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The Cycle of Organic Carbon in Sea Water*

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Abstract

Recent work has demonstrated that the cycle of organic carbon in sea water is not completely under biological control. Several important pathways may be controlled by physical or chemical mechanisms; these mechanisms may ultimately determine the availability of organic carbon to marine organisms, and the varieties and amounts of organic compounds remaining in solution.

Introduction

As human populations and human expectations continue to increase, it is evident that a time is approaching when with even the best agricultural techniques it will not be possible to feed everyone adequately. We are not feeding everyone adequately now, but the present problems are those of economics and distribution, rather than of production. It has become a commonplace to say that man must turn to the sea to find the needed extra food; however, the amount of carbohydrate and protein available from the sea is only beginning to be estimated, and the early estimates have proved to be somewhat discouraging. RYTHER[1] has calculated the maximum sustained yield of fish to be less than double the present-day catch, and feels that any further increase in food from the sea must come from harvesting organisms further up the food chain, such as the Antarctic krill.

Estimates of this kind, based upon present-day productivity and utilization, are perhaps a little misleading. We are now at the hunting and gathering stage in our use of the seas; we must eventually pass to the farming stage, with its concomitant great increase in productivity. However, before we can hope to farm the sea successfully, we must understand the present limitations on productivity. With the chemist's typical oversimplification of a biological problem, we can define productivity as the fixation of inorganic carbon, in the form of bicarbonate or carbonate ion, into organic molecules. The rate of such fixation, and the route of these molecules through the food chain until they are completely metabolized and freed as CO_2, is the subject of our discussion.

A further limitation on both the quantity and quality of life in the future is the degree of pollution of the biosphere. Both inorganic and organic pollutants are dumped into the seas, largely on the assumption that the oceans are a bottomless pit, capable of swallowing up any amount of garbage. That this is not so has been demonstrated by the distribution of DDT and the chlorinated biphenyls over all of the oceans, and by the amounts of mercury found in tuna and swordfish. Here again, the cycle of organic carbon plays a key role in the spread of many of the pollutants; if we are to set reasonable limits on man's use of the oceans as a dumping-place, we must understand how these added materials, many of them organic, are removed from the water, and how they affect the normal cycle of fixation and metabolism of organic carbon.

The standing crop

In the investigation of the cycle of any substance in nature, the first and usually the easiest step is to determine how much is present, and in what form. In the case of organic carbon in the sea, this first step has turned out to be unexpectedly difficult, and even now there are many uncertainties in our analyses.

Excluding the relatively small amounts of material furnished by land drainage and by the growth of rooted algae along the coasts, the source of all of the organic material in the sea is the photosynthetic activity of the phytoplankton, the marine equivalent of the grasses and flowers on land. The phytoplankton have been the objects of study by marine biologists practically since the invention of the microscope. We thus confidently assume that we should know something about the amount of carbon in the standing crop of phytoplankton. Unfortunately, no such assumption can be made. Phytoplankton populations are usually estimated by measuring the amount of chlorophyll present in organisms filtered from a given volume of water, and then converting the chlorophyll value to carbon, or to weight, by the use of a standard factor. The correspondence between chlorophyll and carbon content is a function of the species present and of their physiological state; our estimates

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[1] J.H. RYTHER, *Science 166* (1969) 72.

of standing crop of phytoplankton must therefore suffer from a fairly large variance. Another method of measurement is to estimate the volume of each phytoplankton organism present, and then to convert volumes to weight, again by the use of a standard factor. This method also furnishes a number with a large variance.

The values available range from 0.5 to 5 μg C/l, over that part of the water column where the organisms flourish. Other, larger organisms, such as zooplankton and fish, make up a very small proportion of the organic carbon content of the water, and are noticeable only because the carbon is distributed unevenly, in large lumps (such as whales). It is from the phytoplankton base that all of the authigenic organic carbon in the ocean ultimately stems.

Living organisms represent only a small part of the particulate organic carbon (POC) in the ocean. The dividing line between dissolved and particulate organic carbon is not a clear one; accumulating evidence suggests that there is a continuum of sizes from large, easily-visible particles characterized as "marine snow", through the colloidal range, to large polymers at the borderline of true solution, and finally to small organic molecules such as urea and the amino acids. The definition of "particulate organic carbon" is an operational one, based on the pore size of available filters. The original definition of a particle as anything retained by a filter of 0.5 μ pore size resulted from the standard pore sizes of the early membrane and glass fiber filters. Those workers using the newer, less absorbent silver filters customarily use 0.8 or 1.2 μ as the cut-off size, since the 0.5 μ silver filters have much higher carbon blanks. As most of the particulate carbon seems to be present in the fraction between 0.05 and 0.5 μ, the shift from 0.5 μ to 0.8 or 1.2 μ produces less change in the values reported than does the change from glass fiber to silver filters. Although the definitive work has yet to be done, reports in the literature suggest that glass filters trap a greater proportion of the smaller particles than do silver filters of the same nominal pore size.

The actual measurement of the POC after filtration is relatively easy and precise. The filters are usually treated with acid to remove carbonates, dried, and burned in an atmosphere of oxygen. The resultant CO_2 is measured either by a nondispersive infrared analyzer or by gas chromatography. The accuracy and precision of the method are limited by the variability in the carbon content of the filters themselves. The amounts found range from 5 to 50 μg C/l, with occasional samples where the amount found is within the variability of the blank. This fraction of the organic material was long considered to be completely detrital, originating in the breakdown of phytoplankton and zooplankton after death. However, recent work has proposed a number of other origins for these materials.

The dissolved organic carbon (DOC) is defined as the quantity which passes through the filter chosen. The quantities reported for sea water seem to depend upon the method of analysis. The standard method over the last eight years has involved wet oxidation by persulfate at 140 °C, followed by measurement of the evolved CO_2[2]. A variant on this method uses ultraviolet radiation in the presence of H_2O_2 for the oxidation step[3], with closely comparable results. These methods give values of DOC in sea water ranging from 0.5 to 1.5 μg C/l, roughly a hundred times the concentration of POC. However, the history of wet oxidation methods in sea water has been one of steady increase in carbon values as better oxidants were introduced; some method involving complete combustion would certainly be preferred.

Such a method was developed by Russian scientists[4]. It involved taking the acidified sea salts to dryness at 60 °C, followed by dry combustion in a stream of oxygen, and measurement of the evolved CO_2. The Russian values were typically higher than the wet oxidation values, and ranged from 0.7 to 3.0 mg C/l. Variants of this method have been developed by a number of workers, but at least until now they have all suffered from the problem of contamination. The quantities of carbon are very small, and each successive manipulation of the sample increases the chance of contamination.

A direct injection method for total combustion has recently been developed by SHARP[5]. In this method, the sample is acidified and bubbled with oxygen, to remove carbonates, and a small volume, usually around 0.1 ml, is injected into a combustion tube packed with platinized asbestos and held at 900 °C. The organic carbon is oxidized to CO_2 in a stream of oxygen, and the CO_2 measured with a nondispersive infrared analyzer. The values of DOC found by this technique are closer to those of the Russian workers. Although the method has several advantages over both the Russian and the wet oxidation techniques, the instrument is difficult to operate, and a simplified variation must ultimately be developed for routine use. Since all of these methods require removal of carbonate carbon by acidification and bubbling, they all fail to measure any volatile organic components present in the original sample. There are no reliable estimates of the size of the volatile fraction.

An unexpected benefit of the development of the high-temperature direct combustion method was the demonstration of the high organic carbon content of distilled water. Early trials with this apparatus produced values of 0.6 mg C/l for double-distilled water. Normal methods of purification, including distillation from permanganate and the introduction of a series of spray traps, could only reduce this value by half. A technique involving combustion of the water vapor in a stream of oxygen at 1000 °C was needed to bring the organic carbon content of the water down to the detection limits of the analytical method. Nothing is known of the nature of this organic material, except that its concentration seems to vary with the annual phytoplankton growth cycle in the reservoirs.

Distributions in space and time

Since the particulate and dissolved organic carbon both are a function of the productivity of the phytoplankton, we would expect the distributions of all three components, at least in the surface waters, to be the same. As long as we speak in terms of large horizontal areas, this is roughly true. Regions of high phytoplankton productivity are generally regions with high standing crops of phytoplankton, POC, and DOC. These correspondences are not necessarily temporal, however. RILEY[6] found a winter peak in POC in Long Island Sound, unaccompanied by any increase in phytoplankton, and in fact during the period of minimum productivity.

The distributions with depth show much less correspondence. The phytoplankton maximum is always some distance down in the water column, while the maximum amounts of both POC and DOC are to be found in the surface layer. Surface values of POC are quite often ten times the value to be found even 10 cm lower in the water column[7]. Earlier workers felt that the distribution of living phytoplankton was strictly controlled by the concentrations of inorganic nutrients and by available light. Below the compensation depth, that depth at which photosynthesis is balanced by respiration, only dying phytoplankton were supposed to be expected. More recently, organisms such as FOURNIER's[8] little green beasts have been found at considerable depths, well below the point at which any photosynthesis could occur.

The POC and wet oxidation DOC values show similarities in depth distribution. Both are relatively high in the surface waters, perhaps down to 200–500 m, and both are lower and relatively constant in the deeper waters. Their distributions have led to the concept of the relative biological uselessness of the organic compounds in deep water[9].

While very few profiles of DOC have been run with the newer total combustion method, the results indicate a considerable amount of structure and variability is to be found in the distribution of DOC in deep water. There seems to be an overall decline with depth, suggesting biological utilization, as well as a number of maxima and minima associated with hydrographic features, as would be expected. The biological meaning of the discrepancy between wet and dry oxidation methods is still obscure; its explanation awaits the identification of the compounds present in sea water.

The isolation and identification of the various compounds in the dissolved organic fraction has been made difficult by the lack of a good method for keeping a carbon budget. The uncertainty in the wet oxidation method is greater than the absolute amount of any single component of the organic fraction. Methods of analysis are also complicated by the high salt content and by the number of interferences present. Almost every compound of biochemical interest has been reported from sea water, usually in microgram amounts. However, in no case has the total of identified fractions in a sample come even close to the total carbon content of that sample. To the best of my knowledge, no one has yet attempted a complete identification of the organic compounds of a single sample, much less an entire hydrographic station.

As an example of the complexity of the problem of identification, let us look at the free amino acid content of sea water. A number of workers have reported values ranging from 50 to 150 $\mu g/l$ in the open ocean. In this fraction there may be eighteen to twenty compounds. Methods for measuring such small amounts are difficult at best. In oceanographic problems, the difficulty is increased by the necessity for running many of the analyses at sea, to avoid problems of bacterial decomposition during storage. Many very skilled analysts function at less than their best at sea. Many very sensitive instruments will not function at all on board ship, because of the motion and the uncertainty in the ship's electrical supply. A failure in any of the electronic components cannot usually be repaired on a cruise, particularly if the instrument uses integrated circuits or circuit boards. When you are making a station at the Antarctic convergence, your friendly factory representative would be hard put to furnish you with parts you might need to repair a mass spectrograph. Oceanographic ports-of-call are usually places like Freetown (Sierra Leone) or Punta Arenas (Chile), ports where even IBM isn't likely to maintain an office. Under these circumstances, it is not strange that a maxim of oceanography has been that the optimum number of electronic components for any oceanographic instrument is less than one.

The most satisfactory methods have been those which measured whole groups of related compounds, such as all of the carbohydrates or all of the proteins. However, the data from these methods has been scanty and not always reliable. If such data were accompanied by measurements of total carbon, there would be less of a credibility gap. The best hope for the future may lie in an improved, simplified dry combustion total carbon method and a system of analysis based on the gas chromatograph.

Pathways

The older ideas of the cycle of organic carbon in sea water involved fairly simple pathways (Fig. 1). Carbon dioxide,

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[2] D.W. MENZEL and R.F. VACCARO, *Limnol. Oceanogr. 9* (1964) 138.

[3] F.A.J. ARMSTRONG, P.M. WILLIAMS, and J.D.H. STRICKLAND, *Nature 211* (1966) 481.

[4] B.A. SKOPINTSEV, *Okeanol. 6* (1966) 361.

[5] J.H. SHARP, unpublished Ph.D. thesis, Dalhousie University (1972).

[6] G.A. RILEY, *Limnol. Oceanogr. 8* (1963) 381.

[7] S. NISHIZAWA, *Bull. Plankt. Soc. Japan 18* (1971) 42.

[8] R.O. FOURNIER, *Limnol. Oceanogr. 15* (1970) 675.

[9] D.W. MENZEL and J.H. RYTHER, *University of Alaska Symposium on Organic Matter in Natural Waters, 1968* (1970) 31.

in the form of dissolved carbonate and bicarbonate, was converted into fixed organic carbon by photosynthesis.

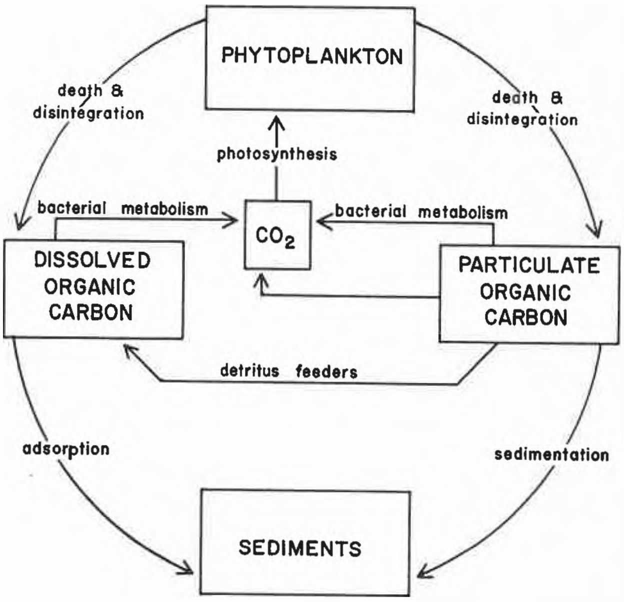

Fig. 1. Organic carbon cycle in sea water, old version

Upon the death and disintegration of the phytoplankton, some of this fixed carbon was released into the water as dissolved organic carbon, while the remains of the organisms formed the particulate fraction. This detritus formed the diet of marine bacteria and of various detritus feeders, both in the water column and at the sea floor. Further components of the dissolved fraction might come from the excretion of urea and other such products by fish and zooplankton, and by bacterial breakdown of particulate material. It was generally considered that the pathway from particulate to dissolved components was unidirectional, and that the major, and perhaps the only, users of the dissolved fraction were the marine bacteria. From both the dissolved and particulate fractions, metabolic processes finally oxidized the organic material to CO_2, and the cycle was closed. It was also generally considered that all of the steps were biologically controlled. The main issues in question were the rates of these processes; we had the cycle, but we didn't know how fast it revolved. With the advent of the C^{14} productivity method, basically a measurement of the rate of incorporation of $HC^{14}O_3^-$ into phytoplankton organisms, we felt that we had an estimate of at least the first step of the cycle, and that in a few more years we might have it all. The results of the last fifteen years of research have shown us how oversimplified our cycle was, and how far, indeed, we were from "having it all".

First of all, a number of investigators demonstrated, almost simultaneously, that many phytoplankton organisms release a portion of the organic carbon as it is being fixed by the processes of photosynthesis. The release seems to be proportionately greater in less productive areas, as in the open sea, than it is in the enriched media used in laboratory cultures. The details of this release are still being debated, and there are several opinions concerning its importance in nature. However, it does furnish another pathway from the phytoplankton to the dissolved state, one not involving the destruction of the organisms. It also complicates the calculation of productivity by the C^{14} method; if productivity is defined in terms of rate of carbon fixation, then the amount of carbon excreted in this fashion must also be measured.

At about the same time, a number of investigators also demonstrated that some phytoplankton species, particularly the dinoflagellates, could not synthesize vitamin B_{12}, and required a source of this vitamin for growth and reproduction. Some species were found to be able to use organic nitrogen compounds, such as urea, as sources of nitrogen when concentrations of nitrate, nitrite, and ammonia were very low. Further work demonstrated that some species could use small organic molecules as carbon sources, and could therefore survive without photosynthesizing. A return pathway, from DOC to phytoplankton, was thus described, and a way of removing DOC from solution without the mediation of bacteria was found. This heterotrophy also helped to explain the existence of apparently healthy phytoplankton organisms below the compensation depth.

A question naturally arose as to whether the ability to utilize the DOC in sea water was limited to phytoplankton. In 1909, **Pütter**[10], on the basis of some very high DOC values, had suggested that some marine organisms, and especially larval forms, might derive such of their food by absorption of DOC. While this particular argument was crushed by **Krogh's**[11] demonstration of the inadequacy of **Pütter's** analytical method, the hypothesis has re-emerged every few years. In the last few years, several investigators, most notably **Stephens**[12] and **Ferguson**[13], have demonstrated that all soft-bodied and many hard-bodied, marine invertebrates are able to absorb simple organic compounds at sea water concentrations, and incorporate them immediately into body structures. At least at the sea floor, then, still another mechanism for the removal of organic carbon exists. Whether this mechanism also appears in larval forms is still unknown.

The absorption of organic materials on suspended inorganic particles has always been considered a possible mechanism for the removal of DOC from the water column. Little research was performed on this mechanism until **Chave's**[14] demonstration that much of the suspended calcium carbonate in sea water was protected from solution by a coating of organic material. Subsequently, **Chave** and **Suess**[15] have shown that such a coating is rapidly accumulated in the presence of surface-active compounds like the stearates. While no one has yet examined the surfaces of suspended clays, I would be very surprised if they did not also absorb such a layer. Here we have a physical mechanism for the removal of DOC from solution, and for its incorporation into particles. This is especially important, since most of the smaller animals in the ocean are particle-feeders, and since marine bacteria are found in greatest concentration on particle surfaces. In this manner, at least part of the great reservoir of DOC is concentrated, and put into a readily available form.

Perhaps the most exciting of the new directions in this research could be described as an excellent example of serendipity. The original interest of the investigators[16] was in the mechanism by which the phosphate in an aerated culture flask accumulated at the surface. They soon discovered that aeration appeared to be the necessary condition for this concentration. Both the inorganic and organic phosphorus compounds were apparently collected on the surfaces of bubbles, and concentrated in the surface layer of the medium as the bubbles burst. If aeration was discontinued, the inorganic phosphate quickly redistributed itself through the medium, in accord with the normal laws of diffusion. The organic phosphorus, however, remained in the surface layer in the form of aggregated particles of organic material.

While the concentration of phosphorus was interesting, the concentration of carbon was even more so. BAYLOR and SUTCLIFFE[17] quickly demonstrated that particles made in this manner would support the growth of *Artemia*, the brine shrimp, and presumably could do the same for other particle-feeders. This was a tremendously important discovery, since it furnished another physical mechanism for the transfer of material from the DOC reservoir, where the amount of organic carbon was immense but diffuse, to the POC, where the amount was small but concentrated into packets. The mechanism is continuous, since it is driven by the breaking of waves. The winter maximum in POC reported by RILEY[6] is now easy to understand; this is the period of storms on the Sound, and therefore of greatest bubble formation.

The exact mechanism of aggregate formation has been a matter of some dispute. It has been demonstrated that both triple filtration through 0.5 μ filters[18] and filtration through 0.22 μ filters to remove bacteria[19] result in great reduction in particle formation. This finding has been interpreted as evidence that bacteria must be present in order for particles to be formed. While such filtration would, in fact, remove most of the bacteria, it would also remove much of the material of colloidal dimensions. SHARP[5] has since demonstrated particle formation in bacteria-free systems, and has suggested that the actual mechanism is the aggregation of smaller particles of colloidal size into the larger, visible particles.

A much more difficult matter to explain is the apparent equilibrium between DOC and POC. If the particles present in normal sea water are removed by filtration, within a short period new particles appear until about the original concentration is reached. If a sample of sea water is bubbled and filtered, usually only a small yield of particles is found. If the water is filtered continuously while it is being bubbled, a much greater harvest of particles results. We know very little about the mechanisms involved in this equilibrium, although KHAILOV and FINENKO[20] have suggested a process of adsorption on existing particles followed by bacterial or enzymatic degradation of the adsorbed material to account for the apparent stability of the POC in any water sample.

While the bubbling mechanism is important in surface waters, it can only work effectively in the upper ten meters or so of the sea. It also seems to function primarily as a collecting or concentrating device. Once the organic matter is present in the surface film, it is subjected to normal daylight, and many reactions, including the denaturation of proteins and the formation of polymers from fatty acids[21], are driven either directly by ultraviolet light or indirectly by reactions with solvated electrons or the byproducts of solvated electron reactions with sea water. Thus dissolved organic materials which have been brought to the sea surface may be altered there into forms which will not go back into solution.

Very early in the study of particle formation we found that almost any energy input, including shaking, stirring, or even simple inversion of the sample flask, would result in particle formation. Some samples would even form particles spontaneously on standing. This was a very heartening discovery, since the bubbling mechanism is limited to surface water, and we really need a way to get at the reservoir of DOC in deep water. SHARP'S[5] work indicates a loss of DOC with depth, but much more work is needed before we can state with any certainty that there is a shift of carbon out of the dissolved fraction at depth.

Another question raised by this work is the nature of the inorganic portion of the aggregates. The particles average only about 30% organic material; the composition of the remaining 70% is as yet unknown. We have found[22] that the particulate fraction usually contains about as much calcium carbonate as organic material,

[10] A. PÜTTER, *Die Ernährung der Wassertiere und der Stoffhaushalt der Gewässer*, Jena 1909.

[11] A. KROGH, *Ecol. Monogr. 4* (1934) 430.

[12] G. C. STEPHENS, *Amer. Zool. 8* (1968) 95.

[13] J. C. FERGUSON, *Biol. Bull. 132* (1967) 161.

[14] K. E. CHAVE, *Science 148* (1965) 1723.

[15] K. E. CHAVE and E. SUESS, *Trans. N. Y. Acad. Sci. 29* (1967) 991.

[16] W. H. SUTCLIFFE jr., E. R. BAYLOR, and D. W. MENZEL, *Deep-Sea Res. 10* (1963) 233.

[17] E. R. BAYLOR and W. H. SUTCLIFFE jr., *Limnol. Oceanogr. 8* (1963) 369.

[18] D. W. MENZEL, *Deep-Sea Res. 13* (1966) 963.

[19] R. T. BARBER, *Nature 211* (1966) 257.

[20] K. M. KHAILOV and Z. Z. FINENKO, *Okeanol. 8* (1968) 776.

[21] J. WHEELER, unpublished Ph.D. thesis, Dalhousie University, (1972).

[22] P. J. WANGERSKY and D. C. GORDON jr., *Limnol. Oceanogr. 10* (1965) 544.

and that there is enough Mn^{++} present to account for all of the manganese content of oceanic sediments. Almost everything still remains to be done in this area.

It would seem, then, that at least some fraction of the DOC can be converted to particulate form by physical and chemical mechanisms, and thus made available to organisms larger than bacteria. This aggregation also renders the material more accessible to bacteria; many particles are heavily bacterized. The main effect of these reactions whould be to increase the rate of cycling, by keeping the organic material in its most available form. However, the cycle has now become considerably more complicated (Fig. 2).

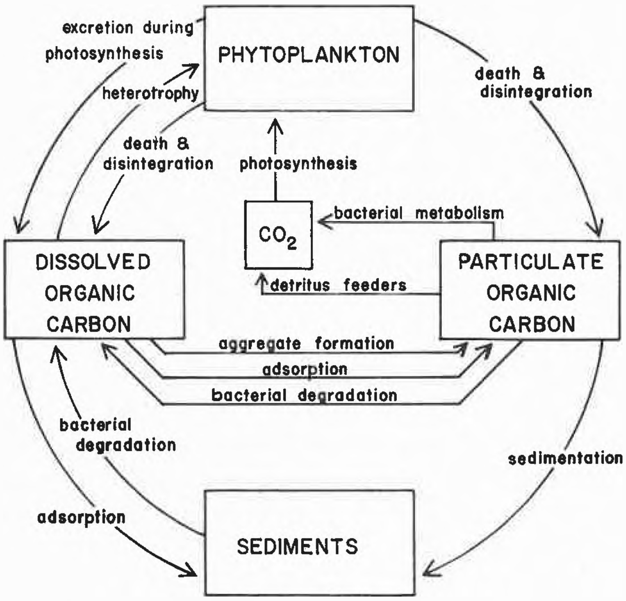

Fig. 2. Organic carbon cycle in sea water, new version

Future work

The details of the mechanisms involved in all of these pathways certainly need further investigation; we know almost nothing of the nature of the compounds involved, or of their distribution in sea water. Newer techniques, such as gas chromatography and mass spectrometry, may enable us to identify and measure compounds even at the low concentrations characteristic of sea water. More important, however, is the study of the kinetics of these reactions. In the past, this study has been considered to be entirely a biological problem. It is becoming evident that physical and chemical equilibria take part in, and perhaps control, important steps in the degradation of organic compounds to CO_2. Understanding the mechanisms and kinetics of these pathways may permit us to predict how long a given pollutant will remain in the system, and whether it will tend to accumulate at any given step.

There is also a possibility that reactions leading to the synthesis of new compounds can take place at or above the sea surface, under the influence of ultraviolet light. Particles of sea salt thrown into the air by breaking waves and bursting bubbles usually contain an organic component. Those particles reaching the upper atmosphere are subjected to intense ultraviolet radiation, as well as increased concentrations of ozone and other reactive species. It would be remarkable if the organic materials were not altered by this stringent environment. Thus the compounds returning to the sea surface in rain may be quite different from those formed in the sea. The effect of these mechanisms on the lighter hydrocarbons and on other pollutants which normally stay in the surface layer must also be investigated.

The solution of problems of this sort calls for a different array of skills than those of the pure chemist. The problems cut across the boundaries of physics, chemistry, biology, and geology, usually involving several sub-fields in each discipline. While much can be done with research teams containing representatives of each of the disciplines involved, the statement of the problem and the synthesis of results are most likely to be carried out successfully by a single mind, rather than by the decision of a committee. If we hope to solve these problems, we must in the future search out and encourage those scientists willing and able to work in a variety of fields, in spite of the longer period of apprenticeship required. We must also change the course structure of our universities, in order to train these people properly, but that is another sermon.