50°S	30	0.126	35.8	33.3	2.5
GEOSECS, Antarctic:					
X, South of 50°S	38	0.131	19.8	16.4	3.4
GEOSECS global area-weighted average			35.9	31.5	4.4
TTO, Atlantic:					
15°N-80°N	320		-8.1	-18.7	10.6
- 15°N-50°N	132		30.8	24.3	6.5
- 50°N-80°N	188		-35.4	-40.3	4.9

Columns contain latitudinal range of regions, the number of samples available within a region, regional area weights (computed as a fraction of the area of the GEOSECS ocean, such that $\sum a_r = 1$), the partial pressures [μatm] and nonlinear contribution [μatm] computed from the data within each region. The GEOSECS data were partitioned into 10 regions as given by *Takahashi et al.* [1981b].

al., 1983]. We chose the minimum value rather than the average sea ice range because, as already indicated, the GEOSECS represents oceanic properties in the warm seasons.

2.2. Transient Tracers in the Oceans Data

The analysis based on the GEOSECS data was supplemented by examination of some data from the Transient Tracers in the Oceans (TTO) cruises. We applied the TTO data to obtain an independent estimate of the nonlinear contribution in the North Atlantic, the region poorly covered during the GEOSECS cruises. First, we treated all the TTO data as belonging to a single region, then we partitioned the data along the 50°N latitude into Arctic and subtropical regions.

We compared the North Atlantic TTO values with those computed on the basis of the GEOSECS data and applied them to recalculate the nonlinear effects at the global scale (appendix). To evaluate whether the nonlinear contribution may be significant at local scales comparable with the resolution of ocean general circulation models (OGCM), we partitioned the TTO data into subsets corresponding to a 3.5° x 3.5° grid and calculated the nonlinear contribution associated with averaging samples within these subsets.

3. Nonlinear Effects on Partial Pressure of CO$_2$

3.1. Terms

To describe the consequences of the nonlinearity of the carbon system on the oceanic partial pressure of CO$_2$ we use the term "nonlinear effects." Whenever necessary we make a distinction between "nonlinear contribution" and "nonlinear error." The first term refers to the difference in partial pressure between the real, nonuniform, waters and the waters assumed to be uniform at the scale of interest. Nonlinear error, on the other hand, reflects the difference between the real ocean and a partially uniform ocean. A partially uniform ocean is made up of a number of parts, each of which is assumed to be internally uniform, but distinct from the others. The word "error" is used to underscore the application of this quantity in carbon models. Carbon models approximate the real ocean as a set of boxes, each of which is assumed to be uniform. As a result of ignoring nonlinearity within the boxes, the estimates of partial pressure of CO$_2$ from the model are subject to a systematic error.

3.2. The Nonlinear Contribution

We define the nonlinear contribution c as the difference between the average partial pressure of CO_2 of a nonuniform body of water and the partial pressure that the same body of water would have if it were uniform, with the same bulk composition as the nonuniform waters.

If we denote the average value of a property X as $\overline{X}$, the nonlinear contribution c may be expressed as

$$c = \overline{p(T, S, A, C, Si, P)} - p(\overline{T}, \overline{S}, \overline{A}, \overline{C}, \overline{Si}, \overline{P}), \quad (1)$$

where p is the partial pressure of CO_2, T is temperature, S stands for salinity, A is alkalinity, and C, Si and P stand for the concentration of dissolved inorganic carbon, silicate and phosphate, respectively. A glossary of the mathematical notation used in this paper appears in the notation section. The first term on the right-hand side represents the partial pressure for the nonuniform case, which is computed as the average of partial pressures associated with each sample, which in turn are calculated from the individual sample values of the controlling variables. The second term is the partial pressure for the uniform case, which is computed by assuming that the seawater properties controlling the partial pressure are uniform within the body of water considered, and equal to the average values of these properties. Note that this approach assumes that the available data are truly representative of the real nonuniform ocean.

As an example, the nonlinear contribution for the case when p is a function of only temperature (with remaining seawater properties kept at average GEO-SECS values) is shown in Figure 1a. The two curves in the figure correspond to the carbonic acid dissociation constants of *Mehrbach et al.* [1973] and of *Goyet and Poisson*, [1989], used in the scheme of *Peng et al.* [1987]. Let us consider two observations with temperatures T_I and T_J, and corresponding partial pressures p_I and p_J. The nonlinear contribution c, graphically represented here as a vector XX', is the difference between the average of the partial pressures associated with the individual values of temperature and the partial pressure computed for the average temperature.

Let us divide the GEOSECS ocean into 10 regions [*Takahashi et al.*, 1981b], each representing a certain oceanographic regime (see Table 1). Based on the assumption of equal weight to every observation in a region, the average of a property X for region r, $\overline{X}_r$, is given by

$$\overline{X}_r = \frac{\sum_{i=1}^{K_r} X_i}{K_r}, \quad (2)$$

where K_r is the number of samples in region r. The nonlinear contribution at the regional scale is given by

$$c_r = \overline{p_r} - p\left(\overline{T}_r, \overline{S}_r, ...\right) = \frac{\sum p_i(T_i, S_i, ...)}{K_r}$$

$$-p\left(\frac{\sum T_i}{K_r}, \frac{\sum S_i}{K_r}, ...\right). \quad (3)$$
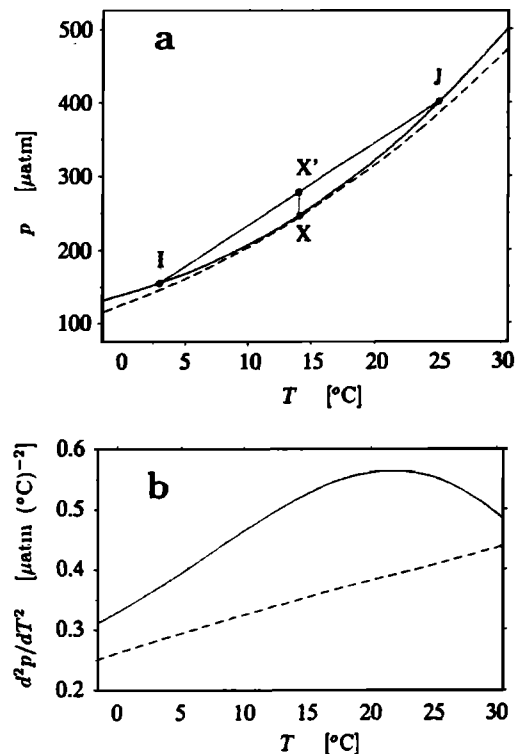
Figure 1. (a) Partial pressure of CO_2 (p) as a function of temperature (T). Note the nonlinearity of this relation: $p_{X'} = (p_I + p_J)/2 > p[(T_I + T_J)/2] = p_X$. (b) Second derivative of p with respect to T (d^2p/dT^2) as a function of T. Solid and dashed lines represent results obtained using dissociation constants of *Mehrbach et al.* [1973] and of *Goyet and Poisson* [1989], respectively. Alkalinity, dissolved inorganic carbon, silicate, and phosphate concentrations are assumed to be average values in the analyzed GEOSECS data: 2320 $\mu eq\,kg^{-1}$, 2010 $\mu mol\,kg^{-1}$, 6 $\mu mol\,kg^{-1}$, and 0.4 $\mu mol\,kg^{-1}$, respectively.

The same rules would apply to computation of the nonlinear contribution in the case of multiple observations within a small grid (local nonlinear contribution), and time series observations at a single station (temporal nonlinear contribution).

If data from two or more regions are combined into a "box," then we have to account for different surface areas associated with regions composing such a box. We assign to each region an area weight, a_r, equal to the fraction of the area of the GEOSECS ocean occupied by region r. Then, the average value of a property X in box b, $\overline{X}_b$, is given by

$$\overline{X}_b = \frac{\sum_{r=1}^{K_b}(a_r\overline{X}_r)}{a_b}, \quad (4)$$

where K_b denotes the total number of regions belonging to box b and a_b is the area weight of box b: $a_b = \sum_{r=1}^{K_b} a_r$.

The nonlinear contribution associated with box b, c_b, may then be calculated from

$$c_b = \bar{p}_b - p(\bar{T}_b, \bar{S}_b, ...) = \frac{\sum_{r=1}^{K_b}(a_r \bar{p}_r)}{a_b}$$

$$-p\left(\frac{\sum_{r=1}^{K_b}(a_r \bar{T}_r)}{a_b}, \frac{\sum_{r=1}^{K_b}(a_r \bar{S}_r)}{a_b}, ...\right). \quad (5)$$

3.3. The Nonlinear Errors

In box models the global ocean is divided into a finite number of horizontally uniform boxes. Within each box the nonlinear contribution is neglected, because p is estimated from the average seawater properties. The estimates of the global partial pressure from box models are therefore subject to the nonlinear error E. We define E as the difference between p_t, the true partial pressure in the global surface ocean, and p_e, the partial pressure estimated for a model ocean composed of the uniform boxes:

$$E = p_t - p_e. \quad (6)$$

Therefore for a model representing the global ocean as a sum of B boxes:

$$E = \sum_{b=1}^{B}(a_b \bar{p}_b) - \sum_{b=1}^{B}\left(a_b p(\bar{T}_b, \bar{S}_b, ...)\right). \quad (7a)$$

Transforming (7a) one may also express E as the area weighted average of the nonlinear contributions associated with each box:

$$E = \sum_{b=1}^{B} a_b\left(\bar{p}_b - p(\bar{T}_b, \bar{S}_b, ...)\right) = \sum_{b=1}^{B}(a_b c_b). \quad (7b)$$

Note that the weights are assigned such that $\sum_{b=1}^{B} a_b = 1$.

Although we defined the nonlinear error with respect to the global scale, similar computations may be performed at various smaller scales, as long as the analyzed area is represented as a sum of distinct boxes.

In the next section we examine the sensitivity of p to the nonlinear effects, and then estimate E for various models that have been used in the past. The models differ from each other in the number of boxes used, and in the demarcation of each box.

4. Partial Pressure of CO2 in the Surface Ocean

4.1. Sensitivity Analysis

The nonlinear effects (both the nonlinear contribution c and the nonlinear error E) depend on six properties of seawater which control the partial pressure of carbon dioxide. The nonlinear dependence on so many variables makes it difficult to interpret the behavior of c and E. To obtain an insight we computed c for several idealized cases. Selected properties were varied systematically within the ranges found in the surface waters of the world oceans, while the remaining properties were held constant at average values in the analyzed GEO-SECS data.

When the partial pressure p is plotted as a function of

one variable at a time, it is seen that, whatever be the selected variable, p is always a convex function (i.e., the line segment between any two points of its graph lies on or above the graph). Convexity of the function ensures that nonlinear contribution is positive.

As an example, we discuss p as a function of temperature T. Figure 1a shows that p is a convex function of T, and, consequently, the nonlinear contribution (vector XX') is always positive. It is also clear from the figure that, with increasing difference between T_I and T_J, the nonlinear contribution increases as well.

To examine the potential for nonlinear effects, we computed $d^2p(T)/dT^2$ as a measure of convexity of the function $p(T)$ (Figure 1b). We found that when the dissociation constants of Mehrbach et al. [1973] are used, $d^2p(T)/dT^2$ reaches maximum at 22°C. Therefore if the partial pressure is controlled mainly by temperature, then the nonlinear effect will be strongest at 22°C.

Calculations with the dissociation constants of carbonic acid of Goyet and Poisson [1989] produced lower values of p than those in which the constants of Mehrbach et al. were used. The plot of $p(T)$ in this formulation has a weaker curvature. Although the value of $d^2p(T)/dT^2$ increases almost linearly with temperature, at no point does it exceed the values calculated previously using the dissociation constants of Mehrbach et al. [1973]. One may expect that the nonlinear effects associated with variations in temperature are weaker when the constants of Goyet and Poisson are applied.

To analyze further the relation between nonlinear contribution and variability of temperature, we computed c for hypothetical data, in which the temperature distribution was assumed to follow a Gaussian distribution (Figure 2). The nonlinear contribution increases with standard deviation of temperature. It also increases initially with mean temperature, but this trend is reversed at higher temperatures. This reversal is consistent with our previous results showing a decline of $d^2p(T)/dT^2$ for temperatures higher than 22°C.

Although some special cases can be conceived wherein the variability in p in natural waters is dominated by
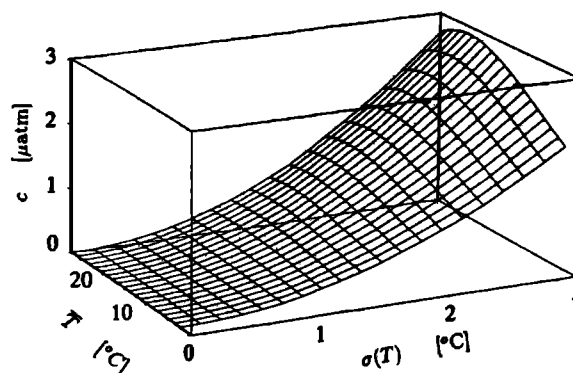

Figure 2. The nonlinear contribution (c) associated with normal distribution of temperature, as a function of its mean ($\bar{T}$) and standard deviation ($\sigma(T)$). Partial pressure of CO2 is assumed to be a function of temperature only. Alkalinity, dissolved inorganic carbon, silicate, and phosphate concentrations are as in Figure 1.

changes in a single seawater property, this is not true in general, and the computation of c usually has to take into account simultaneous variations in more than one variable. We examine the case when p is controlled by temperature and dissolved inorganic carbon.

Models of the carbon cycle often neglect the effect of silicate and phosphate [e.g., *Knox and McElroy*, 1984; *Volk and Liu*, 1988]. It is also a common practice to consider the seawater composition when all the samples are brought to a common salinity. This procedure removes most of the variability in alkalinity, which primarily depends on changes in salinity. Under these simplifying assumptions, p would be mainly a function of just two variables, temperature T and dissolved inorganic carbon C (Figure 3). Note that isolines of p in the C-T coordinate frame are not equally spaced. In waters with high p, even small changes in T or C result in large changes of p and in large values of nonlinear contribution.

Three cases are shown in Figure 3. In the first case (K-L), the differences in T and in C are 10°C and 95 μmol kg^{-1}, respectively, the nonlinear contribution is 36 μatm. In the second case, despite much larger spread in T and C (24°C and 220 μmol kg^{-1}, respectively), p is constant and nonlinear contribution is smaller (10 μatm). In the third case (M-N), with the differences in T and C identical to the first case, but with both values of C moved toward higher concentrations, the difference in p is much larger, and the nonlinear contribution is doubled (75 μatm). Therefore variability in C or T alone was not a good indicator of the nonlinear contribution in these cases. On the other hand, the differences in p (300, 0 and 600 μatm, respectively) were closely related to the nonlinear contribution (36, 10, and 75 μatm, respectively). Therefore variability of the partial pressure seems to be a better predictor of nonlinear contribution, than variability in either T or C. We examine this relation further using the actual data in section 4.3.

Another conclusion drawn from Figure 3 is that the nonlinear effects may be stronger in the future than those estimated for the present conditions. An increasing atmospheric concentration of CO_2 forces the partial pressure of the surface ocean toward higher values, mainly through an increase of inorganic carbon concentration in the surface waters. In such an environment the same variability in T and C may result in stronger nonlinear effects than in the waters with lower C (as seen in the comparison of case M-N with case K-L).

When the nonlinear contribution was examined as a function of other variables taken in pairs, similar tendencies were observed: large nonlinear effects were associated with large variations in p. Similarly, when the variations in p were small so were values of c, sometimes even acquiring slightly negative values, as some combinations of temperature with salinity or alkalinity give rise to slightly concave isolines of p. The results of these sensitivity analyses may be used to interpret the data.

4.2. Nonlinear Contribution at Small Spatial Scales

We used the TTO data to study the nonlinear contribution at scales comparable with the resolution of the three-dimensional (3-D) carbon models. The current carbon models employ 3-D oceanic general cir-
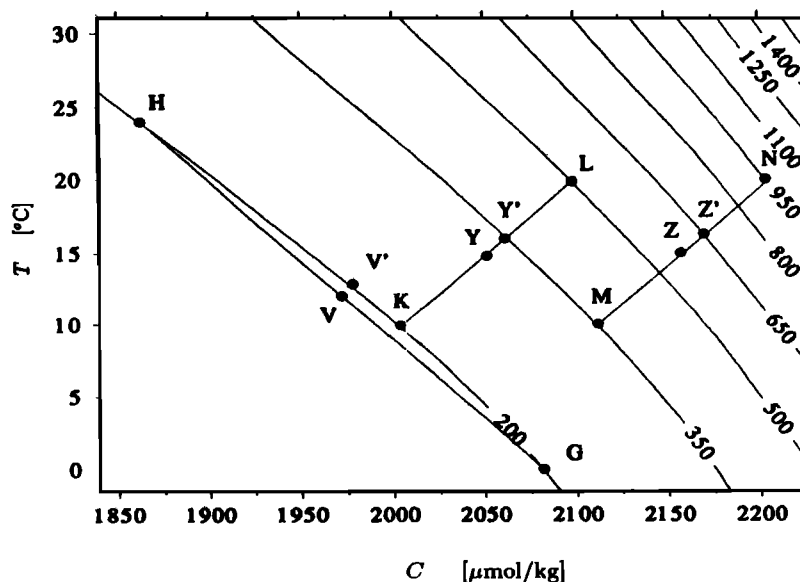
Figure 3. Partial pressure of CO_2 (p) as a function of temperature (T) and dissolved inorganic carbon (C). Note the nonlinearities of this relation: (G-H): $p_{V'} = (p_G + p_H)/2 > p[(T_G + T_H)/2, (C_G + C_H)/2] = p_V$; (K-L): $p_{Y'} = (p_K + p_L)/2 > p[(T_K + T_L)/2, (C_K + C_L)/2] = p_Y$; (M-N): $p_{Z'} = (p_M + p_N)/2 > p[(T_M + T_N)/2, (C_M + C_N)/2] = p_Z$. Alkalinity, silicate, and phosphate concentrations are as in Figure 1.

culation models (OGCM) with a typical resolution of several degrees (for example, 3.75° east-west and 4.5° north-south for the Princeton model [*Toggweiler et al.*, 1989; *Sarmiento et al.*, 1992] and 3.5° x 3.5° (or, in some applications, more) for the Hamburg model [*Maier-Reimer and Hasselmann*, 1987]).

In the subsets of the TTO data covering area comparable to the 3.5° x 3.5° grid we found the nonlinear contribution to vary from 0 up to 11 μatm. The largest value was associated with a grid centered at 42°N, 59°W (TTO stations 243-250). When the depth range was limited to the top 25 m, to avoid incorporation of the samples with properties affected by deep waters, the nonlinear contribution associated with this grid was still 5 μatm. This indicates that even 3-D models with high horizontal resolution are not free from the errors caused by the nonlinearities in the carbonate system, particularly given that there may also be a temporal component of nonuniformity, present even if the grid size was reduced to a single station.

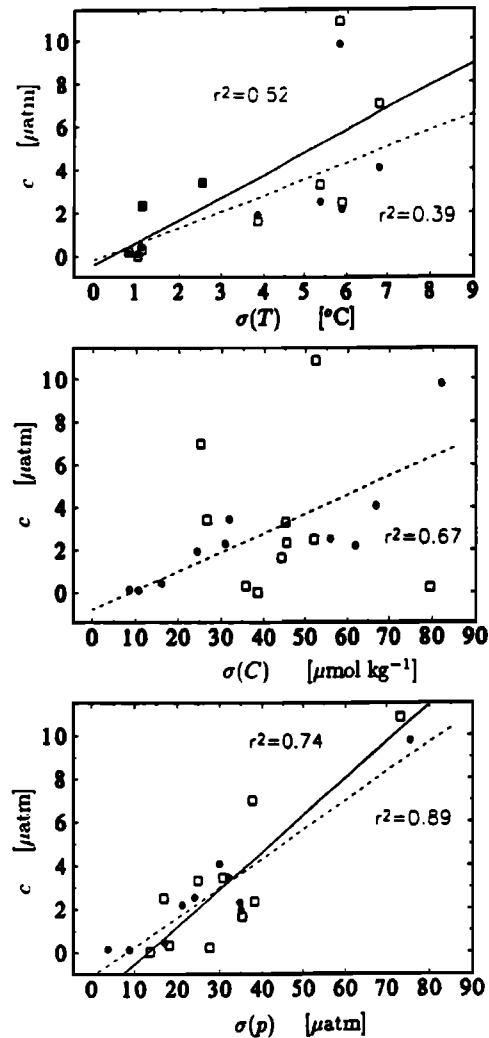## 4.3. Nonlinear Contribution at the Regional Scale

Table 1 summarizes our estimates of the nonlinear contribution for the 10 oceanic regions computed using the GEOSECS data. The regional values of the contribution ranged from 0.03 μatm in the equatorial Indian Ocean to 10.9 μatm in the North Pacific region. The equatorial Indian Ocean also had the lowest standard deviation in p, while the North Pacific region had the highest one.

We further explored this matter by plotting the nonlinear contribution as a function of standard deviation of seawater properties within the 10 regions specified in Table 1 (Figure 4). Results of linear regression are in agreement with conclusions drawn from theoretical considerations. The nonlinear contribution was most closely correlated with standard deviation of p. The coefficient of determination r^2, corresponding to standard deviation from direct measurements and from the salinity-standardized values, was 0.74 and 0.89, respectively.

We also calculated the nonlinear contribution in the TTO data from the North Atlantic (Table 1). When all the TTO data were used, the nonlinear contribution was 10.6 μatm. When only the data south of 50°N latitude were used, the nonlinear contribution was 6.5 μatm. Both values were substantially larger than the 1.6 μatm found in the North Atlantic GEOSECS data. The GEOSECS data in the Atlantic were limited to latitudes below 36°N. Lack of data from high latitudes was responsible for the smaller regional variability of the seawater properties and, consequently, for underestimation of the regional nonlinear contribution. In the subset of the TTO data in the Arctic waters, represented by samples collected north of 50°N, the nonlinear contribution was 4.9 μatm.

4.4. Model Errors at the Global Scale

To evaluate E, the nonlinear error in model estimates of the global p, we tried to recreate the horizontal struc-

Figure 4. The nonlinear contribution (c) as a function of the standard deviations of temperature, dissolved inorganic carbon, and partial pressure of carbon dioxide ($\sigma(T)$, $\sigma(C)$ and $\sigma(p)$, respectively) at the regional scale. Regions are defined as in Table 1. Squares denote values calculated using the actual observations, circles represent values computed after standardization of alkalinity, dissolved inorganic carbon, silicate and phosphate concentrations, to a constant salinity of 34.78. Solid and dashed lines represent the linear regression calculated using direct and the salinity-standardized values, respectively. The regression line between the nonlinear contribution and standard deviation of dissolved inorganic carbon, direct values, is omitted, as in this case $r^2 = 0.03$.

ture of several carbon box models from the literature. We accomplished this by partitioning the GEOSECS data into various boxes. The results are summarized in Table 2.

1. The simplest case considered was the representation of the surface ocean as a single box [e.g., *Revelle and Suess*, 1957; *Craig*, 1957; *Nydal*, 1968; *Oeschger et al.*, 1975; *Takahashi et al.*, 1981a]. This representation underestimated the partial pressure of CO₂ of the GEOSECS ocean by 10.9 μatm.

2. A few schemes for partitioning the world oceans

Table 2. Partial Pressure of CO_2 Above 300 μatm and the Nonlinear Contribution Associated With Various Model Idealizations of the Global Ocean

Model	Regions	Area Weight a_b	Nonuniform Case $\bar{p}_b$	Uniform Case $p(\overline{T}_b, \overline{S}_b, ..)$	Nonlinear Contribution c_b
			Partial Pressure of CO_2		Nonlinear
1. One-box model					
single global box	I-X	1.000	35.9	25.0	10.9
2. Two-box models					
(2a) with high-latitude ocean separated					
high-latitude ocean	X	0.131	19.8	16.4	3.4
balance of ocean	I-IX	0.869	38.3	33.3	5.0
$\sum a_b ...$			35.9	31.1	4.8
(2b) with equatorial Pacific separated					
equatorial Pacific	V	0.127	79.0	76.6	2.4
balance of ocean	I-IV, VI-X	0.873	29.6	18.0	11.6
$\sum a_b ...$			35.9	25.4	10.4
(2c) with equatorial Atlantic separated					
equatorial Atlantic	II	0.040	57.4	57.1	0.3
balance of ocean	I, III-X	0.960	35.0	23.8	11.2
$\sum a_b ...$			35.9	25.1	10.8
3. Three-box model with high-latitude ocean and equatorial Pacific separated					
high-latitude (as in 2a)	X	0.131	19.8	16.4	3.4
equatorial Pacific (as in 2b)	V	0.127	79.0	76.6	2.4
balance of ocean	I, II-IV, VI-IX	0.742	31.3	26.3	5.0
$\sum a_b ...$			35.9	31.6	4.5
4. 10-box model with 10 boxes corresponding to all 10 regions in Table 1					
$\sum a_b ...$			35.9	31.5	4.4

Models are composed of boxes, which are constructed either as a single region, or as a weighted average of several GEOSECS regions (defined in Table 1). "$\sum a_b ...$" denotes the global area-weighted average of the box properties. For instance, "$\sum a_b ...$" for the last column (box nonlinear contributions, c_b), corresponds to $\sum a_b c_b$. Note that $\sum a_b c_b$ corresponds to the global nonlinear error associated with a given model (E in the text).

into two boxes were examined. The nonlinear error was sensitive to how the oceans were partitioned.

Most of the two-box models in the literature separate the high-latitude waters from the rest of the ocean [e.g. *Björkström*, 1979; *Hoffert et al.*, 1981; *Knox and McElroy*, 1984; *Sarmiento and Toggweiler*, 1984; *Siegenthaler and Wenk*, 1984; *Volk and Liu*, 1988; *Joos et al.*, 1991]. As the GEOSECS data set does not cover the Atlantic north of 35°N, the high-latitude box is represented by the Antarctic region only (region X in Table 1). The warm waters are represented by the remaining nine regions. In this case the global partial pressure of CO_2 was underestimated by 4.8 μatm (model 2a in Table 2).

We also analyzed the nonlinear errors associated with two other two-box partitions (following *Volk and Liu* [1988]) that divide the GEOSECS ocean into the equatorial Pacific (region V) and the rest of the ocean (model 2b), or into the equatorial Atlantic (region II) and the remaining ocean (model 2c). The nonlinear errors associated with these models (10.5 and 10.8 μatm, respectively) were larger than that calculated from the model separating the high- and low-latitude waters.

3. We also tested the effect of a further increase in the number of boxes. We used three-box and 10-box parti-

tions. The three-box partition (model 3), composed of the Antarctic and the North Pacific boxes, with the remaining regions pooled into a third box [e.g., *Volk and Liu*, 1988], underestimated global p by 4.5 μatm.

In the 10-box representation all the 10 regions defined in Table 1 were treated as separate boxes. Most of the box models in the literature have only a few boxes representing surface waters, so this case may represent a practical upper limit for the horizontal resolution of box models. This model eliminated the errors caused by pooling data from different regions into boxes, because each box corresponded to a single region. Nevertheless, the model assumed uniformity within each of the regions and, as a result, it underestimated the global p by 4.4 μatm.

Two points are worth noting here. First, a large error was incurred when boxes contained regions with very different properties. Pooling the data originating from the Antarctic waters (characterized by low T, high C, and relatively low p), with those from the other parts of the ocean resulted in large values of the nonlinear error (models 1, 2b, and 2c). Second, an increase in the complexity of the model, expressed as an increase in the number of boxes, does not necessarily lead to a reduc-

tion in the nonlinear error. If a more complex model does not have a more realistic structure than a simpler one, the associated error may remain large. Models 2b and 2c pooled together the data from warm and cold waters into single boxes, hence the structure of the models was still unrealistic. As a result, these models, despite being composed of two boxes, had the nonlinear error comparable with that of a one-box model. A strong reduction in the nonlinear error was possible only if the cold waters were isolated into a separate box (as in models 2a, 3, and 4). Once this separation was accomplished, further subdivision of the warm waters into two (model 3) or nine (model 4) boxes did not reduce the error significantly.

In the appendix we show that our estimates of nonlinear errors were not very sensitive to changes in the algorithm for computing p from seawater properties, and to the alternative selections of the GEOSECS data, except for employing the dissociation constants of carbonic acid proposed by *Goyet and Poisson* [1989]. Models using these constants were less prone to the nonlinear errors (4 μatm and 3 μatm in models containing a single surface box, and warm- and cold-water boxes, respectively).

4.5. Consequences of the Nonlinearity for the Direct Estimates of the Air-Sea Fluxes

Nonlinearity of the carbonate system, coupled with nonuniform distribution of the seawater properties, may affect results of models that estimate the air-sea carbon flux directly from the bulk properties of the surface ocean. In this approach [e.g., *Takahashi et al.*, 1981a] the net air-sea flux is computed from the difference in the partial pressure of CO_2 between the atmosphere and the ocean

$$F = \lambda \Delta p = \lambda(p_a - p_m), \tag{8}$$

where λ denotes the gas transfer coefficient, expressed in mol CO_2 m^{-2} yr^{-1} μatm^{-1}, p_a is partial pressure of CO_2 in the atmosphere, and p_m stands for the partial pressure in the mixed layer.

This approach is sensitive to errors in p_m. Nonlinearity of the carbonate system results in a higher p_m than would be expected from a uniform ocean with the same bulk properties as the real ocean. With $\lambda = 0.067$ mol CO_2 m^{-2} yr^{-1} μatm^{-1} [*Tans et al.*, 1990], the nonlinear error of about 11 μatm for one-box models, and about 5 μatm for the more complicated models, would translate into an overestimation of the oceanic uptake by 3.0 Gt C yr^{-1} and 1.4 Gt C yr^{-1}, respectively. This corresponds to 65% and 30% of fossil fuel emissions in 1973 [*Rotty*, 1987]. Thus neglecting the nonlinear errors could result in overestimation of the uptake of atmospheric carbon by the ocean, when carbon fluxes are computed from the difference in the partial pressure of CO_2 between the ocean and the atmosphere, and the oceanic p is computed from averaged seawater properties.

An example of such a model is that of *Takahashi et al.* [1981a]. In that model a p_m of 300 μatm is calculated from globally averaged observations of T, S, A, and C.

Using the 1973 atmospheric concentration of CO_2 of 321 μatm, these calculations yielded uptake of atmospheric carbon which was greater than the whole anthropogenic carbon emission. This forced Takahashi et al. to consider increasing the value of the global surface-ocean temperature to 20.26°C, despite the recognition that the calculated mean temperature of 19.2°C "appears to be higher by a few degrees than the space-time average values" [*Takahashi et al.* 1981a, p. 278] as a result of sampling mainly during the summer seasons in both hemispheres. This reservation is reinforced by the climatological data of *Levitus* [1982], from which one may calculate the average global ocean temperature in the 0-50 m layer to be 17.7°C. Using a more complete algorithm for calculating p (accounting for the effect of water, silicate, and phosphate dissociation) and applying the nonlinear correction would not only render such an upward adjustment of average temperature unnecessary, but even allow using lower global temperatures, in closer agreement with the space-time average.

Note that the estimates of global p_m derived by averaging individual values of p, directly measured or calculated from the composition of every sample, are not subject to the nonlinear error. For example, the estimates of *Tans et al.* [1990], which are based on such calculations, do not require a nonlinear correction.

5. Implications for Transient Box Models

Predicting the consequences of nonlinear effects is much more difficult in the case of box models in which the computed air-sea carbon flux depends on interactions between the surface ocean, the deep ocean, and the atmosphere. In this chapter we will discuss some transient models that are used to analyze the evolution of the carbon system with time. Diagnostic models, used to study the mechanisms that maintain a steady state, are briefly discussed in section 6.1.

Transient ocean-atmosphere models are run typically for the simulated time period extending from the preindustrial time to the present time or into the 21st century. Using as an example the transient box model composed of the atmosphere, the mixed layer, and the deep ocean [*Bacastow and Björkström*, 1981], we next examine the consequences of nonlinear effects for such models.

5.1. Correction of the Initial Conditions

The initial conditions in transient models typically assume a preindustrial steady state, in which there is no net CO_2 flux between the ocean and the atmosphere. In models with a single mixed layer reservoir this condition is expressed as [e.g., *Bolin and Eriksson*, 1959]

$$k_{am}N_{ao} = k_{ma}N_{mo}, \tag{9}$$

where subscripts m and a denote the mixed layer and the atmosphere, subscript o denotes preindustrial values, N is the amount of carbon in a given reservoir;

k_{am} and k_{ma} are transfer coefficients between the atmospheric and the mixed layer reservoirs.

To meet the condition of no net air-sea flux of CO_2, the partial pressure of CO_2 in the surface ocean (p_m) and the atmosphere (p_a) should be equal (see (8)). This condition can be expressed as $p_{mo} = p_{ao}$, with p_{mo} being a function of N_{mo}, and $p_{ao} = N_{ao}/M_a$, where M_a is the mass of atmosphere.

The overall partial pressure of CO_2 in a nonuniform surface ocean is higher than that of a uniform ocean with the same average properties, by the nonlinear error E (its preindustrial value being denoted E_o). To correct the initial conditions for nonlinear effects one may increase N_{ao} or decrease N_{mo}.

In the first case the initial partial pressure of the atmosphere p_{ao} can be increased to match the p_m of the nonuniform ocean:

$$p'_{ao} = p_m(N_{mo}) + E_o = p_{ao} + E_o, \qquad (10)$$

where the prime denotes a quantity modified to include the nonlinear effects. The fractional change in N_{ao} is given by

$$\frac{\Delta N_{ao}}{N_{ao}} = \frac{N'_{ao} - N_{ao}}{N_{ao}} = \frac{p'_{ao} - p_{ao}}{p_{ao}} = \frac{E_o}{p_{ao}}. \qquad (11)$$

An increase in N_{ao} would also affect the transfer coefficients according to (9). It can be shown that, for this type of model, $k'_{am}/k_{am} = N_{ao}/N'_{ao}$, that is the ratio of the new to the old value of k_{am} is inversely related to a similar ratio for N_{ao}. The transfer coefficient k_{ma} and other initial conditions (describing the exchange between the mixed layer and the deep ocean) are not affected by the correction of N_{ao}.

If the preindustrial nonlinear effects were equal to those computed from the GEOSECS data ($E_o = 10.9$ μatm as in Table 2) and the uncorrected preindustrial atmospheric partial pressure of CO_2 is assumed to be 280 μatm, N_{ao} would have to increase by 4% (=10.9/280).

The second option is to adjust the initial condition by decreasing N_{mo}, such that the new partial pressure, corrected for the nonlinear error E_o, would be equal to the prescribed atmospheric partial pressure:

$$p_m(N'_{mo}) + E_o = p_{ao}. \qquad (12)$$

Due to the buffering properties of the seawater, a required change in partial pressure can be achieved by a much smaller fractional change in the amount of the mixed layer carbon. The buffer factor ξ is defined as the ratio of fractional changes in p and in the concentration of dissolved inorganic carbon C:

$$\xi = \frac{\Delta p/p}{\Delta C/C}. \qquad (13)$$

To correct the initial amount of carbon in the mixed layer, we can rewrite (13) in terms of N_{mo} as

$$\xi = \frac{(p_m(N'_{mo}) - p_m(N_{mo}))/p_m(N_{mo})}{(N'_{mo} - N_{mo})/N_{mo}}, \qquad (14)$$

and from (10), (11), (12), and (14) we get the fractional change in N_{mo}:

$$\frac{\Delta N_{mo}}{N_{mo}} = \frac{N'_{mo} - N_{mo}}{N_{mo}} = \frac{p_m(N'_{mo}) - p_m(N_{mo})}{\xi p_m(N_{mo})}$$

$$= -\frac{E_o}{\xi p_{ao}} = -\frac{1}{\xi}\frac{\Delta N_{ao}}{N_{ao}}. \qquad (15)$$

For a buffer factor of 10, the fractional decrease in N_{mo} is 10 times smaller than the fractional increase that would be required in N_{ao}: the value of N_{mo} would have to be reduced by about 0.4% (=(10.9/280)/10), which is much less than either the uncertainty in N_{mo} or the potential errors caused by other assumptions in box models. For all practical purposes we may assume that the changes required in the initial conditions may be significant if N_{ao} is altered to maintain equilibrium, but not if N_{mo} is modified.

5.2. Modifications at Subsequent Time Steps

Nonlinear effects can modify the calculations at subsequent time steps, by altering the buffer factor. In ocean-atmosphere models with a single surface-ocean box, accumulation of CO_2 in the atmosphere at a given time step can be represented by [e.g., *Bacastow and Björkström*, 1981]

$$dn_a/dt = -k_{am}(N_{ao}+n_a) + k_{ma}(N_{mo}+\xi n_m) + \gamma, \qquad (16)$$

where n_a and n_m represent anthropogenic carbon in the atmosphere and in the mixed layer, respectively, and γ is the input of the anthropogenic carbon into the ocean-atmosphere system during a given time step. Using (9) we can separate the perturbation component from (16):

$$dn_a/dt = -k_{am}n_a + k_{ma}\xi n_m + \gamma. \qquad (17)$$

We use the GEOSECS data to compute a buffer factor correction $\Delta\xi$, a difference between the effective buffer factor of a nonuniform surface ocean and that of a uniform ocean with the same average properties.

5.3. Buffer Factor Correction

To compute the buffer factor of a water parcel using (13), different authors use different reference values of p and C. As a result, different numerical values of the buffer factor are obtained for the same water parcel (as discussed by *Wagener* [1979]). We calculated the buffer factors corresponding to the formulations of *Bolin and Eriksson* [1959], *Bacastow and Keeling* [1973], and *Keeling* [1973], respectively:

$$\xi_1 = \frac{\delta p/p}{\delta C/C}, \qquad (18)$$

$$\xi_2 = \frac{(p - p_o)/p_o}{(C - C_o)/C_o}, \qquad (19)$$

$$\xi_3 = \frac{\delta p/p_o}{\delta C/C_o}, \qquad (20)$$

where δp denotes an increase in the partial pressure of CO_2 of a water parcel (p) if the dissolved inorganic

carbon concentration of the water parcel (C) were increased by a small increment δC; and C_o is the value of C that, at given T, S, A, Si and P of the water parcel, would produce the preindustrial partial pressure p_o.

Assuming $p_o = 280\,\mu$atm and using $\delta C = 0.1\mu$mol kg^{-1}, we calculated ξ according to formulations (18), (19), and (20) for all GEOSECS samples. Then we repeated the procedure described in sections 3.2 and 3.3, calculating the regional and box values of nonlinear contribution and nonlinear error described by (3)-(7) with respect to the buffer factor instead of the partial pressure. Table 3 contains the buffer factor calculated for the one- and two-box model representations of the surface ocean and the correction required to account for the nonlinear effects, which are ignored when uniformity within the boxes is assumed.

The calculated buffer factors differed between definitions, being smallest in the formulation of *Bolin and Eriksson* [1959] and largest when the formulation of *Keeling* [1973] was used. The nonlinear corrections followed the same pattern. Therefore correcting for the nonlinear effects further increases the differences in buffer factor caused by its alternative formulations.

The two-box model required a smaller correction than the one-box model. The nonlinear effects for the high-latitude box were smaller than the low-latitude one, but when the TTO data from the Arctic were added to the GEOSECS data from the Antarctic, the nonlinear correction required for the modified high-latitude box was similar to that of the low-latitude box. The 10-box representation produced almost identical values of buffer nonlinear correction as the two-box representation.

5.4. Nonlinear Effects and Estimates of Oceanic Uptake of Anthropogenic Carbon

Having computed the buffer correction for the GEOSECS data, we may now try to assess the effect of such a correction on the the estimates of oceanic carbon uptake by transient box models.

First, we analyze some simplified cases for which an analytical solution can be obtained. When an exponential growth in anthropogenic emissions (with the time constant μ) and a constant buffer factor are assumed, the airborne fraction of anthropogenic carbon, $r_a(= n_a/\int \gamma dt)$, is given by *Bacastow and Björkström*

[1981]:

$$r_a = 1 - \frac{1}{\mu/k_{am} + h_a\xi/h^* + 1}, \qquad (21)$$

where $h_a = (N_{ao}/N_{mo})h_m$, and h^* for a uniform deep ocean is given by $h^* = h_m + h_d[k_{dm}/(\mu + k_{dm})]$, where h_m and h_d are the mixed layer and the deep ocean depths, respectively, and k_{dm} is the transfer coefficient between the deep ocean and the mixed layer. If one uses a constant buffer factor of ξ =9.64, h_a= 69 m, total ocean depth of 4200 m, $\mu = 1/22.5$ yr^{-1}, $k_{am} = 1/8.1$ yr^{-1}, as by *Bacastow and Björkström* [1981], for $h_m = 500$ m and $k_{dm} = 1/1250$ yr^{-1} the airborne fraction of the anthropogenic carbon in the ocean-atmosphere system would be 0.606, if the nonlinear effects were neglected.

To evaluate the consequences of nonlinearity let us assume that the nonlinear effects were constant in time and take the largest correction of the buffer factor from Table 3 ($\Delta\xi = 0.68$). This correction would increase r_a from 0.606 to 0.618, which corresponds to a decrease in the oceanic uptake of anthropogenic carbon by about 3%. Similar results were obtained for a box diffusion model in which the vertical distribution of carbon in the deep-ocean component of the model was assumed to be controlled by diffusion [e.g., *Oeschger et al.*, 1975]. If N_{ao} were modified instead of N_{mo}, r_a would increase to 0.628, and the decrease in the oceanic uptake would be less than 6%.

However, all these estimates were made for the special case in which the buffer factor was fixed and the nonlinear effects were assumed to be constant. Neither of these assumptions is realistic, particularly when the model simulation time is extended into the future. In reality, when the equilibrium partial pressure of CO₂ of the air-sea system increases, so does the buffer factor. The nonlinear effects can then be incorporated by the addition of a nonlinear buffer correction $\Delta\xi$ to the computed values of the uniform buffer factor. Consequences of such a correction would depend on the structure of the model, the way the uniform buffer factor is computed (section 5.3), and the time dependency of $\Delta\xi$ (as the nonlinear contribution is likely to increase in an environment with elevated partial pressure of CO₂, $\Delta\xi$ may increase in the future). Therefore a more complete

Table 3. Buffer Factors and the Nonlinear Correction Associated With Different Definitions of the Buffer Factor

	Buffer Factor: Uniform Case + Nonlinear Correction		
	ξ_1	ξ_2	ξ_3
One-box model	9.48+0.30	9.88+0.40	10.83+0.68
Two-box model			
low-latitude box	9.10+0.12	9.57+0.16	10.63+0.30
high-latitude box	13.48+0.04	13.88+0.10	15.09+0.25
area-weighted global average	9.67+0.11	10.13+0.15	11.21+0.30

The first term in each column represents the buffer factor calculated for the uniform case, the second term is the nonlinear correction. Formulations of buffer factor of *Bolin and Eriksson* [1959], ξ_1, *Bacastow and Keeling* [1973], ξ_2, and *Keeling* [1973], ξ_3, were used (equations (18)-(20) in the text). The one-box and the two-box models correspond to model 1 and model 2a in Table 2.

assessment of the role of nonlinearity for the results of carbon box models would require running a particular model with a time-dependent buffer factor and prescribing the nonlinear effects for the entire simulation period.

One could consider using a high-resolution 3-D model to obtain insights into changes in the nonuniformity of the seawater properties in time. By pooling data from the model's individual grid points into larger groups one might observe changes of nonlinear effects at successive time steps.

6. Other Issues

6.1. Nonlinear Effects in the Diagnostic Box Models

The nonlinear effect may also modify results of the diagnostic box models. These models are constructed to deduce the rates of mixing and biochemical processes using a set of physical and biochemical constraints [*Rintoul*, 1992], usually assuming various steady states. Partial pressure of CO_2 is one of these constraints which can be modified by nonlinear effects. Introduction of a nonlinear correction in these models would require making assumptions about the degree of variability of seawater properties in different hypothetical steady states.

6.2. Nonlinear Effects in the Real Ocean

So far, our results have been interpreted in the context of carbon models. However, the nonlinear effects are not just mathematical artifacts created by the partitioning of global ocean into a small number of boxes: they also have relevance in the real ocean.

Mixing in the real ocean may be regarded as "physical averaging." Horizontal mixing of different water masses, by homogenization of the seawater properties, usually decreases the overall p of surface waters. A well-mixed surface ocean would typically have a lower overall p than a nonuniform ocean with the same average properties, and consequently could be a stronger sink, or a weaker source, of atmospheric CO_2.

A number of biogeochemical processes, gas exchange with the atmosphere, upwelling of deep waters, biological activity, etc., affect the distribution of seawater properties. The effect of these processes on the carbon fluxes between the atmosphere and the ocean may be changed, even without any change in the overall intensity of these processes, by merely altering their timing and spatial distribution. For instance, without any change in the amount of new nutrients utilized by phytoplankton, an alteration of its distribution (e.g., a change in timing or location of the phytoplankton bloom) may alter the variance in seawater properties and therefore increase or decrease the capacity of surface waters to absorb atmospheric CO_2.

6.3. Representativeness of the GEOSECS Data

Our estimates of the nonlinear effects based on GEOSECS data are conservative and are likely to be on the lower side of the values that might be expected if a more representative data set were available. Poor coverage of some oceanic areas (e.g., Atlantic north of 35°N, coastal waters) and sampling bias toward summer seasons make the GEOSECS ocean different from the actual one. Additional data from waters having properties which differ strongly from the values recorded in the GEOSECS surface samples would probably increase the variability of the seawater properties and consequently the nonlinear error. Incorporation of high-latitude data is likely to increase the nonlinear error as is shown by including the TTO data (appendix). Coastal waters, whose properties often differ from those of the open ocean, have the potential to increase the nonlinear effects but were not represented in the data set we used.

The temporal aspect of the nonlinear effects was not resolved because the data used in our work were collected mainly during summer seasons. This lack of winter data may be important in waters whose properties exhibit a seasonal cycle.

For instance, as indicated in the measurements of *Watson et al.* [1991] and in the model of *Taylor et al.* [1991], properties of seawater in the North Atlantic during winter and immediately after the spring bloom are very different from those prevailing in summer. In the data used here only the postbloom situation was represented, hence a large portion of the annual variability has not been accounted for. The nonlinear effects in the real ocean may therefore be stronger than indicated by our estimates based on the GEOSECS data.

7. Summary

Due to the nonlinearity of the carbonate system, the partial pressure of CO_2 of nonuniform waters is different from that of uniform waters with identical bulk properties. The difference, termed the nonlinear contribution c, is typically positive. However, under specific circumstances, c may take a slightly negative value. Both theoretical considerations and the analysis of the GEOSECS data indicate the largest c to be associated with the highest variability in p.

Carbon models idealize the ocean as a set of internally uniform boxes and therefore underestimate the true value of oceanic p. The resulting nonlinear error depends on the structure of the model.

From the GEOSECS data from depths 0-49 m we estimated the magnitude of the nonlinear error to be about 11 μatm for the models combining the data from the high- and low-latitude waters into a single compartment, and about 5 μatm in a case of models separating data into cold- and warm-water boxes. Once the high-latitude box was isolated from the rest of the ocean, further increases in the horizontal resolution of the box models did not substantially affect the nonlinear error.

Our calculations were not very sensitive to changes in the algorithm for computing p from seawater properties, and to alternative selections of data (appendix). The only exceptions were computations employing the dissociation constants of carbonic acid proposed by *Goyet and Poisson* [1989]. Models using these constants were

less prone to the nonlinear errors (4 μatm and 3 μatm in models containing a single surface box, and warm- and cold-water boxes, respectively).

Our estimates of the nonlinear error based on the GEOSECS data are likely to be lower than the error expected in the real ocean. Addition of data from the Arctic region, coastal regions, and from winter months are likely to increase the estimates of the nonlinear effects. Nonlinear effects of up to 11 μatm were also found at the regional scale and even at the local scale, below the resolution of the carbon models employing 3-D oceanic general circulation models.

The consequences of the nonlinearity of the carbonate system for carbon models depend on the type of model used. When the flux of carbon is estimated directly from the properties of the surface waters, computations based on the average partial pressure of CO_2 should be preferred to models that compute the global partial pressure from average seawater properties, as the latter could overestimate the oceanic uptake of anthropogenic carbon (e.g., by up to 65% of fossil fuel emissions in the case of the GEOSECS data).

In the case of transient carbon models the impact of nonlinear effects on estimates of the uptake of anthropogenic carbon would depend on the structure of the model. In the simple box models and box diffusion models, assuming a constant buffer factor and fixing the nonlinear effects at the values computed from the GEOSECS data, a nonuniform ocean was a weaker sink of anthropogenic carbon than a uniform one. However, as the decrease was about 3%, the errors from nonlinear effects were within the uncertainty introduced by other assumptions in such simplified models. Quantification of the role of the nonlinearity for the results of more realistic carbon box models would require using a time-dependent buffer factor and prescribing time dependency of the nonlinear effects.

The nonlinearity of the carbonate system may have implications not only for models, but for the processes occurring in the real ocean as well. Horizontal and vertical mixing, gas and heat exchange with the atmosphere, precipitation and evaporation, and biological processes, all affect the distribution of properties controlling the partial pressure of CO_2 and thus modify air-sea gas exchange. In other words, carbon fluxes between the ocean and the atmosphere are affected not only by the mean intensity of biogeochemical processes, but also by their timing and spatial distribution. The same process, depending on its spatial and temporal pattern, may either increase or decrease the nonuniformity of the seawater properties and therefore modify the capacity of the surface ocean to act as a carbon sink even if the mean intensity of this process remains unchanged.

Appendix: Sensitivity of the Estimates of the Nonlinear Effects to the Computational Procedure

When computing the effects of nonlinearity for the partial pressure of the surface ocean (sections 4.3 - 4.4)

in the main calculations, we employed the 10-region partition of the GEOSECS data from the depths 0-49 m, (as given by *Takahashi et al.* [1981b]) with area weights based on *Moiseev* [1971], and partial pressure of CO_2 calculated according to *Peng et al.* [1987]. To assess the sensitivity of our results to these assumptions, we repeated some of the computations altering the conditions of this scheme, one at a time.

Table A1 shows how our estimates may be affected by alterations in this basic procedure. We present the results of the alterations for three models described in Table 2: models 1 and 2a, representing the most frequently used box models and, model 4, a likely upper limit of the horizontal resolution of simple carbon models.

Note that modifications of the procedure also change the reference value, which is the estimated global value of partial pressure in the nonuniform ocean (p_t). In each case the nonlinear error E is calculated with respect to the corresponding p_t. We do not discuss at this point which value of p_t is most representative of the actual ocean but merely assess whether any of the modified procedures is less vulnerable to nonlinear errors.

In all cases one-box representations of the global ocean were more susceptible to the nonlinear error, and more sensitive to changes in the computational procedure, than the corresponding two-box or multi-box representations. All but one of the modifications yielded no substantial change in the nonlinear error.

Alternative Algorithms of Calculations of Partial Pressure of CO_2

The only modification that resulted in substantially lower nonlinear error was replacing the carbonic acid dissociation constants of *Mehrbach et al.* [1973] with those of *Goyet and Poisson* [1989], which indicates that models using those constants may be less prone to nonlinear effects. This finding is consistent with the results obtained when p was analyzed as a function of temperature (section 4.1).

Simplified formulations of the carbonate system that approximate total alkalinity as the sum of the carbonate, borate, and water contributions $(A = [HCO_3^-] + 2[CO_3^{2-}] + [H_4BO_4^-] + [OH^-] - [H^+])$, or as the sum of the carbonate and borate contribution only $(A = [HCO_3^-] + 2[CO_3^{2-}] + [H_4BO_4^-])$, were still prone to the nonlinear errors.

Alternative Selection of the Data

Changing the procedure of selection of the data did not strongly affect the estimates of the nonlinear error. First, we modified the values of A, C, Si, and P, by standardization to the GEOSECS average oceanic salinity of 34.78 [*Takahashi et al.*, 1981a]. As standardization eliminates variations in salinity and reduces variability of alkalinity (which is controlled mainly by the addition or removal of fresh water), one might expect weaker nonlinear effects. However, the temperature variations are unaffected. Also, as the concentration of C may be strongly influenced by processes other than the addition

Table A1. Sensitivity of Global Estimates of Partial Pressure of CO_2 (Above 300 μatm) and the Nonlinear Error in Selected Model Representations

	i	ii	iii	iv	v	vi	vii	viii	ix
	Global Partial Pressure Directly Estimated From Data (p_t)								
	35.9	33.6	25.5	21.9	32.9	33.9	32.9	34.6	32.2
	Global Partial Pressure Estimated From Models (p_e)								
one-box model	25.0	23.2	16.6	17.7	23.9	24.1	20.4	24.2	20.7
two-box model*	31.1	29.0	21.6	18.8	28.8	30.1	28.5	29.9	26.5
ten-box model†	31.5	29.4	21.8	19.0	29.2	30.6	28.6	30.4	27.4
	Global Nonlinear Error ($E= p_t - p_e$)								
one-box model	10.9	10.4	8.9	4.2	9.1	9.8	12.5	10.4	11.5
two-box model*	4.8	4.6	3.9	3.1	4.1	3.8	4.4	4.7	5.7
10-box model†	4.4	4.2	3.7	2.9	3.7	3.3	4.3	4.2	4.7

Column i contains the reference values extracted from Table 2, based on the 10-region partition of the GEOSECS data from the depths 0-49 m (following *Takahashi et al.* [1981b]), with area weights based on *Moiseev* [1971] and partial pressure of CO_2 calculated according to *Peng et al.* [1987]. Columns ii-iv were obtained by modification of the algorithm of Peng et al.: ii, alkalinity was approximated as a sum of the carbonate, borate and water contributions; iii, alkalinity was approximated as a sum of the carbonate and borate contributions only; iv, carbonic acid dissociation constants of *Goyet and Poisson* [1989] were used. Columns v-ix were computed using an alternative data selection: v, values of A, C, Si, and P were standardized to salinity S=34.78; vi, the data from the depths 0-24 m were used only; vii, the 7-region partition of the data and area weights based on *Takahashi et al.* [1981a] were employed; viii, a station instead of a sample was the basis of calculation of regional averages of the seawater properties; ix, the Arctic region was added and the TTO data were included. All values are in microatmospheres.

* Here represented by model 2a from Table 2.

† Except column vii, where the ten-box model is replaced by the seven-box one, and column ix, where the eleven-box model was used.

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or removal of fresh water (mixing, gas exchange with the atmosphere, and biological activity), standardization to a constant salinity may actually increase variability of C. As a result, variability in p is only slightly reduced (as seen in Figure 4) and nonlinear errors are not substantially lower than in the nonstandardized case.

Next, we computed the nonlinear errors when observations from the depth range of 0-24 m only were used. Estimates of E were not altered substantially, suggesting that the influence of deep waters in the data from depths 0-49 m is weak.

Then, we considered a station as the basis of computations instead of a sample, i.e., all samples from a given station were averaged and a single value from each station was used in the computation. Although averaging of the observations obtained from different depths within a single location removed part of the data variability associated with differences in seawater within a station, it did not substantially reduce the nonlinear error, as the differences between different stations were still present.

Finally, we examined an alternative scheme for defining regions. Instead of using the 10-box partition of *Takahashi et al.* [1981b] with the area weights based on *Moiseev* [1971], we partitioned the GEOSECS data after *Takahashi et al.* [1981a] into seven boxes and used their area weights with slight modifications. Each ocean was divided at the equator into a northern and a southern part, and all data south of 45°S were pooled into an Antarctic region. *Takahashi et al.* [1981a] extended the average values of alkalinity and dissolved inorganic carbon obtained from the Atlantic 0°-35°N to the rest

of the North Atlantic waters. We found this extension unnecessary, as our calculations concern an idealized GEOSECS ocean, that is, only the part of the global ocean from which there are complete sets of measurements. Therefore we reduced the *Takahashi et al.* [1981a] area weight of the North Atlantic region from 11.9% to 7.0% and increased the weights of other regions proportionally. The computations using this set of regions yielded similar values of E for the two-box and multibox representations, and somewhat larger E for the single-box representation.

The Effect of Incorporation of the TTO Data

We assessed the effect of supplementing the GEOSECS data with those from the TTO cruises. To this point we had not combined these data sets because of methodological differences (for instance, the need of correction of the GEOSECS titration data discussed by *Takahashi et al.* [1981a]) and the time gap between these sampling programs. We made an exception to evaluate how the estimates of the nonlinear error at global scale would change, if the data coverage was extended in the North Atlantic beyond 36°N. We expanded the range of the North Atlantic region from 10°-36°N to 10°-50°N and assigned it an area weight of 9.3%. We also added an eleventh region representing ice-free Arctic waters with area weight of 4.9%. This weight was obtained assuming the Arctic sea ice in its minimal range covers 8×10^{12} m^2 [*Parkinson et al.*, 1987]. The weights of the remaining nine regions were proportionately reduced.

Assuming that the TTO data from latitudes 50°-80°N

and 15°-50°N are representative of the Arctic and the North Atlantic region, respectively, we computed the nonlinear errors using those values and the properties of the remaining nine regions based on the GEOSECS data. We also calculated the nonlinear errors after supplementing the GEOSECS data with the TTO observations. As expected, the addition of the Arctic data, with properties strongly differing from the low-latitude waters, increased the variability of the seawater properties and the nonlinear error in models that pool the high-latitude data with those from low-latitudes into single boxes (models 1, 2b, and 2c). The nonlinear error increased even in the case of the remaining models which isolate the high-latitude waters from the rest of the ocean. As the properties of the Arctic region differ from properties of the Antarctic region, pooling together data from these regions into a single high-latitude box (models 2a and 3) increases the nonlinear contribution in this box to 7.3 μatm, more than doubling the value computed for this box when only the GEOSECS Antarctic data were used.

Notation

T	temperature, °C.
S	salinity.
A	total alkalinity, μeq kg^{-1}.
C	dissolved inorganic carbon, μmol kg^{-1}.
Si	silicate, μmol kg^{-1}.
P	phosphate, μmol kg^{-1}.
p	partial pressure of CO₂, μatm.
$\overline{p(T,S,...)}$	average value of the partial pressure, μatm.
$p(\overline{T},\overline{S},...)$	partial pressure calculated from averaged seawater properties, μatm.
c	nonlinear contribution, μatm.
p_t	true value of p in the global surface ocean, μatm.
p_e	model estimate of p_t, μatm.
p_a	atmospheric partial pressure, μatm.
E	nonlinear error, μatm.
σ	standard deviation.
a	area weight (fraction of the area of the global ocean).
K_r	number of individual samples within a region.
K_b	number of regions composing a box.
n	number of regions composing the global ocean.
B	number of boxes composing the global ocean.
λ	gas transfer coefficient, mol CO₂ m^{-2} yr^{-1} μatm^{-1}.
p_i	partial pressure of CO₂ in the ith reservoir, μatm.
N_{io}	amount of preindustrial carbon in the ith reservoir, mol.
n_i	departure from N_{io} due to uptake of anthropogenic CO₂, mol.
M_a	mass of the atmosphere, mol.
k_{ij}	transfer coefficients from reservoir i to reservoir j, yr^{-1}.

h_a	depth of surface ocean water containing the same amount of dissolved inorganic carbon as the preindustrial atmosphere, m.
h_m, h_d	depth of the mixed layer and the deep ocean, respectively, m.
h^*	the effective mixed-layer depth; that is, h_m increased to reflect transfer of carbon from the mixed layer into the deep ocean, m.
γ	input of the anthropogenic CO₂ into the ocean-atmosphere system, mol yr^{-1}.
μ	reciprocal of e-folding time for anthropogenic CO₂ production, when the production is assumed to grow exponentially, yr^{-1}.
r_a	fraction of anthropogenic CO₂ remaining in the atmosphere.
ξ	buffer factor.
$\Delta\xi$	nonlinear correction of buffer factor (the difference in buffer factor between a nonuniform and a uniform ocean).

Superscripts

Single prime indicates initial properties corrected to account for nonlinear effects.

Subscripts

i	individual.
r	regional.
b	box.
a	atmospheric.
m	mixed layer.
d	deep ocean.
o	preindustrial.

References

Bacastow, R., and A. Björkström, Comparison of ocean models for the carbon cycle, in *Carbon Cycle Modelling (SCOPE 16)*, edited by B. Bolin, pp. 29-79, John Wiley, New York, 1981.

Bacastow, R., and C. D. Keeling, Atmospheric carbon dioxide and radio-carbon in the natural carbon cycle, II; Changes from A.D. 1700 to 2070 as deduced from a geochemical model, in *Carbon in the Biosphere*, AEC Symp. Ser. vol. 30, edited by G. M. Woodwell and E. V. Pecan, pp. 86-136, U.S. Department of Commerce, Washington, D. C., 1973.

Bainbridge, A.E. (Ed.), *GEOSECS Atlantic Expedition, Vol. 1, Hydrographic Data 1972-1973*, 121 pp., International Decade of Ocean Exploration, National Science Foundation, Washington, D. C., 1981.

Björkström, A., A model of CO_2 interaction between atmosphere, oceans, and land biota, in *The Global Carbon Cycle (SCOPE 13)*, edited by B. Bolin, E. T. Degens, S. Kempe and P. Ketner, pp. 403-457, John Wiley, New York, 1979.

Bolin, B., and E. Eriksson, Changes in the carbon dioxide content of the atmosphere and the sea due to fossil fuel combustion, in *Atmosphere and Sea in Motion*, edited by B. Bolin, pp. 130-142, Rockefeller Institute Press, New York, 1959.

Broecker, W. S., D. W. Spencer, and H. Craig (Eds.), *GEOSECS Pacific Expedition, Vol. 3, Hydrographic Data 1973-1974*, 137 pp., International Decade of Ocean Exploration, National Science Foundation, Washington, D. C., 1982.

Craig, H., The natural distribution of radiocarbon and the exchange time of carbon dioxide between atmosphere and sea, *Tellus, 9*, 1-17, 1957.

Goyet, C., and A. Poisson, New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity, *Deep Sea Res., 36*(11), 1635-1654, 1989.

Hoffert, M. I., A. J. Callegari, and C.-T. Hsieh, A box-diffusion carbon cycle model with upwelling, polar bottom water formation and marine biosphere, in *Carbon Cycle Modelling (SCOPE 16)*, edited by B. Bolin, pp. 287-305, John Wiley, New York, 1981.

Joos, F., J. L. Sarmiento, and U. Siegenthaler, Estimates of the effect of Southern Ocean iron fertilization on atmospheric CO_2 concentrations, *Nature, 349*, 772-775, 1991.

Keeling, C. D., 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*, edited by S. J. Rasool, pp. 251-329, Plenum, New York, 1973.

Knox, F., and M. B. McElroy, Changes in atmospheric CO_2: Influence of the marine biota at high latitude, *J. Geophys. Res., 89*, 4629-4637, 1984.

Levitus, S., Climatological atlas of the world ocean, *NOAA Prof. Pap. 13*, U.S. Govt. Print. Offices, Washington, D. C., 1982.

Maier-Reimer, E., and K. Hasselmann, Transport and storage of CO_2 in the ocean — An inorganic ocean-circulation carbon cycle model, *Clim. Dyn., 2*, 63-90, 1987.

Mehrbach, C., C. H. Culberson, J. E. Hawley, and R. M. Pytkowicz, Measurements of apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr., 18*, 897-907, 1973.

Moiseev, P. A., *The Living Resources of the World Ocean*, translated from Russian by N. Kaner and W. E. Ricker, Washington D. C., 1971.

Nydal, R., Further investigation on the transfer of radiocarbon in nature, *J. Geophys. Res., 73*, 3617-3635, 1968.

Oeschger, H., U. Siegenthaler, U. Schotterer, and A. Gugelman, A box diffusion model to study the carbon dioxide exchange in nature, *Tellus, 27*, 168-192, 1975.

Parkinson, C. L., J. C. Comiso, H. J. Zwally, D. J. Cavalieri, P. Gloersen, and W. J. Campbell, Arctic Sea Ice, 1973-76: Satellite Passive-Microwave Observations, NASA Spec. Publ. SP-489, 239 pp., 1987.

Peng, T.-H., T. Takahashi, and W. S. Broecker, Seasonal variability of carbon dioxide in the northern North Atlantic surface water: Observation and a model, *Tellus, 39B*, 439-458, 1987.

Revelle, R., and H. E. Suess, Carbon dioxide exchange between atmosphere and ocean and the question of an in-crease of atmospheric CO_2 during the past decade, *Tellus, 9*, 18-27, 1957.

Rintoul, S. R., Towards coupled physical-biogeochemical models of the ocean carbon cycle, in *Modeling the Earth System*, edited by D. Ojima, pp. 39-75, University Corporation for Atmospheric Research/Office for Interdisciplinary Earth Studies, Boulder, Colo., 1992.

Rotty, R. M., A look at 1983 CO_2 emissions from fossil fuels (with preliminary data for 1984), *Tellus, 39B*, 203-208, 1987.

Sarmiento, J. L., and J. R. Toggweiler, A new model for the role of the oceans in determining atmospheric pCO_2, *Nature, 308*, 622-624, 1984.

Sarmiento, J. L., J. C. Orr, and U. Siegenthaler, A perturbation simulation of CO_2 uptake in an ocean general circulation model, *J. Geophys. Res., 97*, 3621-3645, 1992.

Siegenthaler, U., and T. Wenk, Rapid atmospheric CO_2 variations and ocean circulation, *Nature, 308*, 624-626, 1984.

Takahashi, T., W. S. Broecker, and A. E. Bainbridge, The alkalinity and total carbon dioxide concentration in the world oceans, in *Carbon Cycle Modelling (SCOPE 16)*, edited by B. Bolin, pp. 271-286, John Wiley, New York, 1981a.

Takahashi, T., W. S. Broecker, and A. E. Bainbridge, Supplement to the alkalinity and total carbon dioxide concentration in the world oceans, in *Carbon Cycle Modelling (SCOPE 16)*, edited by B. Bolin, pp. 159-199, John Wiley, New York, 1981b.

Tans, P. P., I. Y. Fung, and T. Takahashi, Observational constraints on the global atmospheric CO_2 budget, *Science, 247*, 1431-1438, 1990.

Taylor, A. H., A. J. Watson, M. Ainsworth, J. E. Robertson, and D. R. Turner, A modelling investigation of the role of phytoplankton in the balance of carbon at the surface of the North Atlantic, *Global Biogeochem. Cycles, 5*(2), 151-171, 1991.

Toggweiler, J. R., K. Dixon, and K. Bryan, Simulations of radiocarbon in a coarse-resolution, world ocean model, I, Steady state, pre-bomb distribution, *J. Geophys. Res., 94*, 8217-8242, 1989.

Volk, T., and Z. Liu, Controls of CO_2 sources and sinks in the Earth scale surface ocean: temperature and nutrients, *Global Biogeochem. Cycles, 2*(2), 73-89, 1988.

Wagener, K., The carbonate system of the ocean, in *The Global Carbon Cycle (SCOPE 13)*, edited by B. Bolin, E. T. Degens, S. Kempe, and P. Ketner, pp. 251-258, John Wiley, New York, 1979.

Watson, A. J., C. Robinson, J. E. Robertson, P. J. le B. Williams, and M. J. R. Fasham, Spatial variability in the sink for atmospheric carbon dioxide in the North Atlantic, *Nature, 350*, 50-53, 1991.

Weiss, R. F., W. S. Broecker, H. Craig, and D. W. Spencer (Eds.), *GEOSECS Indian Ocean Expedition, Vol. 5, Hydrographic Data 1977-1978*, 42 pp., International Decade of Ocean Exploration, National Science Foundation, Washington, D. C., 1983.

Zwally, H. J., J. C. Comiso, C. L. Parkinson, W. J. Campbell, F. D. Carsey, and P. Gloersen, Antarctic Sea Ice, 1973-76: Satellite Passive-Microwave Observations, NASA Spec. Publ., SP-459, 206 pp., 1983.

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