# Source Functions of CO<sub>2</sub> and Future CO<sub>2</sub> Burden in the Atmosphere\*

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A logistic source function for  $CO_2$  was derived which takes into account the input arising from the burning of fossil fuels, the stimulation of photosynthesis by the increasing partial pressure of  $CO_2$ , and the decrease of biomass through deforestation etc. The parameters in a 5-box-model for the kinetics of  $CO_2$  were adjusted to fit the new Mauna Loa data on  $CO_2$  concentrations in air. Using these parameters and a buffer factor  $\xi(t)$  for the absorption of  $CO_2$  into the sea, the future  $CO_2$  burden was calculated for status quo conditions and for different values of the growth coefficient of fossil fuel consumption.

The results show that one can change the deforestation factor in rather wide limits without changing very much the future CO<sub>2</sub> concentration in air during the next 80 years or so (cf. Figure 4). On the other hand, the future CO<sub>2</sub> burden depends strongly on the growth rate of fossil fuel consumption and will double under status quo conditions early in the next century (cf. Figure 5).

Any rational solution to the question of the optimal mix of fossil and nuclear energy sources must take into consideration the future burden of  $CO_2$  in the atmosphere and its climatological consequences. To asses the future  $CO_2$  burden, long-term considerations are clearly called for as already stated in the SCEP report<sup>2</sup>. Since publication of this report, the models for the natural carbon cycle have improved considerably, especially through the work of Keeling et al.<sup>3</sup>, and of Oeschger and co-workers<sup>4</sup>.

As the total amount of fossil fuels is limited, extending only into the next century, any model using an exponential source function will grossly overestimate futur CO<sub>2</sub> concentrations. Therefore, in a previous paper<sup>5</sup> one of the present authors proposed the use of the logistic function for the input of CO<sub>2</sub>. Using such a source function Zimen and Altenhein<sup>6</sup> arrived at predictions for the CO<sub>2</sub> concentration in the atmosphere and the sea over the next century. The 3-box-model used was, however, rather simple, and the growth coefficient for the energy consumption was — according to present knowledge — overestimated. Furthermore, no change of biomass was taken into account.

- \* Preliminary communication at the Dahlem Conf. on Global Chemical Cycles and their Alterations by Man, Berlin, Nov. 1976; cf. Ref. <sup>1</sup>.
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We have, therefore, made a re-evaluation of the problem, using a new source function, the mathematical procedure proposed by Avenhaus and Hartman<sup>7</sup>, and a 5-box-model with a set of reservoir constants and exchange coefficients consistent with the experimental data of CO<sub>2</sub> concentrations in air. As regards global biomass, we have considered both an increase due to the rising partial pressure of atmorpheric CO<sub>2</sub>, and a decrease through deforestation, resulting in a net decrease within the next decades. Alternatively, we have also considered the case of constant biomass. The deforestation parameter is an improvement also compared to our treatment in the recent short communication <sup>1</sup>.

### 1. The Source Function for CO<sub>2</sub>

1.0. CO<sub>2</sub> input from the burning of fossil fuels and the production of cement

Baxter<sup>8a</sup>, Machta<sup>9a</sup> and Keeling<sup>10</sup> have made assessments of the man-made annual releases of CO<sub>2</sub> through fossil fuel burning and cement production since 1860 or so, and Rotty<sup>11</sup> has calculated new data for 1960 through 1971 including flared gas associated with crude oil production.

For our purposes, we have used Keeling's data up to the year 1959 after correction for flared gas as mentioned in his note "added in proof" and Rotty's data (nearly the same as Keeling's) from 1960 to 1965, as the latter provides a more thorough



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assessment of flared gas. For the years 1966 to 1974 more recent data are available from the United Nations 12, and thus we have provided our calculations for this period.

The authors mentioned above have used statistical data from the United Nations for the production, rather than consumption, of fossil fuels and cement. This procedure is correct for flared gas and for cement production, because in each of these cases CO<sub>2</sub> is liberated during the process of production. For fossil fuels, however, it seems more appropriate to use the data for consumption, as CO<sub>2</sub> is only generated when fossil fuels are burned, not while they are produced. In general, the production data of the UN are slightly higher as a result of a net increase of fossil fuels in storage and of losses.

The UN data on fossil fuel production and consumption are given in units of tce a. To convert these figures into mols of CO2 liberated, we have used the following "CO<sub>2</sub> factors".

For coal and lignite:

$$\begin{split} \frac{710\,\mathrm{kg}\,\mathrm{C}^{\,\mathrm{b}}}{1\,\mathrm{tce}} \times 0.99^{\,\mathrm{c}} \times \frac{10^3\,\mathrm{mol}}{12.011\,\mathrm{kg}\,\mathrm{C}} \\ &= 58.52 \times 10^3\,\frac{\mathrm{mol}\,\mathrm{C}}{\mathrm{tce}}\,. \end{split}$$

For crude oil and natural gas liquids:

$$\begin{split} \frac{\text{1 t liquid}}{\text{1.47 tce}^{\,d}} \times \frac{950 \, \text{kg C}^{\,e}}{\text{1 t liquid}} \times 0.915^{\,c} \times \frac{10^3 \, \text{mol}}{\text{12.011 kg C}} \\ = 49.22 \times 10^3 \, \frac{\text{mol C}}{\text{tce}} \,. \end{split}$$

For natural gas:

$$\begin{split} \frac{10^3 \, m^3 \, \mathrm{gas}}{1.332 \, \mathrm{tce}^{\, d}} \times \frac{540 \, \mathrm{g} \, \mathrm{C}^{\, f}}{m^3 \, \mathrm{gas}} \times 0.97^{\, c} \times \frac{1 \, \mathrm{mol}}{12.011 \, \mathrm{g} \, \mathrm{C}} \\ = 32.74 \times 10^3 \frac{\mathrm{mol} \, \mathrm{C}}{\mathrm{tce}} \, . \end{split}$$

- $^{\rm a}$  ''metric tons of coal equivalent' defined through 0.123 toe = 1000 kWh. As 1000 kWh = 3.6000  $\times$  109 J it follows: 1 tce =  $29.268 \times 10^9 \text{ J} \approx 29.3 \text{ GJ}$ .
- b the carbon content corresponding to a heat value of 29.3 GJ is 71% of weight; cf. Keeling 1973 (Ref. 10) Fig. 3, p. 178.
- c fraction of Coxidized according to Keeling 1973 (Ref. 10), Table 11, p. 191.
- d Ref. 12, App. II, p. 909.
   e Keeling 1973 (Ref. 10) uses 840 kg C/t oil and 1.3 tce/t oil. In the new U N statistics (Ref. 11), the latter value is changed to 1.47 tce/t oil and this higher heat value thus corresponds to 950 kg C/t oil.
- f cf. Keeling 1973 (Ref. 10) Table 11, p. 191.

The amount of flared gas associated with crude oil production, as compared to the amount of natural gas consumed, varies widely in different countries and in different years 13. In some instances all resulting natural gas is flared, in others nearly all is consumed. For the early 1970's Rotty<sup>11</sup> calculated 15% flared as an average. As the price of natural gas is rising, this percentage will tend to decrease. Thus, at present the following CO2 factor will be used:

For flared gas:

$$\begin{split} \frac{0.15^{3}m~gas~flared}{m^{3}~nat.~gas~produced} \times &\frac{540~g~C~^{a}}{m^{3}~gas~flared} \times 0.97~^{b} \\ \times &\frac{1~mol}{12.011~g~C} = 6.54 \frac{mol~C}{m^{3}~gas~produced} \end{split}$$

(the reason for using in this case the figures of natural gas *production* has been given above).

For cement, finally, we have applied the following relation:

$$\begin{split} \frac{137 \text{ kg C}^{\text{c}}}{\text{t cement}} \times & \frac{10^3 \text{ mol}}{12.011 \text{ kg C}} \\ &= 11.41 \times 10^3 \frac{\text{mol C}}{\text{t cement}} \,. \end{split}$$

In some cases — up to now rather few — the international SI units have been used in the literature instead of the obsolete tce unit for the resources of fossil fuels. As 1 tce =  $29.3 \times 10^9$  Joules, the corresponding CO<sub>2</sub> factors areas follows:

For coal and lignite 2,00 mol C/MJ; For petroleum liquids 1.68 mol C/MJ; For natural gas 1.12 mol C/MJ; For natural + flared gas 1.29 mol C/MJ.

It should be pointed out that all statistical data on fossil burning refer to commercial production. According to the World Energy Conference 1974<sup>14</sup> about 15% of the global energy production still comes from non-commercial sources like wood, agricultural waste and animal dung, especially in the developing countries. Most of these non-commercial materials belong to the natural carbon cycle; if they

<sup>a</sup> cf. Keeling 1973 (Ref. 10) Table 11, p. 191.

<sup>c</sup> cf. Rotty 1973 (Ref. 11) Table 3, p. 514.

fraction oxidized according to Keeling 1973 (Ref. 10) Table 11, p. 191.

were not burned they would in any case be oxidized naturally within a few years. However, some of this material, like peat and large wood cuttings, oxidizes faster when burned than would happen through natural processes, and thus returns  $\mathrm{CO}_2$  into the atmosphere more quickly. Hence, the  $\mathrm{CO}_2$  production as computed from the statistical data on fossil fuel consumption may result in minimum values.

Furthermore, it should be stressed that, as it is not possible to prescribe error limits for a certain confidence level to the statistical data, the accuracy of the statistics is certainly quite low. The error estimated by Keeling  $^{10}$  for the carbon fraction in various types of fuel is 10-15% standard deviation, and the overall error for the figures on man-made  $\mathrm{CO}_2$  emissions may be much higher, because the estimates concerning the production in many countries are rather uncertain.

With these reservations in mind, we feel that the input data presented in Table 1 are the best available at the present time.

# 1.1. CO<sub>2</sub> input from change of biomass

According to Whittacker and Likens  $^{15}$  the most competent estimate of the global net primary production rate (NPP) of living biomass is 4.41  $\times\,10^{15}$  mols of C or CO<sub>2</sub> per year. In equilibrium the same amount of CO<sub>2</sub> will be released into the atmosphere through oxidation of dead biomass.

Because of anthropogenic alterations the biomass is, however, not in equilibrium with the atmosphere. As is well known, the growth rate of plants can be enhanced to a certain degree by raising the partial pressure of CO<sub>2</sub> as long as other factors (water, nutrients, light) are not limiting. Hence, the industrial input of CO2 may well result in a somewhat higher NPP. Therefore, Oeschger et al. 4, Keeling<sup>3</sup> and Niehaus<sup>16</sup> have considered the biosphere as a sink for industrial CO<sub>2</sub> and evaluated the future burden of CO2 using a biological growth factor in their model computations. Botkin et al. 17, 18 have indicated that the increase in NPP can only be small because when photosynthesis is stimulated by higher partial pressure of CO2 it will soon become limited by other factors.

On the other hand the big forests, representing about 60% of the total biomass, have been harvested and cleared to give room for agricultural land, highways, cities etc. without adequate reforestation;

other formerly green areas have been devastated by erosion. The question as to whether the biomass reservoir is increasing or decreasing has been reviewed by different authors at a recent Dahlem workshop <sup>19</sup> and by Bolin <sup>20</sup>. Even if it is not possible at present to answer the question in an unequivocal and quantitative way, the weight of evidence seems to point in the direction of a net reduction of the living biomass. Hence, the net effect is perhaps, and more probably, that the biomass is not a sink but a source of CO<sub>2</sub>.

The highest estimate was made by Woodwell and Houghton  $^{21}$ , who assume an input of approximately  $0.4 \times 10^{15}$  mol of  $CO_2$  per year at present through reduction of the biomass, that is about the same amount as from burning of fossil fuels (cf. Table 1). We will consider a decrease of the biomass as an alternative.

### 1.2. The logistic function

As pointed out in the beginning of this paper the extrapolation of the exponential increase of the CO<sub>2</sub> input is not appropriate when making long-term projections. We, therefore, have used the logistic function first introduced by Verhulst (1838)<sup>22</sup> and experimentally verified as growth function in biological systems under ideal conditions <sup>23</sup>. Accordingly the input rate of CO<sub>2</sub> can be expressed as:

$$\mathrm{d}n^{\mathrm{i}}/\mathrm{d}t = \alpha \, n^{\mathrm{i}} \left[ (n_{\infty}^{\mathrm{i}} - n^{\mathrm{i}})/n_{\infty}^{\mathrm{i}} \right] = \alpha_{\mathrm{eff}} \, n^{\mathrm{i}}$$
 (1)

and the cumulated input at time t will be:

$$n^{i} = n_{\infty} / \{1 + [(n_{\infty}^{i}/n_{0}^{i}) - 1] \exp(-\alpha t)\}$$
 (1a)

(index 0 for t = 0, i.e. before 1860; index  $\infty$  for  $t = \infty$ ).

Figure 1 shows the input rates of  $CO_2$  from 1860 up to the present as tabulated in Table 1. One finds a growth coefficient of  $\alpha_{\rm eff} = 4.3 \%/\alpha$  for the periods 1860—1910 and 1945—1975 but a disturbed growth in between, for obvious reasons. Hence, for the simulation of the experimental data on  $CO_2$  concentration in air one cannot apply a single value of  $\alpha$  for the whole period. Instead we have used the actual input figures according to Table 1 in our computer model.

For the extrapolation of the curve into the future we need first to discuss the value of  $n_{\infty}^{i}$ .

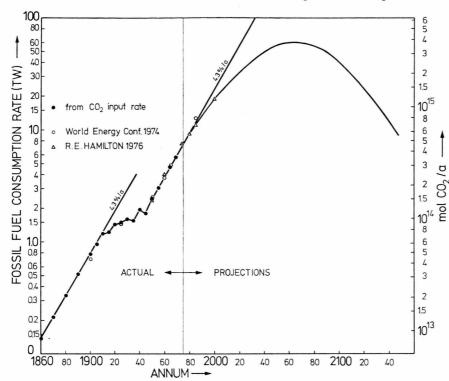


Fig. 1. Input rates of CO<sub>2</sub> from 1860 to 1974 and extrapolation according to Eq. (1) with  $\alpha=4.3\%/a$  and  $n_{\infty}{}^{i}=400\times10^{15}$  mol. WEC 1974 cf. Ref. 14; Hamilton 1976 cf. Ref. 55.

Table 1. CO<sub>2</sub> input rates  $(\dot{n}^i)$  in  $10^{15}$  mols per year up to 1959 according to Keeling 10, from 1960—1965 according to Rotty 11, and from 1966—1974 according to the present authors.

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Year	$\dot{n}^i$	Year	$\dot{n}^i$	Year	$\dot{n}^i$	Year	$\dot{n}^i$
1860	0.0078	1890	0.0292	1920	0.0803	1950	0.1507
1861	0.0082	1891	0.0305	1921	0.0694	1951	0.1627
1862	0.0082	1892	0.0308	1922	0.0747	1952	0.1655
1863	0.0088	1893	0.0302	1923	0.0843	1953	0.1695
1864	0.0096	1894	0.0315	1924	0.0837	1954	0.1736
1865	0.0102	1895	0.0333	1925	0.0844	1955	0.1890
1866	0.0107	1896	0.0344	1926	0.0844	1956	0.2006
1867	0.0115	1897	0.0360	1927	0.0921	1957	0.2097
1868	0.0114	1898	0.0379	1928	0.0916	1958	0.2140
1869	0.0118	1899	0.0415	1929	0.0978	1959	0.2023
1870	0.0121	1900	0.0438	1930	0.0905	1960	0.2223
1871	0.0135	1901	0.0451	1931	0.0814	1961	0.2189
1872	0.0147	1902	0.0462	1932	0.0735	1962	0.2304
1873	0.0157	1903	0.0506	1933	0.0773	1963	0.2439
1874	0.0153	1904	0.0512	1934	0.0838	1964	0.2582
1875	0.0158	1905	0.0540	1935	0.0868	1965	0.2685
1876	0.0160	1906	0.0581	1936	0.0964	1966	0.2820
1877	0.0163	1907	0.0644	1937	0.1032	1967	0.2847
1878	0.0164	1908	0.0615	1938	0.0978	1968	0.3053
1879	0.0173	1909	0.0642	1939	0.1038	1969	0.3241
1880	0.0189	1910	0.0672	1940	0.1094	1970	0.3448
1881	0.0204	1911	0.0687	1941	0.1125	1971	0.3562
1882	0.0219	1912	0.0724	1942	0.1122	1972	0.3714
1883	0.0233	1913	0.0776	1943	0.1147	1973	0.3930
1884	0.0235	1914	0.0701	1944	0.1139	1974	0.3938
1885	0.0231	1915	0.0695	1945	0.1016		
1886	0.0232	1916	0.0748	1946	0.1094		
1887	0.0248	1917	0.0790	1947	0.1248		
1888	0.0269	1918	0.0779	1948	0.1359		
1889	0.0274	1919	0.0694	1949	0.1347		

Table 2. Recent estimates of the global potential resources of fossil fuels. Column 1: recoverable under present conditions (Hubbert 1976\*, Ref. 24), Column 3: total potential resources (WEC 1974, Ref. 14). Columns 2 and 4: corresponding  $CO_2$ -input calculated with the appropriate  $CO_2$  factors given above. The reported figures for  $R_{\rm pot}$  are in all cases the highest estimates and can by their very nature only be considered as very rough figures. The estimate for shale and tar-sand oil is especially uncertain, cf. Ref. 14.

	$egin{array}{l} r\! imes\!R_{ m pot} \ [10^{21}~{ m J}] \end{array}$	$ \begin{array}{ll} \text{correspond.} \\ \text{CO}_2 \text{ input} & R_{\text{pot}} \\ \text{[}10^{15} \text{ mol]} & \text{[}10^{21} \text{ J} \end{array} $		correspond. $CO_2$ input $[10^{15} \text{ mol}]$	
	1	2	3	4	
Coal and Lignite	53	106	300	600	
Petroleum liquids	14	$\bf 24$	79	133	
Tar-sand and shale oil	3	5	11	18	
Natural gas	13	17	43	57	
Sum	83	152	$\overline{433}$	808	

<sup>\*</sup> Hubbert's figures are marked as "original supply recoverable under present economic and technical conditions".

### 1.3. The final cumulated input of CO<sub>2</sub>

According to Eq. (1) we need a value for the final cumulated input of  $\mathrm{CO}_2$   $(n_\infty^{\mathrm{i}})$ . Previously <sup>6</sup> we have used  $n_\infty^{\mathrm{i}} \approx 600 \times 10^{15}$  moles of  $\mathrm{CO}_2$ . The most recent information on the potential global resources of fossil fuels comes from the World Energy Conference 1974 <sup>14</sup> and from Hubbert <sup>24</sup>, and is summarized in Table 2.

It is plausible that the potential resources recoverable under present conditions (col. 1) and the corresponding CO<sub>2</sub> input (col. 2) are minimum values, because when resources dwindle the tendency will be for higher recoveries (according to the figures in Table 2 the over-all recovery factor under present conditions (r) is about 19%). On the other hand, the total potential resources (col. 3) and the corresponding CO<sub>2</sub> input (col. 4) are probably upper limits, because the figures represent the highest estimates and the recovery factor will always stay well below 1.

In view of these recent figures we have now used the lowest of the three alternative values in our short communication (Ref. 1), i.e.  $n_{\infty}^{\rm i} \approx 400 \times 10^{15}$  mol, corresponding to an increase of the over-all recovery factor to roughly 50% over the next 100 years or so, which seems reasonable if the potential resources  $R_{\rm pot}$  in Table 2 are not grossly in error.

The extrapolation of the experimental curve in Fig. 1 is made with this value of  $n_{\infty}^1$ . The results for the future burden of  $CO_2$  are, after all, not very sensitive to the value of  $n_{\infty}^i$  (cf. Fig. 1 in Ref. 1).

### 2. The Model and the Mathematical Procedure

### 2.0. The 5-box-model and kinetics

Figure 2 shows our box-model with 5 reservoirs (or 6 if fossil fuels are considered a reservoir). It is similar to the models used by Machta<sup>9</sup>, Keeling<sup>10</sup>, and others. We consider the diffusion model proposed by Oeschger et al.<sup>4</sup> as probably better adapted to the behavior of CO<sub>2</sub> in the sea, but for the time being we decided to exploit the potentialities of the kinetic box-model.

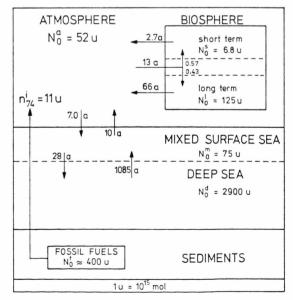


Fig. 2. The 5-box-model with reservoir and time constants corresponding to cases 1 and 3c, cf. Table 4.

### The mathematics

The mathematical description of the model used in this work is — with a few simplifications — essentially the same as that given by Bacastow and Keeling  $^{3}$ c. We have, however, introduced additional fluxes from the biosphere to the atmosphere to take account of the anthropogenic reduction of the biomass through deforestation etc. (index def.). Thus, for the deviations  $n^{j} = N^{j} - N_{0}^{j}$  from the pre-industrial values  $(N_{0}^{j})$  we used the following perturbation equations (cf. Fig. 2 and the list of symbols p. 1554):

Atmosphere:

$$\dot{n}^{a} = -k^{am} n^{a} + \xi k^{ma} n^{m} - \dot{n}^{1} - \dot{n}^{s} + \dot{n}^{i}$$
. (2)

Long-lived biota:

$$\dot{n}^{1} = \beta k^{1a} (N_0^{1} + n^{1}) \ln(1 + n^{a}/N_0^{a}) - \dot{n}^{1}_{def}$$
. (3)

Short-lived biota:

$$\dot{n}^{\rm s} = k^{\rm sa} N_0^{\rm s} [\beta (1 + n^{\rm l}/N_0^{\rm l}) \ln (1 + n^{\rm a}/N_0^{\rm a}) 
+ n^{\rm l}/N_0^{\rm l} - n^{\rm s}/N_0^{\rm s}] - \dot{n}_{\rm def}^{\rm s}.$$
(4)

Mixed surface sea:

$$\dot{n}^{\mathrm{m}} = k^{\mathrm{am}} n^{\mathrm{a}} - \xi k^{\mathrm{ma}} n^{\mathrm{m}} + k^{\mathrm{dm}} n^{\mathrm{d}} - k^{\mathrm{md}} n^{\mathrm{m}}$$
. (5)  
Deep sea:

$$\dot{n}^{\mathrm{d}} = k^{\mathrm{md}} n^{\mathrm{m}} - k^{\mathrm{dm}} n^{\mathrm{d}}. \tag{6}$$

 $\xi$  is the buffer factor defined by

$$p(\xi) = 1 + \xi \, n^{\mathrm{m}} / N_0^{\mathrm{m}} \,, \tag{7}$$

where p is the partial pressure of  $CO_2$  in the surface water relative to the pre-industrial value.  $\xi(p)$  was taken from Fig. 3 in Bacastow and Keeling<sup>3c</sup> and is well described by the parabolic function\*:

$$\xi(p) = -0.122 p^2 + 5.36 p + 3.6$$
. (8)

The main features of the model should be mentioned explicitly:

- (i) All fluxes apart from the exceptions given below — are proportional to the total carbon in the reservoir from which they originate.
- (ii) The flux to the biosphere is governed by the amount of carbon in the long-lived biota.
- (iii) An increase of the net production rates of the biospheres due to enlarged  $CO_2$  concentration in the air is described by a logarithmic function and adjusted by the biological growth factor  $\beta$ . This function will, of course, only hold for a limited time.

(iv) The flux from the ocean surface water to the atmosphere is controlled by chemical equilibria in the sea, where the evasion factor  $\xi$  is evaluated assuming constant alkalinity.

The equations were integrated stepwise starting in the year 1860 (for which  $n^a = n^s = n^1 = n^m = n^d = 0$ ) using the data of Table 1 for the input rate  $\dot{n}^i$  until 1974. Thereafter a suitable "effective" value for  $n_0^i$  was calculated from Eq. 1a to ensure a monotonic input function. After each time step a new value of  $\xi$  had to be determined.

#### The deforestation function

It is not easy to find arguments concerning the time dependence of deforestation. Up to now it has seemed reasonable to assume that deforestation was proportional to industrial activities and thus proportional to global energy consumption, i.e.  $\dot{n}^i$ . When extrapolating into the future one can hopefully assume that the depletion of fossil fuels will force people to treat their environment more carefully. For a first approach we therefore consider

$$\dot{n}_{\text{def}}^{1} = \delta \, \dot{n}^{\text{i}} \, \frac{N^{1}}{N^{1} + N^{\text{s}}} \left( \frac{N^{1}}{N_{0}^{1}} \right)^{q}, \tag{9}$$

$$\dot{n}_{
m def}^{
m s} = \delta \, \dot{n}^{
m i} \, rac{N^{
m s}}{N^{
m 1} + N^{
m s}} igg(rac{N^{
m s}}{N_0^{
m s}}igg)^q.$$
 (9a)

The last factor with q as an arbitrary exponent was introduced to prevent complete disappearance of the biomass (normally q=0 was sufficient). For small perturbations  $n^{s}$ ,  $n^{1}$  one has simply

$$\dot{n}^{\mathrm{def}} = \dot{n}_{\mathrm{def}}^{\mathrm{s}} + \dot{n}_{\mathrm{def}}^{\mathrm{l}} = \delta \, \dot{n}^{\mathrm{i}} \,.$$
 (9b)

The deforestation factor  $\delta$  may be regarded as an adjustable parameter like the biological growth factor  $\beta$ .

# 2.1. The model parameters and their adjustment to experimental data

# Reservoir constants

In pre-industrial times each of the 5 reservoirs contained a certain amount of carbon, with  $N_0^{\rm a}$  probably being the best known value. Oeschger et al. <sup>4</sup>, reviewing the evidence and earlier discussions concerning  $N_0^{\rm a}$ , arrived at 288—295 ppm(V), and used 292 ppm(V) as the most probable value. To

<sup>\*</sup> concerning  $\xi(p)$  cf. also Ref. 28.

convert concentration by volume into amount of CO<sub>2</sub> in mols we have used the following figures:

$$\begin{split} \frac{1\times 10^{-6}\,\mathrm{m}^3\,\mathrm{CO}_2/\mathrm{m}^3\,\mathrm{air}}{1\;\mathrm{ppm}(V)} \times &\frac{10^3\;\mathrm{mol}\;\mathrm{CO}_2}{22.263\;\mathrm{m}^3\,\mathrm{CO}_2} \\ \times &\frac{22.400\,\mathrm{m}^3\,\mathrm{air}}{28.966\;\mathrm{kg}\,\mathrm{air}} \times 5.14\times 10^{18}\,\mathrm{kg}\,\mathrm{air} \\ &= 1.7854\times 10^{14}\,\mathrm{mol}\;\mathrm{CO}_2/\mathrm{ppm}(V)\,. \end{split}$$

Thus, 
$$N_0^a = 292$$
 ppm(V) corresponds to  $N_0^a = 52.13 \times 10^{15}$  mols.

When CO<sub>2</sub> concentration is given in ppm mol fraction the conversion factor is:

$$\begin{split} \frac{1\times 10^{-6}\, \mathrm{mol}\, \mathrm{CO_2/mol}\, \mathrm{air}}{1\,\, \mathrm{ppm}\, (\mathrm{mol})} \times & \frac{1\,\, \mathrm{mol}\, \mathrm{air}}{28.966\, \mathrm{g}\, \mathrm{air}} \\ & \times 5.14\times 10^{21}\, \mathrm{g}\, \mathrm{air} \\ & = 1.7745\times 10^{14}\, \mathrm{mol}\, \mathrm{CO_2/ppm}\, (\mathrm{mol})\,. \end{split}$$

Thus, the atmospheric concentration of  $CO_2$  in mid-year 1974 of  $N_{74}^a = 330.76$  ppm (mol) as determined by Keeling et al. (cf. Table 3), corresponds to

$$N_{74}^{
m a} = 58.69 imes 10^{15} \, {
m mols}$$
 .

For the biosphere we consider in accordance with SCEP<sup>2</sup> a short-term and a long-term reservoir (cf. Fig. 2) containing

$$N_0{
m s}=6.8 imes 10^{15}\,{
m mols}$$

and

$$N_0{}^1 = 125 \times 10^{15} \, \mathrm{mols}$$

with relative fluxes of

$$F^{as}/F^{ab} = 0.57$$
 and  $F^{al}/F^{ab} = 0.43$ . (10)

For the deep ocean we use the value choosen by Reiners  $^{25}$ 

$$N_0{}^{
m d} = 2900 \times 10^{15} \, {
m mols}$$

while we consider  $N_0^{\text{m}}$  as an adjustable parameter, depending on the choice of  $\tau^{\text{ma}}$  (see below).

### Time constants

Concerning the time constants  $(\tau=1/k)$  the one for the exchange between atmosphere and biosphere is known by independent evidence: The net primary production of green plants on land has been assessed <sup>15</sup> to be

$$F^{\mathrm{ab}} = 4.41 \times 10^{15} \, \mathrm{mols/year}.$$

Thus, for the time being

$$\tau^{\rm ab} = N_{74}^{\rm a}/F_{74}^{\rm ab} = 13.3 \, {\rm y} \approx 13 \, {\rm years}.$$

With Eq. (10) it follows (cf. Fig. 2)

$$au^{\mathrm{sa}} = N^{\mathrm{s}}/(0.57 \times F^{\mathrm{ab}}) = 2.7 \mathrm{\ years}$$

and

$$\tau^{1a} = N^{1}/(0.43 \times F^{ab}) = 66$$
 years.

Small errors arising from the fact that  $F_{74}^{ab}$  is not the equilibrium flux are compensated for by an appropriate value of  $\beta$  in the equation for the biosphere.

The time constants governing the exchange between atmosphere and hydrosphere and between surface sea and dep sea are still controversial. Thus, for  $\tau^{\rm am}$  figures between 4 and 10 years have been used, and for  $\tau^{\rm dm}$  figures between 1000 and 3000 years. In accordance with Bacastow and Keeling  $^{3\,\rm c}$  we have used

$$\tau^{am} = 7$$
 years.

The time constant  $\tau^{ma}$  is not known from independent experimental evidence, so we find this parameter by adjusting the model to fit the experimental values of CO<sub>2</sub> concentrations in air as measured by Keeling et al.<sup>26</sup> at the Mauna Loa Observatory, Hawaii (see below).

Finally we have calculated  $\tau^{\rm dm}$  from the equilibrium activities of C-14 in the surface layer of the oceans  $(A_0^{\rm m})$  and in the deep sea  $(A_0^{\rm d})$ . According to Keeling<sup>3</sup>

$$A_0^{\rm m} = 0.95 \, A_0^{\rm a}$$
 and  $A_0^{\rm d} = 0.84 \, A_0^{\rm a}$ 

thus

$$\tau^{\rm dm} = \frac{1}{\lambda} \left\{ (A_0^{\rm m}/A_0^{\rm d}) - 1 \right\} = 1084 \text{ years}$$

with  $\lambda = \ln 2/5736$  y the time constant of C-14 decay.  $\tau^{\rm md}$  then follows from

$$au^{
m md} = au^{
m dm} imes N_0^{
m m}/N_0^{
m d}$$
 .

Thus, this parameter depends on the value of  $N_0^{\rm m}$ , which in turn depends on the adjustment of  $\tau^{\rm ma}$ :

$$N_0{}^{\mathrm{m}} = N_0{}^{\mathrm{a}} imes au^{\mathrm{ma}} / au^{\mathrm{am}}$$
 .

For our calculations we have made different assumptions concerning the biological growth factor and the deforestation factor (cf. below), and for case 1, for example, one can reproduce the Mauna Loa data with  $\tau^{\text{ma}} = 10$  years. In this case, there-

fore it follows (cf. Fig. 2):

$$N_0{}^{
m m} = (52.1 imes 10^{15}) imes 10/7 = 75 imes 10^{15} \, {
m mols}$$
 and

$$\tau^{\rm md} = 1084 \times 75/2900 = 28 \text{ years.}$$

# Adjustment to Mauna Loa data

The experimental data from Mauna Loa, together with those of Bolin and Bischof<sup>27 b</sup> from Swedish flights are summarized in Table 3. (The values are nearly the same if ppm (mol) is converted to ppm(V), substracting one year in the time scale given by Bolin and Bischof). We wanted to consider the following cases:

Case 1. Growth of biomass, no deforestation  $(\beta \pm 0 \text{ and } \delta = 0)$ . Up to now this is the case treated by most authors.

Table 3. Experimental CO<sub>2</sub> concentrations in air. The Keeling data are "seasonally adjusted concentrations ... according to the Scripps 1974 manometric calibration". They are evidently somewhat higher than those reported earlier (cf. Ref. 3b, Fig. 3, p. 56). The data for 1972—1974 are from Ref. 26b.

Mid-	Keeling et al. 26	Bolin and Bischof <sup>27</sup>
Year	ppm (mol)	ppm (V)
1958	315.49	_
1959	316.14	_
1960	317.03	314.3
1961	317.71	315.0
1962	318.57	315.7
1963	319.03	316.4
1964	319.63	317.1
1965	320.25	317.8
1966	320.92	318.5
1967	321.70	319.2
1968	322.58	320.0
1969	324.47	_
1970	325.79	_
1971	326.83	_
1972	328.01	_
1973	330.15	_
1974	330.76	

Case 2. No change of biomass  $(\beta = 0 \text{ and } \delta = 0)$ . This case obviously also can be interpreted as if the increase through stimulation of photosynthesis by rising partial pressure of  $CO_2$  in air is roughly compensated by anthropogenic reductions of the biomass.

Case 3. Net reduction of biomass ( $\beta \neq 0$  and  $\delta \neq 0$ ). We tested the system with a biological growth factor of  $\beta = 0.44$  in accordance with Bacastow and Keeling  $^{3c}$  and a deforestation factor up to  $\delta = 1$ , which corresponds to the estimate of Woodwell and Houghton  $^{21}$ . The results for three different values of  $\delta$  are given in Table 4 (cases 3a, 3b, 3c).

To get a consistent set of parameters we adjusted, as already mentioned,  $\tau^{ma}$  in a way, that the outcome for  $N^{a}(t)$  fits the experimental Mauna Loa data, which seems not only reasonable but necessary for whichever model is applied. Starting from 292 pmm(V) or  $52.1 \times 10^{15}$  mols in the year 1860, using the input data of Table 1 and the reservoir and time constants as derived above, an acceptable fit to the Mauna Loa data (Table 3, col. 2) is obtained with the parameters given in Table 4 (and there are even more possibilities to arrive at the same results). As mentioned before,  $\tau^{am} = 7$  years was chosen in conformity with Bacastow and Keeling<sup>3 c</sup>. It may be noted, however, that the results are predominately dependend on the ratio  $\tau^{\rm ma}/\tau^{\rm am}$  and only secondarily on the absolute values of the time constants. By means of the chosen parameters the calculated curves  $N^{a}(t)$  (Fig. 3) minimize the sum of the deviations of the experimental data and differ from one another by not more than 1% between 1958 and 1974 (there is still no model which simulates the shifting of the experimental data in the sixties). For "no deforestation" ( $\delta = 0$ , case 1 and 2) and  $\beta = 0.0$  to 0.35 the

Table 4. Fitted values of the biological growth factor  $\beta$ , the deforestation factor  $\delta$  and  $\tau^{\rm ma}$  for  $\tau^{\rm am}=7$  a.  $N_0{}^{\rm m}$  and  $\tau^{\rm md}$  are calculated. Col. 6, 7, 8 result from a logistic input function with  $n_{\infty}^{\prime}=400\times10^{15}$  mol and  $\alpha=4.3\%/{\rm year}$ .

	1	2	3	4	5	6	7	8
$ au^{ m am}=7 m a$	β	δ	$ au^{ m ma}$ (years)	$N_0^{ m m} \ (10^{15} \ { m mol})$	τ <sup>md</sup> (years)	$t(2N_0^{ m a})$ (Anno)	$N_{\mathrm{max}}^a \ (10^{15} \mathrm{\ mol})$	$t(N_{ m max}^a) \ ({ m Anno})$
case 1 case 2 case 3a case 3b case 3c	0.35 0.0 0.44 0.44 0.44	$0.0 \\ 0.0 \\ 0.32 \\ 0.18 \\ 0.08$	10 47 47 25 10	75 350 350 186 75	28 149 149 75 28	2029 2029 2027 2028 2028	242 345 310 279 249	2100 2151 2113 2105 2098

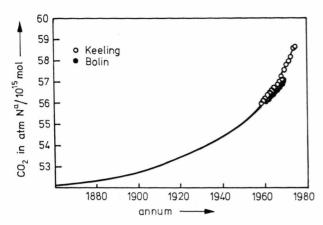


Fig. 3. Experimental CO<sub>2</sub> concentrations as determined at Mauna Loa by Keeling et al.  $^{26}$  and in Swedish flights by Bolin and Bischof  $^{27}$ . Solid line: best fit to the new Mauna Loa data starting from  $52.1 \times 10^{15}$  mols  $\triangleq 292$  ppm (V) in the year 1860.

ratio  $\tau^{\rm ma}/\tau^{\rm am}$  ranges from approximately 1.5 to 7, which seems still reasonable. But for all of the  $\tau^{\rm ma}$  values used  $\beta=0.44$  can also be obtained if one uses the appropriate value of  $\delta$ . A value of  $\delta=1$  leading to  $n^{\rm def}=0.4\times 10^{15}\,{\rm mols/year}$  as currently estimated by Woodwell and Houghton  $^{21}$ , essentially yields too high a concentration in the atmosphere.

# 3. The Future CO<sub>2</sub> Burden in the Atmosphere

### 3.0. Status quo conditions

Continuing the CO<sub>2</sub> input beyond 1974 with a logistic input function ( $n_{\infty}^{i} = 400 \times 10^{15} \text{ mols}, \alpha =$ 4.3%/year) it is found that in all cases given in Table 4 the concentration in the atmosphere will be doubled by the year 2028 (+1) (col. 6). Later there are deviations between the different curves  $N^{a}(t)$ , resulting in maximum values ranging from 242 to  $345 \times 10^{15}$  mols in the atmosphere (col. 7). In all instances the maxima will occur at the end of the next century or thereafter (col. 8). Figure 4 shows the complete results for the cases 1, 2 and 3a together with the changes of  $n^1$  in the long-lived biota. For  $N^{a}(t)$  there are no essential differences between the special cases up to about A.2050. Thereafter the assumed mechanism of the fluxes from and to the biosphere will become more influential, and the decrease in the atmosphere is strongly correlated to the growth of the biota.

The deforestation accumulated until the year 2100 (case 3a) approximately equals the size of the

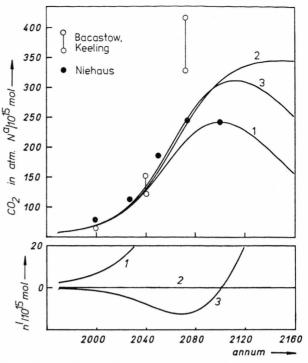


Fig. 4. Future CO<sub>2</sub> burden in the atmosphere for status quo conditions ( $\alpha = 4.3\%/a$ ). Curve 1: growth of biomass, no deforestation (case 1). Curve 2: no change of biomass (case 2). Curve 3: net-reduction of biomass (case 3a with  $\beta = 0.44$  and  $\delta = 0.32$ , cf. Table 4). Open circles: Bacastow and Keeling's<sup>3</sup>c projection with and without increase of the biota ( $\beta = 0.44$  and  $\beta = 0$  resp.). Dark circles: Niehaus'<sup>16</sup> projection for status quo conditions.

present biosphere. The corresponding loss is nearly compensated by the biological growth factor, resulting in a maximum decrease of the biomass of about 10%.

The predictions of Keeling et al.<sup>3</sup> are eventually running much higher than ours because of unrealistic input rates\*. The results of Niehaus <sup>16</sup> are essentially in agreement with our case 1 apart from a slight shift in time.

From the results given here it may be concluded that for the next 80 years or so predictions for the  $CO_2$  increase depend mainly on the source function. If the "free" parameters are adjusted so that the model fits the experimental Mauna Loa data, the

### Note added in proof:

In his latest paper, not yet available to us but referred to in a research proposal (cf. ref. 26b), Keeling 35 has used a logistic function for the input of CO<sub>2</sub>. He still arrives at a future increase of N<sup>a</sup> 8 to 9 times preindustrial level at the maxima. For this discrepancy we have no explanation yet.

question wether or not the biomass is decreasing, and to which extend, seems not to be important for all practical purposes. Of course, the whole model may be unsufficient. When more information will be available about the factual change of the biomass and about the parameters for the mixed surface sea dependend on the adjustment, it will be possible to decide wether or not these facts can be accommodated by the model. For long-term extrapolations beyond the next 100 years the model is, of course, very sensitive to changes in the fluxes to and from the biosphere. They will, therefore, require more insight into these mechanisms, too.

# 3.1. Alternative growth coefficients

The curves in Fig. 4 give maximum values of the  $CO_2$  concentrations to be expected, because the logistic input function used applies to monotonic sigmoidal growth governed only by some natural limit (cf. Figure 1). In reality the growth coefficient  $\alpha$  in the logistic function will not be constant, as non-fossil sources of energy will increasingly play a larger role. Therefore, we have calculated different alternatives with lower values of  $\alpha$ , assuming a net reduction of the biomass as in curve 3, Figure 4.

The results are shown in Fig. 5, where the horizontal line corresponds to a doubling of the pre-industrial concentration, i.e. to an amount of  $105 \times 10^{15}$  mols or a concentration of 584 ppm(V) in the air. According to present estimates (cf.

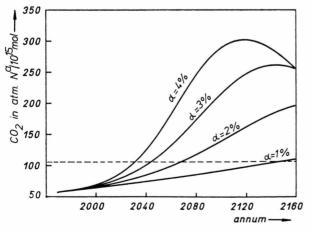


Fig. 5. Future CO<sub>2</sub> burden in the atmosphere for four alternative values of the growth coefficient per year in the logistic function. Biological growth factor  $\beta$ =0.44, deforestation factor  $\delta$ =0.32 (case 3a, cf. Table 3).

Manabe and Wetherald  $^{30}$ ) such a doubling of the CO<sub>2</sub> in air would result in an increase of global temperature between 2 °C in lower latitudes up to 10 °C at the north pole. Together with other anthropogenic alterations of the climate this is at present considered as prohibitive (cf. e.g. Flohn  $^{31}$ , Bach  $^{32}$ ). Of course, the climatic system is extremely complex and much work has to be done before one can make more reliable predictions.

As one can see from Fig. 5 the most important question concerning  $\mathrm{CO}_2$  is not which percentage of our potential fossil fuels can be burned, but how fast one can use up these resources. With an input rate of less than  $0.2 \times 10^{15}$  mols of C per year, for example, one could proceed as long as the supply of fossil fuels lasts, without reaching a doubling of the  $\mathrm{CO}_2$  in air.

Of course, a reduction of the growth coefficient from the present 4.3%/a during the last decades (Fig. 1) to 1 or 2%/a in the near future is unrealistic. According to the latest estimation of the OECD (cf. Hamilton<sup>33</sup>) the consumption rate of fossil fuels will probably increase from 8 TW at present to 18 TW in the year 2000, corresponding to an increase of 3.5%/a for this period.

It thus seems likely at present that the use of fossil fuels will have to be reduced considerably before or soon after the turn of the century.

Finally it should be mentioned that all predictions necessarily assume an uniform rate of development in the whole of world affairs. Another World war, or "Wars of Redistribution", as mentioned by Weinberg and Rotty<sup>34</sup> would alter the picture considerably of course. In this case, however, all predictions will probably turn out to be superfluous.

We appreciated the discussions during the Dahlem Conference with a number of colleagues including Drs. B. Bolin and J. M. Wood. We are grateful to Drs. C. Junge for helpful comments, to Dr. R. Hamilton for referring us to literature relevant to the flaring of natural gas, and to Drs. C. D. Keeling and W. Bach for making the proposal (cf. Ref. <sup>26b</sup>) available to us. The work was supported in part by "Fonds der Chemischen Industrie".

# List of symbols used

Upper indices (cf. Figure 2): a atmosphere, m mixed surface sea, d deep sea, b biosphere (b=l+s), l long-term biosphere, s short-term biosphere, def input from deforestation etc. i input from burning of fossil fuels.

```
N^{j}
    amount of CO_2 in reservoir j (mols);
```

 $N_0^j$   $N^j$  in pre-industrial time, i.e.  $\leq$  annum 1860;

 $= N^j - N_0^j;$  $n^{j}$ 

cumulated input of CO2 into atmosphere from burning fossil fuels;

 $n_{\infty}^{i}$  $n^i$  when all fossil fuels will be burned (=  $N_0^f$ ) (mols);

 $n^j$  $=\Delta n^j/\Delta t \text{ (mols/year)};$ 

 $\dot{n}^{\text{def}}$  input rate from deforestation etc. (b = l + s);

 $A_0^j$  equilibrium activity of C-14 in reservoir j;

1 cf. Report of Group 3, in "Global Chemical Cycles and their Alterations by Man", ed. W. Stumm, Berlin, Dahlem Konferenzen, 1977, p. 292.

<sup>2</sup> Man's Impact on the Global Environment, Cambridge,

Mass., MIT-Press, 1970.

3a C. D. Keeling, in "Chemistry of the Lower Atmosphere", ed. S. I. Rasool, New York-London, Plenum Press, 1973, p. 251.

3b C. A. Ekdahl, Jr. and C. D. Keeling, in "Carbon and the Biosphere", eds. G. M. Woodwell and E. V. Peacon, USAEC 1973, Conf-720510, p. 51.

3c R. Bacastow and C. D. Keeling, in "Carbon and the Biosphere" 1973, p. 86.

<sup>4a</sup> H. Oeschger, U. Siegenthaler, U. Schotterer, and A. Gugelmann, Tellus 27, 168 [1975].

<sup>4b</sup> U. Siegenthaler and H. Oeschger, Science, in press.

<sup>5</sup> K. E. Zimen, Proc. 8th Intern. Radiocarbon Dating Conf., Lower Hutt, New Zealand, Dec. 1972, Vol. 1, p. A86.

<sup>6a</sup> K. E. Zimen and F. K. Altenhein, Z. Naturforsch. 28a, 1747 [1973].

6b K. E. Zimen and R. Brits, Z. Naturforsch. 31a, 854 [1976].

7 R. Avenhaus and G. Hartmann, IISA Research Report RR-75-45, Laxenburg, Austria, Dec. 1975.

8a M. S. Baxter, Thesis, Univ. of Glasgow, 198 p., 1969. 8b M. S. Baxter and A. Walton, Proc. Roy. Soc. London A318, 213 [1970].

9a L. Machta, in Proc. 20th Nobel Symposium, Göteborg Aug. 1971, Stockholm: Almqvist, Wiksell, 1971.

<sup>9b</sup> L. Machta, in "Carbon and the Biosphere", 1973, p. 21.
<sup>10</sup> C. D. Keeling, Tellus 25, 174 [1973].
<sup>11</sup> R. M. Rotty, Tellus 25, 508 [1973].
<sup>12</sup> Statistical Yearbook 1975, United Nations, New York

<sup>13</sup> cf. e.g. OPEC Annual Statistics Bulletin 1974, June 1975.

Survey of Energy Resources. World Energy Conf. 1974,
U.S. Nat. Com. of the W.E.C., New York 1974.
R. H. Whittaker and G. E. Likens, in "Primary Productivity of the Biosphere'', eds. H. Lieth and R. H. Whit-taker, Springer Verlag, Berlin, p. 305. 16a F. Niehaus, Report Jül-1165, Febr. 1975.

<sup>16</sup>b F. Niehaus, Research memorandum RM-76-35, Intern. Institute for Applied Systems Analysis, Laxenburg, Austria, 1976.

17 D. B. Botkin, J. F. Janak, and J. R. Wallis, in "Carbon and the Biosphere", 1973.

 $F^{jk}$  flux from reservoir j to reservoir k (mols/year)  $(F^{jk} = k^{jk} \times N^j)$ :

rate constant for exchange between reservoirs i and k  $(years^{-1});$ 

 $=1/k^{jk}$  (years);  $\tau^{jk}$ 

biological growth factor, cf. Eq. (3), (4);

 $\delta$ deforestation factor, cf. Eq. (3), (4), (9);

ξ buffer factor, cf. Eq. (2), (5), (6), (8); growth coefficient in Equation (1).

<sup>18</sup> D. B. Botkin, Bioscience, in press.

D. B. Botkin, Dioscience, in press.
 cf. Report of Group 2, in "Global Chemical Cycles and their Alterations by Man", 1977, p. 292.

B. Bolin, Science 196, 613 [1977].

G. M. Woodwell and R. A. Houghton III, in "Global Chemical Cycles and their Alterations by Man, 1977, p. 292.

cf. N. S. Goel, S. C. Maitra, and E. W. Montroll, Rev. Mod. Phys. 43, 231 [1971]; or E. W. Montroll, in "Some Mathematical Problems in Biology", Vol. IV", 1972, p. 101.

cf. e.g. A. J. Lotka, Elements of Mathematical Biology New York, Dover Publications, 2nd ed. 1956.

<sup>24</sup> M. K. Hubbert, in "Energy and the Environment, Cost-Benefit-Analysis'', eds. R. A. Karam and K. Z. Morgan, Pergamon Press, New York 1976, p. 3.

W. A. Reiners, in "Carbon and the Biosphere", 1973,

p. 303.

<sup>26a</sup> C. D. Keeling, R. B. Bacastow, A. E. Bainbridge, C. A. Ekdahl, P. R. Guenther, L. S. Watermann, and J. F. S. Chin, Tellus 28, 542 [1976].

<sup>26</sup>b C. D. Keeling, private communication to W. Bach (Ex-

cerpt from a proposal to N.S.F., June 15, 1975). <sup>27a</sup> B. Bolin and E. Eriksson, cited after Ref. <sup>27b</sup>.

<sup>27 b</sup> B. Bolin and W. Bischof, Tellus 22, 431 [1970].

<sup>28</sup> P. Möller and P. P. Parekh, Sci. Total Environm. 4, 177 [1975]

<sup>29a</sup> W. S. Broecker, Y.-H. Li, and T.-H. Peng, in "Impingement of Man on the Oceans", ed. D. W. Hood, J. Wiley Interscience, New York 1971, p. 287.

<sup>29b</sup> W. S. Broecker, Carbon and the Biosphere, 1973, p. 32.

30 G. Manabe and R. T. Wetherald, J. Atmos. Sci. 32, 3 <sup>31</sup>a H. Flohn, Anm. der Meteorol. (N.F.) 9, 25 [1974].

31 b H. Flohn, in "Global Chemical Cycles and their Altera-

tions by Man", 1977, p. 207.

W. Bach, Rev. Geophys. Space Phys. 14, 429 [1976]. 33 R. E. Hamilton, in "Global Chemical Cycles and their

Alterations by Man", 1977, p. 155.

A. M. Weinberg and R. M. Rotty, in "Global Chemical Cycles and their Alterations by Man", 1977, p. 225.

C. D. Keeling, in "Energy and Climate: Outer Limits to Growth", Geophysics Study Committee, Geophysics Research Board, National Academy of Sciences, Washington, D.C., in press (cited after Ref. 26b).