# 2. THE INFLUENCE OF ORGANISMS ON THE COMPOSITION OF SEA-WATER

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## 1. Introduction

A number of components of sea-water enter into biochemical processes to such a degree that their concentrations are highly variable when compared to the total salinity. Whereas the distribution of the major constituents of sea-water are to be accounted for on physical and geochemical principles, additional considerations of a biological nature need to be taken into account where the biologically active components are concerned. Since the changes in such components may take place rapidly, relative to the life of a water mass, their study can illuminate the physical description of the sea.

The object of this chapter is to discuss the special considerations which are required for this purpose. They are of two sorts; the stoichiometric relations which arise from the specific composition of marine organisms, and the dynamic equilibria between biological and physical processes which determine the concentration of elements present at any point in the sea.

The influence of organisms on the composition of sea-water is determined by physiological influences and consequently exhibits the regularity inherent in organic processes. Elements are withdrawn from sea-water by the growth of marine plants in the proportions required to produce protoplasm of specific composition and are returned to it as excretions and decomposition products of an equally specific nature. While significant differences may occur in the requirements of different individuals and species, the statistical effects produced by the entire population present in any body of water have some regularity. Furthermore, ecological principles indicate that certain similarities will occur in populations of any sort when one considers the proportionate activity of the primary producers and of the predators, which occupy later positions in the food chain.

The dissolved components of sea-water are transported from place to place by advection and move from one parcel of water to another by eddy diffusion. These agencies act equally on all dissolved constituents of the water and their effects may be traced by measuring the concentrations of any one of the constituents, such as the chlorides. The biologically active constituents may move from one water layer to another in additional ways: namely, by the sinking of organized matter under the force of gravity and by the active vertical migration of organisms. Such movements of organic matter from one water layer to another provide a fractionating mechanism by means of which the difference in the distribution of conservative and nonconservative properties of sea-water may be explained.

Because of fractionation the biologically active elements circulate in a different pattern than does the water itself or its inactive solutes. We may speak of a biochemical circulation as distinct from, though dependent on, the physical circulation of the water. Since the elements required for the construction of protoplasm are drawn from the water in proportions which have some

uniformity, they are distributed in somewhat similar patterns by the bio-chemical circulation.

## 2. The Biochemical Cycle

The exchange of chemical elements between sea-water and the biomass is a cyclic process. The cycle may be broken down into two phases, synthesis and regeneration. Elements are withdrawn from the water during the synthetic phase by photosynthesis in the proportions required for the growth of the primary producers, which are predominantly the phytoplankton. These elements are ultimately returned to the water in the regenerative phase as the decomposition products and excretions of both the primary producers and the subsequent members of the food chain which prey upon them, including the microorganisms which complete the decomposition of organic debris.

Oxygen occupies a unique position in the biochemical cycle because this element is set free in the course of photosynthesis. The concentration of oxygen consequently increases in the water when synthesis takes place and this oxygen becomes quantitatively available for the subsequent oxidation of the products of this synthesis.

### A. *The Elementary Composition of Plankton*

The proportions in which the elements of sea-water enter into the bio-chemical cycle is determined by the elementary composition of the biomass. Since the plankton comprises the bulk of the biomass these proportions are indicated by the analysis of plankton samples. Earlier analyses of net plankton by Redfield (1934) were substantiated by more extensive data assembled by Fleming (1940) who obtained the atomic ratios for the principal elements present in the organic matter given in Table I. The elementary composition of the zoo-plankton and phytoplankton is very similar and the average ratios may be taken as representative of the biomass as a whole.

TABLE I

Atomic Ratios of the Principal Elements Present in Plankton

|  | C | N | P |
|---|---|---|---|
| Zooplankton | 103 | 16.5 | 1 |
| Phytoplankton | 108 | 15.5 | 1 |
| Average | 106 | 16 | 1 |

The oxygen set free in the synthesis or consumed in the decomposition of the biomass would be 212 atoms for each atom of phosphorus if the oxidation of carbon alone were considered. If, in addition, four atoms of oxygen are con-sumed in oxidizing each atom of nitrogen, the oxidative ratio for phosphorus,

$\Delta O/\Delta P$, is equal to $-276$. This appears to be the most appropriate estimate for general use.

These ratios provide a stoichiometric basis for evaluating the general proportions in which the major nutrients present in sea-water may be expected to change as the result of biological activity. The observed changes in the composition of sea-water in the ocean support this generalization. Their use depends on the assumption that the composition of the plankton is statistically constant. There are, however, a number of considerations which indicate that substantial departures may be found under special circumstances. Riley (1951; 1956a) has discussed the effects of the varying composition of the plankton with respect to lipoid content, skeletal material, etc. He considers that the oxidation of organic matter may lead to $\Delta O/\Delta P$ ratios which vary between $-250$ and $-300$ and that more extreme variations may be noted.

The species composition of the biomass is observably variable both in time and place, and each species may be expected to have a composition which differs somewhat from others (Vinogradov, 1953). The chemical composition of a given species may be expected to vary also with the general nutritional conditions under which it grows. For these reasons statistical uniformity in composition is probably approached only in large masses of water, where deviations of this sort are averaged out.

Analysis of plankton from Long Island Sound by Harris and Riley (1956) indicates that on the average phytoplankton contains nitrogen and phosphorus in the ratio of 16 : 1 atoms, in agreement with Fleming's value. The zooplankton in contrast yields an average N/P ratio of 24 : 1. The individual collections made at different times of year differ from the average by about 25%. In the case of the zooplankton the ratios have a seasonal trend, the higher values being obtained in winter and spring.

### a. Effect of nutrient deficiencies on composition

It has been demonstrated repeatedly in culture experiments that the elementary composition of unicellular algae can be varied by changing the composition of the medium in which they grow. If one element is markedly deficient in the medium, relative to its need by the organism, cell growth and cell division can proceed for a limited period of time. The cells produced under these conditions contain less of the deficient element than do normal cells. When an element is provided in excess in the medium, luxury consumption can increase its content in the cells. It has been shown with radiophosphorus that the excess is readily exchangeable with the medium (Goldberg et al., 1951; Rice, 1953).

The data in Table II illustrate the extremes in phosphorus : carbon : nitrogen ratios which can be produced when deficiencies in phosphorus and nitrogen develop in culture experiments. Perhaps because of the composition of the culture medium, the normal cells contained more than twice as much phosphorus as is observed in phytoplankton populations growing in the marine environment. Deficiency of phosphorus in the medium reduced the ratio of

TABLE II

Experimental Variation of the C : N : P Ratios (by Atoms) in Cultures of the
Freshwater Alga, *Chlorella pyrenoidosa* (after data of
Ketchum and Redfield, 1949)

| Conditions | C | N | P |
|---|---|---|---|
| Normal cells | 47 | 5.6 | 1 |
| Phosphorus deficient cells | 231 | 30.9 | 1 |
| Nitrogen deficient cells | 75 | 2.9 | 1 |

phosphorus to carbon in the cells to about one-fifth and the deficiency of
nitrogen in the medium reduced the ratio of nitrogen to carbon to about one-
fourth of that of the normal cells. Relative to the phosphorus content the nitro-
gen content of the cells could be varied experimentally thirteen-fold.

In natural waters the concentrations of available nitrogen and phosphorus
are greatly reduced during periods of active growth. One or other element
may be almost absent while an excess of the other may remain in the water.
In Long Island Sound, nitrogen appears to be the element available in minimum
proportions relative to the needs of the phytoplankton and its ratio to phos-
phorus varies from nearly zero to about 8 : 1 (Riley and Conover, 1956). The
ratio of nitrogen to phosphorus in the plankton was found by Harris and Riley
(1956) to average 16.7 : 1 with relatively small variations. Similarly, in the
coastal waters south of Long Island the ratio of nitrogen to phosphorus is
lower than that of the requirement of normal plankton. In spite of the ano-
malously low ratio of nitrogen to phosphorus in the water, the plants apparently
assimilate these elements in the normal ratio of 15 atoms to 1 until very low
concentrations are reached (see Fig. 1). However, when the nitrogen is nearly
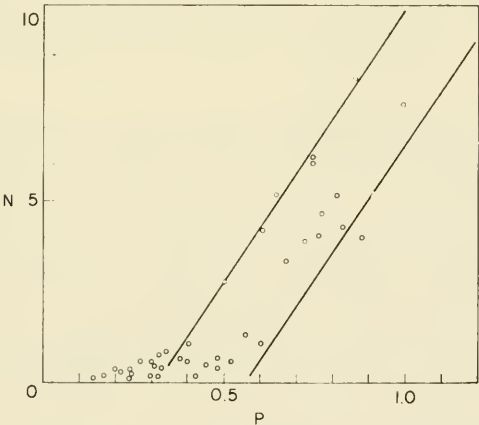depleted from the water the phytoplankton cells can apparently continue to



Fig. 1. Concentration of phosphate phosphorus and nitrate nitrogen in coastal waters
south of Long Island. Units: mg atoms/m$^3$. Slope of envelopes, $\Delta N/\Delta P = 15$. (After
Ketchum *et al.*, 1958.)

assimilate phosphorus, which is then present in excessive proportions in the water.

The ability of phytoplankton to continue to form cells of normal elementary composition, when growing in the sub-surface layers of the sea from which one essential nutrient is practically exhausted, may be explained by the consideration that mixing processes supply nutrients from deeper layers. Eddy diffusion may deliver nitrogen and phosphorus to the euphotic zone in a higher ratio than actually occurs in this layer, as Ketchum, Vaccaro and Corwin (1958) have pointed out. The decomposition of cells *in situ* will also regenerate nitrogen and phosphorus in the higher ratio characteristic of their composition. Under steady-state conditions the net growth of the population is frequently limited by the rate of diffusion of nutrients into the zone of active growth where the phytoplankton assimilates the elements as fast as they are supplied. The nutrients present in the water represent merely the residue of elements supplied which are not required to form cells of normal composition.

Thus, while culture experiments readily show the effects of nutrient deficiencies in the medium on the composition of the organisms, it is by no means certain that such deficiencies are developed by natural populations.

## B. *The Changes in the Nutrient Content of Sea-Water Produced by Biological Activity*

The principal sources of the major elementary components of marine organisms are the carbonate, phosphate and nitrate ions of sea-water. The synthetic process by which these nutrients are removed from the water is limited to the sub-surface layers of the sea into which adequate light may penetrate. The regenerative processes being independent of light may take place at any depth. Owing to the sinking of organized matter under the force of gravity and the vertical migrations of organisms, significant quantities of organic matter are carried downward to decompose at depth. Consequently the cycle does not run to completion in the euphotic zone, where synthesis exceeds regeneration sufficiently to produce the organic matter which decomposes at depth.

The result is a distribution of the biologically active elements in sea-water which is distinct from that of the major salts which results from purely physical motions. The nutrient elements are not only withdrawn from the euphotic zone in quantities sufficient to form the biomass locally present, but are also transported to depth where the water is enriched by the regenerative process. The distribution of oxygen is affected in a converse way. The excess synthesis in the sub-surface layer produces oxygen which causes this layer to be supersaturated, while the regeneration at depth reduces the oxygen content of the water in proportion. The transition level where synthesis balances regeneration is marked by the compensation point where the sea-water is exactly saturated with oxygen.

If the differences in the concentration of nutrient elements which are found at different depths in the ocean are due to the decomposition of organic matter

synthesized near the surface, these differences should not only reflect the quantities of organic matter which have decomposed but also the proportions of the elements present in the plankton from which it has been derived. The latter expectation is confirmed by the data presented in Figs. 2 and 3, in which
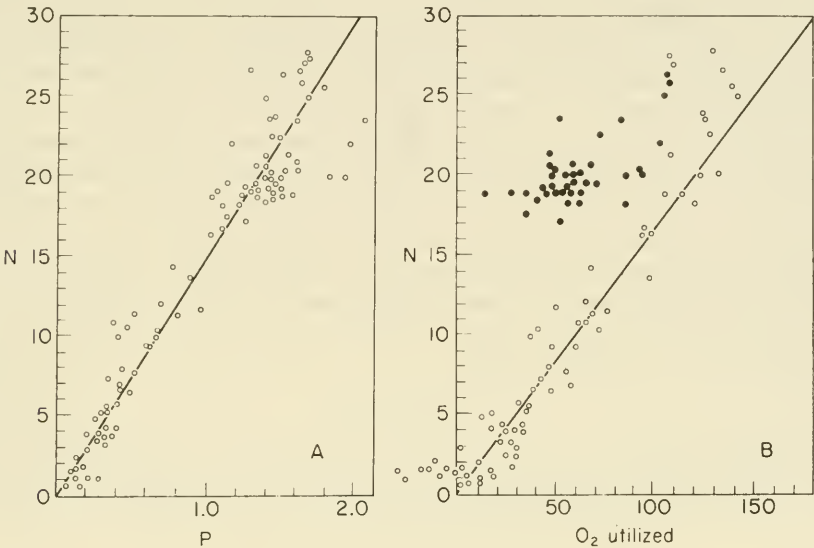


Fig. 2. A. Correlation between nitrate nitrogen and phosphate phosphorus in waters of western Atlantic. B. Correlation between nitrate nitrogen and apparent oxygen utilization in same samples. Open circles represent samples from above 1000 m.
    Concentrations in mg atoms/m$^3$. Phosphorus corrected for salt error. (After Redfield, 1934.)
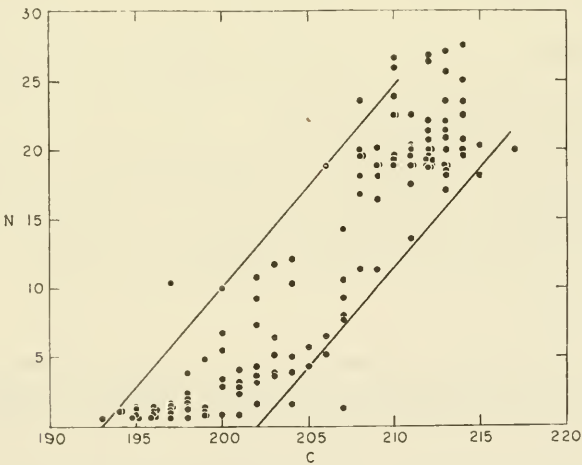


Fig. 3. Correlation between nitrate nitrogen and carbonate carbon in waters of western Atlantic. Concentrations in mg atoms/m$^3$. (After Redfield, 1934.)

each point represents the concentrations of a pair of elements determined from a single sample of sea-water collected at varying depth in the western North Atlantic. In general the low values represent samples from small depths and the high values from greater depths. The slope of the line drawn through the points gives the ratio of the difference in concentration of the elements in question. These differences are assumed to be due to differences in the quantities of organic matter of uniform composition which have decomposed in the different samples. The ratios may be combined to give the relative proportions of the several elements in question in the decomposed material.

Table III gives these ratios as determined from the analysis of sea-water and from analyses of plankton collections. The agreement so far as phosphorus, nitrogen and carbon are concerned leaves little doubt that the changes in concentration at depth arise mainly from the decomposition of plankton and that the ratios are sufficiently precise to be useful in the analysis of oceanographic problems. Similar treatment of data from the Pacific, Indian and South Atlantic Oceans and the Barents Sea shows that the ratio $\Delta N/\Delta P = 15$ applies in sea-water on a world-wide scale.

<div align="center">TABLE III</div>

Ratios of the Elements Involved in the Oxidation of Organic Matter in Sea-Water at Depth and Those Present in Plankton of Average Composition, by Atoms (after Richards and Vaccaro, 1956)

| Sea-water analyses | $\Delta O$ | $\Delta C$ | $\Delta N$ | $\Delta P$ | Ref. |
|---|---|---|---|---|---|
| Northwest Atlantic | −180 | 105 | 15 | 1 [a] | Redfield (1934) |
| Cariaco Trench, upper layers | −235 | — | 15 | 1 | Richards & Vaccaro (1956) |
| Plankton analyses | −276 [b] | 106 | 16 | 1 | Fleming (1940) |

[a] Corrected for salt error after Cooper (1938).
[b] Estimated assuming 2 atoms $O \backsim 1$ atom C and 4 atoms $O \backsim 1$ atom N.

It should be emphasized that these ratios do not represent the proportions in which the elements are available in sea-water, but rather the ratios of change in their concentration which result from biological activity.

## a. The oxidative ratio

The relation of the change in concentration of oxygen in sea-water, shown in Table III, to that of the nutrient elements does not agree well with the expectation raised by the statistical composition of plankton. This discrepancy requires examination.

Oxygen and carbon dioxide are exchanged with the atmosphere when sea-water is at the surface and their concentrations in water sinking to depth is

controlled by this exchange. In order to determine the quantity of oxygen which has disappeared from a sample of water collected at depth, it is necessary to estimate its oxygen content at the time it sank from the surface. The difference between the oxygen concentration of water in equilibrium with a normal atmosphere at the temperature and salinity observed *in situ* and the oxygen concentration as measured is referred to as the *apparent oxygen utilization*, or A.O.U. The conditions specified are met only approximately in nature.

Surface sea-water may be substantially supersaturated with oxygen under conditions favorable for growth, or may be undersaturated under the turbulent conditions obtaining in winter (Redfield, 1948). Some undersaturation is to be expected in high latitudes at the time when deep water is formed. Seasonal variations in atmospheric pressure may also influence the result (Carritt, 1954). Finally, because the saturation values for oxygen are not linear functions of temperature and salinity, the oxygen content of a mixture of sea-waters equilibrated under different conditions would be different from that calculated from the temperature and salinity of the mixture. These considerations introduce errors into the estimation of the utilization of oxygen and its ratio to the regeneration of nitrogen and phosphorus. Probably these errors are not greater than the analytical errors in the determination of phosphate phosphorus or nitrate nitrogen with which they are used, and are not large enough to account for the discrepancy in the ratio as estimated from analyses of plankton and of sea-water.

A more significant source of error in the estimation of oxidative ratios from sea-water analysis is the presence of nutrients in the water which have not been derived from the oxidation of organic matter. The deep water of the oceans is formed in high latitudes in winter where low light intensity restricts the growth of plants. Consequently on sinking it may contain substantial quantities of nutrients which are not in organic form. The presence of such preformed nitrate in the deep water is indicated in Fig. 2B, in which samples from great depth, indicated by solid circles, are seen to contain nitrate in much greater quantity relative to the utilization of oxygen than obtains in the upper 1000 m of water. Preformed nutrients are probably present in smaller quantities in these upper layers. Their presence causes estimates of the oxidative ratio to be too low and to be unreliable. Ratios obtained from the composition of plankton are not subject to this error and consequently are to be preferred.

The $\Delta O/\Delta P$ ratio of $-276$ will consequently be employed in the various estimates to be discussed. The use of ratios derived from sea-water in certain earlier studies (Redfield, 1942. 1948) led to estimates which require revision.

### b. Preformed nutrients and nutrients of oxidative origin

The nutrients present in a sample of sea-water may be separated into two fractions: (1) nutrients of oxidative origin which have been regenerated from organic matter, and (2) preformed nutrients which were present as such in the water at the time it sank from the surface. The quantity of a nutrient of oxidative origin may be estimated from the apparent oxygen utilization by applying

the $\Delta O/\Delta P$ ratio. The difference between this quantity and the total quantity of nutrient present in inorganic form gives the quantity of preformed nutrient present. In estimating the fraction of oxidative origin, it is convenient to note that a $\Delta O/\Delta P$ ratio of $-276$ corresponds closely to the production of 1 mg atom/m³ of phosphorus in the consumption of 3 ml $O_2/l$.

The distribution of these fractions of inorganic phosphorus at two stations in the North Atlantic is shown in Fig. 4. At the station in the subtropics (a)
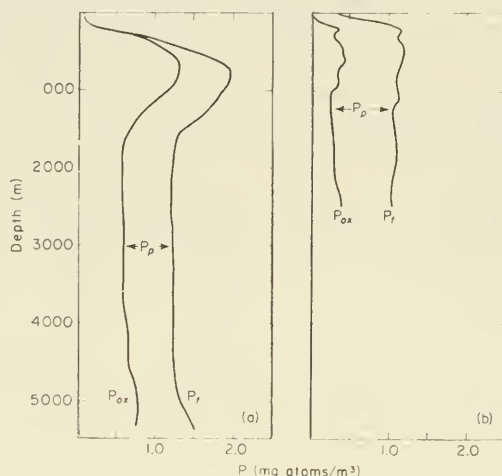


Fig. 4. Fractions of total phosphorus, $P_t$, present as phosphorus of oxidative origin, $P_{ox}$, and as preformed phosphorus, $P_p$, at stations in North Atlantic.

(a) *Crawford* Station 364; 16° 16′N, 54° 44′W.
(b) *Discovery* Station 3849; 55° 25′N, 33° 12′W.

more than half the phosphorus in the deep water is preformed and this fraction is present in practically the same concentration at all depths below 700 m. Above this depth the preformed phosphorus diminishes and is absent in the layers immediately below the surface. At the station in high latitude (b) about three-quarters of the total phosphorus is present in the preformed fraction and it is only in the surface layer that its concentration is reduced by assimilation by the phytoplankton.

As defined, the preformed nutrient concentration is a conservative property, being uninfluenced by the oxidation of organic matter which was present in the water mass at the time of its sinking or which has accumulated in the water at depth. Its value depends on the degree to which conditions at the sea surface influence the synthetic processes at the time the water masses are formed. In contrast, the apparent oxygen utilization, or its equivalent in nutrient, provides a measure of the effect of biological activity on the composition of the water since it sank below the influence of the atmosphere.

The validity of the concept of preformed nutrients and the method of their estimation may be tested by examining the values in water masses which may

be recognized by their composition (see Table IV). In the deep water masses of the Atlantic. characteristic mean values for preformed phosphorus may be assigned which differentiate the North Atlantic deep water, the circumpolar water, and the Antarctic deep water. The dispersion of measurements for samples from each of these water masses is not greater than that of the measurement of inorganic phosphorus.

TABLE IV

Preformed Phosphorus Content ($P_p$) of Deep Water Masses of Atlantic Ocean (mg atoms/m³)

| Water mass | Criteria | No. samples | $P_p$ mean | Dispersion ($\sigma$) | |
|---|---|---|---|---|---|
| | | | | Individual estimate | Analytical method |
| North Atlantic deep water 59°N–34°S | $S$ 34.85–35.0‰ $T$ 2–4°C | 102 | 0.74 | ± 0.13 | ± 0.12 |
| Circumpolar water 24°S–69°S | $S < 34.75$‰ $T$ 0–1.99°C | 41 | 1.50 | ± 0.19 | ± 0.23 |
| Antarctic deep water 49°S–69°S | $S < 34.75$‰ $T < 0$°C | 26 | 1.67 | ± 0.13 | ± 0.23 |

## c. Regeneration of nutrients

It has been implicit in the foregoing discussion that the oxidation of organic matter has gone to completion in the deep water. This is not absolutely correct since the deep sea is inhabited by organisms and various organic residues may be detected in its waters. Intermediate products of decomposition may occur in significant quantities in places where organic matter is decaying in quantity, and their distribution in the sea provides useful information on the regenerative part of the biochemical cycle. Although a variety of organic materials may be detected in sea-water (Duursma, 1960). discussion will be limited to the few which have been sufficiently studied to provide insight into the regeneration of phosphate and the nitrogenous nutrients.

The phosphorus of organisms is present for the most part in organic combination, forming molecules many of which are known to be of great physiological importance. On decomposition such molecules are liberated into the water as dissolved substances. On the oxidation of these materials, presumably by bacterial action, the phosphorus is released as phosphate in the ionic form. The method traditionally employed on shipboard measures only the phosphorus which has been completely regenerated. i.e. that present as inorganic phosphate ions. Treatment of a sample with strong oxidizing agents decomposes the

organic matter completely, enabling the total phosphorus to be measured in ionic form. The difference yields the phosphorus present in organic combination. This fraction may be divided further by filtration into a portion present as particulate matter, including living microorganisms and debris, and a portion representing the phosphorus present in combination with dissolved organic molecules.

The total phosphorus content of a sample of sea-water may thus be separated into several fractions according to the following scheme:

| | |
|---|---|
| Total phosphorus ($P_t$) | Analysis after oxidation |
|    Inorganic phosphorus ($PO_4P$) | Direct analysis |
|       Phosphorus of oxidative origin | $P_{ox} = \text{A.O.U.}/276$ |
|       Preformed phosphorus | $P_p = PO_4P - P_{ox}$ |
|    Organic phosphorus | $P_t - PO_4P$ |
|       Dissolved organic phosphorus | $\Big\}$ Separated by filtration |
|       Particulate organic phosphorus | |

The phosphorus of oxidative origin is merely the apparent oxygen utilization expressed as its equivalent in regenerated phosphorus. This notation is advantageous in reducing all aspects of the phosphorus cycle to common terms. The methods for the determination of phosphate concentration in sea-water are not precise, being subject to errors as large as 10%. Consequently, estimates of the fractions are only approximate and frequently require statistical treatment.

In the process of regeneration, dissolved organic phosphorus represents an intermediate product in the liberation of phosphorus of oxidative origin from the particulate phosphorus of living cells and their debris. In Fig. 5 the distribution of phosphorus among these fractions at various depths and seasons at a
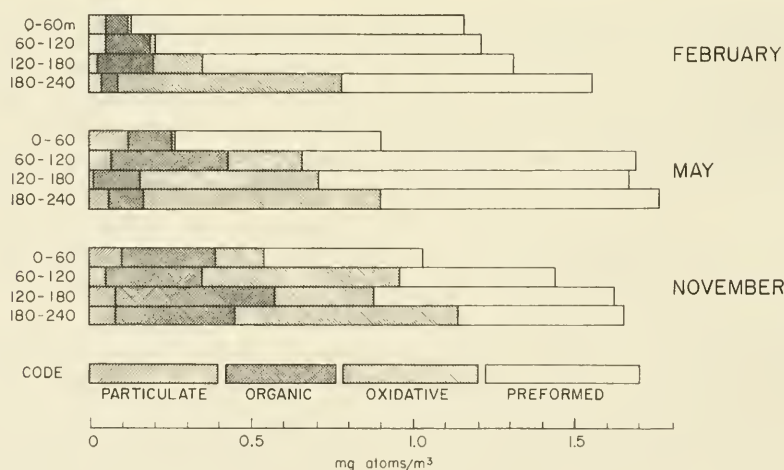


Fig. 5. Seasonal distribution of phosphorus fractions in Gulf of Maine. (From data of Redfield, Smith and Ketchum, 1937.)

station in the Gulf of Maine is shown. In spring, when active growth commences, most of the phosphorus is present in inorganic form; particulate phosphorus occurs chiefly in the photosynthetic zone (0–60 m) and very little dissolved organic phosphorus is present. During the summer and autumn the dissolved organic fraction becomes much greater and is distributed equally at all depths, providing evidence that phosphorus is carried downward by the sinking or migration of organisms. In winter the organic phosphorus decreases as the regeneration of inorganic phosphorus proceeds and in this form phosphorus is returned to the surface layer by the mixing of the water.

Measurements of the rate of phosphate regeneration in the laboratory indicate that up to one-half the total content of decomposing plankton appears in soluble form in the first day (Cooper, 1935; Seiwell and Seiwell, 1938). Vinogradov (1953) estimates that about half the nitrogen and phosphorus in algae is water-soluble. The remainder appears to exist in stable compounds that are decomposed after longer periods. These compounds appear in the water as the soluble organic fractions of phosphorus and nitrogen.

In the upper layers of the ocean, where organisms are decomposing in sufficient quantity, a substantial fraction of the phosphorus may be present in organic combination. Ketchum, Corwin and Keen (1955) found that nearly 50% of surface samples from the North Atlantic contained more than 0.25 mg atom/m$^3$ of dissolved organic phosphorus. As depth increases, however, the proportions of samples in which statistically significant quantities of organic phosphorus were present diminished and in waters deeper than 1000 m none could be detected with certainty.

Rakestraw (1947) found that when samples of water from the oxygen minimum layer and from greater depths were left in the dark at the *in situ* temperature for nearly two years the oxygen content did not change after the first 50 days of storage. During the initial period oxygen was consumed, but not in excess of a few per cent of the total content, so that evidently the fraction of oxidizable organic matter in the deep water is very small.

These two lines of evidence justify the assumption that, in the deep ocean, the oxidation of organic matter has gone so nearly to completion that the unoxidized residues may be ignored for many practical purposes.

The regeneration of nitrate in sea-water is somewhat more complicated than that of phosphate. Dissolved nitrogen compounds are present in sea-water, Robinson and Wirth (1934) having found some 23 mg atoms/m$^3$ of organic nitrogen in Puget Sound and 7 mg atoms/m$^3$ in the off-lying Pacific Ocean. Nitrogen is released from organic combination as ammonia and is subsequently oxidized to nitrite, and then to nitrate. The steps in this process have been followed in laboratory experiments by von Brand and Rakestraw (1941). These experiments showed the successive appearance and disappearance of the fractions as decomposition proceeded. It required three or four months for the regeneration of nitrate to be completed.

In the sea, ammonia and nitrite appear as intermediate products at times and places where organic matter is decomposing in quantity. Ammonia is the

first inorganic product in the regeneration of nitrate. In shallow coastal waters in temperate regions it is present in very small quantities at the end of winter, but increases as the season advances, and may become the principal form in which nitrogen is available in the water (Cooper, 1933). Under such conditions it may be absorbed directly by the phytoplankton without being oxidized to nitrite and nitrate (Harris, 1959). During the autumn and winter the ammonia decreases and nitrate becomes the major fraction of inorganic nitrogen in the water. In the deeper water of the Gulf of Maine ammonia appears in spring immediately below the photosynthetic zone and increases during the summer to occupy the entire water column (Redfield and Keys, 1938). In the deep sea ammonia does not ordinarily occur in significant quantities below the photo-synthetic zone, except in anoxic basins.

Nitrite appears to be more evanescent than ammonia. Both fractions tend to accumulate below the euphotic zone where regeneration may be assumed to be intense. Under these conditions its concentration is much smaller than that of ammonia. In oceanic waters a second zone of increased nitrite con-centration may be found at greater depths if oxygen is greatly reduced. This accumulation is attributed by Brandhorst (1959) to the reduction of nitrate by denitrifying bacteria.

Ammonia and nitrite are intermediate products of the nitrogen cycle which are present where organic matter is decomposing in quantity. In the deep sea where the increment of organic matter is small, relative to the rate of renewal of the water, the regeneration process runs nearly to completion and inorganic nitrogen is present almost entirely in the form of nitrate. Consequently, these intermediate products may frequently be neglected in examining the influence of organic activity on the chemistry of the deeper ocean waters.

There is some evidence that the regeneration of nitrate occurs more slowly than that of phosphate in shallow waters. This has been explained by the time required for bacteria to complete the several stages leading to the formation of nitrate (Atkins, 1926). It has also been observed that the maximum con-centration of nitrate in the nutrient-rich layers of the ocean occurs at a greater depth than does that of phosphorus. This fact has been attributed to the more rapid release of phosphorus from the plankton as it sinks. The matter is of interest in the present connection since it provides a mechanism by which nitrogen and phosphorus may be fractionated and thus may explain the variations in the ratios of these elements in sea-water.

Frequently the minimum concentration of oxygen at stations in the deep ocean does not coincide in depth with that of the maximum concentration of phosphorus or nitrogen. Such deviations may arise because of the presence of preformed nutrients in the water or because the initial oxygen content of the water at different depths has been different owing to its temperature at the time when it sank below the surface. It is only when such influences have been eliminated that departures may be interpreted as indicating differences in the composition of the organic materials being oxidized at different depths. Using procedures to which this stricture does not apply, Riley (1951) has

estimated the oxidative ratios for ocean water and has found them to vary substantially at different depths (see page 68). His investigations throw doubt on the strict application of the statistical composition of the plankton to estimations of the oxidative ratios of nitrogen and phosphorus at different depths in the sea.

### C. The Availability of Nutrient Elements in Sea-Water

In considering the chemical changes in sea-water produced by organic activity it is convenient to establish a norm from which variation in concentration can be measured. Table V has been prepared for this purpose. The norm for phosphorus is based on conditions observed in the deeper water of the Southern Ocean. Nitrogen is derived from this value employing the ratio of 15 : 1 proposed by Cooper (1937, 1938a) as a normal ratio from which anomalies may be measured. The carbon concentration is the value given by Sverdrup, Johnson and Fleming (1942) for water of 19‰ chlorinity and the oxygen saturation value corresponds to water of this chlorinity in equilibrium with the atmosphere at 2°C. Table V shows the ratios in which these elements are available in "average" sea-water and in which they are utilized by plankton in forming organic matter, and also the ratio of availability to utilization. A number of interesting generalizations may be developed from these estimates.

### a. Limiting factors

Liebig's law of the minimum implies that in the growth of a crop of plants, when other factors such as light and temperature are favorable, the nutrient available in smallest quantity relative to the requirement of the plant will limit the crop. The ratios presented in Table V define concretely the relation of availability of the several elements present in sea-water to their utilization. Nitrogen and phosphorus appear to occur in sea-water in just the proportions in which they are utilized by the plankton, a fact first noted by Harvey (1926)

TABLE V

Availability of Nutrient Elements in "Average" Sea-Water ($S = 34.7$‰, $T = 2$°C) and the Ratios of Their Availability and Utilization by Plankton

| | Availability in "average" sea-water | | Utilization by plankton | Ratio of availability to utilization |
|---|---|---|---|---|
| | mg atoms/m$^3$ | ratio | ratio | |
| Phosphorus | 2.3 | 1 | 1 | 1 |
| Nitrogen | 34.5 | 15 | 16 | 0.94 |
| Carbon | 2340 | 1017 | 106 | 9.6 |
| Oxygen saturation value | 735 | 320 | 276 | 1.16 |

who observed the simultaneous exhaustion of nitrate and phosphate in the waters of the English Channel during the growing season. Harvey's observations may be extended to the open ocean as shown in Fig. 2 and by other data reviewed by Redfield (1934).

In contrast, carbon is present in average sea-water in about ten times the quantity which can be utilized if growth is limited by the phosphorus or nitrogen available. This is illustrated in Fig. 3, which shows that the total carbonate in ocean water is reduced by only 10% with the exhaustion of the nitrate nitrogen. Clearly carbon does not become a limiting factor in the growth of marine plants in the sea. In a similar way small residues of phosphate or nitrate are frequently observed in surface waters from which the other nutrient has become exhausted by phytoplankton growth. This may be explained by small variations in the ratios in which these elements are available and are utilized by the population locally present. Thus, under the conditions specified in Table V, a residue of phosphorus amounting to 0.15 mg atom/m$^3$ would remain in the water after the complete exhaustion of nitrogen.

A number of elements known to be of biological importance, such as iron, manganese, copper, zinc, cobalt and molybdenum, are available in sea-water in very small concentrations and might act as limiting factors in the growth of phytoplankton. By adding these elements to samples of surface water from the Sargasso Sea, Menzel and Ryther (1961) have shown that the addition of iron will stimulate the growth of the native plankton when it has come to an end after the exhaustion of the nutrients naturally present. Additions of other trace elements did not produce this effect. In similar experiments with water from the English Channel, Harvey (1947) found that manganese might act as a limiting factor in the growth of *Chlamydomonas*. Similar effects due to the shortage of vitamins and other organic constituents are discussed in Chapters 8 and 9. While it is clear that iron and manganese, and perhaps other essential elements and compounds, are present in sea-water in critically small quantities and may, under local conditions, become limiting, the fact that nitrogen and phosphorus become exhausted so completely over wide areas of the surface waters of the ocean is evidence that their concentrations are in general the factors which control the quantity of phytoplankton produced.

### b. Potential fertility

Harvey (1947a) has proposed that the total phosphorus or total combined nitrogen in natural waters may be used to distinguish their potential fertility. The potential fertility may be defined as the quantity of organic matter which could be produced by photosynthesis from a unit volume of sea-water if it were brought from depth to the surface and illuminated there until the limiting nutrients were exhausted. Assuming the carbon of the organic matter to be 50% of its dry weight it would follow from the information in Table V that the nitrogen would be exhausted when there had been produced organic matter of dry weight equal to 5.48 g/m$^3$ and containing 2.74 g C/m$^3$. Assuming a

dry-weight/wet-weight ratio of 0.2, the wet weight of plankton would be 28 g in 1 million g of sea-water or about 1 part in 36,000.

This estimate serves to indicate the maximum standing crop that could occur on the average in the photic zone under ideally efficient conditions. Actually, the water becomes impoverished while it is at the surface by the sinking of organic matter so that for this and other reasons such crops are not to be expected. Ryther (1960) has estimated that the plankton of oceans as a whole contains 3 g/m² carbon. Assuming this to be concentrated in the upper 100 m. the wet weight of plankton in the water would be equivalent to about 1 part in 3 million. These estimates serve to emphasize the low concentrations at which organisms may be expected to occur in sea-water and the inefficiency with which the potential fertility of the oceans is realized.

## c.  Available oxygen

The concentration of free oxygen in the water at the sea surface is determined by the solubility of the gas when in equilibrium with the atmosphere. The solubility is influenced greatly by temperature and to a less degree by salinity. In water which has sunk below the euphotic zone, the dissolved oxygen is removed by the oxidation of organic matter. The oxygen content of the deep water of the oceans is consequently reduced in proportion to the quantity of nutrients which has been regenerated within it.

The composition of average sea-water, shown in Table V, indicates that such water when equilibrated with the atmosphere at a temperature of 2°C, which approximates that of the deep water of the oceans, will contain 735 mg atoms/m³ of oxygen. This is only 16% more than the quantity required to oxidize all of the organic matter that could be formed from the limiting amounts of phosphorus and nitrogen present.

The concentrations of phosphorus found in the waters of the Pacific and Indian Oceans are more than twice those of the North Atlantic. The effect of this fact on the demand which the oxidation of organic matter may make on the available oxygen content of the water is illustrated in Table VI. The upper part of this table shows the excess oxygen remaining after the oxidation of all the organic matter which could be formed from the limiting quantity of phosphorus present. It may be seen that, in the Atlantic, oxygen is available in large excess and the water would be 53% saturated after oxidation had gone to completion. In the North Pacific, in contrast, more oxygen would be required than is available and the deep water would become anoxic under the assumed conditions.

As a matter of fact, the oxygen of the deep oceanic water is not as completely utilized as these estimates indicate. The reason is that only a part of the nutrients available in the surface waters of high latitudes, where these water masses are formed, is used to form organic matter at the time when the water sinks. The residue of preformed nutrients does not contribute to the utilization of oxygen. In the lower part of Table VI allowance has been made for the preformed phosphorus present in estimating the equivalent oxygen utilization. It

TABLE VI

Comparison of the Excess Oxygen Available in Deep Water of the Oceans
(mg atoms/m$^3$)

| | | North Atlantic | North Pacific |
|---|---|---|---|
| Phosphorus | $PO_4P$ | 1.25 | 3.00 |
| Equivalent $O_2$ utilization | $276 \times PO_4P$ | 345 | 828 |
| $O_2$ saturation value | 100% $O_2$ | 735 | 735 |
| Excess $O_2$ | 100% $O_2 - 276 \times PO_4P$ | 390 | −93 |
| $O_2$ saturation | | 53% | −13% |
| Preformed phosphorus | $P_p$ | 0.75 | 1.50 |
| P of oxidative origin | $P_{ox} = PO_4P - P_p$ | 0.50 | 1.50 |
| Equivalent $O_2$ utilization | $276 \times P_{ox}$ | 138 | 414 |
| Excess $O_2$ | 100% $O_2 - 276 \times P_{ox}$ | 597 | 321 |
| $O_2$ saturation | | 81% | 44% |

may be seen that with this allowance the deep water of the North Atlantic should contain 81% of its original oxygen content and the Pacific about 44%. These estimates approximate the magnitudes actually observed.

These estimates only take account of the oxidation of organic matter which is carried to depth with the movement of the water. Organic matter which sinks from the euphotic zone to depth before decomposing creates an additional demand on the oxygen supply. This effect is important at intermediate depths and contributes to the formation of the oxygen minimum layer. In the Pacific large areas exist at such depths where the oxygen is very nearly exhausted.

The margin of safety against the development of anoxic conditions in the deep ocean is not large. It depends on the limited quantities of nutrients present in ocean water and the incomplete absorption of these elements from the water during its circulation through the euphotic zone.

### D. Anoxic Conditions

Where the accumulation of organic matter is great, the oxygen dissolved in the water becomes completely exhausted, leading to a condition variously designated as anaerobic, anaeric or anoxic. Under this condition, the oxidation of organic matter continues by means of anaerobic bacterial processes in which sulfate, nitrate, nitrite and carbon dioxide serve as hydrogen acceptors. The reduced products of these substances accumulate in the water in addition to the products of the oxidation of the organic matter. The result is to modify the proportions of the components of the water in ways which differ from those characteristic of regeneration in the presence of free oxygen.
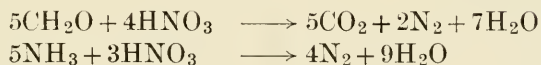
The principal reactions taking place in the presence and in the absence of oxygen may be formally represented by the following equations, in which

$CH_2O$ represents the carbon compounds of the organic matter and $NH_3$ the nitrogen liberated by its oxidation.

Oxidation by oxygen:
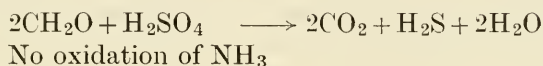
$$CH_2O + O_2 \longrightarrow CO_2 + H_2O$$
$$NH_3 + 2O_2 \longrightarrow HNO_3 + H_2O$$

Denitrification:

$$5CH_2O + 4HNO_3 \longrightarrow 5CO_2 + 2N_2 + 7H_2O$$
$$5NH_3 + 3HNO_3 \longrightarrow 4N_2 + 9H_2O$$

Sulfate reduction:

$$2CH_2O + H_2SO_4 \longrightarrow 2CO_2 + H_2S + 2H_2O$$
No oxidation of $NH_3$

The order and extent to which these steps proceed depends on the free energy available from the respective reactions and on the concentration of the reactants. The free energy decreases in the order oxygen > nitrate > sulfate > carbonate when these serve as hydrogen acceptors (McKinney and Conway, 1957). Consequently, oxygen should be utilized first if it is available. With the exhaustion of oxygen, the oxidation of organic matter should continue by the reduction of the nitrate produced while oxygen was available. Following the exhaustion of the nitrate, oxidation continues by the reduction of sulfate. The free energy available from sulfate reduction is apparently insufficient to oxidize $NH_3$ and, consequently, this product should accumulate during sulfate reduction. Thus the oxidation of organic matter may be expected to proceed in three stages—oxidation by free oxygen, denitrification and sulfate reduction—separated by the exhaustion of free oxygen and of nitrate. In nature, these stages may overlap to some extent. Nitrite is produced and should be present as an intermediate product both of the formation of $NO_3$ and of its reduction.

The limiting concentrations of oxygen below which denitrification occurs in sea-water are not known. In fresh water nitrate reduction takes place only when the oxygen concentration falls below a few tenths of a milligram per liter, depending on the nitrate concentration (Langley, 1958). Relatively large concentrations of nitrite (up to 2.5 mg atoms $N/m^3$) occur below the thermocline in parts of the Pacific where the oxygen is depleted, but only if the oxygen concentration is less than 1.0 ml/l. The presence of nitrite in these places is attributed to the reduction of nitrates as the initial step in denitrification (Brandhorst, 1959).

Free nitrogen appears to be the final product of denitrification. In the Black Sea, the concentrations of gaseous nitrogen increase with depth and supersaturation occurs in the deeper water (Kriss, 1949). In the anoxic water of the Cariaco trench and of the Dramsfjord, Richards and Benson (1961) have examined the accumulation of free nitrogen in excess of that expected from its solubility by comparing the observed nitrogen/argon ratios with those in sea-water equilibrated with air. The excess quantities of nitrogen found correspond

approximately with the amounts estimated to be produced by the decomposition of organic matter as indicated by changes in the oxygen, sulfide and phosphorus content of the water. They found that nitrate and nitrite were present in mere traces in, or were absent from, these anoxic waters. Ammonia, on the other hand, was present and varied in concentration in proportion to the accumulation of sulfides. This observation indicates that sulfate does not act as a hydrogen acceptor in oxidizing the ammonia liberated from organic matter during sulfate reduction.

The most conspicuous change in the composition of sea-water produced under anoxic conditions is the appearance of hydrogen sulfide. The principal source of sulfide sulfur in marine waters is the reduction of sulfates rather than the sulfur of decomposing organic matter. In the Cariaco Trench, the presence of 24 mg atoms/m³ of sulfide sulfur is accompanied by an accumulation of only one-tenth this amount of phosphate phosphorus. If both elements had been derived from the decomposition of plankton, its organic matter must have contained ten times as much sulfur as phosphorus. Data on the sulfur content of plankton are lacking, but in the flesh of fish the sulfur present is somewhat less than the phosphorus (Vinogradov, 1953). Consequently, it is unlikely that much of the sulfide has been derived from the sulfur content of decomposing organisms.

Data from the Black Sea demonstrate in a more positive way that sulfate is the source of the sulfide present in this anoxic basin. Skopintsev (1957) and Skopintsev *et al.* (1958) have found that as the sulfide concentration increases with depth, the ratio of sulfate to chlorinity decreases, indicating that sulfate
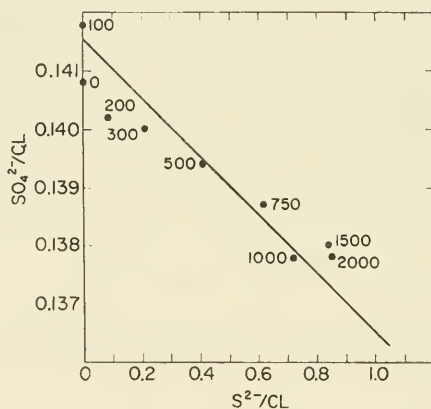


Fig. 6. Relation of sulfide/chloride and sulfate/chloride ratios in waters of the Black Sea. Numbers indicate depths of samples. Slope of line corresponds to $\Delta S^{2-}/\Delta SO_4^{2-} = -1.0$. (From data of Skopintsev *et al.*, 1958.)

has disappeared from the water. Fig. 6 shows that these changes occur in approximately the ratio required if one sulfide ion is formed from each sulfate ion which disappears. By taking the accumulation of phosphorus as an index of the quantity of organic matter which has been oxidized in the water of the

Cariaco Trench and Black Sea, Richards and Vaccaro (1956) have shown that organic decomposition proceeds in proportion to the apparent oxygen utilization until the supply of oxygen is exhausted. After this, the phosphorus continues to increase at a rate which indicates that in its regeneration each sulfide ion is equivalent to approximately four oxygen atoms in accordance with the stoichiometry of the equation for sulfate reduction.

The reduction of carbon dioxide to methane is well known to occur under anoxic conditions in freshwater systems, where it gives rise to the production of marsh gas. We know of no direct evidence that this takes place in sea-water. Perhaps this is because sulfate is present in sea-water in excess of the amounts required for the oxidation of the organic matter.

Carbon dioxide is produced by the oxidation of organic matter by any of the hydrogen acceptors. Because the accumulation of organic matter is greater in anoxic basins, its decomposition produces larger changes in the total concentration than is usual in ocean waters. In the Black Sea, the total carbon present as $HCO_3^-$ and $CO_3^{2-}$ increases from 3275 mg atoms/m³ in the surface water to 4263 mg atoms/m³ at a depth of 2000 m (see Fig. 7). This is an increase of 30%.
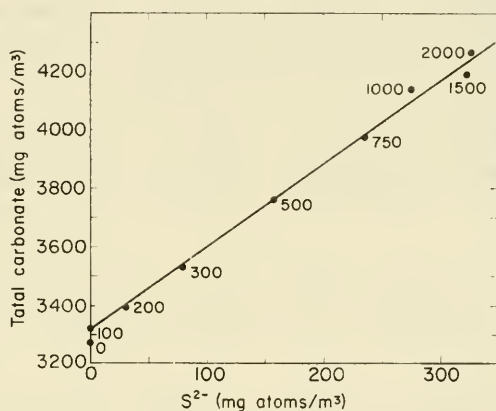


Fig. 7. Relation of sulfide sulfur and total carbonate carbon in waters of the Black Sea. Numbers indicate depth of samples. Slope of line corresponds to $\Delta S^{2-}/\Delta C = 0.36$. (From data of Skopintsev *et al.*, 1958.)

In contrast, the oxidation of organic matter in the depths of oceanic waters increases the total carbonate by only 10%. It follows that the quantity of organic matter which has decomposed in the deep water of the Black Sea is about three times that characteristic of the open ocean basins.

The change in total carbonate carbon with increasing depth is proportional to the change in sulfide content and proceeds in the ratio $\Delta S/\Delta C = 0.36$ (see Fig. 7). This is somewhat less than the ratio of 0.5 given by the equation for sulfate reduction.

When separate components are considered, the changes in chemical composition of sea-water in anoxic basins thus appear to proceed in about the proportions required by the equations shown on page 43. If it is assumed that

decomposed organic matter liberates phosphorus and carbon in the ratio of 1 to 106, the expected ratios of the simultaneous changes in the several components during each step may be estimated from these equations to be as shown in Table VII.

TABLE VII

Ratio of Change in the Atomic Concentration of Products of Decomposition of Organic Matter in the Presence of Oxygen and Under Anoxic Conditions

|  | $\Delta O$ | $\Delta CO_2$-C | $\Delta NO_3$-N | $\Delta N_2$-N | $\Delta NH_3$-N | $\Delta S^{3-}$ | $\Delta P$ |
|---|---|---|---|---|---|---|---|
| *Oxygen present* | $-276$ | 106 | 16 | 0 | 0 | 0 | 1 |
| *Oxygen absent* |  |  |  |  |  |  |  |
| Denitrification | 0 | 106 | $-70.7$ | 86.7 | 0 | 0 | 1 |
| Sulfate reduction | 0 | 106 | 0 | 0 | 16 | 53 | 1 |

By employing these ratios, the changes in concentration of the products of decomposition during the successive stages may be computed and the results shown as a function of the increasing phosphate phosphorus concentrations, as in Fig. 8. It is necessary to know only the initial concentration of oxygen in the water to obtain quantitative values applicable to any natural situation. Such diagrams are not very exact in respect to the products of denitrification because the separate stages probably overlap, and the completeness of the reactions involving these fractions is not understood. The presence of nitrite as
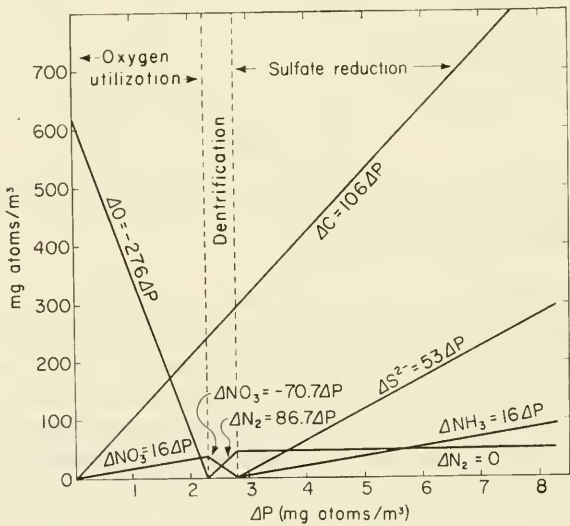


Fig. 8. Simultaneous changes in concentration of products of decomposition of organic matter under oxic and anoxic conditions. Calculated assuming initial oxygen content of 615 mg atoms/m³, appropriate to surface water of Black Sea.

an intermediate product and the possibility that preformed nitrate undergoes denitrification are also neglected.

In Table VIII, the concentrations of various products of decomposition observed in the deep water of the Black Sea and of the Cariaco Trench are compared with the concentrations calculated in this way. The agreement is sufficiently good to indicate that the conditions observed in anoxic basins have resulted in the main from the processes defined by the equations and that the quantitative relations depend on the elementary composition of the plankton.

TABLE VIII

Comparison of Observed and Calculated Values for Concentration of Products of Decomposition in Anoxic Basins, mg atoms/m³

| | Black Sea 750 m | | Cariaco Trench 915 m | |
|---|---|---|---|---|
| Depth | 750 m | | 915 m | |
| Oxygen at surface | 615 | | 471 | |
| Concentrations at depth | Observed | Calcd. | Observed | Calcd. |
| $PO_4$-P | 7.08 | — | 2.42 | — |
| $CO_3$-C | 696[a] | 750 | — | 257 |
| $NO_3$-N | — | 0 | — | 0 |
| $N_2$-N | 44 | 43.8 | 18.6[a] | 33.6 |
| $NH_3$-N | 52.8 | 69.4 | 10.6 | 5.1 |
| $S^{2-}$-S | 235 | 230 | 20.4 | 17.0 |

[a] Corrected for preformed carbonate and nitrogen of surface water.

Data from Danil'chenco and Chigirin (1929, 1929a), Skopintsev et al. (1958), Richards and Vaccaro (1956) and Richards and Benson (1961).

Sulfate is one of the major constituents of sea-water and is present in quantities sufficient to oxidize more than one hundred times the amount of organic matter than can be formed from the phosphorus and nitrogen available. The sulfate reduced under anoxic conditions in the Black Sea is less than 5% of the content of the surface water (see Fig. 6). Under natural conditions in marine waters, sulfate reduction is probably limited only by the amount of organic matter which accumulates. This need not be true of fresh waters in which the available sulfate is more readily exhausted.

The oxygen content of the atmosphere is thought to have been produced in large part by the photosynthetic reduction of carbon dioxide. It has recently been suggested that the reduction of sulfates in anoxic basins or in marine sediments may have contributed substantially in making oxygen available to the atmosphere (Redfield, 1958). The supposition is that sulfides produced in the process of sulfate reduction have been entrapped in the sediments and that the carbon dioxide released at the same time remained in solution and, on ultimate reduction by photosynthesis, supplied oxygen to the atmosphere.

The composition of sedimentary rocks indicates that quantities of oxygen equivalent to those now present in the atmosphere may have been liberated in this way. Since this process would operate only to the extent that the supply of oxygen was inadequate, it may have served to regulate the composition of the atmosphere.

### E. Silicon in the Biochemical Cycle

As a nutrient silicate silicon differs from the inorganic compounds of nitrogen and phosphorus in not being a universal requirement of living matter. It is present, however, in large quantities in the tests of diatoms, which dominate the phytoplankton in the cooler ocean waters. Analyses of diatoms show Si/P ratios varying between 16 and 50, depending on the species (Vinogradov, 1953). Silicon is transported from the surface to the depths by the sinking of these organisms and is liberated there in the course of regeneration.

Studies on the seasonal changes in nutrient concentrations in the water of the English Channel show that the silicate cycle corresponds in many ways with the cycle of phosphorus; silicate and phosphate being depleted or re-generated simultaneously (Atkins, 1930).

The relationship of the distribution of silicate to other elements involved in the biochemical cycle is less obvious in the open oceans than in locally restricted waters. However, Richards (1958) has demonstrated a linear relationship in the simultaneous changes in the concentration of silicate silicon, inorganic phosphate and nitrate nitrogen in much of the water column at stations in the Western Atlantic. The ratios of change were approximately $\Delta O : \Delta Si : \Delta N : \Delta P = -272 : 15 : 16 : 1$. In these waters, silicon appears to enter the biochemical cycle in about the same proportions as nitrogen.

In the oceans, in general, the concentrations of silicate vary greatly in their proportion to the phosphate and nitrate present. Such variation arises from the fact that in different parts of the oceans the proportions of diatoms to other phytoplankton, which does not require silicon, differ greatly. Consequently, the statistical composition of the plankton is variable in respect to silicon. Moreover, the solution of silicate from the diatom tests may be expected to follow a different course from the regeneration of nitrogen and phosphorus, which is related more directly to the oxidation of the organic matter. Consequently, the silicate may be set free at different depths than are nitrate and phosphate. Finally, animals which feed on phytoplankton have no use for silicon. The tests of diatoms will be rejected and will tend to sink to dissolve at depth while nitrogen and phosphorus will be retained by the animal and be regenerated from its excretions and decomposition products in the upper layers of water.

For these reasons, the fractionation of silicate by biological action probably follows a different course from that of the other nutrients. A better analysis of the factors responsible for the distribution of silicate in the oceans might add greatly to our understanding of the biochemical circulation.

### 3. The Biochemical Circulation

The selective absorption of certain elements by organisms, combined with the movement of organized matter from one layer of water to another by sinking or active migration, provides a mechanism for the fractionation of the components of sea-water and the redistribution of these elements in characteristic patterns. The circulation of nonconservative elements and the resulting pattern of their distribution depends on biological as well as hydrographic processes and they thus differ in detail from that of water and its inert solutes.

The concentration of a conservative element at any point in the sea is determined by a dynamic equilibrium between the effects of eddy diffusion and advection. In the case of nonconservative elements the effects of biological processes on the equilibrium must also be taken into account. The theory of this interaction, as developed by Sverdrup (1938), is essentially as follows.

Consider the water in a unit cube of space within the sea in which the concentration of some nonconservative property is denoted by $N$. The value of $N$ is subject to change by biological processes, such as the assimilation or regeneration of nutrients, the consumption of oxygen, etc., which change $N$ at a rate denoted by $R$. In addition, $N$ will be altered by interchange of water with adjacent cubes if they contain water with different concentrations of $N$. These interchanges are of two sorts, eddy diffusion and advection.

If the interchanges along the $x$-axis are considered, the effect of eddy diffusion on the values of $N$ is given by $(A_x/\rho)\,\partial^2 N/\partial x^2$ in which $A_x$ is the coefficient of diffusion in the $x$-axis and $\rho$ is the specific gravity of sea-water. The effect of advection is given by $V_x \cdot \partial N/\partial x$, in which $V_x$ is the component of current velocity in the direction $x$. Similar expressions define the effect of water movement in the $y$- and $z$-axes, and the complete expression is

$$\frac{\partial N}{\partial t} = R + \frac{A_x}{\rho}\cdot\frac{\partial^2 N}{\partial x^2} + \frac{A_y}{\rho}\cdot\frac{\partial^2 N}{\partial y^2} + \frac{A_z}{\rho}\cdot\frac{\partial^2 N}{\partial z^2} - V_x\cdot\frac{\partial N}{\partial x} - V_y\cdot\frac{\partial N}{\partial y} - V_z\cdot\frac{\partial N}{\partial z}. \tag{1}$$

In its complete form the equation is too complicated to be readily usable. With various assumptions it may be simplified and applied to the analysis of oceanographic observations. Since oceanographic data commonly consist of measurements at discrete points, practical application is most easily made by expressing the relations in terms of Eulerian equations in finite difference form. The papers of Riley (1951, 1956, 1956a) may be consulted for a discussion of its application.

The utility of equations for the dynamic equilibrium affecting the concentration of nonconservative properties is of three sorts. When the physical terms can be evaluated the expression may be used to determine the rates of the biological processes expressed by $R$. Conversely, if the value of $R$ can be evaluated from biological data, information on the physical terms may be obtained. When, as is often the case, data are insufficiently numerous or precise to enable quantitative estimates to be obtained, the equations provide a guide to the intuitive reasoning with which observed conditions are interpreted.

The dynamic equilibria obtaining in a series of situations of increasing complexity will be discussed and illustrated in the following pages. These will be (1) cases in one dimension in which the distribution of nonconservative elements results from a balance between the effects of biological activity and vertical diffusion; (2) cases in two dimensions in which advective motion in one horizontal direction must also be considered; and (3) cases in which motion in all three dimensions is taken into account.

### A. Vertical Exchange under Steady-State Conditions

In many situations, the effect of horizontal motions on the composition of sea-water is negligible. This is obviously true where the boundaries of a basin prevent substantial advection, as in an enclosed basin. It happens frequently that conditions are uniform over great horizontal distances, or that the horizontal velocities are very small, in either of which case the influence of advection is small and may be disregarded. If, in addition, conditions do not change with the season so that a steady state exists, in which $\partial N/\partial t = 0$, the dynamic balance on which the distribution of nonconservative elements depends is reduced to the terms defining the rate of change in concentration due to the sinking and regeneration of organic matter, and that due to the vertical diffusion of the regenerated elements toward the surface.

#### a. Stagnant basins

Deep basins in which shallow sills limit the horizontal circulation to a layer near the surface provide the simplest and the most extreme cases of the accumulation of nonconservative elements under the influence of the vertical circulation.

The Cariaco Trench, described by Richards and Vaccaro (1956), is an example of such a basin. It is a depression about 1400 m deep in the continental shelf off Venezuela. The water of the Caribbean flows freely across this depression down to the sill depth at 150 m and is not obviously influenced by the conditions within the depression. Below 250 m the temperature and salinity are nearly uniform and show that the water is isolated from the Caribbean water of comparable depths and can exchange with its surroundings only by eddy diffusion in the vertical across the transition zone separating it from the water above sill depth. In the depths of the Cariaco Trench the total phosphorus concentration is 2.6 mg atoms/m³; at sill depth it is 1.4 mg atoms/m³. Consequently 1.2 mg atoms/m³ have accumulated in the deep water. Water at sill depth, if carried downward by eddy diffusion, would contain only enough oxygen to produce 0.4 mg atom/m³ phosphorus of oxidative origin. Consequently the oxygen has been completely exhausted by oxidation of the excess of organic matter settling from the surface layer. The remaining organic matter has been oxidized by oxygen derived from the reduction of nitrate and sulfate as discussed on page 43.

The accumulation of phosphorus in the depths of the basin may be considered to result from a balance between the gains from the regeneration of

phosphate from sinking organic matter and the losses by eddy diffusion. The steady-state equilibrium may be expressed by

$$\frac{\partial Q_R}{\partial t} - A \cdot \frac{\partial N}{\partial z} = 0 \tag{2}$$

in which $\partial Q_R/\partial t$ is the rate at which the quantity of phosphorus in the water below unit area of the transition zone is increased by regeneration, $A$ is the coefficient of diffusion and $\partial N/\partial z$ is the gradient of phosphorus concentration in the transition zone.

Measurements of the assimilation of carbon in the euphotic zone over the Cariaco Trench indicate that 0.48 g C/m² is absorbed per day. This is equivalent to the production of organic matter containing $4.4 \times 10^{-10}$ mg atom/cm² of phosphorus each second. How much of this organic matter sinks below sill depth is unknown, but Riley (1951) estimates that in the sea only about one-tenth of photosynthetic production sinks to decompose at depths greater than 200 m. Consequently we may assume for purposes of illustration that $\partial Q_R/\partial t = 0.44 \times 10^{-10}$ mg atom/cm² sec. The hydrographic data obtained by Richards and Vaccaro show that at sill depth the gradient in total phosphorus concentration, $\partial N/\partial z$, is $0.75 \times 10^{-10}$ mg atom/cm³ cm. Applying these values to equation (2) the coefficient of eddy diffusion $A$ is found to be approximately 0.6 g/cm/sec. This estimate agrees well with values for intermediate depths in the Atlantic Ocean obtained by Riley (1956) by procedures to be discussed in the following section (Table XI).

This example illustrates how a physical characteristic of the motion of water may be evaluated by the use of biochemical information.

## b. The half-life period

Estimates of the average time a constituent of the water remains below sill depth in a stagnant basin may be made by dividing the content of the basin, $x$, by the rate at which the content is changed by some measured process, $dx/dt$. The time is appropriately expressed as the half-life period, $\tau$, which equals $0.693x/(dx/dt)$. The content of the basin is given by $N \cdot h$, where $N$ is the *mean* concentration of $N$ below sill depth and $h$ is the depth of water below this level. The content is changed at a rate given by $dQ_R/dt$ or by $A \cdot dN/dz$, which are equal according to equation (2). Consequently,

$$\tau_N = 0.693 \, \frac{N \cdot h}{dQ_R/dt} \quad \text{or} \quad 0.693 \, \frac{N \cdot h}{A \cdot dN/dt}.$$

In the case of the Cariaco Trench, $N = 2.4 \times 10^{-6}$ mg atom P/cm², $h = 1.2 \times 10^5$ cm and $dQ_R/dt = 0.44 \times 10^{-10}$ mg atom P/cm² sec. Consequently the half-life period of phosphorus below sill depth, $\tau_N$, is $0.45 \times 10^{10}$ sec or 142 years. This estimate is subject to error in the assumption that one-tenth of the organic matter produced in the euphotic zone sinks and decomposes below sill depth. As an expression of the average for all depths in the water column, it undoubtedly overestimates greatly the rate of exchange of materials in the

deeper layers of the basin. It serves to indicate, however, how very slowly exchange takes place in a stagnant basin of this sort.

It is evident that accumulation of a constituent of sea-water can occur locally only if the constituent circulates through the region more slowly than does the water. If the constituent circulated at the same rate as the water, there would be no change in its concentration. This consideration is overlooked when estimates of the exchange of water are based on the accumulation of nonconservative elements.

The principle involved may be illustrated by a simplified model of a stagnant basin in which a sharp transition zone at sill depth separates an upper layer of water containing a nonconservative element in the concentration $N_U$ from the stagnant lower layer having a concentration $N_L$. The process of eddy diffusion is equivalent to the movement of equal quantities of water upward and downward, each carrying with it quantities of the nonconservative element in proportion to its concentration in the layer from which it comes. If $dx/dt$ is the rate at which water is exchanged, $N_U\,dx/dt$ and $N_L\,dx/dt$ are the rates at which $N$ is transported downward and upward respectively and $(N_L - N_U)\,dx/dt$ is the rate at which $N$ is lost from the lower layer. Under steady-state conditions the fraction of $N$ lost from the lower layer in unit time is $(N_L - N_U)\,dx/N_L \cdot h$ while the fraction of water lost is $dx/h$. Consequently, the fraction of $N$ lost in unit time equals $(N_L - N_U)/N_L$ times the fraction of water lost. Since $(N_L - N_U)/N_L$ is less than one, the fraction of $N$ lost in unit time is less than the fraction of water lost. The half-life period, $\tau$, is inversely proportional to the fraction lost in unit time. Therefore,

$$\tau_{\text{water}} = \frac{N_L - N_U}{N_L} \cdot \tau_N.$$

In the case of the Cariaco Trench the concentration of phosphorus immediately above sill depth is 1.2 mg atoms/m³ while the mean concentration below sill depth is 2.4 mg atoms/m³. If these values be taken for $N_U$ and $N_L$ respectively, $(N_L - N_U)/N_L = 0.5$. $\tau_N$ has been estimated to be 142 years and consequently $\tau_{\text{water}}$ is 71 years. In other words, the water is circulating through the basin twice as fast as is phosphorus. The estimate is not precise because of the simplification of the model but serves to illustrate the principle that accumulation occurs when a constituent circulates through a region more slowly than does the water.

### c. The relation of stagnation to stability

Equation (2) implies that for a given rate of regeneration, and under steady-state conditions, the gradient in concentration, $dN/dz$, resulting from the accumulation of a nonconservative element at depth, will be inversely proportional to the coefficient of diffusivity, $A$. This coefficient in turn tends to vary inversely with the stability of the water column, and consequently the accumulation of the products of regeneration may be expected to be greater where strong density gradients are present.

Richards and Vacarro (1956) have investigated this relation in a number of basins, using the development of anoxia, shown by the concentration of hydrogen sulfide, as a criterion of the accumulation of products of organic decomposition. Table IX shows that the expected relation obtains between the stability of the water column at sill depth, the development of anoxic conditions, and the estimated age of the water in the basin.

TABLE IX

Comparison of Stability, Accumulation of Hydrogen Sulfide and Age in Stagnant Basins (after Richards and Vaccaro, 1956)

|  | Sill depth, m | Stability at sill depth, $\Delta\sigma_t/\mathrm{m}$ | $H_2S$-$S$, mg at/$m^3$ | Age estimate, years |
|---|---|---|---|---|
| Catalina Basin | 982 | $31 \times 10^{-5}$ | nil | — |
| Santa Monica Basin | 737 | 44 | nil | — |
| Santa Barbara Basin | 475 | 88 | nil | 2–20 |
| Kenoe Bay | 40–50 | 520 | 13.4 | — |
| Cariaco Trench | 146 | 440 | 30 | 100 |
| Black Sea | 40–50 | 3000 | 300 | 5600 |

### B. Seasonal Variation in Vertical Exchange

Under steady-state conditions the distribution of concentrations provides no information on the rates of the processes on which these concentrations depend. In the previous example a measurement of the rate of production of organic matter was used to introduce the factor of time into the calculations. The coefficient of diffusion could have served this purpose were its value known. Where the equilibria change with the season, the resulting changes in concentration may be employed to evaluate the rates at which the component processes take place. A study of the seasonal exchange of oxygen across the sea surface, made in the Gulf of Maine by Redfield (1948), will serve to illustrate this procedure, and, in addition, provides an example of the use of stoichiometrical relations in separating changes due to biological and physical processes.

### a. The exchange of oxygen across the sea surface

The quantity of oxygen dissolved in water beneath the sea surface depends on a balance between the rate at which it is exchanged with the atmosphere and the rate at which it is produced or consumed by biological activity, provided the effects of advection may be neglected. Changes in the quantity of dissolved oxygen, $\Delta Q_O$, during the time interval $\Delta t$ consequently result from an equilibrium represented by

$$\frac{\Delta Q_O}{\Delta t} = \frac{\Delta Q_R}{\Delta t} + \frac{\Delta Q_E}{\Delta t} \tag{3}$$

in which $\Delta Q_R/\Delta t$ is the rate of change in quantity due to biological activity and $\Delta Q_E/\Delta t$ is the rate at which oxygen is exchanged with the atmosphere across the sea surface. $\Delta Q_O/\Delta t$ was obtained from hydrographic data by integrating the quantity of dissolved oxygen underlying a square meter of sea surface to a depth of 200 m (below which the changes in oxygen concentration were negligible) at two periods separated by the interval $\Delta t$ and taking the difference. $\Delta Q_R/\Delta t$ was obtained by a similar integration of the inorganic phosphorus concentration, and multiplying the result by the oxidative ratio of phosphorus. If concentrations are expressed in mg atoms, $\Delta Q_R/\Delta t = -276 \, \Delta P/\Delta t$. The mean rate of diffusion of oxygen across the sea surface, $\Delta Q_E/\Delta t$, was obtained by introducing these measurements into equation (3).

The results of the study are illustrated in Fig. 9. During the winter period oxygen entered the water at a greater rate than it was reduced by organic activity. As a result the quantity of oxygen in the water column increased.
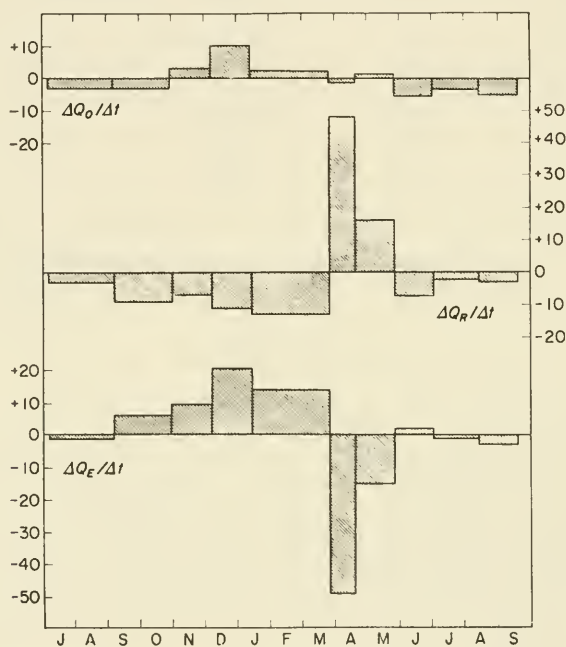


Fig. 9. Seasonal cycle in change in oxygen content of water of Gulf of Maine. $\Delta Q_O/\Delta t$, rate of change of oxygen content of water column; $\Delta Q_R/\Delta t$, rate of change attributed to biological activity; $\Delta Q_E/\Delta t$, rate of change attributed to diffusion across sea surface. Ordinates: rate of change in units of $10^4$ ml per $m^2 \times$ months. Abscissa: time in months. (Recalculated from data of Redfield, 1948, using oxidative ratio $\Delta O/\Delta P = -276$.)

This was possible because of the increased solubility which accompanied the cooling of the water. In the spring, when the growth of phytoplankton is intense, oxygen was produced more rapidly than it was reduced by organic activity. Oxygen escaped to the atmosphere at a nearly equivalent rate during

this period with the result that there was little change in the content of the water column. During the summer the oxygen content of the water decreased at a rate which corresponded closely to the rate of consumption by biological activity. Consequently the exchange with the atmosphere was small during this period.

These estimates show that the changes in the oxygen content of the water are small compared to the processes on which they depend. Thus, during the period between 4 September and 22 March, about $84 \times 10^4$ ml/m$^2$ of oxygen entered the water. The change in the oxygen content of the water column during this time was only one-fourth of this amount, three-quarters being consumed in the decomposition of organic matter. This demonstrates the degree to which the oxygen content of the water is stabilized by exchanges with the atmosphere. The quantity of oxygen crossing the surface of the Gulf of Maine annually is equivalent to that in a layer of air about 4 m in thickness.

The rate of diffusion of oxygen across the sea surface may be expected to vary with the difference in oxygen pressure in the atmosphere and in the surface water, according to the expression $\Delta Q_E / \Delta t = E(P - p)$. $P$ is the partial pressure of oxygen in the atmosphere, and $p$ its tension in the water. $p$ was determined from the degree of saturation of samples drawn from a depth of one meter. $E$ is the exchange coefficient of oxygen.

It was found that the pressure head of oxygen $(P - p)$ was positive during the winter and negative during the remainder of the year, as required by the sign of $\Delta Q_E / \Delta t$. The estimated values of the exchange coefficient $E$ are about $20 \times 10^6$ ml per m$^2$ per month per atmosphere during the winter period and agree in magnitude with estimates of this constant based on laboratory experiments. The values for other periods are not satisfactory and suggest that water samples drawn from a depth of one meter do not give a correct indication of the tension of oxygen in the water at the surface at times when the surface water is stable.

### b. Vertical exchange as a function of depth and season

The factors on which the concentration of nonconservative elements in a vertical water column depend vary greatly with depth. In the sub-surface water of the euphotic zone the growth of phytoplankton tends to reduce the concentration of nutrient elements while at greater depths regeneration tends to increase their concentration in proportion to the quantities of organic matter sinking to decompose at each level. The motion of the water on which the vertical diffusion coefficients depend also varies with depth. The procedures which may be employed to determine the rate of biological activity at different depths and of the vertical diffusion required to maintain the observed concentrations as they varied with the season are illustrated by an investigation of these factors in Long Island Sound made by Riley (1956, 1956a).

For the purpose of the analysis the water column underlying a unit area was divided into a series of segments of which the length, $\Delta z$, was equal, except

that the water immediately below the surface and above the bottom was included in volume units of one-half this length (see Fig. 10). Characteristic values for the temperature and phosphorus concentration based on hydrographic data obtained at stated intervals were assigned to the mid-depth of each segment, and to the water at the surface and bottom. These values were considered to represent the mean temperature, $T$, and mean phosphorus concentration, $N$, of the segment as a whole. It was assumed that horizontal movements of water were negligible in their effect on this distribution of properties.

In the case of the full segments the rate of change in $N$ in the interval $\Delta t$ depends on the balance between the rate of change due to biological activity, $R$, and that due to vertical diffusion across the upper and lower boundaries. Using the subscripts $z$ and $-z$ to distinguish properties of lower and upper boundaries respectively, the equilibrium may be expressed as

$$\frac{\Delta N}{\Delta t} \;=\; R + \frac{1}{\Delta z}\left(A_z \cdot \frac{\Delta N_z}{\Delta z} - A_{-z} \cdot \frac{\Delta N_{-z}}{\Delta z}\right). \tag{4}$$

In the case of the segments immediately below the surface and above the bottom, exchange takes place through only one surface and the appropriate diffusion term in (4) is omitted. Rearranging so that each term expresses a quantity rather than a concentration, (4) becomes

$$\frac{\Delta N \cdot \Delta z}{2\Delta t} \;=\; R \cdot \Delta z + A_z \cdot \frac{\Delta N_z}{\Delta z} \tag{4a}$$

for the sub-surface segment, and

$$\frac{\Delta N \cdot \Delta z}{2\Delta t} \;=\; R \cdot \Delta z - A_{-z} \cdot \frac{\Delta N_{-z}}{\Delta z} \tag{4b}$$

for the segment above the bottom.

In solving these equations for a given segment, $\Delta N/\Delta t$ is obtained from the difference in the mean concentration of $N$ in the segment determined at two times separated by the interval $\Delta t$. $\Delta N/\Delta z$ is the average of the values of the gradients in concentration across the boundary in question at these two times, each of which is given by the difference in $N$ assigned to the adjacent segments divided by the distance between their centers.

Before these equations could be used to evaluate $R$ for each segment, it was necessary to know the value of the diffusion coefficient at the depth of each bounding surface. These values were estimated from the distribution of temperature, $T$. The flux of heat across each boundary was expressed by a modification of (4b) in which $N$ is replaced by $T$, $R$ is omitted because the temperature is uninfluenced by biological activity, and $\Delta z$ is replaced by $h$, to express the length of the water column between the bounding surface in question and the bottom. Thus

$$\frac{\Delta T \cdot h}{\Delta t} \;=\; -A_{-z} \cdot \frac{\Delta T}{\Delta z}.$$

After solving this equation for the value of the diffusion coefficient $A$ at each bounding surface, the information necessary to obtain the value of $R$ characteristic of each segment was available.

As an example of the information obtained by this procedure on the processes determining the phosphate concentrations at depth, a balance sheet of the average rates of these processes in a layer of water in the euphotic zone during a summer period is given in Table X. The phosphate phosphorus

TABLE X

Balance of Factors Changing the Concentration of Phosphorus in Water of Long Island Sound between Depths of 2.5 and 7.5 m, and during Period May 21–August 19. (Data from Riley, 1956a.)

|  | mg atoms/m$^3$ per day |
| --- | --- |
| Diffusion from layer below | $4.8 \times 10^{-2}$ |
| „       to layer above | $-1.3 \times 10^{-2}$ |
| Net change from diffusion | $3.5 \times 10^{-2}$ |
| Change due to biological action | $-3.0 \times 10^{-2}$ |
| Change in concentration in water | $0.5 \times 10^{-2}$ |

concentration in the water increased during the period from 0.51 to 1.0 mg atom/m$^3$ or at a mean rate of about $0.5 \times 10^{-2}$ mg atom/m$^3$ per day in spite of a net loss, due to the excess of photosynthesis over regeneration, at a rate of $3.0 \times 10^{-2}$ mg atom/m$^3$ per day. This was possible because of the excess rate at which regenerated phosphorus was returned to the layer by vertical diffusion. Of the phosphate diffusing into the layer from below about three-quarters remained in the layer to effect the balance while one quarter moved on into the layer above.

The rapid turnover which these exchanges produce is brought out by the consideration that the initial concentration was only 0.51 mg atom, while the biological consumption was $3.0 \times 10^{-2}$ mg atom per day. At this rate the phosphate in the layer would have been completely exhausted in 17 days had it not been renewed by vertical diffusion.

The result of Riley's estimates of the intensity of biological activity in Long Island Sound at various depths and seasons is presented in Fig. 10. They show that, in the summer period, the absorption of phosphorus by growing plankton exceeds regeneration down to a depth of 12.5 m. Below this depth regeneration is in excess and takes place mainly in the layer immediately above the bottom. In spring the total rate of absorption exceeds regeneration, while in summer this relation is reversed. During the winter the overall biological activity appears to be greatly reduced and absorption exceeds regeneration only in the layer immediately below the surface.

It should be emphasized that the procedures reveal only the net result of the balance between absorption and regeneration. In the photic zone substantial quantities of nutrients may be absorbed and returned to the water by regeneration *in situ*. These increments do not appear in the balance. They may be determined by other methods such as those discussed in Chapter 7 which measure absorption directly.
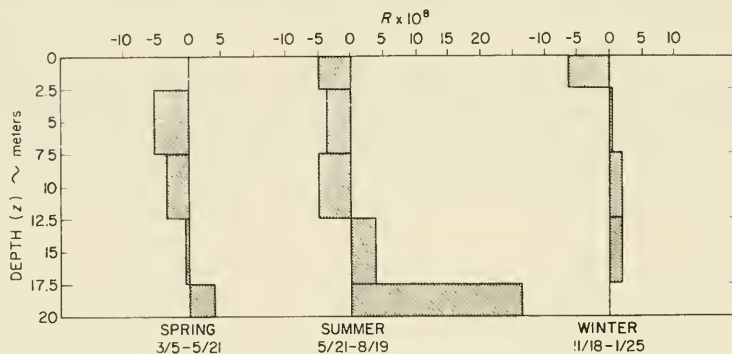


Fig. 10. Rate of change of phosphate phosphorus concentration attributed to biological activity, $R$, in layers of water at different depths and seasons in Long Island Sound. Negative values represent excess of absorption over regeneration. Units: depths, $z$, meters; $R$, $10^{-2}$ mg atom/m³/day. (Estimated from data of Riley, 1956a.)

## C. Differential Advection

Water moves with velocities which vary with depth, usually decreasing downward. Under conditions of differential advection the redistribution of nonconservative properties with respect to depth due to the sinking of organic matter leads to changes in the total quantity of the element present along the path of flow. Differential advection thus provides a mechanism by which geographical differences in distribution of nonconservative elements may be produced.

A simplified model will serve to indicate the principles and relations of the several factors involved in this process. Consider two layers of water of equal depth, $h$, moving with different velocities along the $x$-axis, separated by a surface across which a nonconservative element $N$ is transferred downward by sinking of organic matter and upward by eddy diffusion. At any position along the axis of flow, the concentration of the element is also subject to change by horizontal advection. If $-R$ represents the rate at which the mean concentration of $N$ is being reduced in the upper layer by the synthesis, sinking and decomposition of organic matter, $R$ will represent its rate of increase in the lower layer. If $A$ is the coefficient of vertical diffusion in the surface of separation and $dN/dz$ is the gradient of concentration at this boundary $(A/h) \, dN/dz$ will represent the effect of eddy diffusion on $N$ in the upper layer and $-(A/h) \, dN/dz$ its effect in the lower layer. The rate at which $N$ is altered by

horizontal advection in either layer is given by $V \cdot dN/dx$, where $V$ is the velocity of flow and $dN/dx$ is the gradient in mean concentration along the $x$-axis. Under steady-state conditions the combined effect of the vertical exchanges balances the effect of advection in each layer so that

$$V_U \cdot \frac{dN_U}{dx} = -R + \frac{A}{h} \frac{dN}{dz} \tag{5a}$$

for the upper layer, and

$$V_L \cdot \frac{dN_L}{dx} = R - \frac{A}{h} \frac{dN}{dz} \tag{5b}$$

for the lower layer. The subscripts $U$ and $L$ designate the properties peculiar to the upper and lower layers respectively.

Combining these equations to eliminate the right-hand term,

$$\frac{dN_L}{dx} = -\frac{V_U}{V_L} \cdot \frac{dN_U}{dx}. \tag{6}$$

This states that under steady-state conditions the mean concentration of $N$ in the lower layer will increase along the $x$-axis as that in the upper layer decreases, and at a rate which is proportional to their relative velocities. In the case under consideration the layers are taken to be of equal depth and consequently the quantity of $N$ present is proportional to the concentration in the respective volume units. It follows that if $V_U = V_L$ the quantity of $N$ in the lower layer increases along the $x$-axis at exactly the same rate that it decreases in the upper layer. Consequently there will be no change in the total quantity of $N$ along the $x$-axis. If, as is usually the case, $V_U > V_L$, the quantity of $N$ in the lower layer will increase more rapidly than it decreases in the upper layer and the total quantity present in the two layers will increase in the direction of flow.

If the flow of the lower layer is in the opposite direction to that of the upper layer, $V_L$ is negative and the right-hand term of equation (5) becomes positive. In these circumstances the quantities of $N$ will change in both layers in the same way and will decrease in the direction in which the upper layer is flowing. Consequently countercurrent systems are particularly effective in producing changes in the distribution of nutrients along the direction of flow and lead to accumulation in the direction from which the surface current is flowing.

More complete expressions of the relations of the several factors involved in the effect of differential advection on the distribution of nonconservative properties along the axis of flow may be derived from equations (5a) and (5b). Substituting $dQ/h$ for $dN$ and $dQ_R/h$ for $R$ to express changes in the quantities of $N$ rather than concentrations, the rate of change along the $x$-axis of the total quantity of $N$ in both layers is obtained by adding the equations and rearranging the terms. Thus

$$\frac{dQ_L + dQ_U}{dx} = \frac{1}{V_U} \cdot \left( \frac{V_U}{V_L} - 1 \right) \cdot \left( \frac{dQ_R}{dt} - A \cdot \frac{dN}{dz} \right). \tag{7a}$$

Similarly, the difference in the quantity of $N$ in the respective layers changes along the axis of flow according to

$$\frac{dQ_L - dQ_U}{dx} = \frac{1}{V_U} \cdot \left(\frac{V_U}{V_L} + 1\right) \cdot \left(\frac{dQ_R}{dt} - A \cdot \frac{dN}{dz}\right) \tag{7b}$$

while the rate of change in the difference in mean concentration is

$$\frac{dN_L - dN_U}{dx} = \frac{1}{V_U h_U} \cdot \left(\frac{V_U h_U}{V_L h_L} + 1\right) \cdot \left(\frac{dQ_R}{dt} - A \cdot \frac{dN}{dz}\right). \tag{7c}$$

These expressions indicate that the gradients developed in the horizontal and vertical depend on the ratio of the velocity in the two layers, and vary inversely with the absolute velocities as indicated by the term $1/V_U$. Sluggish currents are more effective than rapid ones in producing differential distribution, other things being equal. It may be noted also that the effects on the gradients in quantity depend on the velocities in the two layers, but that the effects on concentration vary with the product of the respective velocities and depths, that is with the flux in the respective layers, provided the vertical exchange remains the same.

The term $(dQ_R/dt - A \cdot dN/dz)$ indicates that the gradients will develop in proportion to the balance between the biological effect and that of vertical diffusion. As the vertical separation develops along the axis of flow, in accordance with equation (7c), $dN/dz$ will increase in value. Consequently the gradients will not develop linearly with distance along the $x$-axis but will tend to approach a limit at which the biological effect is balanced by the effect of diffusion. The coefficient of eddy diffusion, $A$, varies greatly under natural conditions, and in general in inverse proportion to the stability. Under stable conditions vertical diffusion may be small and have little effect on the gradients developed. If $A$ is large, as in the case of shallow estuaries subject to strong tidal currents, the diffusion term may be so large that gradients in the distribution of nonconservative elements do not develop.

The foregoing discussion is intended to clarify the factors which lead to a differential distribution of nonconservative elements in sea-water in situations where water moves with different velocities at various depths. It will provide a basis for discussion of the natural systems in the following pages.

### a. The estuarine circulation

In estuaries fresh water derived from the land by runoff and seepage mixes with sea-water and is carried seaward in the upper layer of the embayment. A countercurrent of sea-water moves in from the outer sea to replace that entrained in the surface outflow. The estuarine circulation is a special case of differential advection in which $V_L$ is negative. Consequently, the redistribution of nonconservative elements by the sinking of organized matter will tend to cause the concentration of $N$ to increase upstream relative to the motion of the surface layer. The estuarine circulation creates a trap in which nutrients tend to accumulate.

The Gulf of Venezuela is an example of an embayment in which the estuarine circulation is accompanied by an accumulation of phosphorus (see Fig. 11). The upper layers of the Gulf are diluted by fresh water escaping from the Maracaibo basin. The salt water entrained in the surface layer as it moves seaward is replaced by water from the Caribbean. In the deeper water at the head of the Gulf the concentration of phosphate phosphorus is 1 mg atom/m$^3$, which

is twice the quantity found in its offshore source. The total quantity of phosphorus in the water column increases from 11 mg atoms/m² at the shallow sill which divides the Gulf to 16 mg atoms/m² near the head of the Gulf. The oxygen is reduced in the deep water in the proportions expected from the $\Delta O/\Delta P$ ratio (Redfield, 1955).
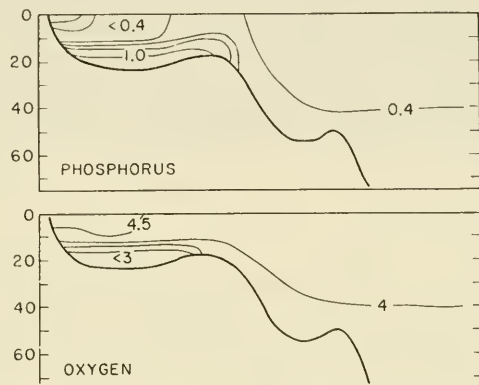


Fig. 11. Distribution of total phosphorus and oxygen in a section along axis of Gulf of Venezuela. Contour interval: Total phosphorus 0.2 mg atom/m³; oxygen 0.5 ml/l. Depths in meters. (After Redfield, 1955.)

The amount of accumulation varies greatly in different estuaries. It may be expected to increase with the rate of production of organic matter and with the length of the basin, to decrease with turbulence and the velocity of flow, and to vary with the relative depth and velocity of the surface and deep layers. Because of the variation in the accession of fresh water with the seasons, steady-state conditions are rarely observed. In shallow estuaries subject to strong tides, vertical advection is so strong that no differential distribution of nutrients can develop. Accumulation may occur, however, in small shallow estuaries if they are sufficiently isolated from tidal effects, as in the case of Great Pond, Falmouth, Massachusetts, studied by Hulburt (1956).

If the velocity of the currents is rapid the deep layer may be replaced before any notable accumulation can develop. This appears to be the case in the Strait of Juan de Fuca, where a well-developed counter current exists. In spite of the high productivity of the surface layer, no clear gradient of phosphate develops in the deeper layer along its length.

Because of the annual variation in the accessions of fresh water, and the influence of climate on the hydrography and the production of organic matter, steady-state conditions rarely exist in estuaries. The balance of the factors leading to accumulation consequently varies with the seasons. In Long Island Sound it is estimated that the countercurrent mechanism causes an accumulation of phosphorus to the order of 0.7–1.5 mg atoms/m³ in summer while comparable losses occur in the winter (Riley and Conover, 1956). Similar annual fluctuations occur in the nitrate exchange (Harris, 1959).

A striking example of the effect of seasonal variation in the influence of the

countercurrent mechanism on the distribution of a nonconservative property is found in the strait connecting Lake Maracaibo with the sea. During the rainy season this strait is swept out by water escaping from the lake. The net movement is seaward at all depths. Although the deeper layers have lower velocities than the surface the strait is too short to permit any notable change in the concentrations of oxygen to develop along its length. With the advent of the dry season the outflow slackens and water of higher salinity crosses the shallow sill separating the strait from the sea, and flows lakeward beneath the outflow of surface water. Within a few months the oxygen content of the deep counter current becomes greatly reduced in the direction of its movement (see Fig. 12).
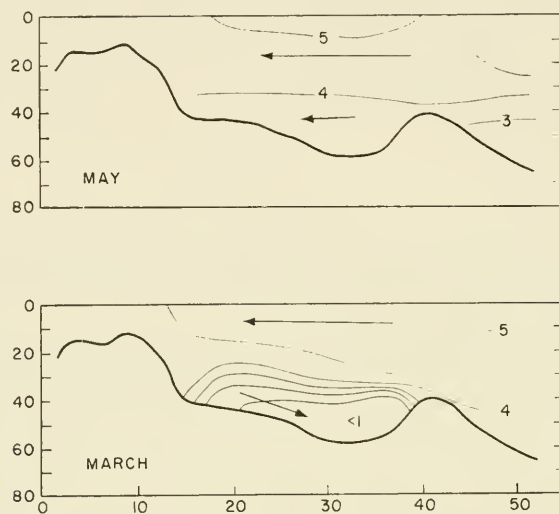


Fig. 12. Distribution of oxygen in section along Strait of Maracaibo during wet season, May, and dry season, March. Lake Maracaibo lies to the right. Arrows indicate the direction of non-tidal currents. Ordinate, depth in feet; abscissa, scale of miles; contour interval, 1 ml oxygen/m³. (After Redfield, 1955.)

Extreme examples of the accumulation of nonconservative elements are provided by fjords. These estuaries are separated from the outer sea by sills which limit the active exchange of water to a relatively shallow layer and thus permit the deep water to stagnate. They thus represent the limiting case of differential advection in which the ratio of the velocities of the upper and lower layers is very large. The sinking of organic matter into the deep basins leads to reduction in oxygen content, the production of hydrogen sulfide and the accumulation of unusual concentrations of phosphate. In a large series of fjords examined by Ström (1936) great variations in the development of these effects are observed, varying from those in which complete anoxia does not occur to others in which as much as 40 ml/l. $H_2S$ is present. In the extreme cases as much as 10 mg atoms/m³ of phosphate phosphorus may accumulate in the deep water.

In fjords with large quantities of fresh water in the upper layers, the deep

water is partially renewed regularly by advection and diffusion. In others seasonal variations in turbulence, stability and productivity lead to some renewal of the upper layers of the deep water each winter. The bottom waters, however, are renewed only periodically when sea-water crosses the sill in sufficient quantity to displace the stagnant water from the bottom upward. Ström suggests that the most general cause of renewal is the gradual warming of the deep water to the point where its density becomes less than that of the water entering over the sill. In the relatively long intervals between renewal, the effects of stagnation gradually develop. In two basins with varying degrees of stagnation, the quantity of $H_2S$ present in the bottom water increased at the rate of 1.0–1.5 ml/year.

### b. The anti-estuarine circulation

In regions where rainfall is small, evaporation from the sea surface may exceed precipitation and the additions of fresh water from rivers. Under these conditions a reversal of the currents characteristic of the estuarine circulation may be expected, since sea-water must flow in to replace water lost by evaporation from the surface, while water concentrated by evaporation will sink and flow out along the bottom. We know of no case where estuaries of this type have been well enough described to show whether the current system actually reduces the nutrient content of the water, as might be expected. However, one large sea, the Mediterranean, is well known to be low in nutrients and is characterized by an anti-estuarine circulation.

### c. The Mediterranean and Black Seas

These seas together illustrate how greatly the characteristics of the circulation can influence the distribution of the biochemically important elements in adjacent bodies of water. The Mediterranean is the most impoverished large body of water known, while in the Black Sea nutrients have accumulated to an extreme degree.

In the Mediterranean evaporation exceeds the accession of fresh water to such an extent that the salinity is increased by about 4%. The dynamics of the situation are such that a much larger volume of water flows in through the Strait of Gibraltar than is required to replace the loss by evaporation. The excess escapes through the Strait as a counter current moving seaward below the inflowing surface layer. Fig. 13 shows the situation diagrammatically. The nutrient content of Mediterranean water, as indicated by the phosphate content, is very much lower than that of the off-lying Atlantic. This is due initially to the fact that water enters the sea across a shallow sill and is thus skimmed from the surface layers of the ocean which are already greatly depleted in nutrients. This fact alone does not explain why a great accumulation of nutrients does not occur in the deep water, as it does in many other basins isolated by shallow sills.

The impoverished condition of the Mediterranean was first described by

Thomsen (1931) and is discussed by Riley (1951) in terms of the circulation pattern. The accumulation of nutrients in the deep water is limited by the exchange through the Strait of Gibraltar. A steady-state condition exists when the income of nutrients in the upper layers of the strait equals the outgo in the deeper layers. Accumulation in the deeper layers can only develop to the point where this condition is met, since any further increase in the concentration in the outgoing water will lead to a net loss of nutrients from the sea as a whole.

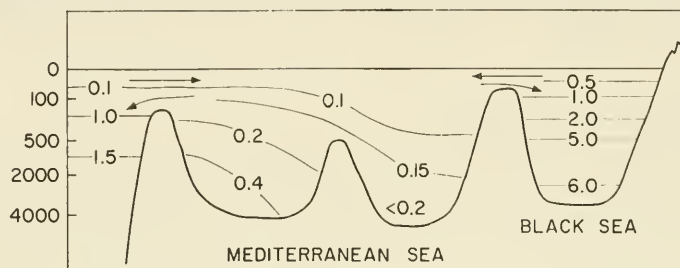Fig. 13 shows that, within the Mediterranean, the concentration of phosphate



Fig. 13. Distribution of phosphorus in Black Sea, Mediterranean and off-lying Atlantic Ocean (diagramatic). Arrows indicate direction of currents in the Bosphorus and Strait of Gibraltar. Contours, phosphate phosphorus in mg atoms/m$^3$. Depths in meters.

decreases progressively in both the sub-surface and deep water as one goes eastward in the direction of flow of the surface layers. This is the relation to be expected in an anti-estuarine circulation.

The circulation of the Black Sea is similar in character to that of a fjord. It receives the discharge of the great rivers of eastern Europe of which the excess escapes through the Bosphorus as a strong surface current. Beneath this flow a counter current transports more saline water from the Mediterranean into the Black Sea. Since the Bosphorus is less than 100 m deep and the deeper part is occupied by an inflowing current, the deep water of the basin cannot escape except by mixing upward into the surface layers. Nutrients accumulated in such deep water re-enter the biochemical cycle when brought to the surface and are returned by sinking as organized matter to the depths (see Caspers, 1957).

The estuarine circulation of the Bosphorus thus produces a trap which hinders the loss of nutrients from the Black Sea and promotes their accumulation. In contrast, water from the depths of the Mediterranean may escape through the Strait of Gibraltar without re-entering the euphotic zone.

A factor which must contribute to the greater accumulation of regenerated nutrients in the Black Sea, as contrasted with the Mediterranean, is the stability of the water column. In the Black Sea the accessions of fresh water at the surface produce strong density gradients in the upper layers which retard the diffusion of deep water into the levels at which escape across the sill is possible. In contrast, the deeper water of the Mediterranean is homogeneous up to depths well

above the critical level at which it can flow across the sill, and its escape is
unimpeded by stability.

### d. Upwelling

Where persistent winds, such as the Trades, blow the surface water off-
shore sub-surface water upwells to replace it. Upwelling takes place off the
western coasts of the continents in the trade-wind zones. It is recognized by the
anomalous coolness of the surface waters, their high nutrient content and
the abundance of life.

A small-scale example of upwelling, and its influence on the distribution of
the components of sea-water, is found in the outer part of the Gulf of Venezuela.
During the winter season, when the northeast trade winds blow persistently,
upwelling occurs in the lee of the peninsula of Paraguana, which forms the
eastern boundary of the Gulf. Fig. 14 shows that along a section extending
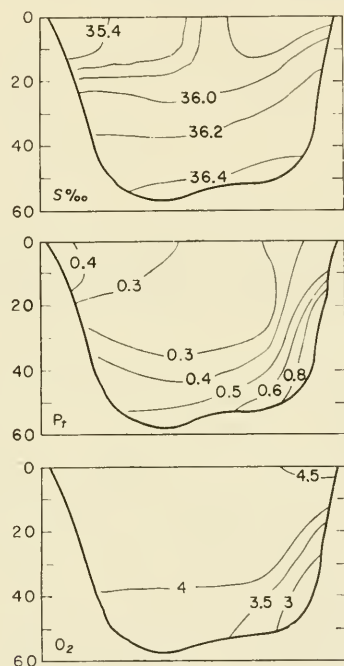
Fig. 14. Distribution of salinity ($S\%_0$), total phosphorus ($P_t$ mg atoms/m$^3$), and oxygen
($O_2$ ml/l.) in a section across Gulf of Venezuela. Ordinate, depths in meters. (After
Redfield, 1955.)

westward from the peninsula the isohalines slope upward as the coast is ap-
proached. This indicates that the more saline water at depth is being drawn
landward and upward by the upwelling process to replace the surface water
being blown offshore. The phosphorus and oxygen isolines slope in much the
same way but more markedly. The concentrations of phosphorus are greater
and those of oxygen less in deep water close to the coast than anywhere off-
shore. Apparently there is an accumulation of phosphorus in the deep water as

it moves toward the site of upwelling, as the result of the sinking of organized matter from the surface layers as they move offshore. In support of this, the oxygen is diminished in about the proportions required for the decomposition of organic matter.

The classic examples of upwelling are found along the eastern boundaries of the oceans in the trade-wind belt. The distribution of total phosphorus in a section crossing the Benguela current off the western coast of Africa, where upwelling occurs, is shown in Fig. 15. At all depths the concentrations of phos-
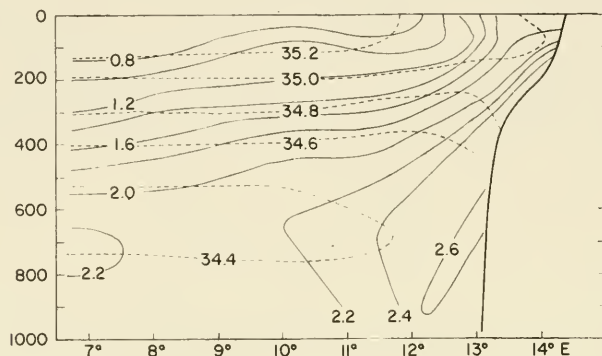
Fig. 15. Distribution of total phosphorus and salinity in a section along 24th parallel off west coast of Africa. Solid contours, total phosphorus, mg atoms/m$^3$; broken contours, salinity, ‰. Depths in meters. (Based on *Crawford* Stations 450–458, October, 1958.)

phorus increase markedly as the coast is approached. If this enrichment were due entirely to the movement of deep water into the upper layers, the isohalines should parallel the phosphorus isopleths, which is not the case. The fact that along any isohaline the phosphorus increases markedly toward the coast indicates that some process other than the physical motions of the water leads to an accumulation of this element in the upwelling area.

Upwelling can only be maintained by a flow of deep water toward the site of upwelling to replace the surface water moved offshore by the wind. Off the coasts of California (Sverdrup and Fleming, 1941) and Peru (Gunther, 1936) counter currents are present in the sub-surface waters during the periods of upwelling. It seems probable that nutrients accumulate in areas of upwelling because of the differential advection of water at different depths and in accordance with the principles which apply in estuaries. This accumulation must contribute substantially to the fertility of the water in such areas.

### D. Dynamic Equilibria in Three Dimensions

In the cases discussed above special considerations have justified a simplification of the problem by the assumption that exchanges in one or two dimensions could be neglected. Such assumptions are not justified when the distribution of properties in large bodies of water are under consideration. The treatment in

such a case is much more complicated, but it has been attempted in one case, that of the distribution of oxygen, phosphate and nitrate in the Atlantic Ocean by Riley (1951). This remarkable paper, which requires and deserves careful study, develops as well a comprehensive account of the physical circulation.

Riley's procedure is to construct a mathematical model to which equation (1) can be applied.

Equation (1) is converted to finite difference form to read:

$$\delta N_0 = R + \frac{1}{\Delta x}\left(\frac{A_x}{\rho}\cdot\frac{\Delta N_x}{\Delta x} - \frac{A_{-x}}{\rho}\cdot\frac{\Delta N_{-x}}{\Delta x}\right) + \frac{1}{\Delta y}\left(\frac{A_y}{\rho}\cdot\frac{\Delta N_y}{\Delta y} - \frac{A_{-y}}{\rho}\cdot\frac{\Delta N_{-y}}{\Delta y}\right)$$

$$+ \frac{1}{\Delta z}\left(\frac{A_z}{\rho}\cdot\frac{\Delta N_z}{\Delta z} - \frac{A_{-z}}{\rho}\cdot\frac{\Delta N_{-z}}{\Delta z}\right) - \frac{1}{2}\left(V_x\cdot\frac{\Delta N_x}{\Delta x} + V_{-x}\cdot\frac{\Delta N_{-x}}{\Delta x}\right)$$

$$- \frac{1}{2}\left(V_y\cdot\frac{\Delta N_y}{\Delta y} + V_{-y}\cdot\frac{\Delta N_{-y}}{\Delta y}\right) - \frac{1}{2}\left(V_z\cdot\frac{\Delta N_z}{\Delta z} + V_{-z}\cdot\frac{\Delta N_{-z}}{\Delta z}\right). \tag{1a}$$

$N_0$ is the concentration at the center of some specified volume unit, $N_0 + \Delta N$ is the concentration at the center of the adjoining volume unit and $\Delta x$, $\Delta y$ and $\Delta z$ are the distances separating the centers along the specified axes. When the centers on any axis are equidistant, $\Delta N_x/\Delta x$, etc. represent the gradients and $A_x$, $V_x$, etc. represent average values of the physical coefficients between successive centers. A steady state is assumed, in which case the array of terms on the right-hand side of the equation equals zero.

The surface of the ocean between 63°N and 36°S is divided into rectangular areas 1000 km on a side and the water column under each area is subdivided into unit volumes separated by surfaces at intervals of 0.2 $\sigma_t$ units. To the center of each of these volumes representative values of the items—temperature, salinity, oxygen, phosphate and nitrate —are assigned, based on oceanographic data. The result is an array of data, distributed geometrically in the horizontal and so that each vertical series lies between the same $\sigma_t$ surfaces, which defines the values of the gradients $\Delta N_x/\Delta x$, etc.

The physical coefficients $A_x$, $V_x$, etc. are evaluated from the data on temperature and salinity. Relative values for the velocity of flow in each $\sigma_t$ surface are obtained by applying standard procedures of dynamic oceanography to the distribution of temperature and salinity. From these the relative transport between the $\sigma_t$ surfaces is then derived by taking account of the difference in their depths. These relative values are adjusted to accord with the principle of continuity to give absolute transports such that the total flow across the southern boundary of the array as a whole is zero. Reversing the procedure the absolute values for the velocity of flow, $V_x$, etc., are obtained. From these values the advective terms of the equation may be evaluated for each volume unit.

The coefficients of eddy diffusion, defining the exchange of water across the boundaries of the unit volumes, are obtained by applying the relaxation method to the salinity distribution. It is assumed that a steady state exists, in which case the quantity of salt entering each unit volume must equal that leaving. The boundary conditions require that, in the array as a whole, this equality shall apply also to the exchange across the southern boundary. Provisional values are assigned to the coefficients of vertical and horizontal diffusion until this condition is met within each unit volume when the advective terms are taken into account. Certain simplifying assumptions are made, including the effect of stability and shear on the vertical diffusivity, for which the original paper may be consulted.

Average values for the coefficients of horizontal and vertical diffusivity obtained are given in Table XI. These coefficients vary somewhat from one area to another.

By these procedures all the terms defining the motion of the water are determined and

the value of $R$, the rate of change of any of the nonconservative properties, may be obtained for any unit volume directly from equation (1a). The average values obtained for the rate of change in oxygen concentration and of phosphorus regeneration at depth are shown in Table XI.

TABLE XI

Average Eddy-Diffusion Coefficients and Rates of Change in Oxygen and Phosphate Concentration, as Estimated by Riley (1951)

| Sigma-$t$ | Diffusion coefficients | | Rate of change in concentration | | $\Delta O/\Delta P$, mg atoms |
| | Vertical, $\dfrac{g}{cm\ sec}$ | Horizontal, $\dfrac{g}{cm\ sec}$ | Oxygen, $\dfrac{ml\ O_2}{m^3\ year}$ | Phosphate, $\dfrac{mg\ atoms\ P}{m^3\ year}$ | $\dfrac{}{mg\ atoms}$ |
|---|---|---|---|---|---|
| 26.5 | 1.5 | $0.57 \times 10^8$ | $-0.21$ | 0.093 | $-190$ |
| 26.7 | 0.56 | 0.18 | $-0.08$ | 0.040 | $-180$ |
| 26.9 | 0.40 | 0.14 | $-0.050$ | 0.024 | $-170$ |
| 27.1 | 2.1 | 0.105 | $-0.055$ | 0.005 | $-1000$ |
| 27.3 | 1.5 | 0.025 | $-0.035$ | 0.003 | $-1000$ |
| 27.5 | 0.8 | 0.024 | $-0.013$ | 0.004 | $-280$ |
| 27.7 | 13.5 | 0.080 | $-0.005$ | 0.004 | $-100$ |
| 1500 m | 0.4 | 0.002 | $-0.0016$ | 0.003 | $-50$ |
| 4000 m | 0.5 | 0.028 | $-0.00013$ | 0.0001 | $-100$ |

The procedure is not well adapted to the analysis of the deep water because of the small gradients present. The results obtained for water below 1500 m are presented by Riley with some reserve. The values entered in Table XI indicate merely the magnitude of the items. Also, it was found impractical to deal with the surface layer by these procedures.

The description of the physical circulation obtained by the analysis of the mathematical model agrees in general with that obtained by other methods. As a check on its utility in accounting for the distribution of nonconservative elements, the results obtained were used to reconstruct the distribution of hosphate and nitrate in a north–south section of the Atlantic basin. The istribution obtained for phosphate is shown in Fig. 16. The distribution estimated from the dynamic balance of the factors evaluated from the model agree in all essential details with that observed in nature.

The estimates of oxygen consumption and phosphate regeneration provide a means of determining the oxidative ratio, $\Delta O/\Delta P$, discussed on page 32. The atomic ratio obtained for the water column as a whole, from 200 m to the bottom, is $-255$. This value differs by only 8% from the theoretical ratio of $-276$ obtained from the analysis of plankton. When the values obtained from the several $\sigma_t$ surfaces are examined, the ratios vary widely and are nearly four times greater than the theoretical ratio in the water of the intermediate layer (see Table XI).

It is difficult to believe that the character of the organic matter being oxidized differs as greatly with depth as the results indicate. Riley finds that errors in the data or analytical procedures cannot account for the discrepancy.
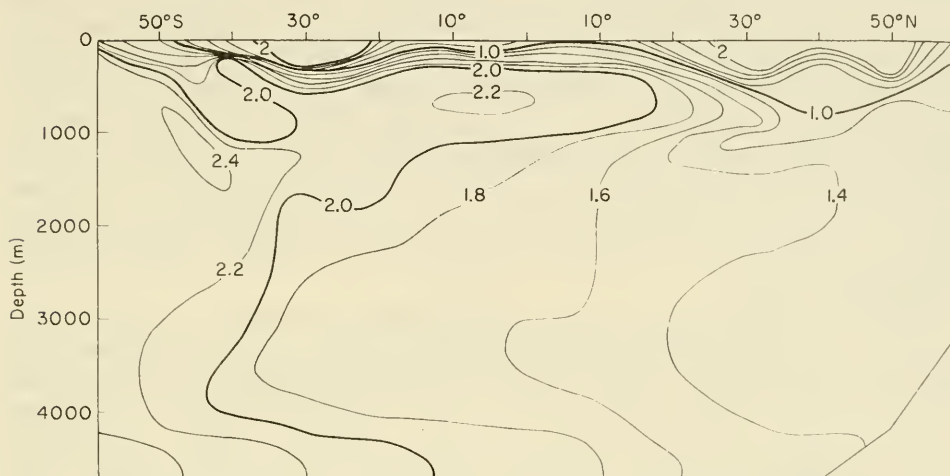


Fig. 16. Mathematical model of phosphate distribution along a north–south profile of the Atlantic Ocean estimated from analytically determined physical coefficients and assumed phosphate regeneration rates that vary in accordance with a generalized hypothesis derived from analysis. Contour interval, 0.2 mg atoms P/m³. (From Riley, 1951.)

The whole analysis is so complicated, however, that it is not possible to make a satisfactory analysis of errors. Some degree of anomaly in the oxidative ratio undoubtedly exists, but it is questionable whether the variations are as extreme as the calculations indicate.

### E. The Biochemical Circulation of the Oceans

Oxygen and phosphorus are distributed in the oceans of the world in characteristic patterns which are described by Sverdrup *et al.* (1942). In the case of the Atlantic Ocean, Riley's analysis evaluates in detail the factors on which the dynamic balance underlying the pattern depends. It is of interest to examine in a more general way the character of the circulation of the oceans to find what dominant physical features create these patterns and account for their differences.

#### a. The vertical distribution of nonconservative elements

The distributions in depth of phosphate and oxygen display a similar pattern in the central basins of all oceans. Phosphate is depleted near the surface, rises to a maximum at moderate depth and then decreases somewhat and is relatively uniform in deep water (see Fig. 4). The distribution of oxygen follows an inverse pattern. The depth at which oxygen is minimal corresponds roughly, but not exactly, with that at which phosphate and nitrate are maximal and

this zone will be referred to as the oxygen-minimum layer. In high latitudes the oxygen-minimum layer is absent and the vertical distributions are more uniform.

There has been general agreement that the oxygen-minimum layer arises from a dynamic equilibrium between the rate at which oxygen is removed from the respective water layers and the rate at which it is renewed by the circulation of water (see Richards, 1957). One group of investigators has emphasized the latter factor and has concluded that the oxygen content is reduced to the greatest extent where the motion of water is minimal. Seiwell (1937) and Sverdrup (1938) have pointed out that this condition is contrary to the facts in certain situations and that the observed distributions of oxygen may be accounted for by assuming various other suitable relations between the dynamic factors.

When the concentration of any nonconservative element in a moving mass of water is considered, its value will depend not only on the changes which have resulted from the balance of dynamic factors operative along its course, but also on the initial condition of the water. If the velocity of flow is great the change due to biological activity may be small and the observed concentrations may depend largely on a state established at the point of origin of the water mass. For example, a core of water of low oxygen content present in the Gulf Stream off New England may be tracked back toward its origin as far south as the Caribbean Sea (Richards and Redfield, 1955). It has been shown that the vertical distributions of oxygen and phosphorus in the Atlantic arise in substantial part from conditions existing near the sea surface at the places where the several water layers are formed, as well as from the decomposition of organic matter in the course of their flow at depth (Redfield, 1942).

The demonstration depends on separating the phosphorus present into its several fractions, as discussed on page 33. The principal motion of the water, by advection and horizontal eddy diffusion, may be assumed to be along surfaces of equal density. It is consequently instructive to plot the data as a function of $\sigma_t$ rather than depth, in which case the principal motion is in the horizontal and the continuity of motion becomes apparent. The convention is not adapted to represent conditions in the deep water with $\sigma_t > 27.8$ because the variation in $\sigma_t$ is insignificant. The conditions below 2000 m are better shown in the usual manner as a function of depth. The conditions at the depth of 200 m may be taken to represent the state of the water masses at the time of their origin. At this depth seasonal variations in the surface layers are largely eliminated.

The distribution of inorganic phosphorus along a north–south section of the Atlantic Ocean is shown in Fig. 17a, using this convention. The close relation of phosphate concentration to density distribution is striking. Maximal concentrations occur in a zone between $\sigma_t$ 27.0 and $\sigma_t$ 27.5 which meets the subsurface in the subantarctic region between 42°S and 50°S, i.e. between the approximate positions of the subtropical and antarctic convergences. This zone will be referred to as the intermediate layer. Maximum concentrations occur at

about $\sigma_t$ 27.3, and their values decrease northward. This trend is interrupted in the equatorial region where a localized increase in concentration occurs.
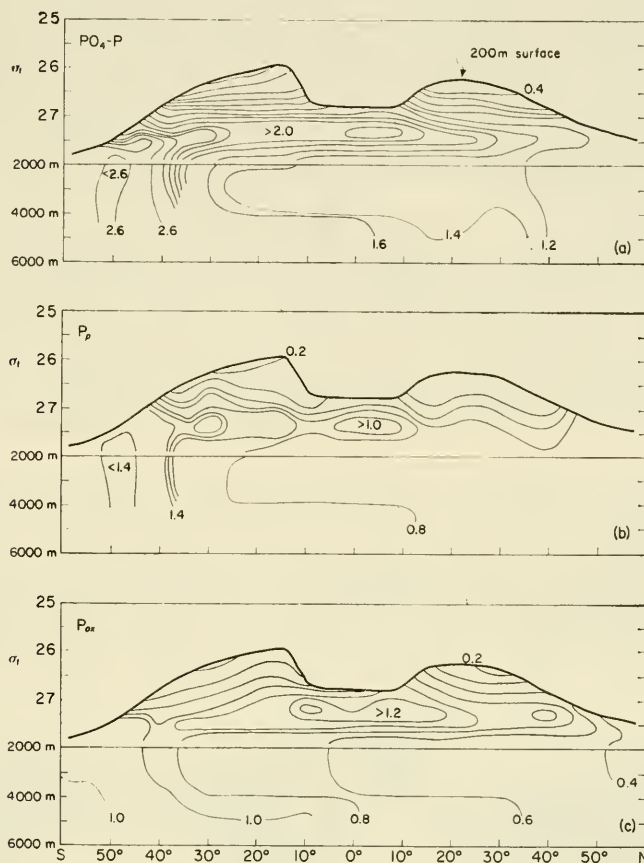
Fig. 17. Distribution of phosphorus fractions along western trough of Atlantic Ocean. (a) Phosphate phosphorus. (b) Preformed phosphorus. (c) Phosphorus of oxidative origin. Ordinates, sigma-$t$ surfaces and depths in meters. Abscissa, latitude. Contour interval, 0.2 mg atom/m$^3$. (Recalculated from data used by Redfield, 1942, and additional stations. Phosphorus corrected for salt error. Phosphorus of oxidative origin estimated using $\Delta O/\Delta P = -276$.)

The origins of the distribution of inorganic phosphorus are illuminated by the distributions of preformed phosphorus and phosphorus of oxidative origin. Preformed phosphorus also has maximal concentrations in the intermediate layer which diminish northward from the sub-surface of the subantarctic region and disappear at about 15°N (see Fig. 17b). This fraction is a conservative property. Its pattern of distribution and attenuation is very similar to that of salinity, which suggests that it is due to the intrusion of subarctic and antarctic intermediate water at an intermediate depth of the ocean. Since preformed phosphorus accounts for about one-half of the inorganic phosphorus in

this layer, its northward flow must produce a substantial part of the inorganic phosphorus maximum.

The distribution of phosphorus of oxidative origin is shown in Fig. 17c. The distribution depends directly upon that of the apparent oxygen utilization from which it is estimated (see page 33). Maximum concentrations are found in the equatorial region of the intermediate layer, from which the concentrations diminish both northward and southward. This maximum must arise from the regeneration of phosphorus from organic matter derived from the surface layers of the tropical ocean.

The sub-surface water in the subantarctic region contains substantial concentrations of phosphorus of oxidative origin. The northward flow of antarctic intermediate water will carry this fraction to the intermediate layer of lower latitudes along with the preformed phosphorus. Allowance for the contribution of this fraction of subantarctic origin to the total phosphorus of oxidation can be made (see Redfield, 1942). When this is done, the occurrence of phosphorus of local oxidative origin becomes restricted in the South Atlantic to the tropical region.

The origin of the phosphate maximum is evidently complex, being due to the combined effects of fractions introduced by the transport of the water of the intermediate layer from its origin in the subantarctic regions, supplemented by local regeneration in the tropics and the subsequent redistribution of the latter by the horizontal circulation. The maximum local regeneration occurs at somewhat lesser depths than the maximum of the preformed phosphate. Accordingly the oxygen minimum lies somewhat above the phosphate maximum.

The depths between the sub-surface (200 m) and the upper boundary of the intermediate layer, in which $\sigma_t < 27.0$, are occupied by the North and South Atlantic Central Water-masses. In the equatorial region these water-masses are separated by the density distribution except for a zone of limited thickness (*ca.* 200 m), so that water can move between them only by passing through the sub-surface layer. In these isolated pools, which circulate as great eddies, the concentrations of the several phosphorus fractions decrease toward the surface depending on the degree of mixing of the rich water of the intermediate layer and the water of the surface layer which is impoverished by the synthesis and sinking of organized matter. The resulting patterns of distribution depend on the circulation which is peculiar to the eddies occupied by the central water-masses, and which also results in gradients in the temperature and salinity distribution.

The depths below the intermediate layer, where $\sigma_t$ is greater than 27.5, are occupied by the North Atlantic Deep Water. This water mass originates in high northern latitudes and flows southward. The concentration of inorganic phosphorus increases slowly from values of about 1 mg atom/m³ in the north to about 1.5 mg atoms/m³ at 32°S. Beyond this point the phosphate concentrations increase rapidly as the North Atlantic Deep Water mingles with deep water of antarctic origin, in which the concentrations are more than 2.6 mg

atoms/m³. At depths greater than 4000 m a layer of relatively high phosphate concentration extends northward under the North Atlantic Deep Water owing to the intrusion of deep water from the Antarctic circumpolar region.

The estimated preformed phosphorus content of the North Atlantic Deep Water remains unchanged wherever its characteristic temperatures and salinities are preserved (see Table IV). The fraction of phosphorus of oxidative origin increases gradually from north to south, providing evidence that some regeneration of phosphorus due to biological activity takes place in the deep water as it drifts southward (see Fig. 17c).

From the foregoing discussion it is clear that the vertical distribution of nonconservative properties below any position on the ocean's surface is due primarily to the pattern of horizontal flow of the underlying water masses, and to characteristics which these water masses acquired at the time they were formed near the sea surface. Biological processes modify the concentrations greatly only near the sea surface, and their effects diminish rapidly with depth, as the estimates shown in Table XI indicate.

### b.  The horizontal distribution of nonconservative elements

The deeper water of the Pacific and Indian Oceans is known to contain substantially more phosphate and less oxygen than that of the Atlantic and Arctic Oceans (Graham and Moberg, 1944). This fact is illustrated in Fig. 18,
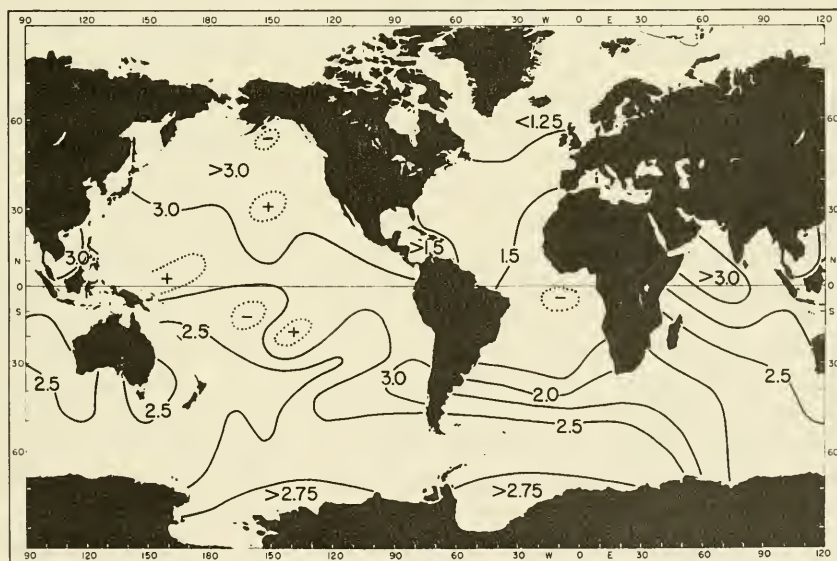


Fig. 18. Distribution of phosphorus at depth of 2000 meters in the oceans of the world. Contour interval, 0.25 mg atom/m³. (From Redfield, 1958. By courtesy of *American Scientist*.)

which shows the distribution of phosphorus at a depth of 2000 m in the oceans of the world. This depth lies below the intermediate layer in which nutrient concentrations are maximal, and the concentrations represent approximately the mean in the great mass of deep water.

In the antarctic circumpolar sea which connects the several oceanic basins the mean concentration of phosphorus is relatively uniform and varies between 2 and 2.5 mg atoms/m³. Proceeding northward in the Pacific and Indian Oceans, it increases gradually to more than 3 mg atoms/m³. In the Atlantic it decreases to less than 1.25 mg atoms/m³ and to about 1 mg atom/m³ in the Arctic basin. Thus the Pacific basin on the whole contains phosphate at about twice the concentration of the Atlantic. If extreme variation is considered, the Arctic waters of the Atlantic contain phosphate in the ratio of 1 : 3.5 when compared to the maximum concentrations present in the North Pacific, and this ratio is increased to 1 : 7 when deep Mediterranean water is compared with the richest part of the Pacific or Indian Oceans.

The differences in the nutrient content of the oceanic basins must depend on the composition of the deep water masses at the time of their origin and their subsequent modification by the balance of biological and physical factors in the course of their drift. This we have seen to be the case for the Antarctic Intermediate Water with its associated minimum oxygen layer, and for the distribution of phosphorus fractions in the North Atlantic Deep Water. The primary cause of the differences found in the deep water of the Pacific and Indian Oceans, in contrast to the Atlantic, quite clearly relates to their respective sources. The deep water of the former originates in the antarctic circumpolar sea (Southern Ocean) and flows northward with an initial concentration of phosphorus of 2 to 2.5 mg atoms/m³. In contrast the North Atlantic Deep Water is formed in the Arctic, where the concentration of phosphorus is 1–1.25 mg atoms/m³. Thus, at their origins, the deep waters of the Pacific and Indian Oceans contain twice as much phosphorus as the Atlantic. To these basic concentrations relatively small additions are made by biological effects.

Superficially, these oceans may be likened to estuaries opening in common on the antarctic circumpolar sea. In the Pacific and Indian Oceans little or no deep water is formed at the northern extremity. In consequence the circulation is estuarine, the surface waters flowing southward to be replaced by an influx of deep water drawn from the Southern Ocean. In the Atlantic the deep water is formed by sinking from the surface in high northern latitudes and is replaced by the flow of surface water northward. From the principles discussed in connection with estuaries, it might be expected that the differential advection, combined with the sinking and decomposition of organic matter at depth, would lead to the accumulation of decomposition products northward in the deep water of the estuarine Pacific and Indian Oceans and southward in that of the anti-estuarine Atlantic. Fig. 18 shows that in the direction of flow in the former oceans the increase in phosphorus concentration, which may be attributed to biological factors, amounts to about 1 mg atom/m³ while in the Atlantic the increase is about half this amount.

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