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PHYTOPLANKTON UTILIZATION OF NITRATE, NITRITE,
AMMONIUM AND UREA NITROGEN IN THE CHESAPEAKE BAY

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We have nearly completed the field work in a program which was designed to assess the relative importance of different forms of nitrogenous nutrients in the Chesapeake Bay. Since some of our laboratory analyses have not yet been completed, and we have a great deal of unreduced data, our remarks today will constitute a preliminary summary of some of the patterns we have observed in the distribution and phytoplankton utilization of nitrogenous nutrients in the Chesapeake Bay. We would like to acknowledge the NSF Grant GA-33445 and AEC Grant AT(11-1)3279 for support of this study.

Through the efforts of Dr. James Carpenter and co-workers in the late 60's, temporal and spatial patterns for nitrate distribution in the northern portion of the Chesapeake Bay were identified. There are high levels of nitrate in the winter and spring, and these are levels which we feel are more than adequate to meet the nutritional needs of the phytoplankton at observed rates of primary productivity. However, during the summer and early fall, the nitrate levels are reduced substantially, and we feel they are low enough to suggest that the phytoplankton are depending heavily upon other forms of nitrogen. The annual range of concentrations for nitrate is from a few tenths to a few tens μg at N/liter. We wanted to investigate this picture more thoroughly and in particular to examine the significance of rapidly recycled nitrogenous nutrients during periods of both high and low nitrate concentrations. Thus, we established a field study which covered the main body of the Chesapeake Bay and adjacent shelf over a 13 month period. The great temporal and spatial variability of nitrogenous nutrient concentrations afforded the opportunity to observe in situ the rate of utilization of a single nitrogenous nutrient when other nitrogenous nutrients were present over a wide range of natural concentrations.

Figure 1 shows the Chesapeake Bay. Major features are the metropolitan areas of Baltimore and District of Columbia which discharge domestic and industrial wastes into sub-tributaries of the Bay and the major rivers are the Patuxent and Potomac in the northern part of the Bay, the Rappahanock, York and James in the lower portion of the Bay. The length of the Bay is approximately 300 kilometers; maximum depth of 53 meters and a mean depth of 8.4 meters.

Without going into detail we would like to simply state that as surprising as it may seem, the waste discharges from Metropolitan Baltimore and Metropolitan District of Columbia are rarely seen in the main body of the Bay, either as dissolved nutrients or as plant biomass. There is a great deal of data accumulated in the past decade by Dr. James Carpenter and Dr. David Flemmer of the Chesapeake Bay Institute and Chesapeake Biological Laboratory, respectively, in the Potomac and Patuxent Rivers which demonstrate that as one moves upstream from the Bay steep gradients of both plant nutrients and biomass are encountered. Concentrations of both nitrate and ammonium increase markedly as one moves upstream towards the point of waste discharges, however, at the mouth of both of these tributaries one can rarely see concentrations of dissolved plant nutrients which are higher than the levels which can be seen in the Bay proper either north or south of the juncture of the tributary and the Bay.

Again referring to Figure 1, we would like to give you some ranges of parameters which we observed in the water during the period of this study from December 1972 through December 1973. The near surface salinity ranged from approximately 5 to 12 ‰ in the vicinity of Baltimore, to 15 to 20 ‰ in the lower portion of the Bay at station 7070. The

temperature ranged from 4 to 29°C in the near surface water and was nearly uniform over the entire Bay during any of our cruises. Plant biomass as measured by chlorophyll is rather surprisingly uniform. Better than 50% of our values for the near surface waters are between 10 and 20 µg chl/liter and better than 90% of our values are between 5 and 25 µg chl/liter. Again these represent a complete annual cycle and nearly the entire length of the Bay. This is not to say there are not blooms or occasional hot spots in this rather high, somewhat uniform level of plant biomass and we did in fact, observe one very intense bloom of Gymnodinium splendens in which the chlorophyll exceeded 1000 µg/liter. This is the most intense bloom that we or anyone else, as far as we know, has observed in the Chesapeake Bay. The euphotic zone varied between approximately 2 and 10 meters and was usually contained within the upper mixed layer of the two-layer estuarine system.

Our field study covered a 13 month period. It consisted of two-week cruises at eight-week intervals. The stations which were occupied are represented in Figure 1, the furthest north of which, 904N, was located immediately below Baltimore Harbor. We found it extremely difficult, sometimes impossible, to work much further north than this because of the high level of suspended inorganic material, particularly during the period of spring runoff. Station 854G was east of the Rhode River-West River area and this is a station which we use in common with Dr. Seliger's group in his studies of the Rhode River and West River. Station 834G is located just below the juncture with the Choptank River. Station 818P is just off the mouth of the Patuxent River. Station 804C is just above and 744 is just below the mouth of the Potomac River. Station 724R is below the Rappahanock River. Station 707Ø is below the mouth of the

York River and in the ship channel at the lower end of the Bay, and Station 0707V is out of the mouth of the Bay and onto the shelf.

Each station was occupied for a full day. Numerous physical, chemical and biological measurements were made. The data which we are presenting were generated from experiments which employed N^{15} as a tracer to measure the rates of utilization of nitrate, nitrite, ammonium and urea nitrogen.

Figure 2 shows the nitrate concentrations observed during the field program. On the abscissa is time from December 1972 through December 1973 and on the ordinate is the position within the Bay represented by the station number. The direction from 904N will be due south to 7070 and from that point due east to 0707V. The concentrations have been represented as ranges. We have established for convenience sake a uniform limit of detection for all of our methods as $0.05 \mu\text{g at N/liter}$. The samples which contain less than a detectable amount of nitrogen in any of the four forms are identified as the open areas in the figures. Concentrations between 0.05 and $0.39 \mu\text{g at/liter}$ represent the range which we feel likely to be limiting the productivity of phytoplankton in the Bay. The samples showing concentrations between 0.4 and $4.9 \mu\text{g at/liter}$ represent a range which we think may possibly be limiting phytoplankton productivity in the Bay. Concentrations between 5 and $10 \mu\text{g at/liter}$ are most likely not limiting phytoplankton productivity in the Bay and those greater than 10 are definitely not limiting. We can see in Figure 2 that through the early part of the year we have very high concentrations of nitrate resulting from the winter and spring runoff of the Susquehanna River; the maximum concentration during this period was $67 \mu\text{g at/liter}$.

The minimum concentration observed over the entire study was at 7070 in December 1973 and this was a sample which had no detectable nitrate. Note particularly the summer and autumn portion of the plot for the lower and mid-bay region in which the lowest concentrations for the entire study occur. In Figure 3 the same type of plot is given for the nitrite concentrations. The concentrations of nitrite range from our limit of detection to 9.1 μg at N/liter, and note again the area of lowest concentrations on this plot is the lower and mid-bay region during the summer. Figure 4 is a similar plot for the ammonium concentrations. Note that the ammonium concentration is far more irregular or patchy than that for nitrate or nitrite and the range of ammonium concentrations was from the limit of detection to 15 μg at/liter; but it can be seen that concentrations in excess of 10 μg at/liter were very rare, and in fact most frequently the concentration was less than 5 μg at/liter. Note again the lower and mid-bay region in the summer in which we have the lowest concentrations of ammonium. Figure 5 is a similar plot for urea nitrogen. Again note a very patchy distribution with concentrations ranging from the limit of detection to 2.4 μg at N/liter, and again note the lower and mid-bay summer area which demonstrates the very low concentrations.

One of our efforts to assess the sufficiency of the nitrogenous nutrition of the phytoplankton of the Chesapeake Bay is demonstrated in Table 1. What we have done is to break down the available nitrogenous nutrient as four separate forms, nitrate, nitrite, ammonium and urea, and represent these as fractions of the total available nitrogenous nutrient. The data selected for this table are for station 804C and they are for months which will show contrasting conditions; February 1973, when the

total nitrogenous nutrient available in the water column was 34.8 μg at N/liter; and in August 1973 when the total available was 0.43 μg at N/liter. Note that in February the partitioning of the available nitrogenous nutrient demonstrates that 97% was available as nitrate, 2% as nitrite, 1% as ammonium and 0.1% as urea. In contrast the partitioning of the nutrient utilized by the phytoplankton gives 35% utilized as nitrate, none used as nitrite, 63% utilized as ammonium, and 3% as urea. By calculating a ratio of the fraction utilized to the fraction available, expressed here as a relative preference index or RPI from this point on, we see values of 0.4 for nitrate, 0 for nitrite, 63 for ammonium and 30 for urea. It is obvious that if the phytoplankton are utilizing a form of nitrogen proportionately to its availability the RPI would be 1, and whereas an RPI in excess unity would demonstrate a preference or selection for a particular form of nitrogen, a value less than unity would suggest that this form is being rejected. In the case of February 1973 at station 804C it can be seen that ammonium was strongly selected for; urea was moderately selected for, whereas relative to availability both nitrate and nitrite were rejected. In August 1973 there was a far more equitable distribution of the total available nitrogen. There is a similar partitioning of the fraction of the total which was utilized and the relative preference index gives values of 0.9, 0.8, 1.4 and 1, suggesting that the different forms of nitrogenous nutrient were utilized essentially in proportion to their availability. August is obviously in contrast with February, not only with respect to total available nitrogenous nutrients, but also with respect to the selection of the forms which were available.

Figure 6 shows RPI values for nitrate plotted in a similar fashion to the concentrations of the nutrients. We have again blocked off ranges of concentration, and we have put rather broad limits around the value of unity; that is, an RPI of 0.5 to 1.5 is the range which we would consider to approximate unity or nearly equitable utilization of a particular form of nitrogen relative to its availability. A value of less than 0.5 will suggest that the particular form of nitrogen is not being selected for. Values of 1.6 to 10 will suggest strong preference for the particular form, and values greater than 10 a very strong preference. Figure 6 shows that for most of the year over most of the Bay, nitrate was definitely not selected for, and only in the lower and mid-bay region in summer when concentrations of all forms of nitrogen were low do the RPI values for nitrate approach the region which suggests equitable utilization. The maximum RPI value for nitrate during this study was 1.1. Figure 7 gives a similar plot for nitrite and here again note that for much of the bay over much of the year we see that nitrite is not selected for, but in the summer lower and mid-bay region we see RPI values in the region of 0.5 to 1.5. There are two points in the upper Bay in the spring and summer in which the RPI values exceeded 1.5. Figure 8 is a similar plot for ammonium and note a strong contrast with both the nitrate and nitrite plots. For a good portion of the Bay and the year, very strong preference for ammonium occurs. Only occasionally, as in the summer period of the lower and mid-bay region, do the RPI values for ammonium approach unity; the minimum value was 1.1. Figure 9 shows the plot for urea nitrogen. Again note the strong preference for urea with RPI

values exceeding 10 during the winter, as was seen for ammonium, and this was the time of the year in which we saw high nitrate concentrations in the Bay. Note again that the RPI values for urea decrease toward a value of unity in the summer lower and mid-bay region.

What is apparent from the plots of the RPI values is a situation in which the RPI for nitrate is nearly always less than 1, while that for ammonium is nearly always greater than 1. Both appear to converge toward a value of unity when the total nitrogenous nutrient becomes scarce. Nitrite is probably utilized by the phytoplankton as if it were nitrate and the condition for urea is somewhat intermediate since urea is utilized simultaneously with both ammonium and nitrate. We have plotted the RPI values against total nitrogenous nutrient, and we do see convergence toward unity. We were in hopes that this would be well enough defined to suggest rather clearly the concentration of total nitrogenous nutrients below which nitrogen limitation of phytoplankton productivity might be expected in the Chesapeake Bay. However, the pattern is not that well defined and our best estimate from this analysis is that such a concentration would be approximately 5 μg at N/liter.

Additional insight is, however, obtained from another analysis. The results of experiments in Eppley's laboratory have suggested that an ammonium concentration of approximately 1 μg at N/liter is sufficient to suppress nitrate uptake by phytoplankton, and our field observations give similar results. Figure 10 is a plot of the fraction of the total nitrogenous nutrient uptake which was due to nitrate and nitrite in the presence of a wide range of ammonium concentrations. There are 120 data points in this plot and the nitrate concentrations range from the limit

of detection to $67 \mu\text{g at/liter}$. The dashed lines are an eyeball approximation intended to include as many data points as possible. Three of the five outside the area enclosed by the dashed lines could be included without changing the point of intersection of the two lines. The point of intersection demonstrates that at ammonium concentrations which exceed approximately $1 \text{ to } 1.5 \mu\text{g at N/liter}$, less than 5% of the total nitrogenous nutrient uptake will be in the form of nitrate and nitrite. What we have then is a demonstration from field data which supports the earlier observations in the laboratory, and these data would suggest that at ammonium concentrations less than the $1 \text{ to } 1.5 \mu\text{g at N/liter}$ the phytoplankton are finding it energetically efficient to activate their enzyme systems for nitrate assimilation and reduction.

In conclusion, what we have presented is one piece of a much larger effort which was designed to assess the significance of rapidly recycled nitrogenous nutrients of the Chesapeake Bay. It is apparent that the rapidly recycled forms of nitrogen are of major importance in the nitrogen economy of the Bay, and at this point we are trying to balance the rest of the equation.

Table 1

Comparisons for availability and utilization of nitrogenous
nutrients at Chesapeake Bay Station 804C.

FEBRUARY 1973

Total N = 34.8 μ gatom/liter

	% of Total Available	% of Total Utilized	Relative Preference Index
NO_3^-	97	35	0.4
NO_2^-	2	0	0
NH_4^+	1	63	63
Urea	0.1	3	30

AUGUST 1973

Total N = 0.43 μ gatom/liter

	% of Total Available	% of Total Utilized	Relative Preference Index
NO_3^-	42	38	0.9
NO_2^-	12	10	0.8
NH_4^+	12	17	1.4
Urea	35	35	1

FIGURE CAPTIONS

Figure 1. Location of stations.

Figures 2-5. Concentration of different forms of nitrogen. See text.

Figures 6-9. Relative Preference Indices for the different forms of nitrogen. See text.

Figure 10. Ratio of the uptake of nitrate + nitrite divided by the total nitrogen uptake plotted against ammonium concentration.

Nitrate
Concentrations
 $\mu\text{g atoms/liter}$

< 0.05

0.4-4.9

0.05-0.39

5-10

>10

Fin

Nitrite
Concentrations
 $\mu\text{g atoms/liter}$

< 0.05

0.4-4.9

0.05-0.39

5-10

>10

Fig 3

Ammonium
Concentrations
 $\mu\text{g atoms/liter}$

< 0.05

0.4-4.9

0.05-0.39

5-10

>10

Fig 4

Urea-N

Concentrations

$\mu\text{g atoms/liter}$

< 0.05

0.4 - 4.9

0.05 - 0.39

5 - 10

> 10

Fig 1

Relative Preference

> 0.5

1.6-10

Index - Nitrate

0.5-1.5

> 10

F-15 C

Relative Preference

> 0.5

1.6 - 10

Index - Nitrite

0.5 - 1.5

> 10

Fig 7

Relative Preference
Index - Ammonium

< 0.5

0.5-1.5

1.6-10

> 10

904 N

854 F

834 G

818 P

804 C

744

724 R

707 Ø

707V

D

F

A

J

A

O

D

Fig 8

Relative Preference

Index - Urea - N

< 0.5

0.5-1.5

1.6-10

> 10

Fig 5

Fig 10