

The carbon cycle: sources and sinks of atmospheric CO₂

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Summary. In this contribution we try to give a synopsis of the more important processes within the global C cycle. Special attention is paid to the mechanisms by which atmospheric CO₂ is interchanged between the biosphere and the oceans, and existing qualitative and quantitative uncertainties are pointed out.

Introduction

Measurements indicate a rising CO₂ content of the troposphere (Kelley, 1964; Pales and Keeling, 1965; Brown and Keeling, 1965; Bolin and Bischof, 1970; Keeling et al., 1976a; Keeling et al., 1976b; Freyer, 1978; Wong, 1978b; Lowe et al., 1979). The present increase is about 2.8 Gt C per year at a reservoir size of about 330 ppm, corresponding to 700 Gt C. On the other hand, climate models show that a doubling of the atmosphere's CO₂ partial pressure should result in an increase of the global average temperature by 3 ± 1.5 K (Manabe and Wetherald, 1975; Augustsson and Ramanathan, 1977; Wetherald and Manabe, 1979) which is most likely to bring about large scale climatic changes with rigorous consequences for the terrestrial and marine biota, especially agriculture.

According to Bach (1978) a well-founded prognosis can be based on 3 aspects which should predict the future energy consumption, the dynamic behaviour of the global C cycle and the earth's climatic system, in a fairly realistic manner. Only the coupling of these may serve to represent the dynamics of man's impact on the climate.

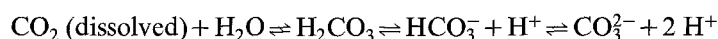
The problem of sources and sinks for atmospheric CO₂ has already been discussed e.g. by Nir et al. (1977) and Zimen (1978). Usually one compares the inputs of CO₂ into the atmosphere (sources) and the outputs from it (sinks) by considering the variation of the atmospheric CO₂ content. In this paper we present such a material balance and point out its limited value for forecasts of the amount of CO₂ in the atmosphere, since the mechanisms of some relevant processes may not yet be sufficiently well established nor are some of the data currently available. In many cases we are far from a reliable mathematical equation describing the flux rates.

Large time scale considerations

The global C cycle may be subdivided into 2 parts: 1. a slow part, with small fluxes connecting large compartments, which comprises most geologic processes such as rock weathering and volcanic ejection of CO₂. Processes within the rock cycle will not be treated in this article; in this context we refer to Garrels et al. (1973) and Kempe (1979b). The former

authors start from the postulate of a long term equilibrium of the rock cycle. 2. a fast part; i.e. the compartments in this part are interconnected by relatively large exchange fluxes as is the case between the troposphere and the oceanic surface layers, as well as between the troposphere and the terrestrial biota.

Let us first in a short survey turn to the effects of the slow processes on the CO₂ partial pressure in the atmosphere. To do this some remarks concerning the sea may be anticipated. The oceanic mixed layer tends to establish equilibrium with the overlying atmosphere. Addition of CO₂ to the atmosphere causes the original surface seawater equilibrium



to raise the concentration of dissolved inorganic C to a new equilibrium level. Now it is assumed that a net transfer takes place from the mixed layer through the thermocline into the deeper layers of the ocean, such that the mixed layer is depleted in the additional dissolved inorganic C. Although transport to the deep sea is slower than equilibration with the atmospheric CO₂ small deviations from the atmospheric equilibrium value can be partly compensated for by the oceans in the long run. This is due to the great reservoir capacity of the oceans in comparison with that of the atmosphere (ratio 50:1). Therefore Degens and Kempe (1978, 1979) assume a relatively constant pre-industrial atmospheric partial pressure pointing out at the same time that it could have altered (slightly) e.g. by the reduction of vegetation during the ice ages and by a changing surface temperature of the sea. Values for the CO₂ content of the pre-industrial atmosphere have been given, e.g. by Freyer (1978) (295 ± 1 ppm corresponding to about 630 Gt C).

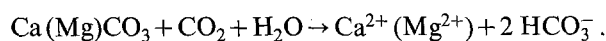
Lithosphere

The earth's crust contains 65.5×10^6 Gt C, of which one quarter is non-carbonate. 35.6×10^6 Gt C are part of the continental sediments, their C content being 1.78% (Kempe, 1979b). The inorganic C in sediments is mainly bound in calcite and aragonite (both CaCO₃) and dolomite, CaMg(CO₃)₂ and less frequently in magnesite, MgCO₃, huntite, CaMg₃(CO₃)₄,

and siderite, FeCO_3 . A small amount of carbonate sediments is weathered each year by CO_2 -containing water.

The washout of atmospheric CO_2 by rainwater is determined by the temperature dependent dissolution equilibrium, i.e. the average CO_2 content of rainwater depends on the temperature of the rain precipitating over the continents. Assuming a dissolution equilibrium at 0°C (strongest washout) one obtains, according to Henry's law, a maximum concentration of $1.13 \text{ mg CO}_2/\text{l}$. The data collected by Miotke (1968) exhibit concentrations mainly between $2.2\text{--}2.7 \text{ mg CO}_2/\text{l}$. The amounts of CO_2 annually washed out by rain can be calculated from these figures together with the annual precipitation of $1.081 \times 10^{20} \text{ g water}$ (Baumgartner and Reichel, 1975) to be $0.033 \text{ Gt C per year}$ (assuming $1.13 \text{ mg CO}_2/\text{l}$) and $0.065\text{--}0.085 \text{ Gt C per year}$, taking the Miotke data.

The main portion of the CO_2 load of soil water, however, comes from soil respiration which may lead to relatively high partial pressures within the soil (Press and Siever, 1974; Kempe, 1979a). Percolation water carrying high concentrations of soil/air derived CO_2 is able to dissolve carbonate rocks according to the equation:



The back reaction of the above equation takes place in the surface waters of the oceans where, through biogenic precipitation of calcium carbonate, CO_2 is released; thus this process does not act as a long term sink for CO_2 .

The total transport of HCO_3^- by rivers to the oceans is estimated by Kempe (1979b) as $0.445 \text{ Gt C per year}$ and according to the same author (determined from figures given by Garrels et al., 1973), the run-off of suspended inorganic C amounts to $0.197 \text{ Gt C per year}$. Discharging of rivers into continental basins

results in the sedimentation of another $0.04\text{--}0.05 \text{ Gt C per year}$ of inorganic C (Kempe, 1979b).

Fossil C input into the atmosphere

We next turn to the problem of how much CO_2 is released to the atmosphere by the combustion of fossil fuels. Figure 1 shows the fossil CO_2 input for the time intervals 1860–1949 after Keeling (1973a), 1950–1969 after Rotty (1977a) and 1970–1976 after Rotty (1977b) in Gt C per year .

As can be seen from this figure the fossil release (\dot{N}_f) at present is about 5 Gt C per year . For different scenarios Rotty (1977a) gives a range of possible values for \dot{N}_f in the year 2000 of $8.2\text{--}14.5 \text{ Gt C per year}$. Perry and Landsberg (1977) estimate \dot{N}_f (2050) as ranging from 13.2 to $26.5 \text{ Gt C per year}$ depending on whether coal or non-fossil energy technologies are employed.

Since fossil resources are non-renewable one may assume, that their consumption is governed by a logistic curve:

$$\dot{N}_f = k_f \cdot N_f \cdot \left(1 - \frac{N_f}{N_{f\infty}}\right) \quad (1)$$

N_f : cumulated fossil input

$N_{f\infty}$: final cumulated input

k_f : growth factor

The term $1 - \frac{N_f}{N_{f\infty}}$ is small for large N_f , and thus

describes the decline of the consumption of fossil fuels when most reserves will have been depleted.

$1 - \frac{N_f}{N_{f\infty}}$ approaches unity for small values of N_f such

that curve (1) takes a nearly exponential increase at the beginning of fossil fuel consumption.

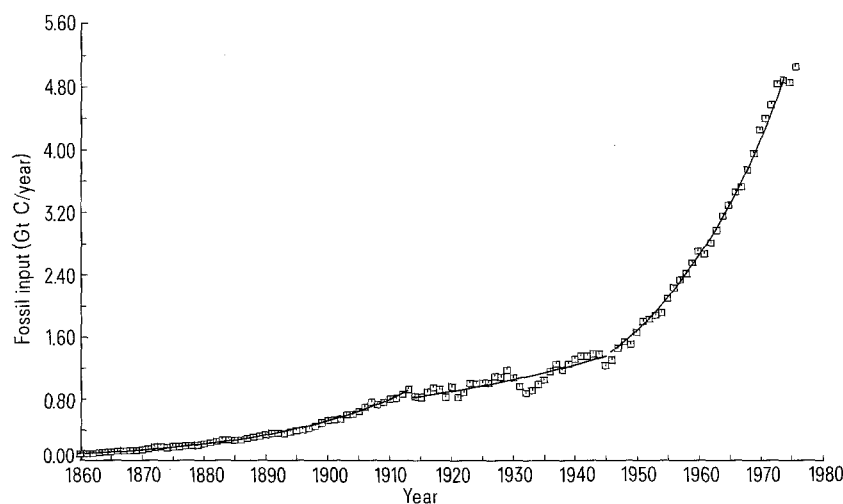


Fig. 1. Input of fossil CO_2 into the atmosphere in Gt C per year .

If one wanted to express a slower or faster depletion of fossil resources, using the same initial growth rate and final cumulated input, this can be done by employing:

$$\dot{N}_f = k_f \cdot N_f \cdot \left[1 - \left(\frac{N_f}{N_{f\infty}} \right)^x \right] \quad (2a)$$

x: cut-off parameter (Keeling and Bacastow, 1977) or by $x > 0$

$$\dot{N}_f = k_f \cdot N_f \cdot \left(1 - \frac{N_f}{N_{f\infty}} \right)^y \quad (2b)$$

(Rotty, 1978); $y \geq 1$

As can be seen from figure 1 the growth coefficient of the fossil input to the atmosphere varies with time. Especially in the time interval between the 2 world wars (1914–1945: 1.6% per year) it deviated strongly from the corresponding values before World War I (4.3% per year) and after World War II (4.4% per year).

Rotty (1978) assumes a growth coefficient of 4.3% per year for future consumption of fossil fuels. The average growth factor for the time interval from 1860 to 1976 is calculated to be 3.5% per year.

Estimations of the final cumulated input ($N_{f\infty}$) carried out by Rotty (1978) and Zimen (1978) yielded values of 7300 and 4800 Gt C, respectively. The difficulty here is to predict depletion of fossil resources under future prices, possible new mining techniques and different techniques of primary energy production (e.g. coal conversion). One distinguishes between the resources recoverable under present economic condi-

tions (reserves) and those presumably recoverable technically.

With the coefficient given by Perry and Landsberg (1977) for the conversion of produced energy (in J) into the amount of C released as CO_2 , the following factors for the individual fossil energy carriers yield:

Coal 1 t SKE¹⁾ \cong 0.7112 t C; 1 TJ \cong 24.273 t C
Crude oil 1 t SKE \cong 0.5673 t C; 1 TJ \cong 19.364 t C
Natural gas 1 t SKE \cong 0.4075 t C; 1 TJ \cong 13.909 t C

From these conversion factors the values in table 1 can be calculated expressing all fossil energy in Gt C. For oil shales and oil sands we have taken the values for crude oil.

Biosphere

We begin this paragraph by sketching the way C would go through a natural ecosystem untouched by man (see Figure 2). The compartments and fluxes are chosen in such a way that they describe the principal processes whereby data are available for the respective reservoir amounts and flux rates of C. The net primary production (NPP) of continental phytomass amounts according to several authors:

77.6 Gt C per year; Bazilevich et al. (1971) (potential)
48.3 Gt C per year; Whittaker and Likens (1973)
45.1 Gt C per year; Lieth (1975)
52.9 Gt C per year; Whittaker and Likens (1975)
59.9 Gt C per year; Ajtay et al. (1979)

For the living phytomass²⁾ of the continents the following values are given:

1081 Gt C; Bazilevich et al. (1971) (potential)
827 Gt C; Whittaker and Likens (1973, 1975)
560 Gt C; Ajtay et al. (1979)

The consumption of a part of the living phytomass by animals (R_{hl}) results in heterotroph respiration and amounts to 3.26 Gt C per year on the continents (Whittaker and Likens, 1973).

Fire is another naturally occurring mechanism of oxidation of living as well as dead phytomass.

The layer of dead plant material on the soil surface is referred to as litter. Its annual production, the litterfall (F_{bl}), is estimated in a model by Reiners (1973) to be 37.5 Gt C per year, a value, which has been taken up by Schlesinger (1977). Ajtay et al. (1979) propose 42.6 Gt C per year. Data for the amount of litter present globally are given by Whittaker (1975) (50 Gt C) and Ajtay et al. (1979) (59.5 Gt C).

Litter is partly oxidized to CO_2 by microbial decomposition, and relatively stable chemical compounds are produced (humus). For the reservoir size of the compartment 'dead organic matter in the soil'

Table 1. Recoverable fossil resources in Gt C

1. Resources recoverable under present economic and technical conditions (reserves)			
	1972 ^a	1975 ^b	1976 ^c
Coal	614	388	1291
Crude oil	72	80	275
Natural gas	29	39	182
Oil shales		27 ^d	21
Oil sands	41	32	35
$N_{f\infty}$ ^e	882	707	1950
2. Resources presumably technically recoverable			
	1972 ^a		1975 ^b
Coal	4301		1314
Crude oil	246		237
Natural gas	161		278
Oil shales			200 ^d
Oil sands	323		222
$N_{f\infty}$ ^e	5157		2392

^a Perry and Landsberg (1977). ^b Bundesanstalt für Geowissenschaften und Rohstoffe (1976). ^c Hubbert (1976). ^d These figures refer to shales with more than 1 t shale oil per 40 t of rock. ^e The values for $N_{f\infty}$ are not only the sum of the individual reserves but also contain the cumulated input until the reference year (126 Gt C for 1972, 141 Gt C for 1975 and 146 Gt C for 1976).

1) 1 t SKE (German coal unit) = 29.3 GJ.

2) For the definitions of the applied terms see e.g., Ajtay et al. (1979).

(N_h) the following figures can be obtained from the literature:

700 Gt C; Bolin (1970)
 1392 Gt C; Kovda (1974)
 3000 Gt C; Bohn (1976)
 1080 Gt C; Baes et al. (1977)
 1456 Gt C; Schlesinger (1977)
 2070; 1635 Gt C; Ajtay et al. (1979)
 1551 Gt C (in 1860) } Schlesinger (1979)
 1515 Gt C (at present)

Dead organic matter in the soil is subject to microbial degradation (R_{h2}) as well; however, decomposition seems to proceed much more slowly in woody parts and humus than in dead leaves (Harris et al., 1975). If organic C is stored in peat or in the subsoil, then it is not very probable that it will return to the atmosphere within a short time. The following data are given for the quantity of peat globally present:

862 Gt C; Bohn (1976)
 165 Gt C; Ajtay et al. (1979)
 500 Gt C; Hampicke (1979c)

The latter author suggests that 0.06–0.24 Gt C are stored in peat annually.

In order to determine those fluxes in figure 2 for which, to our knowledge, no data are available we assume a steady state (subscript o) for all compartments but peat. Furthermore we assume a linear dependent respiration term from N_h to the atmosphere:

$$F_{hao} = \frac{1}{\tau_h} N_{ho} \quad (3)$$

which may be calculated for various biomes if the residence time τ_h is known.

From this we can derive the transfer rate of litter to dead organic matter:

$$F_{lho} = F_{hao} + F_{hmo} + F_{hpo} \quad (4)$$

where F_{hmo} is the transport of organic matter by rivers to the oceans and F_{hpo} is the accumulation rate of C in peat. For F_{hmo} Kempe (1979a, b) gives a value of 0.188 Gt C per year.

Furthermore the flux from litter to the atmosphere is given by

$$F_{lao} = F_{blo} - F_{lho} \quad (5)$$

Heterotroph respiration of organisms in the soil can then be calculated as

$$R_{h2o} = F_{lao} + F_{hao} \quad (6)$$

The C flux from the atmosphere to the living phytomass is of special interest, and it is formulated by some authors in a different, non-linear way. In this context it may be hoped that further insight into the real mechanism is gained by a better knowledge

of gross primary production (GPP) and autotroph respiration (R_a) ($GPP = NPP + R_a$).

The NPP in many models is seen as depending on the atmospheric CO_2 content (N_a) and on the standing living phytomass (N_b) (Keeling, 1973b; Bacastow and Keeling, 1973; Niehaus, 1976; Kohlmaier et al., 1978, 1979).

For the authors of this article the most adequate method of formulating the above dependence is as follows:

$$NPP = k_a \cdot f(N_a) \cdot N_b^\delta \quad (7)$$

$$f(N_a) = \frac{N_a}{K_M + N_a} \quad (8)$$

δ : climax index, in general between 0.15 and 0.4 (Kohlmaier, 1980).

K_M : Michaelis constant (depending on biome type).

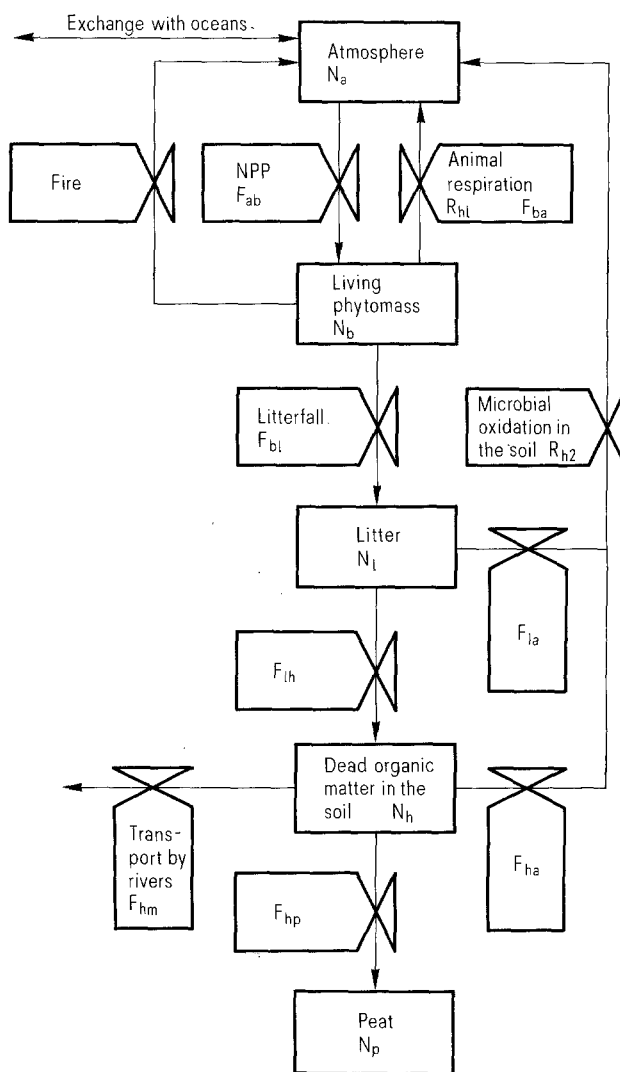


Fig.2. Compartment-model of the terrestrial biosphere as untouched by man (for explanations see text).

$f(N_a)$: passes through the point (0,0) (no growth without CO_2) and approaches for large N_a the saturation value 1.

According to Lemon (1977) and Björkman (1979) no data on the stimulation of growth of trees in open stands by increased p_{CO_2} are available at present. Most experiments with CO_2 fumigation have been carried out in greenhouses where conditions normally differ from the natural ones, as respiration may also be enhanced. Even if photosynthesis may be stimulated by more CO_2 this need not necessarily result in an increased NPP. In addition to temperature and nutrients, the availability of water and the water use efficiency should be of major influence (Lemon, 1977; Goudriaan and Ajtay, 1979). Björkman (1979) proposes that long living plants may exhibit higher NPP with increasing CO_2 content in the atmosphere, whereas short living ones might shorten their life cycle. Hampicke (1979a) suggests that under present conditions an additional 0.3–0.6 Gt C per year may be brought into the biota through stimulation by increased CO_2 . If one assumes that the NPP is in addition proportional to N_b^δ ($\delta < 1$) this means under the conditions of linear respiration terms that after perturbations like fires (natural and anthropogenic), or lumbering, the model system approaches its equilibrium again (Bertalanffy, 1940: equifinality of growth).

The human interference with the biota

The methods used to assess the CO_2 amount released into the atmosphere from the biomass by human activity are based on either direct statistical investigation of the concerned areas or on the analysis of the $^{13}C/^{12}C$ -ratios in tree rings.

We shall present in the following some of the anthropogenic influences on vegetation and the net fluxes resulting from them, the latter always being regarded as educated guesses. Forest reduction in some parts of the tropics is caused by an increasing local population (firewood, shifting cultivation) (Revelle and Munk, 1977; Wong, 1978a) whereas in other parts it is brought about by large landowners and international companies who export lumber and lay out areas to be used for agriculture (Hampicke, 1979c). Woodwell et al. (1978) estimate that by wood combustion in the tropics 3.5 Gt C per year are released. Hampicke (1979c) gives 1.5–4.5 Gt C per year. Bolin (1977) supposes that in the developing countries 0.3 ± 0.1 Gt C per year are stored in wood and that on the other hand 0.8 ± 0.4 Gt C per year by deforestation and another 0.3 ± 0.2 Gt C per year by combustion of firewood are lost to the atmosphere. In the boreal zone according to Hampicke (1979c) 0.1 Gt C per year are stored within peat bogs and an additional 0.1–0.2 Gt C per year or more may be

stored in other waterlogged sites (see table 2). According to the same author, managed forests in the temperate zone may lock up another 0.5–1.0 Gt C per year, whereas Woodwell et al. (1978) assume an input of 1.4 Gt C per year. The fertilization by other gases of anthropogenic origin, mainly NO_x , may provide the possibility of another sink (0.2 Gt C per year, Hampicke, 1979b).

Whenever there is a reduction in above-ground phytomass, organic matter in the soil is increasingly decomposed. Bolin (1977) judges that due to this process 0.3 ± 0.2 Gt C per year enter the atmosphere. The corresponding figures of another authors are 2.8 (Woodwell et al., 1978) and 0.6 Gt C per year (Hampicke, 1979c). In a very detailed investigation Buringh (1979) has presented a low, an intermediate (realistic) and a high estimate of the CO_2 escaping from the soil due to man's interference with values of 2.5, 4.6 and 7.4 Gt C per year, respectively (see table 3).

Revelle and Munk (1977) calculate a cumulated biogenic input in the time interval from 1860 to 1970 as being 72 Gt C and describe it by a time-dependent logistic function. A superposition of 2 such functions has been proposed by Kohlmaier et al. (1979) to describe forest reduction in the northern hemisphere which mainly occurred before World War II (Wong, 1978a) and the reduction in the equatorial regions which goes on at present.

A second method of determining the biogenic input is to measure the $^{13}C/^{12}C$ -ratio in tree rings (Stuiver, 1978; Freyer, 1978, 1979). Stuiver in this way obtains a cumulated non-fossil input of 120 Gt C in the time interval from 1850 to 1950 (60 Gt fossil C), whereas Freyer (1978) estimates the cumulated input from the beginning of industrialization (1860) to 1974 as 70 Gt C from non-fossil sources compared with 136 Gt C from fossil ones. Model calculations with different functions for biogenic input and with evaluation of the resulting $\delta^{13}C$ -values have been performed by Siegenthaler et al. (1978) (see following section).

Table 2. Fluxes between terrestrial biota and atmosphere in Gt C per year

	Woodwell et al. (1978)	Hampicke (1979c)	Bolin (1977)	Buringh (1979)
Forest reduction in the tropics	3.5	1.5–4.5	0.0 ± 0.4	
Peat		–0.1	0 ± 0.1	
Boreal zone	0.8	–0.1	(developed countries)	
Temperate zone	1.4	–1		
Other vegetation	0.2			
CO_2 fertilization		–0.5		
NO_x fertilization		–0.2		
Release from soil	2.0	0.37–1.24	0.3 ± 0.2	4.6 (2.5–7.4)

Inorganic dissolved C in the oceans

The oceans are the major known sink for additional atmospheric CO₂. In lower latitudes they may be subdivided into the well-mixed surface layer, the thermocline layer situated below and the deep sea. In polar regions there is no distinct thermocline; cool surface water sinks to the ocean bottom initiating the oceanic water cycle, which is completed by gradual upwelling of deep water in other parts of the oceans.

The concentration of dissolved inorganic C in the sea varies with geographical position and with depth. Typical concentration profiles (Craig and Weiss, 1970; Kroopnick et al., 1972) exhibit lower values in the mixed layer (about 2.05 moles/m³) than in the deep sea. This may be explained by the fact that dead organic matter in deeper waters is oxidized to inorganic C compounds, in addition to the higher solubility product of CaCO₃ under the increasing pressure at greater depths.

The CO₂ exchange across the air-sea interface between the atmosphere and the surface layer is regulated by the equilibrium between the 2 phases. In addition the concentration of physically dissolved CO₂ (P_m) is influenced by the pH, the concentration of total dissolved inorganic C ($\sum C$) and boron as well as by the alkalinity.

Intending to give a simple relationship between P_m and $\sum C$, one makes use of the so-called buffer factor, ξ

$$\xi = \frac{P_a - P_a^\circ}{P_a^\circ} / \frac{\sum C - \sum C^\circ}{\sum C^\circ} \quad (9)$$

(For different definitions used in the literature see e.g. Wagner, 1979.) The transfer from the atmosphere to the ocean surface is assumed to be proportional to the partial pressure of the atmospheric CO₂ (P_a) or the total mass of C in the atmosphere, respectively:

$$F_{am} = K'_{am} \cdot P_a = K_{am} \cdot N_a \quad (10)$$

Similarly, the transfer of CO₂ from the ocean surface to the atmosphere may be regarded as proportional

to the partial pressure, P_m, which is related to the total dissolved inorganic C by equation (9):

$$F_{ma} = K'_{ma} \cdot P_m = K_{ma} [N_{mo} + \xi (N_m - N_{mo})] \quad (11)$$

The constant buffer factor used is based on a linearization. The exchange of CO₂ between the atmosphere and the sea in the simplest case can be described as molecular diffusion through a stagnant boundary layer, with a linear concentration gradient. Broecker (1974) estimates an exchange of 17 moles CO₂ per m² ocean surface (360 × 10⁶ km²) per year which corresponds to fluxes F_{am} and F_{ma} of 73.5 Gt C per year. Under present conditions these fluxes should not completely compensate such that a net flux into the ocean results.

Compared with the transport into the underlying layers, the equilibrium with the atmospheric CO₂ is established relatively rapidly (Broecker and Peng, 1974). The rate limiting steps of the removal of CO₂ from the atmosphere to the deep sea are transport through the thermocline and cold water downwelling. After arriving in the deep sea it remains there on average for 1000–1600 years.

For the period 1958 to 1978 there was apparently an airborne fraction of 56% CO₂, if no net biotic flux is considered. At a fossil input rate of 5 Gt C per year (1975) this corresponds to an oceanic uptake of 2.2 Gt C per year and the observed increase in the atmospheric C mass of 2.8 Gt C per year. If a biotic contribution of ±10% of the fossil fuel input is assumed, one obtains airborne fractions, with respect to the total input, of 51 and 62%, corresponding to an oceanic uptake of 2.7 and 1.7 Gt C per year respectively. Oeschger et al. (1980) state that this is the range compatible with the box diffusion model (Oeschger et al., 1975).

Organic C in the sea

The difference between the definitions of dissolved organic C (DOC) and particulate organic C (POC) mainly rests on the different particle sizes of the molecular units. POC encompasses particles larger

Table 3. Biogenic input in Gt C per year according to different authors

Woodwell et al. (1978)	2–18 4–8 (most probable range)
Woodwell and Houghton (1977)	5
Adams et al. (1977)	0.4–4
Hampicke (1979c)	1.5–4.5 2.5–3 (most probable range)
Bolin (1977)	1.0 ± 0.6
From soil only:	
Buringh (1979)	4.6 (2.5–7.4)

Table 4. Inputs, reservoirs and losses of organic carbon in the sea (modified from Mopper and Degens, 1979)

Oceanic reservoirs (Gt C)	
DOC (assuming 700 µg C/l)	1000
POC (assuming 20 µg C/l)	30
Plankton	3.0
Inputs (Gt C per year)	
Net primary productivity (assuming 100 g C/m ² /year)	36
Rain (assuming 1 mg C/l)	0.22
Rivers (assuming 5 mg C/l)	0.18
Losses by sedimentation (Gt C per year)	
Nearshore sedimentation	0.0027
Pelagic sedimentation	0.092

than 0.5–1.0 μm diameter. Table 4 shows the most important sources, reservoirs and sinks for oceanic DOC and POC. The sources are considered under 2 general headings: external sources (rain and rivers) and internal sources (net primary production).

The main producer of organic material in the sea is phytoplankton. The amount of C annually fixed by photosynthesis is not precisely known. Values in the literature range from 20 Gt C per year (Ryther, 1969) to 45.8 Gt C per year (De Vooys, 1979). The results of Koblentz-Mishke et al. (1970), assuming 23 Gt C per year as the net primary production of the world oceans, are considered too low by Bruevich and Ivanenkov (1971), pointing out that in tropical regions half of the production occurs in the lower zone of the euphotic layer. Williams (1975) uses a mean value of 36 Gt C per year.

The internal input of organic matter into the sea ranges 1–2 orders of magnitude higher than the external input, although in estuaries the river transport plays an important role. Dead cells of photosynthetically produced phytoplankton are transferred by lysis and partial mineralization into DOC and POC. Besides, different living organisms excrete dissolved and/or particulate organic matter. These products are labile and transformed rapidly. About 10% of the so-formed DOC is converted into high-molecular weight complexes (refractory DOC) which are much more resistant to microbial activity (Ogura, 1975).

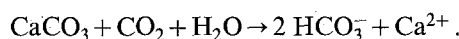
The vertical profiles of DOC (Williams, 1975) and POC (Brewer et al., 1976) show that the concentrations in the euphotic zone are generally highest. A typical value for this zone would be 0.6–1.0 mg C/l for DOC (using wet oxidation analysis) (Williams, 1975). The corresponding value for POC is $> 60 \mu\text{g C/l}$ (Brewer et al., 1976). In productive waters such as those of the Peru current and of the North Atlantic the concentration values may be $> 100 \mu\text{g C/l}$. At depths ranging from 500 to 1200 m there is a sharp minimum both of organic matter and of dissolved O_2 because of areobic oxidation of organic material (Kroopnick et al., 1972). Below this depth a constant concentration of DOC and POC is observed.

Mopper and Degens (1979) give an estimate of the organic fluxes in the sea (table 5). They assume an average primary productivity in the euphotic zone of 100 g C/m^2 per year equivalent to 36 Gt C per year. Nearly the whole primary production is recycled in this zone (upper 200 m of the ocean) through grazing and respiration (De Vooys, 1979; Mopper and Degens, 1979), thus the flux of organic matter leaving the euphotic zone is relatively small (estimated as $4.1\text{--}10.0 \text{ g C/m}^2$ per year). Because of biological oxidation both in the water column and in the sediments and of conversion of labile to refractory DOC the resulting sedimentation rate is $0.2\text{--}0.4 \text{ g C/m}^2$ per year.

CaCO₃ in the oceans

Although the oceanic surface layer is supersaturated with respect to the solubility product of CaCO_3 , chemical precipitation is kinetically hindered. New CaCO_3 is only formed by organisms. The sinking rates range from 1.7 Gt CaCO_3 per year for the Pacific, to 2.9 Gt CaCO_3 per year for the Atlantic (Broecker and Li, 1970) yielding an estimated sinking rate of 0.7 Gt C per year.

These solid CaCO_3 particles may either be sedimented in lower depths or may reach greater depths where they can be dissolved according to



Sediments which are bathed in undersaturated seawater can at least partially redissolve as well. Recently it has been proposed that high magnesian carbonate compounds deposited as coatings on calcite and aragonite can redissolve in the mixed layer under increased CO_2 concentrations (Wollast et al., 1978). If this were the case the oceans would have a greater uptake capacity for atmospheric CO_2 than hitherto accepted.

Conclusion

At present the atmospheric CO_2 content increases by about 2.8 Gt C per year (about 1.55 ppm per year). This is due to several sources: 1st, about 5 Gt C per year from fossil fuel combustion, 2nd, -0.5 to 18 Gt C per year (center of estimates: 2.3 Gt C per year) from reduction of phytomass, 3rd, 0.1 to 7.0 Gt C per year (center of estimates: 2 Gt C per year) from release of soil C.

Table 5. Summary of organic fluxes in the sea (modified from Mopper and Degens, 1979)

Flux	g C/m^2 per year*	Reference
Total flux of organic matter leaving euphotic zone	4.1–10.0	
Particulate organic carbon (POC)		
1. Biological oxidation in the water column	2.0–4.0	Kroopnick and Craig (1976)
2. Biological oxidation in sediment	0.5–3.0	Smith and Teal (1973)
3. Permanently trapped in sediment	0.2–0.4	Degens and Mopper (1976)
Dissolved organic carbon (DOC)		
1. Labile DOC converted to refractory DOC	0.4–0.6	Williams (1971)
2. Deep water oxidation of labile DOC	1.0–2.0	Craig (1971)
Efficiency of recycling per year	94–95%	

*1 g C/m^2 per year = 0.36 Gt C per year.

Table 6. Material balance for atmospheric CO₂ (values in Gt C per year)

	Source Fossil	Biogenic	Soil derived	Increase atmosphere	Sink Oceans	Unexplained surplus
Case I	5	2.3	2.0	2.8	2.2	4.3
Case II	5	1.6	1.3	2.8	2.6	2.4
Case III	5	1.1	1.0	2.8	3.3	1.0

Case I: data as derived from table 3 and 4 (centers of estimates); case II: biogenic and soil release reduced by 30%, oceanic uptake increase by 20% ; case III: biogenic and soil release reduced by 50%, oceanic uptake increased by 50%.

Assuming the lower estimates are correct, a source – sink problem does not exist. This is the situation described by the box diffusion model (Oeschger et al., 1975, 1980), which, regarding the range of uncertainties of some of the model parameters, can account for the atmospheric CO₂ increase under consideration of a biogenic input in the order of $\pm 10\%$ of the fossil one. If, on the other hand, one considers the upper values for biogenic and soil C release then there is a real source – sink problem that cannot be explained by any of the models we are familiar with. Taking the centers of estimates (see table 6, case I) the biota clearly act as a source for atmospheric CO₂ to such an extent that the resulting surplus must be counterbalanced by some yet unknown sink(s), if the ocean uptake capacity is assumed to remain unchanged.

Recently, however, several suggestions have been made resulting both in a lower input of biogenic C to the atmosphere and an enhanced uptake of C by the oceans. Seiler and Crutzen (1980), in analyzing phytomass burning, estimated that incomplete combustion leads to a large fraction of relatively stable, reduced C compounds (e.g., charcoal) which do not reach the atmosphere within the considered time range. A process with a similar effect has been proposed by Lieth (personal communication). Follow-

ing vegetation changes by man's impact, erosion may start or increase leading to an enhanced river discharge of soil C into the oceans. Taking into account both effects, we may reduce the values for phytomass- and humus-derived CO₂ input each by 30% (case II) and by 50% (case III), respectively. A possible increase of the C uptake capacity of the oceans has been suggested by considering downwelling of polar surface waters (Björkström, 1979a; Hoffert et al., 1979) and additional dissolution of CaCO₃ (Keeling and Bacastow, 1977; Wollast et al., 1978). We summarize both effects again in table 6 by assuming an oceanic uptake increased by 20% (case II) and by 50% (case III), respectively.

In the intermediate case (II) 2.4 Gt C per year of atmospheric C input remain unbalanced whereas this figure is reduced to 1 Gt C per year in case III. In that case the source – sink problem is reduced to a large extent, however a lot of detailed work has to be done before a sufficient understanding of the atmosphere – biosphere – ocean system is obtained.

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The effect of the atmosphere-biosphere exchange on the global carbon cycle

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The earth's land vegetation and soils currently comprise $2000\text{--}3000 \times 10^{15}$ g of organic C, roughly 3–4 times the amount stored in atmospheric CO₂ (table 1). If these reservoirs lose or gain only 1% of their organic C, the result will be a net input of CO₂ to, or a net withdrawal from, the atmosphere of $2\text{--}3 \times 10^{15}$ g, equivalent to 40–60% of the current annual anthropogenic CO₂ production from the burning of fossil fuels. Even an annual net transfer of only one tenth of this size, or $0.2\text{--}0.3 \times 10^{15}$ g, will represent a quantity anything but negligible if one attempts to

model the global carbon cycle. This demonstrates the high short-term sensitivity of the atmospheric CO₂-budget to natural or anthropogenic changes in the terrestrial biota's C pool.

Models of the global carbon cycle generally conclude that the amount of organic C stored in land vegetation and soils is, presently, either in a steady state or is slightly increasing (Keeling, 1973b; Bacastow and Keeling, 1973; Oeschger et al., 1975; Keeling and Bacastow, 1977; Broecker et al., 1978; Siegenthaler and Oeschger, 1978; Björkström, 1979). Otherwise,