

THE CARBON CYCLE

The main cycle is from carbon dioxide to living matter and back to carbon dioxide. Some of the carbon, however, is removed by a slow epicycle that stores huge inventories in sedimentary rocks

by Bert Bolin

The biosphere contains a complex mixture of carbon compounds in a continuous state of creation, transformation and decomposition. This dynamic state is maintained through the ability of phytoplankton in the sea and plants on land to capture the energy of sunlight and utilize it to transform carbon dioxide (and water) into organic molecules of precise architecture and rich diversity. Chemists and molecular biologists have unraveled many of the intricate processes needed to create the microworld of the living cell. Equally fundamental and no less interesting is the effort to grasp the overall balance and flow of material in the worldwide community of plants and animals that has developed in the few billion years since life began. This is ecology in the broadest sense of the word: the complex interplay between, on the one hand, communities of plants and animals and, on the other, both kinds of community and their nonliving environment.

We now know that the biosphere has not developed in a static inorganic environment. Rather the living world has profoundly altered the primitive lifeless earth, gradually changing the composition of the atmosphere, the sea and the top layers of the solid crust, both on land and under the ocean. Thus a study of the carbon cycle in the biosphere is fundamentally a study of the overall global interactions of living organisms and their

physical and chemical environment. To bring order into this world of complex interactions biologists must combine their knowledge with the information available to students of geology, oceanography and meteorology.

The engine for the organic processes that reconstructed the primitive earth is photosynthesis. Regardless of whether it takes place on land or in the sea, it can be summarized by a single reaction: $\text{CO}_2 + 2\text{H}_2\text{A} + \text{light} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + 2\text{A} + \text{energy}$. The formaldehyde molecule CH_2O symbolizes the simplest organic compound; the term "energy" indicates that the reaction stores energy in chemical form. H_2A is commonly water (H_2O), in which case 2A symbolizes the release of free oxygen (O_2). There are, however, bacteria that can use compounds in which A stands for sulfur, for some organic radical or for nothing at all.

Organisms that are able to use carbon dioxide as their sole source of carbon are known as autotrophs. Those that use light energy for reducing carbon dioxide are called phototrophic, and those that use the energy stored in inorganic chemical bonds (for example the bonds of nitrates and sulfates) are called chemolithotrophic. Most organisms, however, require preformed organic molecules for growth; hence they are known as heterotrophs. The nonsulfur bacteria are an unusual group that is both photosyn-

thetic and heterotrophic. Chemoheterotrophic organisms, for example animals, obtain their energy from organic compounds without need for light. An organism may be either aerobic or anaerobic regardless of its source of carbon or energy. Thus some anaerobic chemoheterotrophs can survive in the deep ocean and deep lakes in the total absence of light or free oxygen.

There is more to plant life than the creation of organic compounds by photosynthesis. Plant growth involves a series of chemical processes and transformations that require energy. This energy is obtained by reactions that use the oxygen in the surrounding water and air to unlock the energy that has been stored by photosynthesis. The process, which releases carbon dioxide, is termed respiration. It is a continuous process and is therefore dominant at night, when photosynthesis is shut down.

If one measures the carbon dioxide at various levels above the ground in a forest, one can observe pronounced changes in concentration over a 24-hour period [see top illustration on page 127]. The average concentration of carbon dioxide in the atmosphere is about 320 parts per million. When the sun rises, photosynthesis begins and leads to a rapid decrease in the carbon dioxide concentration as leaves (and the needles of conifers) convert carbon dioxide into organic compounds. Toward noon, as the temperature increases and the humidity decreases, the rate of respiration rises and the net consumption of carbon dioxide slowly declines. Minimum values of carbon dioxide 10 to 15 parts per million below the daily average are reached around noon at treetop level. At sunset photosynthesis ceases while respiration continues, with the result that the carbon dioxide concentration close to the

CARBON LOCKED IN COAL and oil exceeds by a factor of about 50 the amount of carbon in all living organisms. The estimated world reserves of coal alone are on the order of 7,500 billion tons. The photograph on the opposite page shows a sequence of lignite coal seams being strip-mined in Stanton, N.D., by the Western Division of the Consolidation Coal Company. The seam, about two feet thick, is of low quality and is discarded. The second seam from the top, about three feet thick, is marketable, as is the third seam, 10 feet farther down. This seam is really two seams separated by about 10 inches of gray clay. The upper is some 3½ feet thick; the lower is about two feet thick. Twenty-four feet below the bottom of this seam is still another seam (not shown) eight feet thick, which is also mined.

ground may exceed 400 parts per million. This high value reflects partly the release of carbon dioxide from the decomposition of organic matter in the soil and partly the tendency of air to stagnate near the ground at night, when there is no solar heating to produce convection currents.

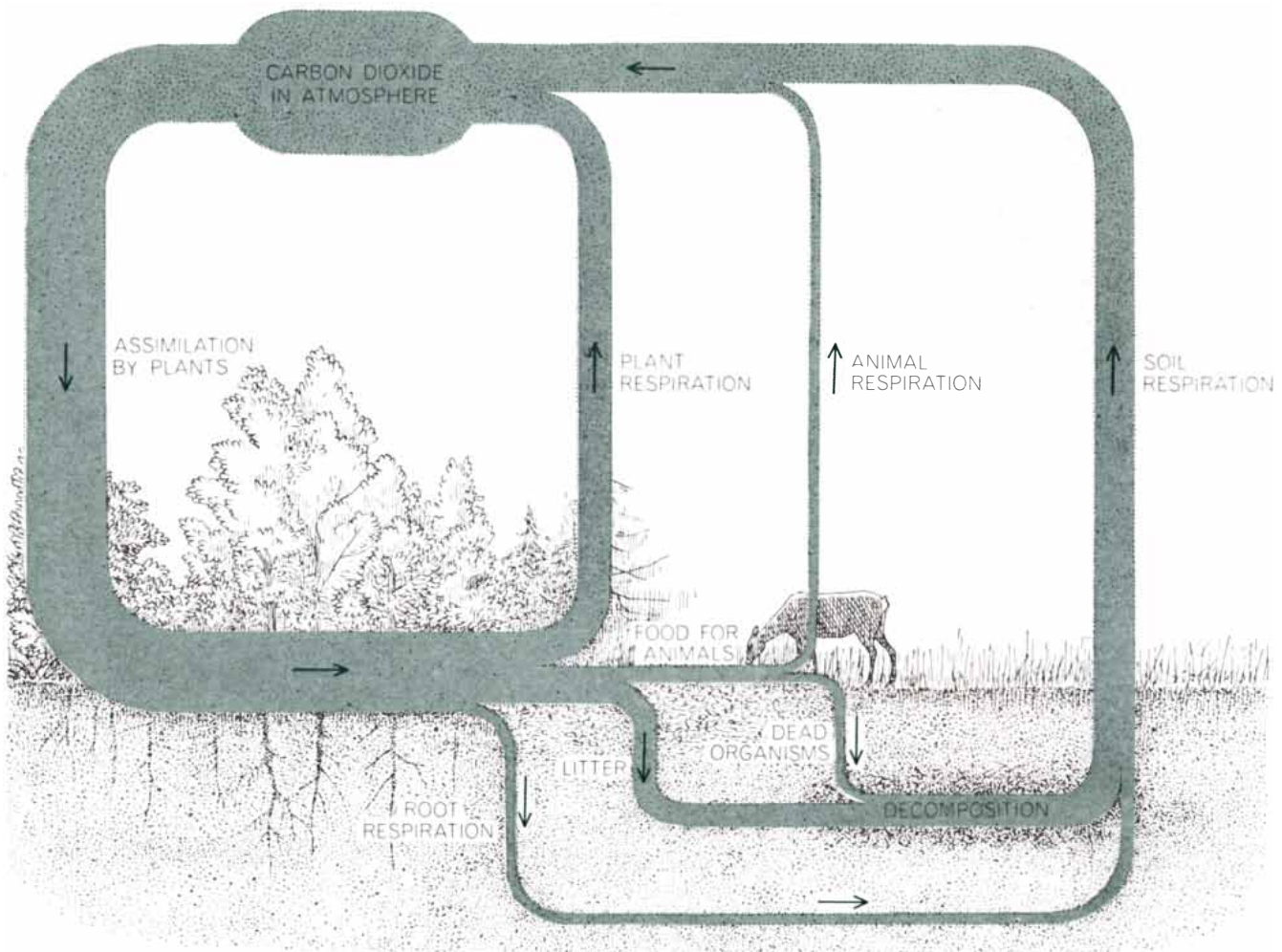
The net productivity, or net rate of fixation, of carbon dioxide varies greatly from one type of vegetation to another. Rapidly growing tropical rain forests annually fix between one kilogram and two kilograms of carbon (in the form of carbon dioxide) per square meter of land surface, which is roughly equal to the amount of carbon dioxide in a column of air extending from the same area of the earth's surface to the top of the atmosphere. The arctic tundra and the nearly barren regions of the desert may fix as

little as 1 percent of that amount. The forests and cultivated fields of the middle latitudes assimilate between .2 and .4 kilogram per square meter. For the earth as a whole the areas of high productivity are small. A fair estimate is that the land areas of the earth fix into organic compounds 20 to 30 billion net metric tons of carbon per year. There is considerable uncertainty in this figure; published estimates range from 10 to 100 billion tons.

The amount of carbon in the form of carbon dioxide consumed annually by phytoplankton in the oceans is perhaps 40 billion tons, or roughly the same as the gross assimilation of carbon dioxide by land vegetation. Both the carbon dioxide consumed and the oxygen released are largely in the form of gas dissolved near the ocean surface. Therefore most of the carbon cycle in the sea is self-con-

tained: the released oxygen is consumed by sea animals, and their ultimate decomposition releases carbon dioxide back into solution. As we shall see, however, there is a dynamic exchange of carbon dioxide (and oxygen) between the atmosphere and the sea, brought about by the action of the wind and waves. At any given moment the amount of carbon dioxide dissolved in the surface layers of the sea is in close equilibrium with the concentration of carbon dioxide in the atmosphere as a whole.

The carbon fixed by photosynthesis on land is sooner or later returned to the atmosphere by the decomposition of dead organic matter. Leaves and litter fall to the ground and are oxidized by a series of complicated processes in the soil. We can get an approximate idea of the rate at which organic matter in the soil is



CARBON CYCLE begins with the fixation of atmospheric carbon dioxide by the process of photosynthesis, conducted by plants and certain microorganisms. In this process carbon dioxide and water react to form carbohydrates, with the simultaneous release of free oxygen, which enters the atmosphere. Some of the carbohydrate is directly consumed to supply the plant with energy; the carbon dioxide so generated is released either through the plant's leaves or through its roots. Part of the carbon fixed by plants is consumed

by animals, which also respire and release carbon dioxide. Plants and animals die and are ultimately decomposed by microorganisms in the soil; the carbon in their tissues is oxidized to carbon dioxide and returns to the atmosphere. The widths of the pathways are roughly proportional to the quantities involved. A similar carbon cycle takes place within the sea. There is still no general agreement as to which of the two cycles is larger. The author's estimates of the quantities involved appear in the flow chart on page 130.

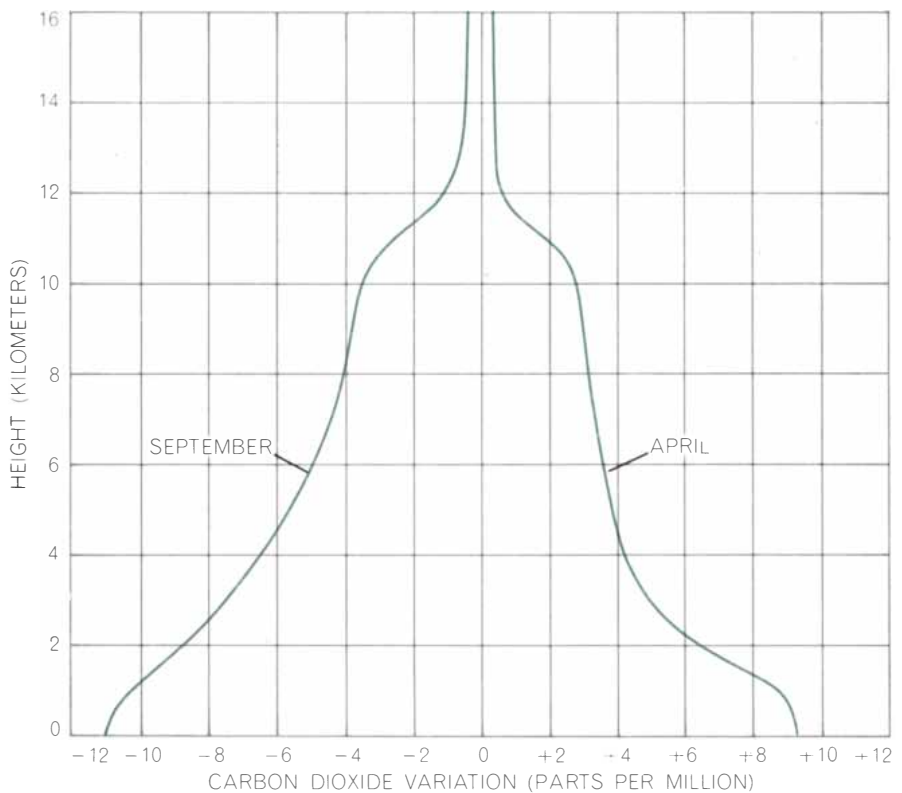
being transformed by measuring its content of the radioactive isotope carbon 14. At the time carbon is fixed by photosynthesis its ratio of carbon 14 to the non-radioactive isotope carbon 12 is the same as the ratio in the atmosphere (except for a constant fractionation factor), but thereafter the carbon 14 decays and becomes less abundant with respect to the carbon 12. Measurements of this ratio yield rates for the oxidation of organic matter in the soil ranging from decades in tropical soils to several hundred years in boreal forests.

In addition to the daily variations of carbon dioxide in the air there is a marked annual variation, at least in the Northern Hemisphere. As spring comes to northern regions the consumption of carbon dioxide by plants greatly exceeds the return from the soil. The increased withdrawal of carbon dioxide can be measured all the way up to the lower stratosphere. A marked decrease in the atmospheric content of carbon dioxide occurs during the spring. From April to September the atmosphere north of 30 degrees north latitude loses nearly 3 percent of its carbon dioxide content, which is equivalent to about four billion tons of carbon [see bottom illustration at right]. Since the decay processes in the soil go on simultaneously, the net withdrawal of four billion tons implies an annual gross fixation of carbon in these latitudes of at least five or six billion tons. This amounts to about a fourth of the annual terrestrial productivity referred to above (20 to 30 billion tons), which was based on a survey of carbon fixation. In this global survey the estimated contribution from the Northern Hemisphere, where plant growth shows a marked seasonal variation, constituted about 25 percent of the total tonnage. Thus two independent estimates of worldwide carbon fixation on land show a quite satisfactory agreement.

The forests of the world not only are the main carbon dioxide consumers on land; they also represent the main reservoir of biologically fixed carbon (except for fossil fuels, which have been largely removed from the carbon cycle save for the amount reintroduced by man's burning of it). The forests contain between 400 and 500 billion tons of carbon, or roughly two-thirds of the amount present as carbon dioxide in the atmosphere (700 billion tons). The figure for forests can be estimated only approximately. The average age of a tree can be assumed to be about 30 years, which implies that about 15 billion tons of carbon



VERTICAL DISTRIBUTION OF CARBON DIOXIDE in the air around a forest varies with time of day. At night, when photosynthesis is shut off, respiration from the soil can raise the carbon dioxide at ground level to as much as 400 parts per million (ppm). By noon, owing to photosynthetic uptake, the concentration at treetop level can drop to 305 ppm.



SEASONAL VARIATIONS in the carbon dioxide content of the atmosphere reach a maximum in September and April for the region north of 30 degrees north latitude. The departure from a mean value of about 320 ppm varies with altitude as shown by these two curves.

in the form of carbon dioxide is annually transformed into wood, which seems reasonable in comparison with a total annual assimilation of 20 to 30 billion tons.

The pattern of carbon circulation in the sea is quite different from the pattern on land. The productivity of the soil is mostly limited by the availability of fresh water and phosphorus, and only to a degree by the availability of other nutrients in the soil. In the oceans the overriding limitation is the availability of inorganic substances. The phytoplankton require not only plentiful supplies of phosphorus and nitrogen but also trace amounts of various metals, notably iron.

The competition for food in the sea is so keen that organisms have gradually developed the ability to absorb essential minerals even when these nutrients are available only in very low concentration. As a result high concentrations of nutrients are rarely found in surface waters, where solar radiation makes it possible for photosynthetic organisms to exist. If an ocean area is uncommonly productive, one can be sure that nutrients are supplied from deeper layers. (In limited areas they are supplied by the wastes of human activities.) The most productive waters in the world are therefore near the Antarctic continent, where the deep waters of the surrounding oceans well up and mix with the surface layers. There are similar upwellings along the coast of Chile, in the vicinity of Japan and in the Gulf Stream. In such regions fish are abundant and the maximum annual fixation of carbon approaches .3 kilogram per square meter. In the "desert" areas of the oceans, such

as the open seas of subtropical latitudes, the fixation rate may be less than a tenth of that value. In the Tropics warm surface layers are usually effective in blocking the vertical water exchange needed to carry nutrients up from below.

Phytoplankton, the primary fixers of carbon dioxide in the sea, are eaten by the zooplankton and other tiny animals. These organisms in turn provide food for the larger animals. The major part of the oceanic biomass, however, consists of microorganisms. Since the lifetime of such organisms is measured in weeks, or at most in months, their total mass can never accumulate appreciably. When microorganisms die, they quickly disintegrate as they sink to deeper layers. Soon most of what was once living tissue has become dissolved organic matter.

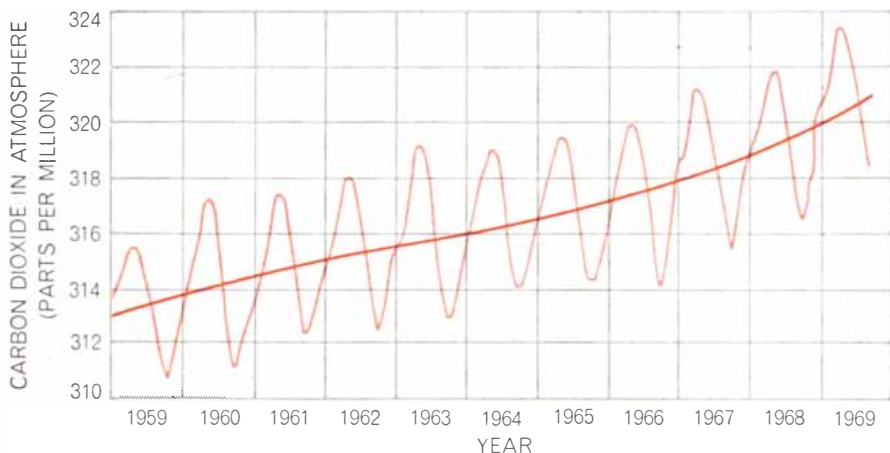
A small fraction of the organic particulate matter escapes oxidation and settles into the ocean depths. There it profoundly influences the abundance of chemical substances because (except in special regions) the deep layers exchange water with the surface layers very slowly. The enrichment of the deep layers goes hand in hand with a depletion of oxygen. There also appears to be an increase in carbon dioxide (in the form of carbonate and bicarbonate ions) in the ocean depths. The overall distribution of carbon dioxide, oxygen and various minor constituents in the sea reflects a balance between the marine life and its chemical milieu in the surface layers and the slow transport of substances by the general circulation of the ocean. The net effect is to prevent the ocean from becoming saturated with oxygen and to enrich the deeper strata with carbonate and bicarbonate ions.

The particular state in which we find the oceans today could well be quite different if the mechanisms for the exchange of water between the surface layers and the deep ones were either more intense or less so. The present state is determined primarily by the sinking of cold water in the polar regions, particularly the Antarctic. In these regions the water is also slightly saltier, and therefore still denser, because some of it has been frozen out in floating ice. If the climate of the earth were different, the distribution of carbon dioxide, oxygen and minerals might also be quite different. If the difference were large enough, oxygen might completely vanish from the ocean depths, leaving them to be populated only by chemibarotrophic bacteria. (This is now the case in the depths of the Black Sea.)

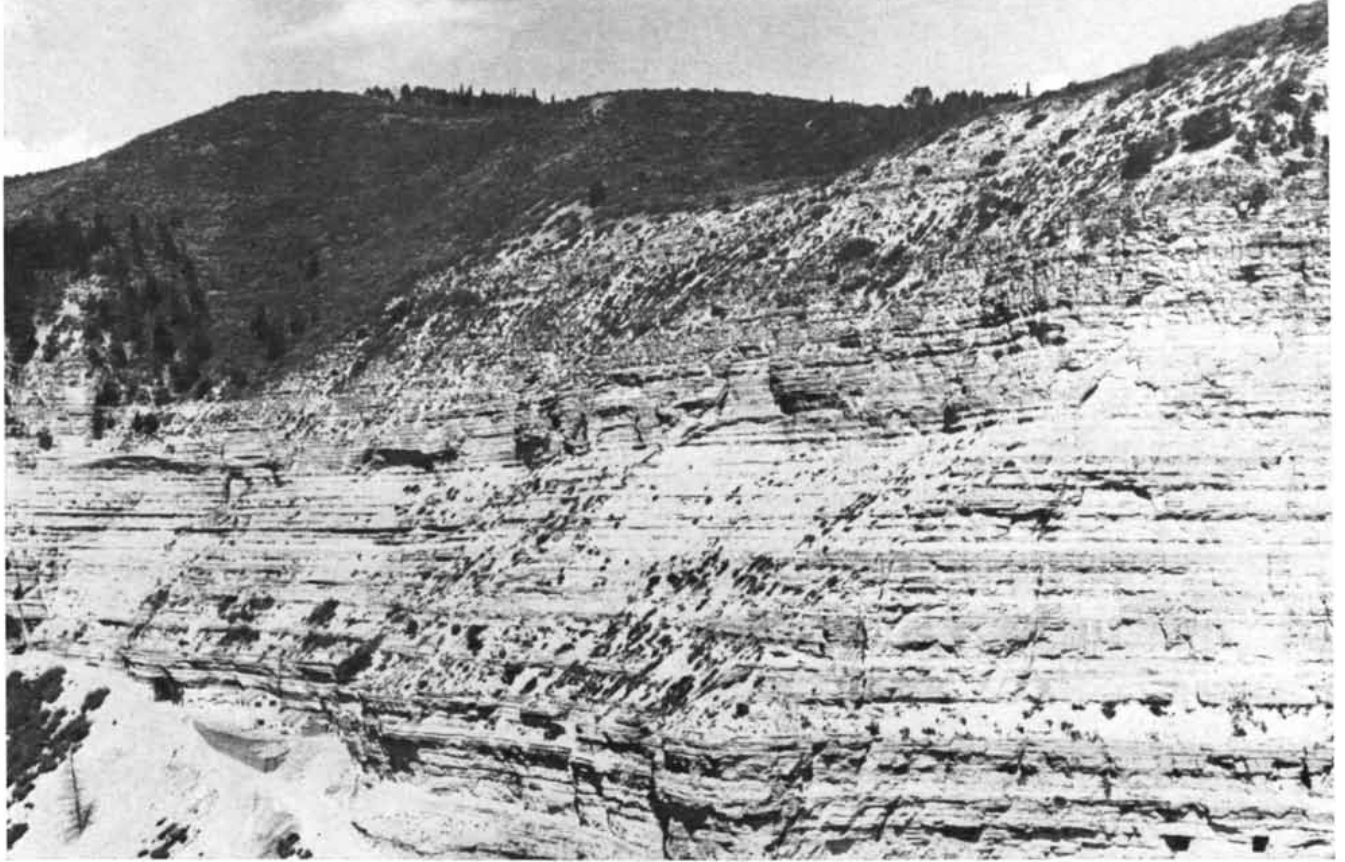
The time required to establish a new equilibrium in the ocean is determined by the slowest link in the chain of processes that has been described. This link is the oceanic circulation; it seems to take at least 1,000 years for the water in the deepest basins to be completely replaced. We can imagine other conditions of circulation in which the oceans would interact differently with sediments and rocks, producing a balance of substances that one can only guess at.

So far we have been concerned only with the basic biological and ecological processes that provide the mechanisms for circulating carbon through living organisms. Plants on land, with lifetimes measured in years, and phytoplankton in the sea, with lifetimes measured in weeks, are merely the innermost wheels in a biogeochemical machine that embraces the entire earth and that retains important characteristics over much longer time periods. In order to understand such interactions we shall need some rough estimates of the size of the various carbon reservoirs involved and the nature of their contents [see illustration on page 130]. In the context of the present argument the large uncertainties in such estimates are of little significance.

Only a few tenths of a percent of the immense mass of carbon at or near the surface of the earth (on the order of 20×10^{15} tons) is in rapid circulation in the biosphere, which includes the atmosphere, the hydrosphere, the upper portions of the earth's crust and the biomass itself. The overwhelming bulk of near-surface carbon consists of inorganic deposits (chiefly carbonates) and organic fossil deposits (chiefly oil shale, coal and petroleum) that required hundreds of



LONG-TERM VARIATIONS in the carbon dioxide content of the atmosphere have been followed at the Mauna Loa Observatory in Hawaii by the Scripps Institution of Oceanography. The sawtooth curve indicates the month-to-month change in concentration since January, 1959. The oscillations reflect seasonal variations in the rate of photosynthesis, as depicted in the bottom illustration on the preceding page. The smooth curve shows the trend.



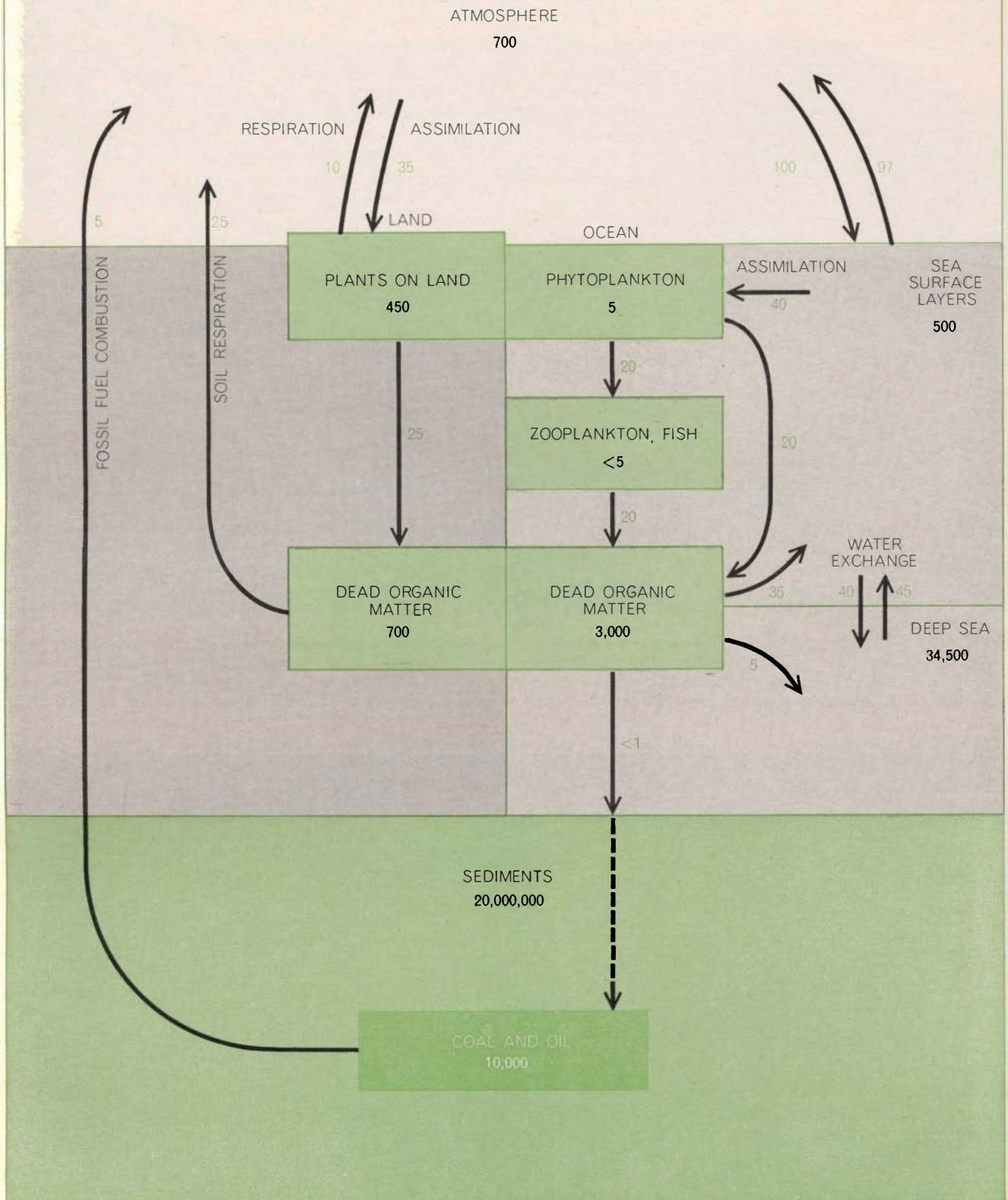
OIL SHALE is one of the principal sedimentary forms in which carbon has been deposited over geologic time. This photograph, taken at Anvil Points, Colo., shows a section of the Green River Formation, which extends through Colorado, Utah and Wyoming.

The formation is estimated to contain the equivalent of more than a trillion barrels of oil in seams containing more than 10 barrels of oil per ton of rock. Of this some 80 billion barrels is considered recoverable. The shale seams are up to 130 feet thick.



WHITE CLIFFS OF DOVER consist of almost pure calcium carbonate, representing the skeletons of phytoplankton that settled to the bottom of the sea over a period of millions of years more

than 70 million years ago. The worldwide deposits of limestone, oil shale and other carbon-containing sediments are by far the largest repository of carbon: an estimated 20 quadrillion (10^{15}) tons.



CARBON CIRCULATION IN BIOSPHERE involves two quite distinct cycles, one on land and one in the sea, that are dynamically connected at the interface between the ocean and the atmosphere. The carbon cycle in the sea is essentially self-contained in that phytoplankton assimilate the carbon dioxide dissolved in seawater and release oxygen back into solution. Zooplankton and fish consume the carbon fixed by the phytoplankton, using the dissolved oxygen for respiration. Eventually the decomposition of organic matter replaces the carbon dioxide assimilated by the phytoplank-

ton. All quantities are in billions of metric tons. It will be seen that the combustion of fossil fuels at the rate of about five billion tons per year is sufficient to increase the carbon dioxide in the atmosphere by about .7 percent, equivalent to adding some two parts per million to the existing 320 ppm. Since the observed annual increase is only about .7 ppm, it appears that two-thirds of the carbon dioxide released from fossil fuels is quickly removed from the atmosphere, going either into the oceans or adding to the total mass of terrestrial plants. The estimated tonnages are the author's.

millions of years to reach their present magnitude. Over time intervals as brief as those of which we have been speaking—up to 1,000 years for the deep-ocean circulation—the accretion of such deposits is negligible. We may therefore consider the life processes on land and in the sea as the inner wheels that spin at comparatively high velocity in the carbon-circulating machine. They are coupled by a very low gear to more majestic processes that account for the overall circulation of carbon in its various geologic and oceanic forms.

We now know that the two great systems, the atmosphere and the ocean, are closely coupled to each other through the transfer of carbon dioxide across the surface of the oceans. The rate of exchange has recently been estimated by measuring the rate at which the radioactive isotope carbon 14 produced by the testing of nuclear weapons has disappeared from the atmosphere. The neutrons released in such tests form carbon 14 by reacting with the nitrogen 14 of the atmosphere. In this reaction a nitrogen atom (${}^7\text{N}^{14}$) captures a neutron and subsequently releases a proton, yielding ${}^6\text{C}^{14}$. (The subscript before the letter represents the number of protons in the nucleus; the superscript after the letter indicates the sum of protons and neutrons.)

The last major atmospheric tests were conducted in 1963. Sampling at various altitudes and latitudes shows that the constituents of the atmosphere became rather well mixed over a period of a few years. The decline of carbon 14, however, was found to be rapid; it can be explained only by assuming an exchange of atmospheric carbon dioxide, enriched in carbon 14, with the reservoir of much less radioactive carbon dioxide in the sea. The measurements indicate that the characteristic time for the residence of carbon dioxide in the atmosphere before the gas is dissolved in the sea is between five and 10 years. In other words, every year something like 100 billion tons of atmospheric carbon dioxide dissolves in the sea and is replaced by a nearly equivalent amount of oceanic carbon dioxide.

Since around 1850 man has inadvertently been conducting a global geochemical experiment by burning large amounts of fossil fuel and thereby returning to the atmosphere carbon that was fixed by photosynthesis millions of years ago. Currently between five and six billion tons of fossil carbon per year are being released into the atmosphere. This would be enough to increase the

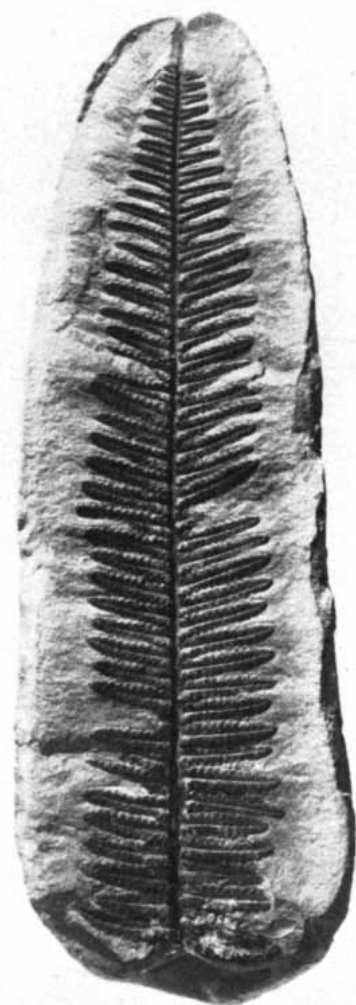
amount of carbon dioxide in the air by 2.3 parts per million per year if the carbon dioxide were uniformly distributed and not removed. Within the past century the carbon dioxide content of the atmosphere has risen from some 290 parts per million to 320, with more than a fifth of the rise occurring in just the past decade [see illustration on page 128]. The total increase accounts for only slightly more than a third of the carbon dioxide (some 200 billion tons in all) released from fossil fuels. Although most of the remaining two-thirds has presumably gone into the oceans, a significant fraction may well have increased the total amount of vegetation on land. Laboratory studies show that plants grow faster when the surrounding air is enriched in carbon dioxide. Thus it is possible that man is fertilizing fields and forests by burning coal, oil and natural gas. The biomass on land may have increased by as much as 15 billion tons in the past century. There is, however, little concrete evidence for such an increase.

Man has of course been changing his environment in other ways. Over the past century large areas covered with forest have been cleared and turned to agriculture. In such areas the character of soil respiration has undoubtedly changed, producing effects that might have been detectable in the atmospheric content of carbon dioxide if it had not been for the simultaneous increase in the burning of fossil fuels. In any case the dynamic equilibrium among the major carbon dioxide reservoirs in the biomass, the atmosphere, the hydrosphere and the soil has been disturbed, and it can be said that they are in a period of transition. Since even the most rapid processes of adjustment among the reservoirs take decades, new equilibriums are far from being established. Gradually the deep oceans become involved; their turnover time of about 1,000 years and their rate of exchange with bottom sediments control the ultimate partitioning of carbon.

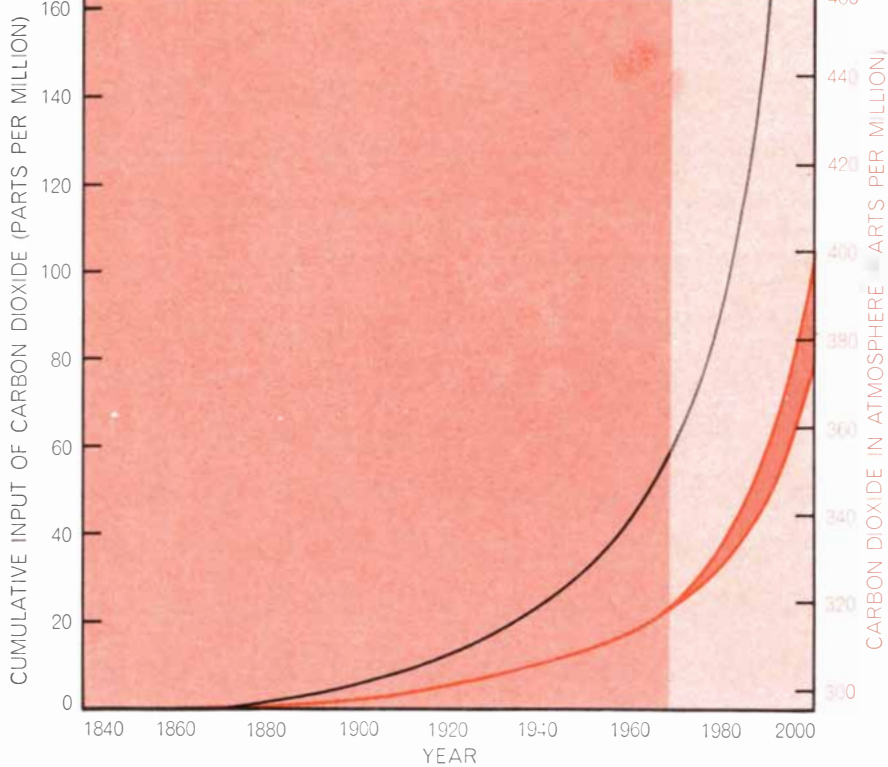
Meanwhile human activities continue to change explosively. The acceleration in the consumption of fossil fuels implies that the amount of carbon dioxide in the atmosphere will keep climbing from its present value of 320 parts per million to between 375 and 400 parts per million by the year 2000, in spite of anticipated large removals of carbon dioxide by land vegetation and the ocean reservoir [see illustrations on next page]. A fundamental question is: What will happen over the next 100 or 1,000 years? Clearly the exponential changes cannot continue.

If we extend the time scale with which we are viewing the carbon cycle by several orders of magnitude, to hundreds of thousands or millions of years, we can anticipate large-scale exchanges between organic carbon on land and carbonates of biological origin in the sea. We do know that there have been massive exchanges in the remote past. Any discussion of these past events and their implications for the future, however, must necessarily be qualitative and uncertain.

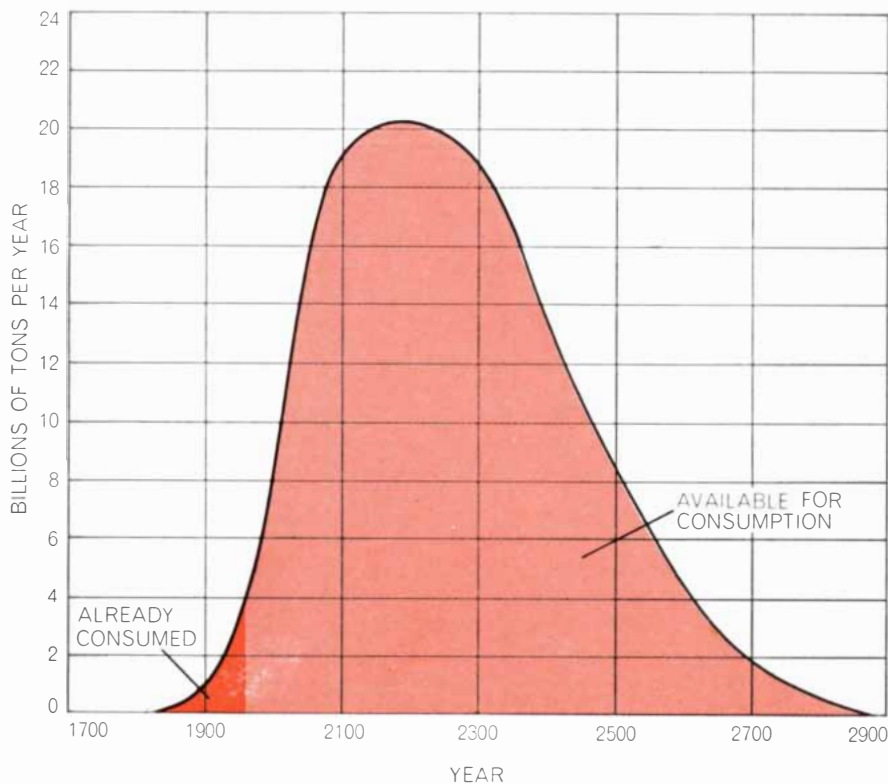
Although the plants on land have probably played an important role in the deposition of organic compounds in the soil, the oceans have undoubtedly acted as the main regulator. The amount of carbon dioxide in the atmosphere is essentially determined by the partial pressure of carbon dioxide dissolved in the



GIANT FERN of the genus *Pecopteris*, which fixed atmospheric carbon dioxide 300 million years ago, left the imprint of this frond in a thin layer of shale just above a coal seam in Illinois. The specimen is in the collection of the Smithsonian Institution.



INCREASE IN ATMOSPHERIC CARBON DIOXIDE since 1860 is shown by the lower curve, with a projection to the year 2000. The upper curve shows the cumulative input of carbon dioxide. The difference between the two curves represents the amount of carbon dioxide removed by the ocean or by additions to the total biomass of vegetation on land.



POSSIBLE CONSUMPTION PATTERN OF FOSSIL FUELS was projected by Harrison Brown in the mid-1950's. Here the fuel consumed is updated to 1960. If a third of the carbon dioxide produced by burning it all were to remain in the atmosphere, the carbon dioxide level would rise from 320 ppm today to about 1,500 ppm over the next several centuries.

sea. Over a period of, say, 100,000 years the leaching of calcium carbonates from land areas tends to increase the amount of carbon dioxide in the sea, but at the same time a converse mechanism—the precipitation and deposition of oceanic carbonates—tends to reduce the amount of carbon dioxide in solution. Thus the two mechanisms tend to cancel each other.

Over still longer periods of time—millions or tens of millions of years—the concentrations of carbonate and bicarbonate ions in the sea are probably buffered still further by reactions involving potassium, silicon and aluminum, which are slowly weathered from rocks and carried into the sea. The net effect is to stabilize the carbon dioxide content of the oceans and hence the carbon dioxide content of the atmosphere. Therefore it appears that the carbon dioxide environment, on which the biosphere fundamentally depends, may have been fairly constant right up to the time, barely a moment ago geologically speaking, when man's consumption of fossil fuels began to change the carbon dioxide content of the atmosphere.

The illustration on page 130 represents an attempt to synthesize into a single picture the circulation of carbon in nature, particularly in the biosphere. In addition to the values for inventories and transfers already mentioned, the flow chart contains other quantities for which the evidence is still meager. They have been included not only to balance the books but also to suggest where further investigation might be profitable. This may be the principal value of such an exercise. Such a flow chart also provides a semiquantitative model that enables one to begin to discuss how the global carbon system reacts to disturbances. A good model should of course include inventories and pathways for all the elements that play a significant role in biological processes.

The greatest disturbances of which we are aware are those now being introduced by man himself. Since his tampering with the biological and geochemical balances may ultimately prove injurious—even fatal—to himself, he must understand them much better than he does today. The story of the circulation of carbon in nature teaches us that we cannot control the global balances. Therefore we had better leave them close to the natural state that existed until the beginning of the Industrial Revolution. Out of a simple realization of this necessity may come a new industrial revolution.