UREA AND OTHER NITROGENOUS NUTRIENTS IN LA JOLLA BAY DURING FEBRUARY, MARCH, AND APRIL 1970

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ABSTRACT

Samples collected from La Jolla Bay twice weekly for 2½ months were analyzed for nitrate, nitrite, ammonium, and urea in addition to other chemical, physical, and biological parameters. On the basis of an infestation of blue sharks (*Prionace glauca*), periods before, during, and after the infestation were defined. Statistical analyses indicated that: 1) Urea concentrations were highest during the period of shark infestation. 2) There was strong positive correlation between phaeo-pigment/chlorophyll ratios and ammonium concentrations during the infestation but none between the pigment ratios and either the ammonium concentrations for the other two periods or the urea concentrations for any of the three periods. 3) There was no correlation between ammonium and urea concentrations before, a strong positive correlation during, and no correlation after the shark infestation. 4) Urea was the only nitrogenous nutrient for which the concentrations above and below the thermocline were not different. 5) Comparisons between two stations 1.5 km distant indicate that on a horizontal scale, the patch structure for urea is smaller than that of the other nitrogenous nutrients although the median urea concentration in the water column was not different at the two stations.

The temporal similarity and the more complex patch structure for urea (as seen in 4 and 5 above) suggest that the blue sharks were responsible for the higher urea concentrations during the infestation. Although the median ammonium concentrations before and during the infestation were not different, the strong positive correlation between ammonium and urea concentrations during the infestation hint that the sources or rates of supply and utilization for both nutrients may have been closely related. The strong positive correlation between phaeo-pigment/chlorophyll ratios and ammonium concentrations during the infestation may imply that the source of ammonium was herbivore excretion.

The nitrogenous plant nutrients in the marine environment classically include the nitrate, nitrite, and ammonium ions. The fixation of dissolved gaseous nitrogen has been observed in both the Sargasso Sea and Arabian Sea (Dugdale, Goering, and Ryther, 1964) and may for certain areas be a significant process (Dugdale and Goering, 1967). More recently, evidence has been presented which suggests that both urea (McCarthy, 1971) and certain amino acids (North and Stephens, 1971) may also be of importance as nitrogenous nutrients. The purpose of the present study was to compare the pattern of distribution for urea with those for ammonium, nitrite, nitrate, and other chemical, physical, and biological parameters in the La Jolla coastal waters.

In contrast to the other nitrogenous nutrients, little is known about the distribution, the importance, or the cycle of either urea or amino acids in marine waters. The results of quantitative analyses for urea in a total of approximately 120 samples of seawater have been reported by Newell (1967) and McCarthy (1970). Newell's samples were collected from a depth of 10 m at 25 stations in the English Channel and 45 of

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McCarthy's were collected from 9 profiles (5 samples each) in the euphotic zone of the Peru Current. One of the obvious features of both sets of data is the high degree of variability between samples, even those only a few meters vertically distant from one another. There was no consistent pattern in the profile data although higher values tended to occur at intermediate depths in the euphotic zone. It has been shown that urea accounts for a significant fraction of phytoplankton nitrogen uptake off the coast of southern California (McCarthy, in press), and it has been suggested that animal excretion is the major source of urea in the euphotic zone of that area (McCarthy and Whitledge, 1972).

Ammonium concentrations are usually low in coastal waters, but this ion can, at times, be the most abundant form of nitrogen available for phytoplankton utilization. It is the major nitrogenous excretory product of most marine animals (Parry, 1960; Baldwin, 1964) and as such is recycled rapidly in surface waters. The importance of ammonium in phytoplankton nutrition has been demonstrated in the eastern tropical Pacific by Thomas (1966) and Thomas and Owen (1971).

Nitrite in neritic waters often shows marked differences with depth, and the concentration is usually somewhat less than that of ammonium (Vaccaro, 1965). Nitrite can be formed by bacteria through either the oxidation of ammonium or the reduction of nitrate. Phytoplankton can utilize nitrite as a source of nitrogen and have been shown to excrete extracellular nitrite when growing on high levels of nitrate (Vaccaro and Ryther, 1960; Carlucci, Hartwig, and Bowes, 1970).

In temperate coastal areas the distribution of nitrate in seawater usually shows a predictable seasonal pattern which is well documented (see Vaccaro, 1965). During the winter, vertical mixing and low rates of plant assimilation keep the nitrate concentration plentiful in near surface waters and rather uniform in vertical distribution. With the onset of spring, density stratification substantially reduces the vertical transfer of nitrate, and it is removed from the wind mixed surface waters via phytoplankton assimilation. Bacteria are probably responsible for regenerating nitrate through the oxidation of ammonium and nitrite (Harvey, 1966).

SAMPLE COLLECTION AND ANALYSIS

Samples were collected with PVC Van Dorn bottles off the coast of La Jolla, Calif., twice weekly from 7 February to 17 April 1970, at three stations in 50 m of water. Station II (Figure 1) was approximately 1 km directly seaward of Scripps Institution of Oceanography pier on the southern edge of Scripps Canyon, Station I was approximately 1.5 km SW of Station II on the southern edge of La Jolla Canyon, and Station III was approximately 1.5 km NW of Station II over the more gently sloping bottom north of both canyons. Water for the analysis of chemical and biological parameters was collected from the surface, 10, 20, 30, and 40 m depths at all three stations on each sampling day. Nutrient analyses were run on samples collected at Station II and alternately on those collected at Stations I and III (with a few exceptions). A Secchi disk reading and bathythermograph cast were always taken at Station II.

Immediately after sample collection, aliquots were drawn for oxygen determinations. They were "pickled" by the addition of the manganous sulphate and alkaline iodine solutions and were returned to the laboratory for the completion of the analysis. Within 2 hr after sample collection, aliquots were analyzed in duplicate for ammonium and urea while others were analyzed for chlorophyll *a* and phaeophytin *a*. Other aliquots were: 1) frozen and later analyzed (within 2 weeks) for nitrate, nitrite, silicate, and phosphate; 2) preserved for microscopic determination of phytoplankton species and numbers; and 3) stored (approximately 3 weeks) for salinity determinations.

The determinations of dissolved oxygen by a modified Winkler technique (Carritt and Carpenter, 1966), chlorophyll *a* and phaeophytin *a* by fluorometry (Holm-Hansen et al., 1965), nitrate by the cadmium-copper reduction and subsequent determination of nitrite (Wood, Armstrong, and Richards, 1967), nitrite by diazotization (Bendschneider and Robinson, 1952),

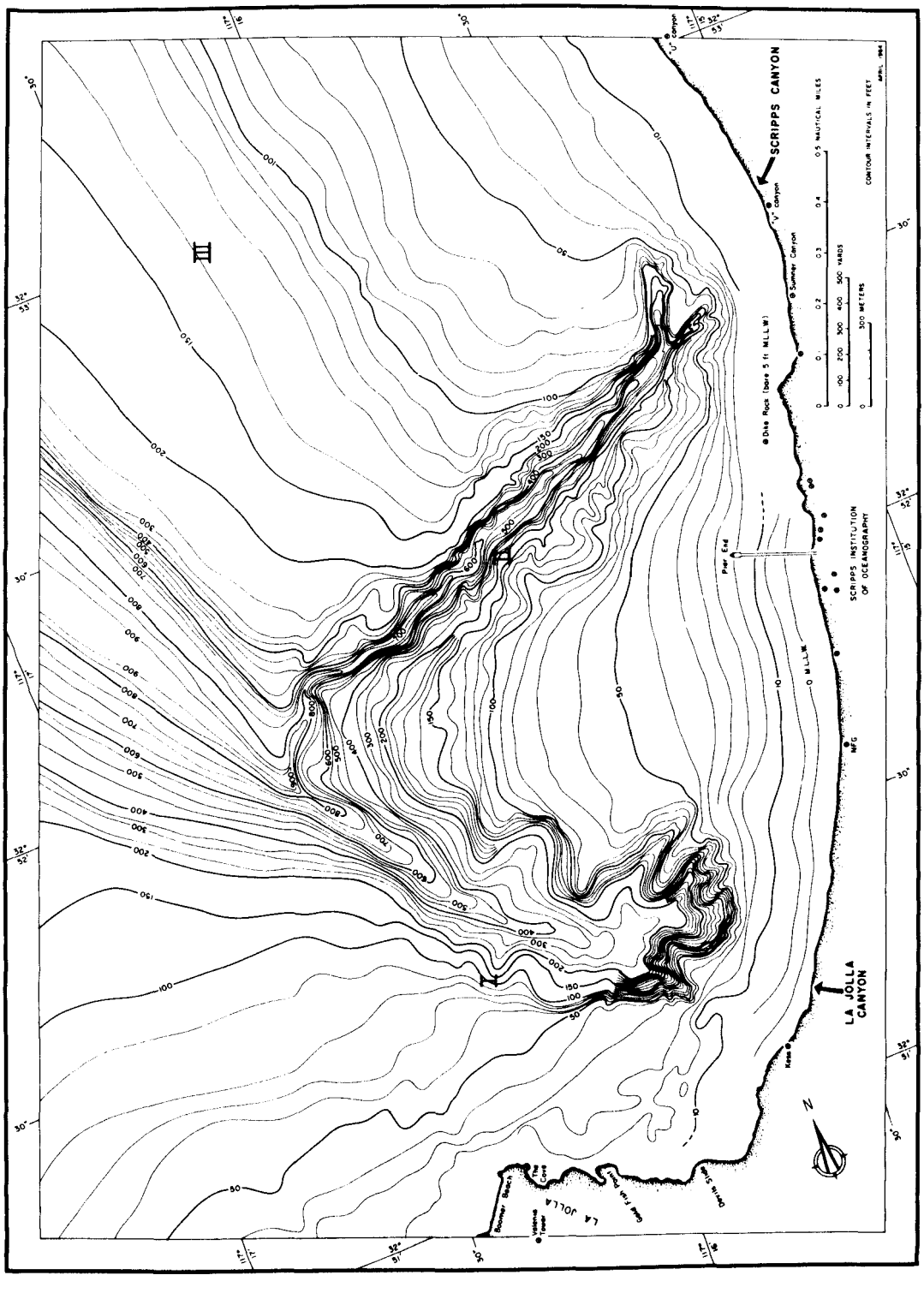

FIGURE 1.—The locations of Stations I, II, and III.

silicate by molybdate complexing (Mullin and Riley, 1955), and phosphate by molybdate complexing (Murphy and Riley, 1962) followed the procedures outlined by Strickland and Parsons (1968). Salinity was determined by conductivity measurements on an Autolab[R] salinometer.[3]

Ammonium was determined by the phenolhyochlorite method (Solórzano, 1969) and urea by the urease method (McCarthy, 1970), but both of these methods deserve additional comment. Solórzano states that for ammonium analyses the absorbance of samples is stable for at least 24 hr when a 0.5% sodium nitroprusside reagent is used, whereas, at higher concentrations a high and unstable blank which increases with time can result. Difficulties such as those expected at higher sodium nitroprusside concentrations were, however, occasionally experienced when using the recommended concentration. Efforts made to determine the source of this problem were complicated by its erratic occurrence, e.g., differences from day to day using the same reagents. No solution to the problem was found. It is, however, of little consequence when absorbances are read within a short interval of time, e.g., 15 min, since the optical density increased uniformly in blanks, samples, and standards. When analyzing as many as 50 samples at once, the reagent additions were staggered in time so that the absorbance of a sample was always read between 1.00 and 1.25 hr later.

A problem was encountered with the Worthington URC crude urease which was recommended for the urease method. Several batches of this product were purchased over a period of a year, and following the outlined purification procedure, the preparations were almost identical in activity and blank. Shortly after the urease-urea method was published (McCarthy, 1970), two batches of the same product were received which yielded both less activity and higher blanks than the preceding preparations. Owing to these difficulties, Sigma Type III urease was used subsequently. The resultant blank is higher (0.030-0.050 OD units/10-cm cell) than previously described and approximately 3 mg rather than 0.5 mg of the enzyme preparation must be added to each sample. A 0.1-0.2 ml Biopipette[R] was found to be accurate and rapid enough to permit direct addition of the concentrated enzyme preparation without dilution. In addition, it was found that by centrifuging the final urease preparation approximately 1,000 $\times$ g for 20 min and discarding the pellet, turbidity of the preparation could be reduced. For laboratory analyses of urea McCarthy (1970) recommended the use of aluminum foil coverings for the reaction vessels, but it should be noted that if the sample contacts the foil an erroneously high ammonium value will result. If foil coverings are used, care should be taken when moving the flasks, and they should be discarded after the addition of the oxidizing solution. After the addition of the last reagent, color will not result from ammonium added to the sample whereas contact with the aluminum foil will still interfere with the results.

The nutrient data were shown to depart from normality in distribution by plotting them on normal probability paper, so parametric statistics could not be applied. The Mann-Whitney U test (Tate and Clelland, 1957) was used for comparing medians from different stations or different periods. This test compares the central tendency of two distributions and does not assume similarity in variance. The Tukey-Siegel modification of the Mann-Whitney U test was used to compare variability between sets of data, the median regression procedure (Tate and Clelland, 1957) was used to calculate the regression lines, and the *tau* coefficient test (Kendall, 1955) was used to determine correlations. The α for significant differences was taken at the 0.05 level except when there was multiple testing, in which cases $0.05/n$ was used where n = the number of times a test was run with interrelated data.

The data for dissolved oxygen, chlorophyll *a*, phaeophytin *a*, silicate, phosphate, phytoplankton species and numbers, temperature, and salinity will be reported elsewhere (Kamykowski).[4]

[3] Reference to trade names in the publication does not imply endorsement of commercial products by the National Marine Fisheries Service.

[4] Kamykowski, D. Some physical and chemical aspects of the phytoplankton ecology off La Jolla, California. Manuscript in preparation.

RESULTS

Representative plots of the nutrient data are shown in Figures 2 and 3. The nitrate concentrations consistently increased with depth. When a thermocline was present, the median nitrate concentration above was 0.49 μg at. N/liter while that below was 12.81 μ at. N/liter. The median nitrite concentration above the thermocline was 0.04 μg at. N/liter while that below was 0.36 μg at. N/liter. The median ammonium concentration above the thermocline was 0.09 μg at. N/liter while that below was 0.34 μg at. N/liter. Both the medians and the variabilities for nitrate, nitrite, and ammonium concentrations above the thermocline were significantly different from those below. The median urea concentration above the thermocline was 0.16 μg at. N/liter while that below was 0.12 μg at. N/liter, and neither the medians nor the variabilities were significantly different.

Urea data for stations made on the same day are plotted in Figure 4. We first noticed that the urea values appeared to vary markedly from one month to another, and since elasmobranches excrete nitrogen primarily as urea (Baldwin, 1964), this pattern suggested that the quantity of urea in the water may have been affected by a heavy infestation of 1-2 m long blue sharks (*Prionace glauca*). The infestation was first noted on 28 February, and initially one could see a few tens of dorsal fins extending above the surface at any time in the vicinity of any of the stations. After a few days the sharks became much more wary of the skiff and although they remained in great numbers, they were usually deeper. Shark sightings continued to be numerous until 21 March and thereafter they were rare. The periods before (7-24 February), during (28 February-21 March), and after (24 March-17 April) the infestation, hereafter referred to as Periods A, B, and C, are indicated in Figure 4. These periods define an initial stage of low urea values, a secondary stage of higher and more variable urea values, and a final stage which appears similar to the first. Medians and ranges for nitrate, nitrite, ammonium, and urea for the three periods are given in Table 1 and were used for the statistical analyses reported in Tables 2, 3, and 4. The highest concentration of urea detected at any time during the sampling program, 1.28 μg at. N/liter, was in a surface sample collected approximately 1 m from a 2½-m blue shark which was near Station I.

Comparisons between Periods A, B, and C Table 4) show that the periods differed with respect to nitrate, nitrite, and ammonium as well as urea. The median nitrate concentration in Period B was significantly lower than those in either Period A or Period C. The median nitrite concentrations were similar for all three periods. The median ammonium concentration for Period C was significantly lower than that for Period A. The median urea concentration for Period B was significantly higher than those for either Period A or Period C. Both the variability and the range of urea concentrations were considerably higher in Period B than in either Period A or Period C.

TABLE 1.—Medians, ranges, and number of samples for nitrate, nitrite, ammonium, and urea within each period. The medians and ranges for each form of nitrogen are in units of μg at. N/liter.

	Nitrate			Nitrite			Ammonium			Urea		
	Median	Range	Number	Median	Range	Number	Median	Range	Number	Median	Range	Number
Period A												
Stations I and III	6.91	0.50-19.07	20	0.25	0.04-0.36	20	0.29	0.00-0.71	20	0.09	0.00-0.18	20
Station II	6.87	0.53-19.00	20	0.21	0.05-0.44	20	0.27	0.00-0.73	20	0.03	0.00-0.25	20
All values	6.58	0.50-19.07	40	0.24	0.04-0.44	40	0.28	0.00-0.73	40	0.07	0.00-0.25	40
Period B												
Stations I and III	0.88	0.00-15.11	30	0.12	0.00-0.61	30	0.21	0.00-1.96	30	0.22	0.00-0.67	30
Station II	1.81	0.00-15.00	30	0.14	0.00-0.58	30	0.25	0.00-1.66	30	0.28	0.00-0.90	30
All values	0.88	0.00-15.11	60	0.13	0.00-0.61	60	0.23	0.00-1.96	60	0.27	0.00-0.90	60
Period C												
Stations I and III	9.43	0.09-23.16	35	0.20	0.00-0.88	35	0.06	0.00-0.59	35	0.09	0.00-0.24	35
Station II	10.09	0.00-20.87	35	0.25	0.00-0.73	35	0.09	0.00-2.38	35	0.12	0.00-0.56	35
All values	9.64	0.00-23.16	70	0.22	0.00-0.88	70	0.08	0.00-2.38	70	0.12	0.00-0.56	70

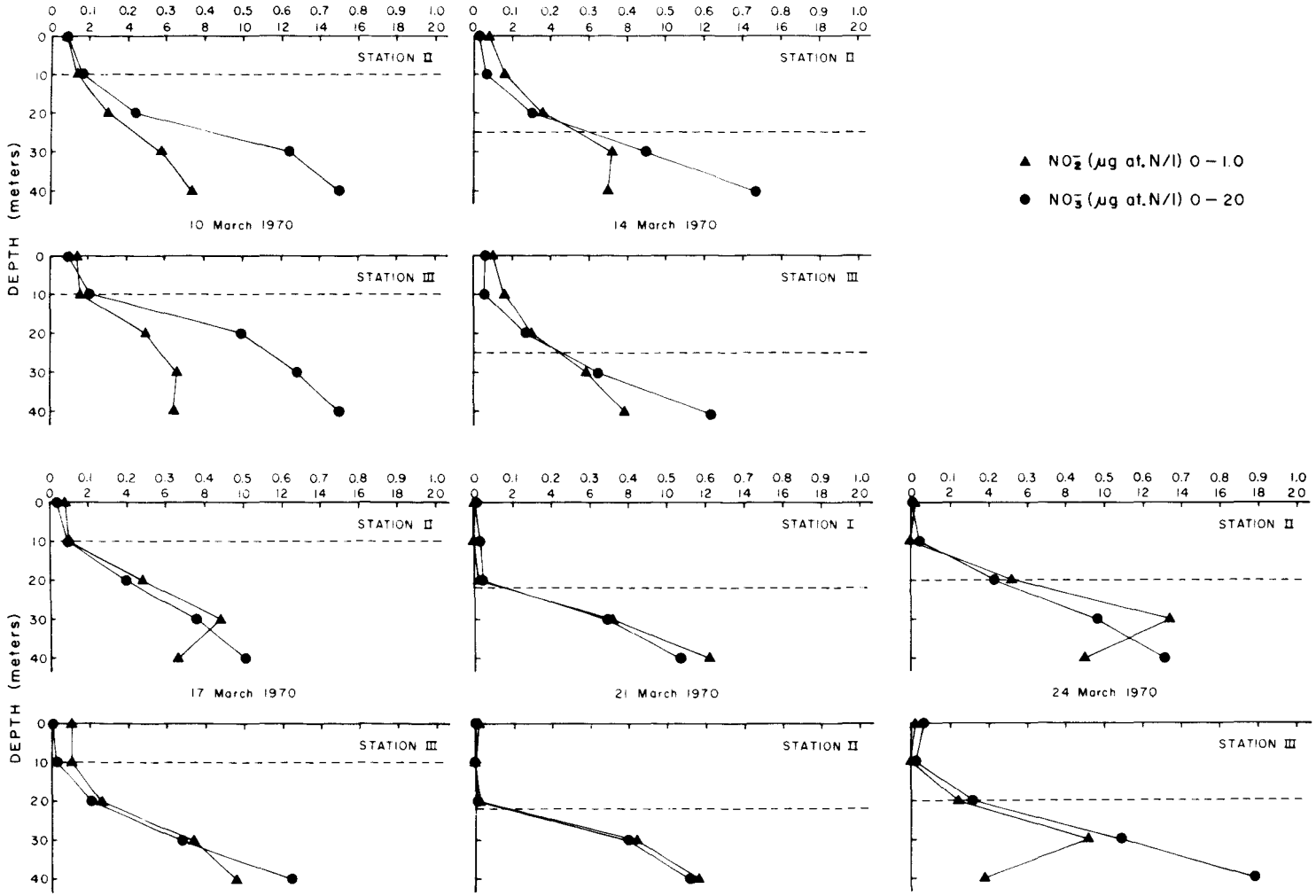

FIGURE 2.—Nitrate and nitrite concentrations for paired stations on five successive sampling days. The depth of the thermocline is indicated by the dashed line.

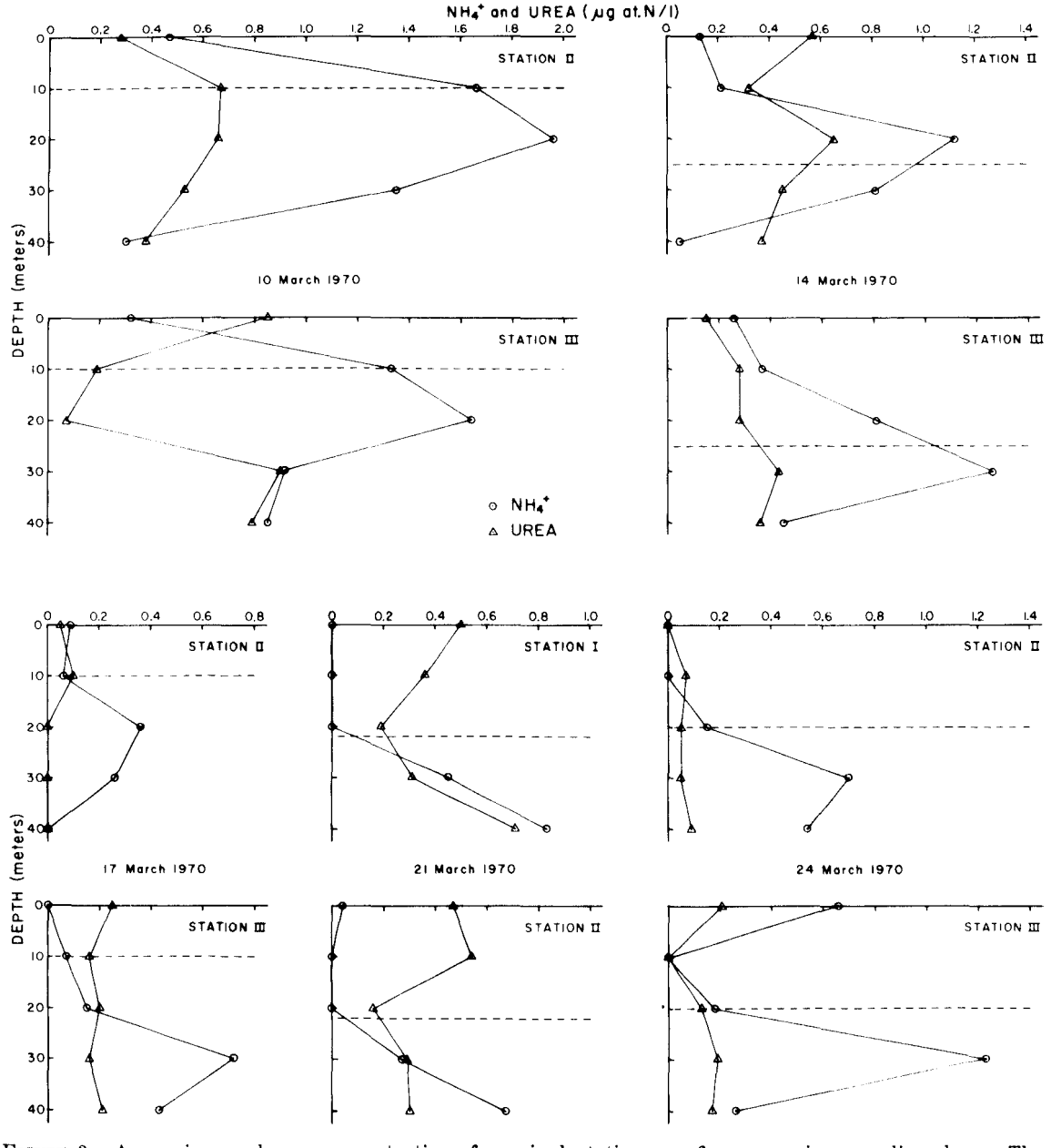

FIGURE 3.—Ammonium and urea concentrations for paired stations on five successive sampling days. The depth of the thermocline is indicated by the dashed line.

The *tau* coefficient was used to examine ammonium and urea concentrations for correlation in each of the three periods. From the z approximation the following pattern emerged: for Period A there was no correlation ($P = 0.030$), for Period B the correlation was positive ($P = 0.009$), and for Period C there was no correlation ($P = 0.124$). Values for the probabilities

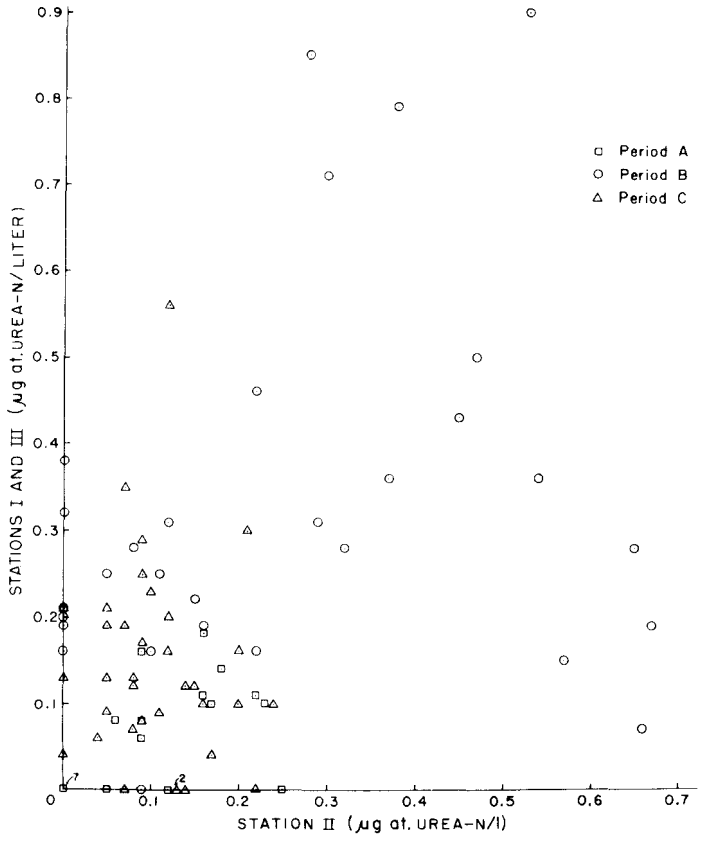

FIGURE 4.—Urea concentrations at the same depth for paired stations sampled on the same day during Period A, Period B, and Period C.

TABLE 2.—Linear regressions of Station I or III vs. Station II for nitrate, nitrite, ammonium, and urea within each period.

Nutrient	Period	Station I or III vs. Station II	P[1]
Nitrate	A	$Y = 1.00X + 0.50$	<0.05
	B	$Y = 0.99X - 0.05$	<0.05
	C	$Y = 0.97X + 1.00$	<0.05
Nitrite	A	$Y = 0.98X + 0.02$	<0.05
	B	$Y = 0.92X + 0.00$	<0.05
	C	$Y = 0.90X + 0.03$	<0.05
Ammonium	A	$Y = 1.10X - 0.02$	<0.05
	B	$Y = 1.76X + 0.17$	<0.05
	C	$Y = 1.42X + 0.02$	<0.05
Urea	A	$Y = 0.65X - 0.02$	<0.05
	B	$Y = 0.52X + 0.16$	>0.05
	C	$Y = 2.00X - 0.06$	>0.20

[1] Probability that the regression slope is not different from zero.

are for the two-sided test and since these same data will be used for another analysis the level of significance (α) is taken as 0.05/2.

Vaccaro and Ryther (1960) observed maximum concentrations of nitrite when both phytoplankton and nitrate were abundant at light limiting depths. *Tau* coefficients indicated that in the present study there were no significant correlations between either 1) the median chlorophyll *a* and the median nitrite concentrations below the thermocline ($P = 0.288$) or 2) the chlorophyll *a* and the nitrite concentrations at or within 5 m of the thermocline ($P = 0.490$).

Lorenzen (1967) suggested that a phaeo-pigment/chlorophyll ratio is indicative of herbivore grazing pressure, and since ammonium is the major nitrogenous excretion product of most marine crustaceans (Parry, 1960), we used the *tau* coefficient to examine the phaeo-pigment/chlorophyll ratios and ammonium and urea data from this study for positive correlation. If one assumes that the single pigment profile taken each sampling day is representative of the whole area

TABLE 3.—Comparisons of medians and variability of the nitrate, nitrite, ammonium, and urea results from stations sampled on the same day.

Nutrient	Period	Medians P	Variability P
Nitrate	A	>0.70	>0.40
	B	>0.70	<0.05
	C	>0.40	>0.20
Nitrite	A	>0.40	>0.70
	B	>0.70	>0.40
	C	>0.90	<0.05
Ammonium	A	>0.90	>0.90
	B	>0.40	>0.60
	C	>0.60	>0.10
Urea	A	>0.20	>0.90
	B	>0.10	<0.05
	C	>0.20	>0.60

for that day, it is reasonable to compare the phaeo-pigment/chlorophyll ratios with the best estimate of average ammonium and urea values for the same area. This is supported by the findings that the phytoplankton species composition was similar at all three stations and that the surface chlorophyll concentrations at Stations I and III were significantly correlated with the surface cell counts at Station II. Thus we paired the phaeo-pigment/chlorophyll ratios with the median ammonium and urea values at each depth for the same day in the following analysis. The phaeo-pigment/chlorophyll ratios were not correlated with the median ammonium concentrations in either Period A ($P = 0.189$) or Period C ($P = 0.171$) but were positively correlated in Period B ($P < 0.001$). The phaeo-pigment/chlorophyll ratios were not correlated with the median urea concentrations in Period A ($P = 0.382$), Period B ($P = 0.397$), or Period C ($P = 0.166$). Since each set of pigment and nutrient data have been used in two correlations, an appropriate α for significance is 0.05/2. Scatter diagrams for phaeo-pigment/chlorophyll ratios and the median ammonium and urea concentrations are presented in Figures 5 and 6 respectively.

DISCUSSION

Earlier studies in the Peru Current (McCarthy, 1970), in the central Pacific (McCarthy, 1971), and the present study have shown that great differences in both ammonium and urea occur on a vertical scale of a few meters. If during this study a small-scale inhomogeniety had been prevalent in the horizontal as well as vertical dimensions, it should have been evident both within and between stations made on the same day. If, on the other hand, there had been horizontal patches large with respect to a 1.5 km distance, the concentration at a particular depth should have been similar at both stations; this was apparently the case for nitrate, nitrite, and

TABLE 4.—Normal deviates (z) and corresponding probabilities (P) for comparisons between medians and variabilities of nitrate, nitrite, ammonium, and urea for all three periods.

Nutrient	Periods	Medians		Variabilities	
		z	P[1]	z	P[1]
Nitrate	A vs. B	3.80	**<0.005**	3.12	**<0.005**
	A vs. C	0.37	0.712	3.17	**<0.005**
	B vs. C	3.82	**<0.005**	2.72	**<0.005**
Nitrite	A vs. B	1.68	0.083	0.60	0.549
	A vs. C	0.48	0.631	4.89	**<0.005**
	B vs. C	1.83	0.067	2.31	**0.021**
Ammonium	A vs. B	0.57	0.569	2.36	**0.018**
	A vs. C	3.19	**<0.005**	1.40	0.162
	B vs. C	2.14	0.032	3.98	**<0.005**
Urea	A vs. B	5.58	**<0.005**	4.90	**<0.005**
	A vs. C	2.74	**<0.005**	1.02	0.308
	B vs. C	5.02	**<0.005**	4.97	**<0.005**

[1] P values are given for the two-sided test. To correct for multiple testing an α of 0.05/2 should be used. Significant differences are in bold type.

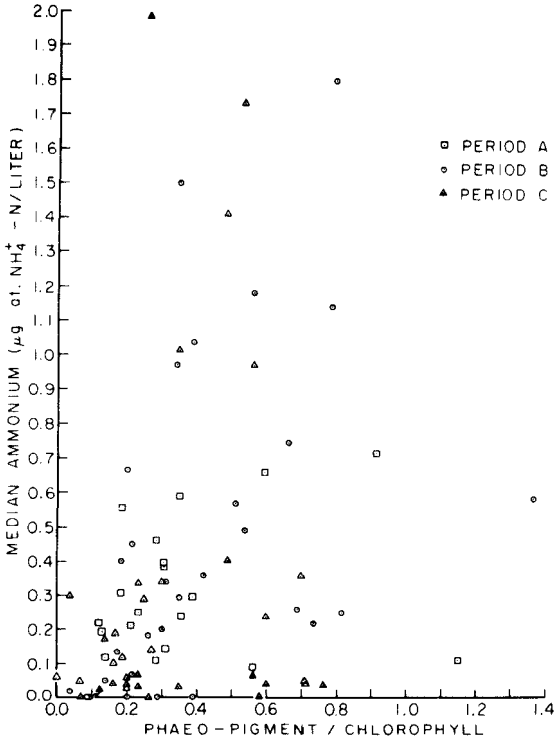

FIGURE 5.—Median ammonium concentrations and phaeopigment/chlorophyll ratios for Period A, Period B, and Period C.

to a lesser degree for ammonium but was not the case for urea.

Table 2 shows that the slopes for nitrate, nitrite, and ammonium regression equations contrasting the two stations sampled on any one day are positive and are significantly different from zero for each period. This implies that the values observed at each depth at one station on a particular day are positively correlated with those at corresponding depths at the other station. This resulted because the nitrate and nitrite profiles were nearly identical for the two stations on a single day and the ammonium profiles generally resembled each other. The regression slopes for the nitrate and nitrite data were all similar to 1.0, but the ammonium and urea slopes were occasionally far from unity. The regression slopes for the urea data were not significantly different from zero for either Period B or Period C. This analysis indicates that the patch structure of urea distribution is probably of a smaller horizontal scale than that of nitrate, nitrite, or ammonium. In comparing a particular depth at one station with the corresponding depth at another station, the two urea values are less likely to be similar than the ammonium values and considerably less than the nitrate or nitrite values.

The similarity of median values for the station pairs sampled on the same day (Table 3) suggests, on the other hand, a homogenous distribution for each nutrient over the sampling area; however, the stations showed markedly more resemblance in nitrate, nitrite, and ammonium than in urea. Comparisons also showed that within each period the median at Stations I and III were not different. This further supports the hypothesis of a smaller patch structure for urea since there was no persistent difference between stations with respect to urea, even though on any one day the stations may have differed significantly.

The three periods were based on the timing

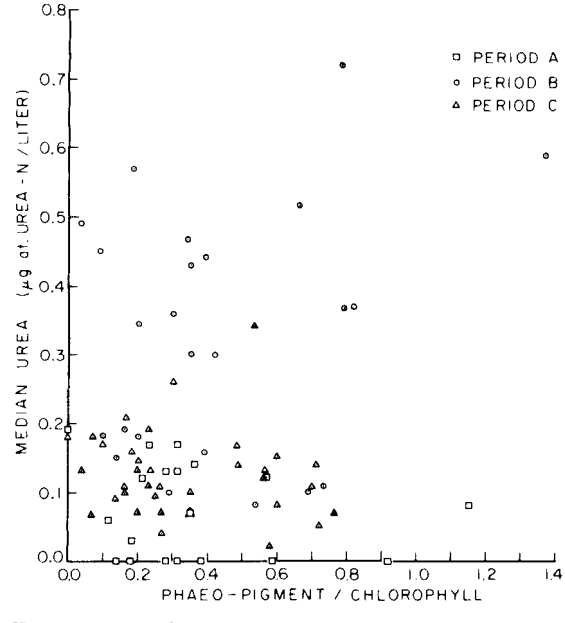

FIGURE 6.—Median urea concentrations and phaeo-pigment/chlorophyll ratios for Period A, Period B, and Period C.

of the shark infestation, and it is evident that the urea values were elevated significantly during Period B. It is unlikely that the significant differences in the medians and variabilities of the nitrate, nitrite, and ammonium values between periods were related to the presence of the sharks per se. The trends for each nutrient were markedly different: For nitrate the Period B median concentration was less than that in either Period A or Period C, for nitrite the median was unchanged, and for ammonium the median in Period B was greater than that in Period C but not different from that in Period A. Kamykowski (see footnote 4) presents data which suggests that a mechanism involving internal waves acting together with intermittent wind-related events (e.g., upwelling) can explain the pattern of increases in surface nitrate and corresponding decreases in surface temperature found in the study. Strasburg (1958) has shown that blue sharks in the central Pacific Ocean were found most frequently where the temperature was between 7° and 15°C; however, the temperature differences with respect to either time or depth which were encountered during the present study were not sufficient to provide an explanation for the shark infestation.

The nitrite regression equations contrasting the two stations sampled on the same day reveal that the dynamics of the nitrite production and utilization is uniform over the scale of a few kilometers. If the greater nitrite concentration below the thermocline represents a greater rate of production, our finding is consistent with the ideas put forth by Vaccaro and Ryther (1960) which suggest that nitrite liberation by phytoplankton in the presence of excess nitrate will be intensified at reduced light levels. The lack of correlation between the chlorophyll *a* and nitrite concentrations, however, implicates a complex interaction between components of the nitrite system.

The lack of correlation between ammonium and urea concentrations for Period A and Period C follows the pattern seen earlier in data from the English Channel (Newell, 1967), the Peru Current (McCarthy, 1970), and the central Pacific (McCarthy, 1971), but the strong positive correlation in Period B deserves further consideration. The median ammonium values for Periods A and B were not different, and although the rates must have been similarly balanced, the sources as well as rates of both supply and utilization could have been considerably different for the two periods. If the shark infestation was responsible for the elevated urea concentrations during this period, was it perhaps not also responsible for enough of the ammonium present to have produced the observed relationship? It would seem unlikely that the sharks were directly responsible since the selachii (modern sharks) are reported to excrete 80-90% of their nitrogenous end products as urea, 2-10% as ammonium, and the balance as amino acids and an unidentified fraction (Scheer, 1963). During Period B a squid (*Loligo opalescens*) spawn was noted off the coast of La Jolla. These usually last approximately 1 week, and during this time the adult squid reportedly do not feed (A. O. Flechsig, personal communication). Sharks collected during this period were found to have been feeding on squid (N. Marshall and G. Sullivan, personal communications), but it seems unlikely that the sharks were attracted to this area by the squid since such spawns are frequently noted without the presence of sharks. The squid spawns do, however, regularly attract birds (*Larus* spp.), and we also noted greater abundances of birds during this time. Nitrogen is excreted principally as ammonium by cephalopods (Barnes, 1963) and as uric acid by birds (Needham, 1931). It has been reported that uric acid is unstable in seawater and rapidly degrades to urea (Williams, 1970)[5] so the birds might have been an additional source of urea.

It is therefore possible that Period B was also unique with respect to the presence of ammoniotelic organisms which were either directly or indirectly supporting or supported by the shark population and which were in sufficient abundances to have resulted in the positive correlation between ammonium and urea concentrations.

[5] Williams, P. M. 1970. The stability of organic nitrogen compounds in seawater. University of California, Institute of Marine Resources. Research on the marine food chain progress report for U.S. Atomic Energy Commission Contract At(11-1)GEN 10, P.A. 20. Part 1, p. 8b. [Unpubl. manuscr.]

The strong positive correlation between phaeo-pigment/chlorophyll ratios and ammonium concentrations in Period B suggests that ammoniotelic herbivores were important, and perhaps the presence or abundances of these organisms were also related to the shark presence.

Another possible explanation for the positive correlation between ammonium and urea concentrations is that bacterial hydrolysis of urea during Period B was responsible for increased ammonium production. ZoBell and Feltham (1935) isolated marine bacteria capable of hydrolyzing urea from the same area used for the present study, but indirect evidence (McCarthy, in press) indicates that bacterial hydrolysis is probably of much less importance than phytoplankton uptake in the fate of urea in near surface waters off the coast of Southern California.

Fish, zooplankton, and phytoplankton have long been known to occur in schools, patches, and layers in near surface waters, and their spatial array probably contributed to the irregular distributions of both ammonium and urea seen in this study. On a scale of a few meters the input due to zooplankton and the utilization due to phytoplankton may approach an equilibrium, but the immediate effect of a large fish or fish school passing through a particular volume would be elevated ammonium and urea concentrations which would decrease with time at rates dependent on both diffusion and biological utilization. Since the blue shark has no urinary sinus (Dr. T. Enns, personal communication), both the branchial and the renal systems would be expected to release urea continuously. One can calculate both branchial (Boylan, 1967) and renal (Forster, 1967) excretion rates for *Squalus*, but it is questionable whether these rates would be representative of *Prionace glauca*. The major problem in attempting to estimate the shark urea production during the present study is, however, that of reliably estimating the shark biomass.

An increased rate of ammonium or urea production in a parcel of water will not necessarily be reflected in an increased seawater concentration of the metabolite. To the extent that rates of utilization are dependent on substrate concentrations, e.g., nitrogen uptake by phytoplankton, then an immediate increase in the rate of utilization might be expected in response to an increased rate of production. There are no sewage outfalls in the vicinity of La Jolla Bay, but the supply of ammonium and/or urea to waters proximate to such discharges may result in significant enrichment with these nutrients (Eppley et al., in press).

Because of the spatial variability in both supply and utilization and the low concentrations usually encountered, it is difficult to interpret, or even detect, short-term changes in ammonium and urea concentrations in near-surface seawater. Surface waters into which fish and crustaceans migrate daily in some degree of synchrony to feed is one setting in which such changes might be expected, and have been observed. Beers and Kelly (1965) presented data which suggested a correlation between variations in ammonium concentrations in the upper 500 m of the Sargasso Sea and the diurnal migration of zooplankton, and Emmet (1969) referred to unpublished work which showed that a diurnal maximum in urea concentration occurs in open ocean surface waters early in the morning.

If, as Lorenzen (1967) has suggested, a phaeo-pigment/chlorophyll ratio is indicative of herbivore grazing pressure, the significant correlation between this ratio and ammonium concentrations reported in Period B of this study might imply that (1) both fecal material and ammonium excreted by herbiverous zooplankton have residence times which are similar, or (2) ammonium is released with the degradation of herbivore fecal pellets. The lack of correlation in Periods A and C might imply that herbivores were not significant sources of ammonium during these periods. The lack of correlation between phaeo-pigment/chlorophyll ratios and urea concentrations might imply that (1) herbivore excretion is not an important source of urea, (2) the residence times of phaeo-pigments and urea are sufficiently different to mask any association, (3) urea excreted by nonherbivores obscured a relationship between phaeo-pigment/chlorophyll ratios and urea concentrations, or (4) urea is not released with the degradation of herbivore fecal pellets. Herbivores zooplankton have been shown to release substantial quantities

of urea (Corner and Newell, 1967; McCarthy, 1971) so the lack of correlation with phaeo-pigments might further implicate the blue sharks as the major source of urea during Period B. The residence times of ammonium and urea may well differ since ammonium is utilized readily by all marine phytoplankters whereas urea is utilized by only some species and even then uptake may be partially suppressed by certain concentrations of nitrate or ammonium (McCarthy and Eppley, in press). It is not known whether urea is released in fecal pellet degradation.

The data from the present study do not show whether the relationship between the presence of the blue sharks and the elevated urea values in Period B is one of cause and effect. If the sharks were a significant source of urea, this may provide an explanation for the similarity in urea concentrations above and below the thermocline, the more irregular distribution of urea, and perhaps the lack of correlation between phaeo-pigment/chlorophyll ratios and urea concentrations. Without estimates of urea input due to excretion by sharks, other fish, zooplankton, and possibly birds, and rates of urea utilization for phytoplankton, the net effect of the shark population's contribution to urea production cannot be rigorously evaluated.

While this manuscript was in review, Remsen (1971) published the results of urea analyses for samples collected from both the eastern tropical Pacific Ocean and coastal waters off northeastern United States. The concentrations he detected were generally higher than those reported either previously or in this communication but his conclusions as to the biological significance of urea in the marine environment are not at variance with those presented here

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