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# THE ANNUAL CYCLE OF PHOSPHORUS AND NITROGEN IN NEW ENGLAND COASTAL WATERS

By

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## ABSTRACT

Distributions of phosphorus and nitrogen in New England coastal waters at various times of year are described. In surface waters the nitrate-nitrogen content is sometimes completely exhausted, even though small concentrations (0.2–0.5 $\mu$g-at/l) of phosphorus are always available. The ratio of concentrations by atoms, N:P, varies in surface waters from maximum values of about 10:1 to values approaching zero as the nitrate is exhausted. However, the ratio of change, $\Delta$N:$\Delta$P, is approximately 15:1 except during summer months when it decreases. During summer, vertical mixing supplies nitrogen and phosphorus to the euphotic zone at higher ratios than the ratios of concentration in the euphotic zone. In deep offshore waters the N:P ratio is about 12.5:1, and no significant seasonal variation in either the phosphorus or nitrate concentration at the oxygen minimum-nutrient maximum layer could be detected.

## INTRODUCTION

Phosphorus and nitrogen concentrations in surface waters of the sea decrease as a result of utilization by phytoplankton but are replenished by decomposition of organic matter *in situ* and by mixing, which brings supplies back to the surface from richer, deeper waters. The concentration of these two elements change in a correlated way. Harvey (1926) commented upon the remarkable fact that during the spring outburst of phytoplankton in the English Channel both nitrogen and phosphorus were reduced simultaneously to negligible concentrations. Redfield (1934) showed that this observation of Harvey's was generally applicable to various oceanic bodies of water and that the ratio of change of concentration was

similar in all of the waters studied. When the phosphorus concentration values are corrected for salt error, as suggested by Cooper (1938), these elements vary in a ratio of 15 atoms of nitrogen to one of phosphorus. As shown by Redfield (1934) and Fleming (1940), the ratio in which the elements vary in sea water is closely comparable to the concentration found within living marine organisms.

When the ratio of concentrations in a single sample of water is calculated, it is frequently found that this has a different value from the 15:1 ratio of change. Cooper (1937, 1938) termed the difference between the 15:1 ratio and the observed ratio the anomaly of the N:P ratio; and he pointed out also that this anomaly is greatest in confined seas such as the Mediterranean. Phifer and Thompson (1937) showed that this ratio had a mean annual value in San Juan Channel of 12.7 but that it varied throughout the year from 11.9 to 13.6. Even more extreme values for the N:P ratio were found by Riley and Conover (1956) in Long Island Sound. There, on a seasonal cycle, the ratio varied from nearly zero to 8:1. The extremely low values reflect the fact that phytoplankton were able to remove practically all of the nitrogen from the water even though there was a small residual concentration of phosphorus (about 0.5 $\mu$g-at/l).

Over the last two years, during investigations in coastal waters off New England at stations shown in Fig. 1, concentrations of nitrogen and phosphorus have been measured on each cruise. Even in these exposed coastal waters the ratio of concentrations in surface waters is low, and, as in Long Island Sound, values fluctuate from near zero in the summertime to 5–10 in midwinter. In spite of these low ratios of *concentration*, the ratio of *change* of nitrogen and phosphorus in the surface waters corresponds closely to a ratio of 15:1, excepting changes in surface waters in summertime.

## METHODS

The cruises which have been made to the area indicated in Fig. 1 are listed in Table I. Aliquots of samples taken from various depths were frozen immediately in 500 ml plastic bottles at a temperature of about −15° C. Duplicate analyses of fresh samples at sea and of frozen samples have confirmed the fact that frozen samples give satisfactory results for inorganic phosphorus, nitrate, nitrite and
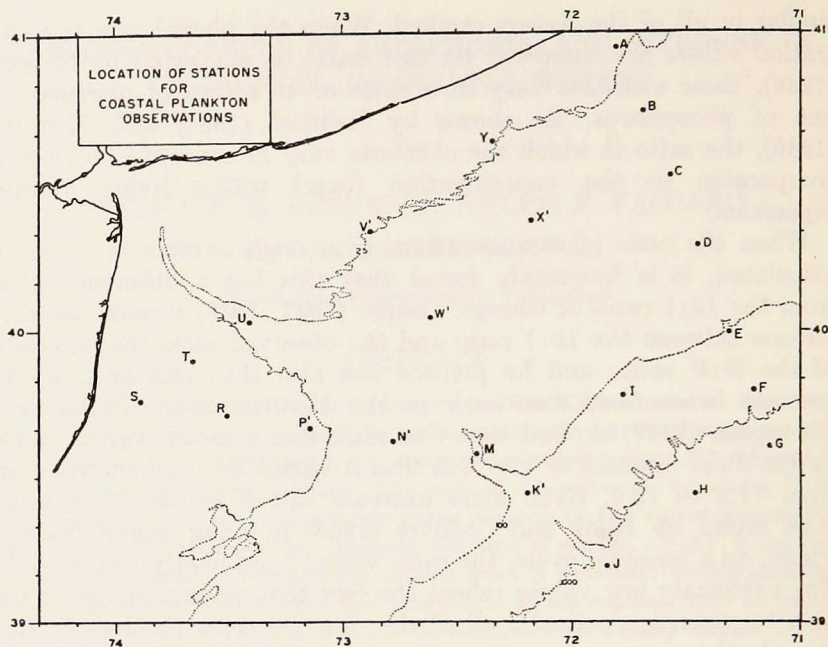
Figure 1. Location of stations occupied during coastal cruises, September 1956–1958.

ammonia nitrogen and silicate analyses for periods of at least a month of frozen storage.

The method for inorganic phosphorus determination has been described by Wattenberg (1937), Robinson and Thompson (1948), and Wooster and Rakestraw (1951). The color developed was measured in a photoelectric colorimeter (Ford, 1950), using a red light filter (Corning 2408) and absorption cells of 29 and 8 cm light path for concentrations of less than 1.0 and more than 1.0 $\mu$g-at P/l, respectively. The reproducibility of the method was discussed by Ketchum, *et al.* (1955), who have given analytical variations of $\pm 7 \, ^0/_0$ for the low concentrations in the 29 cm tube and of $\pm 9 \, ^0/_0$ for the higher concentrations in the 8 cm tube. Total phosphorus was determined by the method described by Harvey (1948) as modified by Ketchum, *et al.* (1955).

The nitrate concentration was determined by hydrazine reduction according to the method of Mullin and Riley (1955). The nitrite produced was reacted with alpha napthylamine, and the concen-

TABLE I. Dates of Cruises Made to the New England Coastal Waters

| Vessel and Cruise No. | Date |
|---|---|
| ATLANTIS, 227 | 10–15 September 1956 |
| CRAWFORD, 8 | 28 November–3 December 1956 |
| BEAR, 159 | 13–17 February 1957 |
| BEAR, 162 | 21–25 March 1957 |
| BEAR, 165 | 29 April–3 May 1957 |
| CRAWFORD, 13 | 10–20 July 1957 |
| BEAR, 174 | 16–20 September 1957 |
| BEAR, 179 | 18–23 November 1957 |
| BEAR, 181 | 21–27 January 1958 |
| BEAR, 183 | 6–10 March 1958 |
| BEAR, 185 | 12–16 May 1958 |
| CRAWFORD, 19 | 7–19 July 1958 |
| BEAR, 195 | 5–8 September 1958 |

TABLE II. Reproducibility of the Determination of Nitrate-Nitrogen based on Standardization Data. Analyses were made in a Beckman DU Spectrophotometer at a Wavelength of 524 $m\mu$

| Concentration Range ($\mu g$-$at/l$) | Cell Length (cm) | No. of Standards | Calibration Factor | Standard (units) | Deviation ($^0/_0$) |
|---|---|---|---|---|---|
| 0– 3.75 | 10 | 25 | 5.85 | .75 | 12.9 |
| 1.0–50 | 1 | 67 | 53.2 | 7.38 | 13.9 |

tration was then determined in a Beckman DU Spectrophotometer using a wavelength of 520 $m\mu$. The result will be referred to in this paper as nitrate-nitrogen, but both nitrate and nitrite-nitrogen are included in the analysis. The concentration of nitrite-nitrogen, which has also been determined for these samples, is generally less than 10 $^0/_0$ of the nitrate plus nitrite-nitrogen.

The reproducibility of the method has been evaluated by comparing standard solutions at various concentrations. Standards were prepared by adding known amounts of nitrate to nitrate-free sea water and, after correcting for reagent blank and for the quantity of nitrate-nitrogen in the sea water used, the factor relating optical density of the photometer with concentration was calculated for each sample. For low concentrations ($< 4 \mu g$-$at/l$) a 10 cm cell has been used; the ratio of concentration to optical density is $5.85\pm.75$, or a variability of about 13 $^0/_0$ (see Table II). For samples containing

more nitrogen than this, a one centimeter cell was used; an average factor of $53.2 \pm 7.38$ was found for these concentrations, indicating a variability of about $14 \, ^0/_0$.

Total nitrogen is the sum of the concentrations of nitrate and nitrite-nitrogen, ammonia nitrogen and amine-amide nitrogen. Ammonia nitrogen has been determined by the method of Riley (1953). Amine-amide nitrogen has been determined by micro-Kjeldahl digestion according to Pregl (1946) followed by distillation of the ammonia according to Riley (1953).

## THE ANNUAL CYCLE IN SURFACE WATERS

Variations in the nitrogen and phosphorus concentrations and in the N:P ratio for surface waters in Sections A-G-J (see Fig. 1) are shown in Figs. 2, 3 and 4. Five of the 13 cruises have been selected as representing adequately the seasonal variations. The density structure for the same five cruises is presented in Fig. 5 for comparison. In July and September, when the density stratification is greatest, the concentration of both nutrients in the surface layers is small, the lowest values being observed during the September cruises. In waters below 100 m at these times there is considerable parallelism not only between the distribution of the two nutrients but between each of these and the distribution of density. Thus, for example, there is always present just off the Continental Shelf, at St. E, a high concentration of nutrients in the same area; this shows as an upward bulge in the density contours. In contrast, lower values are found at Sts. G and H where comparable density contours are at greater depths than at St. E.

By November the density stratification has decreased markedly and surface concentrations of nitrogen and phosphorus have increased. Over the Continental Shelf, the increases in waters of less than 50 m are accompanied by decreases in waters below 50 m, indicating that much of the observed change may be due to mixing of the water column rather than to regeneration of nutrients *in situ*. Beyond the edge of the Continental Shelf, however, the nitrogen and phosphorus content has increased below 100 m of depth, indicating that mixing here has extended to greater depths.

In January, waters over the Shelf are vertically homogeneous in density, and the nutrient concentrations, though much less than those found in the deeper offshore waters, have reached maximum

values for the year. By May, stratification in the water column has been intensified, both by freshening of the inshore water (at St. A) and by warming of the surface layers. The surface nitrate values at this time are almost all less than 1 $\mu$g-at/l and the surface phosphorus concentrations less than 0.5 $\mu$g-at/l—conditions which represent closely the concentrations observed in July and September.

The ratio of N:P (in atoms) in the surface waters, shown in Fig. 4, is consistently below 5 in July, September and November, with minimum values of zero in some of the September observations indicating complete exhaustion of the nitrate. By January the ratio of concentration has increased to values generally above 5 in surface waters over the Continental Shelf and commonly above 10 at the offshore stations. By May, when the growth of plants has again depleted the supply of nutrients, the ratio of concentration in surface waters is again less than 5.

The fact that the growth of plants in surface waters over the Shelf reduces the N:P ratio implies that plants are assimilating these elements in a higher ratio than the ratio of concentration which is presented to them. In regard to the constancy of the ratio of change, Redfield (1934) commented that "it appears to mean that the relative quantities of nitrate and phosphate occurring in the oceans of the world are just those that are required for the composition of the animals and plants which live in the sea". In the case of the coastal waters of New England, these elements are presented to the population in quite a different ratio from the *normal* 15:1 ratio. It is pertinent to inquire, therefore, whether these coastal populations have become adapted to these low ratios and utilize these elements in a ratio comparable to the ratio of concentration in the water.

An evaluation of the ratio by which biological populations modify the concentrations of phosphorus and nitrogen can be obtained from our data. This is done by plotting one against the other so that the slope of the line joining the high and low concentrations represents the ratio of *change* rather than that of concentration which has been discussed so far. This has been done for all of the 10-m water samples obtained on the 13 cruises at stations of intermediate depth over the Continental Shelf (B, C and D). The results are shown in Fig. 6. The slope of the envelope which encloses the majority of the points corresponds to the *normal* ratio of *change* of 15 atoms of nitrogen to one of phosphorus. The shaded area
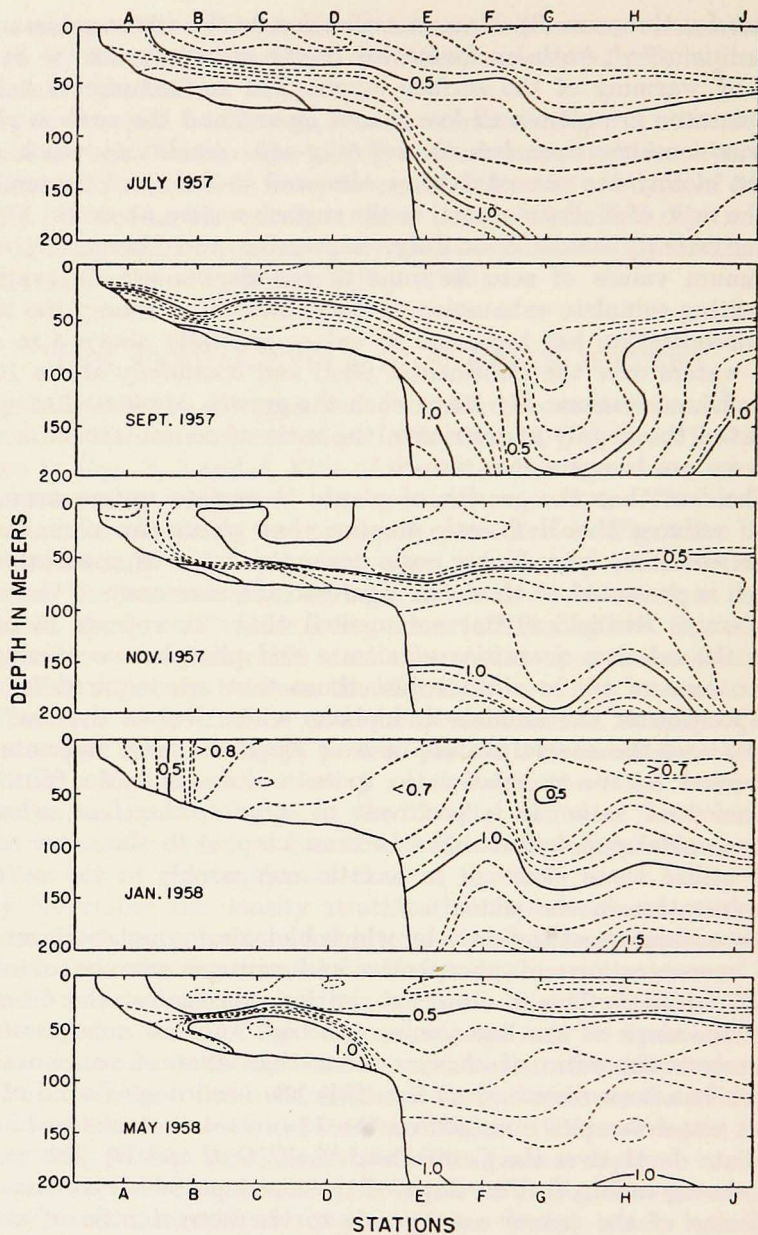
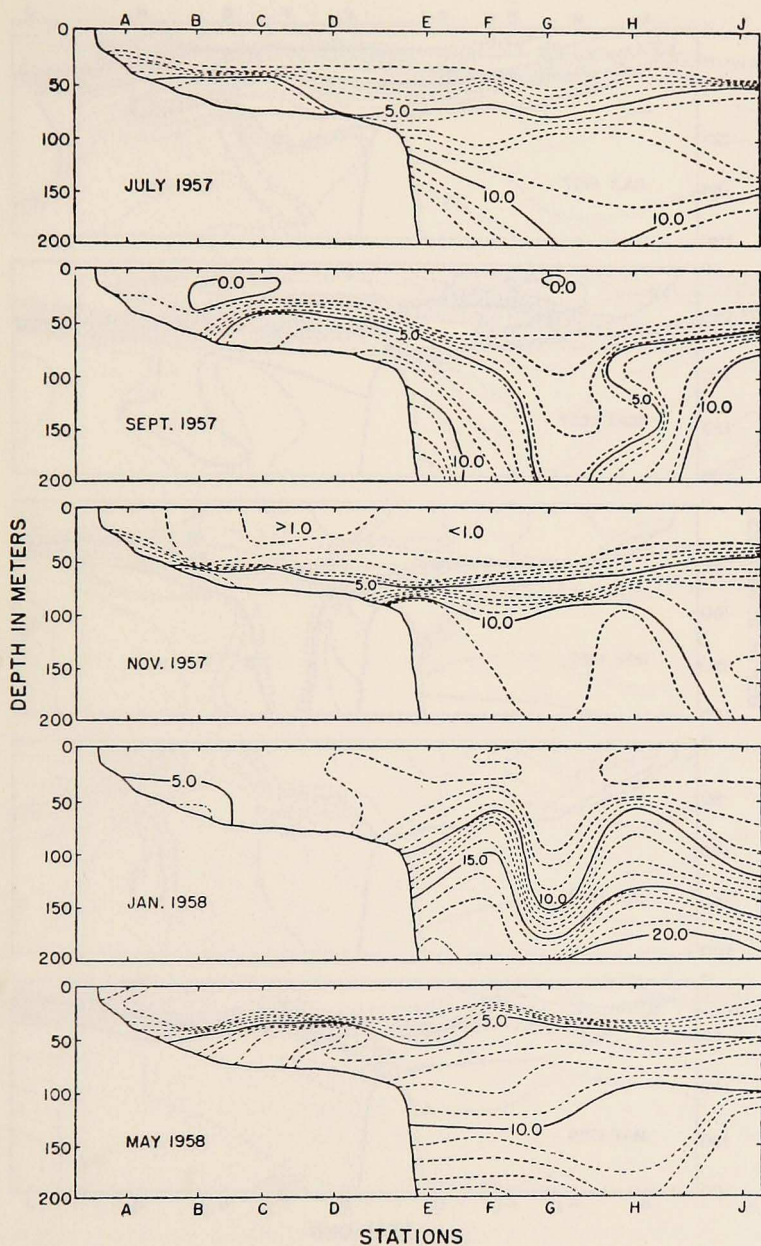Figure 2. Distribution of inorganic phosphorus (Vertical exaggeration 400:1).

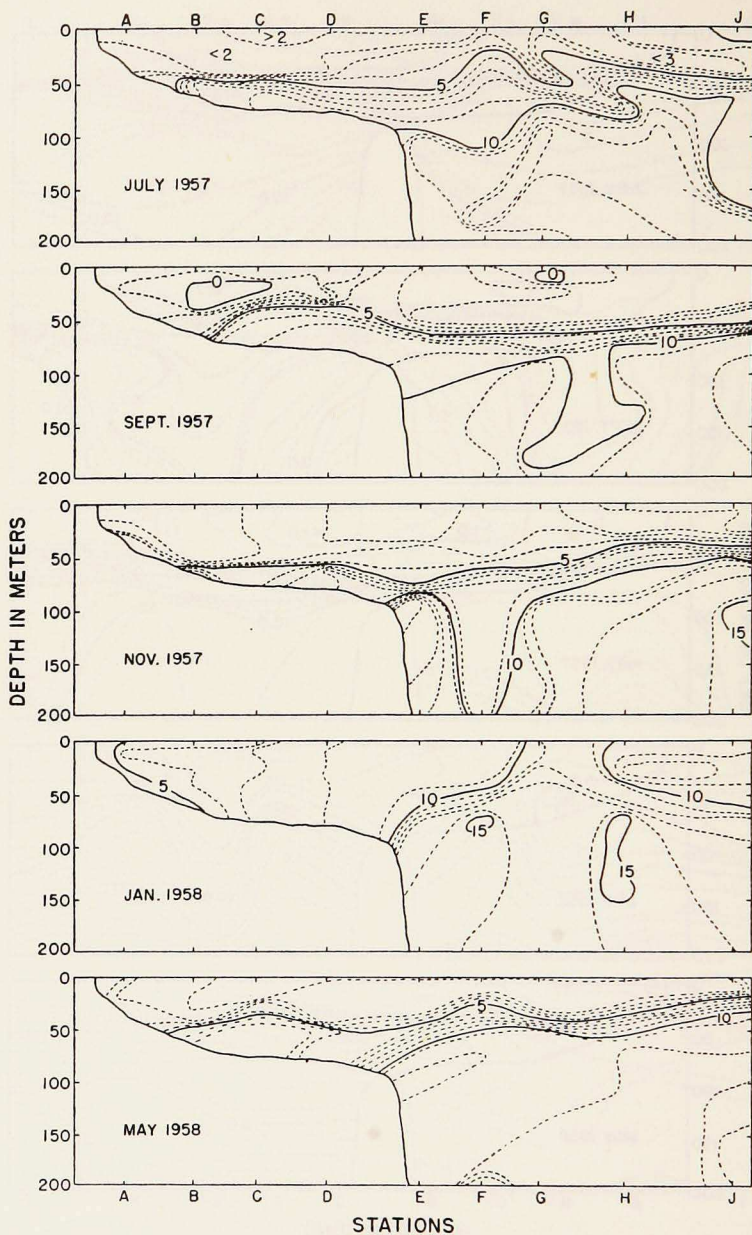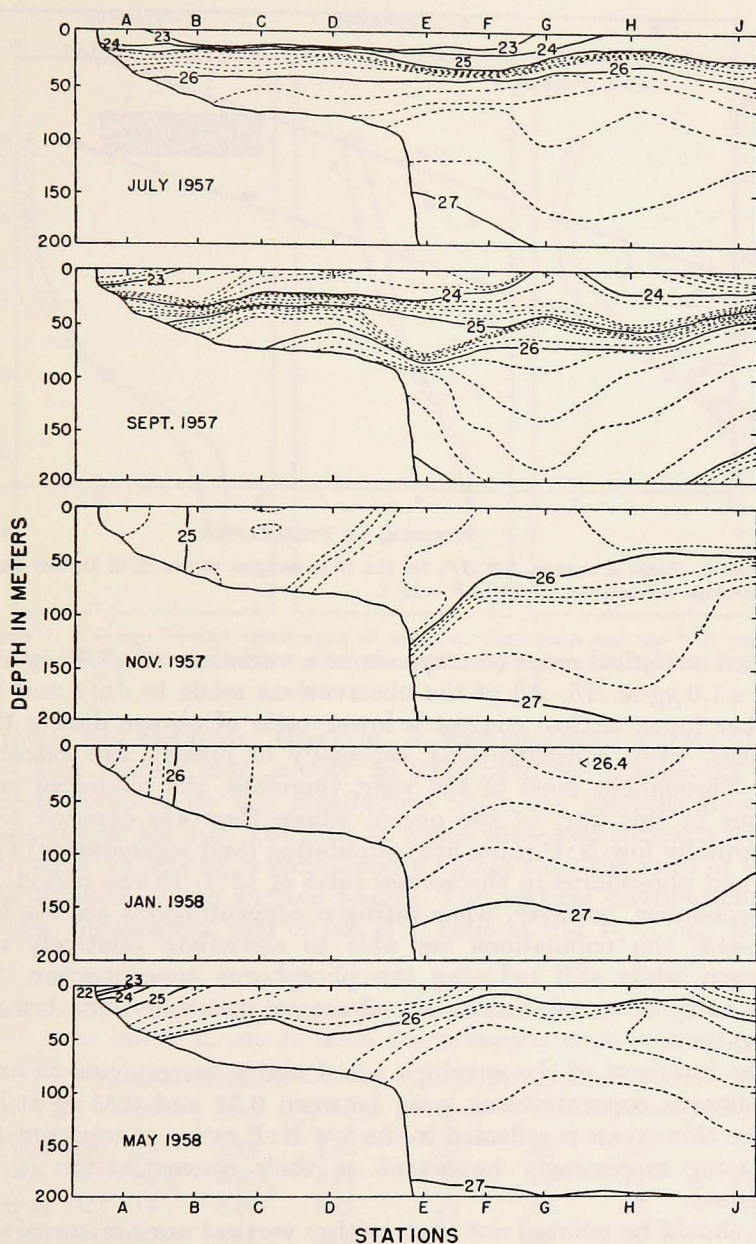Figure 3. Distribution of nitrate-nitrogen.

Figure 4. Distribution of N:P ratios.

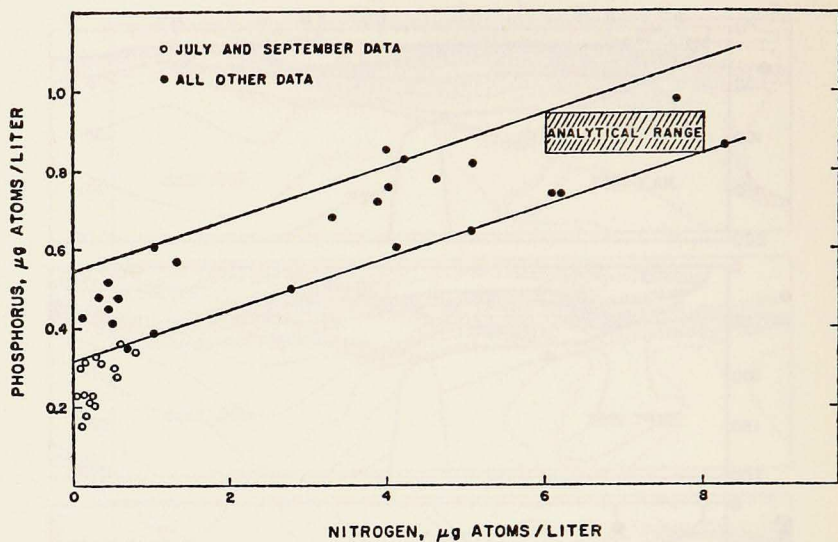Figure 5. Distribution of density ($\sigma_t$).

Figure 6. Ratio of change, $\Delta N : \Delta P$, for the 10 m samples at Sts. B, C, D. The slope of the envelope corresponds to $\Delta N : \Delta P = 15 : 1$.

labeled *analytical range* corresponds to a variation of $\pm 0.05$ $\mu$g-at P/l and $\pm 1.0$ $\mu$g-at N/l. All of the observations made in July and September (open circles) suggest a lower ratio of *change* during these months, when concentrations, especially of nitrate, are extremely low. Throughout most of the year, therefore, the biological populations in this part of the ocean, where they are exposed to an abnormally low N:P ratio, are assimilating (and regenerating) nitrogen and phosphorus in the *normal* ratio of 15:1. In the period July to September, however, when nitrogen concentrations are less than 1 $\mu$g-at/l, the populations are able to assimilate relatively little nitrogen while still reducing the phosphorus concentration. This may imply accomodation to the abnormal ratios at these low concentrations.

The intercept of the envelope noted above corresponds to excess phosphorus concentrations lying between 0.32 and 0.55 $\mu$g-at/l. Of course this excess is reflected in the low N:P ratios of concentration, becoming increasingly important as their concentrations are diminished.

It should be pointed out that neither vertical nor horizontal mixing processes in this area can account for a ratio of change of 15:1
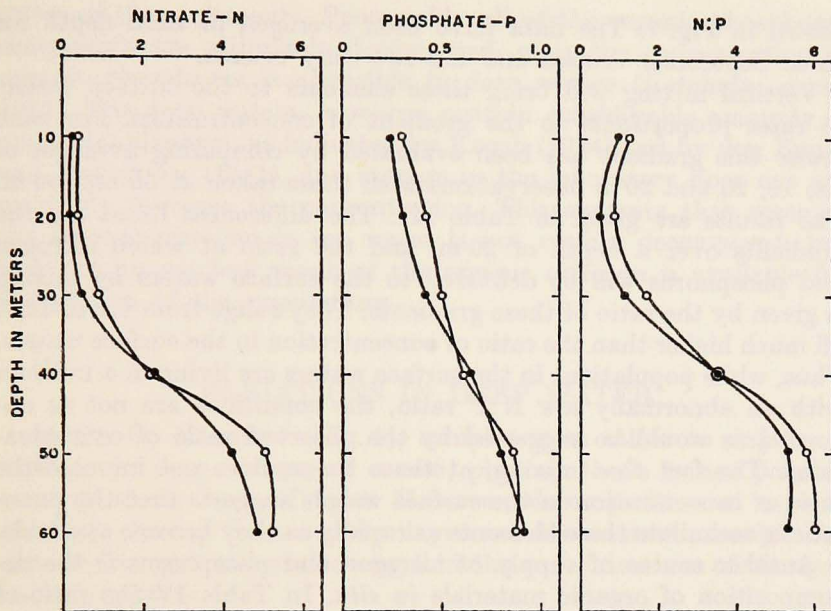
Figure 7. Average vertical distribution of nitrogen, phosphorus and the N:P ratio at stations of intermediate depth (B, C, D); open circles, September; solid circles, July.

for these two elements. However, it was suggested by Mr. John Steele that mixing must supply, in large part, the phosphorus and nitrogen required by the populations while the concentrations in surface waters are low. The ratio in which these two elements would be supplied by mixing is considerably higher than the ratio of their concentrations in the surface waters. The vertical distributions of nitrogen, phosphorus, and of the N:P ratio at Sts. B, C, and D are

TABLE III. GRADIENTS OF NITROGEN AND PHOSPHORUS IN JULY AND SEPTEMBER AT STS. B, C, AND D. MEAN CONCENTRATION IN $\mu$G-AT/l.

| | Nitrate-N | | | Phosphorus | | | |
|---|---|---|---|---|---|---|---|
| | Surface | Deep | Difference | Surface | Deep | Difference | $\Delta N:\Delta P$ |
| September 1956 | .23 | 3.78 | 3.55 | .35 | .93 | .58 | 6.1 |
| July 1957 | .63 | 6.07 | 5.44 | .35 | .86 | .51 | 10.7 |
| September 1957 | .13 | 5.56 | 5.43 | .21 | .86 | .65 | 8.4 |
| July 1958 | .46 | 4.11 | 3.65 | .44 | .91 | .47 | 7.8 |
| September 1958 | .48 | 3.96 | 3.48 | .40 | .74 | .34 | 10.2 |

shown in Fig. 7. The data have been averaged at each depth for three September cruises and for two July cruises.

Vertical mixing will bring these elements to the surface waters at rates proportional to the gradient of concentrations. For each cruise this gradient has been evaluated by comparing averages of the 10, 20 and 30 m observations with those taken at 50 and 60 m. The results are given in Table III. The differences listed are the gradients over a depth of 20 m, and the ratio at which nitrogen and phosphorus will be delivered to the surface waters by mixing is given by the ratio of these gradients. They range from 6.1 to 10.7, all much higher than the ratio of concentration in the surface waters. Thus, while populations in the surface waters are living in a medium with an abnormally low N:P ratio, the conditions are not as abnormal as would be suggested by the observed ratio of concentrations. The fact that mixing, at these times, does not increase the ratio of concentration in the surface waters suggests that the populations assimilate these elements as rapidly as they become available.

Another source of supply of nitrogen and phosphorus is the decomposition of organic materials *in situ*. In Table IV the ratio of

TABLE IV. AVERAGE INORGANIC AND TOTAL N:P RATIOS (BY ATOMS) FOR 10-M WATER SAMPLES AT STATIONS OF INTERMEDIATE DEPTHS ON THE CONTINENTAL SHELF

| Cruise Date | Inorganic | Total |
|---|---|---|
| September 1956 | 1.21 | 16.3 |
| November-December 1956 | 4.55 | 25.9 |
| February 1957 | 5.78 | 15.9 |
| July 1957 | 2.41 | 30.2 |
| September 1957 | 1.55 | 23.1 |
| November 1957 | 1.81 | 21.0 |
| January 1958 | 7.08 | 14.9 |

total nitrogen to total phosphorus is compared with the inorganic ratio observed in the 10 m samples for stations of intermediate depth on various cruises. Some of the cruises have been omitted because ammonia and amine-amide nitrogen, necessary to derive the total, were not determined. The ratio of concentration of total N:total P is considerably higher than the ratio of the inorganic concentrations. Decomposition of the organically combined nitrogen and phosphorus would thus supply the populations with high

ratios of these elements. Presumably all of the organic phosphorus compounds are ultimately decomposed, since the concentration of organic phosphorus is negligible in deep waters (Ketchum, *et al.*, 1955). The deep waters, however, contain considerable amounts of combined nitrogen, as indicated by Krogh (1934) and by von Brand and Rakestraw (1941), and storage in the laboratory does not appreciably decrease the concentration. This suggests that some of the organic nitrogen in sea water is not readily decomposed, but it is not known how much of the organic nitrogen is available for metabolism of the populations.

## VARIATIONS IN DEEP WATER

At Sts. G, H and J (Fig. 1), samples were taken to depths of 2000 m. In deep waters, of course, photosynthesis is not possible because of the lack of light. However, decomposition of organic material sinking from surface layers at these stations might be expected to give seasonal changes in the concentrations of nitrogen and phosphorus.

In order to permit comparison of the results, concentrations of nitrogen and phosphorus at depths greater than 100 m have been plotted against density ($\sigma_t$). This was done for the cruises which were made between February 1957 and May 1958 inclusive, with one exception[2]. Thus results from three stations were available, and for each cruise an average curve relating nitrogen and phosphorus to density was constructed. These average curves were then traced on a single graph, and the envelope in Fig. 8 describes the range of concentrations observed at various times of year.

Throughout most of the water column the range of variation in the nitrogen and phosphorus concentrations is no more than would be expected from analytical variation. The values of the maximum concentration for each cruise are presented in Table V. The average

[2] Results of BEAR cruise 165 made in April and May 1957 are not included in this treatment. In the nitrate analysis, calibration of the one centimeter cell gave anomalously low color development, and results calculated with the factor from this calibration are all considerably lower than any for the other cruises. We believe that, for some reason, reduction by the hydrazine in the high concentrations was incomplete for this set; however, the calibration and the concentrations for the more dilute samples measured in the 10 cm cells were apparently satisfactory and have been used in the previous section.

concentration of nitrate-nitrogen at the maximum was 20.7 $\mu$g-at/l, with a standard deviation of $\pm 1.97$. This corresponds to a variation of approximately 10 %, which would be expected for this analysis. The average phosphorus concentration was 1.65 $\mu$g-at/l, with a standard deviation of 0.11, or about 7 %. This variation is also to be expected from analytical errors.

The N:P ratios vary from 11.2 to 14.6 at the maximum concentration of these elements, with a mean value of 12.5. Even for the deep waters immediately off the Continental Shelf in this region, therefore, there is an excess of phosphorus over nitrogen, producing a low N:P ratio.

For all depths at the deep stations, the concentration of phosphorus has been plotted as a function of the concentration of nitrogen. All of the results for each cruise can be enclosed in an envelope with a
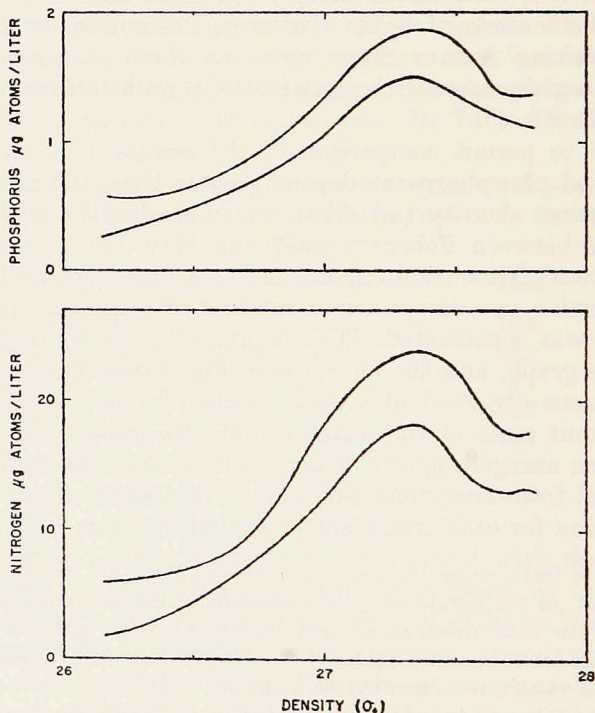


Figure 8. The relationship between phosphorus and nitrogen and the density of the water at depths greater than 100 m. The envelope describes the maximum range of concentrations observed at various times of year.

TABLE V. MAXIMUM CONCENTRATIONS OF INORGANIC PHOSPHORUS AND NITRATE-
NITROGEN IN μG-AT/l AT STS. G, H AND J

| Date | Phosphorus | Nitrogen | N:P (atoms) |
|---|---|---|---|
| February 1957 | 1.86 | 20.8 | 11.2 |
| March 1957 | 1.72 | 19.8 | 11.5 |
| July 1957 | 1.63 | 20.0 | 12.3 |
| September 1957 | 1.64 | 18.2 | 11.1 |
| November 1957 | 1.52 | 18.8 | 12.4 |
| January 1958 | 1.54 | 22.5 | 14.6 |
| March 1958 | 1.67 | 24.2 | 14.5 |
| May 1958 | 1.62 | 21.4 | 13.2 |
| Mean | 1.65 | 20.7 | 12.5 |
| Standard deviation | 0.11 | 1.97 | — |

slope of 15 atoms of nitrogen to 1 of phosphorus, provided it is assumed that the waters contain excess phosphorus, *i. e.*, the median line of the envelope intercepts the ordinate at a phosphorus concentration greater than zero. However, the width of the envelope exceeds the standard deviation of the method of analysis. The excess phosphorus determined by extrapolation and the ranges of variation are presented in Table VI. The mean value for excess phosphorus for the deep stations is 0.22 μg-at/l, somewhat less than that found

TABLE VI. RELATIONSHIP BETWEEN NITROGEN AND PHOSPHORUS IN μG-AT/l AT
STS. G, H, J. THE EXCESS PHOSPHORUS IS THE INTERCEPT OF THE MEDIAN LINE
OF AN ENVELOPE ENCLOSING ALL POINTS, HAVING A SLOPE OF $\Delta N:\Delta P = 15:1$.
THE RANGE IS THE DISTANCE FROM THE MEDIAN LINE TO THE BOUNDARIES OF
THE ENVELOPE

| Cruise | Excess P | Envelope Range | |
|---|---|---|---|
| | | P | N |
| September 1956 | 0.31 | ±0.30 | ±4.5 |
| November 1956 | 0 | ±0.25 | ±3.8 |
| February 1957 | 0.25 | ±0.25 | ±3.8 |
| March 1957 | 0.25 | ±0.25 | ±3.8 |
| July 1957 | 0.35 | ±0.35 | ±5.25 |
| September 1957 | 0.25 | ±0.25 | ±3.8 |
| November 1957 | 0.25 | ±0.25 | ±3.8 |
| January 1958 | 0.13 | ±0.22 | ±3.3 |
| March 1958 | 0.22 | ±0.28 | ±4.2 |
| May 1958 | 0.26 | ±0.25 | ±3.8 |

for the shallow inshore waters, which ranged from 0.32 to 0.55. Variations in the data, as defined by the distance between the envelope and median line, are generally two or three times the standard analytical deviation, even at the highest concentrations observed (*c. f.* Table V). This excess variation, suggesting inhomogeneity in the water masses, is as yet unexplained. These differences are apparently not accompanied by related variations in either temperature or salinity of the water, which would have been apparent in the plots as a function of density (Fig. 8). They thus demonstrate an inhomogeneity which would have escaped detection by the usual oceanographic techniques.

## DISCUSSION

In his original paper on the proportions of organic derivatives in sea water, Redfield (1934) speculated that biological processes might determine these proportions. He has recently (1958) presented a discussion of the ways in which this could be accomplished. It is also possible, of course, that the sea, when it originated in eons past, had concentrations of the essential nutrients in the same proportions as the sea today. The fact that marine organisms, and indeed all living matter, contain in their protoplasm nitrogen and phosphorus in approximately the same ratio as they are found in the deep sea would then be attributed to the adaptive ability of the biological system. Ketchum (1939) showed that, for a given concentration of phosphate, the marine diatom *Nitzschia closterium* (*Phaeodactylum tricornutum*) absorbs constant proportions of phosphorus and nitrogen from the water, regardless of the ratio of their concentration. As the concentration of phosphorus in the medium was increased, the ratio of assimilation (($\Delta N : \Delta P$) decreased. No variation was apparent with nitrogen concentrations at constant phosphorus except when the nitrogen content was less than 1 $\mu$g-at/l, which produced low values for the ratio of assimilation. Ketchum (1939a) showed that, when either nitrogen or phosphorus was exhausted from the water, the plants continued to grow and divide but developed a deficiency in the internal concentration of the exhausted element. The maximum nitrogen deficiency in *Chlorella pyrenoidosa* produced an internal N:P ratio of 2.35 (by atoms) and the maximum phosphorus deficiency produced a ratio of 31.2.

Our observations on surface coastal waters confirm these con-

clusions. In spite of the anomalously low N:P ratio, plants apparently assimilate these nutrients in the *normal* ratio of 15:1 until extremely low concentrations are reached. At such times the cells can apparently assimilate relatively little nitrogen while still depleting the phosphorus which is present in excess. It would clearly be desirable to have analyses of photyplankton collected in September, when the low ratio of assimilation is inferred to have taken place over a period of about three months. Harris and Riley (1956) did make such analyses of phytoplankton growing in Long Island Sound, where the ratio of concentrations is comparable to that found in our coastal waters. Their average value for the N:P ratio in phytoplankton was 16.7:1, suggesting that the plants generally maintained a high ratio of composition in spite of the low ratio of concentration in the waters in which they had grown. However, their lowest value, 13.1:1 by atoms, was obtained in August, approximately four months after the nearly complete removal of nitrogen from the water, as shown by Riley and Conover (1956).

The nearly complete assimilation of nitrate-nitrogen from the surface waters suggests that it may be an important nutrient limitation to the growth of phytoplankton. Phosphorus is always present in some excess in these waters, hence it may not be limiting, although its concentration does fall below the value of 0.55 $\mu$g-at/l, frequently quoted as limiting the rate of phytoplankton growth (Ketchum, 1939). The nutrient concentrations in surface waters did not change appreciably from July to September. Ryther and Yentsch (1958) have shown, however, that phytoplankton production continues during this period, but at a low rate. This production must be supported by nutrients supplied through turbulent mixing or by regeneration *in situ*. Both of these processes require more rigorous evaluation.

Our observations emphasize the dangers inherent in an interpretation of the nutritional status of plankton populations from observations of only one nutrient element. It is probable that a more complete understanding of phytoplankton periodicity will require observations not only of nitrogen and phosphorus but of other nutrients as well.

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