NUTRIENTS IN WATERS ON THE INNER SHELF

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INTRODUCTION

High productivity has been observed in many areas of the oceans adjacent to land (ref. 1). A significant portion of the living resources from the seas is derived from these regions. This increased productivity may be caused by nutrients, trace metals or organic growth-promoting factors originating from land (ref. 2). The major route for the transport of materials from land to the coastal oceans is via rivers. In its pristine state, the composition of river waters is controlled by weathering processes. However, with increasing population and industrial activities in coastal regions and along river banks, anthropogenic inputs such as domestic sewage effluents and industrial wastes may have a significant direct or indirect influence on the composition of rivers, estuaries, and coastal oceans. Goldberg (ref. 3) suggested that river water may affect primary productivity in coastal water in several ways:

- (a) By bringing in, diluting or removing (by sedimentation) plant nutrients
- (b) By bringing in suspended material or dissolved colored substances and thus altering the depth to which sufficient light can penetrate to support photosynthesis
- (c) By establishing the stability of the water column with a low density surface layer. The increased stability of the water column may increase production by reducing the tendency of cells to be carried below the critical depth for photosynthesis.

The primary objective of the project Superflux is to assess the influence of the outflow of water from the Chesapeake Bay on the adjacent shelf waters of the southern tip of the Middle Atlantic Bight. We shall discuss the distribution of nutrients in this region during three cruises in the summer and fall of 1980.

THE SOUTHERN MIDDLE ATLANTIC BIGHT

Our study area is considered to be the part of the shelf bound by Virginia and North Carolina to the west, the 100-m isobath to the east, and the imaginary lines extending due east from Cape Hatteras, North Carolina to the

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south and Cape Charles, Virginia to the north. It is part of the Middle Atlantic Bight which extends from Cape Cod (Massachusetts) to Cape Hatteras. A large scale systematic study of the oceanography of the northern Middle Atlantic Bight (the New York Bight) which stretches from Cape Cod to Cape May (New Jersey) has been completed and the results were reported in a special Symposium volume (ref. 4). However, the southern Middle Atlantic Bight was much less extensively studied.

The annual outflow of freshwater from the Chesapeake Bay to the Atlantic Ocean estimated from the inflow of water into the Chesapeake Bay is about 60 km³/yr (ref. 5). This constitutes over 50% of the freshwater inflow to the Middle Atlantic Bight (ref. 6) and virtually the total freshwater inflow to the study area. The Chesapeake Bay is the largest estuary in the United States. It has a drainage basin of $1.66 \times 10^5 \text{ km}^2$. The population in the drainage basin is projected to be 30 million by the year 2020 (ref. 7). Land use in the drainage basin is highly diversified. There are urban, industrialized as well as agricultural areas. Significant amounts of anthropogenic materials are introduced directly or indirectly via the tributaries into the Bay. These inputs will affect the composition of the outflow that reaches the study area.

The major input of water to the study area is the alongshore transport over the shelf, which is estimated to be 8000 km³/yr (ref. 6). Thus, the total freshwater input from the Chesapeake Bay is less than 1% of this alongshore flow. The cross-shelf exchange of shelf water with slope water has not been quantified. The volume of water in the study area is estimated to be about 3×10^2 km³. Therefore, the maximum residence time of the water is about 0.5 month.

EXPERIMENTAL

A grid of stations was established for the Superflux cruises as shown in figure 1. In June, 1980 (Superflux II) 30 stations were occupied between June 17 and 23 by R/V Delaware II and 11 stations were occupied between June 24 and 27 by R/V Kelez. Between October 14 and 22, 1980 (Superflux III) 26 stations were occupied by the R/V Kelez. Samples were collected with Niskin bottles and analyzed for phosphate, nitrate, ammonia, and silicate. Nitrite was determined in the samples from Superflux II only. (Salinity was measured by investigators from the Northeast Fisheries Center, Sandy Hook Laboratory of the National Oceanic and Atmospheric Administration, and the data were made available to all participants in the Superflux program). Stations were occupied usually along east-west transects. No special attention was given to tidal conditions. It was not uncommon that the first and last stations of a transect were occupied more than a tidal cycle apart.

Dissolved reactive phosphate was determined by the method of Murphy and Riley (ref. 8) by the reduction of the phosphomolybdate complex with ascorbic acid. Nitrate was first reduced to nitrite by passing the samples through a Cd-Cu column and then measured as nitrite (ref. 9). Nitrite was

diazotized with sulfanilamide and the concentration of the azo dye formed was determined by spectrophotometry (ref. 10). Ammonia was measured by the indophenol blue method of Solorzano (ref. 11). Dissolved silicate was measured by spectrophotometry after the silicomolybdate complex had been reduced with metol (ref. 12). The precision of these methods for the determination of nutrients was about $\pm 5\%$. The detection limits were about 0.03, 0.01, 0.05, 0.1, and 0.1 µmole/& for phosphate, nitrite, nitrate, ammonia, and silicate, respectively (ref. 13). About half of the samples were analyzed onboard ship. The remaining ones were filtered, frozen and returned to shorebased lab for analyses.

RESULTS AND DISCUSSION

Distribution at 1 m

In June, a tongue of water with lower salinities (<29 o/oo) extending southward from the southern portion of the mouth of Chesapeake Bay (~37°N) to about 36°20' can be readily identified from the data obtained between June 17 and 23 (figure 2a). This water mass, which represented the influence of the outflow of freshwater from the Chesapeake Bay to the Atlantic Ocean, hugged the coast initially and turned eastward offshore as it spread southward. This distribution of salinity is in accord with the first order description of the circulation at the mouth of the Bay (ref. 14) since seawater enters the Bay through the northern portion of the mouth and freshwater leaves the Bay via the southern portion. Wong (ref. 15) also reported similar but less extensive data on the distribution of salinity at the mouth and within the southern part of the Bay. A closer examination of the distribution of salinity indicates that salinity did not increase monotonically away from the mouth of the Chesapeake Bay. Patches of water with salinities significantly higher than the surrounding waters were observed. Moreover, when the same station was occupied a week later, different salinities were observed (table 1). This patchiness and the short-term temporal variation in salinity are expected as a result of the tidal influence on the outflow of waters from the Chesapeake Bay and they clearly demonstrate the limitations of non-synoptic data for studying a nonsteady-state phenomenon.

In October, the distribution of salinity was significantly different (figure 2). Waters with salinities below 31 o/oo were confined to the immediate vicinity of the mouth of the Chesapeake Bay. This longer term variation in salinity (table 1) is probably caused by the seasonal variations in the outflow of fresh water from the Chesapeake Bay. It should be noted that the summer and fall of 1980 were exceptionally dry. Thus, the influence of Chesapeake Bay water on the adjacent Atlantic water decreased as the drought continued.

The distributions of phosphate, nitrate, ammonia and silicate during the first cruise in June are shown in figures 3a - 3d. The distribution of nitrite is not presented because the concentrations rarely exceeded the detection limit. In the case of nitrate, phosphate, and silicate, with the exception of

station 800 at the southern side of the mouth of the Chesapeake Bay, the concentrations were also frequently at or close to the detection limits. Significant quantities of ammonia were detected at many stations although the distribution was patchy. In general, the concentrations of the nutrients decreased southward and seaward away from the mouth of the Bay (table 2 and ref. 16). The elevated concentrations of the nutrients at the mouth of the Bay suggest that the outflow of waters from the Chesapeake Bay may be a source of nutrients for the adjacent Atlantic waters. As expected, the patterns of the distributions of the nutrients were not similar to that of salinity since they do not have the same sources and sinks. The elevated concentrations of nutrients did not extend noticeably offshore or southward suggesting that they are not conservative and may be utilized and exhausted rapidly by organisms.

Ammonia was frequently the most abundant form of combined inorganic nitrogen. The concentrations were at times an order of magnitude higher than the sum of nitrate and nitrite. In marine waters, the common limiting nutrient is nitrogen (ref. 17). An N/P atomic ratio lower than 15:1 implies that the availability of inorganic nitrogen limits the phytoplankton produc-At the mouth of the Bay as at station 800, nitrogen limitation was tion. apparently observed as the ratio of N/P in both June and October was below 15 (table 2). However, at other stations such as station 816, phosphate was exhausted while significant amounts of ammonia remained. The N/P ratio greatly exceeded 15. In these cases, phosphate may be the limiting nutrient. The complex and patchy distribution of ammonia in comparison with that of the other nutrients reflects the higher degree of complexity of the chemistry of the nitrogen system. During the photosynthetic uptake and remineralization process of phytoplankton, in addition to the removal or replenishment of combined inorganic nitrogen in the water column, the speciation can also be modified by processes such as assimilatory nitrate reduction, preferential uptake of ammonia, and nitrification (refs. 18 and 19). The concentration of ammonia is further affected by the excretions of higher organisms such as zooplankton.

As in the case of salinity, the concentrations of the nutrients at a single station displayed short-term temporal variations. Significantly different concentrations were observed during the two cruises in June (table 2). These short-term variations render a precise estimation of the fluxes of material from the Bay to the adjacent Atlantic waters difficult, even if the outflow of water can be accurately measured. An intensive sampling program is clearly essential if such quantifications are to be made.

The distributions of phosphate, nitrate, ammonia, and silicate during October are shown in figures 4a - 4d. Again, a decrease of concentration from the mouth of the Chesapeake Bay seaward and southward was observed (table 2). A pocket of water with higher concentrations of nutrients was observed in the immediate vicinity of the Bay mouth. However, other pockets of nutrient-rich waters were found in some cases further south and further east. The distribution of ammonia was again more patchy than the other nutrients. Between June and October, the salinity at the Bay mouth (station 800) increased significantly (table 2). The nutrient concentrations had increased also. However, the magnitudes of the changes in concentrations were similar to the short-term variations observed in a period of a week in June. Thus, real seasonal variations in the concentrations of the nutrients cannot yet be established.

East-West Transects

The distributions of salinity, phosphate, nitrate, ammonia, and silicate along a northern transect (stations 69, 802, 803, and 804) and a southern transect (stations 814, 815, 72, and 816) in June and October are shown in figures 5 to 8. In each east-west transect, salinity increased with depth and seaward. During each cruise, salinity increased southward. In June, a water mass with salinities below 30 o/oo was clearly defined in both transects. In October, waters with salinities below 30 o/oo were confined to the immediate vicinity of the mouth of the Chesapeake Bay and at depths of less than 2 m. In the southern transect, salinities were all above 32 o/oo. These distributions of salinities suggest a decreasing outflow of freshwater from Chesapeake Bay from June to October.

In June, in the northern transect, the concentrations of phosphate decreased seaward and increased towards the bottom at some stations. In the southern transect, with the exception of two samples, the concentrations were uniformly low, being less than 0.1 µM. In October, a decrease in concentration seaward was observed in both transects and an increase in concentrations towards the bottom was again observed at some stations. Similar concentrations and distributions of phosphate have been reported in the New York Bight (ref. 20). In the northern transects, the elevated concentrations in the top few meters of water close to the mouth of Chesapeake Bay may be related to the outflow of Chesapeake Bay water. The increase in the concentration of phosphate towards the bottom may be caused by a diffusive flux of phosphate from the sediments. Nutrients, including phosphate, are regenerated by the decomposition of organic matter in the sediments and elevated concentrations of phosphate in the interstitial waters relative to the bottom waters have been reported in coastal sediments (ref. 21). The resulting concentration gradient leads to a diffusive flux of phosphate to the water column. The elevated concentrations of phosphate in the bottom may also be explained by an advective mass of bottom water with high phosphate concentrations from areas north of the study area. Indeed. bottom waters with similar concentrations of phosphate were observed in the New York Bight (ref. 20). Thus, there are at least three possible sources of phosphate to the study area: (1) outflow from Chesapeake Bay; (2) diffusive flux of phosphate from the sediments; and (3) advection of nutrient-rich water from areas north of the study area. Thus, although water from the Chesapeake Bay is a potential source of phosphate to the study area, its contribution cannot yet be isolated from those of the other sources.

During June, the concentration of nitrate was uniformly low in both transects, being mostly less than 0.5 μ mole/ ℓ . In October, in the northern transect, significantly higher concentrations were observed at the mouth of the Chesapeake Bay. In the southern transect, no definite pattern similar to the

distribution of salinity was observed. The concentrations of nitrate at the stations close to shore were below 0.5 µM. The bottom water at the seaward stations had somewhat elevated concentrations. These distributions and seasonal variations were similar to those observed in the New York Bight (ref. 20). The distribution of ammonia was patchy although definite patterns were observed in each transect. As discussed previously, this patchiness might be caused by the higher level of complexity of the chemistry of the nitrogen system. Again, as in the case of phosphate, elevated concentrations were observed at some stations in the bottom waters and similar mechanisms can be proposed to explain these observations. The concentrations and depth profile of ammonia are not unlike those observed in the New York Bight (ref. 22). Thus, an advective flux of ammonia cannot be ruled out. Ammonia is also one of the initial products in the decomposition of organic matter in sediments. Τn coastal sediments, which are likely to have a thin oxidizing zone, ammonia is not further oxidized to nitrite or nitrate in such a reducing environment (ref. 23). Consequently, in the interstitial waters, concentrations of ammonia that are orders of magnitude higher than those in the bottom water have been observed (ref. 21) resulting in a diffusive flux of ammonia to the water column.

In June, the concentrations of silicate were uniformly low, being mostly less than 1 μ mole/ ℓ . In October, the concentrations of silicate decreased seaward and increased towards the bottom. The elevated concentrations in the bottom water may again be caused by an advective flux from the north or a diffusive flux from the sediments. The concentration gradient of dissolved silicon in the interstitial water can be maintained by the dissolution of solid phases such as skeletal parts of siliceous organisms (ref. 24) and such a concentration gradient has been observed in coastal sediments (ref. 21).

CONCLUSION

The outflow of freshwater from Chesapeake Bay is a potential source of nutrients to the adjacent shelf waters. However, a quantitative estimation of its importance cannot yet be made because (a) there are other sources of nutrients to the study area and these sources cannot yet be quantified and (b) the concentrations of nutrients in the outflow from Chesapeake Bay exhibit significant short-term and long-term temporal variabilities.

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	DEPTH m		SALINITY (0/00)*			
STATION		A	В	С		
70	1	26.55	29.02	31.65		
	5	27.16	30.87	31.72		
	10	31.69	31.36	32.26		
805	l	25.97	25.07	31.98		
	5	28.06	27.74	31.82		
	10	33.97	31.97	32.14		

Table 1. Time variability of salinity at two stations

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*Samples were collected on June 19 (A), June 25 (B), and October 17 (C), 1980.

	Bay Mouth			Innershelf		Open Ocean* (Gulf stream)
Station No.	800	800	800	816	816	212
Sampling date	6/17/80	6/24/80	10/14/80	6/22/80	10/19/80	3/30/73
Salinity (o/oo)	21.63	N.D.	27.09	31.50	32.72	36.430
Phosphate (µM)	0.38	0.52	0.56	0.01	0.06	0.05
Nitrate and Nitrite (µM)	2.7	0.4	1.5	סט	0.51	0.07
Nitrite (µM)	UD	0.04	ND	UD	ND	
Ammonia (µM)	ND	1.1	4.7	2.38	0.96	ND
Silicate (µM)	0.2	6.6	8.4	0.15	0.25	0.9
N/P		3	11	234	25	14

Table 2. Nutrients and salinity at 1 m at the Bay mouth and in offshore waters.

*Geochemical Ocean Sections Study at 3m at 35° 59.4'N, 67° 59.0'W (Ref. 16).

- UD Undetected
- ND No data
- N/P Atomic ratio of inorganic nitrogen to phosphate



Figure 1.- Location of the stations of the Superflux cruises.



Figure 2.- Distribution of salinity in $^{\rm O}/{\rm oo}$ at 1 m in June and October 1980.



(c) Ammonia (μ M).

(d) Silicate (µM).





Figure 4.- Distribution of phosphate, nitrate, ammonia, and silicate at 1 m in October, 1980.



(a) Salinity (0/00).



(b) Phosphate (µM).

Figure 5.- Distribution of salinity, phosphate, nitrate, ammonia, and silicate in a transect across the northern part of the study area in June, 1980.



(c) Nitrate (µM).

(d) Ammonia (µM).



(e) Silicate (µM).

Figure 5.- Concluded.



(a) Salinity (⁰/oo).



(b) Phosphate (μM).

Figure 6.- Distribution of salinity, phosphate, nitrate, ammonia, and silicate in a transect across the southern part of the study area in June, 1980.









(a) Salinity (⁰/oo).



(b) Phosphate (µM).

Figure 7.- Distribution of salinity, phosphate, nitrate, ammonia, and silicate in a transect across the northern part of the study area in October, 1980.



(c) Nitrate (µM).

(d) Ammonia (µM).



(e) Silicate (µM).

Figure 7.- Concluded.



(b) Phosphate (μM).

Figure 8.- Distribution of salinity, phosphate, nitrate, ammonia, and silicate in a transect across the southern part of the study area in October, 1980.



Figure 8.- Concluded.