On the role of the atmosphere in biogeochemical cycles

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1. INTRODUCTION

Man's activities on earth have reached a pitch where he is becoming a factor of importance in global biogeochemical cycles. In order to understand man's impact on his environment – intentional or unintentional – we must not limit our studies to what we observe in our immediate vicinity: a much more thorough knowledge is required of the natural biogeochemical cycles which form the basis for the existence of the biosphere. This calls for an interdisciplinary approach, in which atmospheric scientists will have to play an important role. Of particular concern is an understanding of the basic mechanisms that maintain a quasi-equilibrium; of the extent to which the system may be sensitive to disturbances; and of the way in which the equilibrium may then change.

The following presentation does not represent a well-balanced synthesis, since this is hardly possible at present: it is rather an attempt to emphasize some important general principles and to discuss also some specific questions, such as the likely further increase of carbon dioxide in the atmosphere, the sulphur cycle and the acidity of rain, and the nitrogen cycle and agriculture, since they are much debated at this time.

2. CHARACTERISTIC TIMESCALES AND MODEL DEVELOPMENT

In attempting to describe the processes on earth that maintain the circulation of those constituents that are important for the existence of the biosphere, we must realize the need to distinguish between processes operating on very different timescales. Life in the surface layers of the world's oceans, which is of prime importance for many problems in atmospheric chemistry, interconnects several such cycles with a rather short timescale – of the order of weeks or months. The carbon dioxide flux from the atmosphere to the sea has a characteristic timescale of some years. On average, oxygen stays in the atmosphere for about 10,000 years before it takes part in biological processes in plants or animals on land. The nitrogen molecule has to wait some millions of years before passing into solution in sea water.

Even though the daily variations of atmospheric constituents are the most conspicuous, and air pollution problems as experienced in metropolitan and industrial areas certainly deserve attention, we are, in the present context, interested in the quasi-equilibria existing before man intervened significantly on a regional or global scale and their possible drift over periods of decades, centuries, millennia or maybe even longer. In this context rapid processes may be treated as dynamic equilibria, as, for example, the way in which biological activity in the surface layers of the sea maintains assimilation of carbon, nitrogen and phosphorus, and the emission of oxygen, in fixed ratios, whereby the cycles of these four elements are quantitatively linked. Similarly the atmospheric processes of cloud scavenging, rain-out and wash-out need to be dealt with statistically in order to reveal their role in determining global and regional depositions of various elements as we observe them.

To simplify the overall treatment of global ecological problems it has been customary

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to define a number of reservoirs—atmosphere, land biota, soil, the fresh water system, oceans, marine biota, sediments—and initially to focus attention on transfers between these reservoirs. Some overall relationships are thereby obtained, but obviously we need to consider in some detail also transfers and conversions within these major reservoirs, not considering them merely as 'well-mixed', the fluxes between them being deduced by assuming first-order exchange processes. One may justifiably question the extent to which such models can be used with confidence in attempting quantitative assessments of likely future changes arising from the increasing importance of man as an ecological factor. It is most important to assess how well they do describe reality before conclusions are drawn.

It may, on the other hand, not be possible to develop very complex models, because data are often missing for their proper validation. We need rather to proceed stepwise in the further development of our understanding of biogeochemical cycles to maintain a balance between increasing complexity of the overall models, the development of sub-models for the specific physical-chemical biological processes of relevance and the compilation of a data base for the validation of both the overall models and the relevant processes.

For the following discussion it is important to clarify in some detail concepts of turnover time, exchange rate and 'average age' of constituents in a reservoir, which are sometimes misused or misunderstood (Bolin and Rodhe 1973). Consider a reservoir (say the atmosphere or an ocean) which is in exchange with other reservoirs. Assume for simplicity steady-state conditions. The total mass of the reservoirs is, say, \( M_0 \) and we define an 'age distribution function' \( \psi(\tau) d\tau \) as the mass that has spent time \( \tau \) to \( \tau + d\tau \) in the reservoir, then

\[
M_0 = \int_0^\infty \psi(\tau) d\tau .
\]  

(1)

Similarly we define fluxes \( F_0 \) to and from the reservoir (equal in steady state). Further let \( \phi(\tau) d\tau \) be the 'transit time distribution function', i.e. the mass leaving, that has spent time \( \tau \) to \( \tau + d\tau \) in the reservoir. We have

\[
F_0 = \int_0^\infty \phi(\tau) d\tau .
\]  

(2)

The distribution functions \( \psi(\tau) \) and \( \phi(\tau) \) are related by the expression

\[
\phi(\tau) = -\frac{M_0}{F_0} (d \psi(\tau)/d\tau).
\]

(3)

We further define the 'turnover time', \( \tau_0 \); the 'average age' of particles in the reservoir, \( \tau_a \); and the 'average transit time', \( \tau_t \); of a particle in the reservoir by

\[
\begin{align*}
\tau_0 &= \frac{M_0}{F_0} \\
\tau_a &= \int_0^\infty \tau \psi(\tau) d\tau \\
\tau_t &= \int_0^\infty \tau \phi(\tau) d\tau
\end{align*}
\]

(4)

It can be shown that \( \tau_0 = \tau_t \) but generally \( \tau_a \neq \tau_t \). In a so-called well-mixed reservoir \( \tau_a = \tau_t \) and the distribution functions \( \psi(\tau) \) and \( \phi(\tau) \) are exponential functions (Bolin and Rodhe 1973).

The case \( \tau_a < \tau_t \) prevails when rather few elements leave the reservoir soon after having entered it, i.e. \( \phi(\tau) \) is small (or zero) for small \( \tau \). This is, for example, the case for the 'age' of water in a lake with inlet and outlet at opposite sides.
More interesting in the present context is \( \tau_a > \tau_t \), which is the case when most of the elements that enter the reservoir stay there only for a short time. This is, for example, the case for sea salt aerosols in the atmosphere. Most of these quickly return to the sea; \( F_0 \) is large and \( \tau_0 = \tau_t \) small, while on the other hand \( \tau_a \) is considerably larger since those aerosols that survive the first minutes have comparatively a much better chance of staying in the atmosphere for days. This fact also implies that an estimate of the flux of sea salt aerosols into the atmosphere is very much dependent on whether the flux is at the ocean surface or at some short distance above. In many estimates of fluxes between major reservoirs in biogeochemical cycles this distinction is not adequately considered.

Of particular interest in this context is transfer between two reservoirs associated with a chemical transformation. The exchange of carbon dioxide between the atmosphere and the sea is an important example (Bolin 1960). The average transit time of carbon dioxide in the atmosphere before returning to the sea, 5–10 years, is controlled by the rapidity of the hydration and dissociation process in a layer some tens of microns thick. Another interesting example of a similar kind is the emission of hydrogen sulphide or dimethylsulphide into the atmosphere and its oxidation to sulphur dioxide. The turnover times of the sulphides are obviously directly dependent on the oxidation rate, but so is the average transit time of sulphur dioxide. The more rapid the oxidation, the closer to the sea surface it occurs and the more likely it is that the sulphur dioxide is dissolved in the sea rather than transferred to higher levels in the atmosphere. The different estimates for the magnitude of the natural sources of sulphur in the atmosphere may be partly due to inadequate consideration of the transfer process between reservoirs. The average transit time may be considerably less than the average age and therefore the flux into (and away from) the atmosphere rather large, even though the sulphur concentration (due to natural sources) is small. We shall return to this question later.

Often \( \tau_a \) can be estimated on the basis of the distribution of some radioactive tracer present in the reservoir. \( \tau_a \) for the oceans relative to transfer across the sea surface is directly obtained from the average \(^{14}\text{C} \) age of the carbon in the sea (with due regard to fractionation at the sea surface) and can be estimated to be roughly 1000 years. Due to mixing processes we do not, however, know \( \psi(\tau) \) and therefore cannot deduce \( \phi(\tau) \), which otherwise would be possible with the aid of Eq. (3). We do not therefore know whether \( \tau_t > \tau_{as} \) or the reverse. The former seems the more likely, however, as will be discussed below.

Furthermore, most values of \( \tau_{as} \) (and \( \tau_t \)) are deduced on the basis of steady-state considerations as in the case of the ‘average age’ of the oceans referred to above. The results are then not necessarily applicable to the transient behaviour with which we are often concerned when wishing to assess man’s possible interference. If the timescales in which we are interested are larger than \( \tau_a \) (and \( \tau_t \)), and thus most of the reservoir is involved, the characteristic average time can be used for reasonably good estimates. If, on the other hand, the relevant timescale is small in comparison with \( \tau_{as} \), we may need to know the characteristics of the transit time distribution function \( \phi(\tau) \), since only a portion of it is of significance during the short period considered. This can most easily be seen from the following consideration: reservoirs (a) and (b) are in exchange with each other and, due to a source \( \gamma \) in reservoir (a), they contain amounts \( n_a \) and \( n_b \), respectively, above the equilibrium values that prevailed before the source came into action. We assume that reservoir (a) is well mixed and that (b) is characterized by the transit time distribution function \( \phi_b(\tau) \) and has average transit time \( \tau_t \). If we assume a first-order exchange process between the two reservoirs we obtain (Bolin 1975)

\[
\frac{dn_a}{dt} = \gamma - \frac{1}{\tau_t} \int_0^\infty \phi_b(\tau)n_b(t - \tau) \, d\tau
\]  

(5)
The first term within the parenthesis expresses the loss from (a) to (b), while the integral describes the return of the tracer from (b) to (a). If the source $\gamma$ began at a time $(t - T)$ the integral need only be extended over a time $T$, and $\phi_b(\tau)$ for $\tau > T$ is of no importance for the changes of $n_e$. If $T \ll \tau$, it is hardly possible to extrapolate with any great certainty the future behaviour from observations that are dependent on only a small part of the function $\phi_b(\tau)$. We notice also that continuous observations of $n_e$ and $\gamma$ permit us to deduce $\phi(\tau)$. Such a procedure is equivalent to the 'black-box' approach in systems analysis. If we know something about the physical characteristics of the reservoir, however, which is often the case in reality, we may be able to deduce (directly or indirectly) some characteristics about $\phi_b(\tau)$, as we shall see later.

3. SINK MECHANISMS FOR CONSTITUENTS IN THE ATMOSPHERE

The transit time for compounds present in the atmosphere depends on the relative roles of: (a) chemical reactions in the atmosphere; (b) removal by dry deposition at the earth's surface; (c) wet deposition due to precipitation. If we are interested merely in the cycles of the basic elements (carbon, sulphur, nitrogen) we obviously need not concern ourselves with chemical reactions in the atmosphere except to the extent that the particular chemical form of the element influences the efficiency of the other removal processes, (b) and (c). An understanding of the complex set of chemical reactions in the atmosphere is, of course, still fundamental in trying to interconnect the various biogeochemical cycles. The formation of ammonium sulphate interconnects the nitrogen and sulphur cycles. In the present context we shall not deal with this vast field but rather limit ourselves to physical processes of relevance.

Dry deposition of sub-micron particles is rather inefficient, with a characteristic deposition velocity of the order of 0·1 cm s$^{-1}$. If the particles originate from the earth's surface (e.g. sea salt aerosols) dry deposition may still represent an important sink mechanism; this is usually less so if they are emitted by elevated sources, as is often the case with air pollution, or if they are formed in situ by inhomogeneous chemical reactions. Rain-out and wash-out are then more effective removal processes, since the characteristic vertical exchange time in the atmosphere is of the order of about a month, while the frequency of rain from an air parcel is once every few days in middle latitudes or maybe once every few weeks in arid regions, except possibly in vast desert areas.

For gaseous compounds the situation is rather different. Solubility in water and chemical reactions in the water phase are decisive. Since a very small amount of carbon dioxide at any given moment is present in solution in water drops, precipitation is an unimportant sink mechanism, and the same is true for many other gases, such as the chloro-fluoro-methanes. Sulphur dioxide, on the other hand, is oxidized in the water phase, for example by the catalytic effect of iron (Brosset 1976), whereby sulphate or sulphuric acid is formed, depending on the ion composition of the water in the cloud drop. In such a case the frequency of cloud and precipitation formation is decisive in determining the removal rate from the atmosphere (Rodhe and Grandell 1972). The same is in principle true for ammonia gas, if there is excess acid in the drops. The formation of ammonium sulphate is therefore an efficient sink process for both nitrogen and sulphur in the atmosphere.

It is of interest to note, however, that not all cloud drops become rain drops. When some evaporate, other chemical processes may take place. If gases and particles have been incorporated into the drops and changed their ion composition, we can compute the volatility of the gases in solution as a function of the ion concentration when the drops decrease in size (Söderlund 1978). Clearly, sulphur will remain in the drop since the partial pressure of sulphuric acid is very small, but to the extent that chlorine and nitrate ions are
present HCl and NNO₃ will again escape during the evaporation phase. Since most evaporating clouds are found at rather high levels, this chemical transformation is combined with an efficient vertical transfer. The much higher sulphur emissions in industrialized areas may therefore, in principle, have influenced the cycles of chlorine and fixed nitrogen in the atmosphere and permitted an increased flux of these compounds to the upper troposphere. An assessment of the importance of such a process requires reasonably good estimates of the probability of a cloud drop escaping development into a rain drop or being scavenged during precipitation formation. We hardly have sufficient knowledge in this regard to justify further elaboration of the idea here, but it may still serve as an example of the intricate ways whereby the various biogeochemical cycles are interconnected.

4. THE GLOBAL CYCLES OF CARBON, SULPHUR AND NITROGEN AND THEIR INTERRELATIONS

(a) A few general comments

A few examples of how uncertainties relating to the definitions of the major natural reservoirs influence the accuracy with which we can define the characteristics of the biogeochemical cycles were given in section 2. The assumption that these major reservoirs are well mixed, which is not the case in reality, implies that the overall descriptions of the global cycles, as commonly given and as also presented in the following, are considerably more uncertain than they may appear. This also means that attempts to assess the possible future changes that may occur due to man’s interventions are equally uncertain. A prime aim of the following presentation will be to point out such uncertainties. On the other hand few attempts have as yet been made to explore how these various cycles are quantitatively interconnected. A second aim will therefore be to point out where and how such relations may reduce uncertainties of the assessments made. As yet there are rather few examples where specific results in this regard are available, but this possibility should be systematically explored further.

(b) The carbon cycle

The overall characteristics of the carbon cycle are reasonably well known, even though considerable uncertainties exist with regard to the magnitude of the reservoirs and the fluxes between them. Figure 1 shows a schematic diagram of its major features, essentially based on estimates as presented by Bolin (1970), Reiners (1973), Bolin (1975), and material assembled by a study group created by SCOPE (Bolin et al. 1979). This is not the place to describe in detail the way all the numbers in Fig. 1 have been derived but a few general comments are relevant particularly with regard to uncertainties and also to the slow change that occurs due to man’s interventions.

The present (1977) amount of carbon in the atmosphere in the form of carbon dioxide is 695 Pg (Pg = petagram = 10¹⁵ g = gigatonne, Gt), which is equivalent to 329 ppm by volume. This represents an increase of 16 ppm = 34 Pg since 1960. The average annual increase during the 1970s has been 1.1 ppm (≈2.3 Pg) in comparison with an average release of about 4.2 Pg due to fossil fuel combustion. The so-called airborne fraction of the release by combustion has on the average been somewhat above 50% (Keeling and Bacastow 1977). Since the middle of last century altogether about 140 Pg carbon has been emitted into the atmosphere. The fossil fuel reserves have been estimated to be about 5000 Pg (Perry and Landsberg 1977).

Recent detailed inventories of carbon in land biota have yielded values between 700 and 1000 Pg (Bolin et al. 1979). The higher figure, however, is most likely a considerable
overestimate and we may accept a value of 800 Pg as the best estimate at present. Assessments of organic carbon in the soil are even more variable, with a value of 3000 Pg as the maximum (Bohn 1976). A considerable portion of the carbon in soil is in peat, and exchanges very slowly with the atmosphere.

Man is also changing the amount of carbon in land biota and in the soil. Bolin (1977a) estimated that, since the first half of last century, the decrease of forests has added $45 \pm 15$ Pg to the atmosphere and decomposition in the soil $25 \pm 15$ Pg; in total $70 \pm 30$ Pg. In a somewhat more detailed analysis, Revelle and Munk (1977) arrive at a value of about 75 Pg, while Bohn (1978) estimates that cultivation of soil has meant a flux of 150 Pg carbon to the atmosphere. Finally Stuiver (1978) has analysed the change of $^{13}$C in wood during the last 100 years. The departure ($\delta^{13}$C) of the $^{12}$C/$^{13}$C ratio from the international standard is larger for wood ($-25\%$) than for CO$_2$ in air ($-7\%$), due to fractionation during the assimilation process. A net flux of carbon to the atmosphere by burning, and by bacterial decomposition of organic matter, will therefore decrease $^{13}$C for atmospheric CO$_2$. More recently-formed organic compounds would therefore have a lower $^{13}$C value because assimilation has taken place from this more $^{13}$C-deficient atmospheric CO$_2$. Observations show that a decrease of 1–1.5 per mille has occurred during the last 100 years, but the precise value is still quite uncertain and does not permit a very accurate determination of the net return of CO$_2$ to the atmosphere. The value deduced by Stuiver, 120 Pg, is also dependent on a model for the CO$_2$ exchange between the atmosphere and the sea. We shall return to this later.

The oceans present the largest carbon pool in comparatively rapid exchange with the atmosphere. There is about 35000 Pg of inorganic dissolved carbon, and about 1000 Pg in the form of dissolved organic carbon, in the oceans. In addition there are small amounts of phytoplankton and zoo-plankton ($\approx 3$ Pg) and also inorganic and organic particulate matter, being remnants of life in the surface layers of the ocean settling to deeper strata while being decomposed.

In order to understand the role of the oceans in the carbon cycle we need to know the mechanisms of exchange with the atmosphere and with sediments at the bottom of the sea, as well as internal exchange processes. Gaseous exchange between the atmosphere and the surface layers of the sea is primarily determined by molecular diffusion and hydration of carbon dioxide molecules in a thin ($\approx 20$–50 µm) surface film (Bolin 1960). The fact that only about one per mille of the inorganic carbon in the sea is in the form of dissolved CO$_2$ gas, limits the exchange rate so that the mean residence time for CO$_2$ in the atmosphere is 5–10 years. In the light of the discussion in section 2 one should note here that in estimating this residence time we have disregarded those molecules that enter the surface film, but are never transformed into ionic form and therefore stay there merely for a fraction of a second. Gaseous exchange between the atmosphere and the sea is also influenced by chemical reactions in the sea in that a net flux in one direction or the other will shift the ionic equilib-

Figure 1. The carbon cycle according to Bolin et al. (1979). The reservoir inventories are given in $10^8$Mt = Pg = 10$^9$ g and the fluxes in Pg yr$^{-1}$. The oceans have been divided into 11 reservoirs to permit a more accurate description of the ocean circulation and associated carbon fluxes in the oceans. The three numbers in these reservoirs refer to dissolved inorganic carbon, dissolved organic carbon and carbon in living matter. The double arrows between ocean surface water and intermediate water indicate turbulent exchange. The estimates for the carbonate bottom sediments are based on the assumption that a layer of about 10 cm can be in exchange with the ocean water due to bioturbation. For terrestrial biota the net assimilation has been assumed to be 30% of the gross assimilation. The circled figures show the fluxes caused by man during a single year (Pg yr$^{-1}$). Emissions to the atmosphere by fossil fuel combustion (5 Pg yr$^{-1}$), deforestation (1 Pg yr$^{-1}$) and soil decomposition (1 Pg yr$^{-1}$) are partly balanced by increased assimilation (1–3 Pg yr$^{-1}$) and dissolution in the oceans (1–3 Pg yr$^{-1}$), whilst the remainder (2.5 Pg yr$^{-1}$) is the annual increase in the atmosphere. Since pre-industrial times the amount of carbon in the atmosphere has increased by about 80 Pg. For a discussion of the uncertainty of the figures see text and Bolin et al. (1979).
rium. Because of this, the ratio of the change of carbon in the atmosphere, and the change of total amount of inorganic carbon in the sea required to maintain equilibrium, is not unity but is a factor $\alpha \neq 1$, often called the buffer factor. The value of $\alpha$ at prevailing partial pressures, $p(\text{CO}_2)$, for CO$_2$ in air, and for a carbonate–borate solution such as sea water, is between 9 and 10 and increases considerably for increasing values of $p(\text{CO}_2)$ (Keeling 1973).

The crucial question in trying to assess the role of the oceans in the carbon cycle, and particularly its role as a sink for excess CO$_2$ in the atmosphere, is how effectively and quickly the oceans are mixed. Measurements of $^{14}$C in the deep sea clearly show an overall characteristic mean age of the deep sea of about 1000 years. We do not know, however, whether the mean transit time is longer or shorter, nor do we know the transit time distribution function, which is of prime interest if we want to assess the role of the deep sea as a sink for excess atmospheric CO$_2$ due to man’s activities. So far, models of the sea to describe the carbon cycle have been very simple (Craig 1957; Bolin and Eriksson 1959; Keeling 1973; Oeschger et al. 1975). Little use has been made of our knowledge of the real circulation of the oceans as developed in physical and dynamical oceanography. Recently, a much more detailed model of the oceans has been developed (Bolin 1977b; Björkström 1978) to resolve some of the ambiguities that we find if using the simple two- or three-box models referred to above.

The surface layers of the oceans are divided into warm surface water, which is found in tropical and temperate latitudes, where a well-defined thermocline separates the surface water from the deep sea, and cold surface water, which is the top layer of the oceans ($\approx 100$ m thick) in polar and arctic regions. Between about 100 and 1000 m depth we define a few layers that describe the intermediate water, which is primarily formed by slant convection originating from the polar surface waters in the vicinity of the major ocean currents and circumpolar convergence zones found at those latitudes. The deeper layers of the oceans are mainly renewed by deep penetrating convection within very limited areas in the Iceland–Greenland area and around the Antarctic continent. The sinking water penetrates to a depth where its density is equal to that of the deep water; it then spreads horizontally. For continuity, a slow upward motion is assumed to take place over most of the deep oceans, amounting to a few m yr$^{-1}$.

Transfer of carbon to the deep sea is accomplished not only by the water motions described above, but also by the sinking of dead organic matter in particulate form and carbonate shells from the plankton. The organic matter is decomposed by bacteria, which requires oxygen and takes place mainly in the upper 1000 m of the oceans, and by dissolution of carbonate shells, since solubility increases as pressure increases with depth. By considering the transfer of oxygen by water motions in a similar manner, we are able to determine approximately the flux of carbon brought about by detritus fall in the oceans.

The application of a complex model of the carbon cycle based on a more detailed description of the various reservoirs of carbon, as outlined above, requires careful testing and the utilization of many more data than in the case of simpler models, since the number of degrees of freedom is much greater. This has by no means as yet been completed and, as a matter of fact, in some regards available data may at present be inadequate for the proper testing of the model. It should, however, still be possible to assess the uncertainties in the ‘best possible’ diagnosis of the carbon cycle achieved in this way and a prognosis of likely changes due to man’s intervention both by burning fossil fuels and by changing land utilization. At this stage we limit ourselves to some preliminary results, and, in presenting these, dwell particularly on the importance of proper consideration of the transit time distribution function concept as outlined in section 2 and the considerable uncertainties which still prevail with regard to changes that are being brought about by man.

The most crucial questions at present are:
(1) What role has the deep sea played, and what role will it play, as a sink for the net emissions of carbon dioxide to the atmosphere that man brings about?

(2) How effective is exchange between the cold surface water and the intermediate water of the ocean, and what is its importance for the carbon cycle?

(3) How will land biota respond to an increasing amount of carbon in the atmosphere, and to what extent could it serve as a sink for excess carbon dioxide in the atmosphere?

(4) Is it possible to say into which reservoirs CO$_2$ emitted by man's activities has gone in the past?

(5) What is the likely future increase of atmospheric CO$_2$ due to different scenarios of the expected CO$_2$ releases to the atmosphere due to man, and what is the uncertainty of such projections?

For a more detailed account of model experiments to resolve these questions reference is made to Björkström (1978).

It is obvious that the characteristic circulation of the deep sea described above means a delay in the return of water to the surface layers in comparison with the so-called well-mixed reservoirs that have been used in the simple models considered so far. This implies that $\tau_s = \tau_\alpha > \tau_a$. It also follows that such a reservoir for periods from some decades to centuries, i.e. for times small compared with $\tau_\alpha$ ($\approx 1000$ years), is a more effective sink than a well-mixed reservoir with the same value for $\tau_a$. Nevertheless, during the time in which appreciable emissions of carbon dioxide to the atmosphere have occurred, a rather small percentage may have found its way into the deep sea, which, therefore, has so far played only a minor role as a sink for excess carbon dioxide in the atmosphere.

The tritium and radiocarbon measurements recently reported by Östhlund et al. (1974) show that the intermediate water is formed rather rapidly. Few measurements are available from the upper 1000 m from times before bomb-produced radio-activity was introduced into the atmosphere, and then also into the oceans. Our present idea about the renewal rate of intermediate water is therefore still quite uncertain. At present, observations seem to support the idea presented by Keeling (1973) that a layer of several hundred to a thousand meters is exchanging rather rapidly with surface waters. This implies a transient time distribution function for ocean water below the top layer of the ocean that has rather large values for transit times less than 50–100 years, which would considerably increase its role as a sink for excess carbon dioxide in the atmosphere. A more detailed analysis and the simultaneous use of several tracers (above all, oxygen) are required to ascertain the precise role of intermediate waters in this regard.

It has been generally accepted that the pre-industrial level of carbon dioxide in the atmosphere was 290–295 ppm. This value has been derived on the basis of careful scrutiny of all measurements before 1900. About the same value is obtained from an extrapolation backwards from observed concentrations in the atmosphere during 1957–1977, knowledge about total emissions from fossil fuel combustion since 1860, and an assumption that the airborne fraction has remained about the same during the last century, at about 50%. Recent results, that man may have added considerable amounts of carbon dioxide to the atmosphere by changing land use, imply that such an extrapolation back in time is not permissible. Such considerations, as well as Stuiver’s $^{14}$C measurements, indicate that the CO$_2$ concentration during the first half of last century may have been anywhere between 265 and 290 ppm.

Even if the pre-industrial level of CO$_2$ were somewhat lower than is so far believed, the large emissions due to decrease of living land biota and more rapid decomposition of soil organic matter imply that even greater demands are placed on the oceans as a sink for excess CO$_2$ in the atmosphere. It therefore does not seem unlikely that the higher CO$_2$ concentrations in the atmosphere during this century have led to increased photosynthesis.
and thus to a significant flow of carbon into land biota. This could have been so only if assimilation were not seriously limited by lack of water and nutrients. It should, however, be noted that higher CO₂ values in the air imply more rapid diffusion of CO₂ to stomata while evapotranspiration does not increase. Also, a given amount of nutrient available for a forest may still permit an increase of the production of cellulose if no other environmental factors limit growth, since it contains very small amounts of nitrogen and phosphorus.

It follows from the discussion above that it is possible to account for the CO₂ released into the atmosphere due to man’s activities. The atmospheric CO₂ concentration may have been significantly less than 290 ppm in the early part of last century; the intermediate ocean waters may have been a more effective sink than has been so far believed; and some increased photoassimilation due to higher atmospheric CO₂ concentrations may well have increased the biomass in those parts of the world forests until recently untouched by man. We do not know, however, what the relative importance of these three factors has been in the past. It is particularly important to be able to distinguish the relative importance of the land biota and the sea as sinks in the past, since in the long run their roles will have to be quite different. Even though Revelle and Munk (1977) have advanced a model in which a threefold increase of the biomass in land biota might take place, it is difficult to imagine that this really could occur because of the likely continued exploitation of the world forests.

In view of the great uncertainties in assessing the size of the carbon pools in the form of living and dead organic matter on land, it seems unlikely that we shall be able to establish firmly by direct observation the magnitude of possible changes until they are quite large. Integrations, indirect methods based on, for example, the observed change of δ¹³C in wood, are therefore of great value. Extensive measurements of δ¹³C of wood are urgently needed. The interpretation of such data also requires a careful analysis of the complex fractionations that occur in the assimilation process and an analysis of the resulting δ¹³C changes in the atmosphere. The model described briefly above and presented in some detail by Björkström (1978) is also being used for quantitative interpretation of the δ¹³C data.

Obviously any projection of future atmospheric CO₂ concentrations will be quite uncertain because of our limited knowledge of the characteristics of the most important sinks. We first note that changes of energy policy or of exploiting the world forests are slow. For the next two or perhaps three decades we may with reasonable certainty predict that the increase will remain close to 50% of the CO₂ emissions due to burning of fossil fuels. If we assume that combustion will increase by 2-4% annually, the atmospheric concentration will be 365-375 ppm at the turn of the century. With the same increase of the rate of emissions during the next century and an unchanged airborne fraction, atmospheric CO₂ will double by year 2065, or 2035, respectively. Such a simple extrapolation, however, probably cannot be extended that far into the future.

Keeling and Bacastow (1977) have made projections of the probable future CO₂ increase by assuming that in total 5000 Pg will be emitted during the next one or two centuries, i.e. 8.2 times the total pre-industrial content of the atmosphere, assuming a concentration of 290 ppm. They assume that the land biota will not be a significant sink and that the airborne fraction of CO₂ emitted by fossil fuel combustion in the past has been 50%. The latter will, however, increase as the atmospheric CO₂ concentration, and associated with it the buffer factor, increase. A maximum of 2200-2100 ppm would be reached sometime between years 2150 and 2250, which implies an average airborne fraction of 80%. This is most likely an upper limit of the future increase due to an emission of the given magnitude. If in the past a significant net flux of carbon has occurred from land biota to the atmosphere, as δ¹³C data seem to indicate, and the pre-industrial atmospheric CO₂ concentrations were not significantly below 290 ppm, the airborne fraction up to now must have been less than 50%. The intermediate waters of the ocean would then have been a more
effective sink than assumed by Keeling and Bacastow and would presumably remain so in the future. Also some dissolution of CaCO₃ from the bottom sediments in the Atlantic Ocean with comparatively rapid turnover, might in the long-run further add somewhat to the capacity of the sea as a sink (Broecker and Takahashi 1977). If the biomass of land biota were to increase in the future, which might be possible if present reductions of forest extension were stopped, this would obviously further reduce the airborne fraction of man’s emissions. At present we cannot assess with any certainty the importance of these factors, but the projections of future CO₂ concentrations could possibly be reduced to half the values given by Keeling and Bacastow, but probably not by more than that.

(c) The sulphur cycle

Since the first attempt to present a global sulphur cycle was made by Eriksson (1960) a number of more detailed analyses have appeared (Junge 1963; Robinson and Robbins 1970; Kellogg et al. 1972; Friend 1973; Granat et al. 1976). Even though some general characteristics of these are the same, quite major revisions of the quantitative assessments have been made, generally in the direction of decreasing the fluxes due to natural processes and thereby making modifications by man relatively more important. It should, however, be emphasized that the global picture of the sulphur cycle is much less satisfactory than that for the carbon cycle, because the mean transit time, or average age for sulphur in the atmosphere, is merely a few days and therefore very marked spatial inhomogeneities exist. The following general discussion should be seen against that fact; we shall also specifically consider regional differences (Fig. 2).

Sulphur in the form of gas (H₂S, SO₂) or particulate matter (SO₄²⁻) is present in the atmosphere naturally by release of gaseous compounds during the decay of organic matter, by emissions of sulphur dioxide from volcanoes, and from sea spray. The appearance in the atmosphere is, in this sense, secondary and it is therefore appropriate to begin a discussion of the sulphur cycle by considering the lithosphere (for details see Granat et al. 1976).

Weathering can be estimated as denudation rate, survival rate (i.e. the ratio between the volume of a sedimentary system and the duration of the corresponding geological period), or total river load. Different attempts to estimate the pre-industrial rate of weathering using these different means show surprisingly coherent results, about 33 Tg yr⁻¹ (teragram = Mt = 10¹²g), but the uncertainty is still considerable. River run-off can be reasonably well estimated on the basis of chemical analyses of the major rivers of the world. There are also clear indications that man’s expanding activities in industry, agriculture and forestry have significantly changed the river transport of dissolved and suspended matter. According to Granat et al., and based on Berner’s (1971) discussion of present total dissolved sulphur in river water, we may conclude that man probably has doubled this weathering rate by his various activities. The numbers given in Fig. 2 for pre-industrial conditions of river run-off are more definite than those for weathering, but are still quite uncertain. The difference between weathering and river run-off is, however, significant – a consequence of the flow of sulphur from the sea to the continents via the atmosphere.

Sulphur is an important constituent in biological matter and the latter therefore, is a source for volatile sulphur compounds from decay, both on land and in the sea. There are considerable difficulties in assessing the magnitude of this flux, because a great part is oxidized to sulphate in the soil, in sediments, in marshland or tidal flats, or in the sea before ever being transferred to the atmosphere. Not until very recently have reliable measurements been made in the atmosphere (Georgii 1978) and most previous attempts to estimate this flux have primarily been through a balance of the overall sulphur budget. The first estimates (Eriksson 1960 and Junge 1963) yielded values larger than 200 Tg. Recently,
however, Granat et al. have made a very careful analysis of all data on SO$_2$ in the air and sulphate in precipitation and arrive at a figure of about 40 Tg. It is interesting to note that Georgii's measurements seem to support the latter figure. The vertical distribution of hydrogen sulphide up to a height of about 1 km both over the North Sea (Isle of Sylt) and over rural land in Germany seems to indicate that the transit time, or turnover time, for H$_2$S in the atmosphere is more than a few hours, probably 10–20 hours. Accepting the measurements made by Georgii as representative (0.3–1 µgS m$^{-3}$) and assuming that emissions essentially occur only from moist soils and coastal waters, which together constitute merely about 10% of the earth’s surface, we arrive at an annual flux of sulphur to the atmosphere of the order of tens of Tg yr$^{-1}$. This figure might, however, be higher if tropical moist soils produce considerably more H$_2$S than assumed above. On the other hand measurements of SO$_2$ concentrations in air above the tropical Atlantic show low values (Georgii 1978). It is therefore likely that earlier estimates of global H$_2$S emission were considerably too large.

Finally, we note that the amount of sulphur transferred to the atmosphere by sea spray is of interest only to the extent that a transfer to the continents also occurs. The figure given here is reasonably accurate, since rather little is brought far inland and estimates are therefore not too difficult to make.

The present emissions of sulphur from fossil fuel combustion have been estimated at
65 Tg yr\(^{-1}\). Some emissions may also result from the nutrient pollution of lakes and coastal areas, but are probably small in comparison with those due to combustion. For further discussion of the fate of man-made emissions it is necessary to have a rough idea of the mean transit time for sulphur in the atmosphere, which in turn requires a knowledge of the mechanisms for oxidization of SO\(_2\) to sulphate aerosols, and of the characteristics of the removal processes for both SO\(_2\) and SO\(_4\). We shall not discuss these further here but merely refer to current literature: Rodhe (1978) has summarized the role of these various transfer mechanisms in terms of turnover times (or mean transit times):

<table>
<thead>
<tr>
<th>Process</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry deposition of SO(_2)</td>
<td>60</td>
</tr>
<tr>
<td>Wet deposition of SO(_2)</td>
<td>100</td>
</tr>
<tr>
<td>Transformation of SO(_2) to SO(_4)</td>
<td>80</td>
</tr>
<tr>
<td>Turnover time for SO(_2)</td>
<td>25</td>
</tr>
<tr>
<td>Dry deposition of SO(_4)</td>
<td>large</td>
</tr>
<tr>
<td>Wet deposition of SO(_4)</td>
<td>80</td>
</tr>
<tr>
<td>Turnover time for SO(_4)</td>
<td>80</td>
</tr>
</tbody>
</table>

Turnover time for sulphur, 50 h.

Most measurements on which these figures are based have been made in middle latitudes, where most man-made emissions of sulphur take place. The values therefore cannot be directly applied in subtropical or tropical latitudes. Furthermore the transit time distribution function need not be exponential. Small but significant amounts of SO\(_2\) and particulate SO\(_4\) escape through clouds, and penetrate into the upper troposphere and the stratosphere (Junge 1974; Bolin and Charlson 1976). Nevertheless the rather short turnover time for sulphur and the very varying concentrations that are found in the atmosphere imply that deposition patterns are equally variable. In the areas of major industrial activity the natural fluxes of sulphur through the atmosphere are small in comparison with those due to human activity. The amount of sulphur deposited on the ground during any one year is small in comparison with that in the soil, often less than 1%. The major impact of sulphur deposition is, however, associated with the fact that it appears in rain and in dry deposition as sulphuric acid and that the pH of the soil thereby may change. In this way both microbial activity and ion composition are influenced. As yet our knowledge of the long-term effects is quite incomplete. We note, however, that microbial activity is obviously of importance for cycles of other key elements of organic compounds, notably nitrogen, a matter to which we return in the following section.

The soils of natural ecosystems have been created during periods of many millennia, usually even much longer. They represent some kind of quasi-equilibrium between biological processes, weathering of the bedrock and the inorganic content of the soil, and the flux of compounds due to air and water motions. It is obvious that the fluxes of key elements to and from the soils have changed very significantly due to man. The ecosystems respond to these changes and strive towards some new quasi-equilibrium and the question arises: what are the likely changes that will occur in this process of adjustment? It is worth noting that the immediate changes must not simply be extrapolated, but rather that the dynamics of the ecosystem need to be considered in detail. The deposition of sulphuric acid, for example, may well release more positive ions into the soil moisture than would be the case naturally, and, since these (Ca, K, Mg, etc.) are essential to plant growth, may thus stimulate primary production. On the other hand, to the extent that these will be lost to ground water and ultimately to the oceans, the nutrient content of the soil may in the long run decrease very significantly. Within decades such soils may become considerably less productive and the original biome may be replaced by a less demanding kind. The base saturation (which is a measure of the amount of nutrients) of the podsoils on which most of the boreal forest
Figure 3. Caption on facing page.
grows is quite low, often merely 10–15%. It is obviously essential to clarify their resilience to a continued deposition of acid rains.

Finally it should be remarked that so far only a few percent of the total fossil fuel reserves have been used. Some of the unexploited oil and coal deposits contain more sulphur than those being used today. The amount of sulphur in accessible fossil fuel reserves is 50–100 times the amount so far emitted. It is therefore most important to foresee what the consequences might be for the natural ecosystems, if such an amount of sulphur were emitted from power plants in the industrialized areas of the world. Undoubtedly the consequences might be very drastic in some areas.

(d) The nitrogen cycle

The nitrogen cycle is intimately coupled to the carbon cycle in that nitrogen compounds are essential nutrients in the assimilation process because of their fundamental role in protein formation. A presentation of our current knowledge of the nitrogen cycle was recently made at the Nobel Symposium 38 (Bolin and Arrhenius 1977). The following attempt to summarize the nitrogen cycle into one diagram, and assign approximate values to the various transfers and conversions, has been based on work by Söderlund and Svensson (1976), Bolin and Arrhenius (1977) and Hahn and Junge (1977). Figure 3 shows the major fluxes and conversions as given in these papers. Notwithstanding its complexity, many details have been left out, particularly with regard to photochemistry, which is of basic importance for conversions of N\textsubscript{2}O, NO, NO\textsubscript{2} and NO\textsubscript{3} in both the troposphere and the stratosphere (see also Crutzen and Ehhalt 1977).

It is clear from the figure that there are considerable uncertainties in many of the estimates given. As was the case for the sulphur cycle, this is partly because there are great regional differences on land with regard to the distribution of nitrogen compounds. Also, the mean transit times through the atmosphere of NO\textsubscript{3}, NO\textsubscript{2}⁻ and NH\textsubscript{3} are merely of the order of days, which implies great spatial variations. It is necessary to account explicitly for such regional differences in order to be able to balance properly the conversions between different nitrogen compounds and transfers between different parts of the ecosystem. The present global survey, as well as the basic data provided by Söderlund and Svensson, does not account for this in any detail, but it may still be of some use as a starting point.

The amounts of both NO\textsubscript{3}, NO\textsubscript{2}⁻ and NH\textsubscript{3}, NH\textsubscript{4}⁺ are significantly influenced by man due to combustion and cattle raising, respectively. It is clear that anthropogenic sources already present are significant in comparison with natural ones, although percentagewise

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**Figure 3.** The nitrogen cycle according to Söderlund and Svensson (1976), Bolin and Arrhenius (1977), Hahn and Junge (1977). The estimates of the inventories are given in Mt = Tg = 10\textsuperscript{12}g and the fluxes in Tgyr\textsuperscript{−1}. In many instances attempts have been made to give the range of uncertainty of the estimates, which is then indicated within parentheses. Man’s modification of the nitrogen cycle has been shown by circled figures. The nitrogen cycle is characterized by a number of chemical transformations and some indication of this fact is given by the shadings of the reservoirs.

- Inorganic nitrogen compounds in oxidized form, except N\textsubscript{2}O (valence ≥2)
- N\textsubscript{2}O (valence 1)
- Inorganic nitrogen compounds in reduced form (valence ≤−1)
- Nitrogen in living matter
- Nitrogen in dead organic matter
still less so than for the sulphur cycle. We also note that sulphate and nitrate ions dominate in comparison with ammonium ions and that the modification of these two nutrient cycles implies an acidification of atmospheric aerosols and thus of precipitation.

The amount of nitrogen being cycled annually between the soil and land biota is (stoichiometrically) of the order of 3–5% of the amount of carbon, reflecting the rather low N/C ratio in the organic compounds being formed on land, compared with the ratio 1:15 approximately holding for plankton formation. On the other hand the N/C ratio for dissolved organic matter in the sea has been put at about 1:25, as experimentally determined, showing the fractionation in the process of bacterial decomposition. We also note that there is a deposition of organic nitrogen at the bottom of the sea which also implies a sink for carbon. The fact that increased assimilation has occurred in lakes and coastal waters due to man’s increasing use of nitrogen (and phosphorus) fertilizers means also that some of the excess carbon in the atmosphere has been withdrawn from the carbon cycle. Still, the amount could hardly be more than a few percent of the total excess, which is small but not totally insignificant (Bolin 1977b).

The magnitudes of the conversion and transfers (from a few thousand Tg for the uptake of nitrogen by plants in the sea and on land to merely a few Tg for the in situ destruction of N₂O in the troposphere or conversion of NH₃ to NO₂), as well as the considerable uncertainties assigned to many of these estimates, imply that it is usually not possible to balance the budget for the different reservoirs more accurately. The N₂O cycle has been discussed most extensively in this regard (Hahn and Junge 1977) and it has been shown that the flux to the atmosphere, primarily due to transfer from the oceans, cannot be balanced by the known N₂O sinks. Further, there are presently no means of determining accurately the return of molecular nitrogen to the atmosphere or of establishing the way in which a total balance of the natural nitrogen fixation is maintained in nature. Our estimates of how increased use of nitrogen fertilizers in agriculture could possibly change the present N₂O balance of the atmosphere are therefore quite uncertain. We should note, however, that:

1. the mean transit time for nitrogen in inorganic form in the soil is merely a few years;
2. the mean transit time for nitrogen in organic matter in the soil is of the order of a century; most of this nitrogen again becomes available to plants in inorganic form and only a small fraction is returned to the atmosphere in gaseous form;
3. the mean transit time for fixed nitrogen in the oceans is at least 10,000 years, probably much longer;
4. the annual fixation of nitrogen by the terrestrial biosphere is probably less than one per mille of the nitrogen reservoir in the soil;
5. man’s fixation of nitrogen is already today quite significant in comparison with that due to natural processes, and may well exceed it before the turn of the century.

The response of the natural system to man’s interventions will much depend on the characteristics of the transit time distribution function of nitrogen in the terrestrial biosphere, which is primarily influenced and will respond more quickly than the marine biosphere. If the mean transit time is very much less than the mean age of nitrogen in the soil, and thus a comparatively large part of the nitrogen recently fixed and added to the soil returns to the atmosphere in the course of decades, one would soon expect a significant change of the N₂O balance in the atmosphere. If, on the other hand, the transit time distribution function is close to exponential it may be centuries before changes will be noticeable. Obviously very much better knowledge will be needed of the processes of bacterial decomposition of organic matter in the soil before this question can be settled.

Even though changes of the nitrogen cycle on a global scale are probably slow they may in the long run be very significant. It is remarkable that man will probably soon be adding more fixed nitrogen to the global ecosystem than is done naturally, which fact may have
far-reaching consequences if maintained long enough, i.e. for centuries or more. It is likely that any such global changes will first be observed in the atmosphere and the monitoring of relevant constituents, notably N₂O, should therefore be given priority.

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