United States Environmental Protection Agency
Environmental Research Laboratory
Gulf Breeze FL 32561
Middle Atlantic Region 3
6th and Walnut Sts
Philadelphia PA 19106
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Nutrient Work Paper #1

A NUTRIENT BALANCE OF THE CHESAPEAKE BAY: WITH APPLICATIONS TO MONITORING OF NUTRIENTS

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A NUTRIENT BALANCE OF THE CHESAPEAKE BAY: WITH APPLICATIONS TO MONITORING OF NUTRIENTS

by

Gerard F. Laniak

University of North Carolina
School of Public Health
Department of Environmental Sciences and Engineering

U.S. ENVIRONMENTAL PROTECTION AGENCY
CHESAPEAKE BAY PROGRAM
MIDDLE ATLANTIC REGION 3
6TH AND WALNUT STREETS
PHILADELPHIA, PA 19106

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INTRODUCTION

The study of nutrients in the Chesapeake Bay is of growing concern. Algal blooms, resulting primarily from increased nitrogen and phosphorus loadings, are appearing with greater frequency and abundance in the Upper Bay. These blooms can cause many undesirable effects such as producing anoxic conditions in the bottom wastes after decay and settling take place. There are many necessary analyses to be performed before the efficient management of nutrients is possible.

The first step in resolving this problem is to gain a knowledge of the sources and the major transport mechanisms associated with nutrients within the system. A general mass balance approach, that is, one which assimilates "first cut" data, illustrates the essential features of the nutrients and their movement in the Bay. A mass balance shows the relationship between inputs and outputs. As such, the sensitive areas of the Bay, those which would show most immediate and desirable results from control, can be determined.

The scale, or the combination of study area size and time increment, is important in performing a mass balance. This study considers a nutrient budget (i.e., mass balance) for the entire Chesapeake Bay area on a monthly basis. Of course, finer detail would yield more information, but because of the character of available data this is not presently possible. Indeed, it is the purpose of this "first cut" approach to yield information necessary to future nutrient monitoring efforts. Data resulting from these monitoring efforts will provide for the refinement of scale in mass balance studies and the ultimate management of nutrients in the Chesapeake Bay.

The primary objectives of this study are:

1) To develop a nutrient budget for the Chesapeake Bay. This budget is to include total nitrogen, reactive nitrogen, total phosphorus, and reactive phosphorus.

2) To assess the temporal and spatial variations of nutrients in the Chesapeake Bay.

3) To make recommendations for future monitoring of nutrients in the Bay.

The study consists of the following tasks:

1) Review the literature to obtain pertinent existing data.

2) Using these data estimate both nutrient loadings to and outputs from the Bay. This analysis considers a mass balance of nutrients with respect to the water column.

3) Examine data on Bay quality to establish cause and effect relationships.

4) Assimilate results from above tasks and make recommendations concerning future monitoring of the Chesapeake Bay.

THE STUDY AREA

The study area includes the main body of the Chesapeake Bay from its mouth at the Virginia Capes to the Susquehanna River. Also included are the tidal segments of all connecting tributaries, the most notable being the Susquehanna, Patuxent, Potomac, Rappahannock, York, and the James Rivers.

To facilitate analysis, the study area was sectioned into seven segments as shown in Figure 1. Sections are assumed to be uniform with respect to water quality. Pertinent physical characteristics of the segments are listed in Table 1. The study area is approximately 250 kilometers long with

TABLE 1. STATISTICAL SUMMARY OF CHESAPEAKE BAY SEGMENTS

SECTION	LENGTH (N. Mi.)	VOLUME (10^6 M^3)	SURFACE AREA (10^6 M^2)	AVERAGE DEPTH (M)
1	26	3100	900	3.4
2	20	5800	900	6.4
3	20	7300	1000	7.3
4	25	9300	1100	8.5
5	25	24200	3800	6.4
6	30	17800	2500	7.1
7	10	6400	1200	5.3
TOTAL	156	73900	11400	6.5

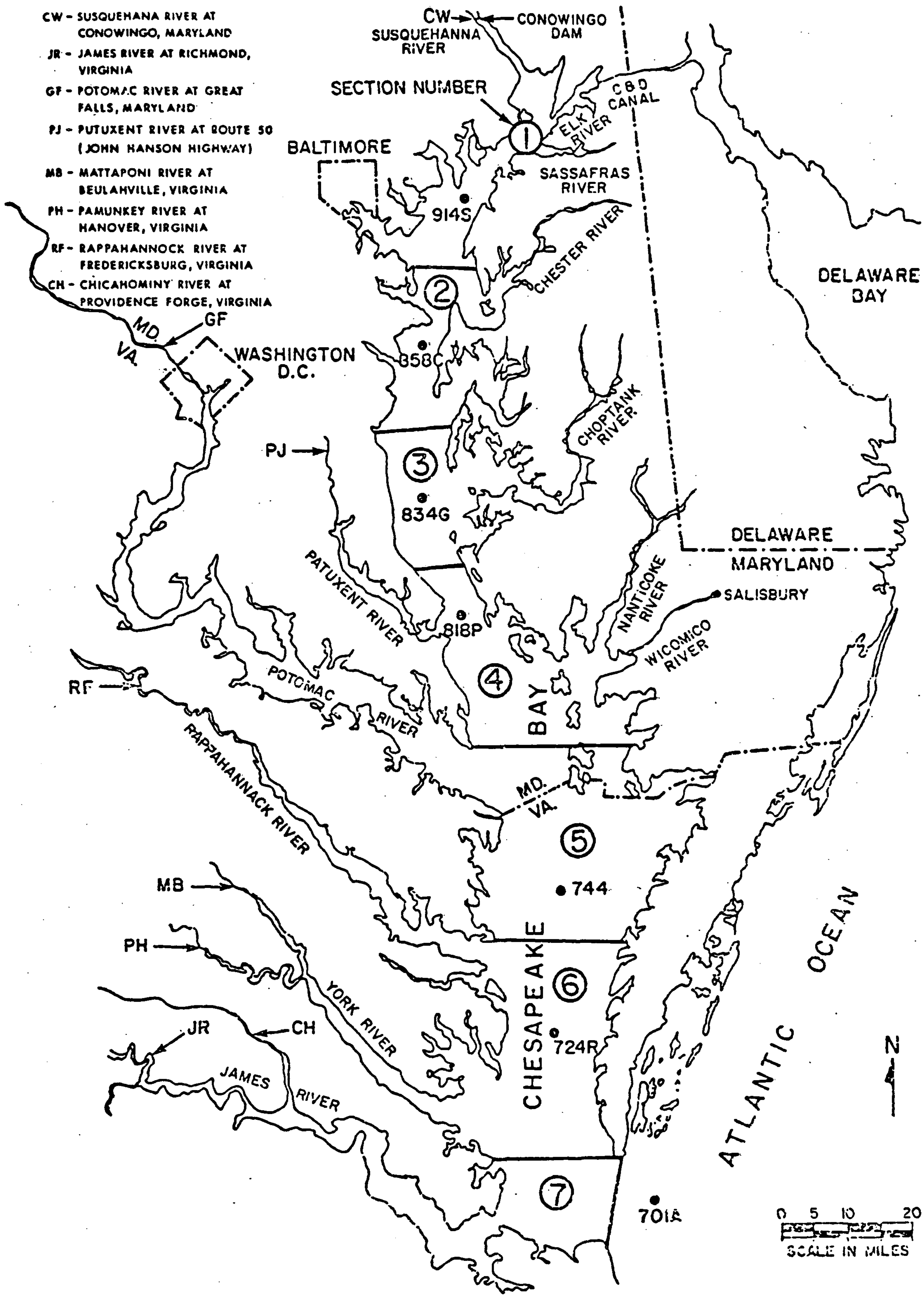

Figure 1. Chesapeake Bay Study Area

an overall volume of nearly $74x10^9$ cubic meters, a surface area of $11.4x10^9$ square meters, and has an average depth of 6.5 meters.

In addition to the segmentation, a computer program was constructed to manipulate all raw data into a form suitable for the analysis of both individual sections and the entire Bay with respect to time.

DATA BASE

A literature search was conducted to locate a period of time in which the four major types of nutrient data: tributary loadings, instream concentrations, point source loadings, and air loadings were simultaneously collected.

Within the period 1969 to 1971 two extensive monitoring programs were conducted. The EPA (3) monitored fresh water inflows from major tributaries for flow and the following species: total phosphorus, inorganic phosphorus, TKN, NO_2+NO_3, ammonia, and total organic carbon. This study consisted of several samples per tributary per month extending from June 1969 to August 1970.

Concurrently, the Chesapeake Bay Institute (CBI) (2) carried out monthly sampling at seven stations along the length of the Bay. CBI reported the following concentration data at various depths for each station: NO_2, NO_3, ammonium, ortho-phosphate, dissolved organic phosphorus, particulate phosphorus, inorganic carbon, dissolved organic carbon, and various chlorophyll-a pigments. This study extended from April 1969 to June 1971.

EPA tributary sampling stations as well as CBI instream stations are shown on Figure 1.

Point source loadings are represented by data collected in 1974 (6) and later by EPA. These loadings include all municipal and industrial discharges occurring within the study area.

Air loadings are based upon a study of the Rhode River Watershed (7) performed from 1974 through 1976. In this study seasonal loadings of reactive nitrogen and reactive phosphorus were determined on the basis of continuous monitoring of selected sites.

On the basis of these data the time frame of this analysis is from June 1969 to August 1970. The following assumptions are made concerning the various data:

1) Point source loadings and air loadings, although obtained at later dates, are assumed to apply directly to the study period.
2) Point source data do not vary with time.
3) Air loadings vary by season only.
4) Monthly values for loadings and concentrations represent an average of all data reported for a particular month.
    a. With respect to tributary data as many as fifteen and as few as two samples were reported per month.
    b. In the case of instream concentrations reported by CBI samples at various depths were averaged and applied uniformly to the entire section. One such average is computed per month per station.
5) Point source loading and air loading data are reported as total nitrogen and total phosphorus. It is assumed that total nitrogen equals reactive nitrogen and total phosphorus equals reactive phosphorus for these data.
6) Instream concentrations of total nitrogen are not reported by CBI due to sample analysis difficulties. To compute this quantity the following procedure was used.

An independent study (9) of the Upper Chesapeake Bay does report total nitrogen at eleven stations periodically between 1969 and 1971. All results were plotted against concurrent reactive nitrogen data. A regression analysis was run and the resulting linear relationship applied to CBI data throughout the study area.

PROCEDURE FOR NUTRIENT BUDGET

The nutrient budget represents a mass balance performed on each segment with respect to time. In words, the mass balance expression in section i is as follows: $\text{ACCUMULATION}_i = \text{NET INPUTS}_i - \text{NET SINK}_i$

The accumulation term is computed as the difference between the mass of the quality constituent within the water column at $t+\Delta t$ and t (i.e., accumulation $= M_{t+\ t} - M_t$, where M represents the product of section volume and average section concentration, t represents time and Δt represents a time increment of one month.). Net inputs is the difference between the sum of all external loadings (i.e., tributaries, point sources, air loadings, and transport in by advection and dispersion) and outputs (i.e., advection and disperson out of a section). The net sink term represents that mass which is removed from the water column by internal mechanisms such as decay, biological uptake, or sedimentation.

In terms of the mass balance expression data is available for both the accumulation and net input terms. No such data is available to describe the net sink term. For purposes of this analysis the mass balance is performed to determine the magnitude and significance of the net sink term.

The results of this study are discussed in the following order:

1) Annual external loadings of nutrients to and outputs from the study area.

2) System response to these loadings. This is shown as average seasonal concentration plots of nutrients along the length of the Bay.

3) Average seasonal molar ratios (reactive nitrogen/reactive phosphorus and total nitrogen/total phosphorus) of instream concentrations.

4) Monthly plots of total system mass, loadings, and net sink terms. This is a direct result of the budget and includes total and reactive nitrogen and total and reactive phosphorus.

5) Monthly molar ratios of mass balance components (i.e., water column masses, loadings, and the net sink term).

EXTERNAL LOADINGS AND OUTPUTS

Table 2 shows annual total nitrogen and total phosphorus loadings to the Chesapeake Bay by section. The following observations concerning this data are made:

1. Air loadings of nitrogen and phosphorus are generally in the order of 5% of the total and therefore insignificant.
2. Of the total nitrogen loadings 70% enters via tributaries and 25% via point source discharges.
3. Total phosphorus loading figures are: 65% from point sources and approximately 30% from tributaries.
4. There are three significant regions of the study area through which nutrients enter. Section 1, which includes the Susquehanna River and Baltimore Harbor, receives 55% and 35% of the total nitrogen and total phosphorus loadings, respectively. Section 5, which

includes the Potomac River, receives 25% and 35% of the nitrogen and phosphorus loadings, respectively. Section 7, which includes the James River, receives 10% of the nitrogen loading and 20% of the phosphorus loading. In all, these sections receive approximately 90% of both the total nitrogen and total phosphorus loadings.

5. Total annual loadings to the Chesapeake Bay are 1212 x 10^5 kg/yr total nitrogen and 164 x 10^5 kg/yr total phosphorus. Outputs, via advection and dispersion to the ocean are 390 x 10^5 kg/yr total nitrogen and 2 x 10^5 kg/yr total phosphorus. This shows that 70% of the total nitrogen and essentially all of the total phosphorus (99%) loadings remain in the Bay.

SUMMARY OF LONGITUDINAL CONCENTRATION DISTRIBUTIONS (FIGURES 2 THROUGH 5)

1. Reactive nitrogen concentrations vary widely both with respect to season and location.
   - In all seasons the highest concentrations are located in the upper Bay near Baltimore Harbor. Concentrations are highest here during the winter and spring, 1.0 mg/l as N and 0.65mg/l as N, respectively.
   - During the summer reactive nitrogen in the headwaters is 0.2 mg/l as N. This decrease is believed primarily due to lower river flows and is reflected in the general loading curves (Figure).
   - While during winter and spring reactive nitrogen decreases significantly along the entire length of the Bay, the summer concentrations reduce from 0.2 mg/l as N in the upper Bay to

TABLE 2. YEARLY TN/TP LOADINGS TO CHESAPEAKE BAY

SECTION	POINT SOURCES TN (10^5 KG/HR)	POINT SOURCES TP	TRIBUTARIES TN (10^5 KG/YR)	TRIBUTARIES TP	AIR TN (10^5 KG/YR)	AIR TP
1	126	32.3	523	23.5	4.1	.70
2	3.7	.3	0	0	4.2	.7
3	0	0	0	0	4.7	.8
4	12.1	3.8	9.9	2.8	5.3	.9
5	97.9	40.7	214	17.2	17.8	3.1
6	3.6	1.3	27.7	2.2	11.6	2.0
7	79.3	26.8	61.4	4.1	5.7	1.0
TOTAL	322.6	105.2	836	49.8	53.4	9.3

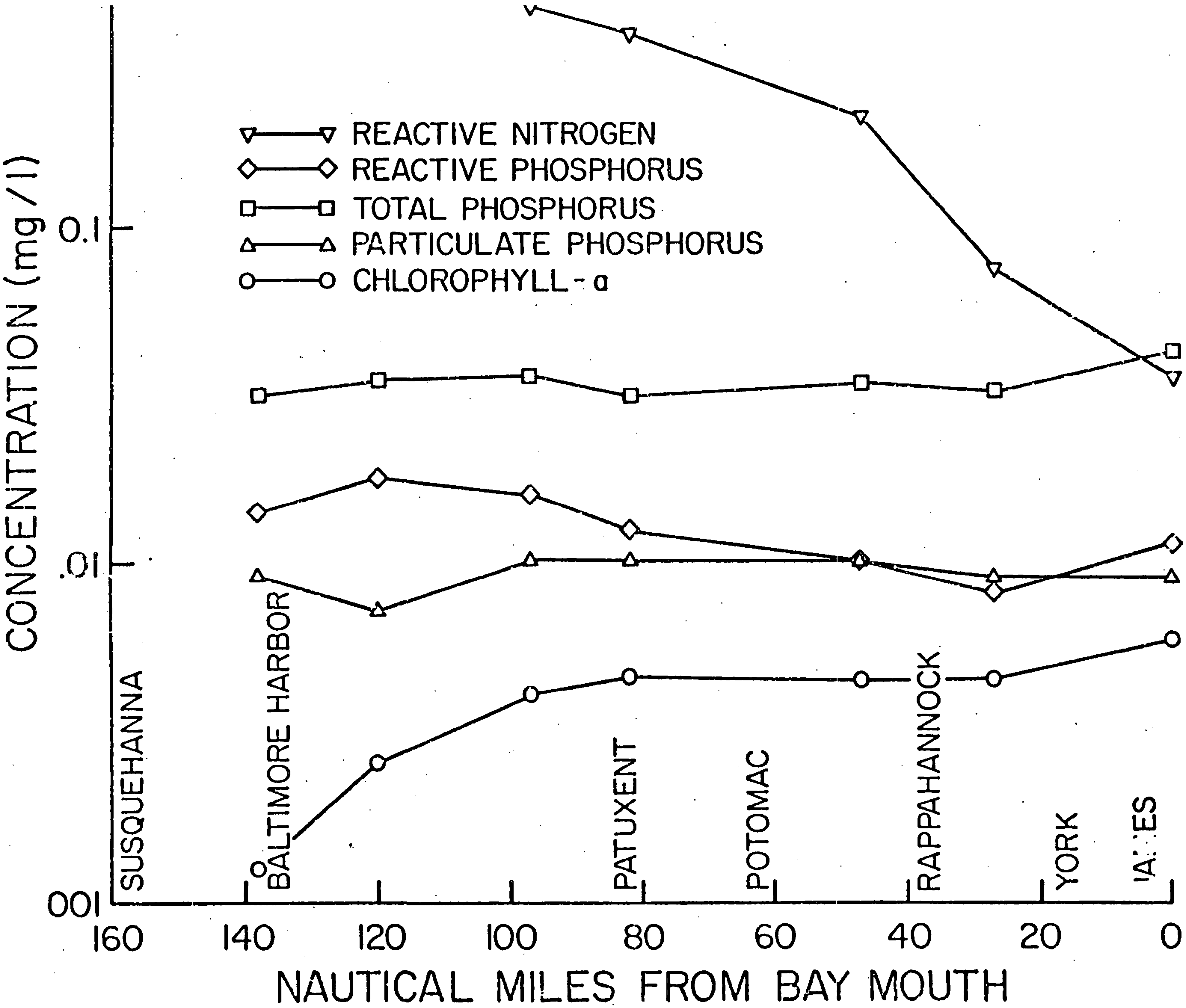

Figure 2. Longitudinal Concentration Distributions: Winter

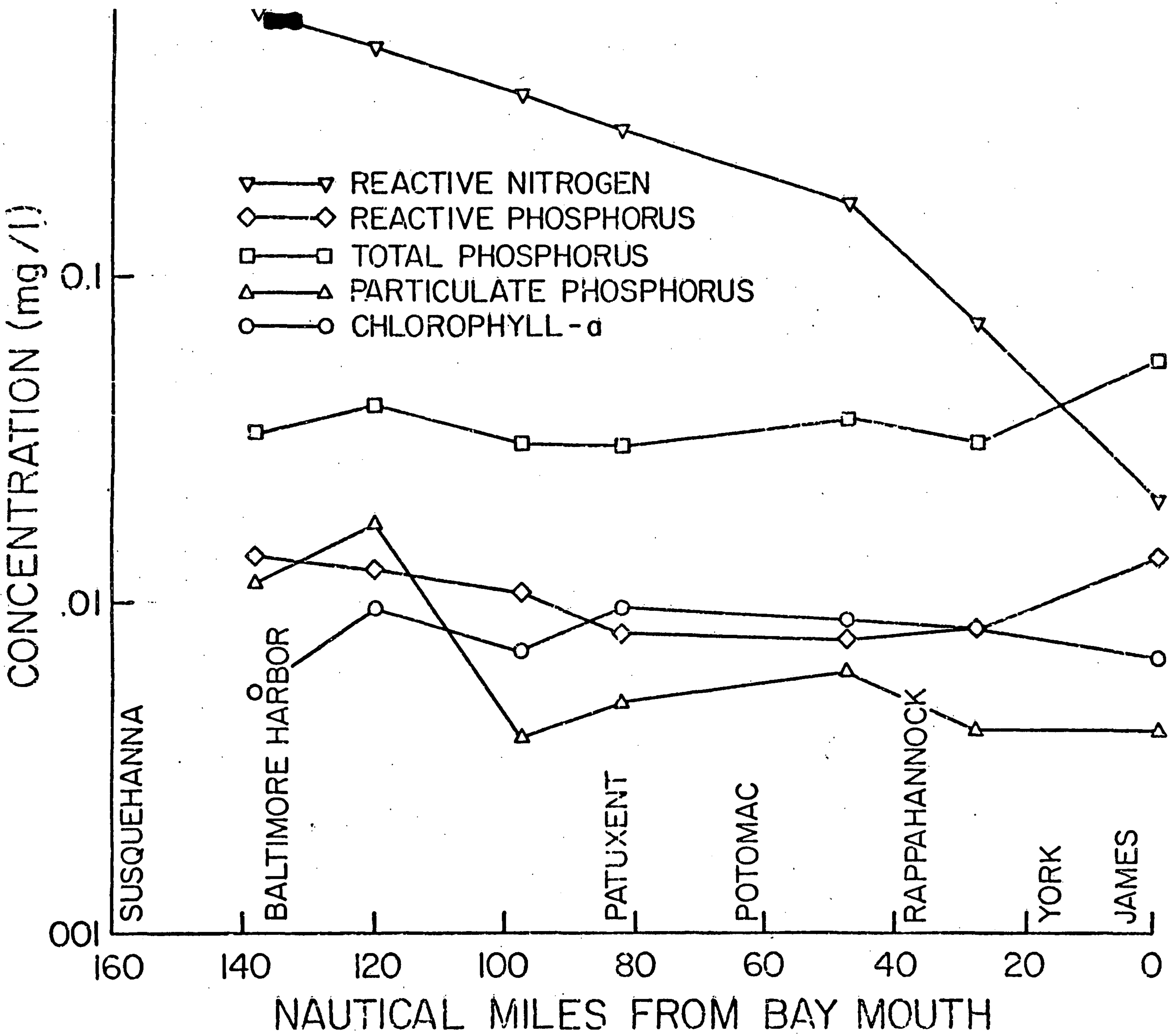

Figure 3. Longitudinal Concentration Distributions: Spring

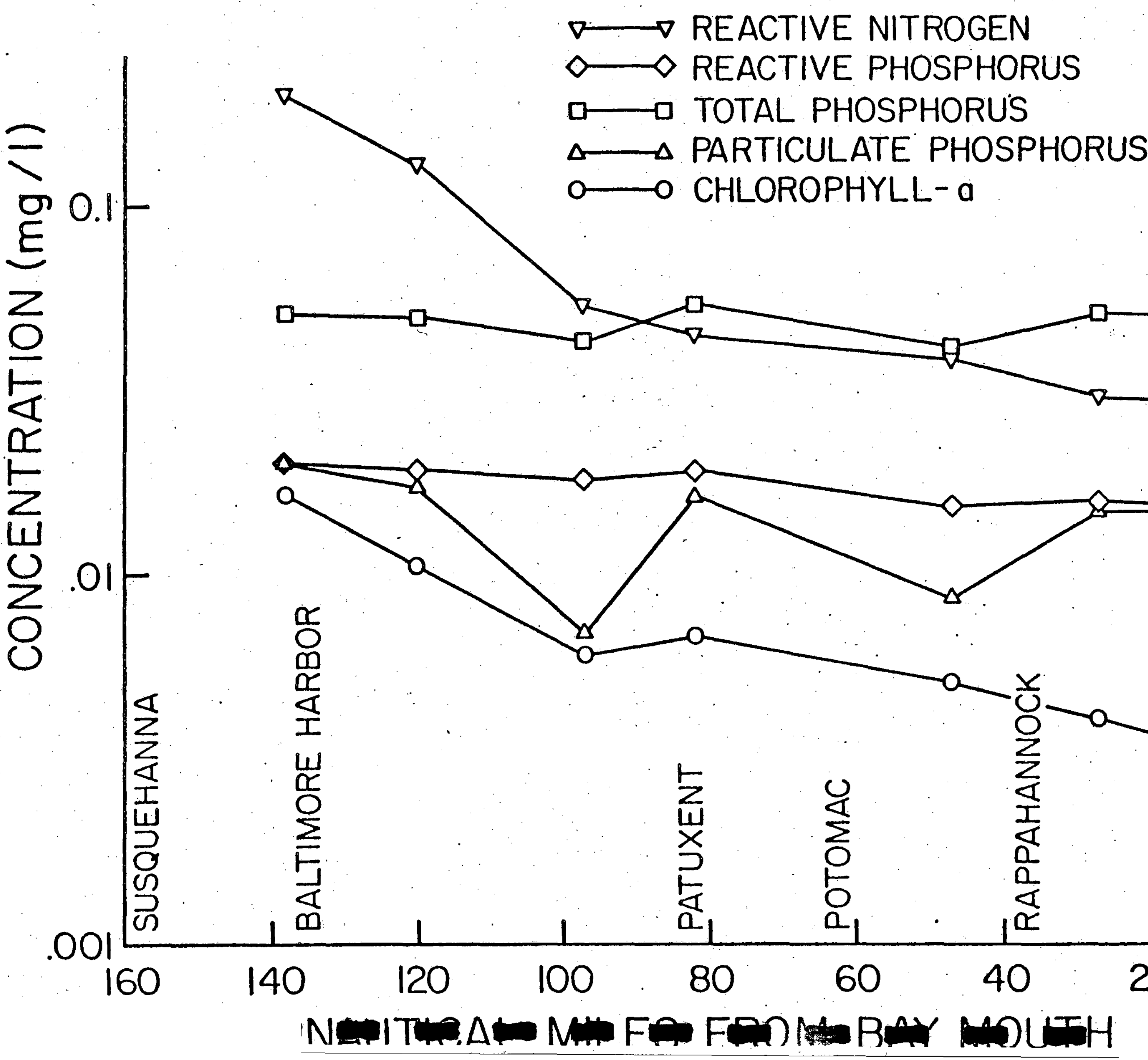

Figure 4. Longitudinal Concentration Distributions: Summer

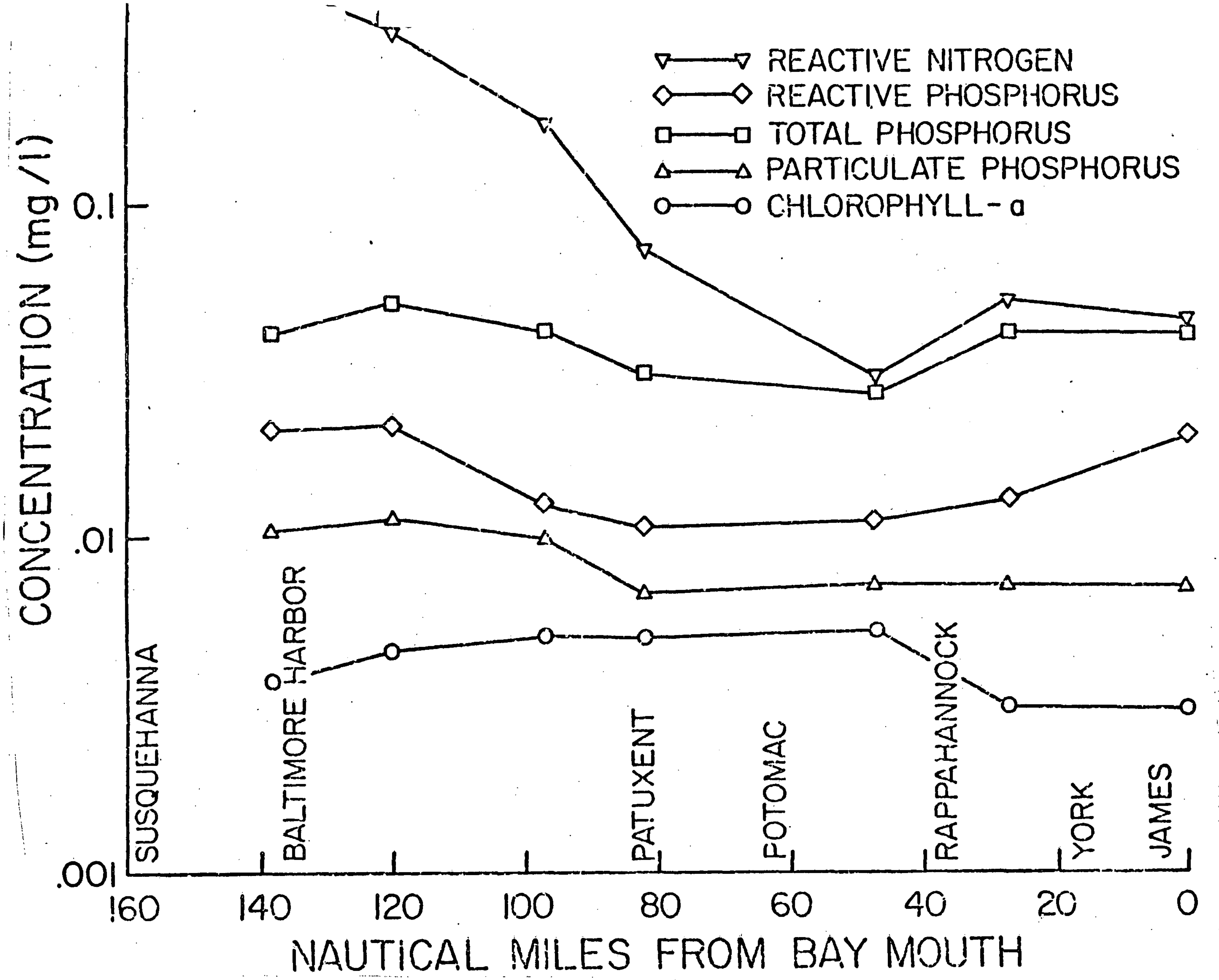

Figure 5. Longitudinal Concentration Distributions: Fall

approximately 0.04 mg/l as N at mid-Bay and remain essentially constant with a low point of 0.03 mb/l as N at the ocean interface.

2. Reactive phosphorus concentrations during all seasons lie between 0.01 mg/l as P and 0.02 mg/l as P. Typically, upper and lower Bay experience slightly higher concentrations than does the middle region. This tendency is altered during the summer where concentrations fall from 0.02 mg/l as P in the upper Bay to 0.015 mg/l as P in the middle region and then remain constant.

3. The spatial variation in total phosphorus is not significant. Summer concentrations are highest and average 0.05 mg/l as P throughout the Bay. During the remainder of the year concentrations generally vary between 0.03 mg/l as P and 0.04 mg/l as P.

4. Particulate phosphorus in the upper Bay varies between 0.01 mg/l as P and 0.02 mg/l as P during winter-fall and summer-spring respectively. Spatial variation is most significant during the summer where a low of 0.007 mg/l as P is seen just above the Patuxent River and a high of 0.02 mg/l as P is seen in both the upper and lower Bay.

5. In all seasons but summer chlorophyll-a is lowest in the upper Bay, rises in the middle region, and remains essentially constant to the ocean. This range is from 0.003 mg/l to 0.01 mg/l. During the summer, however, concentrations are greater than 0.015 mg/l, more than double other seasons, in the upper Bay. This is followed by a steady decrease toward the lower Bay to a value less than 0.003 mg/l.

SEASONAL INSTREAM MOLAR RATIOS (FIGURE 6)

1. RN/RP ratios are generally highest in the upper Bay, and steadily decrease downstream.
2. Spring and winter show ratios greater than 100 in the upper end. These values decrease to approximately 50-75 in the middle regions and further decrease to a low of 10 at the extreme lower boundary.
3. During the summer, molar ratios in the upper end range between 15 and 20. These ratios are near those measured in algae and therefore suggest that either nitrogen or phosphorus could be limiting algal growth.
4. Middle and lower Bay values for the summer are well below 15 which suggests that nitrogen only would limit algal growth.

MONTHLY MASS-LOADING-NET SINK CURVES (FIGURES 7 through 10)

Loadings

1. Nutrient loadings in general are highest during winter and spring. Because point source discharages are essentially constant and air loadings are insignificant, the variation of loadings is a function of tributary flow.
2. During the summer and fall, the reactive phosphorus loading remains essentially constant at 10^6 kg/mo. Loadings are then increased by an average factor of 1.3 during the winter. The winter loadings, and thus flows, show more variation than do summer loadings.
3. Total phosphorus loadings are similar to reactive phosphorus except the winter increase factor is approximately 1.6. This shows an increased organic fraction.
4. Nitrogen loadings show identical temporal characteristics as do

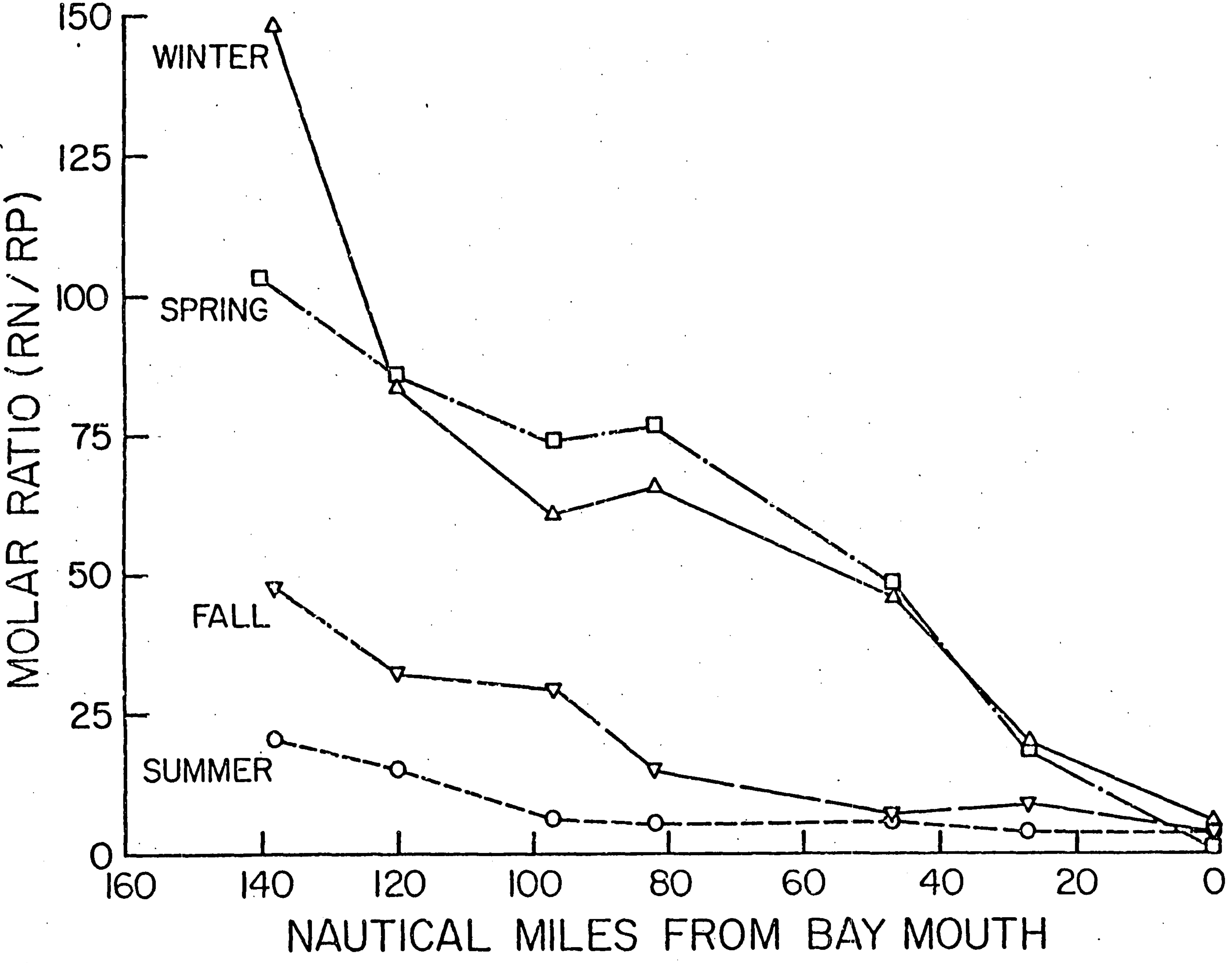

Figure 6. Seasonal Molar Ratios (RN/RP) Along Chesapeake Bay

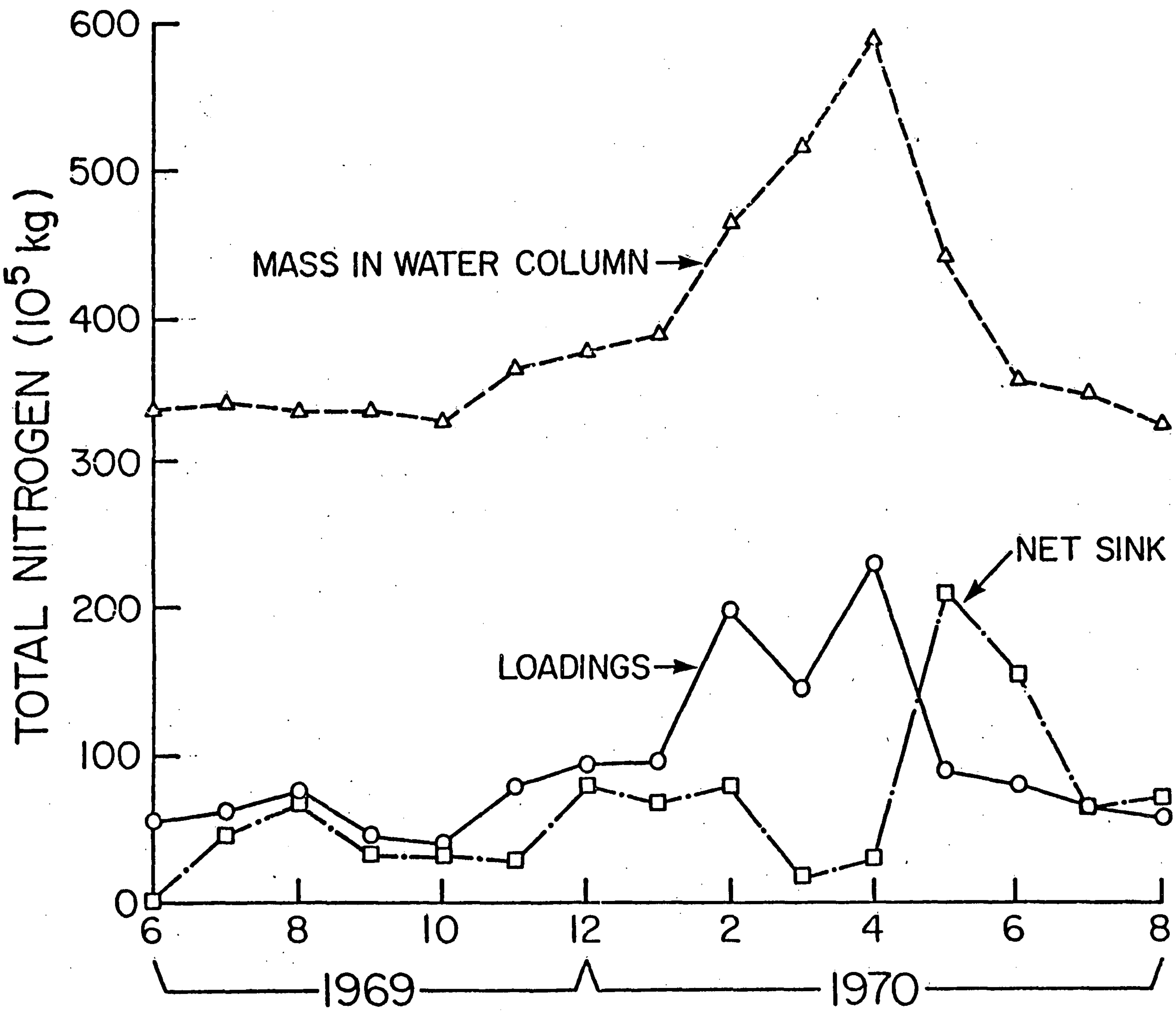

Figure 7. Monthly Measures of Nutrient Budget Components

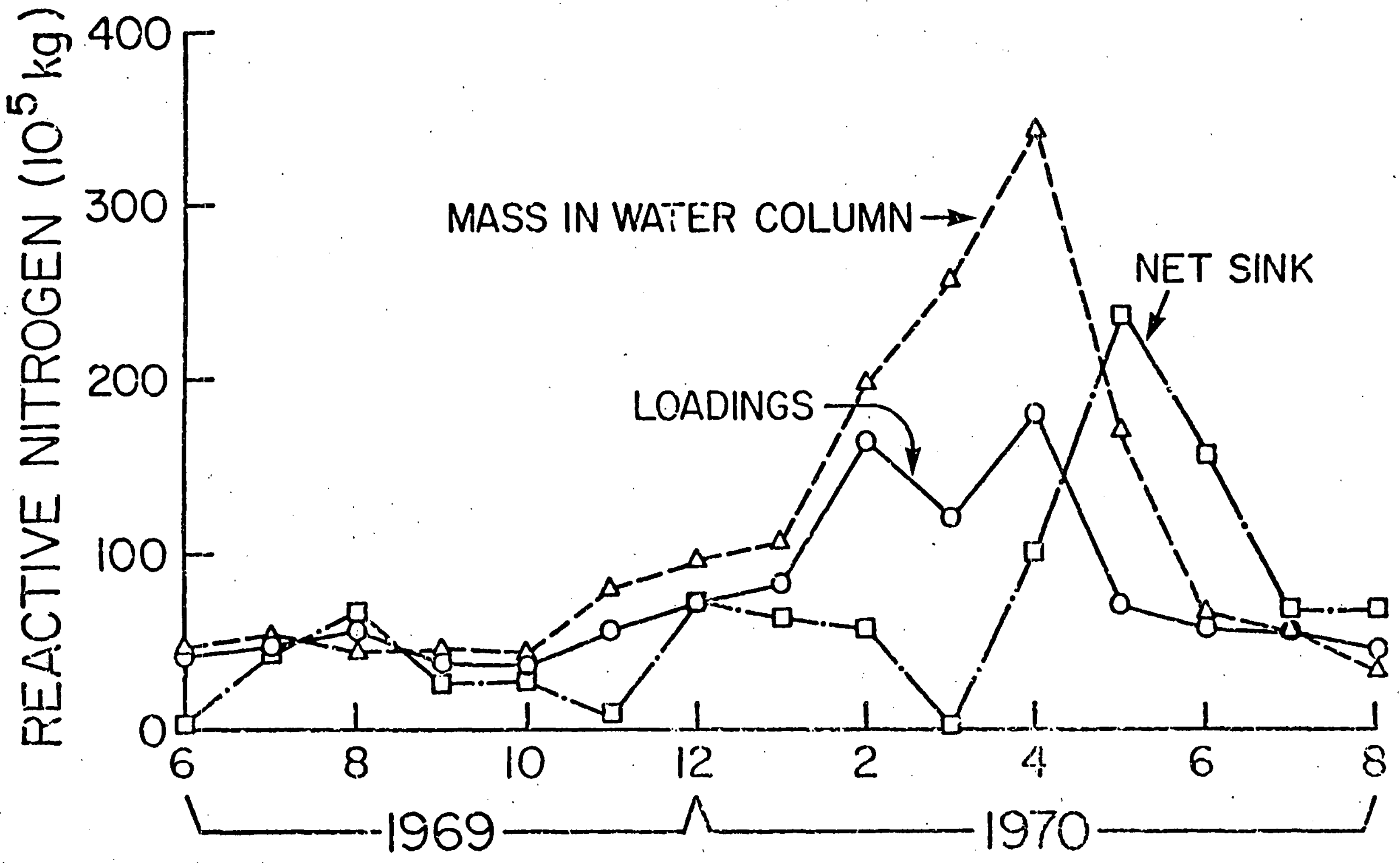

Figure 8. Monthly Measures of Nutrient Budget Components

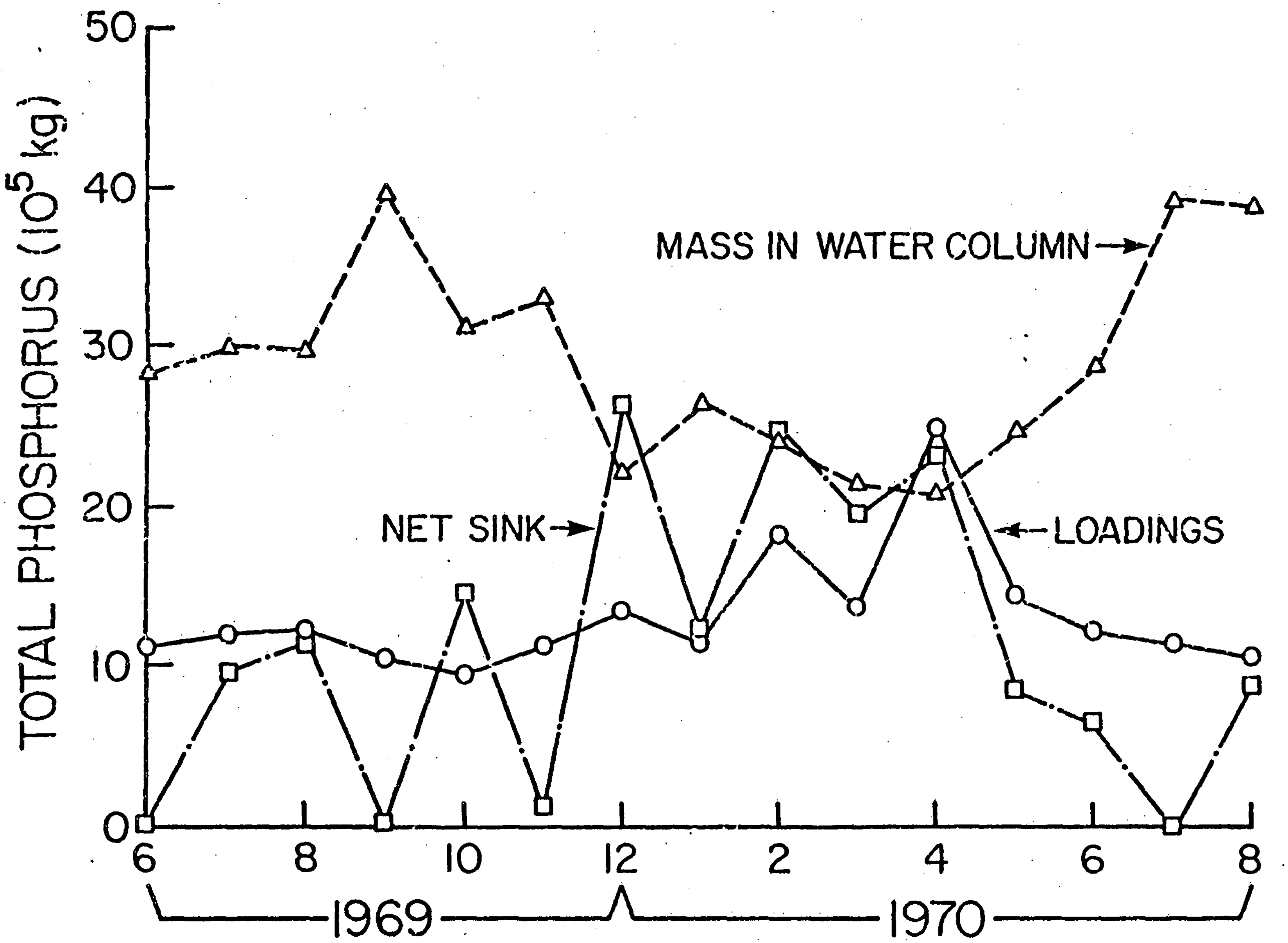

Figure 9. Monthly Measures of Nutrient Budget Components

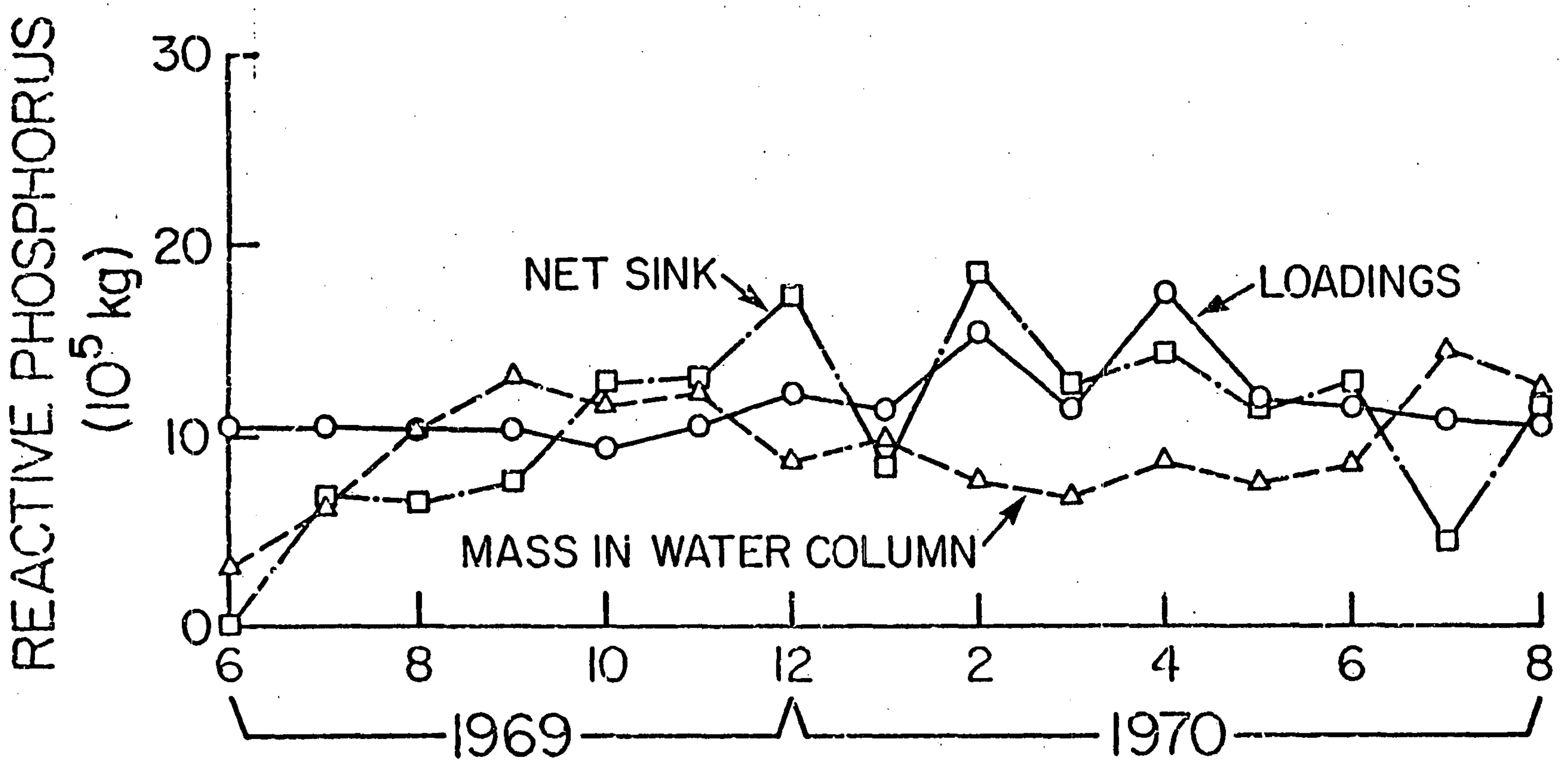

Figure 10. Monthly Measures of Nutrient Budget Components

the phosphorus loadings. During the summer, reactive nitrogen loadings are approximately $5x10^6$ kg/mo and constant. Total nitrogen is slightly higher.

5. During the winter both total and reactive nitrogen increase by a factor of approximately 2.4. The increased organic fraction, as seen in the phosphorus loadings, is not evident with nitrogen.

Water Column Mass

If total mass is divided by a loading rate, the result represents an average retention time.

1. The total mass of reactive phosphorus in the Bay fluctuates little during the year. The average value is approximtely 10^6 kg. Coupled with the average reactive phosphorus loadings, it is concluded that there is a residence time of one month during the summer and slightly less than a month in the winter for reactive phosphorus in the water column.
2. Total phosphorus undergoes large seasonal variation. Average summer values of water column mass lie between $3.0x10^6$ and $4.0x10^6$ kg. Winter values are noticeably lower and range from $2.0x10^6$ kg and $2.5x10^6$ kg. Residence times for total phosphorus appears to be three months during the summer and fall and as little as one month during the winter and spring.
3. Because water column concentrations of total nitrogen is a direct function of reactive nitrogen temporal variations are identical. Nitrogen masses, unlike phosphorus, increase dramatically during the winter. This is because the major portion of the total nitrogen loading enters via tributaries.

4. Residence times for reactive nitrogen are approximately one month during the summer. This is identical to reactive phosphorus and approximately two months during the winter, compared to less than a month for reactive phosphorus. Tentative explanations for these results are:

   a. The removal of both reactive species during the summer is by the same mechanism, possibly algal comsumption.

   b. Removal of the reactive species during the winter is by a different mechanism which does not seem common to both reactive nitrogen and reactive phosphorus.

5. Total nitrogen residence times appear highest, more than four months, during the summer and decrease to approximately three months during winter and spring.

6. It should be noted that these residence times are related to the water column only and therefore do not represent flushing times from the Bay. Indeed, the greatest portion of the nutrients seem to be accumulated within the Bay region.

<u>Net Sink</u>

1. "Net sink" is a term for describing all the processes by which constituents leave the water column. This removal can be via sedimentation, biological uptake, etc. For purposes of discussion this will be referred to as losses or removal.

2. Total phosphorus losses undergo large fluctuations throughout the year. Summer and fall see as much as 10^6 kg/mo and as little as zero kg/mo removed. Winter and spring values are higher with average removal of approximately $20x10^6$ kg/mo. This high winter

loss coincides with the dramatic reduction of total phosphorus in the water column.

3. Reactive phosphorus also disappears at a higher rate during the winter. The increased removal during winter months may be due to increased sediment loading associated with high flows and resulting in adsorption of nutrients to suspended sediments and subsequent settling.

4. The decreased removal rate during the summer months may simply reflect a lessening sediment load accompanied by a relatively low algal uptake rate.

5. The removal of both total and reactive nitrogen is temporally similar. Highest removal, approximately $20x10^6$ kg/mo, occurs during the spring. For the remainder of the year both total and reactive nitrogen losses vary between zero and $8x10^6$ kg/mo.

6. As was reported earlier, relatively small amounts of nitrogen and especially phosphorus are flushed into the ocean. This suggests that the inverse correlation betweeen water column mass and removal mass should be strong. From the curves shown this is true.

<u>MOLAR RATIOS (FIGURE 11)</u>

1. RN/RP is essentially the same for the water column and loadings during the summer and early fall and measure approximtely 10. This would seem to say that, on the whole, the Chesapeake Bay may be nitrogen limiting during the summer. However, as was seen earlier, the upper Bay experiences higher molar ratios than the remainder of

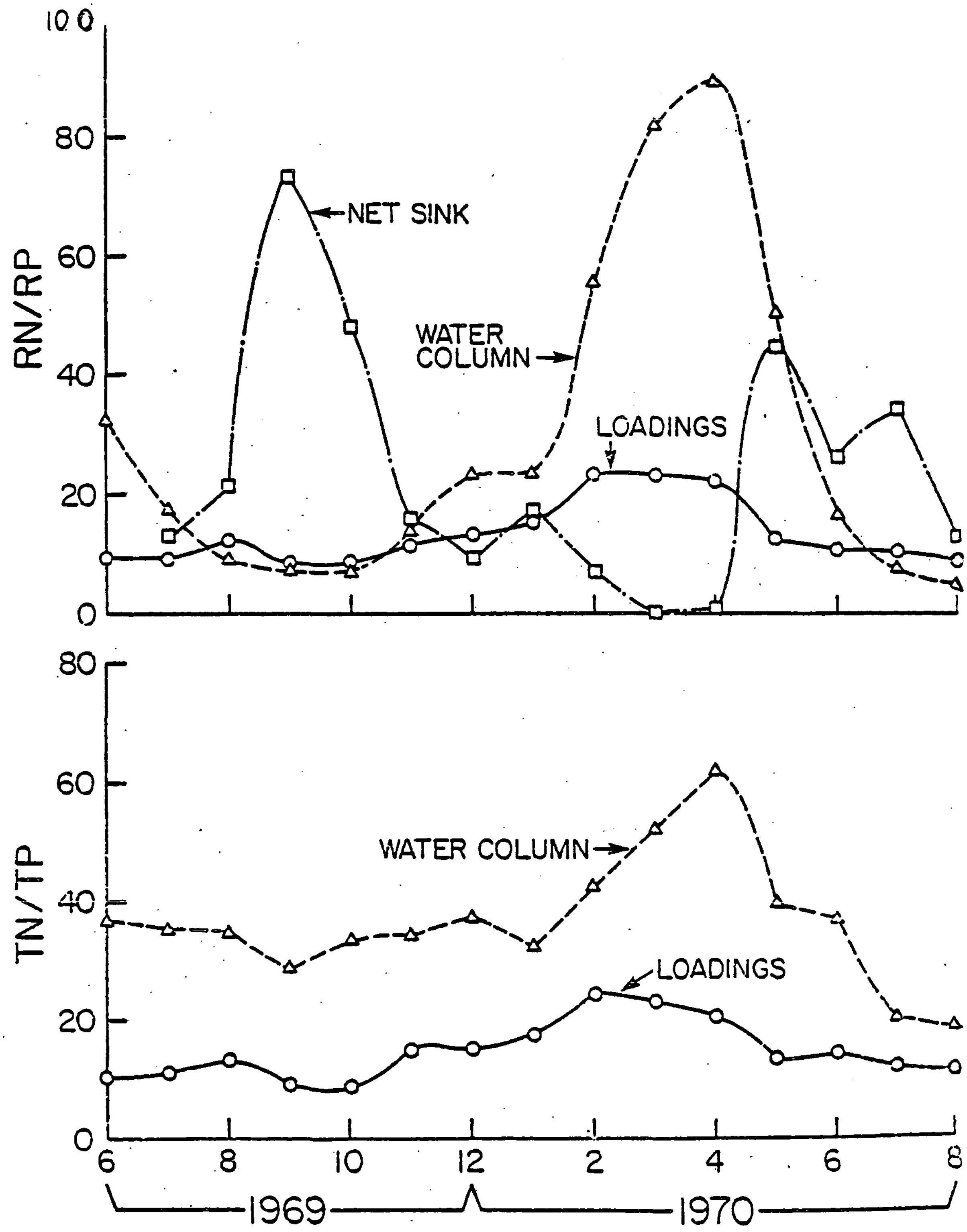

Figure 11. Monthly Molar Ratios of Nutrient Budget Components

the Bay.

2. During the winter months the RN/RP ratio increases to as much as 80 in the water column while an increase to approximtely 20 is seen in the loadings. The sharp increases in water column ratios is suggested by the longer residence time of nitrogen during the winter coupled with the relatively shorter holding time for phosphrous.
3. Total nitrogen/total phosphorus for loadings is similar to RN/RP in all respects.
4. TN/TP in the water column is approximately 35 during the summer and reaches a peak of 60 during the spring. Again, this variation is suggested by increased total nitrogen and decreased total phosphorus in the water column during the winter.
5. The RN/RP ratios for the net sink term lies between 15 and 30 during the late spring and summer and is widely variant during winter and early spring. This may describe the major removal mechanisms as being adsorption to suspended sediments during the high flow months and algal uptake during the summer. The widely variant nature of the winter RN/RP ratios suggests multiconditional removal mechanisms.

RAMIFICATIONS FOR NUTRIENT MONITORING

When considering a monitoring program the two primary decisions are where to sample and how often are samples to be taken. Some of the major factors affecting these decisions are as follows:

Location of Sampling Stations

1. Point source, upstream and downstream
2. Segments with high variability of water quality parameters
3. Critical points with respect to a parameter
4. Substantial flow changes
5. Changes in regional classification
6. Freshwater limits of estuaries
7. Interstate borders
8. Location of sensitive receptors
9. Areas of environmental concern
10. Areas of potential development
11. Areas susceptible to storm flows
12. Locations that can provide baseline information.

Frequency of Sampling

1. The response time of the system
2. Expected variability of the parameter
3. Half-life and response time of constituents
4. Seasonal fluctuations and random effects
5. Representiveness under different conditions of flow
6. Short term pollution events
7. The magnitude of response
8. Variability of the inputs

Of these many factors this report concentrates on only the variability of nutrient conditions with respect to space and time within the Chesapeake Bay region. With the background provided by the data the following observations and recommendations are made:

1. Air loadings are shown to be an insignificant factor in determining nutrient loadings to the Chesapeake Bay. However, this conclusion reflects a uniform extrapolation of conditions representative of a single watershed located within the Bay region. Because of possible heightened local effects, it is felt that air loadings should be studied for additional regions of the study area.
2. Nutrient loadings to the Bay vary significantly during winter and spring months and remain relatively constant during summer and fall. This is due to the temporal variations associated with freshwater flows entering the Bay. Because of these facts, monitoring efforts aimed at determining nutrient loadings need not be as temporally extensive during low flow months.
3. Spatially, these loadings enter the Bay region primarily at three locations: the upper Bay from the Susquehanna River and Baltimore Harbor, the mid-Bay region from the Potomac River, and the lower Bay from the James River. All other contributions total approximatley 10%. This fact suggests that conclusions concerning Bay-wide loadings may be made on the basis of data from these three regions.
4. Flushing of nutrients from the Bay shows only fractional overall removal, approximately 30% and 1% annually for total nitrogen and total phosphorus, respectively. These numbers are dependent upon limited concentrations data at the Bay-ocean interface area. Further monitoring of this area is necessary to verify results.
5. Of the water quality constituents studied, only nitrogen and particulate phosphorus show significant spatial variation in waste column concentrations. Only nitrogen shows significant seasonal

variation throughout the Bay. These tendencies suggest that not all constituents need be monitored on the same basis. Interparameter correlations would also help in determining constituent preference in monitoring.

6. Chlorophyll-a concentrations vary seasonal only in the upper Bay regions where algal growths are most common. Continued monitoring of this parameter is particularly important in this region.

7. Nutrient molar ratios are helpful in determining the potential for algal growth. Based on the analysis instream molar ratios, it is concluded that nitrogen limits algal growth in the middle and lower regions of the Bay. In the upper regions of the Bay reactive nitrogen to reactive phosphorus ratios fluctuate about a mean representative of ratios found in the biomass. This suggests that either nitrogen or phosphorus could limit algal growth depending upon local conditions. These comments are directed to the low flow summer months only.

8. Perhaps the most important monitoring consideration is the further definition and quantification of nutrient removal mechanisms. As is reported, the majority of the nitrogen and phosphorus loadings to the Bay are not flushed to the ocean, rather they are removed from the water column by various internal mechanisms. On the basis of this analysis the removal mechanisms are varied with respect to both season and the particular nutrient. It is postulated that the major mechanisms are adsorption to suspended sediments during the high flow months and uptake by the algal cells during the low flow summer months.

SUMMARY

Using the approach of elementary raw data manipulation, a nutrient budget for the Chesapeake Bay is performed. Results of this budget analysis show that major portions of the nitrogen and phosphorus loadings to the Bay are removed from the water column internally; that is, they are not discharged to the ocean. Further, removal mechanisms seem to vary from season to season and among the various nutrient species. On the basis of this analysis it is necessary to construct appropriate monitoring programs to enable a more complete understanding of these mechanisms.

Coupled with this budget analysis the data from tributary loadings, air loadings, point source loadings, and instream concentrations of nutrients, are studied with respect to spatial and temporal variation within the Chesapeake Bay. Results are then utilized in forwarding recommendations concerning the future monitoring of nutrient conditions in the Chesapeake Bay region.

Obviously, the appropriate management of Chesapeake Bay resources depends heavily upon the effectiveness of data collected through monitoring. Monitoring, while its main product is data, is also constrained in efficiency by previously collected data. It is therefore necessary to apply exhaustive measures to the analysis of all previously collected data to discern its usefulness as a component in future decision-making processes.

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