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PHOSPHORUS DYNAMICS IN SOME COASTAL PLAIN ESTUARIES

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ABSTRACT

Phosphorus availability in estuaries may have a seasonal cycle with a maximum usually occurring in the summer when orthophosphate is released into oxygen depleted deep water and transported to the euphotic zone by turbulent mixing. Superimposed on the annual fluctuation of total phosphorus is the rapid turnover of orthophosphate and phosphorus monoesters in the euphotic zone. The concentrations of these materials in surface waters are similar and phosphate uptake kinetics from each type by natural phytoplankton assemblages are similar which suggests that phosphorus monoesters may be significant in phytoplankton phosphorus nutrition.

Introduction

One of the most important and interesting questions that can be addressed in an estuary is: What factors are regulating phytoplankton primary productivity? Studies of rapid nutrient recycling indicate that the answers to this question are complex and vary with region. However, another question which seems to have simpler answers is: What factors are regulating the level of phytoplankton biomass?

The upper limit of phytoplankton biomass is usually established by the nutrient and/or light regimes. In estuaries, phosphorus, nitrogen and light availability may temporally and spatially alternate as the single regulating factor. This paper deals with the role of phosphorus in regulating phytoplankton biomass in several estuaries through consideration of the literature and presentation of some recent data of our own. It also reviews some of our recent thoughts on the significance of phosphorus monoesters in phytoplankton nutrition. For the most part we will concentrate our discussion on a few estuaries of the mid-Atlantic coastal plain (Figure 1).

Figure 1

The Annual Cycle

Newcombe and Lang (10) reported an annual cycle of phosphate availability in Chesapeake Bay in which the highest concentrations were present in summer and lowest concentrations were found in winter. Smayda (17) made a similar observation for lower Narragansett Bay, R.I., and cited the work of Ferrara who also observed a summer phosphate maximum in upper Narragansett Bay. Smayda termed

the cycle "atypical" compared to the annual temperate open ocean cycle in which the phosphate maximum occurs in winter. Jeffries (8) observed a summer phosphate maximum in Raritan Bay, N.J. He also found high phosphate waters entering the bay along the northern shore. Patten, Mulford and Warriner (11), working in the York River and lower Chesapeake Bay, found a late summer and early fall phosphate maximum. Whaley, Carpenter and Baker (24), in an intensive study of upper Chesapeake Bay and its rivers and embayments, frequently found summer phosphate maxima in deep water. Hobbie, Copeland and Harrison (7) and Copeland and Hobbie (4) also observed summer phosphate peaks in the Pamlico River estuary.

Figure 2

Data from some of these studies is summarized in Figure 2. Two data points for Delaware Bay (14) are included with the Chesapeake Bay data. Although not definitive, they suggest that Delaware Bay may be subject to summer phosphate maxima as are some of its inshore marshes (15, 16).

The mechanism for the summer phosphate influx into these estuarine waters is not well explained. It appears that during most of the year the phosphate remineralized by bacterial activity from organic matter in the sediments reacts with iron (III) to form insoluble ferric phosphate which remains on the sediment surface or in the upper interstitial waters. As summer progresses, oxygen in deep waters is removed faster than it is replaced. Hypoxic and anoxic conditions favor phosphate release from ferric phosphate into the overlying water where physical circulation returns the phosphate

to the euphotic zone. It has been demonstrated that oxidation of anoxic sediments during sampling significantly decreases the dissolved orthophosphate measured in sediments rich in iron II (1, 22, 23).

It has been suggested that suspended sediment particles "buffer" the inorganic phosphate concentration of the water (3, 13) so one would not expect the sediments to readily release phosphate unless iron binding is a principal mechanism for phosphate retention on sediment particles.

A second explanation for the observed annual cycle could be continual orthophosphate release from sediment interstitial water and its uptake by bacteria in the upper few cm of aerobic sediment. With the onset of hypoxia and anoxia in the overlying water the high metabolic activity of the aerobes is checked and replaced by the slower metabolic processes of anaerobic bacteria which cannot utilize all phosphate available. The excess phosphate then escapes into the water column. This hypothesis has not been tested but it is unlikely that even aerobic bacteria near the sediment surface could consume virtually all of the phosphate diffusing from the interstitial water. However, it is plausible that both ferric phosphate formation and bacterial uptake contribute to phosphate retention in aerobic sediments.

Once dissolved in deep water, phosphate is transported vertically at the same rate as sea salts. Upon entering the euphotic zone the phosphate is taken up by phytoplankton and its presence is reflected as increased particulate and total phosphorus. We have discussed this observation elsewhere (19).

In fall, the surface waters cool, oxygen input to the deep waters exceeds demand and phosphate release from the sediments is no longer detectable. Particulate phosphate in the euphotic zone is flushed out of the estuary, is remineralized in the water column or settles onto the bottom. The net removal of phosphate from the surface layers is reflected in decreased total phosphorus concentrations.

Release from the sediments represents the only detectable inorganic phosphate source for open Chesapeake Bay waters. Most phosphorus entering from major tributaries is organic and must be remineralized to be useful to indiginous phytoplankton assemblages (2, 19).

The wetlands draining into Chesapeake Bay are potential phosphorus sources. At present, we cannot estimate the actual phosphorus input from all wetlands but we can calculate the minimum input which could impact on open bay waters. The Maryland portion of Chesapeake Bay contains about 30×10^{12} LITERS of water and has about 100 Km^2 of tidal marsh draining into it either directly or through tributaries. The MARSH water depth at high tide is usually less than 10 cm so a volume of about 1×10^{11} LITERS flows onto and off the marshes daily.

As a yearly average, the total phosphorus concentration of bay waters is about 1 $\mu gat \cdot liter^{-1}$ so the instantaneous mass of phosphorus in the water would be about 30×10^{12} µgat P in the Maryland portion of the bay. A 10% change in total phosphorus, or 0.1 $\mu gat \cdot liter^{-1}$, in the open bay would require a marsh input of 3×10^{12} µgat P dissolved in 1×10^{11} liters of water, if all marsh water were exchanged on each tidal cycle. The instantaneous concentration in the marsh effluent would then be 30 $\mu gat \cdot liter^{-1}$. Total phosphorus is about 5 $\mu gat \cdot liter^{-1}$ at the mouth of

a low salinity marsh (6). If this is typical of other marshes, then the marsh input to Chesapeake Bay is small compared to the mass of phosphorus already present. Also, the marsh water is not completely exchanged on each tidal cycle so some phosphate is carried back into the marsh (6).

Rapid Cycling

In late summer phosphate appears to be abundant in relation to phytoplankton requirements, but for the rest of the year it is scarce and the significance of recycling within the euphotic zone increases. In a recent study of Chesapeake Bay, turnover times for orthophosphate, dissolved organic phosphate, polyphosphate and particulate phosphate ranged from a few minutes to about 100 hours (20). All soluble phosphate pools appeared to contain fractions which were metabolically useful to the phytoplankton. The dissolved organic phosphate pool contained phosphorus monoesters in low concentration and a large quantity of seemingly refractory organic phosphate.

Many phytoplankton species produce alkaline phosphatase enzymes (9) when intracellular orthophosphate or polyphosphate levels decline below some threshold value. These enzymes are frequently located near the outer cell surface where they hydrolyze organic phosphorus monoesters to release orthophosphate ions which are then available for incorporation into the cell.

Recent studies have revealed that phytoplankton in Chesapeake Bay, Potomac River, Delaware Bay and Pamlico Sound may produce alkaline phosphatase enzymes when orthophosphate supply is restricted.

Hydrolysis rate depends both on substrate concentration and ambient pH, and seems to follow Michaelis-Menton kinetics in natural phytoplankton assemblages (21). Table 1 compares half-saturation constants for orthophosphate uptake and alkaline phosphatase activity for natural phytoplankton assemblages in these four coastal regions. The ambient concentrations of both orthophosphate and phosphorus monoester are ~~frequently~~ USUALLY low in Chesapeake Bay (21). The comparable ranges in half-saturation constants for phosphorus utilization in both forms suggests that monoesters may be a significant phosphorus source ~~which~~ AND may equal orthophosphate in importance when orthophosphate concentrations and resupply rates from outside the euphotic zone are minimal. Ranges of maximum uptake velocity for phosphorus in both forms are also similar for the four regions (Table 2).

Table 1

Table 2

Alkaline phosphatase activity in Chesapeake Bay shows some seasonal patterns (21). Hydrolysis rate per unit phytoplankton biomass is generally higher in spring and lower in late summer. In August, 1975 alkaline phosphatase activity was virtually undectable throughout Chesapeake Bay (Taft, unpublished data). Alkaline phosphatase activity in phytoplankton has been interpreted as a symptom or consequence of phosphorus deficiency (5), so these trends in enzyme activity may reflect trends in the availability of new inorganic phosphate with respect to new inorganic nitrogen.

Biomass Regulation

Seasonal trends in alkaline phosphatase activity and the results of a previous study (20) suggest that phytoplankton biomass

in Chesapeake Bay could be regulated by phosphorus availability during spring and early summer and by nitrogen availability during late summer and fall.

To examine this further, data for the vertical distribution of inorganic nitrogen and phosphorus were compared for May and August 1975. A spring maximum in nitrate input from the Susquehanna River is a normal occurrence. At the end of May, 1975, the upper bay still contained about 10 $\mu gat \cdot liter^{-1}$ of inorganic nitrogen but virtually no inorganic phosphate (Table 3). Nitrogen to phosphorus ratios for the water were not calculated due to low SRP concentrations, but nitrogen was clearly abundant with respect to phosphorus. In August, deep waters were anoxic and ~~both~~ ammonia and orthophosphate ~~were present~~ CONTAINED in high concentration ~~in deep waters.~~ Table 4 shows ammonium and SRP concentrations and their atomic ratios with depth at station P-12 in the estuarine region of the Potomac River. (Nitrate and nitrite made very small contributions to the total inorganic nitrogen concentration and are omitted from the table.) ~~Data for Chesapeake Bay proper were similar~~. Figure 3 shows a vertical profile of salinity, soluble reactive phosphorus (SRP) and oxygen at station P-12 in the Potomac River. Data for open Chespaeake Bay waters in August 1975 are very similar.

Table 3

Figure 3

Table 4

The inorganic nitrogen to phosphorus ratios (Table 4) in the deep water were about 10 to 1 and in surface water about 4 to 1, indicating abundant phosphate supply with respect to nitrogen, further suggesting that phytoplankton biomass in the euphotic zone

could be nitrogen regulated. This interpretation is supported by very low levels of alkaline phosphatase activity which is indicative of phosphorus rich cells.

We examined the hypothesis that nitrogen was regulating biomass at Potomac River station P-12 with surface water collected by bucket and screened through 35 μm mesh into a carboy. A one liter sample was placed in a glass bottle, enriched with about 15 μgat NH_4-N and incubated on deck in natural light attenuated to 73% of the incident value with stainless steel screen. The sample was maintained at the temperature of near surface water flowing through the incubator from the ship's seawater system.

Subsamples were taken with time for analyses of ammonium concentration (18), alkaline phosphatase activity (11) and for intracellular polyphosphate (Poly P). For the Poly P analyses a 10 ml subsample was pipetted onto a 25 mm Nucleopore^R filter with pore size 0.45 μm which was irradiated with ultraviolet light for 1 hr in a quartz tube containing 10.2 ml distilled water and 0.1 ml 30% hydrogen peroxide. a 5 ml aliquot was analyzed for SRP (18) and the remaining 5 ml was heated with 0.1 ml 40% HCl in boiling water (18) for 1 hr to convert Poly P to orthophosphate and the SRP was measured by the molybdate method. Corrections for sample turbidity were applied to the optical densities. Filter phosphate blanks were significant (0.1 μgat·liter^{-1}), but were constant and small compared to the particulate phosphate retained. Particulate organic phosphate values were identical in UV irradiated whole water samples and in distilles water containing particulates retained on Nucleopore^R filters.

F re 4

The results in Figure 4 show that as ammonium was taken up, intracellular polyphosphate decreased to less than one-half the initial value and alkaline phosphatase activity increased sharply. During the experiment SRP was 0.1 μgat·liter^{-1} or less.

These results suggest that, when collected, the phytoplankton contained sufficient internal phosphorus stores to suppress alkaline phosphatase induction. As nitrogen was supplied, polyphosphate stores were depleted and, without new orthophosphate to draw on, the cells mobilized alkaline phosphatase to hydrolyze extracellular phosphorus monoesters.

It is a popular notion that alkaline phosphatase activity is a sign of "phosphorus limitation" in phytoplankton. This may be correct if "phosphorus limitation" is applied to biomass only, which may have an upper limit set by the total amount of phosphorus available. However, in a natural system, primary productivity per unit biomass may be influenced more by the turnover rate of the nutrient in least supply than by the total amount of that nutrient in all forms. Therefore, alkaline phosphatase production enables phytoplankton to increase the turnover rate of available phosphorus and may not necessarily be symptomatic of primary productivity "limitation" by phosphorus.

Summary

1. Several coastal plain estuaries have annual phosphorus cycles featuring maxima in summer and early fall.

2. In some of these estuaries phosphorus availability seasonally establishes the upper limit for phytoplankton biomass.
3. During periods of restricted inorganic phosphate supply, phosphorus monoesters may become a significant phosphorus source for the phytoplankton.

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CAPTIONS

Figure 1. Map showing locations of stations sampled in this study. Delaware Bay station at Fourteen Foot Bank; Chesapeake Bay station 834G; Potomac River Station P-12; Pamlico Sound station at Waves, N. C.

Figure 2. Concentrations of soluble reactive phosphorus during the year in five coastal plain estuaries.

Figure 3. Vertical distribution of salinity ($S‰$), soluble reactive phosphorus (SRP) and oxygen at station P-12 in the Potomac River.

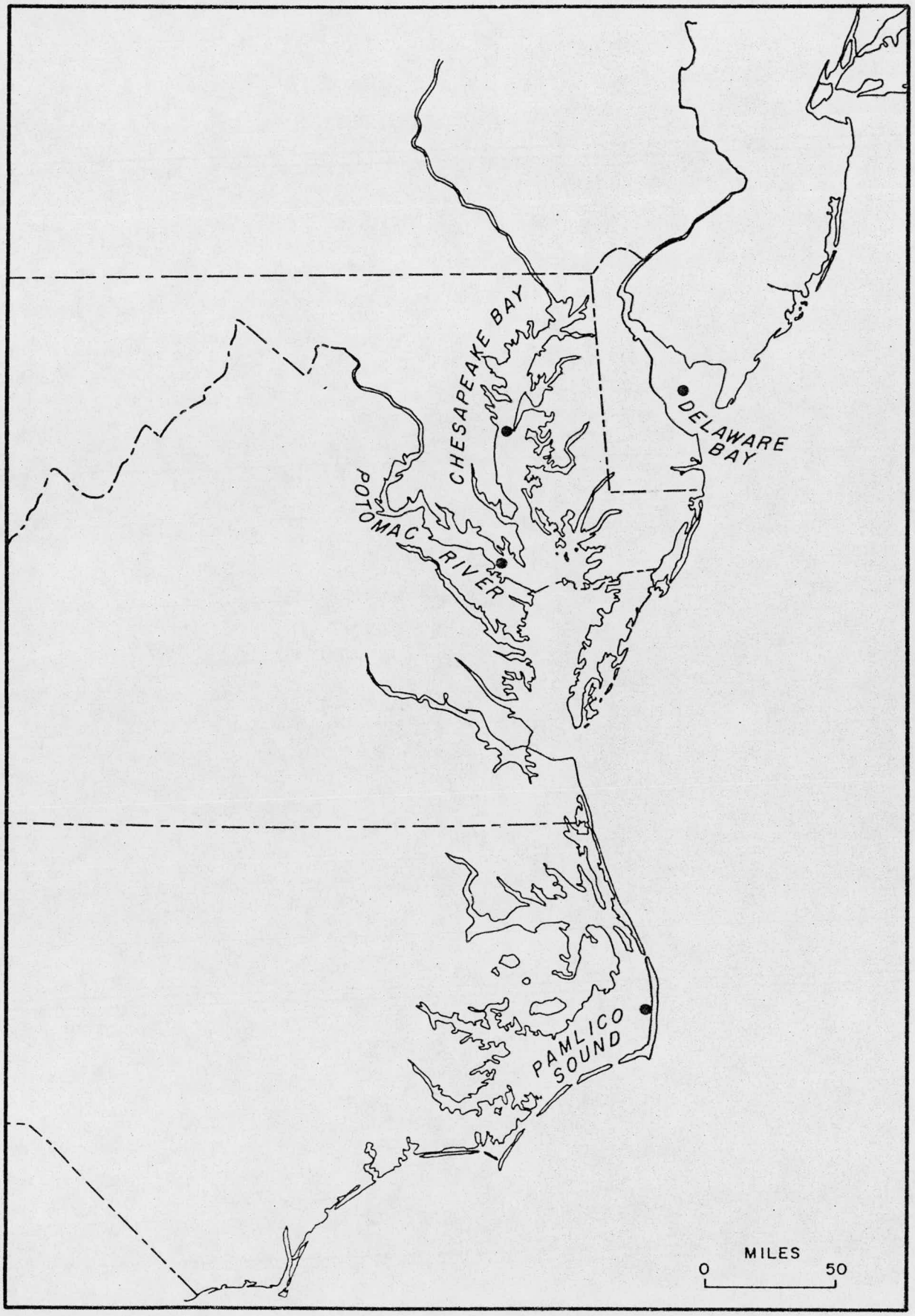
Figure 4. Ammonium concentration change in the water and polyphosphate (Poly P) and alkaline phosphatase activity change in phytoplankton from Potomac River Station P-12.

Table 1. Half-saturation values for orthophosphate uptake and hydrolysis of phosphorus monoesters by alkaline phosphatase.

Table 2. Maximum velocity for orthophosphate uptake and hydrolysis of phosphorus monoesters by alkaline phosphatase.

Table 3. Vertical distribution of combined inorganic nitrogen and soluble reactive phosphorus at Chesapeake Bay station 834G on 28 May 1975. U = undetectable.

Table 4. Vertical distribution of ammonium ion and soluble reactive phosphorus and the nitrogen to phosphorus atomic ratios at Potomac River station P-12 on 19 August 1975.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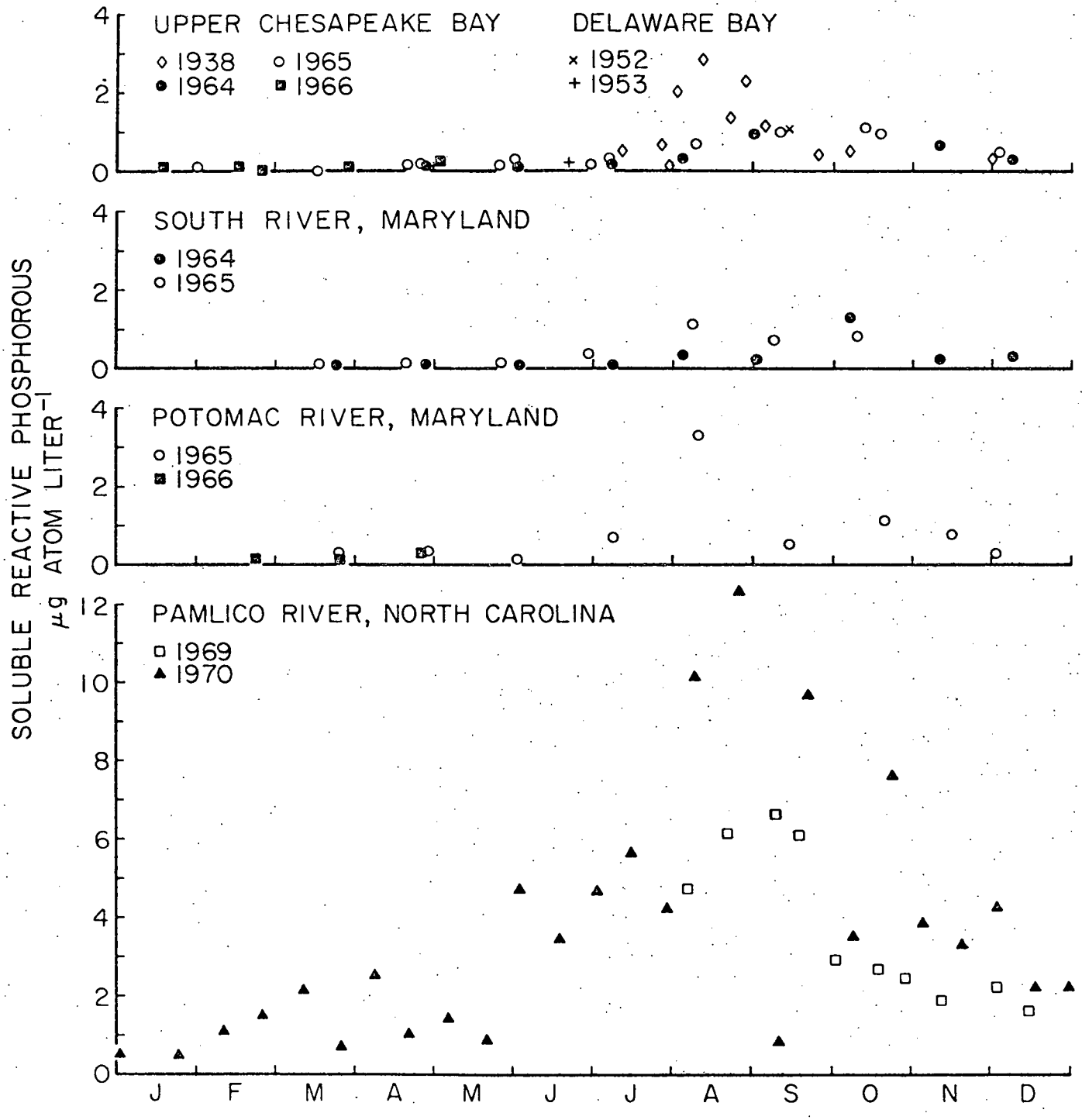
DELAWARE BAY
POTOMAC RIVER
PAMLICO SOUND
MILES
0
50


UPPER CHESAPEAKE BAY
◇ 1938
● 1964
○ 1965
▣ 1966
DELAWARE BAY
× 1952
+ 1953
SOUTH RIVER, MARYLAND
● 1964
○ 1965
POTOMAC RIVER, MARYLAND
○ 1965
▣ 1966
PAMLICO RIVER, NORTH CAROLINA
□ 1969
▲ 1970
SOLUBLE REACTIVE PHOSPHOROUS
μg ATOM LITER⁻¹
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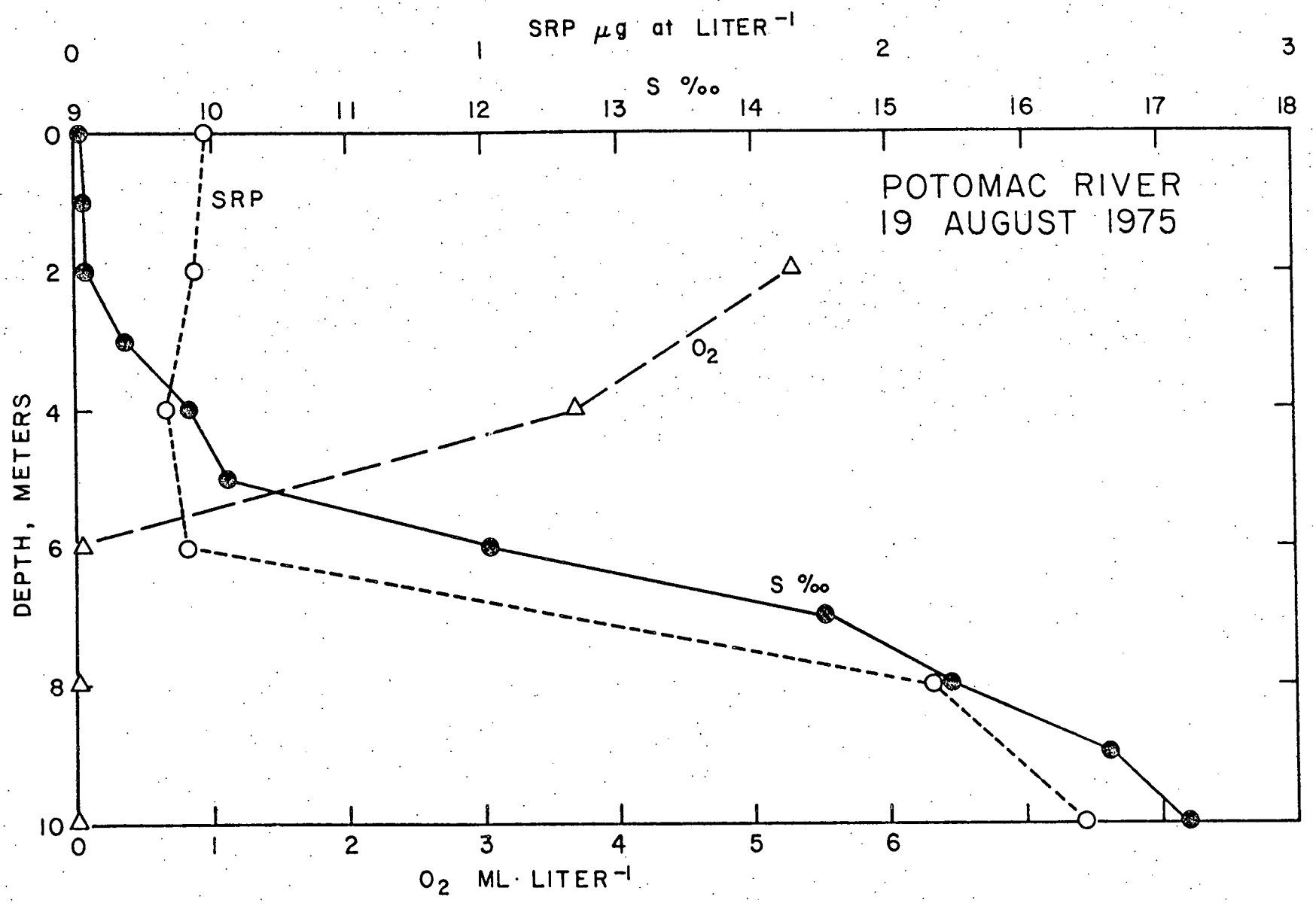
SRP μg at LITER⁻¹
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1
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POTOMAC RIVER
19 AUGUST 1975
SRP
O2
S ‰
DEPTH, METERS
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2
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6
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1
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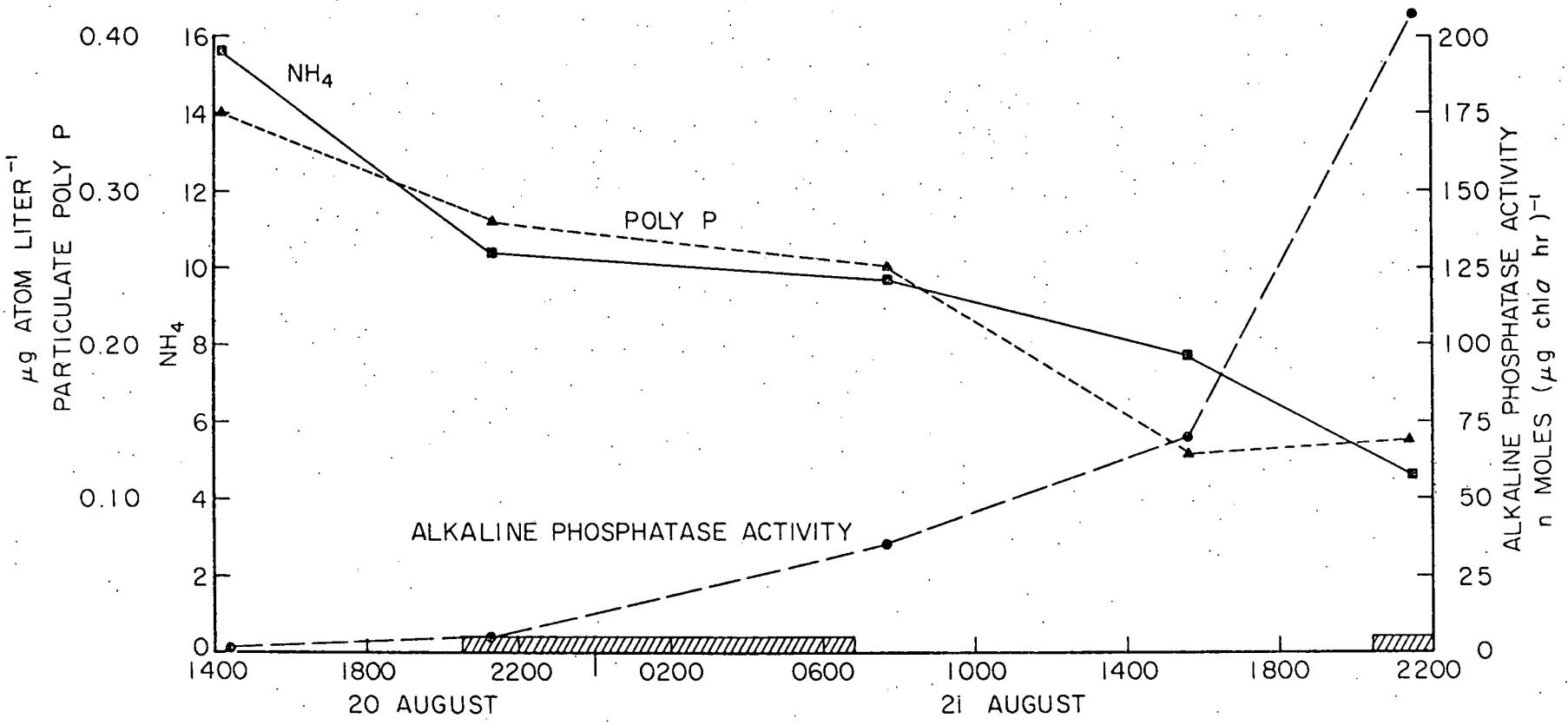
O2 ML· LITER⁻¹


0.40
0.30
0.20
0.10
µg ATOM LITER⁻¹
PARTICULATE POLY P
16
14
12
10
8
6
4
2
0
NH4
NH4
POLY P
ALKALINE PHOSPHATASE ACTIVITY
200
175
150
125
100
75
50
25
0
ALKALINE PHOSPHATASE ACTIVITY
n MOLES (µg chlσ hr)⁻¹
1400
1800
2200
0200
0600
1000
1400
1800
2200
20 AUGUST
21 AUGUST

HALF-SATURATION VALUES FOR ORTHOPHOSPHATE UPTAKE AND ALKALINE PHOSPHATASE ACTIVITY.

$\mu gat \cdot liter^{-1}$

	PO_4 Uptake	Alkaline Phosphatase Activity
CHESAPEAKE BAY	0.09 to 1.72	0.14 to 1.0
DELAWARE BAY	0.13	0.50
PAMLICO SOUND		0.06
POTOMAC RIVER	2.5	

MAXIMUM VELOCITY FOR ORTHOPHOSPHATE

UPTAKE AND ALKALINE PHOSPHATASE ACTIVITY

	PO_4 Uptake ngat (µg Chl$\underline{a}$·hr)$^{-1}$	Alkaline Phosphatase Activity nmoles (µgat Chl$\underline{a}$·hr)$^{-1}$
CHESAPEAKE BAY	3.5 to 156	3.2 to 53.2
DELAWARE BAY	>70	3.6
PAMLICO SOUND		41
POTOMAC RIVER	63	

CHESAPEAKE BAY STATION 8340

28 MAY 1975

Depth m	NH_4	NO_3	NO_2	SRP
		$\mu gat \cdot liter^{-1}$		
1	0.4	9.6	0.6	U
5	0.9	8.0	0.5	U
7	1.9	8.3	0.5	U
9	4.6	6.9	0.4	0.06
11	5.2	7.6	0.4	0.06

POTOMAC RIVER STATION P-12

19 AUGUST 1975

Depth m	NH_4 $\mu gat \cdot liter^{-1}$	SRP $\mu gat \cdot liter^{-1}$	N:P
0	1.2	0.3	4.0
2	0.9	0.3	3.0
4	0.5	0.2	2.5
6	2.0	0.2	10.0
8	19.9	2.0	10.0
10	21.8	2.3	9.5