THE RELATIVE SUPPLIES OF PHOSPHATE, NITRATE AND SILICATE IN THE MEDITERRANEAN SEA (1)

by David A. Mc Gill

INTRODUCTION

Among the most curious aspects of the chemistry of the Mediterranean Sea are the general depletion of nutrient resources and the decline in concentration as one goes eastward. These phenomena have been noted by even the earliest of the modern expeditions using acceptable analytical techniques, the Dana Expedition of 1928-1930 (Thomsen, 1931). No comprehensive survey has been conducted for the entire region, although a number of countries have surveyed some parts of the area. A summary of seasonal patterns in oxygen and phosphorus distribution was presented by McGill (1961), and the physical data from a series of recent expeditions to various Mediterranean areas were reported by Miller (1963). The present paper will

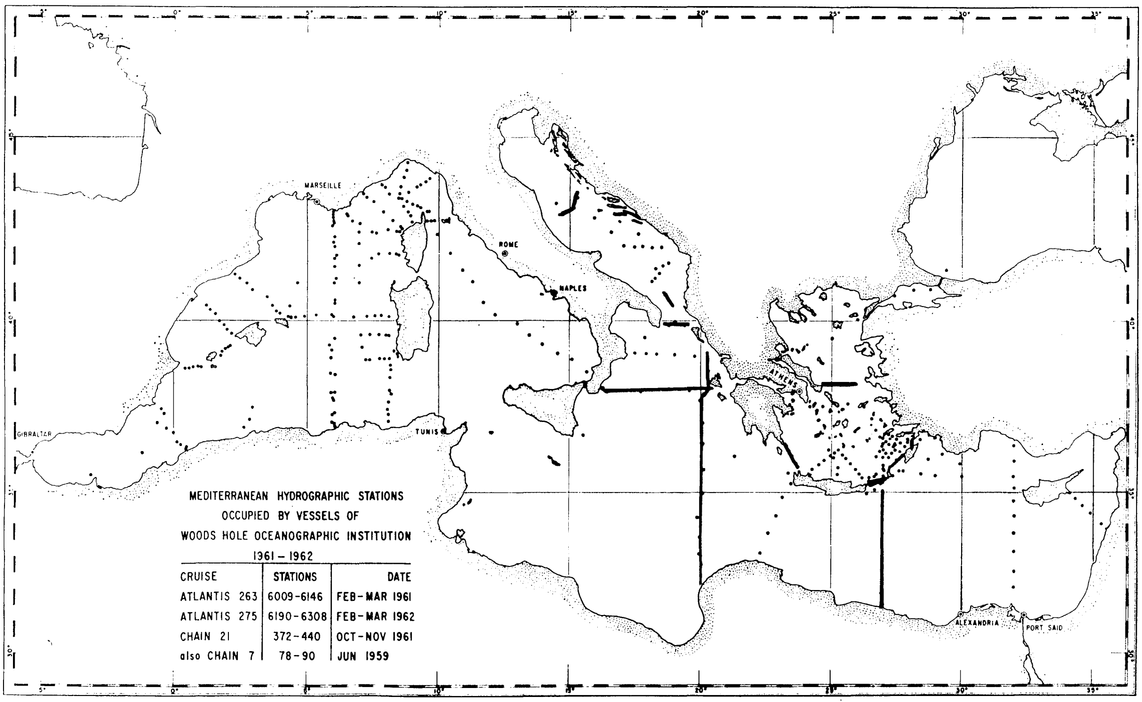

Fig. 1. — *General distribution of station sampling in the Mediterranean Sea* (after Miller, 1963). The sections shown by a solid line are those areas in the eastern Mediterranean where nutrient samples were collected.

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discuss those nutrient data which were collected from these same expeditions, with emphasis particularly on the latest data from the eastern Mediterranean.

Methods.

Not every station could be sampled for the nutrient concentrations, so data collections were concentrated in the regions shown in figure 1. « Chain » cruise 7 in 1959 obtained inorganic phosphate and total phosphorus samples on a section at 6°E in the Balearic Sea which were included in the seasonal summary (McGill, 1961). This section was repeated on « Atlantis » cruise 263 in February-March 1961, but only total phosphorus was obtained. On « Chain » cruise 21, October-November 1961, to the Aegean Sea and the Levantine Basin, phosphates were measured at sea and frozen samples were returned to the laboratory for silicate and nitrate determinations. Frozen samples were collected for all three nutrients on « Atlantis » cruise 275 in February-March 1962 which surveyed the Adriatic Sea and the Ionian basin. Total phosphorus samples from all cruises were collected at sea and analysed at Woods Hole.

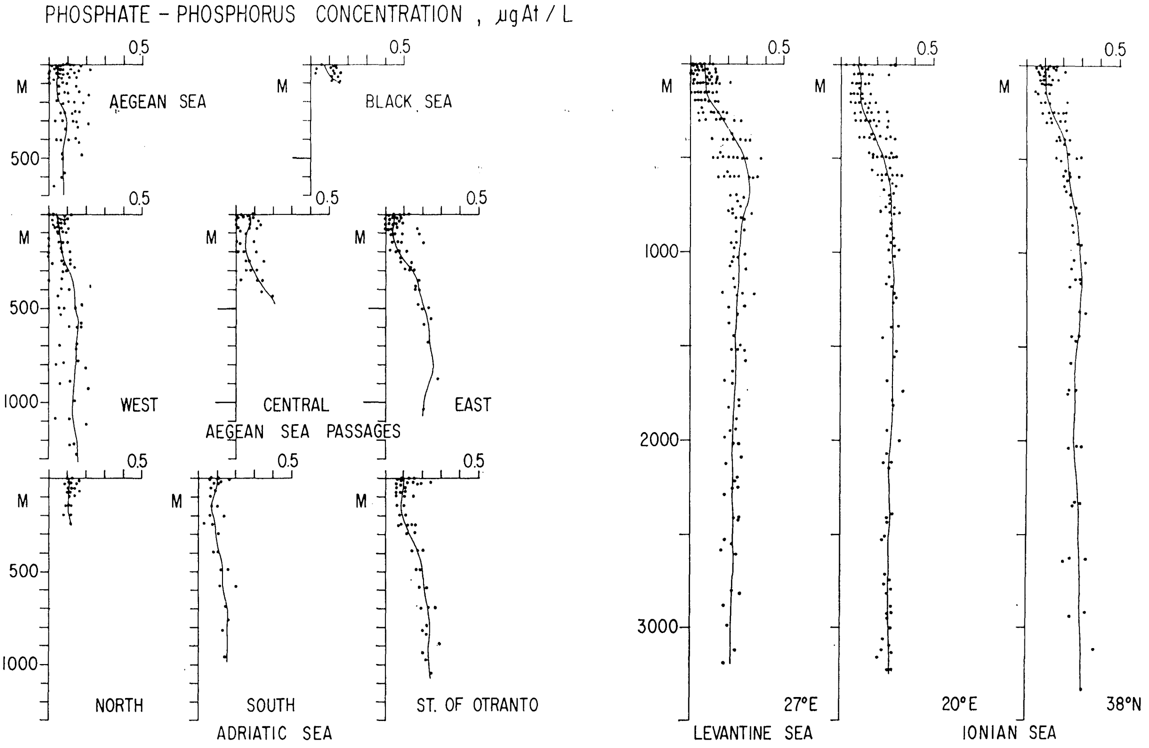

Fig. 2. — *Distribution of values obtained for inorganic phosphorus concentration in the indicated areas* (µgA/L). Refer to figure 1 for position of the sections.

Inorganic phosphate was measured by the technique of Denigès (1920) as modified by Robinson and Thompson (1948), using either an electric-eye photometer (Ford, 1950) or a Beckman DU spectrophotometer. Total phosphorus was analysed by the procedure of Ketchum *et al.* (1955). Nitrate and silicate analyses were done colorimetrically by methods of Mullin and Riley (1955*a*, 1955*b*). Nitrite-nitrogen and ammonia-nitrogen in the eastern Mediterranean were determined using methods simmarized in Strickland and Parsons (1960). M. Ralph F. Vaccaro carried out the nitrogen chemistry; the remainder of the work was done with the assistance of M. Nathaniel Corwin and M. John Schilling.

Observations.

All available data from the eastern Mediterranean are presented in figures 2, 3 and 4 with a line of best visual fit for each section which simmarizes the trend within the region. Figure 2 shows the concentrations of inorganic phosphate measured for stations in the central Aegean, at the various passages of the South Aegean, at places in the Adriatic Sea and in the Levantine and Ionian basins. The spread of the distributions reflects the accuracy of modern analytical techniques. The distributions of nitrate are similarly shown in figure 3 for the same areas, but it should be noted that the scale of concentration is increased by a factor of 10. The silicate distributions for the eastern Mediterranean are presented in figure 4. In all cases the concentrations in the Mediterranean below about 500 meters are essentially constant to the bottom of the basin. There is no linear increase in silicate in the deep waters, as seen in data from the Atlantic ocean studied by RICHARDS (1958). Data from a station in the Black Sea near the Bosporus are included in the figures, and the very high silicate concentration of the Black Sea (fig. 4) is especially notable.

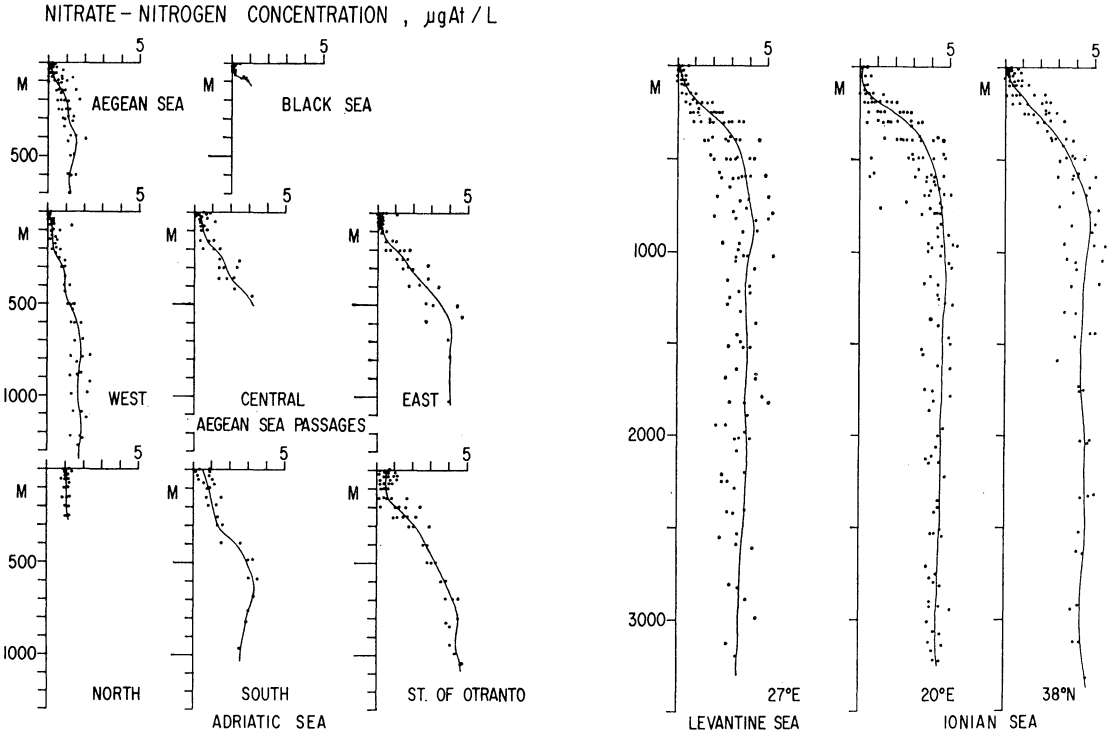

FIG. 3. — *Distribution of values obtained for nitrate-nitrogen concentration in the indicated areas* (ugA/L). Refer to figure 1 for position of the sections.

The nutrient concentrations in the various Mediterranean basins are summarized in figure 5. Additional data for the western Mediterranean and Atlantic Ocean added to complete the figure. There is no appreciable difference between nutrient concentrations in the Strait of Otranto and the Ionian basin at 20°E or 38°N-- all these sections may be considered typical in character of the Ionian Sea. The lowest concentrations are found in the Aegean Sea in every case and this area thus serves as the base line for comparisons with the other regions. The Adriatic Sea has only slightly greater concentrations of nutrients. Levels in the Levantine basin represent an increase of 2 to 3 over those in the Aegean, as is also the case in the Ionian Sea. In deep water (below 1000 m) the Ionian basin is slightly richer in nutrients than the Levantine. All these data are from northern areas of the eastern basin.

Stations in the Ligurian Sea occupied by « Atlantis II » In 1963 provide curves for nitrate and phosphate in that region : phosphate is about four times higher than the concentration in the Aegean, and the nitrate has likewise increased four to five times over its Aegean level.

	Aegean Sea	Adriatic Sea	Ionian Sea	Levantine Sea	Ligurian Sea	Alboran Sea[1]	East Atlantic Ocean	Indian and Pacific Oceans[2]
PO_4-P	1	2	3	3	4	8	12	24
NO_3-N	1	2	3	3	4	7	12	24
SiO_3-Si	1	1	3	3	—	—	8-12+	Up to 60

1. From Thomsen (1931). Data are uncorrected for salt error, but converted to modern units for the purposes by this comparison.
2. From Sverdrup *et al.* (1942).

Tabl. 1. — *The variation in nutrient concentrations in the Mediterranean Sea and the World Ocean, expressed as factors of increase over the level in the Aegean Sea.*

Thomsen (1931, fig. 2 and 3) has presented data in the southern regions of all basins of the Mediterranean which continue the picture and show increasing concentrations to the westward. However, he noted that « although the quantity of nitrate and phosphate increases considerably as we go from the eastern part of the Mediterranean to the western, yet the quantity of phosphate and nitrate even in the westernmost part is considerably less than at the same depths in the oceanic regions. » (Thomsen, 1931, p. 6-7). Recent IGY data from the eastern Atlantic at 32°N are given for phosphate and silicate; a nitrate curve is shown for older observations of « Atlantis I » near 36°N (cruise 151, 1948). These curves may be compared with distributions in other major oceanic regions, as given in Sverdrup *et al.* (1942 : Phosphate, figure 48, p. 241;

Area	RATIO, BY ATOMS			Mean depth of Section (m)
	SiO_3-Si	NO_3-N	PO_4-P	
Aegean Sea	1.78 ± 3.32 (78)	2.13 ± 2.10 (78)	1	525
Aegean Passages				
West	13.32 ± 3.81 (91)	5.97 ± 1.88 (90)	1	1160
Central	8.47 ± 5.55 (38)	8.81 ± 3.83 (38)	1	423
East	22.88 ± 4.13 (66)	14.83 ± 2.62 (66)	1	556
Levantine Sea (27°E)	26.33 ± 2.61 (212)	13.81 ± 1.27 (207)	1	2458
Adriatic Sea				
North	8.49 ± 7.45 (28)	1.39 ± 2.37 (28)	1	251
South	15.91 ± 6.36 (30)	17.74 ± 8.33 (30)	1	920
St. of Otranto	25.17 ± 5.49 (62)	21.26 ± 3.42 (62)	1	719
Ionian Sea				
38°N	32.35 ± 3.28 (123)	19.66 ± 1.87 (121)	1	2060
20°E	29.94 ± 3.18 (180)	18.49 ± 1.69 (180)	1	2347
Ligurian Sea		23.44 ± 3.98 (32)	1	2400

The value for the least squares regression is followed by the 95 % confidence interval and the number of pairs in the comparison is given in parentheses. The mean depth of the stations involved in each area is given at the far right.

Tabl. 2. — *The ratio by atoms of the nutrient concentrations within various regions of the Mediterranean Sea.*

Nitrate, figure 50, p. 242; Silicate, figure 55, p. 245), which show that the nutrient concentrations of Atlantic deep water are only about 1/2 the maximum values found in the Indian and Pacific oceans. In figure 5 it is seen that the phosphate concentration of the western Mediterranean is 1/2 to 1/3 of that in the eastern Atlantic, and the nitrate concentration has a similar relationship in the same areas. This bears out the observation of Redfield (1958) of a sixfold difference between the phosphate level of the eastern Mediterranean and that for the Atlantic. The very low levels of the eastern Mediterranean are clearly shown in figure 5. The relative factors of increase from this base line are summarized in table 1.

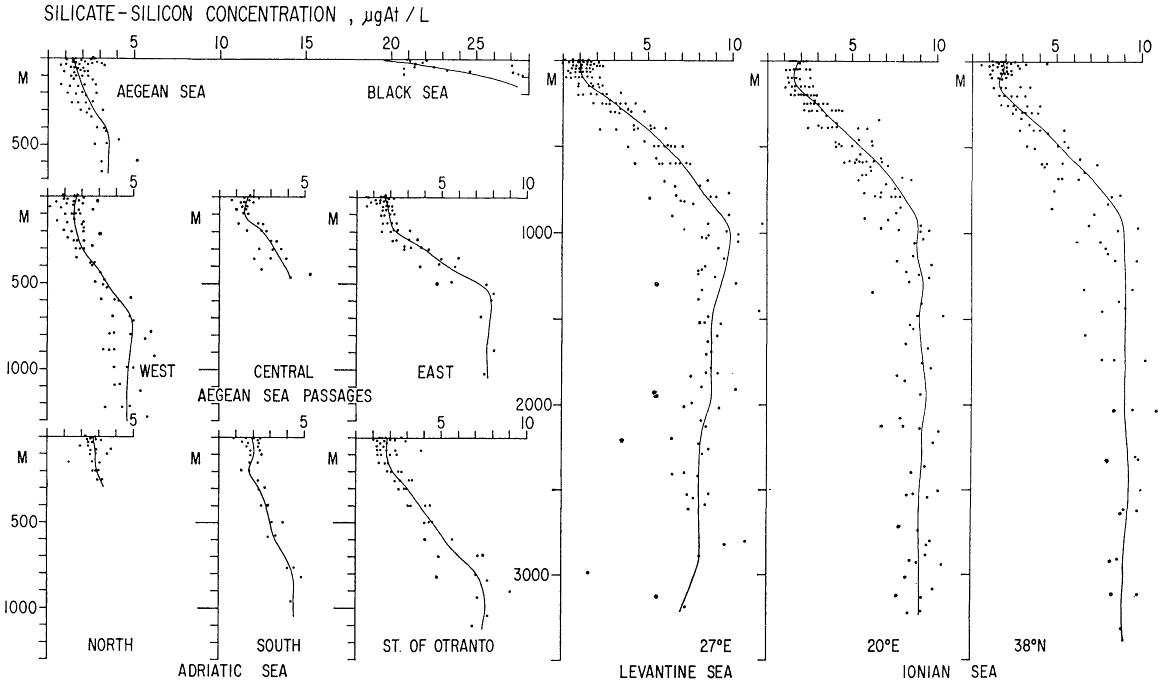

Fig. 4. — *Distribution of values obtained for silicate-silicon concentration in the indicated areas* (µgA/L). Refer to fig. 1 for position of the sections.

The ratios by atoms of the silicate and nitrate to the phosphate concentration in a given area also show much variation between regions. This is presented in table 2, where the ratios are derived as simple regressions from the grouped data represented in figures 2 through 4. The 95 % confidence interval and the number of paired samples in each case are also indicated in the table. Surprisingly low values are obtained in the Aegean Sea and in the north Adriatic Sea. These are the shallowest of the regions, as indicated by the calculated mean depth shown at the far right of table 2. Elsewhere, the ratios approach more closely the average relationship in the western North Atlantic of 16 : 16 : 1 (Richards, 1958). It is probable that the low values found between Crete and Scarpanto represent an outflow of Aegean water in the Caso Strait, as noted by Miller (1963). Likewise, the higher values in the south-east passage between Scarpanto-Rhodes and Asia Minor presumably relate to an influx of Levantine water there. The values found in the South Adriatic correspond with those for the Ionian basin, as might be expected from the suggestion of Pollak (1951) that the deep water of the Ionian basin is mainly formed in this region.

Discussion.

The lowest nutrient concentrations occur in the Aegean and the Adriatic Seas. However, it is difficult from the available data to find any fully adequate explanation for these greatly reduced levels. Consideration may be given to the factors contributing to the supply of nutrients, such as (1) contributions from river runoff and land drainage, (2) mixing and overturn of the water column by physical processes, and (3) biological regeneration of nutrient material.

The northern Adriatic receives the runoff from the rivers of northern Italy. The major drainage of southeastern Europe, however, is not to the Mediterranean but into the Black Sea via the Danube system. Even in the Black Sea, Carter (1956) has shown that the contribution from rivers has large seasonal variation in its relative importance to the water balance. The eastern Mediterranean area is distinguished by him as « a large area of small streams with a low intensity of runoff. » (Carter, 1956, p. 163). Hence, any contribution of nutrients from land drainage is an extremely small amount of the nutrient budget for the eastern Mediterranean. Erosion, however, may be a local factor in coastal areas, especially in the Aegean Sea.

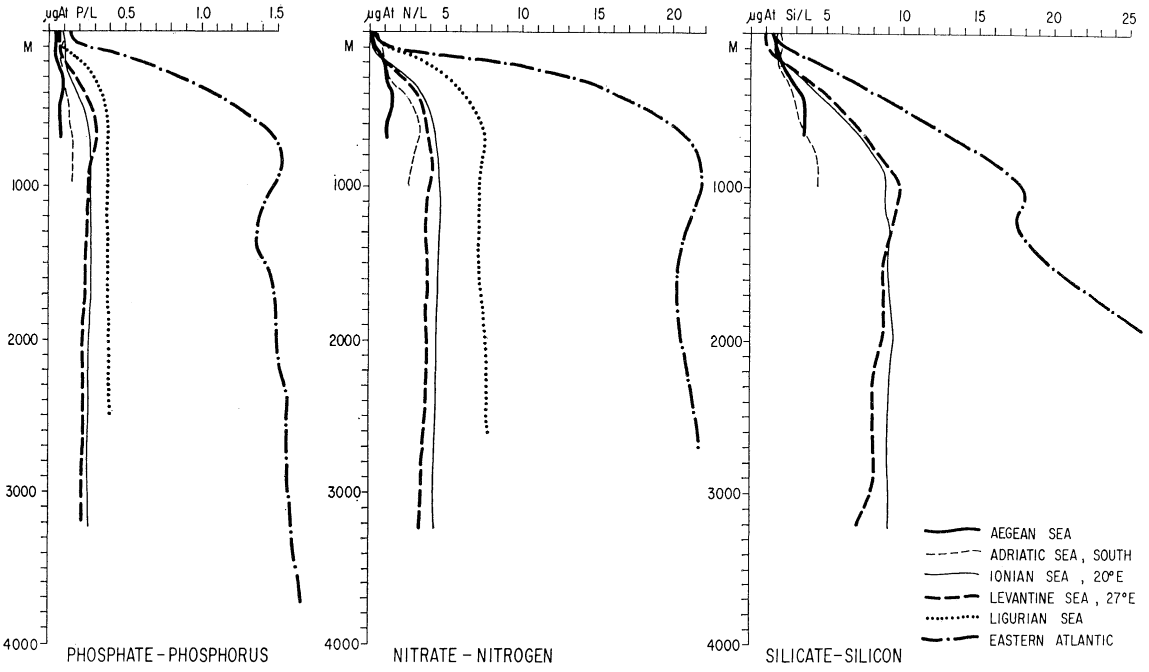

Fig. 5. — *Summary of the concentration changes in different areas of the Mediterranean Sea, compared with available data from the eastern Atlantic Ocean.*

In the relatively shallow regions of the Aegean and the Adriatic, it has been suggested that mixing through the water column is an effective means of maintaining the nutrient level. Pöllak (1951, p. 150) emphasized the mixing conditions in the Adriatic in winter, saying, « due to its restricted size and shallow mean depth it is particularly susceptible to short term weather fluctuations. » Wust (1959) has also emphasized this characteristic for the Adriatic and the Aegean. The deep water T-S diagram presented by Miller (1963) indicates some mixing in the northern Adriatic but considerable more stratification in the Aegean, the Sea of Marmara and the area near Crete, since the density of the deep water in these latter regions shows a regular increase with depth. Bompus (1948) found that the rate of vertical transfer for phosphorus was unusually low in the Aegean Sea and from this the concluded that enrichment o the surface from the deep water was not taking place. In the Ionian Sea and the western Mediterranean, however, Bumpus obtained a good correlation between turbulence and the change in nutrient concentration. However, the exchange over the sill at Gibraltar constantly withdraws nutrients at intermediate depths and thus reduces the accumulation in deeper layers (Redfield, *et al.*, 1965). This limits the effectiveness of vertical turbulence as a mechanism of enrichment in the western Mediterranean.

Evaluation of the biological regeneration may be attempted from the ratios between the nutrient elements. These elements occur in sea water in approximately the same proportion as in organisms, with growth and decay transforming them proportionately so that the ratio remains relatively constant. The N : P ratio is normally about 16 : 1. The data for the Aegean Sea and the Adriatic in table 2 show extremely low N : P ratios with a wide standard deviation, which indicates little or no correlation between the two nutrient elements in these shallow basins. Low ratios have been obtained in Atlantic waters in summer when the nutrient levels in surface water are depleted by the growth of phytoplankton (Ketchum *et al.*, 1958). Redfield (1958) suggests that where the elements are substantially depleted, small unused residues of one or another element may greatly alter the ratios. Further, in the process of decomposition phosphorus tends to be regenerated more rapidly than nitrogen. Hence, low ratios may be often found in near surface depths, which represent the majority of the samples for the Aegean and Adriatic.

Area	0-1000 m	Over 1000 m
Aegean Sea at 38°N	0.0532 ± 0.0147 (77)	—
Aegean Sea Passages		
West	0.0472 ± 0.0125 (90)	—
Central	0.0703 ± 0.0306 (37)	—
East	0.0530 ± 0.0184 (66)	—
Total, All Passages	0.0534 ± 0.0108 (193)	—
Levantine Sea		
At 27°E	0.0522 ± 0.0123 (157)	0.0625 ± 0.0169 (56)
At 32°E	0.0379 ± 0.0110 (165)	0.0272 ± 0.0169 (46)
Adriatic Sea		
North	0.0571 ± 0.0237 (28)	—
South	0.0339 ± 0.0155 (28)	—
Strait of Otranto	0.0369 ± 0.0135 (61)	—
Ionian Sea		
At 38°N	0.0400 ± 0.0100 (90)	0.0466 ± 0.0227 (29)
At 20°E	0.0620 ± 0.0153 (117)	0.0292 ± 0.0171 (48)
Ligurian Sea	0.1070 ± 0.0360 (43)	0.0594 ± 0.0321 (16)
Balearic Sea at 6°E	0.1592 ± 0.0300 (131)	0.0767 ± 0.0196 (86)

Tabl. 3. — *Mean concentration of organic phosphorus (µgA/L) and* 95 % *confidence limits for selected regions of the Mediterranean Sea.*

A relatively large amount of ammonia is found in surface waters of the Adriatic and in the Aegean passages. This is presumably produced by rapid regeneration at shallow depths in much the same way as phosphate. However, the ratio of N :P remains quite low even when recalculated using total nitrogen (nitrate plus ammonia), which suggests the nitrogen is the limiting factor in these waters.

Variations in the level of organic phosphorus, which is found from the difference of total phosphorus and inorganic phosphate determinations, serve as an index of the changes in the biomass in the absence of direct measurements. The values may be treated as a frequency distribution in order to obtain statistical limits. The mean and 95 % confidence limits as well as the number of samples are given in table 3 for the areas under discussion. Very little variation is seen in any part of the eastern Mediterranean in winter, but the values indicate a retention of phosphorus biologically that varies from 15 % of the total phosphorus to nearly 50 % in the Aegean. To produce such a high percentage, the populations in the Aegean must make very efficient use of the available nutrient supply. Summer data for the Ligurian Sea from «Atlantis II » in 1963 and for the Balearic Sea at 6°E from « Chain » cruise 7 in 1959 (McGill, 1961) are also given in table 3. Although the actual amount of organic phosphorus present is increased, the phosphorus in organic form represents only about 30-35 % of the total phosphorus available, Regional differences in the amount of organic phosphorus are similar to those seen in quantitative estimates of phytoplankton and zooplankton in the eastern and western basins, such as Jesperson (1923) and Bernard (1961).

No single factor is the predominating cause of the observed low nutrient concentrations. The major portion of the nutrient concentrations in the Mediterranean is supplied to the surface water by mixing and biological regeneration. This nutrient supply is in turn utilized by the surface populations. There is a need for systematic seasonal investigations of the nutrient cycle and corresponding productivity and biomass measurements to further elucidate the changes in the various areas of the Mediterranean.

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