Seasonal Variations of Minor Chemical Constituents in the Waters of the Zunan-Kuroshio Region. I.* On Nitrogen-phosphorus Content Ratio with the Behaviors of Nitrate and Phosphate

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Introduction

Whereas a large number of observations have been made on nutrient salts in sea water in various periods as well as in various localities of Europe and America, observations made in the western Pacific near Japan have been restricted to coastal waters and such observations were seldom carried out during and after the war.

Determinations of nutrient salts in sea water have been made by the present author on the waters of the Zunan-Kuroshio region, where the Kuroshio, a warm current, is passing over the Izu submarine ridge, in connection with studies on other hydrographical conditions and fisheries resources.

In the present paper, data concerning nitrate and phosphate determinations which were made by the present author are selected from those concerning the observations which had been made from January 1950 to February 1951, by the author and other workers, and their seasonal variations are investigated with reference to N-P ratio.

The relationship between the contents of nitrate-nitrogen and those of phosphate-phosphorus in the sea water, was first suggested by Harvey[1] in 1928. Later, it was discussed by Redfield,[2] Cooper,[3] Fleming[4] and other workers. Of the normal ratio of nitrate-N/phosphate-P, the value, 6.8 (by weight), which was proposed by Cooper is widely accepted.

The purpose of this study is as follows: to answer the question whether the normal ratio of N/P can be accepted for the waters of the Zunan-Kuroshio region, and if any deviation from the normal ratio is found, whether it has a connection with other conditions.

Analytical Methods Adopted

For nitrate: Colorimetric determination with Harvey's reduced strychnine reagent.[5]

For phosphate: Denigès-Atkins' method.[6] Colorimetric determination with blue color resulting from the reaction with complex phosphomolybdic acid and the following reduction by stannous chloride solution.

Stations Under Consideration

Two stations were chosen on a line between Sunosaki and Hachijō as follows: Station 3, on the shelf slope about 20 miles south of Sunosaki (Lat. 34°40'N, Long. 139°45'E); Station 6, in the main current of the Kuroshio (Lat. 33°50'N, Long. 139°45'E). (Fig. 1)

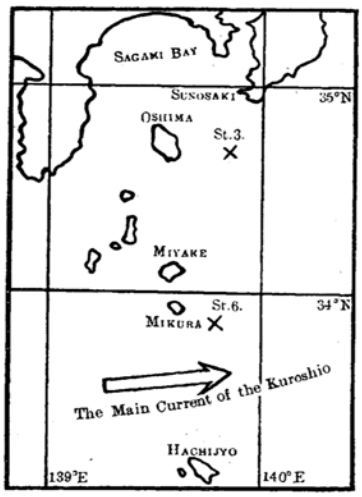

Fig. 1.—Stations under consideration.

Results and Discussion

Attention is called to the fact that in the sea region under examination, the spacial position of the Kuroshio itself may be altered

* Contribution B. No. 64 from Tokai Regional Fisheries Research Laboratory, Tokyo, Japan.

(1) H. W. Harvey, "Biological chemistry and physics of sea water", Cambridge University press, 1928, p. 48.

(2) A. C. Redfield, "James Johnstone Mem. Vol.", 1934, p. 176.

(3) L. H. N. Cooper, *J. Mar. Biol. Assoc.*, **22**, 177 (1938).

(4) R. H. Fleming, "Proc. Sixth Pacific Sci. Congress", Vol. **3** (1939).

(5) H. Wattenberg, *Rapp. et Proc.-Verb. des Reunions*, **103**, 1 (1937).

(6) R. J. Robinson, *J. Mar. Res.*, **7**, 33 (1948).

in course of time. If so, variations in contents of chemical substances which appear in such spacially fixed stations do not always represent those that relate to seasonal changes. From hydrographical data, however, it can be assumed on the whole that a stationary state has been reached in so far as the current is considered.

Considering the data, water columns are assumed, and the columns are divided into several parts in which the integral mean concentrations of chemical substances are calculated (in order to avoid fluctuation of individual datum). Based upon these values, the values of N/P are calculated in each part of the water columns for each month. The vertical distributions of these ratios for each month are shown in Fig. 2 (at Station 3) and Fig. 3 (at Station 6).

In these figures, vertical broken lines represent the normal value of N/P, proposed by Cooper. If the values of N/P in sea water remained constant and had the normal one, the points plotted in the figures should lie on the lines. The results obtained are not in good agreement. But this does not always give the conclusion that the actual values of N/P deviate from the normal one, since considerable errors accompany the estimation of chemical substances in sea water.

In order to obtain reliable ranges for the calculated values of N/P, probable maximum and minimum values of N/P were computed of each value, introducing the numerical values of probable maximum error given in Table 1

Table 1

Probable Maximum Errors in Determination

found Nitrate-N (μg./l.)	Error (μg./l.)	found Phosphate-P (μg./l.)	Error (μg./l.)
< 25	$\pm$ 5	< 20	$\pm$ 2
25– 50	$\pm$ 10	20–50	$\pm$ 3
50–100	$\pm$ 15	> 50	$\pm$ 5
100–300	$\pm$ 20		
>300	$\pm$ 30		

in the computation. These probable ranges are shown by two dotted curves for each month in the figures. Then, it can be considered that the deviations from the normal ratio take place only when the normal lines do not lie between two dotted curves.

In Fig. 2, from these points of view, nitrate content below subsurface layers was relatively higher than phosphate content in January and February 1950, while in March and April 1950 and February 1951, phosphate content was predominant. Although these variations in vertical distribution of N/P might suggest some character of a phenomenon occurring in this sea region, any conclusion may not be given until further observations will be accumlated.

In Fig. 3, the distribution of N/P for each month are regular except those in May and July, 1950. In upper layers (0-200 m.) the ratios are much lower than the normal ratio. On the contrary, in deep layers (400-800 m.)

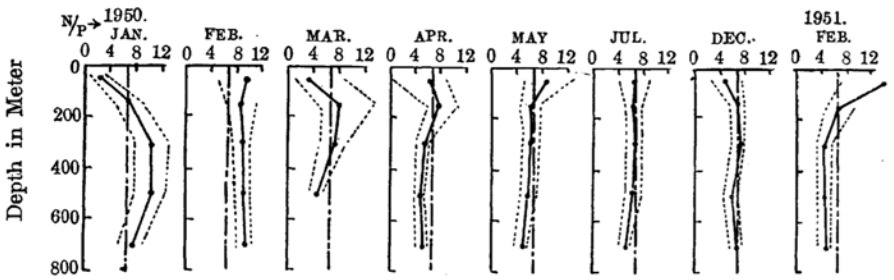

Fig. 2.—Vertical distribution of N-P ratios for each month (at Station 3).

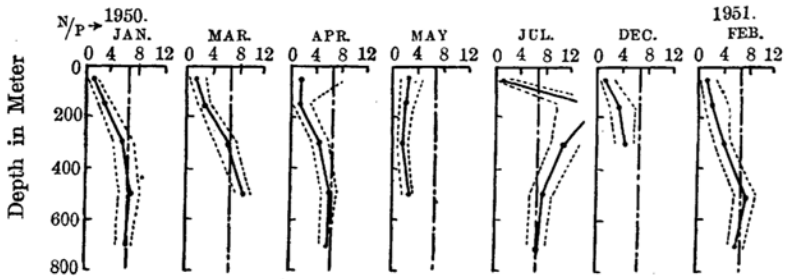

Fig. 3.—Vertical distribution of N-P ratios for each month (at Station 6).

the ratios are nearly equal to the normal ratio.

The average values of N/P in these regular cases are 1.4 and 6.9 for upper layers and deep layers, respectively. The rejection limits are 0-2.8 for upper layers and 4.7-9.1 for deep layers (level of significance: 0.05). These values indicate the possibility of difference of water masses that are present in upper and lower layers.

It is a remarkable fact that the values of N/P in May and July 1950, deviated considerably not only from the normal ratio but also they deviated in opposite directions from each other.

In order to examine the processes of deviation from the normal ratio systematically, the rates of change in nitrate, $\delta[N]/\delta t$, and phosphate, $\delta[P]/\delta t$, were computed. Further, on the base of $\delta[N]/\delta t$, theoretical rates of change of phosphate, $\delta[P']/\delta t$, were also computed. These computations were based upon the assumption that phosphate was accompanied in the ratio of 6.8 by nitrate.

The values of $\delta[P]/\delta t - \delta[P']/\delta t$ are given in Table 2. Due to the experimental errors introduced in the computations, it is impossible

Table 2

Values of $\delta[P]/\delta t - \delta[P']/\delta t$ in Each Layer for Each Period (unit: μg./l./month)

Depth(m.)	0–100	100–200	200–400	400–600	600–800
	at Station 3				
'50 JAN.–FEB.	−10	−4	+ 1	− 2	−16
FEB.–MAR.	+ 4	+2	+ 6	+29*	
MAR.–APR.	− 3	+1	+14	+ 4	
APR.–MAY	− 2	+5	− 7	−13	+ 6
MAY–JUL.	+ 1	0	0	− 2	+ 3
'50 DEC.–'51 FEB.	− 3	0	+ 5	+ 3	+11*
	at Station 6				
'50 JAN.–MAR.	− 2	−1	0	− 4	
MAR.–APR.	− 5	−4	+ 3	− 2	
APR.–MAY	+ 2	+3	+17*	+36*	
MAY–JUL.	− 1	−6*	−14*	−20*	
'50 DEC.–'51 FEB.	0	−1	− 1		

to deduce the correlation between nitrate and phosphate from most of the values. But from the values which were marked by *, it can be concluded that net increase or decrease of phosphate has occurred.

As above mentioned, it is evident that the deviations from Cooper's normal ratio have occurred in this sea region.

As the causes of deviation, the following may be assumed:

1. The effect of coastal water masses in which the ratio of N/P is different from the normal ratio.

2. Increase in amount of planktons, of which the N/P ratios are widely different from the normal ratio.

3. Difference in rates with which nitrate and phosphate are regenerated in decomposition processes of dead marine organisms.

It is difficult to decide among these three causes, which one is the most probable for the elucidation. But in view of the peculiar features of the sea region under question, (1) should be discarded. (2) is the most improbable one. Consequently, (3) is the most probable. But plankton populations in the upper layers of the Kuroshio in the region under question correspond to phosphorus content equivalent to 0.5-2 μg./l., and it can not give a decisive explanation for the deviation of N/P in the intermediate layers. Abundant plankton populations, such as found in the Oyashio, which is a cold current originating in the northern part of the North Pacific and penetrating under the Kuroshio, must be taken into consideration as the cause of deviation in N/P.

Summary

Data of nitrate and phosphate detrminations have been selected from those of the Zunan-Kuroshio observations which were made from January, 1950 to February, 1951, and their seasonal variations were investigated with reference to N/P ratio.

As a result, it was proved that no change was recognised in deep layers (400-800 m.) at Station 6 (in the main current of the Kuroshio) throughout the period, but deviations from Cooper's normal ratio were found in surface and subsurface layers. The cause of these deviations may partly be due to the decomposition processes of dead marine organisms.

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