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The standard notation of Ref. 2 has been adopted.

10 These approximations should not be confused with the first and second approximation of the Chapman-Enskog method (see Ref. 11).

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R. S. Devoto, Tables of the Composition and Transport Coefficients of Partially Ionized Argon, NASA CR-85559.

In this work all charged-charged collision integrals have been calculated according to the shielded Coulomb potential (see Ref. 7). It is worth noting that the use of the Coulomb potential with a cut-off to the Debye length for charged-charged interaction decreases the convergence as can be appreciated from Ref. 16 (Table 2, columns 1, 2).

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Relaxation Phenomena in the Biological Carbon Cycle under Conditions of Variable Atmospheric CO2-Content

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Under normal conditions the carbon cycle is a stationary process. A varying CO2 partial pressure would cause deviations from the steady state. This process is analysed using a differentiated flow scheme of the carbon through the biosphere. For this purpose the biomass on land is divided into three reservoirs with average fixation times of 1 day (day-night-cycle), 2 years (annual period), and 100 years (timber, humus), respectively. The kinetic analysis shows that about 70% of the global respiration follow fluctuations of the rate of photosynthesis immediately, so that this portion of the excess of fixed carbon will be returned in the atmosphere within a few years. Only 30% of the total cycle passes through the largest reservoir (timber, humus) which could serve as a buffering system. But since the time constant of this partial cycle is about 100 years, the CO2 exchange with the ocean is the faster process.

1. The Problem

In the natural carbon cycle CO_2 , water, O_2 , and organic material are cyclically transformed, and thus the stoichiometric relationships follow from the gross-equation (1):

$$CO_2 + H_2O \xrightarrow{\text{Photosynthesis}} [CH_2O] + O_2.$$
 (1)

With respect to the carbon, there is an almost completely cyclical conversion. From a geochemical material balance, which covers long periods of time,

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comes the result that a carbon atom will pass through cycle (1) 10,000 times on the average, before it is buried unoxidized in sediments, and in this manner is removed from the cycle 1. The global conversion rates of photosynthesis and of respirative processes are thus equal to each other to a very good approximation. (In comparison, volcanism and carbonate formation have no importance.)

The material conversion rate on the land is estimated to be 1011 tons CO2 per year 2. This value depends on a number of factors which, however, from a global view, will change very slowly in comparison to the conversion time of carbon in the biological cycle; i. e., the average fixation time of car-



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bon in the biomass amounts to about 30 years, and the CO_2 reservoir of the atmosphere will be transformed once in about 20 years. We therefore must expect that under natural conditions all of the reservoirs of carbon involved in the cycle will show a stationary material content. In addition the CO_2 partial pressure in the atmosphere will be in equilibrium with the ocean.

This system is increasingly disturbed by human activity, whereby additional CO2 gets into the atmosphere through the combustion of fossil carbon. Moreover, the oxidation of dead organic material is accelerated by the cultivation of natural soils (particularly of wooded areas). The combustion rate of fossil carbon will have reached the natural CO2 conversion rate by the turn of the century 3. The result will be an increased CO2 partial pressure in the atmosphere since the absorption of the excess by the ocean can take place only at a limited rate 4. Under these circumstances, a stimulation of the photosynthesis rate must be reckoned with, this leading to an increased production of organic material⁵. The respirative processes follow this increased conversion rate only with a certain delay. so that relaxation phenomena in the carbon cycle will result. These relationship will be investigated in a more detailed manner, in what follows. In this context, of particular interest is the question: will increasing the biomass lead to a damping or retardation of the atmospheric CO2 disturbance?

2. Kinetics of the Carbon Cycle after a Stimulation of the Photosynthesis Rate

It is a very substantial fact that there are fast and slow processes in the biological cycle. The fixation time of a C-atom in the biosphere can be very different before the atom is returned to the atmosphere, after oxidation to CO_2 . Consequently, in order to calculate the kinetics of the carbon cycle after a CO_2 stimulation, we have to divide the total cycle into partial cycles of different velocity, the material flows of which are coupled with each other. Thus we divide the biological material into three reservoirs of different fixation periods:

 Fixation periods on the order of 1 day: about 30% of the primary organic material produced by photosynthesis is respired again by the plants (day-night-rhythm).

- II. Fixation periods on the order of a few years: the renewal of the plant mass (leaves, for example) taking place in an annual rhythm leads to no significant accumulation of the dead material in the soil.
- III. Fixation periods on the order of tens of years; timber and organic products which are difficult to decompose (humic acids, for example).

Undoubtedly, such a scheme represents a considerable simplification of the actual relationships; in particular, the reservoir III consists of a very complex mixture of substances, in which the duration of fixation extends from decades to centuries ⁶. However, there are still no sufficient data available for a more differentiated picture. Figure 1 shows the flow diagram of carbon through the biosphere, using the simplified approach of three reservoirs. The values indicated for the partial flows, the amounts of carbon in the individual reservoirs and the duration

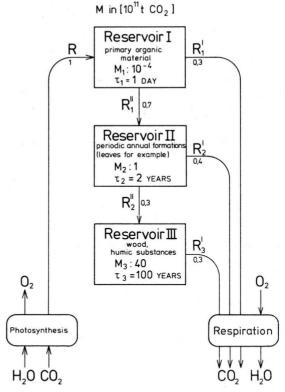


Fig. 1. Flow diagram of carbon in the land cycle. Comments on the numerical values are in the text. The stationary carbon quantities in the three reservoirs were computed as CO_2 -mass, given in 10^{11} t CO_2 . τ =average fixation duration of a carbon atom in the reservoir. The distribution into partial flows R_1' , R_2' , R_3' is indicated in fractions of the total cycle R.

of fixation were determined or estimated as follows:

The division into the partial flows R_2 and R_3 (indicated as fractions of the total cycle R) was estimated, whereas the value $R_1' = 0.3 R$ (plant respiration) can be regarded as certain. Then the arbitrariness of the division into $R_2^{\ \prime}$ and $R_3^{\ \prime}$ is no longer great. In addition, $\tau_1 \leq 1$ day for the duration of fixation is also certain. A more accurate indication is unnecessary in this context. $\tau_2 \approx 2$ years represents an estimated average value for the plant growth (leaves, for example) produced in the annual rhythm. $\tau_3 \approx 100$ years is an approximate average value which takes into account the complex path via wood, decay products, humus precursors, humic substances and decomposition products. The stationary amounts of material M_1 , M_2 , M_3 in the three reservoirs, thus, result from the following equations:

$$M_1 + M_2 + M_3 = 40 \cdot 10^{11} \text{ t CO}_2$$
 (2)

(the carbon being computed each time as CO₂-mass; numerical value according to ⁷), as well as:

$$M_i = \gamma_i R \tau_i \tag{3}$$

(γ_i = fraction of the total flow R, passing through M_i ; $R = 1.3 \cdot 10^{11}$ t CO_2 /year).

One most easily perceives the kinetic behavior of the biological C-cycle, which follows from the reaction scheme in Fig. 1, after a stimulation of photosynthesis, if one imagines a sudden change from R to $R+\Delta R$ and then analyzes the resulting relaxation in the respiration rate. For this purpose R_1' , R_1'' , R_2' , R_2'' will be considered as first order reactions (with respect to their dependence on M_1 or M_2 , respectively), which is undoubtedly a satisfactory approximation in the scope of this consideration. Then the branching ratios R_1'/R_1'' and R_2'/R_2'' remain constant with a change in R (and thus of M_i).

After a sudden jump from R to $R + \Delta R$ the following equation is valid for the time rate of change of substance M_1 :

$$dM_1/dt = R + \Delta R - (M_1/\tau_1)$$

from which one obtains:

$$(M_{\infty} - M_{\rm t})/(M_{\infty} - M_{\rm 0}) = \exp\{-t/\tau\}.$$
 (4)

The increase in the amount of substance up to the new stationary value takes place with the relaxation time τ_1 . According to the above statement, $R_1^{\ \prime\prime}$ will increase to the same degree, so that M_2 also in-

crases. Since τ_2 is nearly three orders of magnitude greater than τ_1 , the increase of R_1 ", with regard to the material balance of the reservoir M_2 , takes place practically just as suddenly, so that Eq. (4) also holds for the growth of M_2 , but with the relaxation time τ_2 . The same statement will be applicable to the delayed increase in M_3 , since τ_3 is large in comparison to τ_2 . The delayed increase of the total respiration rate after a (assumed) sudden increase in the photosynthesis rate R results in a superposition of the three relaxation processes as shown in Figure 2.

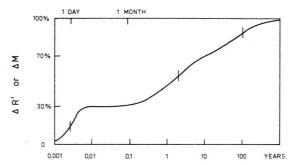


Fig. 2. The increase of respiration rate on land by $\Delta R'$ (or of the biomass by ΔM) as a function of time, after a sudden increase of the photosynthesis rate R. The diagram was based on the scheme in Figure 1. $\Delta R' = \Delta R_1' + \Delta R_2' + \Delta R_3'$. The total curve represents the superposition of three relaxation processes.

3. Discussion

The considerations in Sect. 2 show the relaxation in the various reaction paths of the carbon cycle. In this connection, it was not taken into account that a change in te CO₂-content occurring primarily in the atmosphere (which was originally stationary) will gradually disappear through a transfer to the other carbon reservoirs. (The influence of the sea should remain unconsidered for the time being.) In order to obtain quantitative statements, we must make a further assumption, namely the dependence of the photosynthesis rate on the CO₂ partial pressure. In accordance with the present state of knowledge, a proportional relationship:

$$R \cong (M_{\rm A}/M_{\rm A}^{\rm o}) \ R^{\rm o} \tag{5}$$

 $(M_{\rm A}={\rm atmospheric~CO_2}{\rm \cdot mass};$ the superscript $^{\rm o}$ refers to the original undisturbed condition) seems to be the most reasonable approximation in the expected range of variation of the partial pressure $^{\rm 5}.$ It is doubtful whether this assumption is correct

under all ecological conditions; however, it might be justified for our purposes, as a global mean value.

Thus, an atmospheric disturbance $\Delta M_{\rm A}$ (if the participation of the sea is left out of consideration) would finally be distributed among the three carbon reservoirs of Fig. 1, as well as the reservoir of the atmosphere. As a result, increases in R immediately produce an increase in the material content of reservoir I, within a few days, whereas M_2 proceeds with a phase shift of a few years. Due to the smallness of these reservoirs in comparison to $M_{\rm A}$,

$$(M_1 + M_2)/M_A \cong 0.04$$
,

a change in their amount of substance, has practically no influence on ΔM_{Λ} . On the other hand, the respiration rate from these two reservoirs amounts to 70% of total respiration, so that this portion of additionally bound carbon, according to Eq. (5), will get back into the atmosphere very rapidly. According to the reaction scheme of Fig. 1, the remaining 30% will go to M_3 , where it remains bound for about 100 years. The amount of carbon in reservoir III is comparable to that in the atmosphere: $M_3/M_{\Lambda}=1.6$, so that finally ΔM_{Λ} would be distri-

buted in this proportion between M_3 and $M_{\rm A}$. However, this would be realized only in part, for, due to the slowness of the partial cycle 3, the absorption by the sea (as a result of the disturbed solution equilibrium), which we had left out of consideration so far, is the more rapid process in this instance.

Thus, we come to the result that the influence of the biocycle on a disturbed CO₂-content of the atmosphere is slight. For the damping of fluctuations in the CO₂-content of the atmosphere, the kinetics of the exchange with the ocean is rate-determining.

Finally, it should be mentioned that the concept of "mean fixation time of carbon", which is, in the terminology used here:

$$\bar{\tau} = (M_1 + M_2 + M_3)/R \cong 30$$
 years,

does not permit any conclusions about the behaviour of the carbon cycle in the domain of the questions posed. The differentiation of the complete cycle into partial cycles which was attempted in Fig. 1 is decisive. The data used there still cannot be final numerical values. However, the total result could not be substantially modified by adding any corrections at this point.

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