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Biological and chemical study of Virginia's estuaries

Morris L. Brehmer

Virginia Institute of Marine Science

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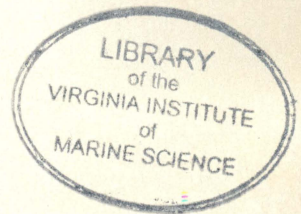
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OWRR Project No. B 003 Va

Biological and Chemical Study
of Virginia's Estuaries



Morris L. Brehmer

Virginia Institute of Marine Science
Gloucester Point, Virginia
21 June 1970

ANNUAL REPORT INFORMATION -- SUBMIT THIS NARRATIVE PROGRESS REPORT SEPARATELY FOR EACH ANNUAL ALLOTMENT AND MATCHING GRANT PROJECT, INCLUDING THOSE PROJECTS IN PROGRESS IN THE FISCAL YEAR ENDING JUNE 30 AND THOSE ADDITIONAL NEW PROJECTS APPROVED FOR SUPPORT IN THE NEW FISCAL YEAR BEGINNING JULY 1

OWRR PROJECT NO. B 003 Va.
 ANNUAL ALLOTMENT OR MATCHING
 GRANT AGREEMENT NO. 14-01-0001-
 FGST RESEARCH CATEGORY: _____

PROJECT TITLE:
 Biological and Chemical Study of
 Virginia's Estuaries

NAME AND LOCATION OF UNIVERSITY WHERE PROJECT IS BEING CONDUCTED:

Virginia Institute of Marine Science, Gloucester Point, Virginia 23062

PROJECT BEGAN--MONTH: July ; YEAR: 1967 SCHEDULED COMPLETION--MONTH: June ; YEAR: 1970

PRINCIPAL INVESTIGATORS	DEGREE	DISCIPLINE
Morris L. Brehmer	Ph.D.	Marine Science
STUDENT ASSISTANTS 1/	DEGREE HELD, IF ANY	DISCIPLINE OR ACADEMIC BACKGROUND
Thomas Bernard*	B.S.	Marine Science
Thomas Cain*	B.S.	Marine Science
Richard Peddicord*	B.S.	Marine Science

*Not funded from contract.

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IN THE SPACE BELOW, USING ADDITIONAL SHEETS AS NECESSARY, PROVIDE THE FOLLOWING:

- (A) A DESCRIPTION OF RESEARCH PERFORMED AND FINDINGS, RESULTS, OR CONCLUSIONS RELATING THERETO;
- (B) A LISTING BY TITLE, AUTHOR, VOLUME, PAGE NUMBER, ETC., OF PROJECT-RELATED PUBLICATIONS OR REPORTS ISSUED AND PAPERS PREPARED. ONE COPY ONLY OF EACH SUCH PUBLICATION, REPORT OR PAPER SHOULD BE TRANSMITTED TO OWRR BY THE INSTITUTE DIRECTOR EXCEPT IN THOSE INSTANCES WHERE ONE COPY HAS ALREADY BEEN PROVIDED TO OWRR IN ACCORDANCE WITH OWRR'S PROJECT "REPORTING GUIDELINES";
- (C) IF A PROJECT WAS COMPLETED DURING THE FISCAL YEAR ENDING JUNE 30 AND A COMPLETION REPORT HAS BEEN SUBMITTED TO OWRR, PLEASE SO INDICATE, BUT RECORD ON THIS FORM PERTINENT FINDINGS, RESULT OR CONCLUSIONS (SEE "A" ABOVE), AND LIST PUBLICATIONS AND THESES (SEE "B" ABOVE);
- (D) STATEMENTS OF PROJECT WORK REMAINING TO BE ACCOMPLISHED, IF APPLICABLE; AND
- (E) AN INDICATION OF WHAT ADDITIONAL PROJECT PROGRESS IS CONTEMPLATED FOR THE REMAINDER OF THE CURRENT CALENDAR YEAR. (SUCH INFORMATION TO ASSIST OWRR IN PREPARING ITS CALENDAR YEAR REPORT TO THE PRESIDENT AND THE CONGRESS AS REQUIRED BY P.L. 88-379, AS AMENDED.)

RESEARCH PERFORMED

The field program of the chemical and biological investigation of Virginia's three main estuarine systems--the James, York and Rappahannock rivers--was completed during this period. Eighteen regular cruises plus daily special cruises involving three vessels were made following the passage of Hurricane Camille. The final months of the period were utilized for the analyses of sediment samples and for data reduction.

VIRGINIA'S ESTUARIES

Virginia's major estuarine systems, the James, York and Rappahannock rivers, are tributaries of the Chesapeake Bay system. These three rivers discharge into the lower third of the Bay and contribute approximately 23% of the freshwater to the primary estuary (Figure 1). The tributaries are typical drowned valley systems characterized by relatively wide reaches (2-5 nm), extensive shoal areas, and rather narrow natural channels.

GENERAL DESCRIPTION

James River

The James River is the largest of Virginia's estuarine systems. The drainage basin includes approximately 10,000 square miles in Virginia and a small area in West Virginia. The James River drains all of 13 counties and parts of 27 counties, a total of nearly 24% of the Commonwealth.

The basin lies in four physiographic provinces, the Coastal Plain, Piedmont, Blue Ridge, and Ridge and Valley. The tidal reach extends from the mouth at Fort Wool in Hampton Roads to Richmond at the fall line, a distance of approximately 90 nm. Freshwater discharges are gaged at Richmond above the fall line. Flows as low as 320 cfs were recorded during the drought of 1931 and the estimated maximum discharge was 325,000 cfs in 1771. The mean annual discharge is approximately 7,500 cfs.

The James River receives significant artificial enrichment above the usual forest and agricultural sources. Approximately 2.7 metric tons

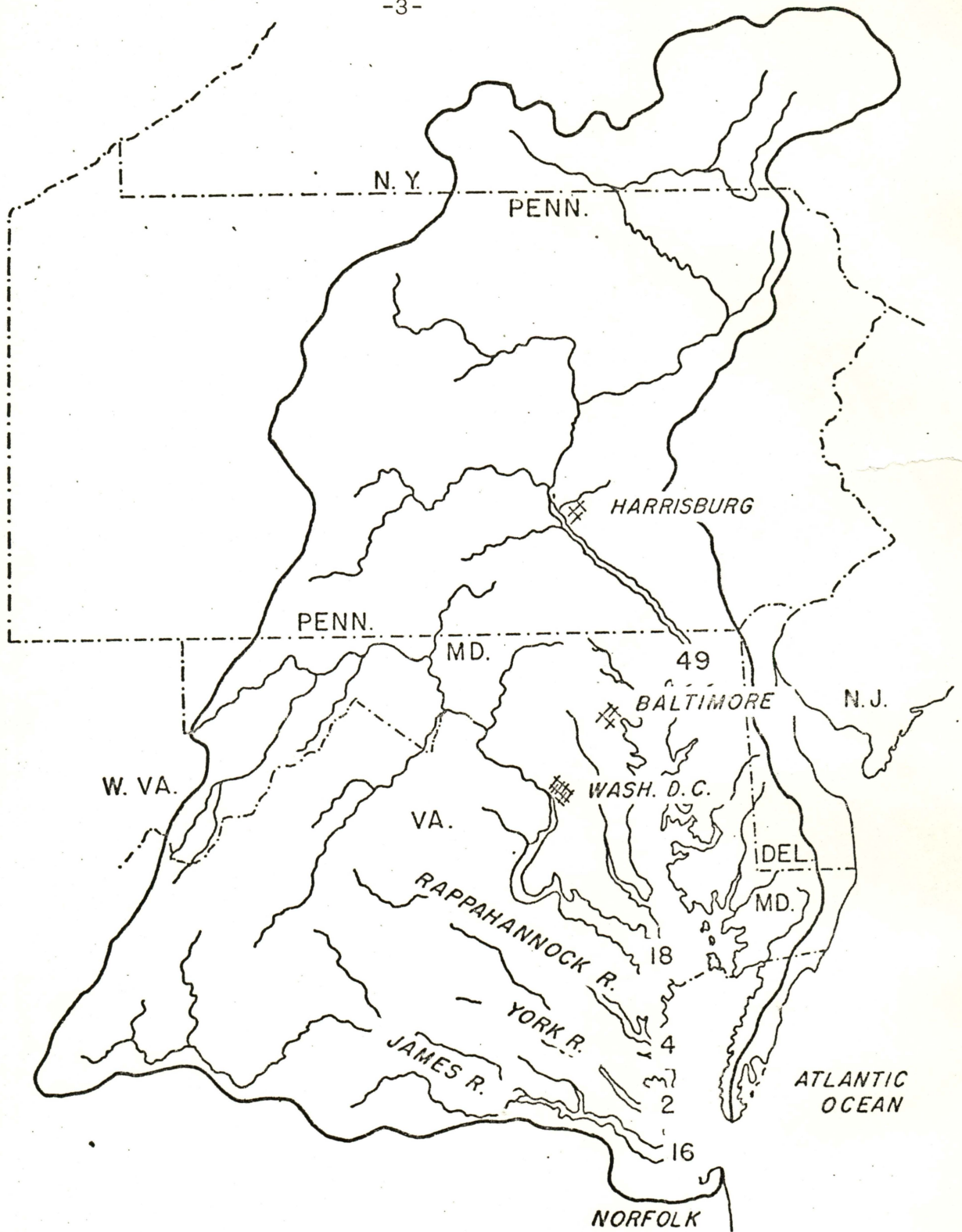


FIGURE 1. Chesapeake Bay drainage basin showing location and watersheds of tributary streams with percentage of total discharge.

of phosphorus and 8.2 metric tons of nitrogen in various organic and inorganic forms are discharged in the effluents of the metropolitan Richmond area each day. The data also indicate heavy loadings from Hopewell industrial and domestic sources and a detectable but slight increase in the Hampton Roads area. Aquatic nuisance conditions and environmental degradation resulting from nutrients loadings have been observed in the tidal freshwater reaches but no atypical phytoplankton responses have been measured in the estuarine section of the James River.

York River

The York River is the smallest of Virginia's major estuaries. It is a unique and complicated system in that the lower portion from the mouth to the constriction between Gloucester Point and Yorktown apparently is more strongly influenced by Mobjack Bay and Chesapeake Bay than is the remaining 26-mile reach to West Point. At West Point the river bifurcates with the Pamunkey River and its tributaries draining the southern portion of the drainage and with the Mattaponi River and its tributaries draining the northern portion.

The York River basin includes only 2,660 square miles in the Piedmont and Coastal Plain physiographic provinces. The Pamunkey River drains approximately 1,475 square miles, the Mattaponi 900, and the York below West Point 275. The two major tributary streams are tidal through most of their length, and dissolved solids of marine origin were measured 38 nm above the confluence during the low freshwater discharge period which accompanied the drought of 1968. Sampling was

conducted from the York River mouth to the transition zone between salt and freshwater in the Pamunkey River.

Mean annual freshwater discharge of the York River is approximately 2,200 cfs. Extremes of 300 and 37,800 cfs have been recorded. This flow represents only approximately 2% of the total freshwater inflow into Chesapeake Bay.

The York River basin is primarily rural in character, and nutrient enrichment from sources other than agricultural and forest drainage is insignificant. The Pamunkey and Mattaponi tributaries differ from the other systems, however, in that the lower 30 miles of each are meandering with extensive marshes within each bend.

Rappahannock River

The Rappahannock River is the most northerly of Virginia's major estuaries. It is tidal from its mouth at Chesapeake Bay to the fall line at Fredericksburg, a distance of 95 nm. The drainage basin, encompassing approximately 2,700 square miles, lies in three physiographic provinces, Coastal Plain, Piedmont and Blue Ridge, including all of four counties and parts of eleven.

The mean annual freshwater discharge into the tidal reach as measured at the Fredericksburg gaging station is approximately 1,600 cfs. The maximum flow recorded was 140,000 cfs during the October flood of 1942, and a minimum flow of 5 cfs was recorded in 1931. The Rappahannock River contributes approximately 4% of the total freshwater entering Chesapeake Bay.

In addition to forest and agricultural nutrient sources, the tidal Rappahannock receives nitrogen and phosphorus with the industrial and

domestic effluents from the Fredericksburg-Falmouth area just downstream from the fall line. The levels of enrichment have not been quantified, but partially due to the low assimilation capacity of the freshwater tidal reach, aquatic nuisance conditions have been observed during low-flow conditions.

HYDROGRAPHY

Salinity

The James, York and Rappahannock rivers are typical coastal plain estuaries in which the salinity decreases from the mouth of the estuary, the source of saltwater, to the head of the estuary at the transition zone between fresh- and saltwater. The salt content of the water also increases with depth although no strong stratification exists. The isohalines across the estuary typically extend downstream a greater distance on the right side than on the left when the system is viewed from upstream. The dynamics of estuarine transport are a function of freshwater inflow and tidal movement, with the latter being the dominant factor. Field and hydraulic model studies clearly show that the upper layer has a longer ebb excursion than flood excursion. The opposite is true in the lower layer. The net flows, therefore, result in a net downstream transport in the upper layer and a net upstream transport in the lower layers, with a layer of "no net motion" dividing the two. This complex transport system has an influence on the distribution of nutrients and plankton forms in coastal plain estuarine systems.

The surface salinity at the mouth of the James River ranges between 15 and 25 ‰. Variations are due to the volume of freshwater flowing

into the system from the tidal river and to changes in the salinity regime of Chesapeake Bay. The range between surface and bottom values also responds to the same factors although they are more strongly influenced by the freshwater inflow levels and by temperature differences which may exist between the incoming freshwater and Chesapeake Bay.

The James River was nearly homogeneous from surface to bottom at the station 5 miles upstream from the mouth from October through February (Figure 2). Salinity values show very little variation with depth. Other physical and chemical parameters which will be discussed in later sections verified that complete mixing had occurred within the system.

Differences between surface and bottom salinities increase during the spring months when freshwater discharge values are high. During this period the lower Bay salinities have not yet been influenced by high freshwater discharges from the Susquehanna and Potomac river basins. Also, the temperature of the freshwater in the tidal James is characteristically 2-5°C higher than the temperature of the Bay waters. The difference in the sigma t value is, therefore, sufficient to prevent a high degree of mixing between the upper and lower layers.

During the summer months when freshwater flows decrease and water temperatures become more uniform throughout the system, the differences between surface and bottom salinities become less pronounced and the water mass approaches homogeneity. This modification of the salinity structure may have a pronounced effect on biological systems in that as it weakens, the transport mechanism weakens. Planktonic early-life stages of many of the molluscan and crustacean species indigenous to the James River are thought to be dependent upon the net upstream movement

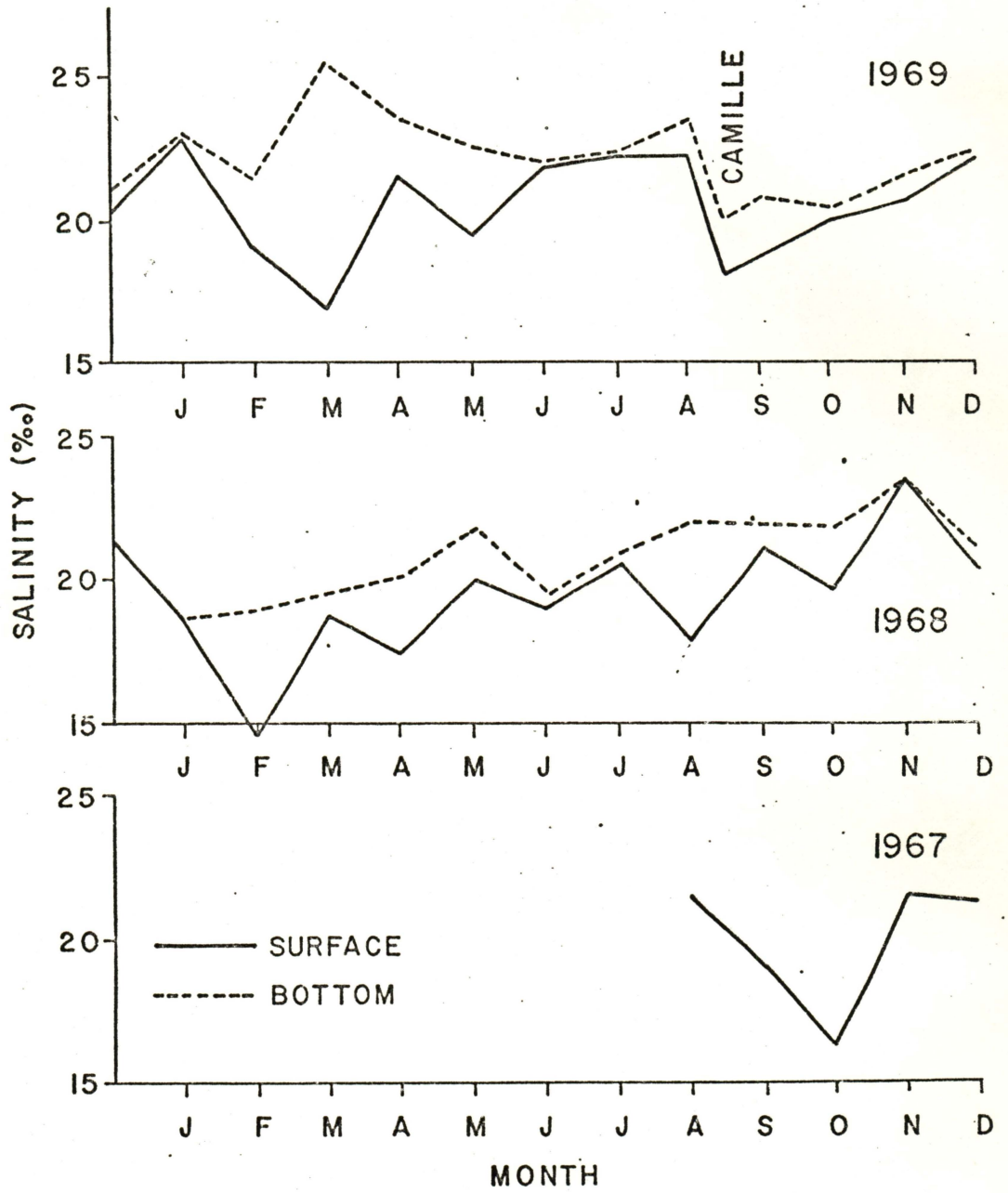


FIGURE 2. Surface and bottom salinities recorded at slack before flood tide at a station 5 miles upstream from the mouth of the James estuary.

of the lower layers to reach the setting and nursery areas upstream. Comprehensive investigations extending over 20 years indicate that the oyster set on the James River racks is very low during the summer months even though the larval stages are present in the water column.

Stratification near the mouth of the river developed again in August and was maintained through October of 1968 and November of 1969. The difference between years within the river is thought to be due to the higher freshwater discharge values during Hurricane Camille and their residual effect upon the system.

The salinity structure at the York River station located 5 miles upstream from the mouth showed a greater variation between years than did the James River (Figure 3). In 1968, the structure was similar to that of the James River through the month of June. The system developed a more defined structure in July but this weakened as the freshwater inflow decreased during the fall.

During 1969, the salinity gradient at Mile 5 of the York River was maintained throughout the year. A comparison of the parameters affecting density indicates that the only differences between years within the system were a more rapid warming trend during the spring of 1968 after the season's minimum temperature was reached in March and generally higher surface and bottom salinity values in 1969 than were recorded in 1968.

The passage of Hurricane Camille through the upper part of the York River drainage basin had a pronounced effect on the salinity structure at Mile 5. Fresh warm water flowing out of the river in the upper layer depressed the surface salinity to 11 o/oo but the bottom

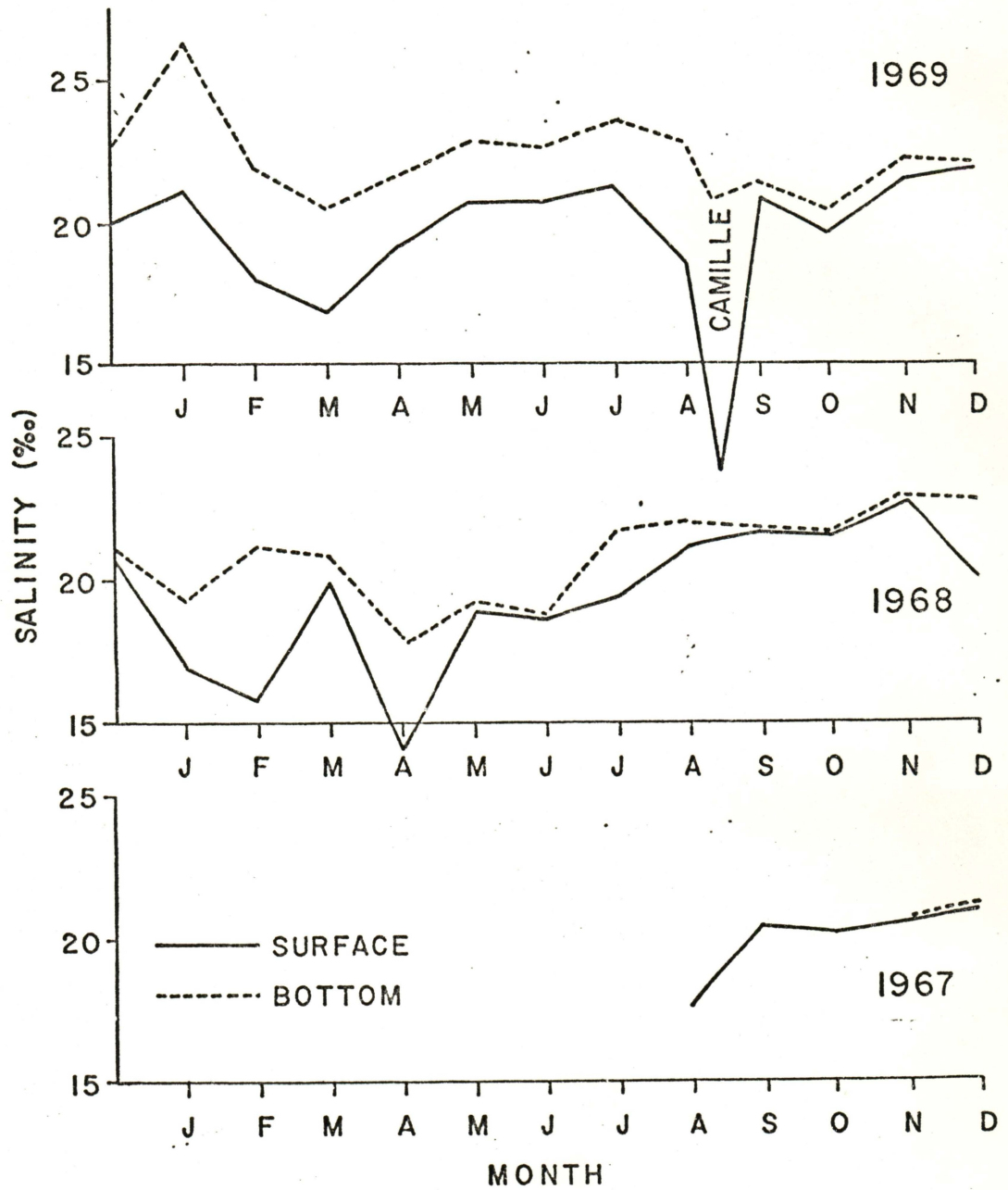


FIGURE 3. Surface and bottom salinities recorded at slack before flood tide at a station 5 miles upstream from the mouth of the York estuary.

salinity was only reduced to 20.6 o/oo. This storm was intense in only a small area of the watershed and the volume of water was augmented by that of several reservoirs in which the retaining structures failed. The resulting freshwater discharge as measured at the gaging station above the fall dropped rapidly after the passage of the flood crest, and the salinity gradient near the mouth recovered within two weeks after the low-salinity values had been recorded.

Surface and bottom salinities at Mile 5 on the Rappahannock River showed less variation both within and between years than was recorded for the James and York (Figure 4). The effects of the spring runoff were detectable during 1968 but no significant change was noted in 1969. Although the salinity levels were significantly higher in 1969 than in 1968 (3-5 o/oo), the Rappahannock River did not develop the gradient at the mouth that was recorded in the York River.

During 1968, a year of relatively low Chesapeake Bay salinities, the Rappahannock River remained relatively homogeneous from surface to bottom from March through December. In 1969, however, the gradient did not develop during the spring freshet period, but differences between surface and bottom values were recorded during the summer until after the passage of Hurricane Camille. This storm crossed the Rappahannock in the middle estuarine reach where the drainage basin is narrow and, therefore, did not affect this system as severely as the York River.

The location of the 5 o/oo isohaline in an estuary is an important factor in the distribution of oligohaline marine species. This varies with the freshwater inflow patterns and the Bay salinities, although the former is more important than the latter.

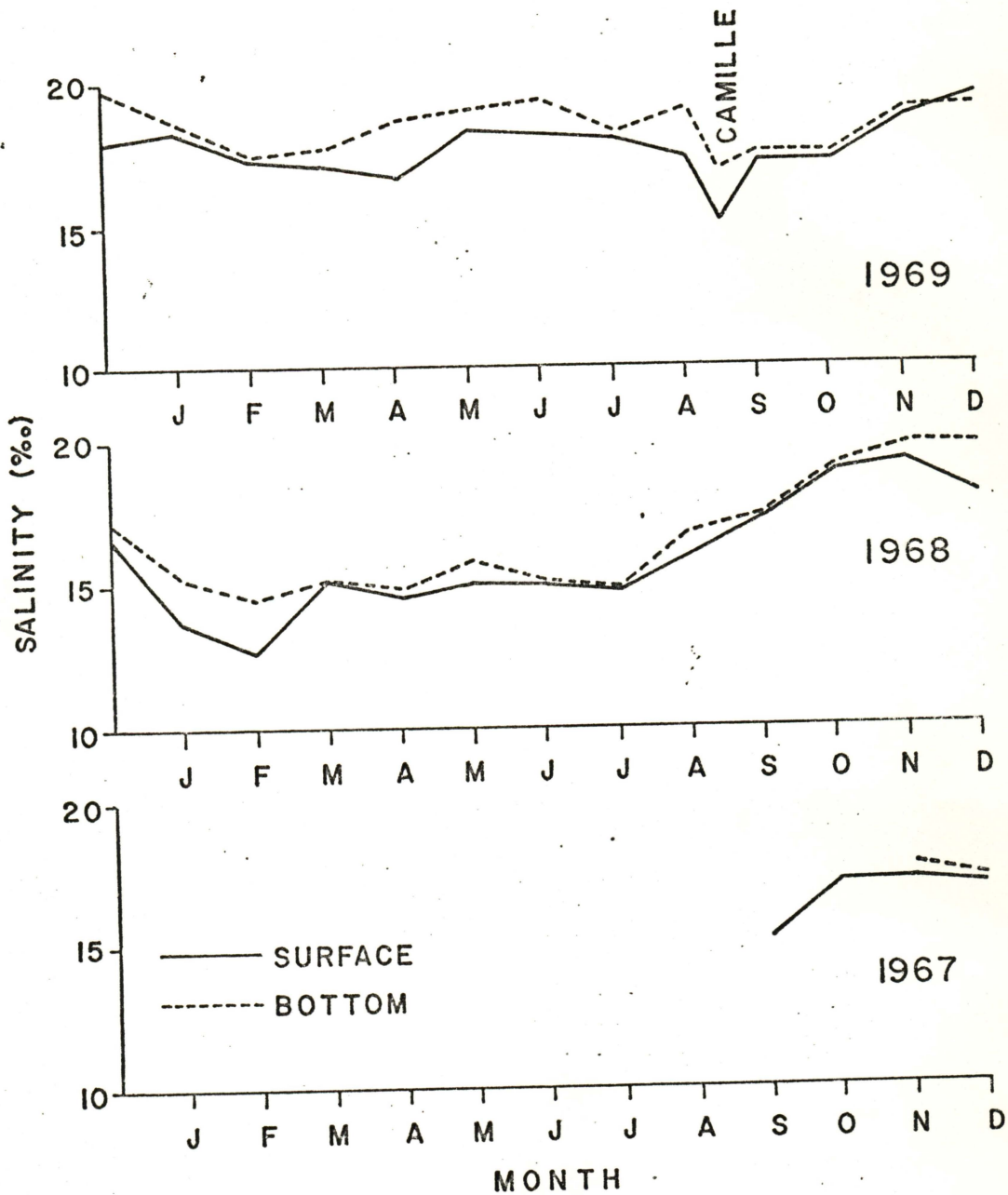


FIGURE 4. Surface and bottom salinities recorded at slack before flood tide at a station 5 miles upstream from the mouth of the Rappahannock estuary.

Oligohaline variations in the three systems follow similar patterns although the location of the upper limit as expressed in miles from the mouth differs both within and between the rivers (Figures 5, 6 and 7). The James estuary, having a watershed area nearly five times as large as either the York or Rappahannock, has a correspondingly higher fresh-water inflow. In addition, the mouth is located in lower Chesapeake Bay only 12 miles from the ocean, thus increasing the salinity in the lower reaches. These two factors result in a more compressed estuary in which the 5 o/oo level as measured at the 3-m depth is nearer the mouth than in the other two systems.

In 1968, the freshwater inflow decreased rapidly during the June-July period. The upstream migration of the 5 o/oo isohaline is clearly demonstrated in the figures. Although 1968 did not approach the low flow of record, a maximum intrusion of water containing 14% seawater was 40 miles on the James, 47 miles on the York, and 43 miles in the Rappahannock. The shift in location in the James was from Mile 18 to Mile 40, a distance of 22 nm.

The York River, being a bifurcate estuary with the Pamunkey and Mattaponi rivers having drainage basins of 1,475 and 900 square miles, is more responsive to low flows than is the James. During January of 1968 the 5 o/oo isohaline was located at Mile 25, 4 miles downstream from the confluence of the two tributaries. In November of 1968, the 5 o/oo isohaline was located at Mile 47 in the Pamunkey River, 18 miles upstream from the confluence, a shift of 22 nm also. No measurements were made in the Mattaponi River during this period.

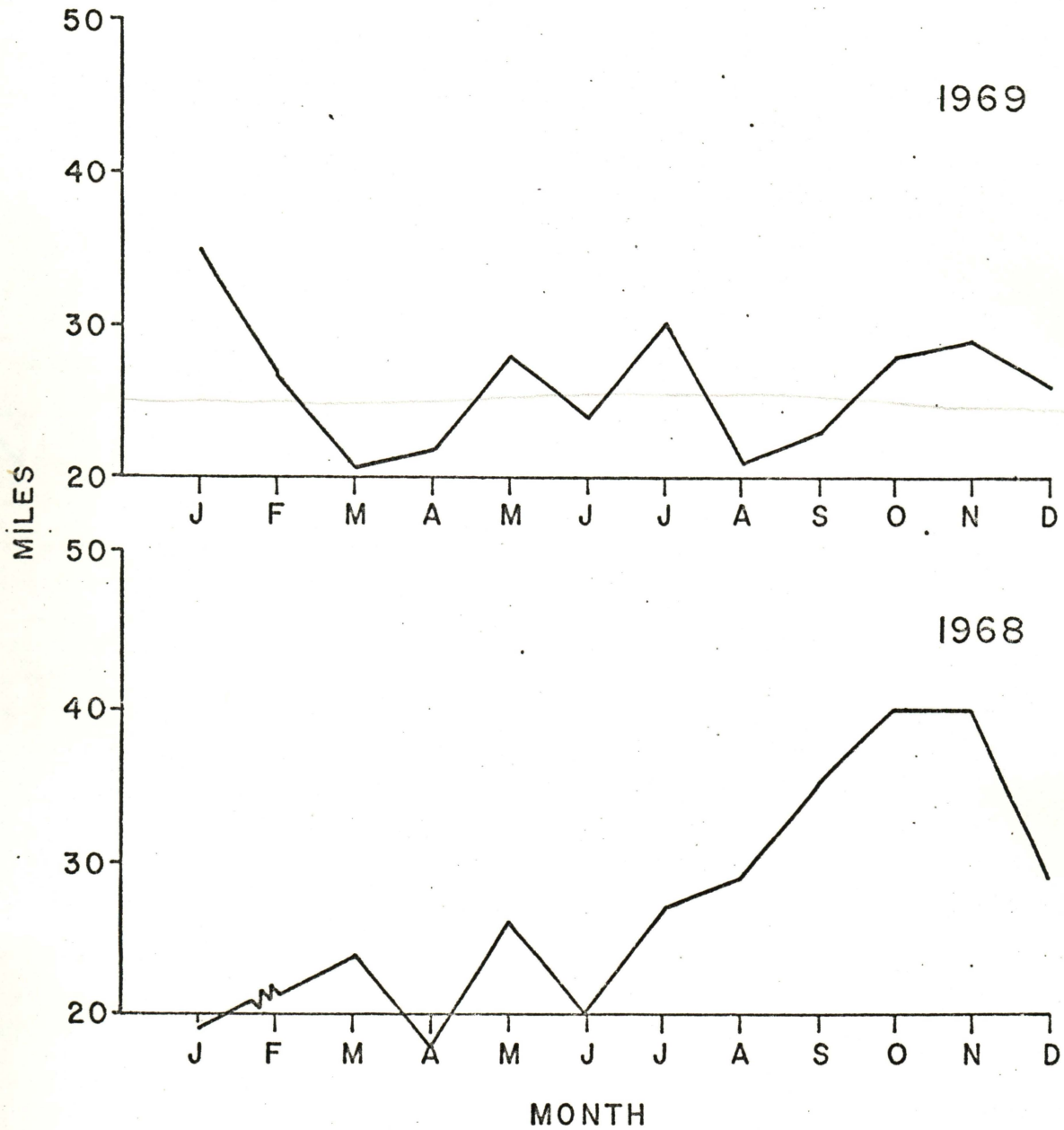


FIGURE 5. Location of the 3 meter depth 5 o/oo isohaline in the James estuary.

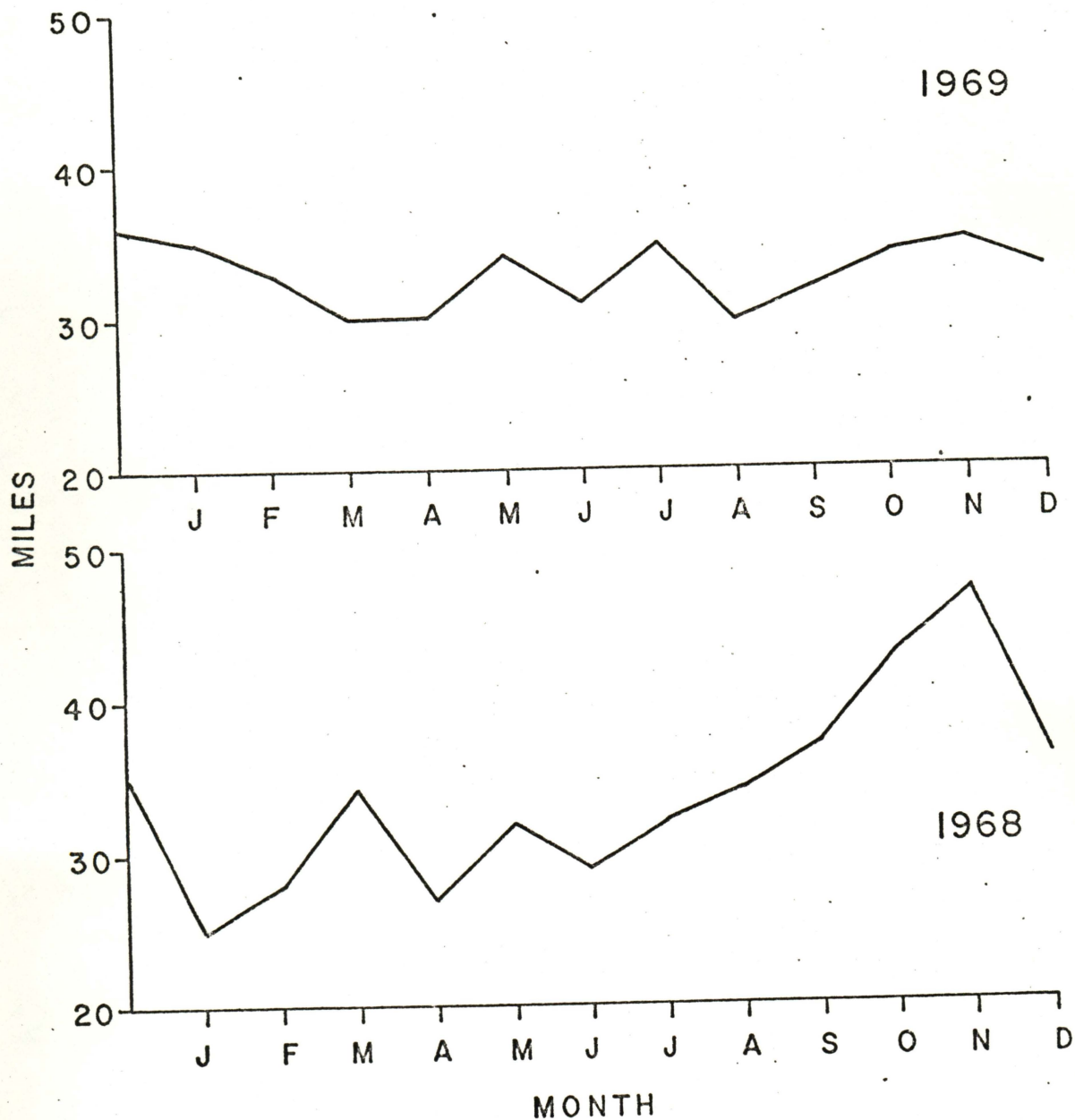


FIGURE 6. Location of the 3 meter depth 5 o/oo isohaline in the York estuary.

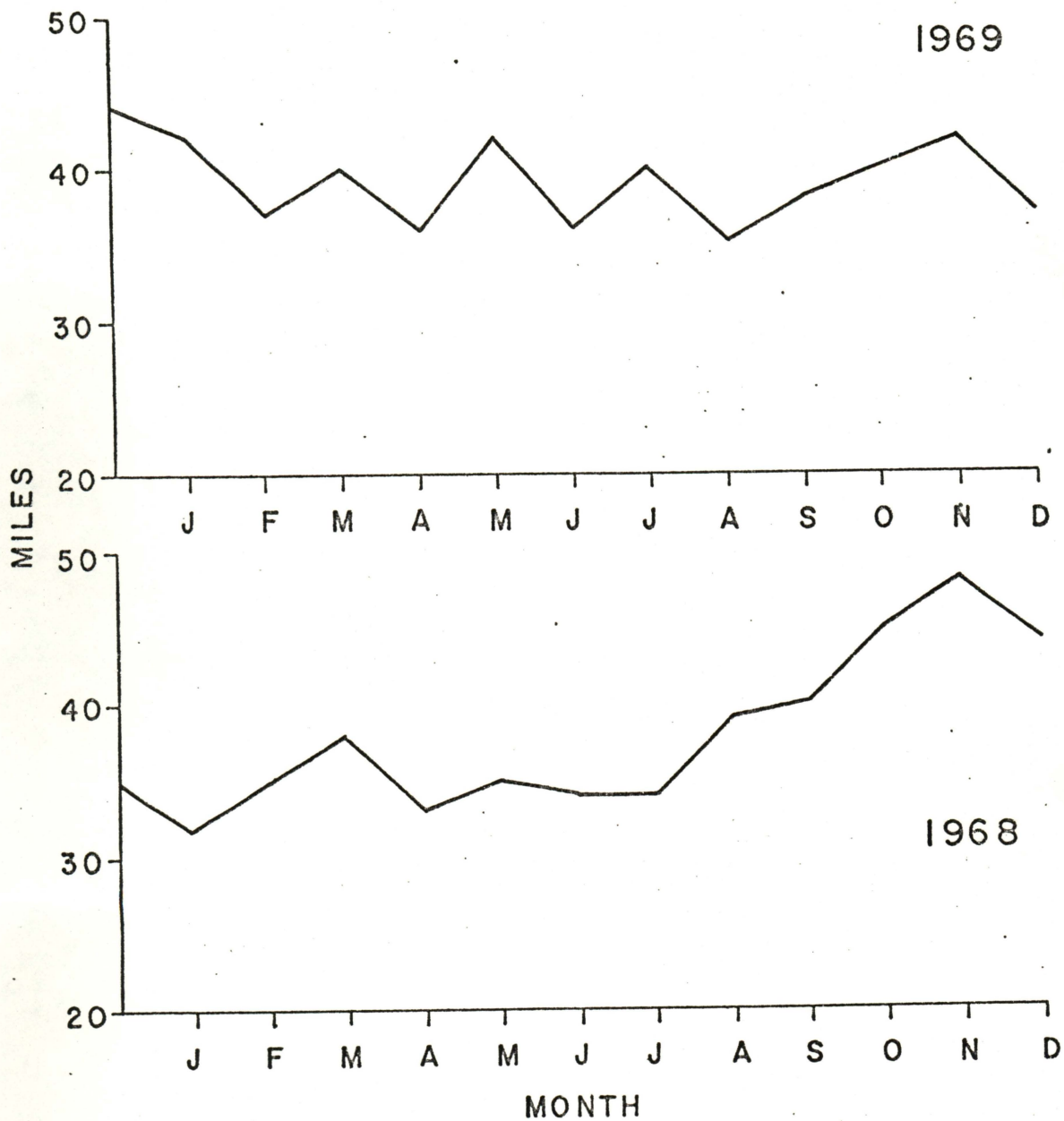


FIGURE 7. Location of the 3 meter depth 5 o/oo isohaline in the Rappahannock estuary.

The Rappahannock River is the least "compressed" of the three systems. Although the surface salinity at the mouth only ranged between 12 and 18 o/oo during 1968, the location of the 5 o/oo isohaline was never found to be downstream from Mile 32. This system also had a higher level of stability in that the location of the 5 o/oo isohaline did not go above Mile 43 during the early winter period. This was due in part to a less severe drought in the upper drainage basin than was experienced in the southern part of Virginia.

Although Bay salinities were higher in 1969 than they were in 1968, the drainage basins of Virginia's estuaries received more rainfall and the runoff levels were higher (mean 1969--14,000 cfs; 1968--11,200 cfs; USGS data). Also, the distribution of the runoff was such that values were relatively high during the period of the highest transpiration-evaporation rates. This resulted in a more stable location of the 5 o/oo isohaline, with a maximum range in location after the spring freshet period of less than 10 miles (Hurricane Camille period omitted) during the summer and fall (Figures 5, 6 and 7).

The James estuary showed the greatest variation in the location of the oligohaline zone in response to upstream freshets. Rappahannock estuary salinities showed variations but the location of the 5 o/oo isohaline showed a range of only 7 miles during the regular monthly sampling periods. The location of the 5 o/oo isohaline of the York River varied only 6 miles as compared to 22 miles in 1968.

Runoff waters resulting from the passage of Hurricane Camille produced drastic changes in the salinity structure of the upper estuarine reaches of the James and York rivers. Freshwater carried in the upper layer

resulted in stratification in which the surface and bottom salinities differed by as much as 14 o/oo. On 5 September 1969, the salinity at Mile 16 on the James River was 5.97 o/oo at 1 m, 9.93 o/oo at 3 m, 16.79 o/oo at 5 m, 20.17 o/oo at 7 m, and 20.33 o/oo at 9 m. York River values on 27 August at Mile 20 were 2.62 o/oo at 1 m, 4.94 o/oo at 3 m, 14.36 o/oo at 5 m, 15.20 o/oo at 7 m, and 15.60 o/oo at 9 m. The freshwater discharge into the estuaries occurred over such a short period that the lower layers were not grossly modified as the less dense freshwater flowed over the surface. The salinity gradient increased and the stratification was pronounced. This, however, resulted in a severe loss to the shellfish industry in the upper reaches as the loading of organic material increased and very little mixing between surface and bottom layers occurred, producing anaerobic conditions over the shellfish beds. Oyster mortalities exceeding 60% were recorded in some areas.

The salinity structure in the middle estuarine reach may vary from that measured at the mouth or the head (Figures 8, 9 and 10). Also, considerable variation was noted among seasons-within rivers, within seasons-between rivers, and between years both within and between rivers. The months of January, April, July and September were chosen to point out the differences. In January 1968, the Bay salinities were low and the freshwater inflow volumes were high. This resulted in a "compression" of the James and York estuaries with high levels of stratification as indicated by the "slope" of the isohalines. The Rappahannock River, which is characteristically a less "compressed" estuary, showed a high level of stratification but less shift in the isohaline locations.

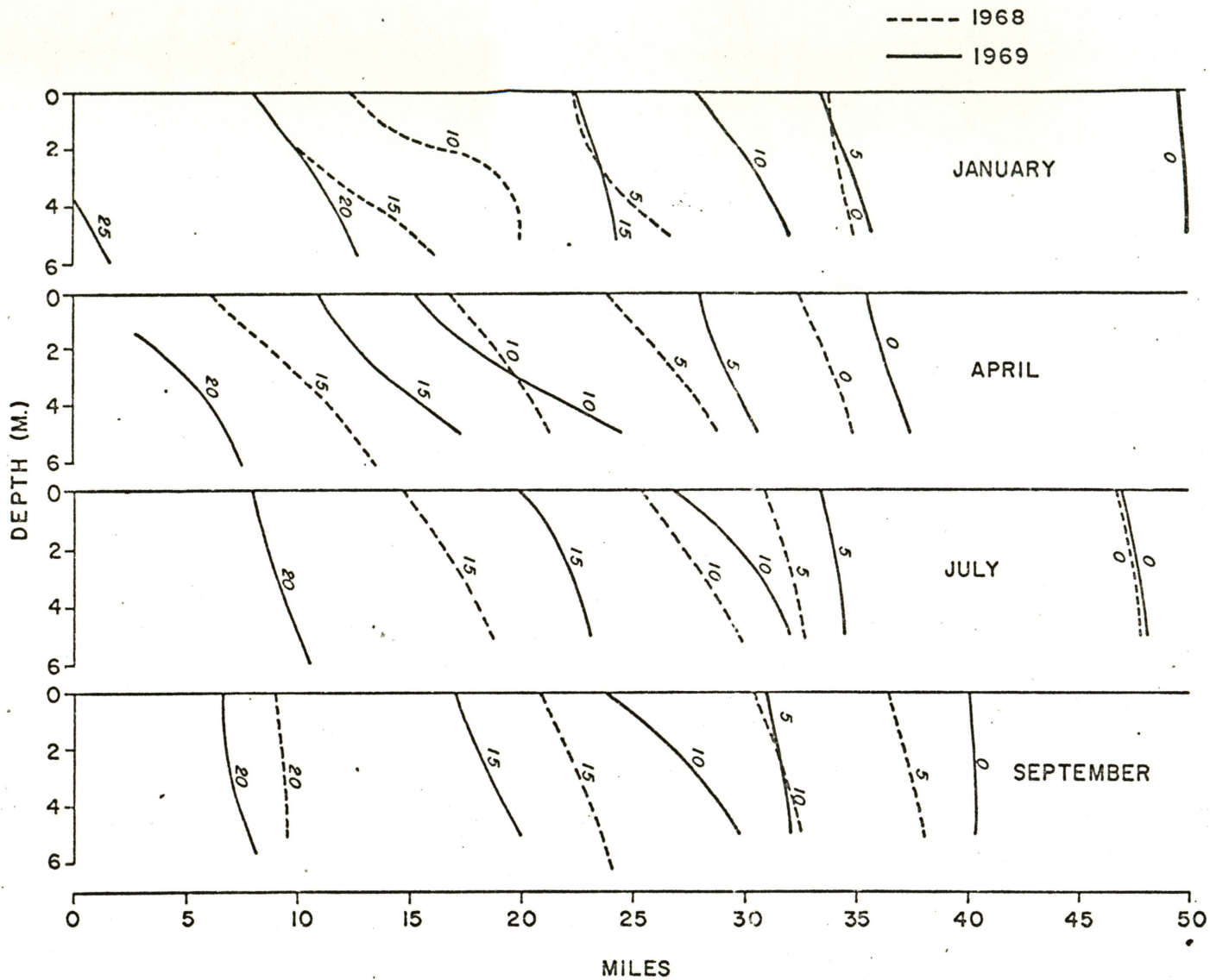


FIGURE 9. Vertical and longitudinal salinity structure of the York estuary at slack before flood tide during 1968 and 1969.

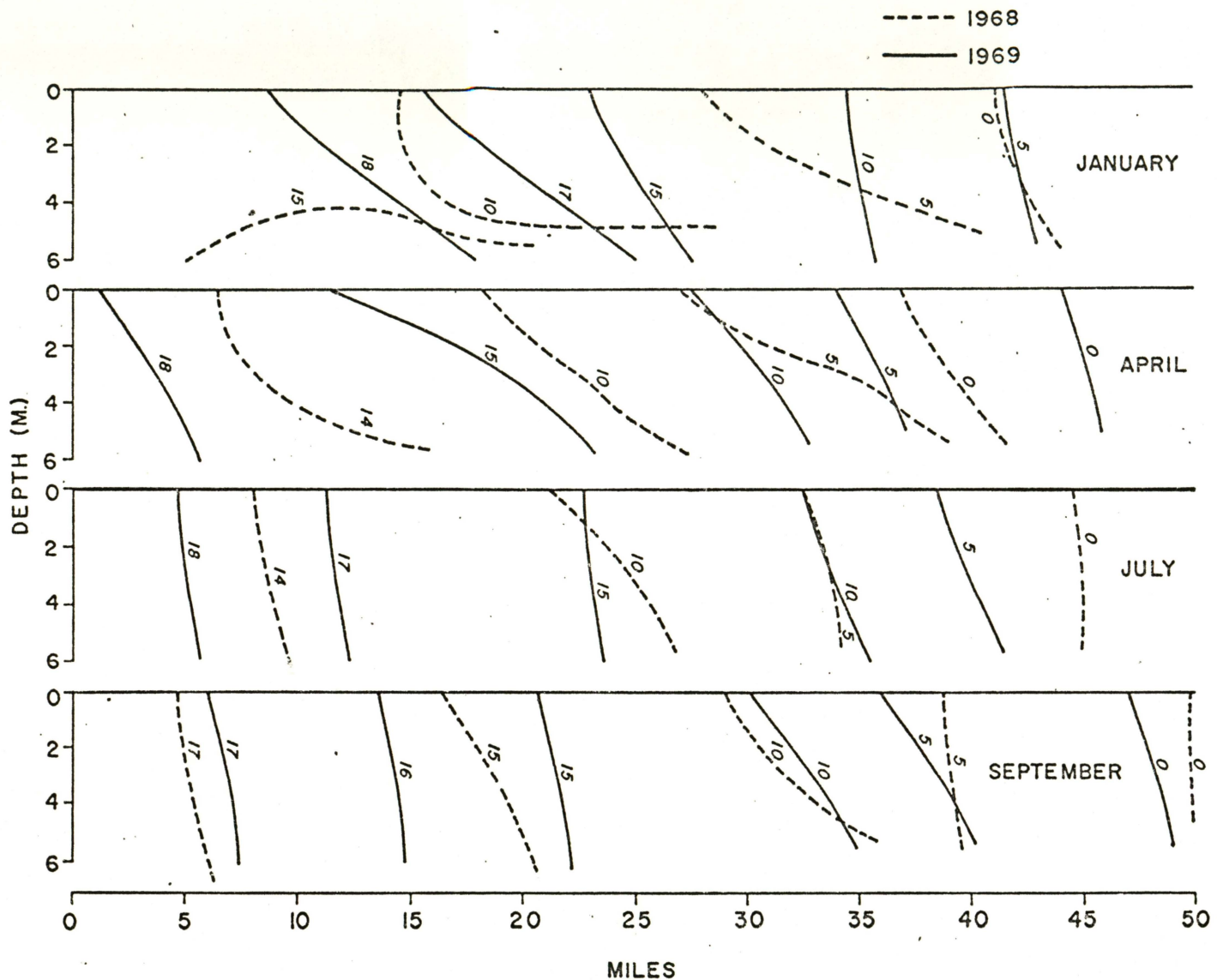


FIGURE 10. Vertical and longitudinal salinity structure of the Rappahannock estuary at slack before flood tide during 1968 and 1969.

In 1969 when Bay salinities were higher and freshwater discharge values were lower, the salinity gradient between surface and bottom was less than in 1968 and the transition zone between fresh- and saltwater was shifted from 15 to 25 miles upstream.

April data from the three estuaries indicate salinity structures were similar between years within rivers but the gradients between surface and bottom were greater in 1969 than they were in 1968. The similarity of positions of the transition zones and the shifting of the higher isohalines show the influence of the higher Bay salinities. In addition, water temperatures were lower in 1968 than in 1969 because of cold weather in March 1968.

In July salinity gradients appear to decrease even though the location of the isohalines may be shifted due to differences in freshwater discharges. The James and York estuaries showed a high level of similarity between years even though the 1969 meso-salinity isohalines were shifted approximately 5 miles upstream from the 1968 values. The Rappahannock River showed a greater upstream shift in isohalines in 1969 and also a higher gradient between surface and bottom salinities in the middle reach. Although this is contrary to what might be predicted, the salinity structure at the head and the mouth of the system shows a high degree of mixing from surface to bottom.

September data from the three estuaries show the influence of the higher freshwater discharge from the tidal river sections. James River salinities were nearly 5 o/oo lower in 1969 than in 1968 at a given mileage. The transition zone between fresh- and saltwater was located at Mile 35 in 1969, whereas it was at Mile 57 in 1968. This shift in

the isohalines did not, however, appear to affect the vertical salinity structure in the mesohaline reach.

Isohalines in the York River were also shifted downstream in 1969. Again, the gradient accompanying this shift was stronger in the middle reach but not markedly different near the mouth or at the head of the estuary. The transition zone had shifted, however, from near Mile 44 in 1968 to Mile 40 in 1969.

The Rappahannock River, which was not seriously affected by Hurricane Camille, did not show a distinct shift in either isohaline or transition zone location between years. The vertical salinity structure differed between years, however, in that the gradient between surface and bottom was much stronger in 1969 than it had been in 1968.

Temperature

Estuarine water temperatures are strongly influenced by air temperatures, wind velocities, and ocean water temperature. The latter influence is most obvious in late fall and winter when ocean temperatures are higher than those in the tidal freshwater reach and in the spring and early summer when they are lower. Generally, however, the temperatures throughout a calendar year follow the same curve as air temperatures, with the rapidity of change within a short period of time influenced by wind conditions.

Surface and bottom water temperatures follow the same patterns within years between Virginia's three major estuaries but show differences between years within systems (Figures 11, 12 and 13). 1968 was an atypical year with cold weather extending into March. The James estuary,

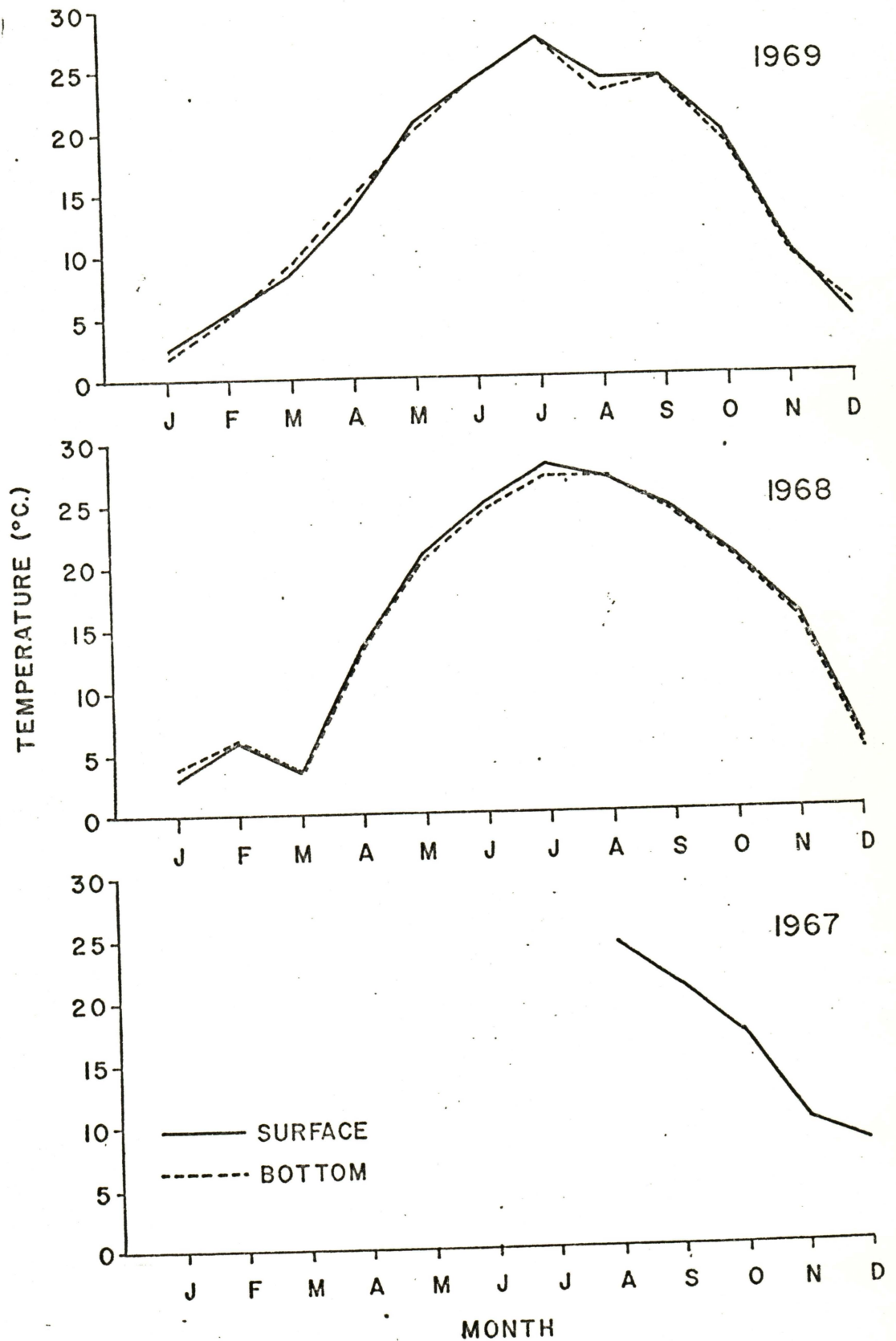


FIGURE 11. Surface and bottom water temperatures recorded at Mile 5 in the James estuary during 1967, 1968 and 1969.

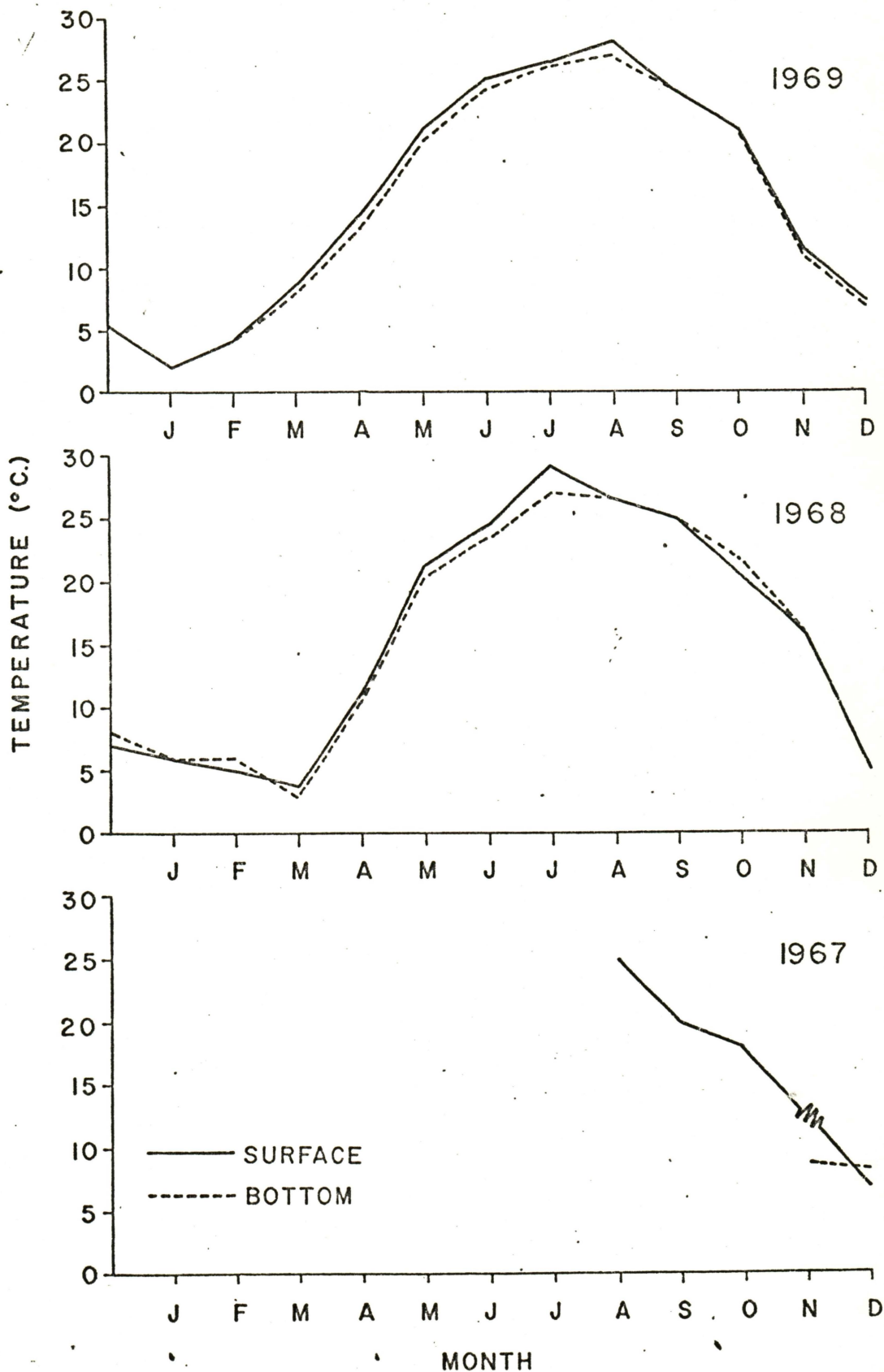


FIGURE 12. Surface and bottom water temperatures recorded at Mile 5 in the York estuary during 1967, 1968 and 1969.

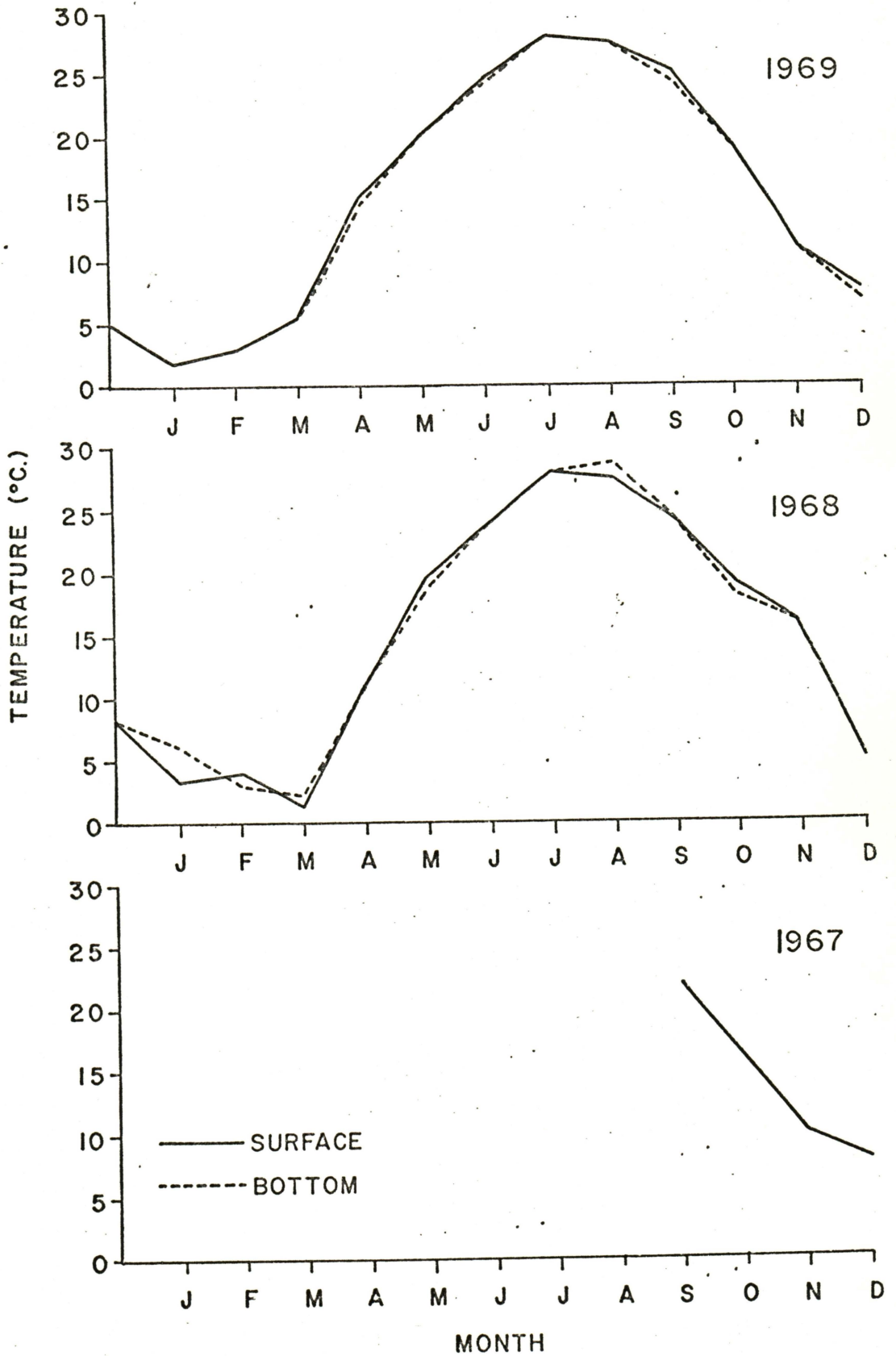


FIGURE 13. Surface and bottom water temperatures recorded at Mile 5 in the Rappahannock estuary during 1967, 1968 and 1969.

located nearest the ocean, responded to the influence of the warmer water and had a slightly different late winter temperature pattern than the other two rivers. A surface and bottom temperature of 3.5 was recorded in March. The middle system, the York, did not show an increase in temperature in February and the temperature decreased steadily to the March low. The Rappahannock River, the most northerly of the three, also reached the lowest level in March with a value of 1.5°C recorded.

When compared to the years of thermograph data from the VIMS pier station, 1969 was a more typical temperature year. The season's low values were recorded in January and temperatures then increased until the maximum was reached in July. Water temperatures normally decrease after the July maximum, and although the slope may vary slightly between years, the lowest point is reached in December.

CHEMISTRY

Dissolved Oxygen

Dissolved oxygen levels in estuarine systems are governed by the solubility coefficient as influenced by temperature and salinity and by man-made or organic loadings capable of producing an oxygen demand exceeding reaeration rates. Data from calculations of percent saturation, which are based upon solubilities as related to temperature and salinity, indicate that the percent saturation in the lower reaches of the estuaries ranges between 90 and 100 percent. Percent saturation in the upper estuarine reaches frequently falls below the 90 percent level due to high organic material oxygen demand from marsh drainage and the presence of industrial wastes.

Data from the 1968 cruises on the James River are given in Table 1. Although all of the values recorded both at surface and bottom are well above the minimum values required to maintain the biological health of the system, the values at the transition zone during the early fall show the effects of the oxygen sag zone downstream from the industrial complex at Hopewell. The data indicate that reaeration occurs between the transition zone and the 5 o/oo isohaline and that no additional modification occurs below this point.

Organic loadings from an industrial source at Mile 30 and a high volume of marsh drainage upstream from this point modify the dissolved oxygen levels in the York estuary (Table 2).

Dissolved oxygen values in the lower estuary showed the normal variation with season, with the highest values recorded in the early part of the year during the low water-temperature period. As the water temperatures increased, the absolute values decreased as the solubility decreased and the salinity increased. Surface values were usually higher than bottom values due to higher photosynthetic activity in the trophogenic layer and the higher salinity and respiration in the tropholytic layer.

The influence of the industrial effluents discharged at Mile 30 was obvious during January, February, April, May, June and July. During these months the 5 o/oo isohaline was located within the range of one flood or ebb tide excursion of the outfall location (see Figure 6). During these months the oxygen values were lower at the 5 o/oo isohaline than at the 10 o/oo isohaline even though the oxygen solubility was higher because of the lower salinity.

TABLE 1. Dissolved oxygen values (mg l^{-1}) recorded at surface and bottom at five stations on the James estuary during 1968.

Salinity (o/oo)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
20--S	11.1		11.7	9.5	7.8	6.8	6.9	6.8	8.2	7.6	7.4	10.8
--B	11.1		10.8	9.4	6.8	6.5	6.1	5.5	6.6	6.6	7.4	10.4
15--S	11.3	11.1	11.8	9.4	7.8	7.9	6.8	6.4	6.6	7.7	8.1	11.1
--B	11.0	10.9	10.7	8.7	7.0	6.2	5.8	5.6	6.6	7.2	7.8	11.3
10--S		10.1	11.2	9.4	7.8	7.1	6.5	6.8	7.0	7.9	8.5	11.3
--B		10.0	11.1	8.9	7.0	6.5	5.3	6.1	6.6	7.9	8.3	11.4
5--S	11.8	11.1	11.6	9.2	8.0	7.5	7.3	7.7	7.5	9.1	8.7	11.7
--B	10.5	11.2	11.4	8.9	7.4	6.7	7.2	6.8	6.9	7.5	8.4	11.5
0--S	11.9	10.7	11.8	9.1	7.4	6.7	6.0	4.1	3.9	6.2	4.8	9.7
--B	11.9	10.7	11.8	9.0	7.5	6.7	5.6	4.3	4.3	5.9	4.5	9.6

TABLE 2. Dissolved oxygen values (mg l^{-1}) recorded at surface and bottom at five stations on the York estuary during 1968.

Salinity (o/oo)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
<i>% Sat:</i>	<i>91</i>		<i>96</i>		<i>93</i>	<i>89</i>	<i>92</i>	<i>85</i>	<i>82</i>	<i>89</i>	<i>86</i>	<i>86</i>
20--S	10.1		11.0		7.4	6.7	6.3	6.1	6.0	6.9	7.3	9.4
--B	10.1		10.7		6.9	6.3	4.9	4.9	4.5	7.1	7.4	10.1
<i>% Sat:</i>	<i>92</i>		<i>91</i>		<i>86</i>	<i>84</i>	<i>69</i>	<i>69</i>	<i>62</i>	<i>91</i>	<i>87</i>	<i>89</i>
15--S	10.2	11.3	10.5	10.3	7.4	7.0	6.4	6.5	6.0	7.2	6.7	9.8
--B	10.3	10.5	10.5	9.7	7.1	6.6	5.7	5.5	6.7	7.3	6.9	9.8
10--S	10.0	10.0	9.9	9.3	6.9	6.4	5.5	4.4	4.6	7.0	7.5	9.1
--B	10.0	10.9	10.3	9.1	6.6	6.2	5.1	4.5	4.0	6.6	6.8	9.9
5--S	9.7	9.6	10.1	8.0	5.7	5.0	5.2	4.4	5.3	7.2	8.1	9.6
--B	9.8	9.2	9.9	8.4	6.3	4.7	4.7	5.3	5.1	7.0	7.7	10.1
0--S	10.0	10.2	11.2	8.6	6.2	5.9	6.3	6.7	6.7	7.3	7.2	10.6
--B	10.1	10.5	11.2	8.4	7.3	5.7	6.1	6.4	6.5	7.0	8.3	11.1

Dissolved oxygen values in the Rappahannock estuary followed the pattern expected for an unmodified estuary (Table 3). This system has a bathymetric characteristic, however, which apparently produced low dissolved oxygen values at the 15 o/oo isohaline in August. A shelf exists at the mouth which prevents free circulation of bottom waters in and out of the river. Occasionally during the late summer months the water behind the shelf becomes stagnant and anaerobic conditions develop. The data indicate that in August the station was located on the shelf at slack before flood tide and it is quite likely that water from the oxygen-deficient upstream reach was in the area.

pH-Alkalinity

Seawater is a slightly alkaline solution having a pH ranging between 7.8 and 8.2. It is a highly buffered solution containing borates in addition to the carbonates and bicarbonates which are normally present in freshwater. The anions capable of accepting protons prevent significant changes in the pH of the water due to biological activity or through minor influences of man's activities.

The 1968-69 data indicate that the pH values in Virginia's estuaries are nearly equal between rivers, within years, and between years (Tables 4, 5 and 6). In comparing the ranges of pH at the various isohaline locations, it appears that the range of values recorded during the 24-month period is greater in the low-salinity areas than at the downstream stations near the mouth of the rivers. Occasionally, pH values slightly below 7 were measured at the upstream

TABLE 3. Dissolved oxygen values (mg l^{-1}) recorded at surface and bottom at five stations on the Rappahannock estuary during 1968.

Salinity (o/oo)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
20--S									7.9	7.0	9.0	11.1
--B									6.8	7.4	8.8	10.5
15--S	12.5	12.0	11.5	10.4	7.7	7.3	6.0	4.8	8.1	7.8	9.0	11.2
--B	12.1	12.0	11.3	10.5	6.8	7.2	5.4	4.3	6.9	7.4	8.1	9.9
10--S	12.0	11.7	11.8	9.4	7.4	7.4	7.4	7.9	7.9	8.0	8.1	11.4
--B	11.6	11.3	11.3	9.3	7.2	6.6	6.0	6.2	6.7	8.0	8.5	5.7
5--S	11.9	11.3	12.0	9.4	7.8	7.2	6.7	6.5	7.5	10.0	8.8	11.4
--B	11.6	10.7	12.4	8.8	7.1	7.2	6.5	6.3	7.4	8.5	8.5	11.4
0--S	11.5	11.8	12.4	9.5	8.3	8.0	5.3	6.8	8.2		9.8	8.6
--B	11.3	11.2	12.4	9.5	8.0	7.4	4.8	6.3	7.9			9.0

TABLE 4. Mean and range of pH and alkalinity values at five salinity levels in the James estuary.

	<u>1968</u>	<u>1969</u>
20 o/oo		
Mean pH	8.0	8.0
Range	7.7-8.4	7.7-8.2
Mean Alkalinity	1.50	1.56
Range	1.26-1.71	1.24-1.69
15 o/oo		
Mean pH	7.9	8.0
Range	7.6-8.4	7.7-8.4
Mean Alkalinity	1.20	1.25
Range	0.97-1.36	1.03-1.42
10 o/oo		
Mean pH	7.8	7.9
Range	7.4-8.2	7.5-8.5
Mean Alkalinity	0.97	1.03
Range	0.74-1.27	0.76-1.26
5 o/oo		
Mean pH	7.7	7.8
Range	7.3-8.2	7.5-8.5
Mean Alkalinity	0.76	0.81
Range	0.51-0.96	0.62-1.04
0 o/oo		
Mean pH	7.4	7.9
Range	6.8-7.9	7.3-8.6
Mean Alkalinity	0.69	0.71
Range	0.41-1.18	0.38-1.04

TABLE 5. Mean and range of pH and alkalinity values at five salinity levels in the York estuary.

	<u>1968</u>	<u>1969</u>
20 o/oo		
Mean pH	7.8	7.9
Range	7.6-8.0	7.6-8.0
Mean Alkalinity	1.59	1.57
Range	1.45-1.76	1.31-1.72
15 o/oo		
Mean pH	7.8	7.8
Range	7.6-8.5	7.4-8.2
Mean Alkalinity	1.36	1.26
Range	1.20-1.58	0.92-1.59
10 o/oo		
Mean pH	7.6	7.6
Range	7.3-8.1	7.2-8.2
Mean Alkalinity	1.08	1.00
Range	0.61-1.33	0.40-1.57
5 o/oo		
Mean pH	7.4	7.5
Range	7.2-7.9	7.1-8.1
Mean Alkalinity	0.73	0.69
Range	0.41-1.00	0.30-0.95
0 o/oo		
Mean pH	7.4	7.6
Range	6.6-8.3	7.0-8.1
Mean Alkalinity	0.45	0.41
Range	0.26-0.59	0.32-0.63

TABLE 6. Mean and range of pH and alkalinity values at five salinity levels in the Rappahannock estuary.

		<u>1968</u>	<u>1969</u>
20 o/oo	Mean pH	7.8	7.9
	Range	7.7-7.9	7.1-8.4
	Mean Alkalinity	1.39	1.34
	Range	1.35-1.45	1.00-1.59
15 o/oo	Mean pH	8.0	7.9
	Range	7.6-8.4	7.6-8.1
	Mean Alkalinity	1.21	1.13
	Range	0.91-1.42	0.81-1.52
10 o/oo	Mean pH	7.7	7.7
	Range	7.2-8.2	7.2-8.0
	Mean Alkalinity	0.72	0.60
	Range	0.31-0.99	0.08-0.90
5 o/oo	Mean pH	7.3	7.4
	Range	6.3-8.1	6.4-8.1
	Mean Alkalinity	0.36	0.36
	Range	0.03-0.64	0.03-0.59
0 o/oo	Mean pH	7.4	7.8
	Range	6.6-8.1	7.2-8.5
	Mean Alkalinity	0.31	0.35
	Range	0.13-0.46	0.21-0.49

stations and this is attributed to marsh drainage water. This conclusion is substantiated by the visual observations of stained water on occasional runs.

Alkalinity or base reserve values indicate more clearly the differences within stations within rivers and within stations between rivers. The James River, which drains four physiographic provinces, discharges a more highly buffered water into the estuary than does the York. The York in turn is more highly buffered than the Rappahannock. These differences are not apparent downstream from the 10 o/oo isohaline as the percentage of freshwater decreases to five-sevenths of the solution.

Nutrients--Nitrogen and Phosphorus

Nitrogen and phosphorus are generally regarded as the primary nutrients responsible for phytoplankton productivity in natural waters. These elements, in addition to trace substances, are discharged in large volumes into tidal and estuarine systems with runoff water from agricultural activities, as the result of sewage treatment which is designed to stabilize and mineralize organic wastes, with liquid effluents containing detergents, and in the effluents of certain types of industrial activities. The role of these nutrients in producing "secondary pollution" through over-enrichment and environmental degradation has been well documented. The author has described the conditions which develop in the upper tidal James River during low-flow conditions and high water temperatures in which the river is

adversely affected from Mile 50 to Mile 90 at Richmond. Enrichment resulting from man's activities is minimal in the York tidal river and moderate in the upper Rappahannock.

Nitrogen

Total nitrogen levels in the three estuarine systems generally reflect the upstream loadings although the chemical state usually differed within rivers and between rivers both within and between years (Figures 14-21).

January 1968 and 1969 James estuary values are inversely related to the freshwater discharge values. In 1968, the discharge was high as indicated by the location of the 5 o/oo isohaline at Mile 18 and the total nitrogen values at all stations were less than ^{1.4 ppm} 100 ug-at l⁻¹. The soluble organic nitrogen (SON) values increased towards the middle of the estuary as the particulate organic nitrogen (PON) values decreased. Downstream from the 10 o/oo isohaline the PON values tended to increase while the SON values remained essentially the same. The nitrate plus nitrite values remained nearly constant throughout the system.

1969 was a relatively low discharge period (5 o/oo isohaline at Mile 35) and the estuary was in a quasi-steady state. Total nitrogen values were not only higher but the levels decreased towards the mouth and the chemical form of the nitrogen showed the influence of the ammonia discharges at Hopewell. Total nitrogen values decreased towards the mouth of the James estuary but the PON fraction increased slightly.

The York estuary total nitrogen or nitrogen fraction values did not reflect the 1968-1969 freshwater discharge-quantity relationship previously demonstrated for the James. PON levels were slightly higher

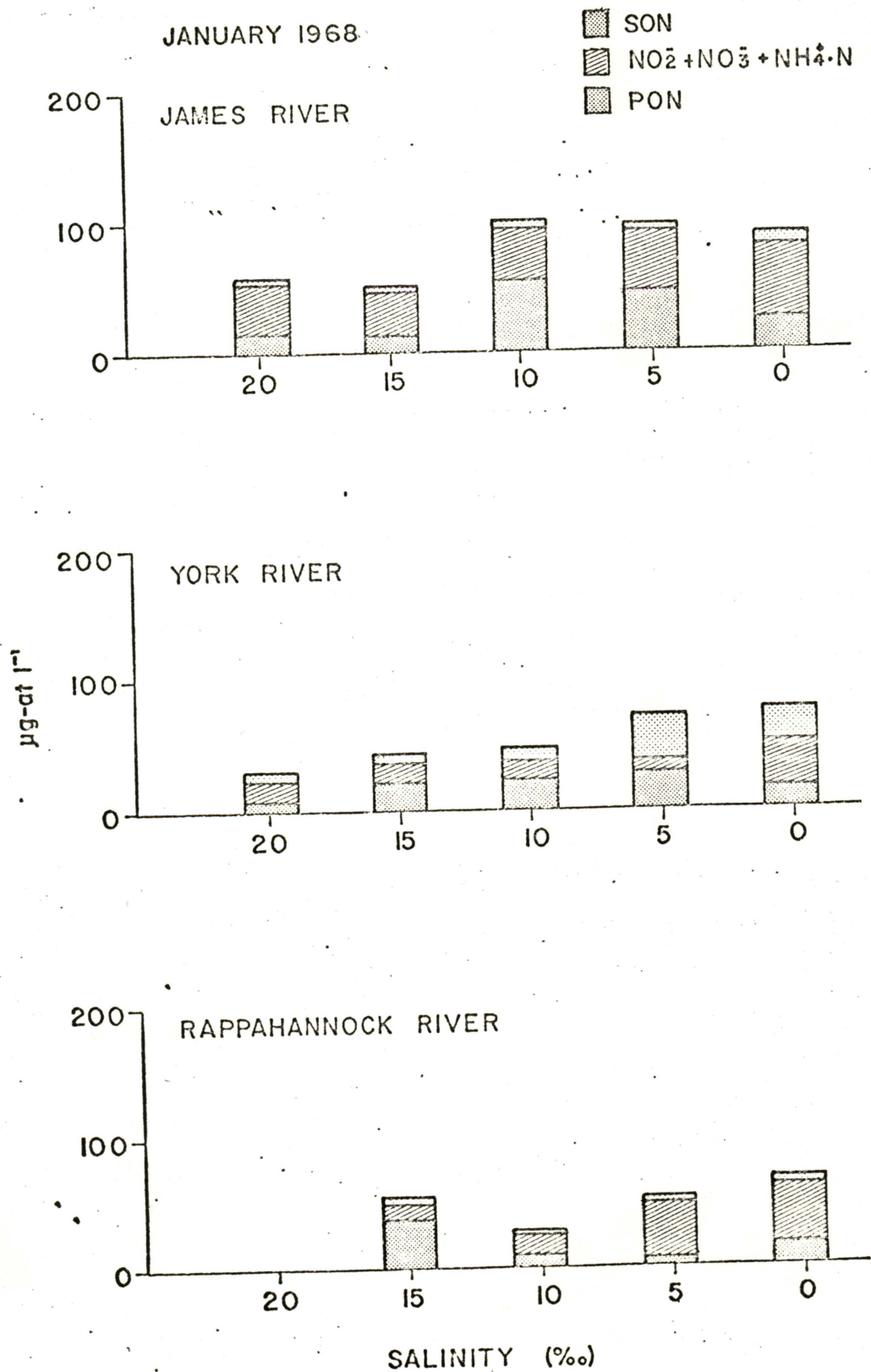


FIGURE 14. Organic and inorganic nitrogen levels at five stations in Virginia's estuaries during January 1968.

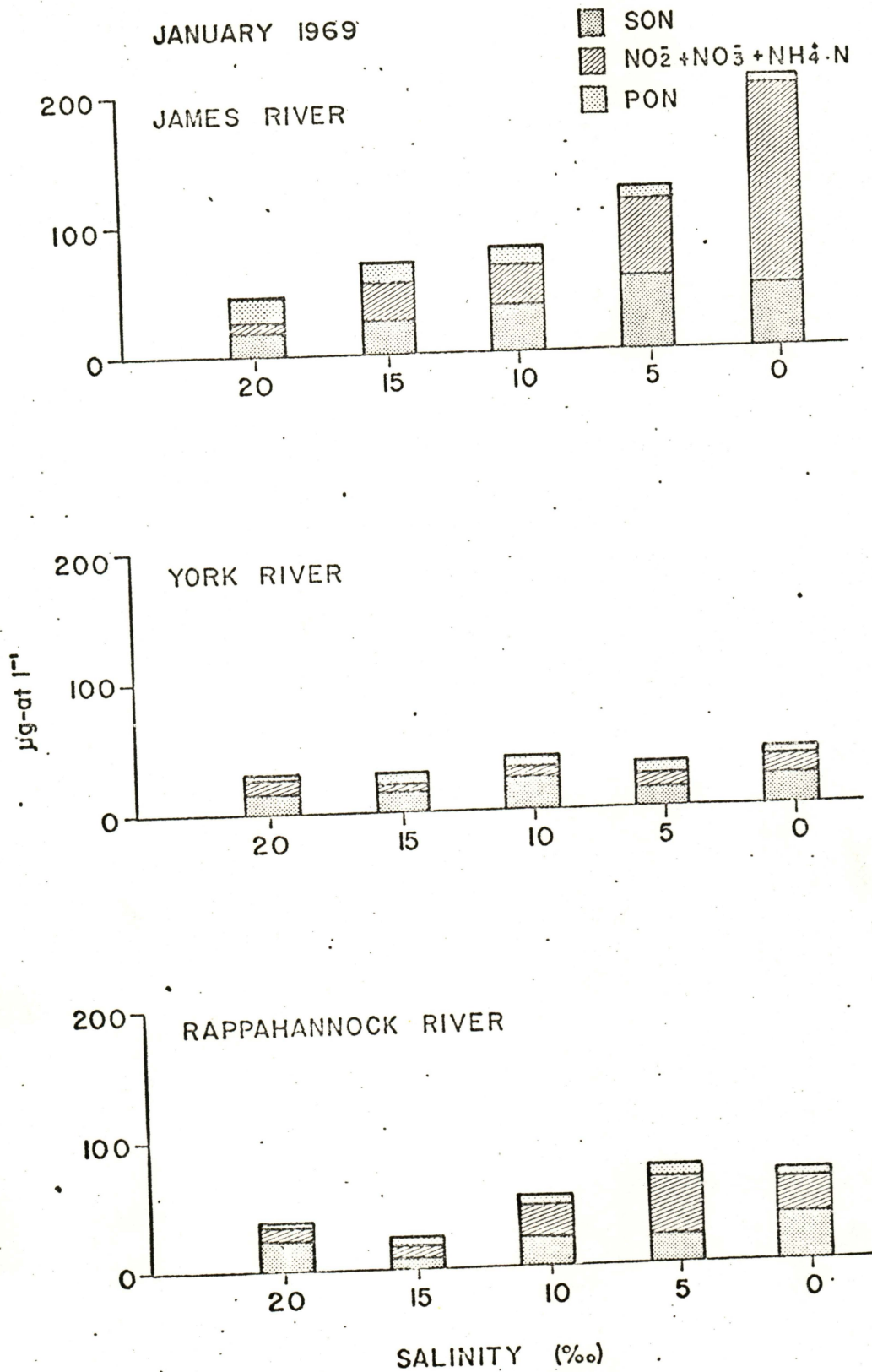


FIGURE 15. Organic and inorganic nitrogen levels at five stations in Virginia's estuaries during January 1969.

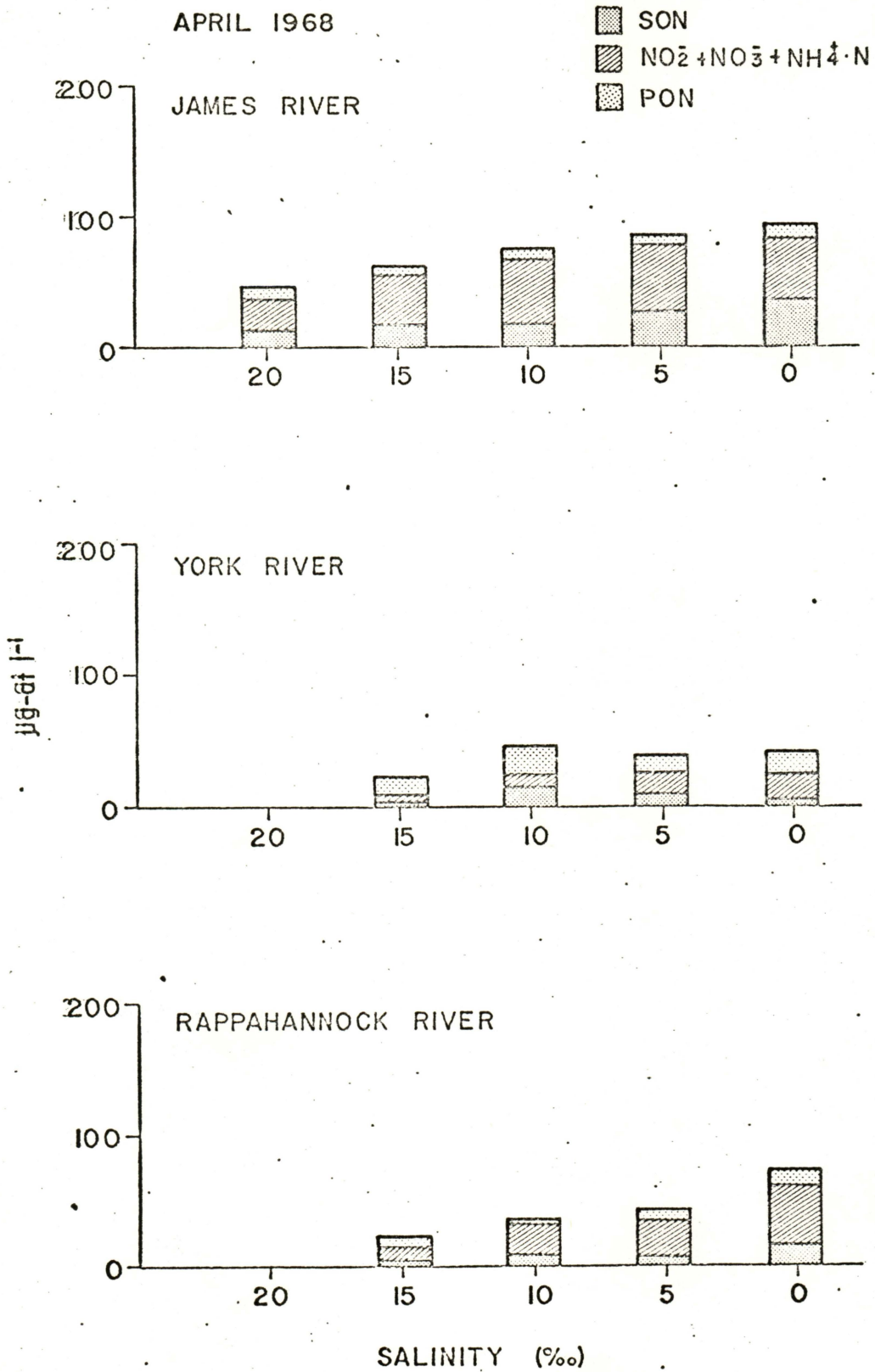


FIGURE 16. Organic and inorganic nitrogen levels at five stations in Virginia's estuaries during April 1968.

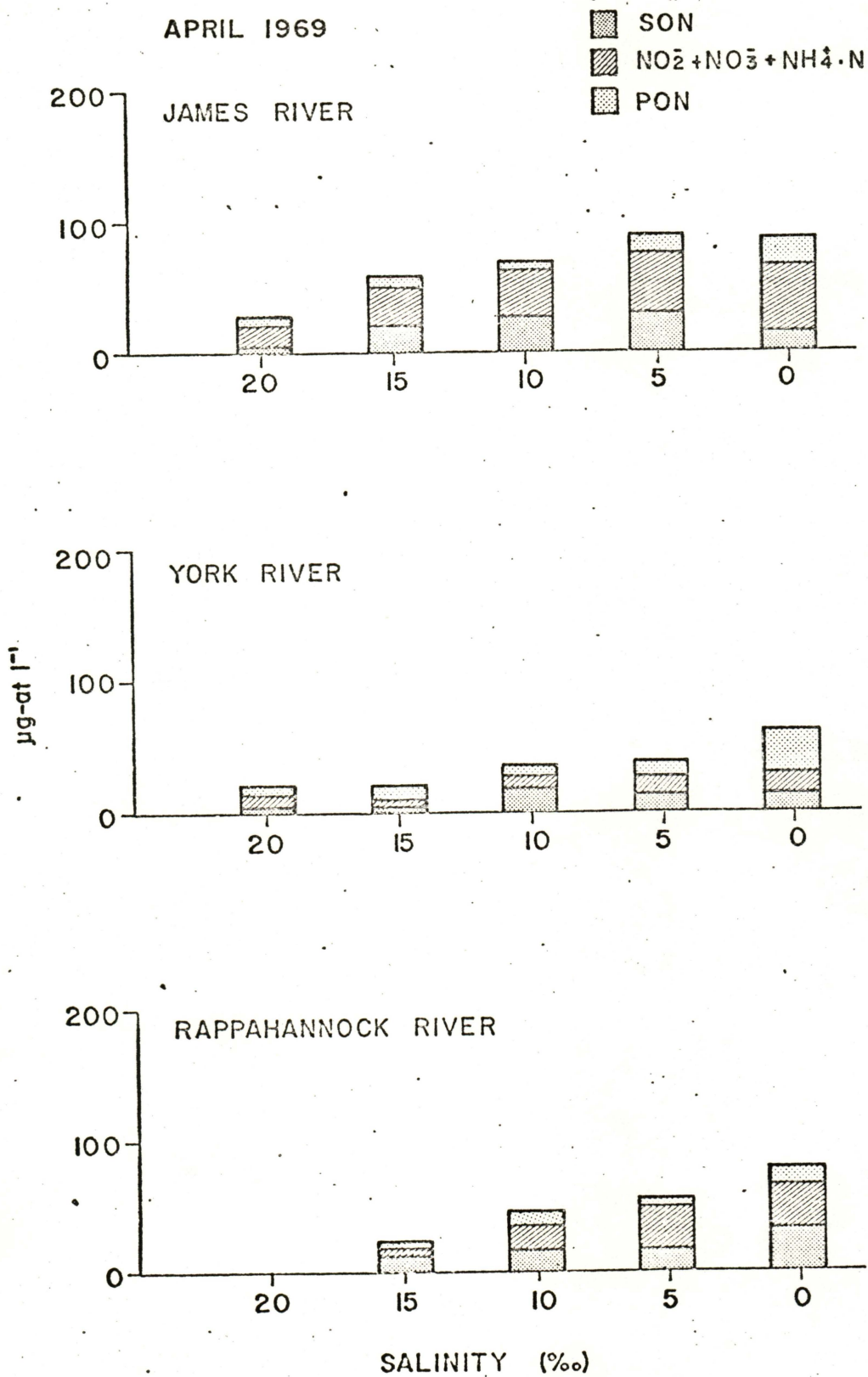


FIGURE 17. Organic and inorganic nitrogen levels at five stations in Virginia's estuaries during April 1969.

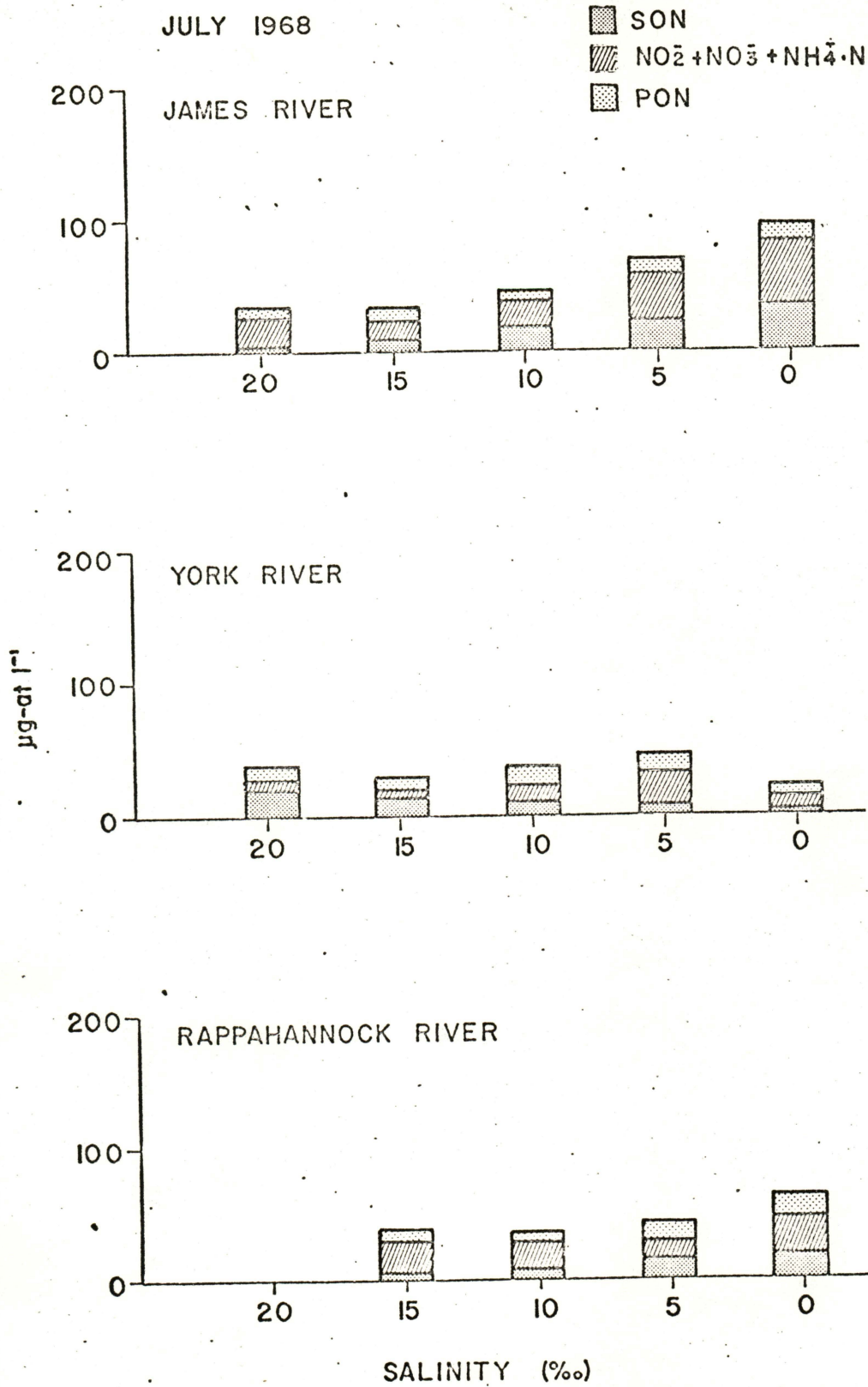


FIGURE 18. Organic and inorganic nitrogen levels at five stations in Virginia's estuaries during July 1968.

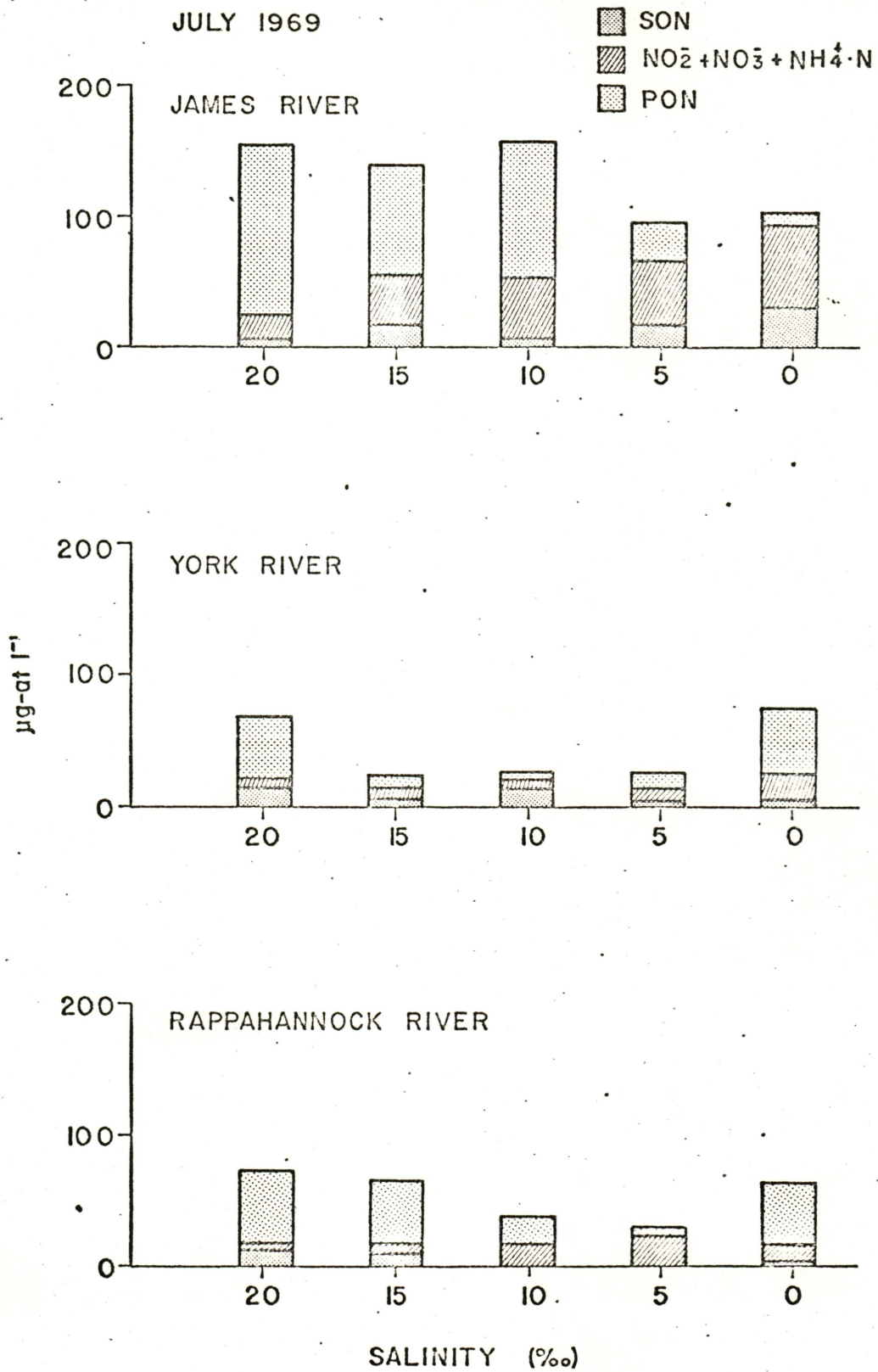


FIGURE 19. Organic and inorganic nitrogen levels at five stations in Virginia's estuaries during July 1969.

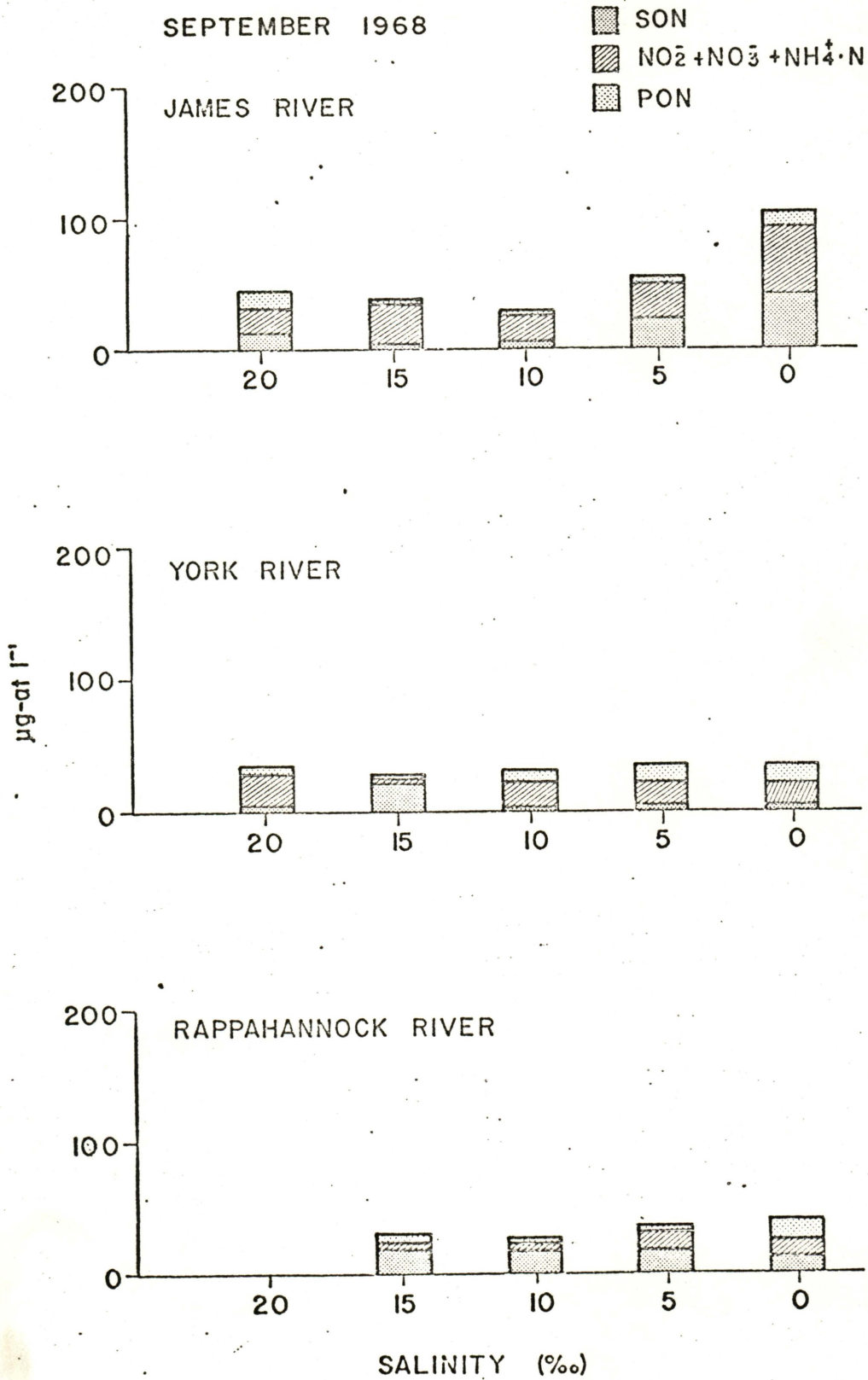


FIGURE 20. Organic and inorganic nitrogen levels at five stations in Virginia's estuaries during September 1968.

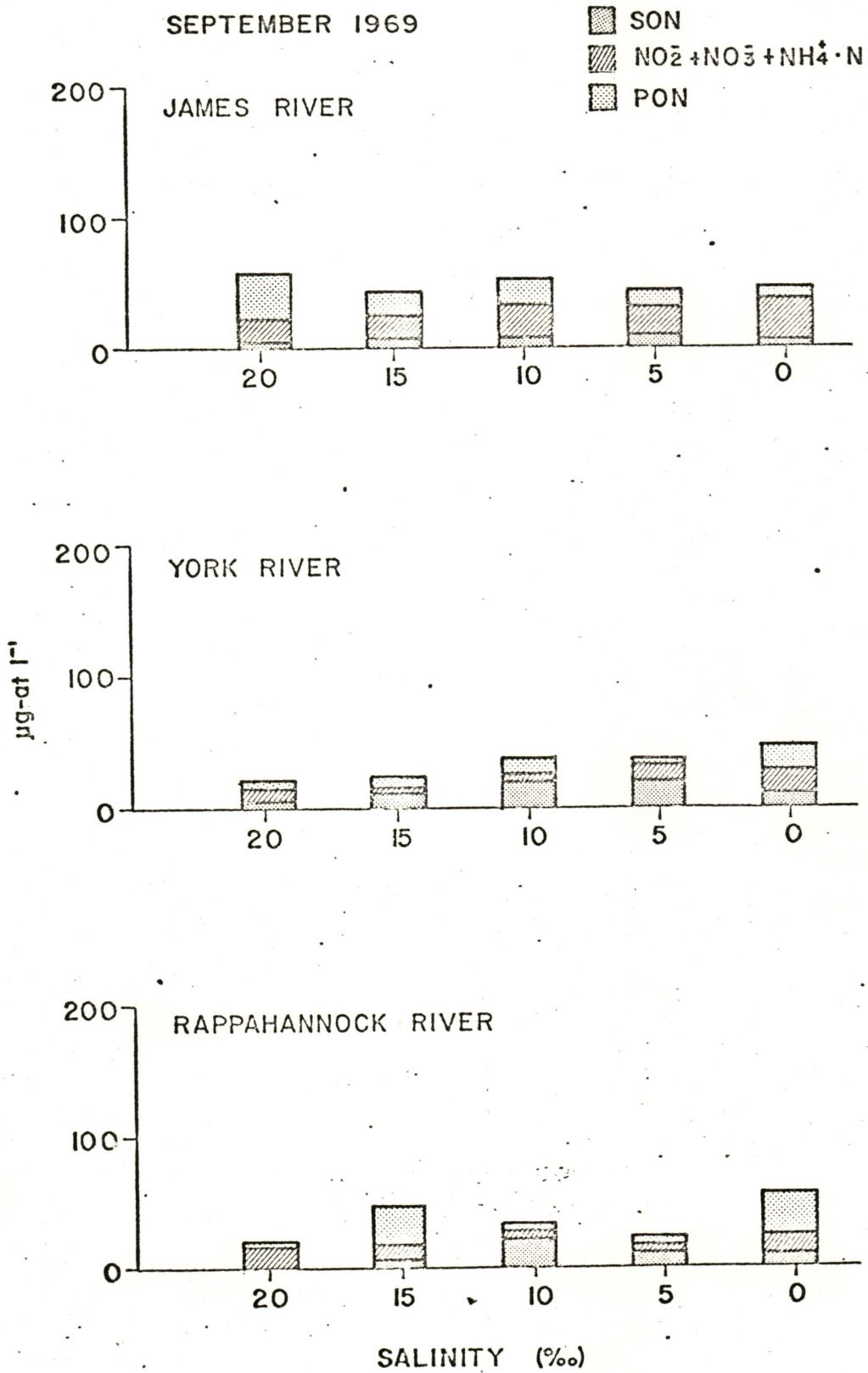


FIGURE 21. Organic and inorganic nitrogen levels at five stations in Virginia's estuaries during September 1969.

at the head of the system in 1968 than in 1969 in the oligohaline reach than at the mouth but the relationship between the forms did not occur at the mouth. Although the freshwater discharges between years as indicated by the location of the 5 o/oo isohalines (Mile 25 and Mile 35) were different, the differences in nitrogen were small.

Nitrogen levels and chemical forms were also similar in the Rappahannock estuary during the two January samplings. A slight downward trend was noted towards the higher salinities and an increase in SON towards the mouth. The 5 o/oo isohaline was located at Mile 32 in 1968 and at Mile 42 in 1969, reflecting the higher freshwater discharges during the former year.

Data from the April 1968 and 1969 cruises show higher total nitrogen levels at the head of the estuaries than at the mouth. The species of nitrogen also reflects the source. The largest quantities were in the oxidized forms in the James and upper Rappahannock reach, whereas in the York the PON dominated in 1968 and at the transition zone in 1969 but showed no definite pattern in the downstream areas. SON was also present in significant quantities in the James and Rappahannock but was a factor only in the mesohaline reach of the York in 1969.

Freshwater discharges as indicated by the location of the 5 o/oo isohalines in the three estuaries were very similar in 1968 and in 1969. Distinct differences were detected within estuaries between years, however, both in total nitrogen levels and in the forms present. Salinities at Mile 5 of each system were approximately 5 o/oo higher in 1969 than in 1968, indicating the influence of the Bay.

The James estuary showed the greatest difference between years of the three systems. The data indicate that relatively high nitrogen levels in the oxidized forms were entering the system at the transition zone during both periods. In 1968, however, the PON levels indicate that the available nitrogen was not incorporated into biological material to be retained as a part of the water mass as the values decreased towards the mouth at a rate only slightly higher than the calculated rate based upon the dilution with nitrogen-poor seawater. In 1969 the values for the oxidized forms decreased towards the mouth and the PON values increased to become the dominant form. The total level also increased, indicating either concentration or an additional source. The latter cannot be accounted for as no new activities were added.

York River nitrogen data from July 1968 and 1969 do not follow an identifiable pattern although the low and high salinity reach PON levels were higher in the second year. The levels in the Rappahannock River were similar for both years although again the PON form was dominant at four of the five stations.

September nitrogen levels in the three systems again indicate differences between years. Values for the James estuary were higher in the oligohaline reach during the low flow year of 1968 than during the higher flow year of 1969. This is similar to the pattern observed during January of the two years. Again, the oxidized forms of nitrogen were dominant in the composition of the levels.

No definite differences were observed between years in either the York or Rappahannock estuaries. Total values were relatively low and the predominant form varied between stations within rivers.

Phosphorus

Phosphorus determinations were made on each water sample collected during the cruises. Samples were split and treated as the soluble reactive phosphorus (SRP), soluble unreactive phosphorus (SUP), particulate reactive phosphorus (PRP), and particulate unreactive phosphorus (PUP). The form of the element present in natural waters not only describes its chemical state and availability to biological organisms but also the quantities that are combined with organic materials within the water column.

Data gathered in 1968 and 1969 indicate a definite relationship between total values and seasons within and between estuaries although the absolute values vary between systems. Levels in the James are generally higher than those found in the York and levels in the York considerably higher than those of the Rappahannock. The high James levels were predictable because of the major sources of domestic sewage effluents discharged into the system in the Hampton Roads area and in the upper tidal reach at Richmond. The York, with no significant artificial sources but with a high marsh and wetlands-basin area ratio, frequently showed a high POP ratio. The Rappahannock River, with artificial enrichment at the fall line and a duck farm at Mile 13 having a population equivalent of approximately 20,000, did not contain the phosphorus levels as observed in the other two systems.

In January of both 1968 and 1969, the total phosphorus (TP) values in the three estuaries were recorded at the transition zone, with PUP being the dominant form (Figures 22-29). SRP levels in the James increased in 1968, the low-salinity year, but did not show this increase

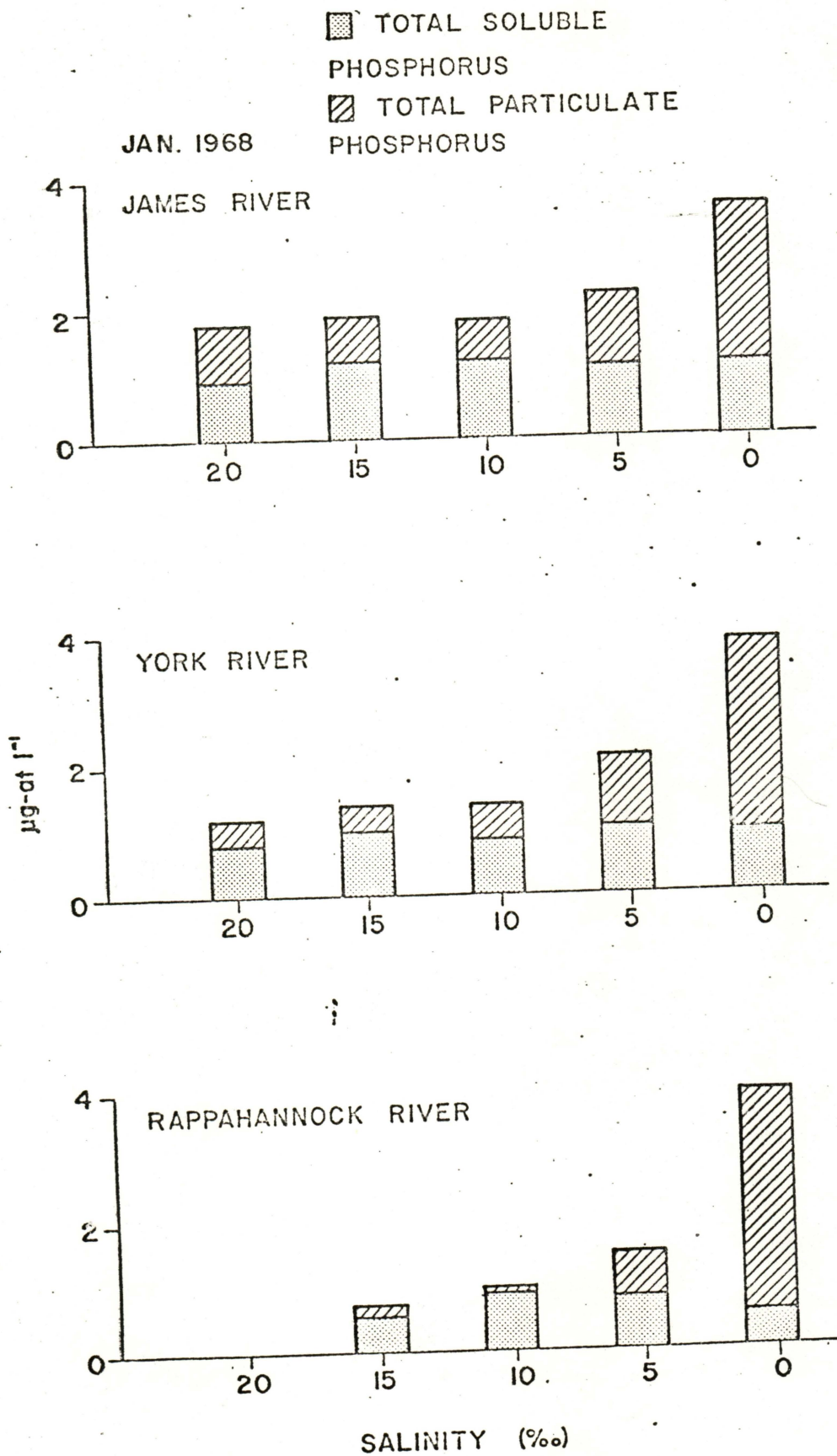


FIGURE 22. Total soluble and particulate phosphorus at five stations in Virginia's estuaries during January 1968.

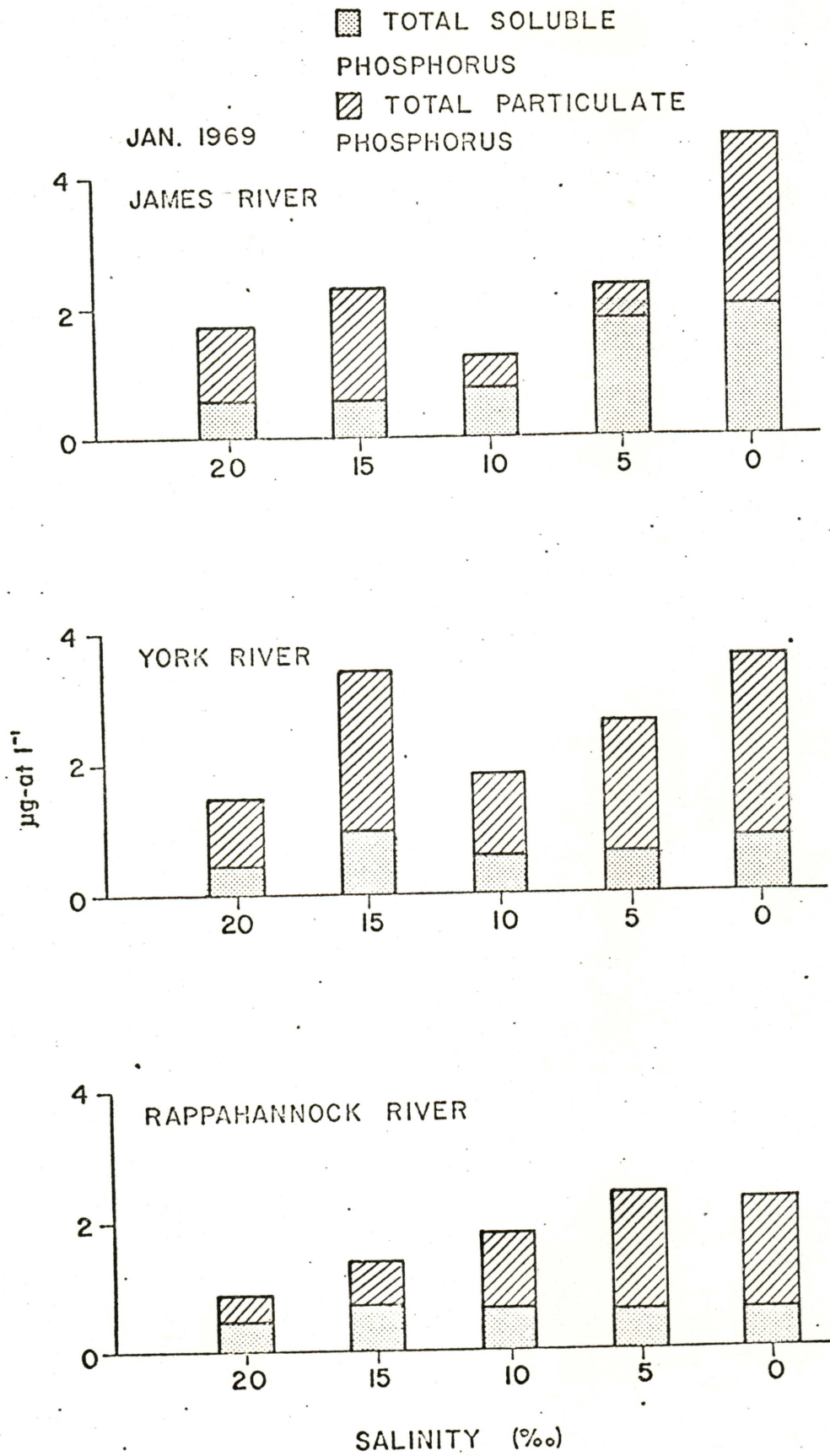


FIGURE 23. Total soluble and particulate phosphorus at five stations in Virginia's estuaries during January 1969.

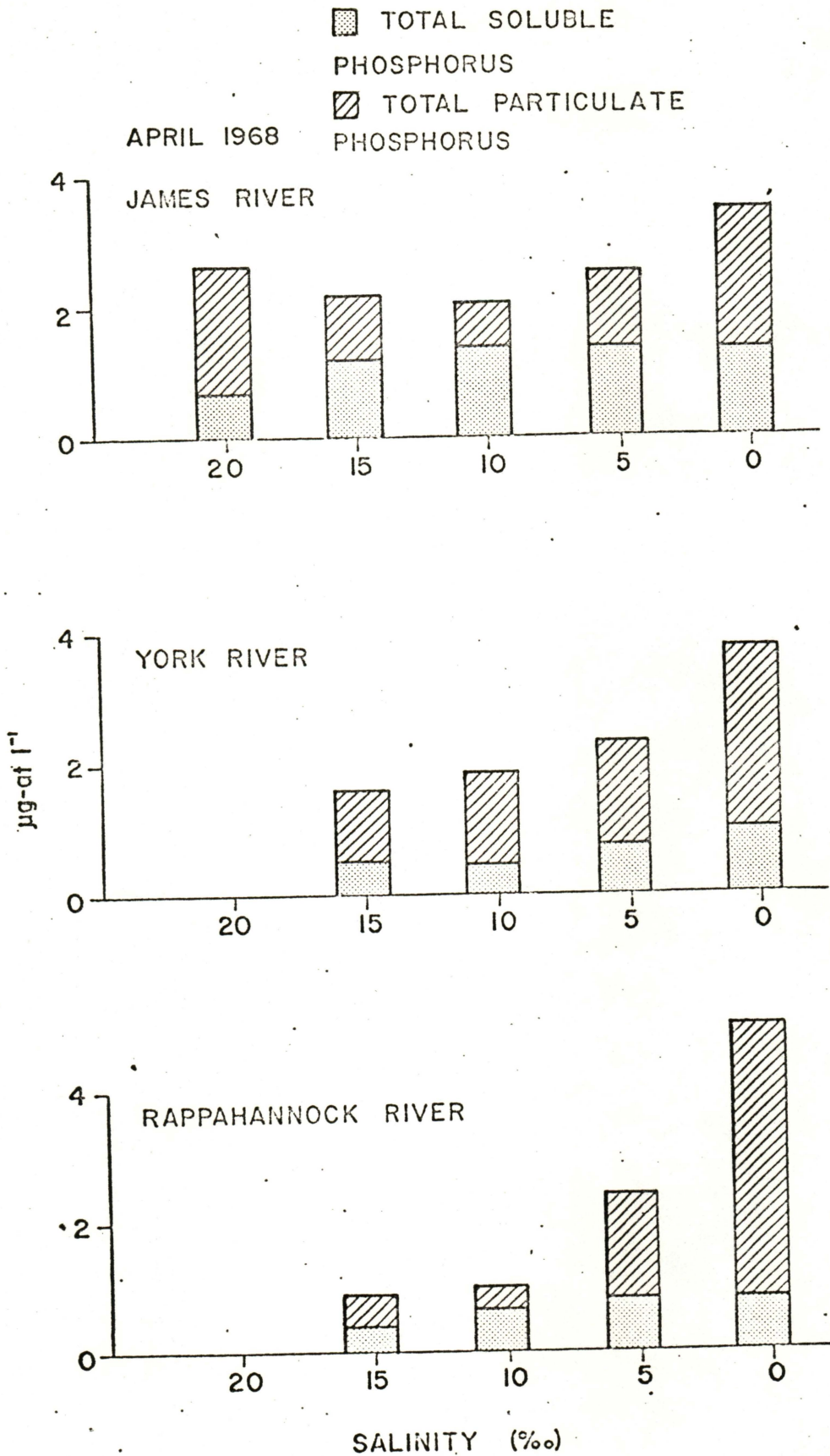


FIGURE 24. Total soluble and particulate phosphorus at five stations in Virginia's estuaries during April 1968.

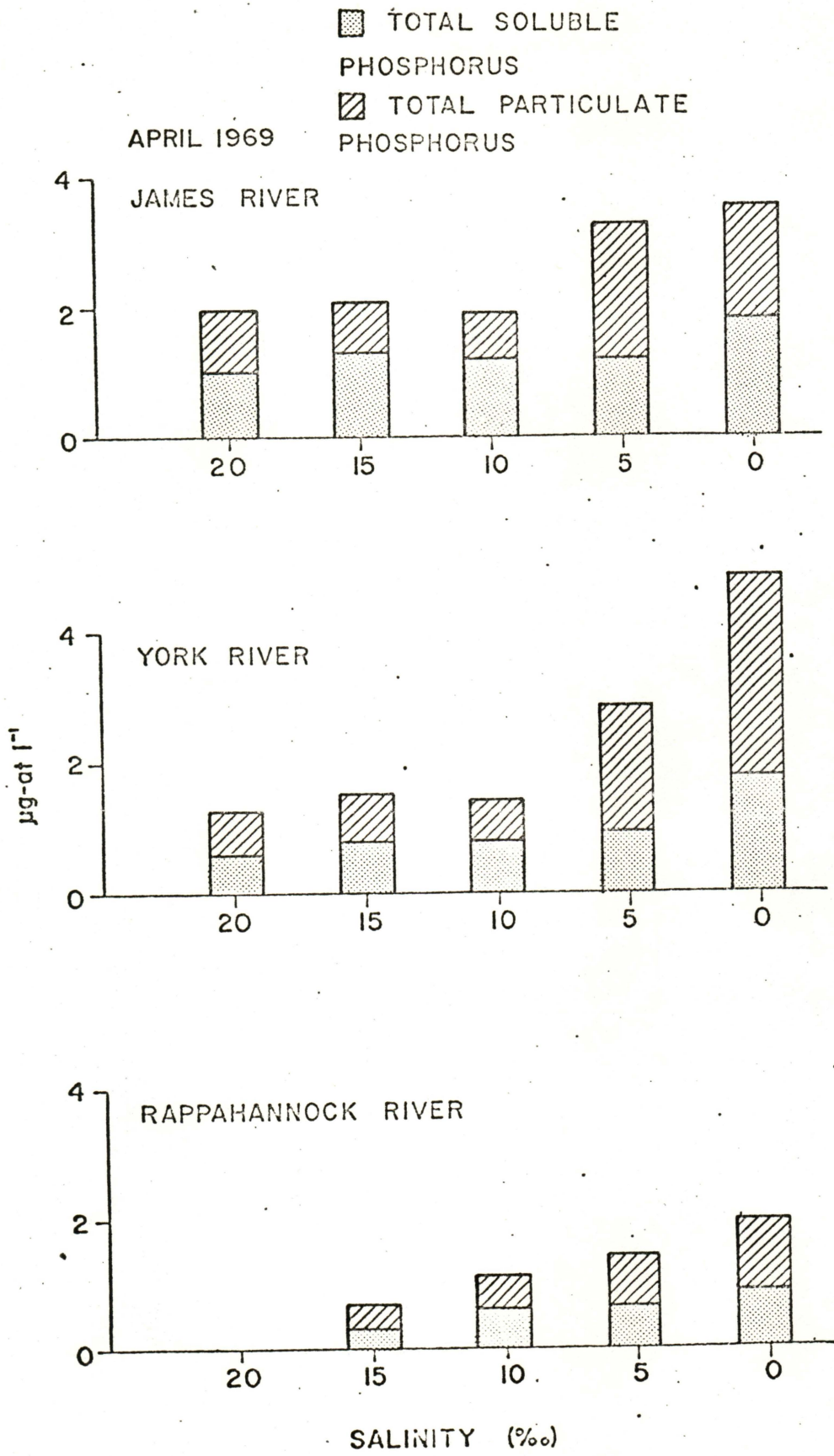


FIGURE 25. Total soluble and particulate phosphorus at five stations in Virginia's estuaries during April 1969.

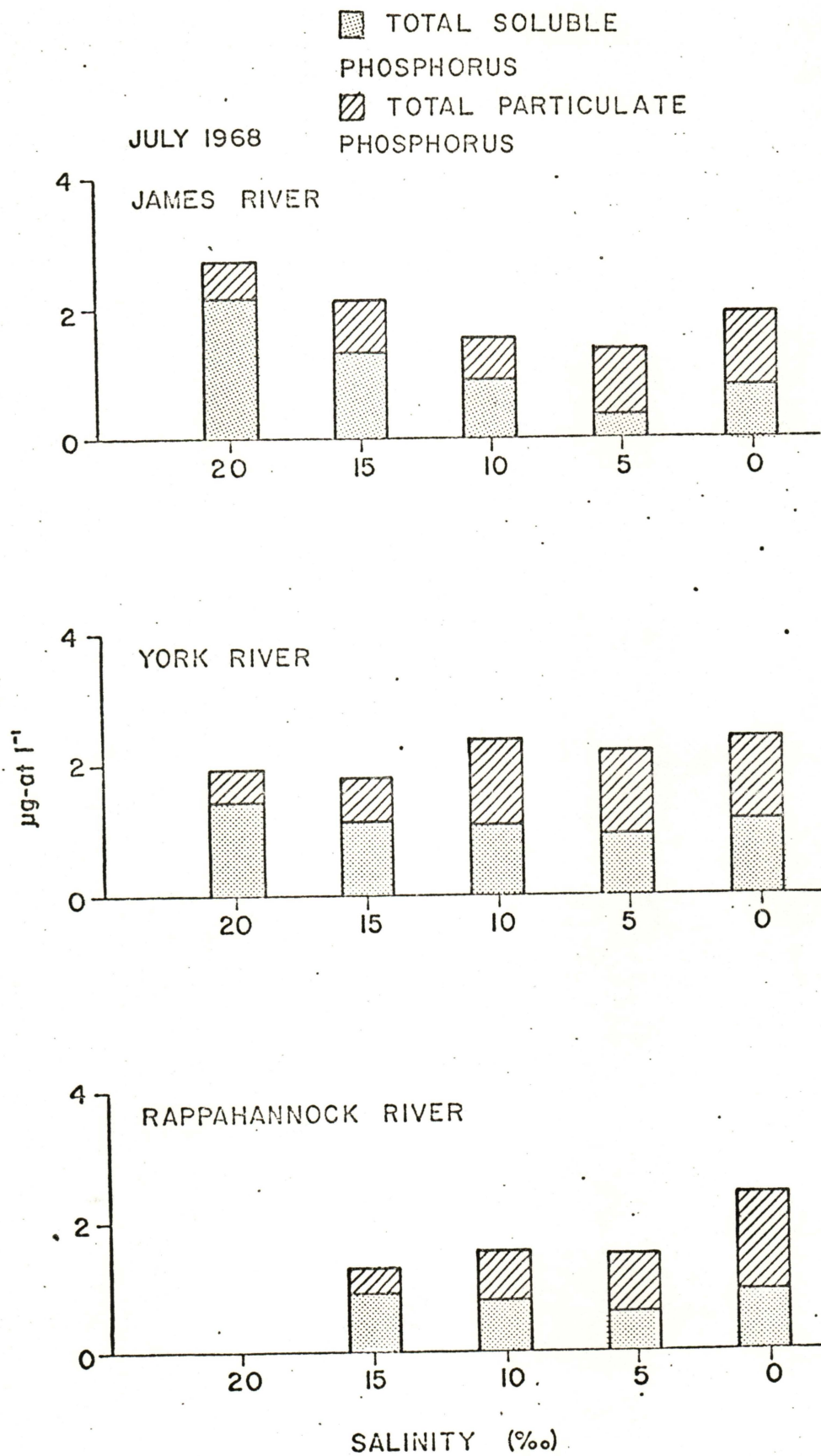


FIGURE 26. Total soluble and particulate phosphorus at five stations in Virginia's estuaries during July 1968.

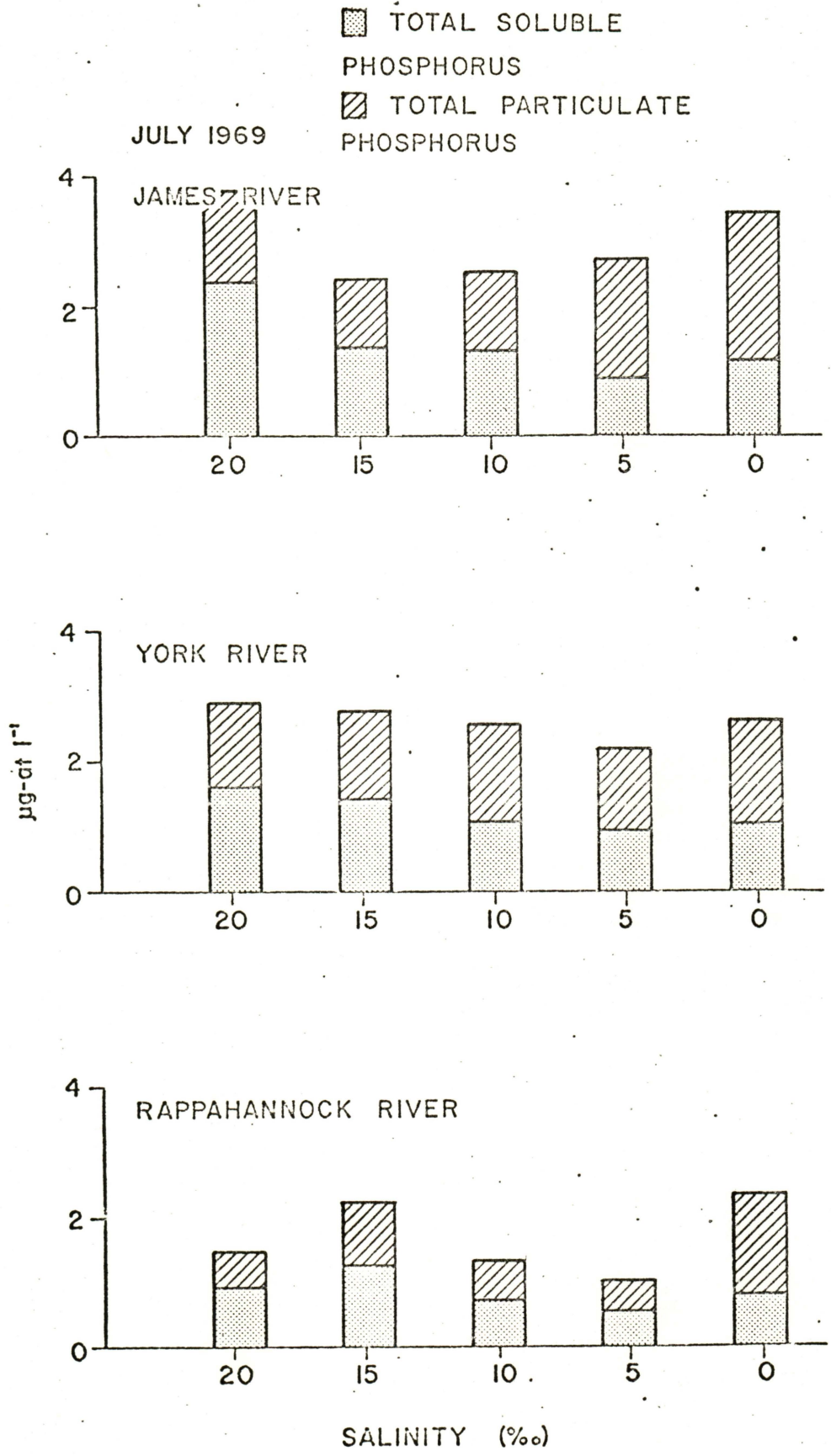


FIGURE 27. Total soluble and particulate phosphorus at five stations in Virginia's estuaries during July 1969.

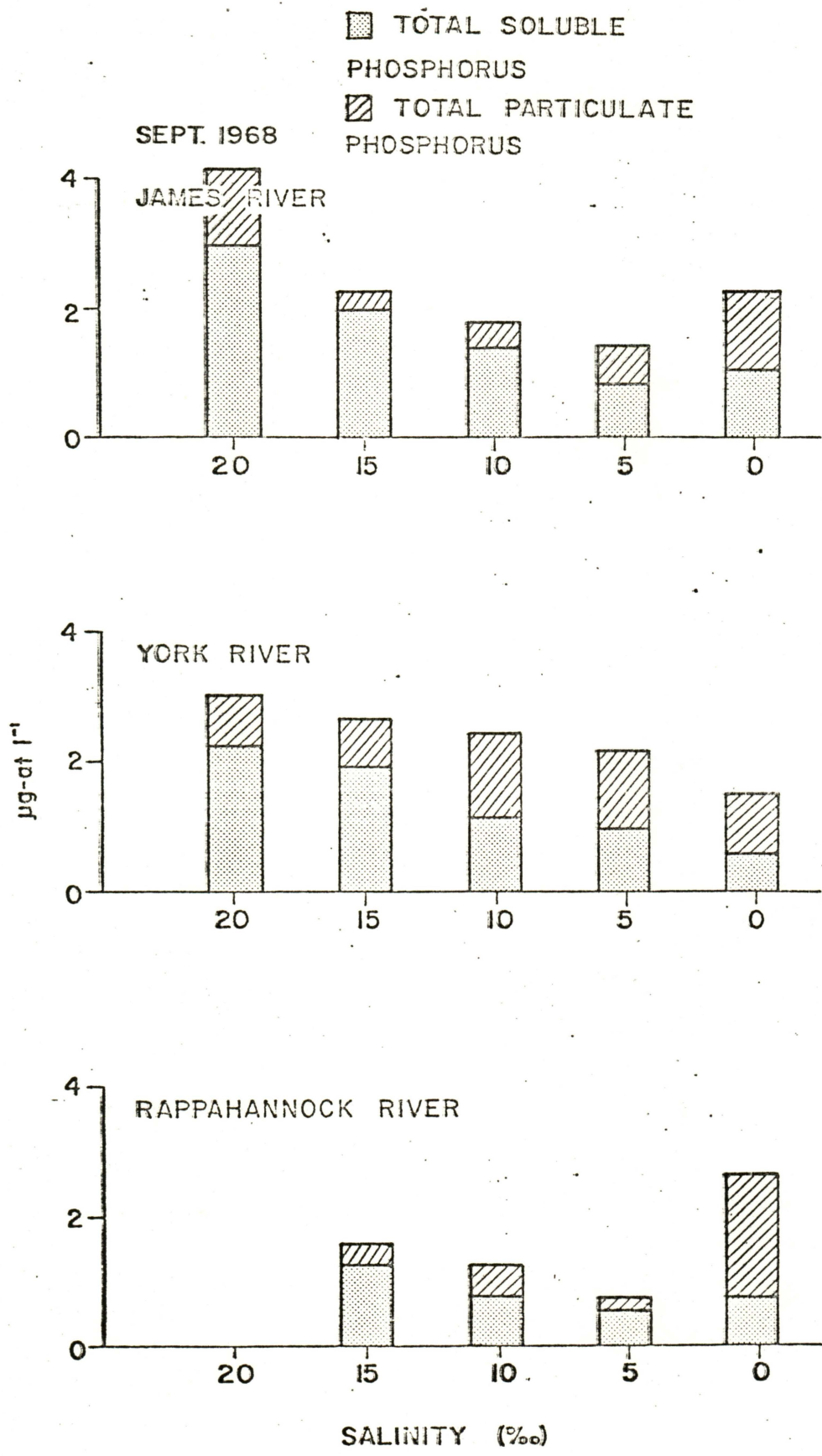


FIGURE 28. Total soluble and particulate phosphorus at five stations in Virginia's estuaries during September 1968.

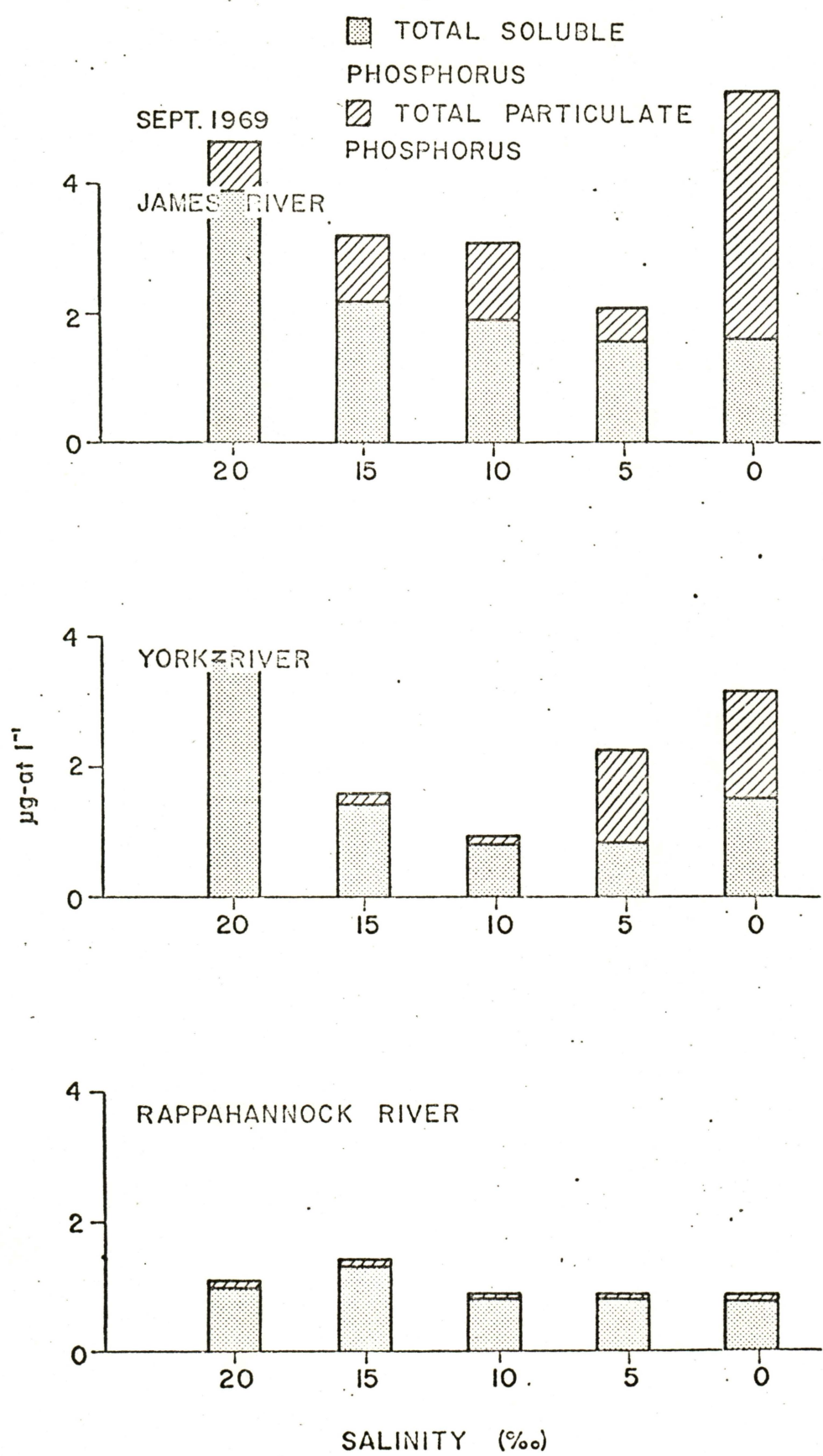


FIGURE 29. Total soluble and particulate phosphorus at five stations in Virginia's estuaries during September 1969.

in 1969, the high-salinity year. A similar pattern was observed in the York River in 1968, with very high PUP values at the head and a sharp decrease towards the mouth. The SRP values did not follow the pattern previously described for the James; however, nearly equal values were recorded from the transition zone to the mouth even though the freshwater discharges and the Bay salinities were quite different. In 1969 the PUP values were much higher at all isohalines than in 1968 but the levels followed the same general reduction in levels towards the mouth.

Rappahannock estuary values also indicate a reduction in TP from the head towards the mouth, again with PUP being the dominant form. The total phosphorus within this system was generally lower than that of the other two estuaries, with the highest values recorded during the relatively dry year of 1969 when the 5 o/oo isohaline was located at Mile 42.

Total phosphorus and the relationship between the four forms show a close correlation in April with the January levels. Again, PUP was the dominant form at the head of the estuaries, with SRP levels higher in the James than in the York or Rappahannock. Freshwater discharges as indicated by the location of the isohalines were nearly equal between years although the water temperatures increased more abruptly in 1968 after the March low than in 1969. The values at the time of sampling were nearly equal between years.

The James estuary data indicated a decrease in total phosphorus levels in the middle reach. Several factors may be responsible for this pattern.

Coastal plain estuaries are characterized by a turbidity maximum which is usually located in the region of the 2-5 o/oo isohalines. This is the area where the energy of the net upstream transport system on the bottom is approximately equal to the energy of the net downstream transport forces of the tidal river and the upper layer. This nullification of the forces results in the concentration of suspended material and high turbidity levels.

Suspended solids affect both SRP and PUP levels. Phosphate phosphorus is adsorbed on the edges of clay lattice structures under alkaline pH conditions. As the suspended materials settle to the bottom, the phosphate phosphorus and unreactive phosphorus in organic material are removed from the water column and the biochemical cycle.

The middle reach of the James estuary is also characterized by broad shoals. During windy weather wave characteristics develop in which they "touch bottom" over the shoal areas. This results in very high "temporary turbidity" levels. As the winds subside and the suspended solids coagulate and settle to the bottom, particles of organic matter are mechanically entrapped and "coprecipitated." This phenomenon affects the PUP values in the water column.

The James estuary, with the largest drainage basin and broadest reaches, is the most turbid of Virginia's systems. The less turbid York and Rappahannock did not show the phosphorus sag in the middle reach except in a few of the months investigated.

July phosphorus levels in the James River show a shift in forms present and differences within stations between years. The SRP which had been relatively uniform throughout the estuary or the highest at

the transition zone was the highest at the mouth and decreased towards the head against the seawater dilution factor with freshwater. This appears to indicate that either the levels in the Bay were high and contributing to the estuary or that the known sources in Hampton Roads were affecting the system. SRP levels in the high-salinity areas of the York and Rappahannock suggested that the source was the Bay. SRP levels from the mouth to the transition zones during August, September, October and November of 1968 confirmed the source as the Bay, especially in the James and York where the values were as much as ten times higher at the mouth than at the transition zone. This was observed in both years even though the fall of 1968 was an extremely low freshwater discharge period and the lower two systems were purged by the runoff resulting from the passage of Hurricane Camille in the latter part of August 1969.

The Rappahannock estuary, which is the least "dynamic" of the three systems, generally reflected the same general phosphorus level patterns as the other two systems but the total values were frequently 25-75% lower.

Sediment-Nutrient Relationships

Investigators often suggest that sediments adsorb the various forms of nitrogen and phosphorus in natural aqueous systems, thus removing them from the water column and storing them for future cycling. These statements are somewhat deceiving in that the ionic charges of the species are of the wrong sign for adsorption on clay minerals. This does not imply that nutrients cannot be adsorbed but rather that true

adsorption, governed by zero point charge, is of less importance than perhaps nutrients incorporated in living or dead plants and animal material.

By actually analyzing the sediment for the various nutrient forms rather than assuming the nutrient concentrations by difference, the function of bottom sediments in the total nutrient budget was assessed. The bottom sediments of each river were sampled and stored by freezing until such time as analysis was possible.

No standard procedures were available for the analytical determinations. However, procedures were developed which provide both accurate and precise data.

Three samples were taken at each 5-mile interval in the estuarine segments of the James, York and Rappahannock rivers. One sample was taken in the channel and one on either side, halfway between the channel and shore. These samples were stored in a freezer until analytical procedures were available. The thawed and dried samples were ground until particle sizes were below 65 microns. These homogeneous sediments were then analyzed for ammonia plus organic nitrogen, nitrate plus nitrite, and total phosphorus. A part of each sample was also ignited at 600°C and loss on ignition (LOI) was calculated.

The results are plotted in Figures 30-35. The mean of all three stations at a given mileage plus the extremes are given.

The most obvious correlation between the sediment data and the data from the water column is that the former is a factor of 10^3 higher when units of $\mu\text{g}(\text{g})^{-1}$ are used for both water and sediment.

Sediment Nitrogen

Most of the nitrogen incorporated in the sediment of the estuaries was in the form of ammonium ion plus organic nitrogen ($\text{NH}_4^+ + \text{ON}$). The James River showed a linear increase from the mouth to Mile 35 (Figure 30). The York River showed an erratic pattern, with the mouth of the estuary being three times as high as the similar stations on the James or Rappahannock (Figure 31). The Rappahannock River showed high levels between Miles 15 and 20, after which the concentration dropped and rose again towards Mile 45 (Figure 32). This peak in the lower part of the Rappahannock may be attributed to a duck farm which is located at Mile 13 and has the waste equivalent of a city of approximately 20,000 persons. Without this increase, Figures 30 and 32 would be similar in shape.

Sediment Phosphorus

Total phosphorus was determined on each sample. The data showed the James River sediment to increase in concentration from mouth to fresh-water. This trend also held for nitrogen but the slope was much higher for the latter (Figure 33). The York River sediment-phosphorus pattern was erratic, as it had been for nitrogen. Again, the highest average was at Mile 5. This concentration is higher than either the James or Rappahannock (Figure 34). The Rappahannock River data showed the sediment to be fairly constant with respect to phosphorus (Figure 35). The large increase in the nitrogen concentration at Miles 15 and 20 can again be seen in the phosphorus data, however not nearly as pronounced.

Loss on Ignition

The results of the loss on ignition analyses are given in Table 7. This analysis is an indication of the organic content of the sediment

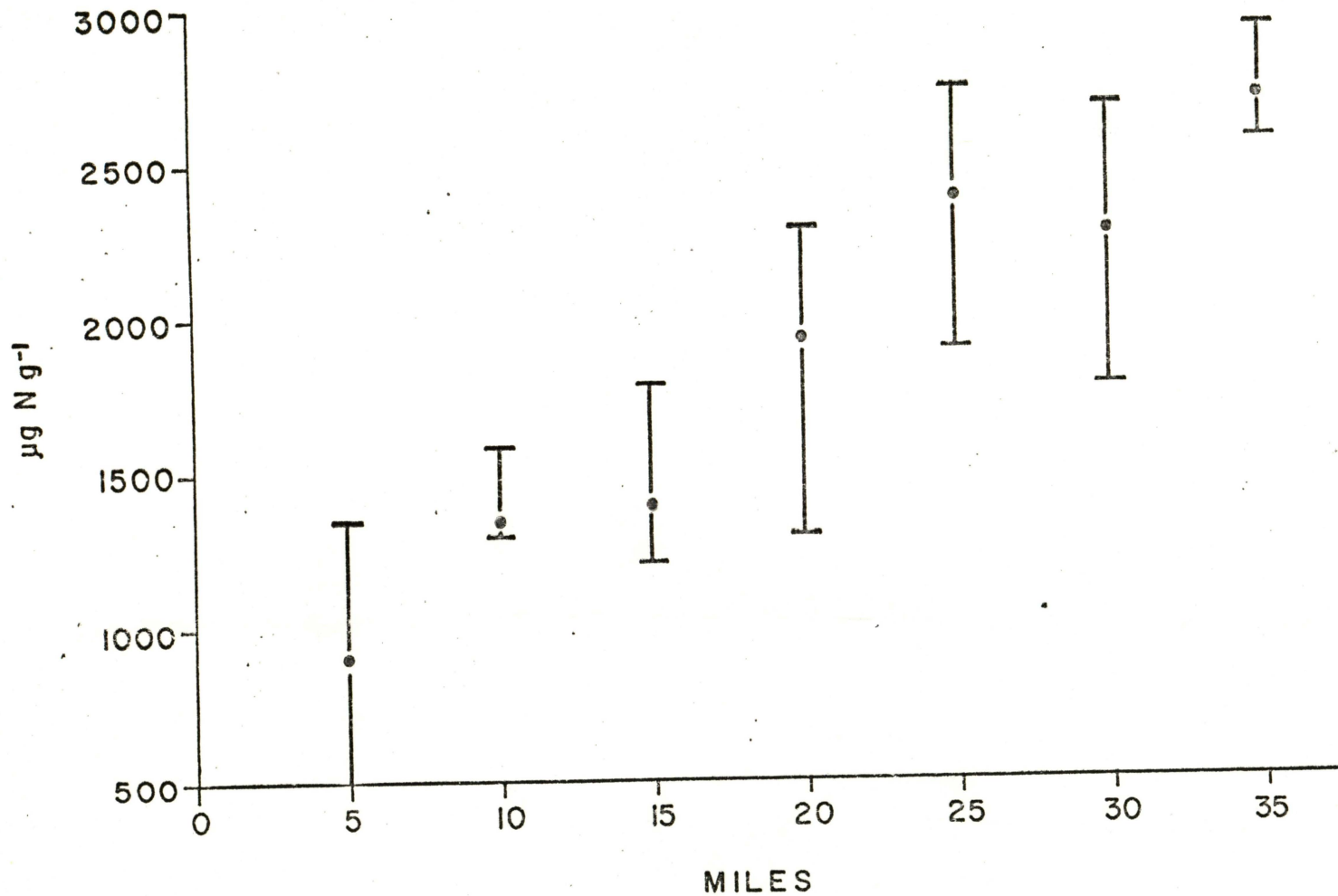


FIGURE 30. Total nitrogen in top 1 cm of sediments from seven stations in the James estuary.

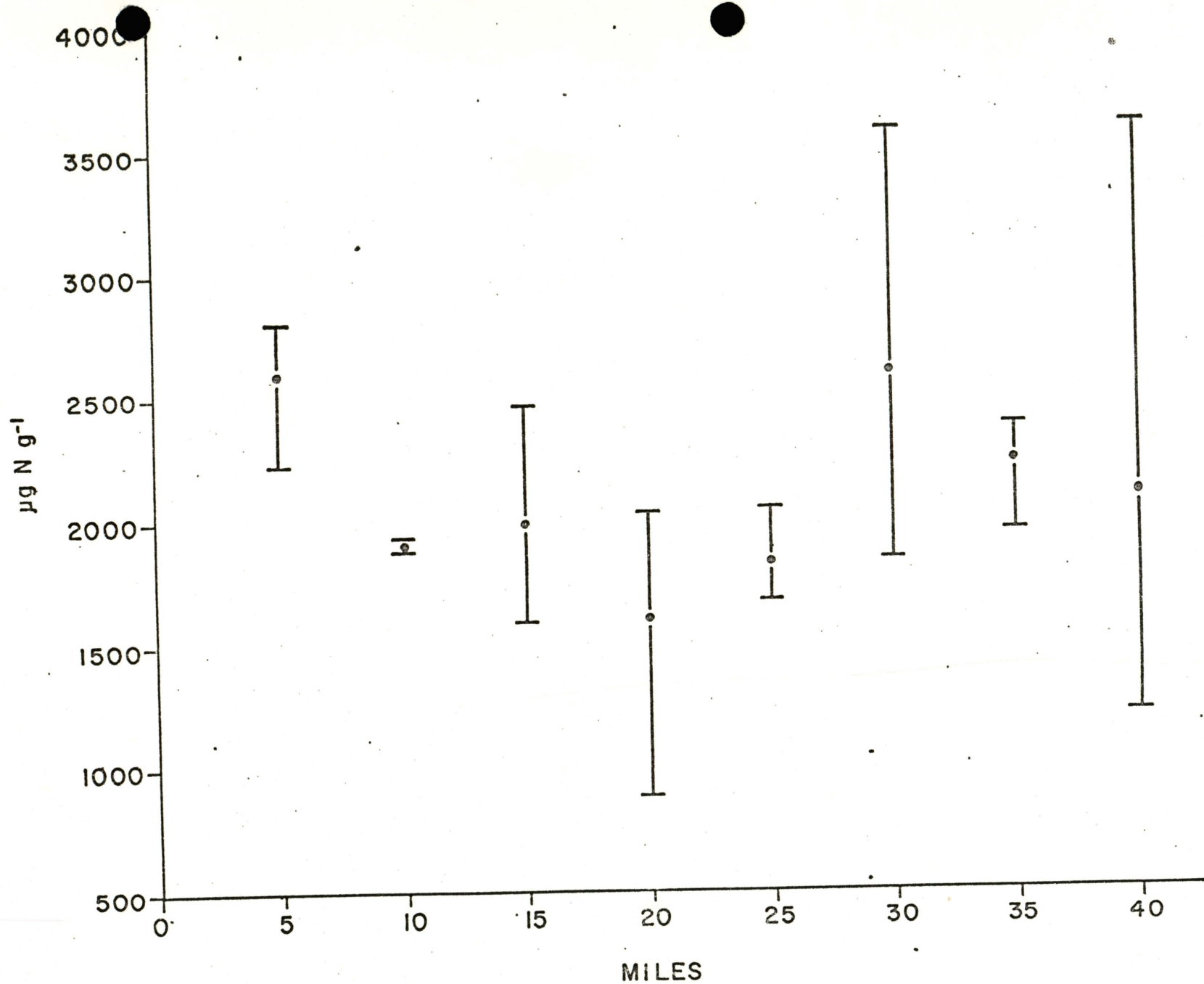


FIGURE 31. Total nitrogen in top 1 cm of sediments from eight stations in the York estuary.

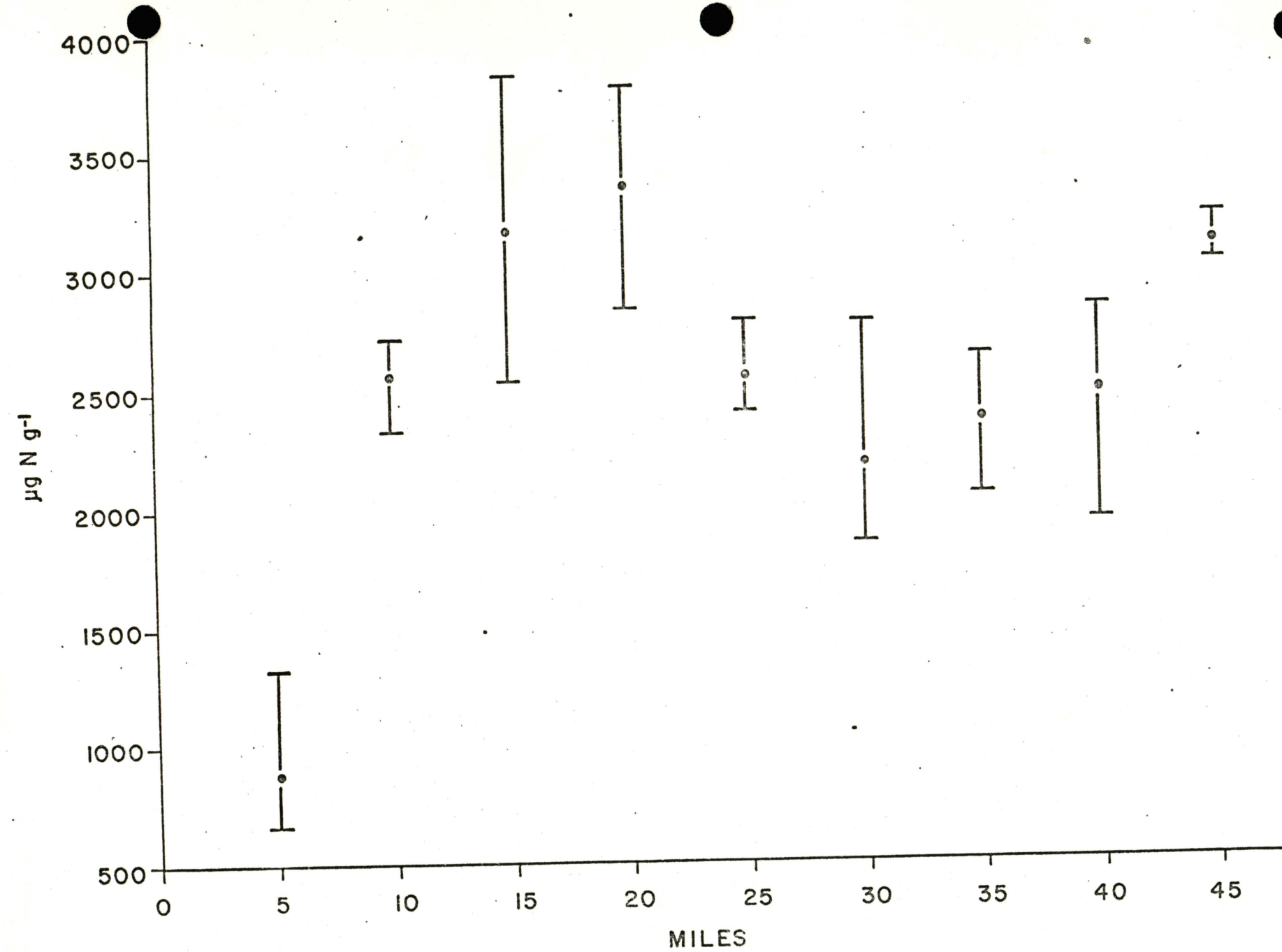


FIGURE 32. Total nitrogen in top 1 cm of sediments from nine stations in the Rappahannock estuary.

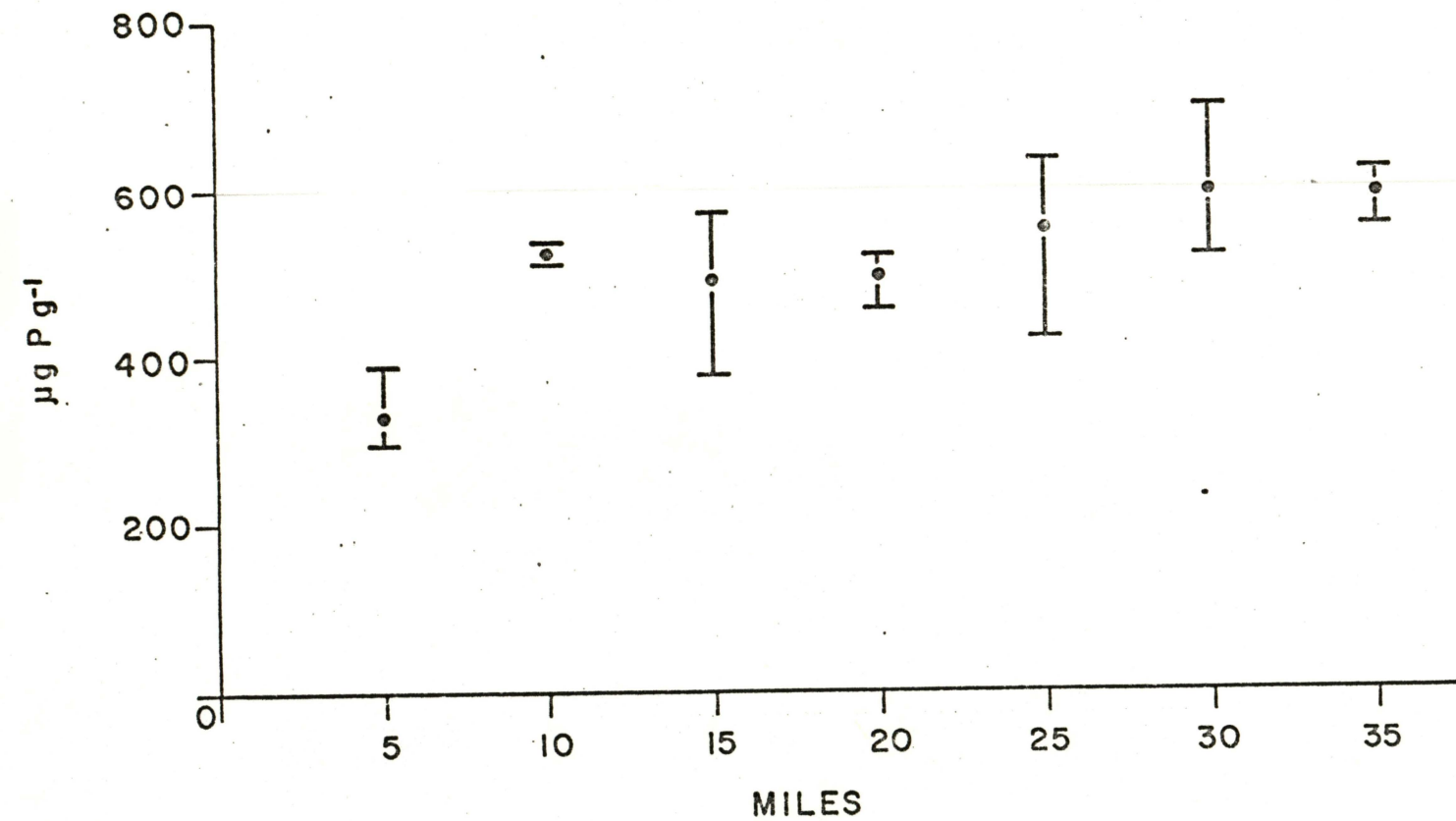


FIGURE 33. Total phosphorus in top 1 cm of sediments from seven stations in the James estuary.

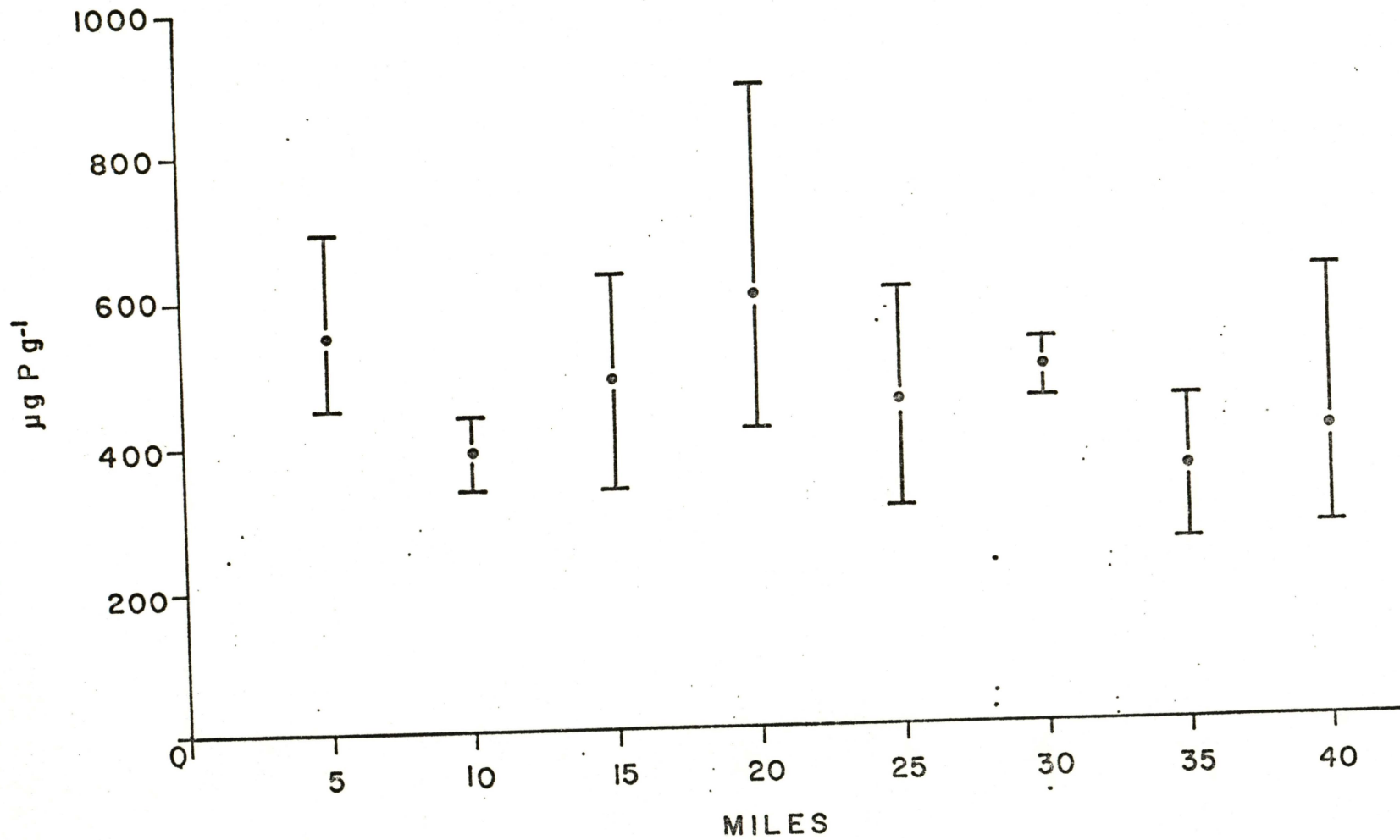


FIGURE 34. Total phosphorus in top 1 cm of sediments from eight stations in the York estuary.

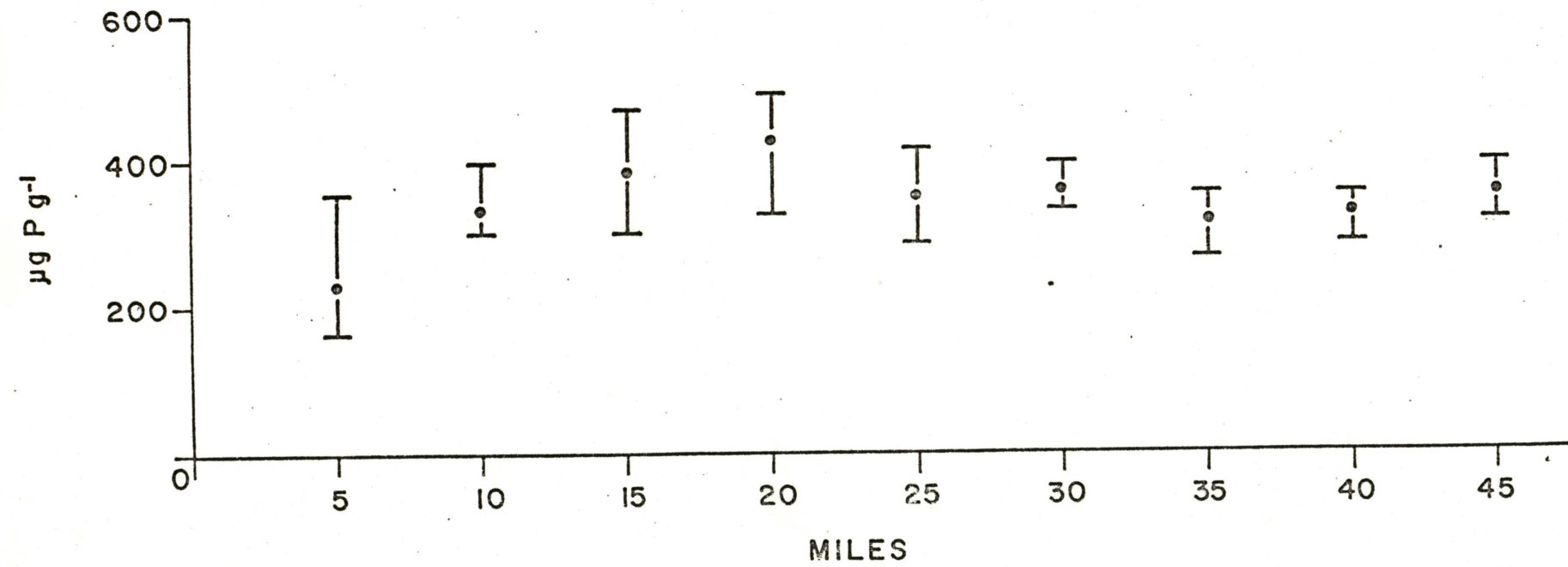


FIGURE 35. Total phosphorus in top 1 cm of sediments from nine stations in the Rappahannock estuary.

TABLE 7. Bottom sediment sampling stations and organic composition of top 1 cm layer as indicated by percent loss on ignition (LOI).

<u>Estuary</u>	<u>Miles</u>	<u>Station</u>	<u>LOI</u>
James	5	Channel	7.7
	10	Channel	5.9
	15	Channel	6.3
	20	Channel	9.8
	25	Channel	11.1
	30	Channel	12.2
	35	Channel	11.0
York	5	Channel	10.9
	10	Channel	8.4
	15	Channel	9.2
	20	Channel	9.5
	25	Channel	7.8
	30	Channel	9.8
	35	Channel	9.0
Rappahannock	5	Channel	2.6
	10	Channel	9.2
	15	Channel	12.1
	20	Channel	10.8
	25	Channel	12.0
	30	Channel	10.4
	35	Channel	11.7
	40	Channel	7.6
	45	Channel	13.3

and the two are assumed to be proportional. The data indicate that approximately 10% of the bottom sediment in all three estuaries is organic material. It is also noted that the LOI and nitrogen data are related. This relationship seems to be one of direct proportion. The percent LOI vs. the total nitrogen are plotted in Figure 36. The straight line indicates the proportion and suggests that very little, if any, of the nitrogen is adsorbed to the inorganic fraction of the sediment.

Assuming that the nitrogen in bottom sediments is in the organic fraction, then a percent nitrogen in the combustible material can be calculated. Such a calculation was performed and the result was near 2%.

The phosphorus data showed no correlation with LOI and it is concluded that most phosphorus in sediments is either adsorbed to the sediment grains or in the form of a chemical precipitate, such as the common marine mineral Apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$). The latter hypothesis seems more valid in view of the zero point charge.

In summation, the relatively high concentration of nitrogen and phosphorus in the sediments may act as a sump for recycling. These nutrients, however, are more closely related to the combustible fraction of the sediments than to the inorganic segment.

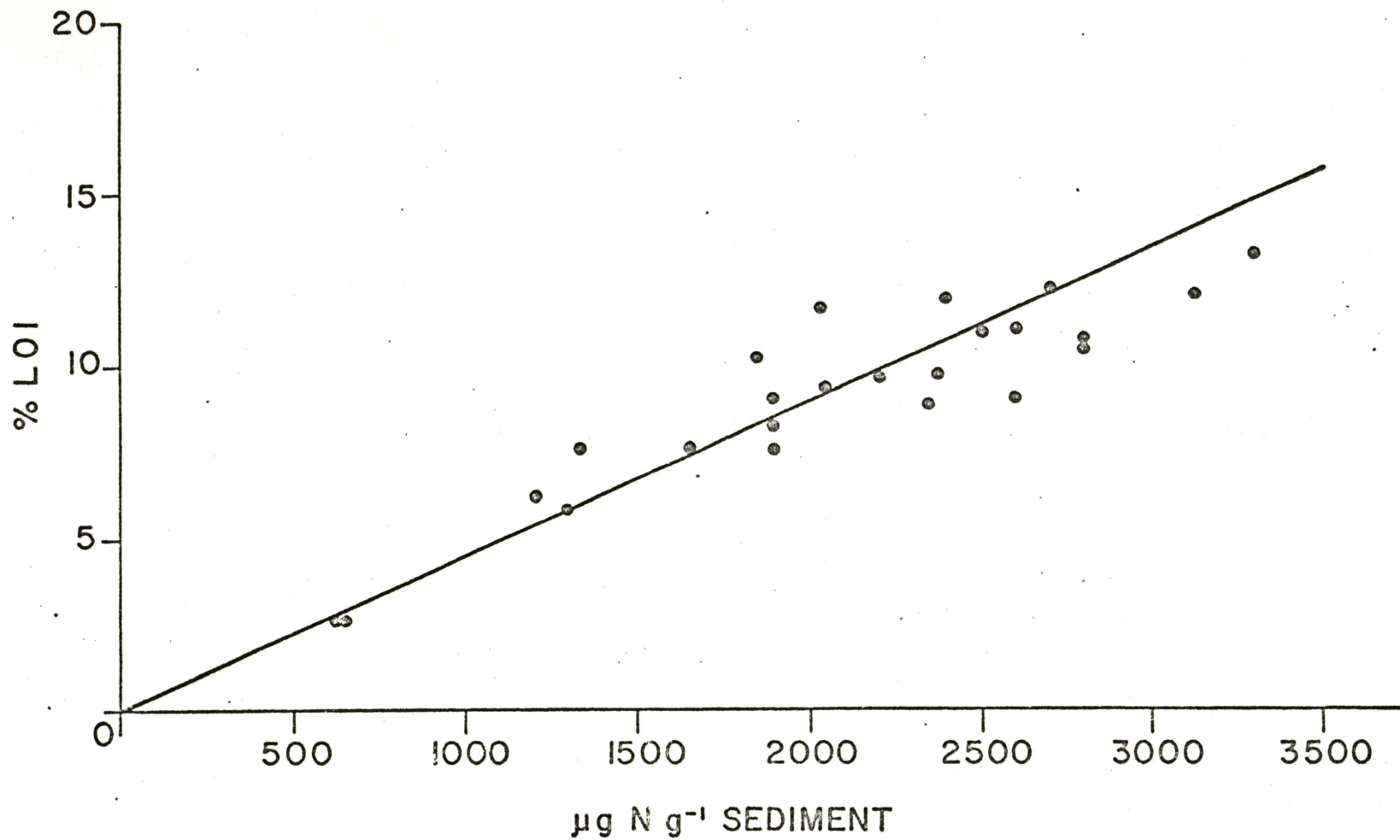


FIGURE 36. Relationship between total nitrogen levels and organic material in the three Virginia estuaries.

BIOLOGY

Phytoplankton

The standing crop of phytoplankton as determined by chlorophyll "a" concentrations in the water was measured at each 5 o/oo break in the longitudinal salinity structure. Plankton samples were also collected for qualitative and quantitative determinations of the five most abundant genera in the population.

Phytoplankton levels in the upstream tidal freshwater reach of the James River frequently are sufficiently high to reduce the aesthetic value and modify the dissolved oxygen content of the water. Undesirable aesthetic conditions and fish kills are reported each summer. The dominant organism in the blooms is usually the freshwater blue-green alga, Anacystis cyanea. This form cannot tolerate high dissolved solids levels and is eliminated at the transition zone between fresh and salt water. Data from special cruises through the tidal river indicate that only summer genera such as Anacystis are available within the the system and during low flow periods in late fall and early winter the "excess" nutrients introduced at Richmond and Hopewell are not utilized in the freshwater reach by phytoplankton forms.

The data indicate that distinct differences in phytoplankton levels exist within estuaries between seasons and stations and between estuaries (Figures 37 and 38).

The James estuary which is the most highly enriched but also the most turbid was usually characterized by lower phytoplankton levels in the water column than found in the other two systems. Chlorophyll "a" levels were usually below 10 ug l^{-1} , a value considered within the the normal range for coastal plain estuaries.

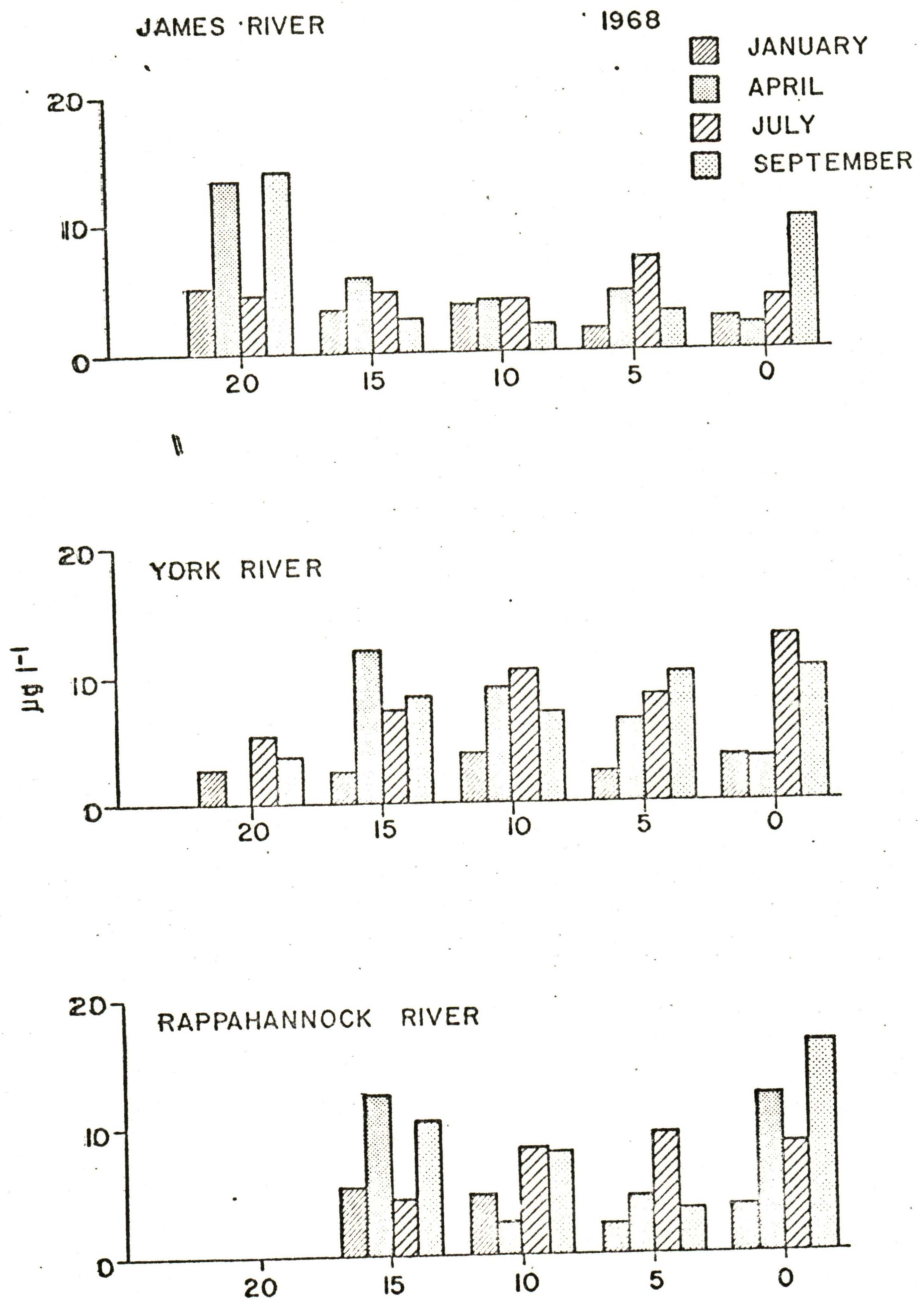


FIGURE 37. Phytoplankton standing crop as indicated by chlorophyll "a" concentrations in Virginia's estuaries for four months during 1968.

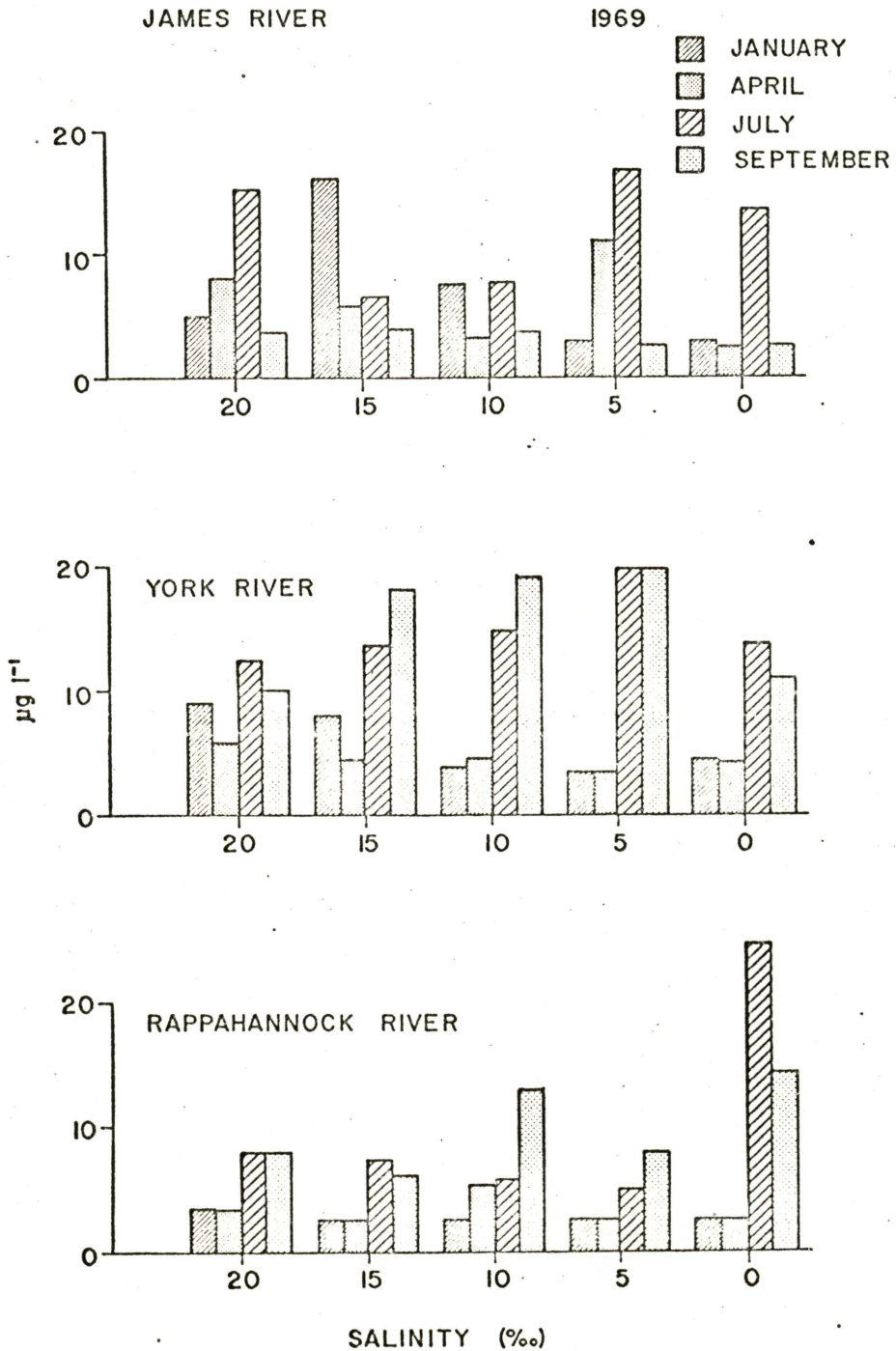


FIGURE 37. Phytoplankton standing crop as indicated by chlorophyll "a" concentrations in Virginia's estuaries for four months during 1969.

If phosphorus was the limiting factor governing the standing crop, the population level as indicated by chlorophyll "a" would be highest at the low salinity isohalines during January and April and the highest near the mouth during July and September. The data, however, do not indicate that this relationship exists. Also, a relationship between phytoplankton levels and the oxidized forms of nitrogen in the water column cannot be established.

Freshwater discharge as indicated by the location of the isohalines was nearly the same in July of both study years; however, the standing crop of phytoplankton was much higher in 1969 than it was in 1968. In September the system was less fresh in 1968 than in 1969 but the standing crop was nearly equal or lower in the latter year.

The York estuary is a completely different system from the James. Upstream from Mile 30 the two tributaries are narrow and bordered by extensive marsh areas. The contributions of these marshes and the influence of the basin characteristics are obvious in the data as the chlorophyll "a" levels were usually nearly equal between stations and within years in the lower salinity reach. Greater variations were noted in the lower river.

Phytoplankton levels as indicated by chlorophyll "a" were significantly higher during the "wet" years of 1969 than during the low discharge year of 1968. Rainfall over a marsh area would tend to wash sessile forms into the drainage system and also increase the flushing rates of the small streams within the marshes. Values for September, after the passage of Hurricane Camille, indicate complete recovery after the flushing that occurred during the period.

Chlorophyll "a" values in the Rappahannock estuary were usually less than those of the York but as high or higher than the James River levels. This system also showed a higher level of stability within stations between months than the other systems.

The dominant genera of phytoplankton present in the population was evaluated semi-quantitatively at each sampling station on each cruise. Samples were taken from the 1-meter depth, preserved with modified Lugol's solution and returned to the laboratory. Sediment containing the plankton was mounted on microscopic slides and identified using oil emersion. Relative abundance was based upon the average number of organisms (individual cells or colonies) per field. Genera with counts averaging less than 1 were not recorded. Organisms averaging more than 20 per field were classified as abundant, 10-19 common, 3-9 occasional, and 1-2 rare.

Chlorophyll "a" levels exceeding 10 ug l^{-1} were usually associated with an abundant or common classification of a single genera. In April 1968, for example, Cerataulina was abundant in the James, whereas in December of that year Peridinium was common. In the Rappahannock River during the same months Skeletonema was common, while in September Gymnodinium was abundant and Amphidinium was common. The latter forms are small flagellates having very low quantities of chlorophyll "a" per cell. Cerataulina was abundant in the York in April of that year. Dominant genera at the transition zone stations were usually filamentous Chlorophyta or Cyanophyta which had been transported into the reach from the freshwater tidal stream.

Dominance of a genera at one station within an estuary seldom indicated that this form would be dominant at the other stations or in

the other estuaries. The greatest degree of uniformity was found during the winter and early spring months when the diatoms Skeletonema and Nitzschia were frequently present at most stations. Thalassiosira was observed most frequently throughout the study period at a higher range of salinities and the flagellate forms were common during the summer months.

SUMMARY

Virginia's estuaries are dynamic systems characterized by high levels of instability. The reaches near Chesapeake Bay are the most stable since they are least affected by variations in freshwater inflow from the tidal river. The middle reach encompasses the gradient zone in which the water may be completely fresh during extremely high discharge periods and approach 17 o/oo or 50% seawater during drought conditions. The location of the transition zone between fresh and salt water also shifts with discharge levels and may vary as much as 20 miles upstream and downstream from the "average" point within a season.

The salinity structure in the James estuary is relatively compressed longitudinally, whereas the structure in the Rappahannock is extended. During low flow summer months the 15 o/oo isohaline may be as much as 20 miles upstream from the 20 o/oo isohaline in the latter system. Differences were also noted in the vertical structure of these systems both within and between seasons and years. This appeared to be influenced by Bay salinities, temperature, and freshwater discharge volume levels.

Dissolved oxygen levels in Virginia's three major estuarine systems did not approach sub-minimal values during the study period. An oxygen sag zone was noted in the vicinity of Mile 30 in the York River, a source of kraft process pulp and paper mill effluent. Low values were also recorded in the James River for one month where the location of the transition zone moved upstream into the oxygen sag zone produced by the industrial complex at Hopewell.

Virginia's estuarine waters are slightly alkaline with no significant differences in pH either within or between systems. The alkalinity values, however, differ both within and between estuaries with all three systems increasing in buffering capacity from the transition zone to the mouth, a relationship directly proportional to salinity. The James estuary had the highest buffering capacity, the York was intermediate, and the Rappahannock was the lowest.

Nitrogen and phosphorus nutrient levels and chemical states of the nutrients varied widely within systems within months and years and between systems. Total nitrogen levels generally reflected the upstream loadings with the James estuary usually showing the heaviest enrichment. A relationship between freshwater discharge levels and total nitrogen could be established for the James estuary; however, this relationship did not hold for the relatively unenriched York or the moderately enriched Rappahannock. Also, in the James estuary the relatively high levels of the oxidized forms of nitrogen in the oligohaline reach were indicative of the source. During 1968 the particulate organic nitrogen levels did not indicate that the available nitrogen was being utilized

by aquatic plants within the estuary, whereas in 1969 the organic levels increased as the inorganic levels decreased. Nitrogen levels and forms in the York and Rappahannock estuaries varied within stations between years and no definite correlations could be established. Nitrogen levels in the range capable of contributing to the development of algal populations sufficient to produce aquatic nuisance conditions and environmental degradation were not recorded in Virginia's estuaries during the study period.

Total phosphorus values in the James estuary were generally higher than those observed in the York and Rappahannock. Reactive phosphorus levels in the James and York showed a definite shift with seasons. Values were usually highest in the oligohaline areas during the winter and spring and in the lower reaches during the summer and fall. The ratio of particulate unreactive phosphorus to the other forms was usually higher in the York and Rappahannock than in the James.

All systems, but especially the James, consistently contained the lowest phosphorus levels in the middle reach. This may be the result of the action of temporary turbidity produced by wind action, settling after winds subside, and "coprecipitating" organic material containing high phosphorus levels.

Estuarine sediments contain on the order of 10^3 higher nutrient levels than the overlying water column. James estuarine sediments contained the highest nitrogen concentrations in the upper reach and the concentration decreased towards the mouth; no pattern could be established for the York; the Rappahannock was similar to the James except for an increase near a possible source at Mile 13.

The sediment phosphorus levels were similar to those described for sediment nitrogen except that the Rappahannock values were more uniform from mouth to transition zone.

Calculations based upon the organic matter content as indicated by the loss on ignition and nutrient levels indicate a direct relationship between organic matter content and nitrogen concentrations at all stations in the three systems. This correlation did not exist for phosphorus.

Phytoplankton levels as indicated by chlorophyll "a" concentrations in the middle and lower reaches of the three estuaries were usually below 10 ug l^{-1} . Levels in excess of 50 ug l^{-1} are considered to indicate overenrichment. Values exceeding 100 ug l^{-1} have been measured in the degraded freshwater tidal section of the James River. Concentrations of chlorophyll "a" were usually higher in the York estuary than in the highly turbid James and the Rappahannock although the latter system indicated a higher level of stability than the other two.

No relationship could be established between concentrations of the oxidized forms of nitrogen and phosphorus and the standing crop of phytoplankton. Chlorophyll "a" values were higher in the York estuary during the "wet" year of 1969 than in the "dry" year of 1968 but this difference was not significant in the other two estuaries. With the exception of the summer of 1969 in the York, the levels varied greatly between stations within estuaries and within stations between estuaries.

The generic composition of the phytoplankton also showed high levels of variability. Filamentous Chlorophyta and Cyanophyta genera

were usually dominant at the transition zone but were replaced by salt water forms in the estuary. Thalassiosira, Skeletonema, Nitzschia and Cryptomonas were recorded most frequently from the estuarine stations.