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ON THE PROPORTIONS OF ORGANIC DERIVATIVES IN SEA WATER AND THEIR RELATION TO THE COMPOSITION OF PLANKTON[1]

ALFRED C. REDFIELD

PROFESSOR OF PHYSIOLOGY, HARVARD UNIVERSITY, AND SENIOR BIOLOGIST, WOODS HOLE OCEANOGRAPHIC INSTITUTION

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> "Chemical analysis shows that the animal and plant body is mainly built up from the four elements, nitrogen, carbon, hydrogen, and oxygen. Added to these are the metals, sodium, potassium and iron, and the non-metals, chlorine, sulphur and phosphorus. Calcium or silicon are also invariably present as the bases of calcareous or siliceous skeletons. All these, with some others, are indispensable constituents of the organic body, and in an exhaustive study of the cycle of matter from the living to the non-living phases, and *vice versa*, we should have to trace the course of each." JAMES JOHNSTONE, "Conditions of Life in the Sea," p. 273. 1908.

IT is now well recognized that the growth of plankton in the surface layers of the sea is limited in part by the quantities of phosphate and nitrate available for their use and that the changes in the relative quantities of certain substances in sea water are determined in their relative proportions by biological activity. When it is considered that the synthetic processes leading to the development of organic matter are limited to the surface layers of the sea in which photosynthesis can take place, it becomes evident that the chemical changes which occur in the water below this zone must arise chiefly from the disintegration of organic matter. In so far as this disintegration goes to completion, the changes in the derived inorganic constituents of sea water must depend strictly upon the quantity and composition of the organic matter which is being decomposed. This is true quite irrespective of the agencies of decomposition, be they bacterial action,

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the autolytic enzymes of the original tissues themselves, or the metabolic processes of deep sea animals which utilize the organic matter as food. Thus, in the decomposition of a given quantity of organic matter, the quantity of oxygen consumed must be determined by the quantity of carbon, nitrogen, hydrogen, sulphur, and phosphorus to be oxidized, and the relative changes in the quantity of oxygen, nitrate, phosphate, carbonate, and sulfate must depend exactly on the elementary composition of the plankton.

It has seemed possible that the chemical composition of the population of the seas may be sufficiently uniform, and the contributions of the substances in question from other sources sufficiently limited, to permit the discovery of relations between their concentration in sea water which would be serviceable in the study of oceanic problems.

An examination of the data on nitrate and phosphate in the water of various seas secured by the "Dana" in the course of the Carlsberg Foundation's oceanographical expeditions around the world in 1928-1929 proved encouraging from this point of view. Thanks to the collaboration of Dr. Norris Rakestraw a more complete set of data, showing the relative concentrations of oxygen, nitrate, phosphate, and carbonate at different depths, was obtained from a number of stations made by the "Atlantis" in the deep waters of the western Atlantic Ocean. Six stations were occupied in the Sargasso Sea between Bermuda and the southern coast of the United States. In this region water samples were obtained at successive depths from at least three distinct water masses: (1) the surface water in intimate relation with the atmosphere and in which photosynthetic activity has reduced the nutrient substances to a minimum; (2) the layer of intermediate depth—most clearly marked at 700 meters and characterized by minimal oxygen concentrations and high concentrations in organic derivatives; and (3) the deep water of polar origin of relatively uniform composition below 1,500 meters, which has also been the seat of organic decomposition. Between these layers lie zones in which the water has intermediate characters due to the mixing of the primary water masses.

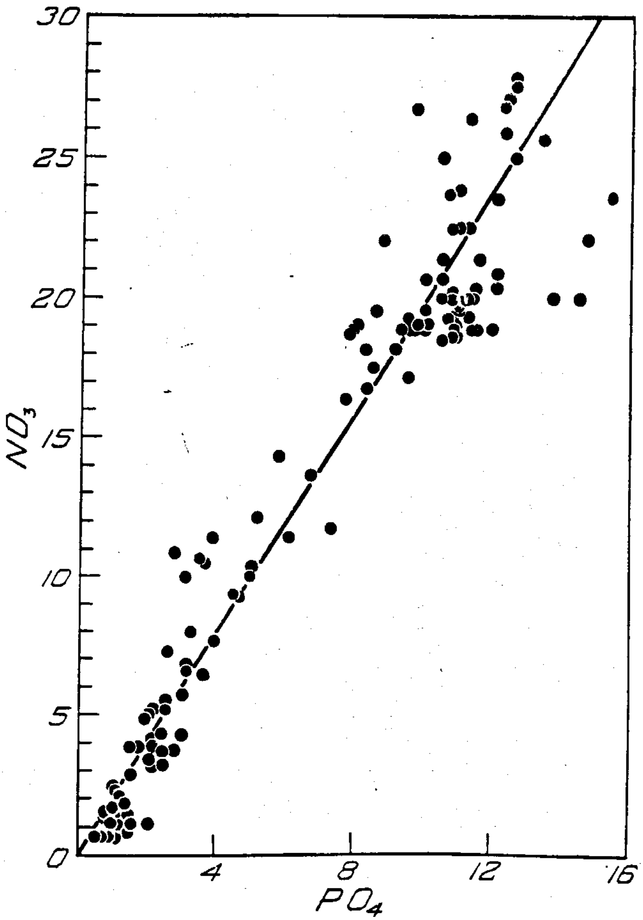
The characteristics of the water at the various stations occupied are unusually uniform both as regards temperature and salinity and the concentrations of the biologically significant substances. A seventh station was occupied in the western edge of the Gulf Stream outside the Gulf of Maine. Here the layer characterized by minimal oxygen concentration is nearer the surface and the deep cold water lies within 500 meters of the surface. The numbers and positions of the stations are given in Table I. The station data will be published in the Bulletin Hydrographique of the International Council for the Exploration of the Sea.

TABLE I

Ship	Station No.	Position	Date
" Atlantis "	1463	34°02′ N. 68°15′ W.	February 8, 1933
"	1465	31°25′ N. 66°30′ W.	" 13, 1933
"	1467	30°30′ N. 68°30′ W.	" 14, 1933
"	1469	29°26′ N. 70°42′ W.	" 15, 1933
"	1472	27°56′ N. 73°53′ W.	" 17, 1933
"	1475	26°49′ N. 76°09′ W.	" 19, 1933
"	1677	40°53′ N. 66°21′ W.	June 25, 1933

From the data for oxygen content and temperature, the amount of oxygen which has disappeared from the water since its exposure to the atmosphere has been estimated, assuming that the water was saturated at that time and had the temperature which characterized it *in situ*. While neither of these assumptions are probably strictly correct, they provide the only definite method available to arrive at the amount of oxygen utilized at the various depths. From the data for pH as measured at the temperature of the ship's laboratory the total carbonate content, Σco_2, of the water samples was estimated with the aid of the tables provided by Buch, Harvey, Wattenberg, and Gripenberg (1932). These, together with the direct analyses of nitrate and phosphate, give a measure of the principal products formed by the complete oxidation of the carbon, nitrogen, and phosphorus of the biological population, together with the amount of dissolved oxygen which has disappeared in the process.

FIG. 1.



Correlation between concentrations of nitrate and phosphate in the waters of western Atlantic Ocean. Ordinate, concentration of nitrate, units 10^{-3} millimols per liter; abscissa, concentration of phosphate, units 10^{-4} millimols per liter. The line represents a ratio of $\triangle N : \triangle P = 20 : 1$ milligram atoms.

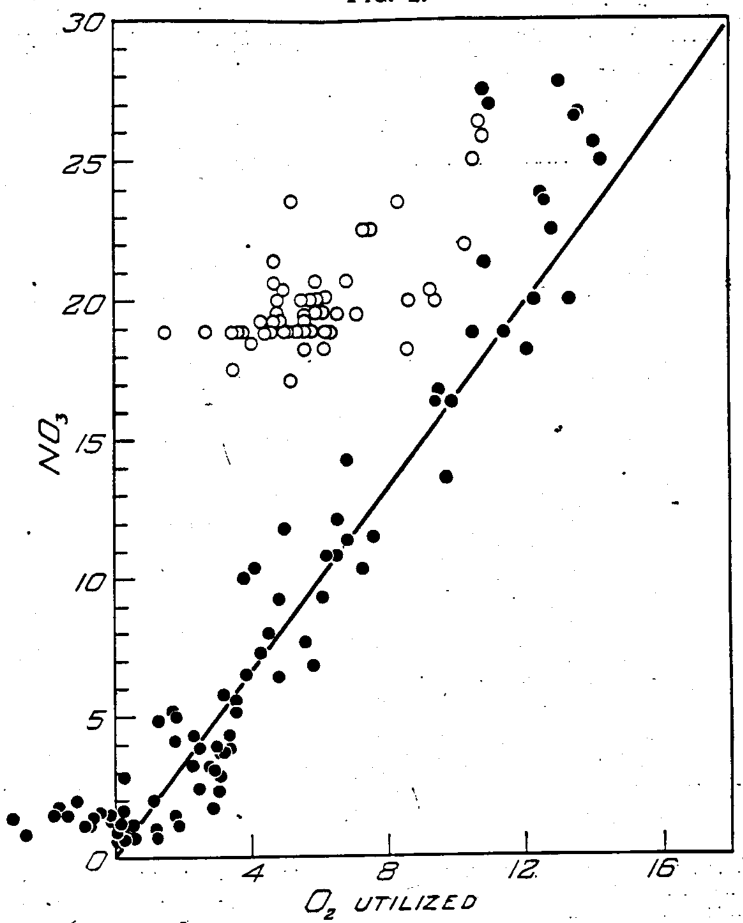
The data obtained for the water masses underlying the various stations are plotted in Figs. 1, 2 and 3. In these diagrams the concentration of nitrate characterizing each water sample is plotted against one of the other constituents in order to show whether the concentrations of these constituents vary in a correlated fashion. The concentrations are expressed in milligram atoms or in millimols per liter, as suggested by Cooper (1933), since this notation yields values proportional to the number of atoms of nitrogen, carbon, and phosphorus present in the constituents in question.

To consider first the relation between nitrate and phosphate concentration in the water samples, shown in Fig. 1, it is apparent that a very close correlation exists. Any gain or loss in nitrate content observed in comparing one water sample with another is accompanied by a strictly proportional gain or loss in phosphate content. The water samples in which the concentrations were low were from near the surface; the quantities of nitrate and phosphate increase with increasing depth. The straight line drawn through the points describing the nitrate-phosphate correlation has the slope demanded if, for every three grams of nitrogen added to or subtracted from the water, one gram of PO_4 (or $\frac{3}{4}$ gram of P_2O_5) also made its appearance or disappearance. This corresponds to a ratio of 20 atoms of nitrogen to 1 atom of phosphorus. On the assumption that these changes are due solely to the decomposition or synthesis of organic matter, these ratios may be taken to reflect the proportions of nitrogen and phosphorus in the plankton community taken as a whole.

The correlation between the gain in concentration of nitrate and the loss in concentration of oxygen, as shown in Fig. 2, is almost equally good for the water samples collected from depths less than 1,000 meters in the Sargasso Sea, and 400 meters in the Gulf Stream,—depths which mark the transition between the intermediate layer of low oxygen content and the deeper layer of cold water. The data for greater depths, indicated by open circles in the figure, depart strongly from the expected correlation—an anomaly to which we will return. Above these depths, however, the variation of nitrate concentration and oxygen utilization is in the proportion of 1 millimol of nitrate to 6 millimols of oxygen.

The correlation between the concentrations of nitrate and carbonate shown in Fig. 3 is less precise owing to the greater variation in the carbonate measurements. This is due to the fact that the total variation in carbonate content is

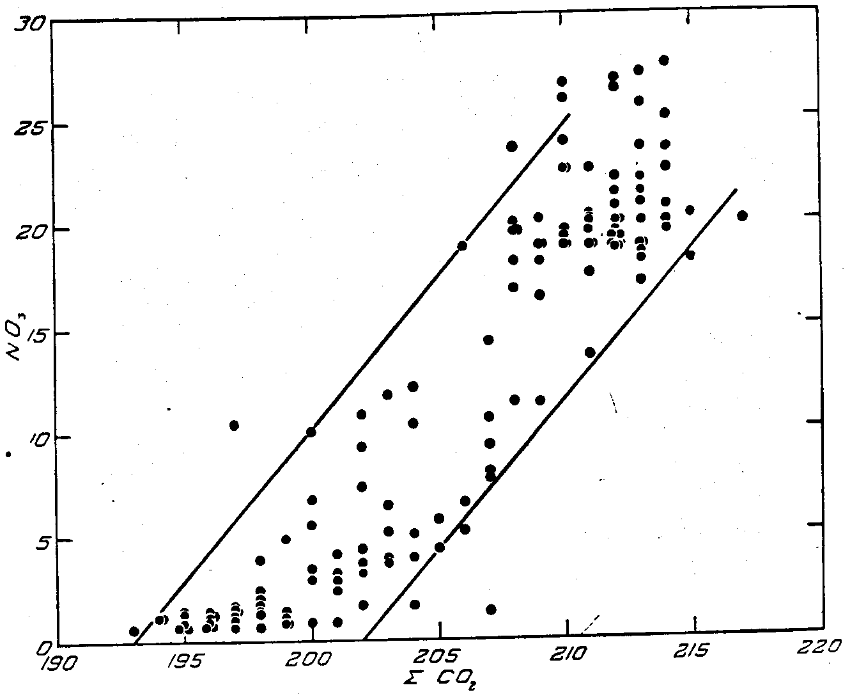
FIG. 2.



Correlation between concentration of nitrate and amount of oxygen utilized in waters of western Atlantic Ocean. Ordinate, concentration of nitrate, units 10^{-3} millimols per liter. The line represents a ratio of oxygen used : $\Delta N = 6 : 1$. Points representing stations from a depth below 400 meters in the Gulf Stream and below 1,000 meters in the Sargasso Sea are represented by open circles.

only a small part of the amount present, to the indirect nature of the method of estimating carbonate, to possible variations in buffer capacity which have been neglected in these estimations, and to exchange in CO_2 between air and the surface waters. Nevertheless, taking the data as a whole, it is clear that carbonate content is correlated with nitrate content. The envelopes drawn about the points in Fig. 3 have a slope corresponding to a ratio of 1 millimol of nitrate to 7 of carbonate. The value of this ratio is not as securely established as that relating nitrate to phosphate and to oxygen utilization.

FIG. 3.



Correlation between concentration of nitrate and total carbonate in waters of western Atlantic Ocean. Ordinate, concentration of nitrate, units 10^{-3} millimols per liter; abscissa, concentration of carbonate, units 10^{-2} millimols per liter. The slope of the envelopes corresponds to a ratio of $\triangle C : \triangle N = 7 : 1$ milligram atoms.

If we take the ratio of change in nitrate to carbonate to be 7 : 1 and that of nitrate to oxygen utilization to be 6 : 1, it follows that the ratio of carbonate to oxygen is 7 : 6 or 1·17 : 1. This ratio is close to that characterizing photosynthetic processes and the decomposition of the principal classes of organic compounds. Its variation from the theoretical is not greater than the uncertainty of the carbonate measurements.

It appears from the foregoing data that, with the exception of the anomaly quoted in connection with the oxygen content of the deep water, the concentrations of nitrate, phosphate, and carbonate in samples of oceanic sea water of widely different origin vary in such a way as might be expected if the different samples contained the products of the complete disintegration and oxidation of organic material of similar composition, and that they differ only in the quantity of such material which has arrived at and remains in this degree of decomposition. Furthermore, the loss in oxygen agrees approximately with that to be expected from the quantity of carbonate gained. The proportions of carbon, nitrogen and phosphorus present in the organic material from which the carbonate, nitrate, and phosphate may be supposed to be derived are approximately 140 : 20 : 1 atoms or 100 : 16·7 : 1·85 grams.[1]

It is pertinent to inquire how these proportions agree with those actually found in various members of the plankton community. Naturally each kind of organism is found to have a characteristic composition different from that of other kinds, and unfortunately no adequate means of obtaining a truly representative sample of the entire population is available. However, by considering the composition of the plankton yielded by various kinds of haul, some idea may be obtained as to the validity of the foregoing considerations.

A number of elementary analyses of various kinds of plankton are recorded in Table II. They show that the proportions of carbon, nitrogen, and phosphorus as calculated from the carbonate, nitrate, and phosphate composition of the sea are not greatly different from those observed in

1. This comparison presupposes that nitrate nitrogen may be regarded as the sole source of nitrogen available to the plankton. Strictly speaking, this is not the case. Of other sources of nitrogen, nitrite is known to occur in oceanic waters in concentrations too small to be significant in computations of this sort. Professor Krogh has recently made observations on the nitrogen present as ammonia and as organic compounds in the deeper waters of the western Atlantic. His results indicate that ammonia is present in only small quantities. Organic compounds in the sea water contain relatively large amounts of nitrogen, but as the concentration of these does not vary greatly from surface to bottom, this source of nitrogen does not appear to be readily available for conversion into living matter.

various plankton, and on the whole the latter differ among themselves much more than their average differs from the calculated ratios.

TABLE II

Proportions of carbon, nitrogen, and phosphorus in various samples of plankton.

Sample	Parts by Weight		
	Carbon	Nitrogen	Phosphorus
Mixed copepods from Buzzards Bay ..	100	21	1·98
Centropages typicus, Gulf of Maine ..	100	25·6	1·06
Calanus finmarchicus, Gulf of Maine ..	100	13·4	2·04
Calanus finmarchicus, Gulf of Maine ..	100	15·8	2·26
Diatoms—Bay of Fundy, almost entirely *Thalassiosira nordenskiöldi*.	100	18·2	1·36
Diatoms—Off Nova Scotia coast—17 species of somewhat the same abundance.	100	15·6	2·26
Peridinians—Meyer (1914)	100	13·2	2·2
Chiefly peridinians—average of samples No. 1, 2, 3, 4, of Brandt (1898).	100	8·1	—
Chiefly diatoms—average of samples No. 6 and 7, Brandt (1898).	100	12·4	—
Chiefly copepods—average of samples No. 8 and 9, Brandt (1898).	100	15·3	—
Mixed plankton—sample no. 10, Brandt (1898). ..	100	11·3	—
Average all samples	100	15·4	1·88
Estimated from analyses of sea water ..	100	16·7	1·85

In this connection it is of interest to note that Braarud and Føyn (1930) have observed that each cell of *Chlamydomonas* removes $2{\cdot}98 \times 10^{-12}$ gr. NO_3 nitrogen and $0{\cdot}98 \times 10^{-12}$ gr. P_2O_5 from the sea water in which it grows. Here we see in a laboratory experiment an organism modifying the concentration of nitrate and phosphate in the medium in a ratio ($\Delta N : \Delta P = 15 : 1$) not very different from that observed in the oceans as a whole.

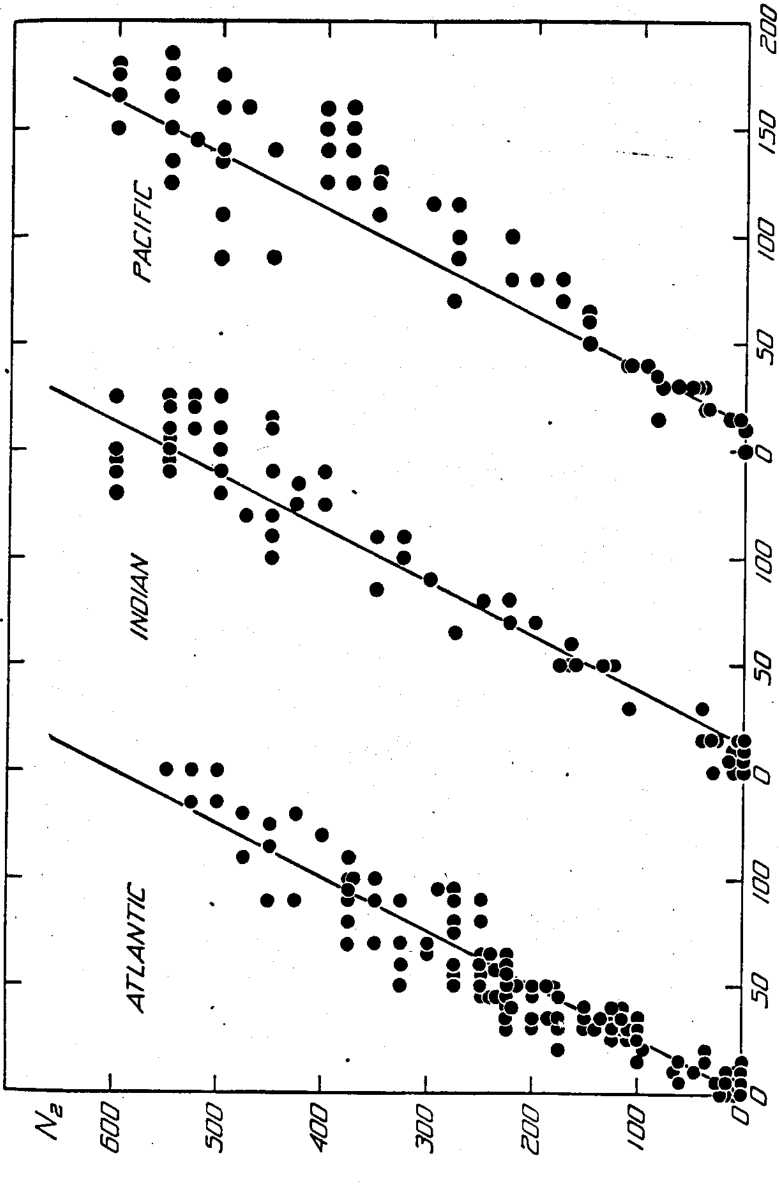


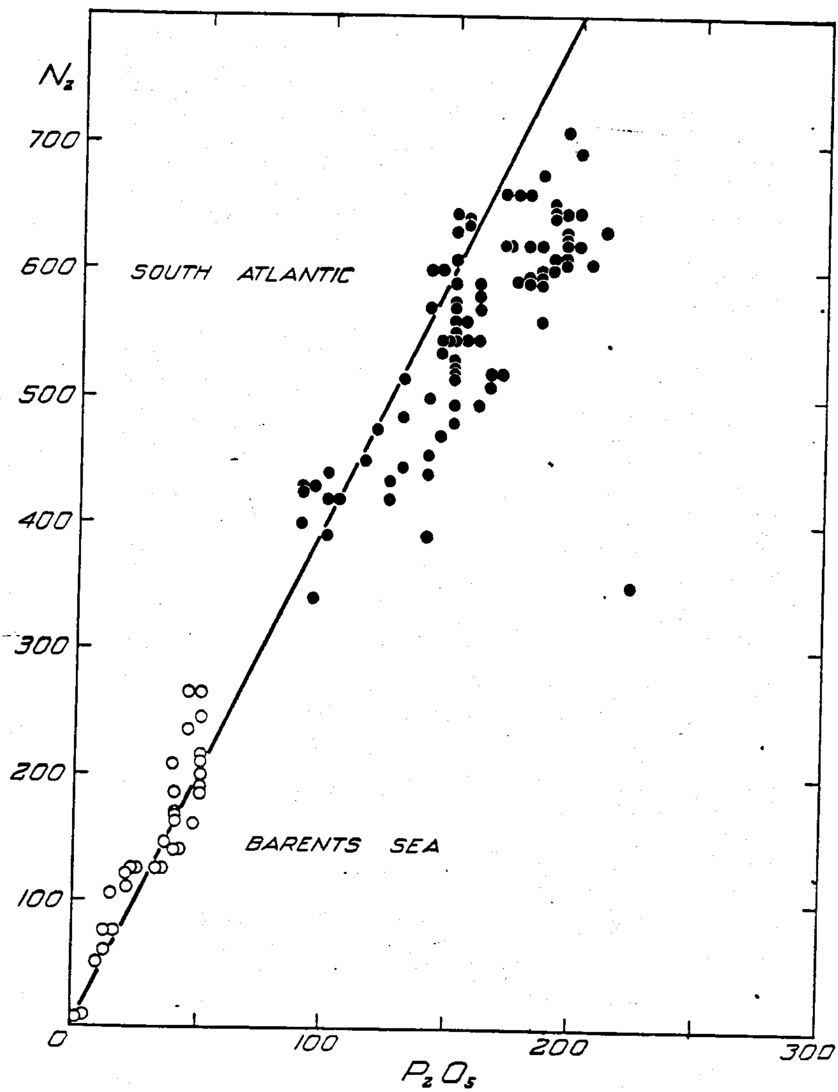
FIG. 4. Correlation between concentration of nitrate and phosphate in waters of the Atlantic, Indian, and Pacific Oceans. Data of Thomsen. Ordinate, concentration of nitrate nitrogen, units milligrams of nitrogen per cubic meter; abscissa, concentration of phosphate, units milligrams P_2O_5 per cubic meter. The lines correspond to a ratio of $\Delta N : \Delta P = 20 : 1$ milligram atoms.

The establishment of a general, if approximate, relation between the concentration of the various organic derivatives in sea water and the chemical composition of plankton would provide a valuable tool in the analysis of many oceanographic problems. Observations made at a single group of stations such as that reported cannot be considered to establish such a relation, though the results doubtless are encouraging. The data collected by the "Dana" (Thomsen, H., 1931) enable the generalization to be tested more widely—at least so far as nitrate and phosphate are concerned, for the measurements were made in the most diverse regions by the same investigators using uniform methods. In Fig. 4 I have plotted the simultaneous measurements of phosphate and nitrate obtained by the "Dana" at all stations and depths in the three oceans traversed. No attempt has been made to separate the data obtained at different stations within each ocean, for, as in the case of the observations collected by the "Atlantis," the water underlying a given station at various depths has quite different origins. It is apparent that a definite correlation exists between the quantity of nitrate and phosphate occurring in any sample. The proportions between these constituents, as indicated by the lines drawn through the points, are essentially the same in the three oceans visited by the "Dana," and in the Atlantic stations occupied by the "Atlantis".

The stations occupied by the "Dana" and the "Atlantis" were all in temperate or tropical latitudes. In Fig. 5 are plotted data selected at random from the stations in Barents Sea, 70°-76° N, reported by Kreps and Verjbinskaya (1932) and from stations in the south Atlantic Ocean between 55° and 62° S. published by Ruud (1930). Here the proportions between phosphate and nitrate nitrogen vary in the same ratio as in the more temperate waters found at low latitudes, though the quantities of these constituents are much lower in the north than in the south.

These results indicate that the relations observed in the western Atlantic may be of general application, at least so far as the oceanic waters are concerned. By inference they

FIG. 5.



Correlation between concentration of nitrate and phosphate in waters of Barents Sea (data of Kreps and Verjbinskaya) and south Atlantic (data of Ruud, from stations between 55°-62° S., 0°-40° W.). Ordinate, concentration of nitrate nitrogen, units milligrams of nitrogen per cubic meter, abscissa, concentration of phosphate, units milligrams P_2O_5 per cubic meter. The line corresponds to a ratio of Δ N : Δ P= 20 : 1 milligram atoms.

suggest a remarkable uniformity in the chemical composition of the planktonic communities occupying the various oceans. It is scarcely to be expected that these relations will hold in water bodies of limited extent, where local conditions such as the proximity of land, the inflow of rivers, and the peculiarities of a local flora and fauna may alter the picture. Examination of data for such regions as the Baltic (Buch, 1932), the Norwegian fjords (Braarud and Klem, 1931), the Denmark strait (Bohnecke, Føyn, and Wattenberg, 1932), indicate that this is the case. In the English Channel the ratio in the variation in nitrate and phosphate in the surface water with season was about 2 mg. nitrate nitrogen to 1 mg. P_2O_5 ($\Delta N : \Delta P$ = 10 : 1 mg. atoms) according to data published by Harvey (1928). Cooper (1933) has shown that in this region where active regeneration takes place, variation in the ratio of nitrate to phosphate is attributable to the longer time required to complete the regeneration of nitrate from decomposing albuminous matter. In the Gulf of Maine data recently secured by Dr. Rakestraw indicate that the ratio of the variation of nitrate and phosphate with depth is lower and more variable than in the open ocean outside the Gulf. However, the value of a generalization such as that suggested by the data from the open oceans lies in the fact that it makes clearer the exact nature of the anomalous conditions found in local situations and thus defines more precisely the questions which must be answered before the local situation is understood. This point can be illustrated by a consideration of the anomaly in the concentration of oxygen which is present in the data secured by the "Atlantis".

Below 1,000 meters there is less oxygen removed from the water than is to be expected from the amount of nitrate present. This expectation, however, is based on the assumption that the nitrate has all appeared as the result of decomposition of organic matter after the water was removed from contact with the atmosphere. The observations suggest that the deeper water of the Atlantic contained a considerable amount of nitrate at the time it sank. Actually one must assume most of the samples from the greater depths to have contained about 140 mg. nitrate nitrogen per cubic meter (equivalent to 10×10^{-3} mg. atoms per liter) at the time they became separated from the atmosphere. Now the water at these depths is thought to originate at high latitudes where nutrient substances are commonly observed at high concentrations in the surface water. Thus Kreps and Verjbinskaya (1932) observed nitrate nitrogen concentrations in the surface water of Barents Sea of 128 to 200 mg. per cubic meter in March and April, and Bohnecke, Føyn and Wattenberg (1932) record values of 125 mg. per cubic meter in the mixed water of the polar front east of Greenland. The values of nitrate nitrogen recorded by Ruud (1930) in the surface waters of the Antarctic exceed 600 mg. per cubic meter in many cases. Thus the history of the deep water suggested in explanation of the anomalous character of the ratios in which oxygen enters is confirmed by independent observations.

One fact of great general interest emerges from an examination of the data recorded in Figs. 1 and 4. It may be noted that as the quantities of nitrate and phosphate diminish, as they do as one approaches the surface layers of the sea, they diminish simultaneously in such proportions that no great excess of one element is left when the supply of the other has been exhausted. In 1926 Harvey wrote: "It is a remarkable fact that plant growth should be able to strip sea water of both nitrates and phosphates, and that in the English Channel the store of these nutrient salts, formed during autumn and winter, should be used up at about the same time." The relation noted by Harvey is thus of much wider application than he could have known at that time. It appears to mean that the relative quantities of nitrate and phosphate occurring in the oceans of the world are just those which are required for the composition of the animals and plants which live in the sea. That two compounds of such great importance in the synthesis of living matter are so exactly balanced in the marine environment is a unique fact and one which calls for some explanation, if it is not to be regarded as a mere coincidence. It is as though the seas had been created and populated with animals and plants and all of the nitrate and phosphate which the water contains had been derived from the decomposition of this original population.

Professor Huntsman has suggested to me that the correspondence between the proportions of phosphate and nitrate in the seas and the statistical composition of living matter may be due to the fact that, although different members of the plankton community have different requirements in regard to phosphorus and nitrogen, the numbers of each of these members may depend on the relative availability of the substances they most need. Thus a population requiring relatively much nitrogen may thrive until the nitrate supply has been depleted, when it will be replaced by a population requiring relatively more phosphorus. By the balancing of such communities the ratio of the elements in the plankton as a whole might come to reflect the ratio of the nutrient substances in sea water rather closely.

Another explanation of the correspondence between the proportions of nitrate and phosphate in the sea and the composition of living matter may be sought in the activities of those bacteria which form nitrogenous compounds from atmospheric nitrogen or liberate nitrogen in the course of the decomposition of organic matter. In the case of the nitrogen-fixing bacterium, *Azotobacter*, it is known that for every unit of nitrogen fixed or assimilated and synthesized into microbial protein, about one half a unit of P_2O_5 must be available. The physiological activity of such organisms must tend to bring the relative proportions of organic nitrogen and phosphorus toward the ratio in which these substances occur in the bacterial protoplasm. Comparable studies upon the physiology of the denitrifying bacteria do not appear to have been made. It is evident, however, that the composition of these organisms must be more or less fixed in regard to their relative phosphorus and nitrogen content and that when living in an environment containing an excess of nitrate, considered in relation to phosphate, the growth and assimilation of the organisms may continually tend to bring the proportions of nitrogen and phosphorus nearer to that characteristic of their own substances. It would appear inevitable that in a world populated by organisms of these two types the relative proportion of phosphate and nitrate must tend to approach that characteristic of protoplasm in general and that, given time enough and freedom from systematic disturbing influences, a relationship between phosphate and nitrate such as that observed to occur in the sea must inevitably have arisen. On this view the quantity of nitrate in the sea may be regulated by biological agencies and its absolute value determined by the quantity of phosphate present.

These explanations are in no wise mutually exclusive; nor do they exclude other possibilities. Whatever its explanation, the correspondence between the quantities of biologically available nitrogen and phosphorus in the sea and the proportions in which they are utilized by the plankton is a phenomenon of the greatest interest.

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