

Global Carbon Budget and Ocean Buffering against Rising Atmospheric CO₂ Concentration

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The natural carbon cycle has been perturbed since the mid-19th century by anthropogenic CO₂ emissions from fossil fuel combustion and deforestation due to population growth and industrialization. The current study simulated the global carbon cycle for the past 42 years using an eight-box carbon cycle model. The results showed that since the terrestrial biospheric carbon sink was roughly offset by the deforestation source, the fossil fuel emission source was partitioned between the atmospheric and oceanic sinks. However, the partitioning ratio between the atmosphere and the ocean exhibited a change, that is, the carbon accumulation rate was faster in the atmosphere than in the ocean, due to a decrease in the so-called ocean buffering capacity. It was found that the ocean buffering capacity to take up excess CO₂ decreased by 50% in terms of the buffer factor over the past 42 years. Accordingly, these results indicate that if the current CO₂ emission trend continues, the future rate of increase in the atmospheric CO₂ concentration will accelerate.

Key words : carbon dioxide, carbon cycle, partitioning, ocean buffering capacity

1. Introduction

Carbon is the most important element for living forms on the Earth because it is both a carbon and energy source. Carbon exists in a variety of chemical forms as either organic carbon or inorganic carbon, and incessantly changes its form through a variety of physical, chemical, and biological interactions between living forms and surrounding environments.

On a global scale, plants in the terrestrial biosphere take up carbon dioxide from the atmosphere and store it as organic carbon for tree growth. Plants also release carbon dioxide into the atmosphere by oxidizing organic carbon as an energy source. Plants pass the organic carbon to the soil in the form of tree death, fallen leaves, and

root decay, where microorganisms decompose it and release carbon dioxide into the atmosphere. The ocean then interacts with the atmosphere through gas exchange at the air-sea interface.

However, this natural carbon cycle has been perturbed since the mid-19th century by anthropogenic CO₂ emissions from fossil fuel combustion and deforestation due to population growth and industrialization. Currently, 6.3 ± 0.4 Gt C/yr (1 Gt C = 1 gigaton as carbon = 10^{15} g as carbon) is emitted from fossil fuel combustion and $0.6 \sim 2.5$ Gt C/yr from deforestation (or land use change)¹⁾. Accurately measured records since 1958, such as the Mauna Loa records, show that the atmospheric CO₂ concentration has rapidly increased to the present 370 ppm and is still increasing at a rate of ~ 1.5 ppm/yr¹⁾. Since the atmosphere is currently accumulating 3.2 ± 0.1 Gt C/yr¹⁾, the remainder is found in the terrestrial and oceanic sink.

Numerous studies have already been conducted on solving the carbon cycle and budget. Most previous ocean-atmosphere interaction studies^{2~5)}

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have focused on the oceanic uptake of CO_2 . However, since these studies have generally assumed a neutral state in the biosphere, the carbon budget of the biosphere has not been accounted for or inferred when balancing the total carbon budget. As such, these studies have omitted the biospheric role in the perturbed global carbon cycle.

Previous terrestrial biosphere-atmosphere interaction studies also fall short in resolving the carbon cycle and budget from a global point of view because the terrestrial biosphere system is relatively heterogeneous compared to the ocean system. As a result, many terrestrial biosphere-atmosphere interaction studies⁶⁻⁸⁾ have been limited to the study of individual species and/or regional scale studies in response to global change.

Kwon and Schnoor⁹⁾ developed the Simple Global Carbon Model(SGCM), which is a coupled ocean-atmosphere-biospheric system. The model includes CO_2 fertilization and temperature effects in the terrestrial biosphere and inorganic chemistry in the ocean. However, it is still limited as regards

quantifying the global carbon budget because it assumes a constant CO_2 emission from deforestation for the model calibration period. Recently reported global deforestation(or land use change) shows that the CO_2 emission from deforestation is continuously increasing.

Accordingly, the current paper reanalyzes the global carbon cycle and budget using SGCM. Throughout the carbon budget study, the ocean's buffering capacity to take up excess CO_2 will be discussed. Plus, to overcome the limitation of the previous model, literature-reported deforestation data are used. The model is calibrated using 42 years of data(1958-1999), including measured atmospheric CO_2 records, observed global temperatures, fossil fuel emissions, and deforestation.

2. Model Description

Figure 1 presents a scheme of the model, which is composed of three large carbon pools, the atmosphere, the terrestrial biosphere, and the ocean.

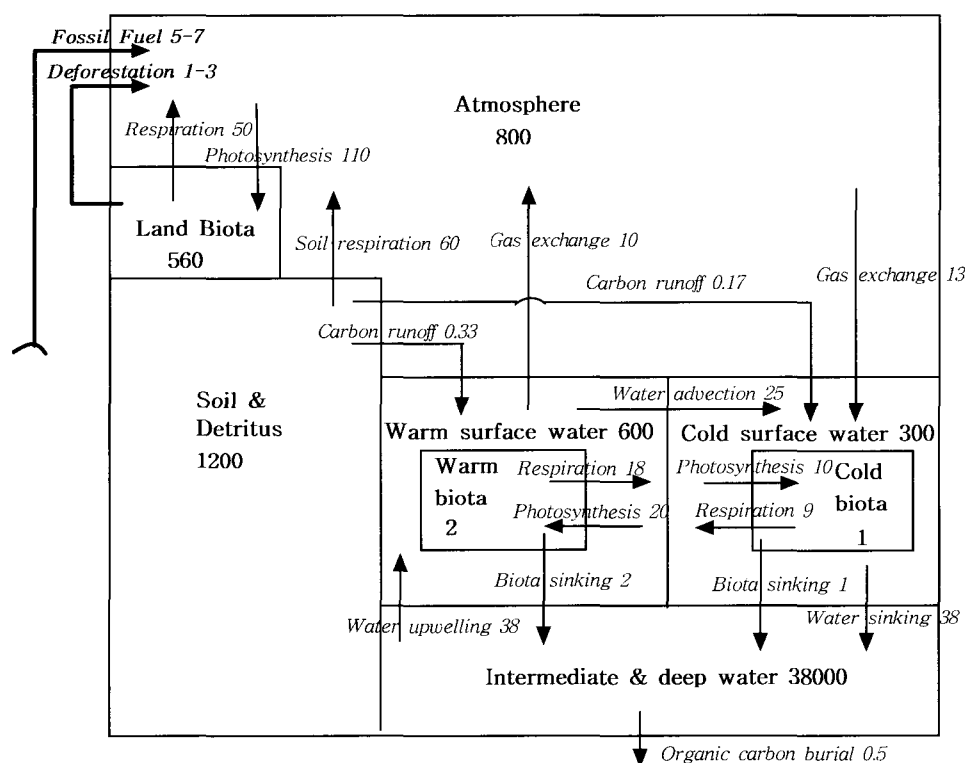


Fig. 1. Schematic diagram of eight-box carbon model with roughly estimated reservoirs and fluxes. Carbon reservoirs are gigatons as carbon(Gt C) and fluxes are Gt C/yr.

The terrestrial biosphere is compartmentalized into the land biota and the soil and detritus. The ocean is compartmentalized into warm ocean surface water, cold ocean surface water, intermediate and deep water, and the ocean biota compartments in both surface waters. Consequently, the model consists of eight compartments and 19 fluxes, which are presented as boxes and arrows, respectively, in Figure 1.

The mass balance equation of the general box modeling can be expressed as follows :

$$V_i \cdot \frac{dC_i}{dt} = \sum_j F_{ji} - \sum_j F_{ij} + \sum_e F_{ei}(\text{Input}) - \sum_e F_{ie}(\text{Output}) \quad (1)$$

in which V_i is the volume of the i^{th} compartment, [L^3]; C_i is the carbon concentration in the i^{th} compartment, [M/L^3]; F_{ij} is the mass flux from the i^{th} compartment to the j^{th} compartment, [M/T]; F_{ei} is the mass flux into the i^{th} compartment from outside the model system (e.g., CO₂ influx into the atmosphere by fossil fuel emission), [M/T]; F_{ie} is the mass flux to outside the model system from the i^{th} compartment (e.g., organic carbon burial in the ocean bottom by carbon sinking in deep water).

Most processes are formulated with first-order kinetics, as is usual in box modeling. However, certain processes, such as the CO₂ gas exchange between the atmosphere and the ocean or the CO₂ fertilization effect on the land biota, are formulated with nonlinear kinetics.

The land biota compartment is composed of plants. Plants fix CO₂ from the atmosphere and store it as organic carbon (photosynthesis). They also release carbon in the form of CO₂ (respiration). In addition, organic carbon in the stems, leaves, and roots are incorporated into the soil compartment seasonally when plants die (litter fall). These processes are influenced by the atmospheric CO₂ concentration and temperature. The CO₂ fertilization effect is assumed to follow the Michaelis-Menton kinetic expression ($k = k_0 \frac{C_{atm}}{K_M + C_{atm}}$), while the temperature effect follows an exponential function ($k = k_0 \theta^{\Delta T}$), where k is the rate of activity, [T^{-1}]; k_0 is the maximum rate of activity, [T^{-1}]; C_{atm} is the CO₂ concentration in the atmosphere, ppm; K_M is the half saturation velocity, ppm; θ is the temperature-variable coefficient of the activity, unitless; and ΔT is the temperature

variation relative to the initial temperature, °C.

Therefore, the flux for photosynthesis can be written as

$$k_{ph} \cdot \frac{C_{atm}}{K_M + C_{atm}} \cdot \theta_{ph}^{\Delta T} \cdot C_{lb} \cdot V_{lb} \quad (2)$$

in which k_{ph} is the maximum rate constant for photosynthesis, [T^{-1}]; θ_{ph} is the temperature-variable coefficient of photosynthesis, unitless; C_{lb} is the carbon concentration in the land biota compartment, [M/L^3]; and V_{lb} is the volume of the land biota compartment, [L^3]. The fluxes for land biota respiration and litterfall are similarly expressed as for photosynthesis.

Plant-derived organic carbon is primarily oxidized by soil microbes and returned to the atmosphere in the form of CO₂ (soil respiration). Because soil microbial activity is strongly influenced by temperature, the flux for soil respiration is written as

$$k_{sr} \cdot \theta_{sr}^{\Delta T} \cdot C_{soil} \cdot V_{soil} \quad (3)$$

in which k_{sr} is the maximum rate constant for soil respiration, [T^{-1}]; θ_{sr} is the temperature-variable coefficient of soil respiration, unitless; C_{soil} is the carbon concentration in the soil compartment, [M/L^3]; and V_{soil} is the volume of the soil compartment, [L^3].

Carbon in the form of CO₂ is exchanged between the atmosphere and the ocean surface waters (gas exchange). The driving force of CO₂ gas exchange is the difference in the CO₂ partial pressure between the atmosphere and the ocean surface water. Therefore, the flux of CO₂ gas exchange between the atmosphere and the ocean surface water is written as

$$k_l \cdot S \cdot (P_{atm} - P_{ocean}) \cdot A_{ocean} \quad (4)$$

in which k_l is the gas transfer velocity, [L/T]; S is the CO₂ solubility (function of temperature and salinity), [$M/L^3/\text{ppm}$]; P_{atm} is the CO₂ partial pressure in the atmosphere, ppm; P_{ocean} is the CO₂ partial pressure in the ocean surface water, ppm; and A_{ocean} is the surface area of the ocean, [L^2].

Carbon is internally cycled based on the ocean circulation. CO₂ is more soluble in cold and saline water. Dense and cold surface water, primarily composed of Antarctic cold water and water near

Greenland, absorbs atmospheric CO₂, which then sinks to intermediate and deep water (cold surface water sinking), meanwhile part of the intermediate and deep water upwells to become warm surface water, primarily in the equatorial area (deep water upwelling). To balance the water mass, water is transported from warm surface water to cold surface water (surface water advection). In addition to the ocean circulation, the ocean biota, which is mainly composed of organic carbon, also contributes to the carbon cycle through biological, chemical, and physical processes. Phytoplankton photosynthesis (ocean biota primary production) lowers the CO₂ partial pressure in the surface water, thereby promoting the absorption of atmospheric CO₂. The ocean biota primary production follows first-order kinetics and the function of the dissolved CO₂ concentration in the surface water. As such, the primary production is remineralized into dissolved CO₂ mostly within surface water (ocean biota respiration), with some sinking to intermediate and deep water (organic carbon sinking), while a small amount is buried in the ocean bottom as organic carbon (organic carbon burial). Some soil organic carbon is also washed out to ocean surface water (runoff), where it is oxidized into inorganic carbon, thereby contributing to an increase in the total inorganic carbon in surface water. Therefore, the flux for the above-mentioned processes is written as

$$k_{ij} \cdot C_i \cdot V_i \quad (5)$$

in which k_{ij} is the mass flux rate constant, [T⁻¹]; and V_i is the volume of the i^{th} compartment.

Consequently, the mass balance equation for the atmosphere can be written as

$$\begin{aligned} V_{atm} \frac{dC_{atm}}{dt} = & F(t) + D(t) - k_{ph} \frac{C_{atm}}{K_M + C_{atm}} \theta_{ph}^{dT} C_{lb} A_{lb} \\ & + k_{br} \frac{C_{atm}}{K_M + C_{atm}} \theta_{br}^{dT} C_{lb} A_{lb} + k_{sr} \theta_{sr}^{dT} C_{soil} V_{soil} \\ & + k_{fso} (P_{uo} - P_{atm}) A_{uo} - k_{fco} (P_{atm} - P_{co}) A_{co} \end{aligned} \quad (6)$$

in which $F(t)$ is the C influx due to fossil fuel use, [M/T]; $D(t)$ is the C influx due to deforestation, [M/T]; and the subscripts are *atm* for atmosphere, *ph* for photosynthesis, *br* for biota respiration, *lb* for land biota, *sr* for soil respiration, *soil* for soil,

wo for warm ocean surface water, and *co* for cold ocean surface water.

Therefore, the eight mass balance equations form a set of ordinary differential equations that can be solved numerically. For more detailed model equations, including a physical description, refer to Kwon and Schnoor⁹.

3. Results and Discussion

3.1. Model Calibration and Results

The model was calibrated with a 42-year record (1958-1999) of atmospheric CO₂ concentrations measured at Mauna Loa¹⁰, which was assumed to represent the global average CO₂ concentration for the purpose of the current study. The annual CO₂ emission data from fossil fuel combustion¹⁰ and deforestation¹¹ are shown in Figure 3. Since deforestation data was not reported after 1991, the 1990 value was assumed for the entire 1990s. The temperature change ΔT , which appears in the temperature-related flux terms was the difference between the temperature at time t and the pre-industrial temperature that was assumed to be -0.4 °C based on historical data¹². The annual mean global surface air temperature for the temperature input was taken from observed data reported by Jones *et al.*¹³ and adapted to meet the above-mentioned preindustrial temperature.

Most rate constants were initially derived from the carbon reservoirs and fluxes reported in previous literature^{1,14,15} and adjusted. Some parameter values, such as the half saturation velocity K_M in the Michaelis-Menton kinetic equation, and gas transfer velocity k_b , were also taken from previous literature^{16,17}. The ocean CO₂ partial pressure and solubility, as a function of the alkalinity, temperature, salinity, and solubility, were calculated using the method proposed by Peng *et al.*¹⁶. In addition, the total alkalinities and surface water temperatures were assumed constant based on Geochemical Ocean Section Study data¹⁹.

Figure 2 shows the simulated results of the carbon reservoir changes in the atmosphere, ocean, and ocean water compartments.

The atmospheric compartment in Figure 2 represents the best fit of the model with the measured atmospheric CO₂ concentration. Table 1 shows

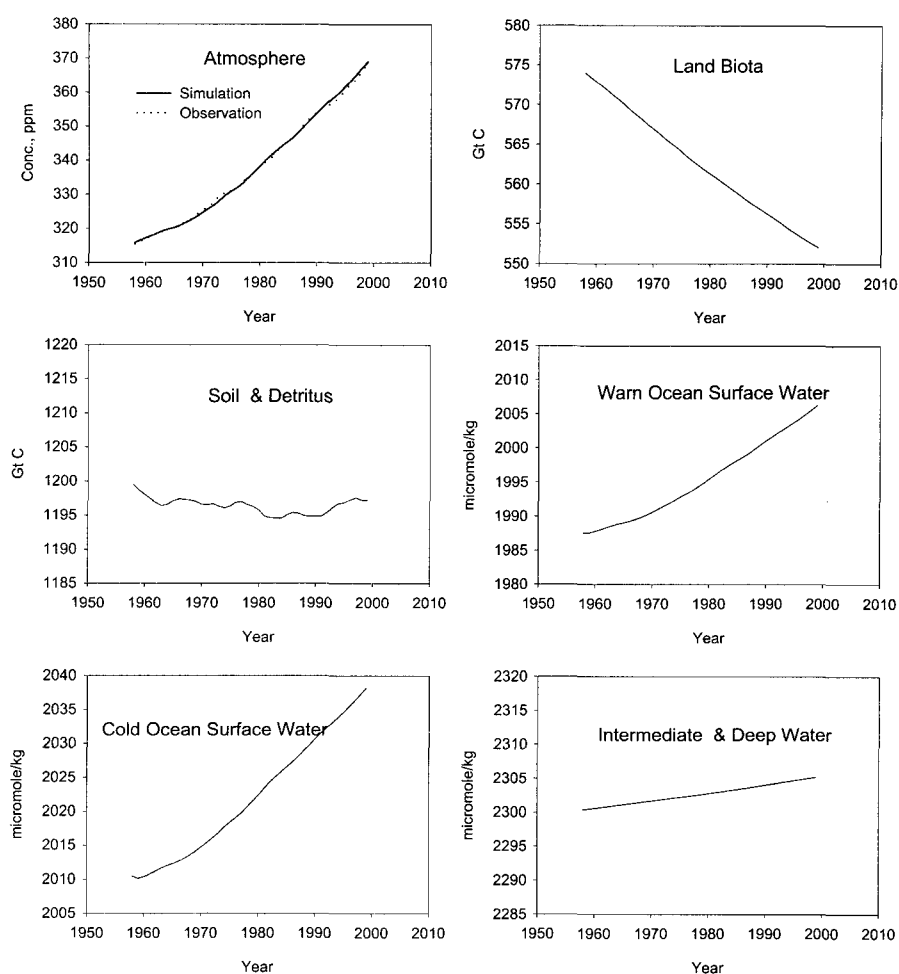


Fig. 2. Simulated carbon reservoir changes. Atmospheric compartment shows simulation vs observation in ppm, Land biota and Soil and detritus in total carbon, and ocean compartments in micromole/kg.

Table 1. Statistical information on calibration results of atmospheric CO₂ concentration

Parameter	Equation	Value
Range of residuals, R	$R = x_{\max} - x_{\min}$	2.30 ppm(-1.101.20)
Mean of residuals, x_{ave}	$x_{ave} = \frac{\sum_{i=0}^n (P_i - O_i)}{n}$	0.048 ppm
Standard Error of mean, SE	$SE = \sqrt{\frac{\sum_{i=0}^n (x_i - x_{ave})^2}{n}}$	0.079 ppm
Root Mean Squared Error, $RMSE$	$RMSE = \sqrt{\frac{\sum_{i=0}^n (P_i - O_i)^2}{n}}$	0.448 ppm

Note : x_{\max} and x_{\min} = maximum and minimum residuals, respectively
 P_i and O_i = simulated and observed concentrations, respectively, at time i
 x_i = residual at time i ($P_i - O_i$)
 x_{ave} = average residual for calibration period
 n = number of observations ($n = 42$)

detailed statistical information on the model calibration result of the atmospheric CO₂ concentration. The standard error was 0.079 ppm and the RMSE was 0.448 ppm.

The atmospheric CO₂ concentration was found to increase from 318 ppm to the current 370 ppm. Meanwhile, the land biotic carbon decreased by 22 Gt C over the 42 years due to competition between deforestation and biotic growth stimulated by CO₂ fertilization and temperature effects. The soil and detritus carbon remained roughly stable within ± 2 Gt C throughout the simulation period despite the continuous release of 0.5 Gt C/yr (see Figure 1) into the ocean (carbon runoff). Since the total carbon runoff over the 42 years was 21 Gt C, the soil and detritus compartment took up an additional 21 Gt C from the land biota. Therefore, the terrestrial biosphere (land biota + soil and detritus) exhibited approximately no change in the carbon reservoir when ignoring the soil carbon runoff, thereby implying that the amount of terrestrial biospheric carbon sink was equivalent to the amount of deforestation over the past 42 years.

The ocean carbon reservoirs are presented in terms of the carbon concentration. Both surface waters exhibited a similar increase to that of the atmospheric carbon dioxide concentration. However, the rate of carbon increase in the surface waters was slower than that in the atmosphere. This was due to the so-called ocean buffering capacity, which is explored later in this paper. The carbon concentration in the intermediate and deep waters was much higher than that in the surface waters. This was due to the so-called "solubility pump" and "biological pump", where dense and cold surface water with a high CO₂ solubility absorbs atmospheric CO₂ and then sinks to become intermediate and deep water. In addition, some portion of the organic carbon formed by photosynthesis in the surface water continuously sinks to become intermediate and deep water, where it is oxidized, thereby increasing the dissolved inorganic carbon.

3.2. Carbon Budget

Figure 3 represents the annual emission sources from fossil fuel use and deforestation, which were used as inputs in the model. Figure 4 represents the model-derived carbon sinks in the atmosphere, ocean, and terrestrial biosphere (land biota + soil

and detritus) during the calibration period using straight lines, thereby showing their linear regression lines. The fluctuation of the atmospheric carbon sink exhibited a reverse pattern and was correlated with that of the terrestrial biospheric carbon sink due to the temperature effect. As seen in Figures 3 and 4 and mentioned in the previous section, during the calibration period the terrestrial biospheric sink was roughly the same as deforestation. Therefore, it can be approximated that the fossil fuel emission source was partitioned between the atmospheric sink and the oceanic sink. Based on the regression results, the atmospheric sink and the oceanic sink increased with an increase in the CO₂ emission from fossil fuel use. However, the increase in the carbon sink was faster in the atmosphere than in the ocean due to the so-called "buffering capacity" of the ocean. CO₂ gas exchange leads to a rapid equilibration between the atmosphere and the surface water. Upon dissolution in water, CO₂ forms a weak acid that reacts with carbonate anions and water to form bicarbonate. The capacity of the oceanic carbonate system to buffer changes in the CO₂ concentration depends on the addition of cations from the weathering of rocks. However, since this process is extremely slow, the effect was negligible for the relatively short time scale used in the current study. Consequently, the ocean buffering capacity was found to decrease with the rising atmospheric CO₂ concentration. Quantitatively, the ocean buffering capacity can be described as buffer factor β

$$\beta = \frac{\Delta pCO_2}{pCO_2} / -\frac{\Delta TIC}{TIC} \quad (7)$$

in which ΔpCO_2 is the change in the atmospheric CO₂ concentration; pCO_2 is the atmospheric CO₂ concentration at a preindustrial level; ΔTIC is the change in the total inorganic carbon concentration in the surface water; and TIC is the total inorganic carbon concentration in the surface water at a preindustrial level. The buffer factor β reported for present ocean surface waters is of the order of 10^{20} . This means that a relative increase of pCO_2 in the atmosphere by 10 % corresponds to a relative increase in the total inorganic carbon in surface water by 1 %. The ocean buffering capacity decreases with an increase in the atmospheric CO₂ concentration because an increased ocean CO₂

partial pressure retards the CO₂ uptake. As such, the carbon concentration changes in both surface waters showed a very similar pattern to that of the atmospheric CO₂ concentration. However, the rate of increase was slower in the surface waters than in the atmosphere; i.e., the buffer factor β increased relative to an increase in the atmospheric CO₂ concentration. This was proved by a quantitative analysis of the model results. Using Eq. 7 with the assumed steady state concentrations of the surface waters (1980 μ mole/kg in the cold ocean surface water and 1955 μ mole/kg in the warm ocean surface water), which satisfied the buffer factor of 10.0 in 1980 (338 ppm in the atmosphere), the calculated average buffer factors for both surface waters are given in Figure 3. The buffer factor exhibited a near linear increase from 7.8 in 1958 to 12.3 in 1999.

Table 2 shows a summary of the annual average source and sink based on the model results. The

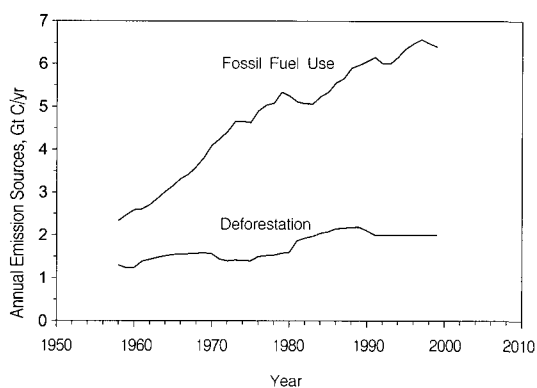


Fig. 3. Annual carbon sources from fossil fuel use and deforestation.

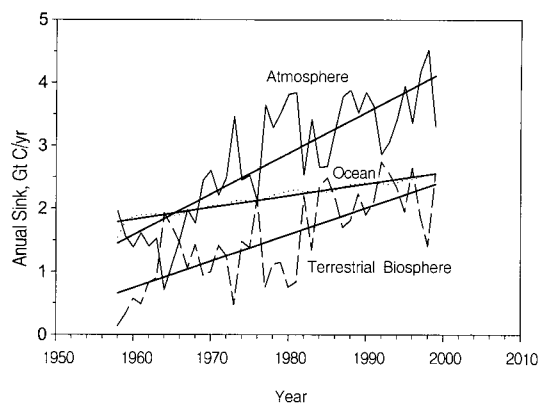


Fig. 4. Model-derived carbon sinks in the atmosphere, ocean, and terrestrial biosphere. Straight lines are the linear regression lines of carbon sinks.

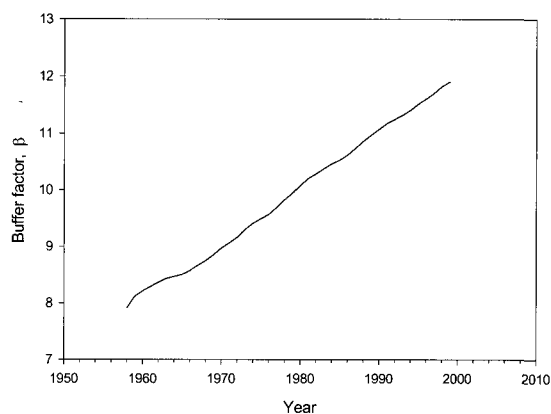


Fig. 5. Model result of average buffer factor in the ocean surface waters.

annual average sources in the 1960s were 2.52 Gt C/yr from fossil fuel use and 1.51 Gt C/yr from

Table 2. Simulated annually averaged global carbon budgets with reported values (in Gt C/yr)

Source and Sink		Current Study				IPCC ¹⁾	
		1960s	1970s	1980s	1990s	1980s	1990s
Source	Fossil Use	3.106	4.702	5.416	6.266	5.1 ~ 5.7	5.9 ~ 6.7
	Deforestation	1.485	1.474	2.017	2.010	0.6 ~ 2.5	N.A.
Total Source		4.591	6.176	7.433	8.276		
Sink	Atmosphere	1.546	2.832	3.337	3.612	3.2 ~ 3.4	3.1 ~ 3.3
	Terrestrial Biosphere	1.129	1.218	1.792	2.211	-0.3 ~ 3.8	N.A.
	Ocean	1.916	2.126	2.304	2.453	1.3 ~ 2.5	1.2 ~ 2.2
Total Sink		4.591	6.176	7.433	8.276		

deforestation, while the sinks were 1.85 Gt C/yr in the atmosphere, 2.00 Gt C/yr in the ocean, and 0.99 Gt C/yr in the terrestrial biosphere. These results increased in the 1990s such that sources were 6.02 Gt C/yr from fossil fuel use and 2.11 Gt C/yr from deforestation, while the sinks were 3.55 Gt C/yr in the atmosphere, 2.10 Gt C/yr in the ocean, and 1.50 Gt C/yr in the terrestrial biosphere. These values were within the range of the reported values with some exceptions where the model results of the atmospheric and oceanic sinks in the 1990s were slightly higher than the reference values¹⁾.

4. Conclusions

The Simple Global Carbon Model, which is an eight-box model and includes a coupled ocean-atmosphere-biospheric system, was used to study the global carbon budget and ocean buffering against rising atmospheric CO₂ concentrations. The following conclusions were made based on the model study.

Over the past 42 years, increased carbon sources from fossil fuel use and deforestation have been allocated to the atmospheric, terrestrial biospheric, and oceanic sinks. The atmospheric and terrestrial biospheric sinks exhibited a yearly high fluctuation due to the direct effect of global temperature variations, while the oceanic sink exhibited a yearly smooth variation due to the indirect effect of global temperature variations.

Since the terrestrial biospheric sink was roughly offset by the source of deforestation, the source from fossil fuel use was partitioned between the atmospheric and oceanic sinks. However, the rate of increase in atmospheric carbon was faster than that in the ocean due to the ocean buffering capacity. The model result showed that the ocean buffering capacity decreased by about 50 % in terms of the buffer factor during the model calibration period. This indicates that the rate of increase in the atmospheric CO₂ concentration will accelerate with a future increase in fossil fuel use.

Acknowledgement

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