Carbon Dioxide in the Ocean Surface Layer: Some Modelling Considerations

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ABSTRACT

Equilibrium with the atmosphere controls the general distribution of values for sea surface total dissolved inorganic carbon concentrations and homogeneous buffer factors. In the absence of carbonate dissolution, future ocean surface uptake of CO_2 can be accurately approximated by equilibrium between the atmosphere and a single average surface seawater. These observations imply that CO_2 box models can treat the atmosphere and the ocean surface together as a single "box". The principal remaining uncertainties in modeling oceanic CO_2 uptake are 1) the nature of future alkalinity changes, and 2) the nature of mixing between surface and deep waters.

In a separate publication (Sundquist, *et al.* 1979), it has been shown that the homogeneous reactions which buffer carbon dioxide uptake by the ocean surface are very well known relative to other uncertainties in the global carbon cycle. Spatial varations in the homogeneous buffer factor depend systematically on sea surface temperatures, and do not contribute significantly to uncertainties in the present or future CO_2 budget. In this paper, we extend these conclusions to carbon cycle modeling.

The homogeneous buffer factor is defined as

$$B_{\text{hom}} = \left(\frac{\delta P_{\text{CO}_2}}{\delta \Sigma C}\right)_{\text{TA}} \cdot \frac{\Sigma C}{P_{\text{CO}_2}} \tag{1}$$

where ΣC is the total concentration of dissolved inorganic carbon in surface seawater equilibrated with the atmospheric CO₂ partial pressure P_{CO2}; and TA is the total alkalinity, which remains constant in the absence of heterogeneous reactions.

Figure 1 (from Sundquist *et al.* 1979) shows that B_{hom} values calculated from the GEOSECS ocean surface data* reflect equilibrium between the ocean surface and

^{*}The results reported here and in Sundquist *et al.* (1979) are based on the GEOSECS data sets available at the time the work was done. These were the Atlantic and Pacific Ocean leg report data. The titration Σ C and TA data were corrected according to the recommendations of Takahashi *et al.* (1976) and Broecker and Takahashi (1978). Takahashi (personal communication) has pointed out that subsequent refinements of the GEOSECS Σ C and TA data may slightly alter some of the data presented here. These refinements, however, do not affect our arguments and conclusions.



Figure 1: Ocean surface values for the homogeneous buffer factor, calculated from GEO-SECS Σ C and TA data (from Sundquist *et al.*, 1979). The line represents B_{hom} values calculated for an average surface sea water (TA = 2330 μ eq/kg., salinity = 35.05 per mil) equilibrated with a P_{CO2} of 325 μ atm. at the temperatures shown.

the atmosphere at varying sea surface temperatures. Figure 2 shows that the same condition controls the general distribution of Σ C values in the ocean surface. Unlike the observed values for B_{hom}, sea surface Σ C values are susceptible to large variations caused by local salinity fluctuations. These variations can be eliminated by normalizing to a single salinity value. The data points plotted in Figure 2 were calculated by normalizing the Atlantic and Pacific GEOSECS sea surface Σ C values to the overall average ocean surface salinity, 35.05 per mil (see Table 1), using the equation

$$\Sigma C_{norm} = \Sigma C \times (35.05/S)$$
(2)

where S is the salinity (in per mil) of the same sample. The connected points in Figure 2 were calculated by first averaging the Atlantic and Pacific surface GEO-SECS temperatures, salinities, and TA values for each of 7 latitude zones (Table 1). The zonal TA averages were then normalized to the overall average ocean surface salinity, 35.05 per mil, using the equation

$$TA_{norm} = TA \times (35.05/S) \tag{3}$$

where S is the zonal salinity average in per mil. At the global average salinity and zonal average temperature, each normalized TA value implies a calculated ΣC value in equilibrium with a P_{CO2} of 325 μ atm., the approximate atmospheric CO₂ partial pressure during the time the GEOSECS samples were taken. The calculated equilibrium ΣC values for each of the 7 latitude zones are connected by the solid lines shown in Figure 2. They were determined using the apparent carbonic and boric acid dissociation constants of Lyman (1956) and the CO₂ solubilities of Weiss (1974). The equilibrium values agree very well with the trend of the individual station titration

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 Σ C data. Thus, although ocean surface P_{CO2} values are seldom in equilibrium with the atmosphere (see, for example, Takahashi, 1979), the disequilibrium does not significantly affect the general tendency of ocean surface Σ C and B_{hom} values to be controlled by atmospheric equilibrium. This condition is not merely statistical happenstance, but a systematic result of the fact that mixed layer Σ C and B_{hom} values are not very sensitive to the nonequilibrium deviations in ocean surface P_{CO2}.



Figure 2: Ocean surface GEOSECS titration Σ C values normalized to a salinity of 35.05 per mil. The lines connect values calculated by assuming equilibrium with the atmosphere for normalized average surface waters of the 7 latitude zones defined in Table 1.

Will this systematic tendency toward equilibrium continue into the future? The answer to this question depends on the relative rates at which the ocean surface will equilibrate with atmospheric CO₂ and at which CO₂ will be added to the atmosphere by human activities. If the process of gas exchange is not fast enough to maintain equilibrium between the mixed layer and the expected exponential rise in atmospheric CO_2 , then the ocean surface will lag farther and farther behind equilibrium with the atmosphere. According to the model calculations of Oeschger et al. (1975, p. 189), this effect is already operating, and the present ocean surface has equilibrated with only 85 percent of the atmospheric CO_2 increase since preindustrial times. On the other hand, Takahashi (1979) has presented data from the Atlantic Ocean which suggest that the equilibrium surface water P_{CO2} increased twice as fast as the atmospheric CO₂ concentration between the years 1958 and 1972.* Some modeling efforts (e.g. Bacastow and Keeling, 1973, and Oeschger et al., 1975) have shown that severalfold excursions from reasonable values for the model gas exchange rate do not significantly alter the model CO_2 budgets; this observation is consistent with the hypothesis that the reasonable gas exchange rates are so fast that the model atmosphere and sea surface remain virtually at equilibrium.

*Takahashi (1979, p. 66) found an average surface water P_{CO2} increase of $1.8\pm0.4 \,\mu$ atm/yr. for the years 1958–1972, whereas the observed average atmospheric P_{CO2} increase was 0.9 ± 0.1 ppm/yr. (Keeling and Bacastow, 1979, p. 76).

We have examined this question by means of a modeling experiment. We have compared a simple standard CO_2 box model; which features separate boxes for the atmosphere, surface ocean, and deep ocean; to a model which differs only in that it treats the atmosphere and surface ocean together as a single box (see Figure 3). Mathematically, this difference means that the latter model has one less differential equation. Instead of two mass balance equations for the separate atmosphere and surface ocean boxes, there is only one such equation for the combined atmosphere-mixed layer box. Instead of the gas exchange flux terms which appear in the mass balance equations for the separate atmosphere and ocean surface boxes, the new model determines atmospheric P_{CO_2} and mixed layer ΣC by an iterative routine which assures that they are always at equilibrium.

The standard box model closely resembles the three-reservoir tandem model described by Keeling (1973). We have ignored biospheric carbon because it is not directly involved in our experiment. We also assumed constant ocean alkalinity, although this assumption may not be reasonable (see below). In order to incorporate the effects of large changes in B_{hom} on CO_2 gas exchange between the atmosphere and surface ocean, the standard model expresses gas exchange by the term

$$k' \left(P_{CO_{2}a} - P_{CO_{2}m} \right)$$

where P_{CO2a} is the atmospheric CO₂ partial pressure, P_{CO2m} is the calculated equilibrium P_{CO2} of the surface ocean, and k' is a constant calculated + o be consistent with the model of Bacastow and Keeling (1973) for the case in which their r_{am} is 5 years. In both models, the deep ocean exchange term and reservoir sizes were calculated to be consistent with the model of Bacastow and Keeling (1973) for the case in which their N_{mo}/N_{ao} is 2 and their r_{dm} is 1500 years*. Initial conditions for the year 1970, based on the GEOSECS Atlantic and Pacific data, are shown in Table 2. The anthropogenic CO₂ flux was calculated according to the equations

$$y = 2.7 \times 10^{12} \exp \left[0.0435 \left(t - 1860 \right) \right]$$
 (4)

for the years 1970-1974, and

$$y = 0.0387 \text{ K} \left[1 - \frac{\text{K}}{(4.2 \times 10^{17})}\right]$$
(5)

where

 $K = [2.381 \times 10^{-18} + 8.659 \times 10^{-17} \exp (0.038668 (1975 - t))]^{-1}$

for the years 1975-2300 (see Keeling and Bacastow, 1977). The model calculations were performed using a 5 th- and 6 th-order Runge-K utta subroutine at step intervals which produced convergence to at least 7 significant figures for all the dependent variables.

Table 3 shows clearly that the models are virtually identical throughout the period 1970-2300. The atmospheric P_{CO2} values predicted by the two models during this

*Bacastow and Keeling defined N_{mo} as the steady state mass of dissolved carbon in the surface ocean and N_{ao} as the steady state mass of carbon in the atmosphere. They defined r_{am} and r_{dm} as the reciprocals of the atmosphere-surface and surface-deep ocean exchange coefficients, respectively. Of course, r_{am} is effectively equal to 0 years in the experimental model.

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Figure 3: Ocean surface ΣC values at increasing atmospheric P_{CO2} values. Values were calculated by assuming equilibrium with the indicated P_{CO2} values at the average temperatures and normalized TA values for the 7 latitude zones indicated in Table 1. A salinity of 35.05 per mil was used in normalizing the TA values and in calculating the equilibrium constants.

time do not differ by more than $1.14 \,\mu$ atm. The modeling experiment confirms that, at constant total alkalinity, CO₂ uptake by the surface ocean can be accurately approximated as an equilibrium function of the atmospheric uptake. Because this effect is determined entirely by the rapid rate of gas exchange relative to the rate of atmospheric perturbation, we believe that a comparable equilibrium approximation will also be accurate for model calculations which take into account changes in ocean alkalinity.* We cannot explain the calculations by Oeschger *et al.* (1975) which suggest that the surface ocean has lagged 15 percent behind equilibrium with the atmospheric P_{CO2} increase. We suspect that the discrepancy between their calculations and ours arises at least partially from their incorrect assumption of a constant buffer factor value.

Thus, it is reasonable to surmise that future global mixed-layer ΣC and B_{hom} values may continue to be dominated by equilibrium with the atmosphere. If changing alkalinities are not involved in this equilibrium (see below), then future ocean surface ΣC and B_{hom} values can be calculated easily from the homogeneous equilibrium relationships. However, our modeling experiment-and most other global CO₂ models-has approximated surface ocean behavior as that of a single average surface water, whereas we have seen a large range of ΣC and B_{hom} values in the real mixed layer (Figures 1 and 2). In order to substantiate our conclusions, we must show that a single average surface water reasonably approximates the global ocean surface.

*Our arguments in favor of a global air-sea equilibrium approximation do not imply any relationship between ocean alkalinity values and the equilibrium behavior of marine carbonate solids.





Figure 4 shows the salinity-normalized ocean surface ΣC values which might be expected if they are determined by equilibrium with future atmospheric P_{CO_2} levels. The values were calculated for each of the 7 latitude zones defined in Table 1, assuming equilibrium with the indicated P_{CO_2} values at the global average salinity and the zonal average temperatures and normalized alkalinities.

Figure 5 shows the expected ocean surface B_{hom} values, calculated in the same manner for each latitude zone. In addition, this figure shows curves for B_{hom} calculated by assuming equilibrium between a single average surface seawater (see Table 1) and the indicated P_{CO_2} values. These curves are very close to the B_{hom} values for each latitude zone at the corresponding P_{CO_2} values, implying that the homogeneous mixed-layer buffering of CO_2 may be closely approximated by the equilibrium behavior of a single average seawater.

This conclusion is supported by the data in Table 4, which compares the net equilibrium uptake of CO₂ for a homogeneous average ocean mixed layer with that calculated by summing the net equilibrium uptakes for each of the 7 latitude zones. The uptakes were determined by calculating the increases in Σ C values from equilibrium with an initial P_{CO2} of 325 μ atm. to equilibrium with P_{CO2}'s ranging from 400 to 1800 μ atm. A uniform mixed layer depth of 100 meters was assumed, and ocean surface areas were taken from Sverdrup, Johnson, and Fleming (1942). The uptake calculated for a homogeneous mixed layer is never more than one percent different from the uptake calculated by summing the latitude zones.

These observations should be encouraging to the many CO_2 modelers who have approximated the surface ocean by a single "box" (e.g., K eeling and Bacastow, 1977; Siegenthaler and Oeschger, 1978). In fact, if the ocean surface uptake of CO_2 is completely determined by homogeneous reactions at equilibrium with the atmospheric CO_2 content, then the ocean surface is not really an independent "box" at all, but rather an extension of the atmosphere "box". Of course, this conclusion does not apply to model mixed layers which are given unrealistic depths in order to parameterize mixing between shallow and intermediate ocean waters. It applies only to realistic mixed layer depths, for which our estimate of 100 meters is probably near an upper limit. Moreover, because atmosphere-ocean carbon exchange attains isotopic equilibrium much more slowly than chemical equilibrium, our modeling experiment does not imply that the distribution of carbon isotopes in the atmosphere and mixed layer can also be modeled by equilibrium relationships.

The results displayed in Table 3 and in Figures 4 and 5 show how equilibrium calculations can provide a convenient means for modeling future relationships between atmospheric and ocean mixed layer CO_2 budgets. However, before these relationships can be meaningfully applied to predicting oceanic CO_2 uptake, two remaining uncertainties must be resolved. These are 1) the extent to which heterogeneous reactions will change ocean alkalinities; and 2) the rates and mechanims by which CO_2 will be mixed downward from the surface ocean to the deep ocean.

It is possible that the ocean's response to anthropogenic CO_2 may be significantly influenced by heterogeneous reactions which affect alkalinity values; for example, carbonate minerals may dissolve, or organisms may alter their metabolic processes



Figure 5: Schematic representations of the modeling experiment. (a) is a standard CO_2 box model; (b) is modified so that the atmosphere and surface ocean are modeled as a single box.

in response to changing pH values. The range of uncertainties associated with these influences can be assessed by examining the total buffer factor, which is defined as

$$B_{tot} = \frac{\Sigma C}{P_{CO_2}} \cdot \frac{dP_{CO_2}}{d\Sigma C} = \frac{\Sigma C}{P_{CO_2}} \cdot \left[\left(\frac{\delta P_{CO_2}}{\delta \Sigma C} \right)_{TA} + \left(\frac{\delta P_{CO_2}}{\delta TA} \right)_{\Sigma C} \cdot \frac{dTA}{d\Sigma C} \right]$$
(6)

at constant temperature and salinity. B_{hom} is merely a special case of B_{tot} for the condition dTA = 0. Whenever the term d Σ C is positive, the value of the term dTA/d Σ C can theoretically vary from 0 (in the case of constant TA) to 2 (in the case where all of the Σ C change is attributed to carbonate mineral dissolution)*. Because $(\delta P_{CO2}/\delta TA)_{\Sigma C}$ is negative, any amount of carbonate dissolution will imply a value for B_{tot} less than the value for B_{hom} , and a corresponding increase in the surface ocean's effective capacity to absorb CO₂. For example, in average surface seawater, at constant pH or constant total carbonate (individual plus complex) ion concentration, the value of dTA/d Σ C is close to 1. This implies that B_{tot} is close to 2, whereas B_{hom} is about 10.

It is also known that downward transport of CO_2 occurs much more rapidly in some areas of the oceans than in others. For example, Broecker and Takahashi (1977) have shown that CO_2 is injected directly into the North Atlantic Deep Water by downward advection of Norwegian and Labrador Sea surface waters. This surface water is much colder and richer in ΣC than the average surface water. Thus, although CO_2 uptake by the surface ocean as a whole may be reasonably approximated by equilibrium between the atmosphere and a homogeneous average mixed layer, significant vertical CO_2 transport within the oceans occurs in areas where the mixed layer is not "average". In fact, downward advection may occur in some high-latitude areas where the ΣC of the surface water is significantly lower than that expected for equilibrium with the atmosphere. A simplified relationship between the atmosphere and the ocean surface does not eliminate the complicated uncertainties of vertical ocean mixing.

In conclusion, we have shown that, at constant total alkalinity, surface ocean CO_2 uptake can be approximated using well known equilibrium relationships. These relationships appear to be so systematic that the ocean surface might be modeled as a single homogeneous box, and even as a non-independent extension of the atmosphere. However, these simplifications cannot be applied to global CO_2 predictions until we know much more about alkalinity changes and vertical mixing within the oceans. If these important uncertainties can be resolved, surface seawater equilibrium approximations will greatly simplify the task of predicting future oceanic CO_2 uptake.

Table 1: Ocean surface averages calculated from GEOSECS Atlantic and Pacific Ocean data, as detailed in text. Values on bottom line are overall averages calculated by weighting the latitude zone averages according to the sea surface area of each zone.

Latitude	Surface	Temp.	Salinity	Density	TA
(degrees)	(10^6 km^2)	(°C)	(per mil)	(g/cm ³)	(µeq/kg)
70-60	22.696	0.7	33.84	1.027	2310
60-50	36.322	5.1	33.82	1.027	2290
50-45	21.305	7.5	33.54	1.026	2273
45-40	24.244	15.9	34.76	1.026	2295
40-30	53.100	21.2	35.35	1.025	2332
30-15	87.117	24.1	35.59	1.024	2356
15-0	101.469	26.8	35.53	1.023	2350
70-0	346.253	19.3	35.05	1.025	2331

Table 2: Initial conditions for the modeling experiment.

Atmospheric P _{CO2} (atm.)	320×10^{-6}
Surface ocean ΣC (moles/kg.)	2.023×10^{-3}
Surface ocean TA (eq/kg.)	2.330×10^{-3}
Deep ocean ΣC (moles/kg.)	2.305×10^{-3}
Deep ocean TA (eq/kg.)	2.415×10^{-3}

Table 3: Values for atmospheric P_{CO2} (P_{CO2a}) and ocean surface $\Sigma C(\Sigma C_s)$ from the modeling experiment. Columns (a) were generated by the model shown in Figure 3(a); columns (b) were generated by the model shown in Figure 3(b). The initial (1970) values in columns (b) were slightly adjusted by the model in order to conform to the assumption of atmospheresurface ocean equilibrium.

Year	рС (µа	O _{2a} tm.)	ک (mmo	C _s ol/kg.)
	(a)	(b)	(a)	(b)
1970	320.0	319.9	2.023	2.023
1980	338.8	338.5	2.034	2.035
2000	407.1	406.5	2.070	2.072
2020	544.1	543.2	2.124	2.126
2040	791.3	790.3	2.187	2.189
2060	1158.6	1157.7	2.245	2.246
2080	1573.4	1572.5	2.287	2.288
2100	1918.9	1918.0	2.314	2.314
2120	2137.0	2136.0	2.328	2.329
2140	2245.3	2244.3	2.335	2.335
2160	2285.0	2284.0	2.337	2.338
2180	2288.3	2287.3	2.337	2.338
2200	2273.9	2272.9	2.337	2.337
2220	2251.4	2250.3	2.335	2.336
2240	2225.4	2224.3	2.334	2.334
2260	2198.0	2196.9	2.332	2.332
2280	2170.4	2169.3	2.330	2.331
2300	2142.9	2141.7	2.329	2.329

Table 4: Ocean surface uptake of anthropogenic CO_2 , assuming equilibrium with atmospheric P_{CO_2} values. (a) was calculated by summing the uptake for each of the 7 latitude zones; (b) was calculated for a single average surface seawater (Table 1, bottom line).

 Σ (area × Σ C increase × density × mixed-layer depth) in 10¹⁵ moles carbon at P_{CO2} (μ atm.) of:

	325	400	600	1200	1800
(a)	0	1.492	4.170	8.075	10.119
(b)	0	1.507	4.191	8.038	10.014

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