Immediate Filtration Processing Of Water Samples To Separate Particulate and Dissolved Nutrient Parameters: What Is The Critical Time Interval Between Sample Collection and Filtration?

Carl Zimmermann and Carolyn Keefe
University of Maryland System
C.E.E.S.
Chesapeake Biological Laboratory
Solomons, MD 20688-0038

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Maryland Department of Natural Resources
Resource Assessment Administration
Water and Habitat Quality Program, D-2
Tawes State Office Building
580 Taylor Ave.
Annapolis, MD 21401

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EXECUTIVE SUMMARY

- Results of this study reaffirm the importance of immediate partitioning of dissolved and particulate fractions for Chesapeake Bay Mainstem samples.

- Expected nutrient concentrations, the expected phytoplankton turnover time and the data quality objectives of a proposed study for a specific body of water must be addressed in order to help determine how long a sample can be held prior to filtering. The sample from the Upper James River frequently typifies the type of water which would be collected as part of a watershed water quality monitoring program. It probably depicts a scenario where the nutrient supply is high and the demand is low. These conditions suggest a long turnover time. The data indicate, with one exception (phosphate), that whole water samples from high nutrient freshwater can be kept chilled and in the dark for several hours without appreciable change in nutrient concentration. However, the data cannot describe what conditions (phytoplankton and nutrient concentrations) will be like at other times of the year or at other locations on the river.

- The immediacy of partitioning a sample depends on the ambient concentrations and turnover time at the season of the year when nutrient concentrations are lowest and their turnover times shortest. Field sampling and sample partitioning protocols should remain constant throughout the study to avoid the possibility of changes in protocols that are instituted too tardily or where unanticipated changes in the phytoplankton population might occur.

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INTRODUCTION

The most appropriate sample collection and processing techniques are critical first steps in obtaining quality nutrient data in any water monitoring program. Standard oceanographic procedures call for the immediate partitioning of dissolved and particulate fractions after sample collection and this procedure has been adhered to within the mainstem portion of the Chesapeake Bay Program. All research vessels collecting samples from the mainstem are large enough to contain laboratory space where these samples are immediately processed.

The recent shift in emphasis by managers to the "watershed approach" to control nutrients entering the Chesapeake Bay has seen the initiation of new monitoring efforts in tributaries, tidal creeks, etc.; where immediate filtration of water samples is difficult, at best. The question of how long a whole water sample can be held before being processed into particulate and dissolved components is a question that needs to be answered for field personnel and data users alike. For example, it would be more practical to process samples collected from remote areas the next day, rather than immediately after collection. Certain practical considerations play into this decision.

Biological activity does not cease once a whole water sample has been collected from a surface body of water. A microcosm of organisms is contained in that whole water sample and under certain conditions nitrogen and phosphorus components can rapidly change, largely as a result of microbiological activity (Geological Survey, 1960).

These changes can be greatly retarded by keeping a whole water sample in the dark and at a low temperature (APHA, 1985). Just how long a whole water sample can be kept under these conditions before significant changes in nutrient concentrations occur is the purpose of this study.

MATERIALS AND METHODS

Sample Collection: The water sample analyzed by each laboratory was collected at different times and places around the Chesapeake Bay or its tributaries. A description of the location, sampling methods, etc. employed by each laboratory follows:

Lower Chesapeake Bay: Old Dominion University (ODU) collected Chesapeake Bay surface water on September 11, 1995 from the pier on the first island of the

Chesapeake Bay Bridge Tunnel in the lower mainstem of the Chesapeake Bay. This location is approximately two miles from station CB7.4. The sample was collected during an outgoing tide and based on historical data, the surface salinity was approximately 27 ppt.

Mid Chesapeake Bay: On 23 May 1995, Chesapeake Biological Laboratory (CBL) collected a surface water sample from the CBL pier. The pier is located at the approximate mouth of the Patuxent River where the salinity that day was approximately 13 ppt. Samples for particulate parameters were sampled on 24-26 February 1996.

Upper James River: A surface water sample was collected by Virginia Institute of Marine Science (VIMS) personnel on 22 March 1995. This was a freshwater sample collected at Jordan Point Marina, approximately 64 nautical miles from the mouth of the James River. This area of the James River is designated as non-tidal fresh.

In each case, a 50 liter Nalgene carboy was filled by compositing bucket filled surface water at each location into the carboy until the carboy was filled. After the carboy was filled and the initial sample processed, the following processing schedule was adhered to: 1, 2, 4, 12, 24 and 48 hours.

Volumes filtered (ml) for particulate analytes by each laboratory are:

PARAMETERS	VIMS	CBL	ODU
TSS/PP	200	500	600
PC/PN	25	220	50
CHL-A	200	250	400

Sub-sampling Procedure and Method of Refrigeration

Lower Chesapeake Bay: The carboy was contained in a 180 liter pickle barrel which was modified to facilitate packing the sample in ice. A platform was placed in the bottom of the barrel to allow ice to be placed beneath the carboy. A one inch diameter PVC extension pipe was manufactured to enable extension of the carboy spigot to the outside of the barrel. The PVC extension pipe was leached using ultrapure water, then cleaned using a dilute solution of nutrient free soap, deionized water rinses, acid rinses and numerous ultrapure water rinses. Stirring was begun twenty minutes prior to removing a subsample, the sample was stirred using a rectangular paddle fitted to a constant speed motor. This method ensured complete sample homogeneity.

Mid Chesapeake Bay: The sample was kept chilled by placing the carboy inside a 136 liter plastic trash can. Ice was packed around the sides of the carboy and a slot was cut out of the trash can to remove melted ice as well as to provide a means to remove subsamples from the carboy. Prior to removing a subsample, the entire apparatus was shaken to provide adequate mixing. All particulate analytes (PC/PN, TSS, PP and Chl A) were also sampled on 24-26 February 1996. The sampling scheme and protocol were exactly the same as that carried out on 23 May 1995. A major reason for repeating this part of the experiment was that the original particulate results indicated that a sampling /processing error was the most probable cause for the continued decline of concentrations as a function of time. It was felt that these differences may have been due to inadequate mixing of the sample carboy prior to withdrawing the sub samples, causing particles to adhere onto the side of the carboy. Only particulate results from the repeated sampling are discussed in this report.

Upper James River: The 50 liter carboy containing the sample was kept in a refrigerator. When a subsample needed to be withdrawn, the carboy was removed from the refrigerator, rolled vigorously on the floor, after which a 4-6 liter sample was removed. The carboy was then returned to the refrigerator.

Sample Processing and Analysis: Each laboratory utilized its usual field filtration procedures to separate the dissolved from the particulate components. These filtering procedures are the same as used on Chesapeake Bay monitoring cruises.

The laboratories used almost identical analytical techniques. All laboratories utilize the alkaline persulfate technique (Valderrama, 1981; D'Elia, et al, 1977) to determine total dissolved nitrogen and phosphorus. All laboratories utilize elemental analyzers for the determination of particulate carbon and nitrogen (EPA, 1992) and a high temperature/HCl extraction technique (Aspila, et al, 1976) for the direct determination of particulate phosphorus. Inorganic nutrients are analyzed colorimetrically by automated analyzers (ODU used EPA Method 365.3 for total dissolved phosphate). ODU and VIMS analyze chlorophyll spectrophotometrically while CBL uses a fluorometric technique. VIMS analyzed dissolved organic carbon using a Shimadzu 5000 DOC Analyzer, while CBL amd ODU utilized a persulfate oxidation technique using Oceanography International instrumentation (Model 524 and 700, respectively). Complete descriptions of methods and instrumentation can be obtained by contacting each of the participating laboratories (Appendix A).

DATA ANALYSIS

Mean concentrations of each analyte over the 7 subsampling periods were compared separately for CBL, VIMS and ODU using a 1-way ANOVA. It should be noted that data sets with small standard deviations will be significantly different from data sets exhibiting small changes but with small standard deviations as well. A follow-up analysis using a Tukey (HSD) pairwise comparison of means was conducted for analyte concentrations showing significant differences among subsampling periods. An alpha level of 0.05 was used for all statistical inferences.

RESULTS and DISCUSSION

Sampling location as well as the seasons in which they were collected provided quite diverse water types. Sample results provided a wide range of concentrations and salinity. Particulate loads ranged from high to very low.

This portion of the report is divided into two sections: dissolved and particulate. The results from each sampling area are discussed in relation to sampling times and comparisons between sites are also made. Data from each laboratory is found in Appendix B.

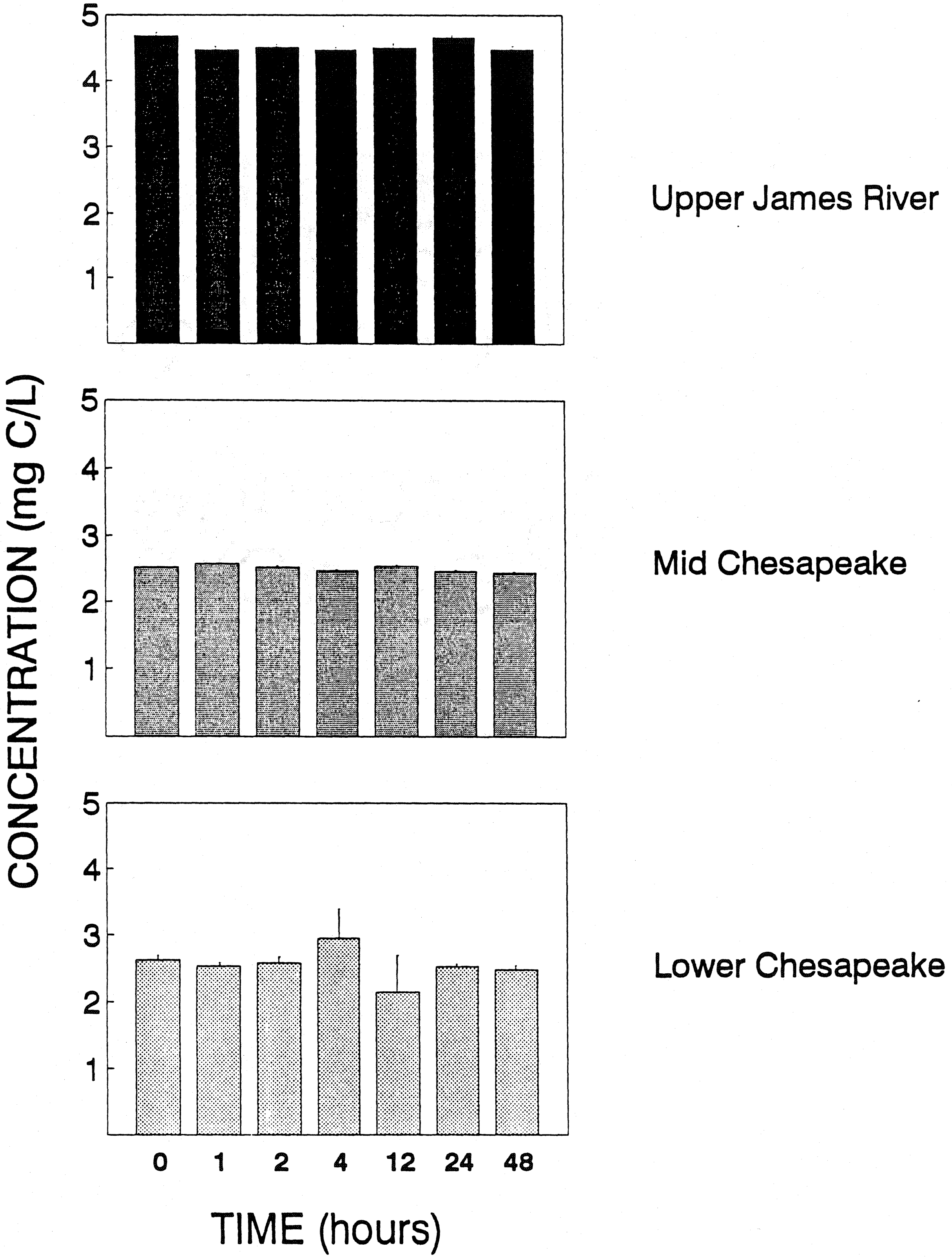
DISSOLVED PARAMETERS

Dissolved Organic Carbon (DOC): Results for DOC are found in Figure 1 and Appendix B. The Upper James River concentrations were approximately 2 mg C/l higher than the other two sites. There was little variation in concentration among time periods with no distinct trends of change. Within each individual time period reproducibility was very close. Coefficients of variation (CV) were all less than 4%. Only a 5% decrease in mean concentration between time 0 and 48 hours was observed. The 1-way ANOVA for subsampling period showed a significant (P=0.0187) difference over time in mean DOC concentration; however Tukey's pairwise comparison of means showed no significant pairwise differences among means.

Little change over time (3% decrease between time 0 and 48 hours), excellent within time period reproducibility and no distinct trends as a function of time summarize the DOC results from the Mid Chesapeake Bay site. The 1-way ANOVA for subsampling period showed a significant (P=0.0003) difference in mean DOC concentration with time. Tukey's pairwise comparison of means indicated that the mean DOC concentration at time 1 hour was significantly greater than at times 4, 24 and 48 hours and mean DOC concentration at time 12 hours was significantly greater than at time 48 hours. There were no significant differences among mean DOC concentrations measured at times 0, 2, 4, 12 and 24 hours using Tukey's pairwise comparison of means.

DOC values from the Lower Chesapeake Bay site approximated those from the Mid Chesapeake Bay. Within sampling reproducibility indicated coefficients of variation of less than 10%. In instances where fewer than five replicates were analyzed, percent coefficients of variation were much higher (>30%). The 1-way ANOVA for subsampling period showed no significant (P=0.4005) differences with time in mean DOC concentration.

Figure 1. Dissolved organic carbon in the upper James River and mid and lower Chesapeake Bay.



Ammonium (NH_4-N): Ammonium concentrations for each site are given in Figure 2. Ammonium concentrations in the Upper James River (~2.6 mg NH_4-N/l) were more than 100 times higher than those concentrations reported for the two Chesapeake Bay sites. Within sampling variability of the Upper James River ammonium concentrations was less than 4%. The 1-way ANOVA for subsampling period showed no significant ($P=0.0687$) differences over time in mean NH_4-N concentration.

Ammonium concentrations for the Mid Chesapeake Bay site were near the detection limit (0.003 mg N/l) and large (13-60%) coefficients of variation were obtained as estimates of within sampling variability. No clear downward or upward trends were noted as a function of time; however, the difference in mean concentration between time 0 and 48 hours was large (50%). The 1-way ANOVA for subsampling period showed significant ($P=0.0001$) differences over time in mean NH_4-N concentration. Tukey's pairwise comparison of means showed mean NH_4-N concentration at time 48 hours was significantly greater than at times 0, 1, 2, 4 and 24 hours. Mean NH_4-N concentration at time 4 hours was significantly lower than at times 12 and 48 hours. There was no significant difference among mean NH_4-N concentrations at times 0, 1, 2, 12 and 24 hours.

A rapid decrease in ammonium concentration during the first four hours of sample collections was evident in the Lower Chesapeake Bay data. All subsequent ammonium concentrations were undetectable. The 1-way ANOVA for subsampling period showed significant ($P<0.00001$) changes over time in mean NH_4-N concentration. Tukey's pairwise comparison of means revealed a steady significant decline in mean NH_4-N concentrations from times 0 to 4 hours. There was no significant difference among mean NH_4-N concentrations measured from 12 through 48 hours.

Nitrite+Nitrate (NO_2+NO_3-N): Figure 3 illustrates the results for nitrite+nitrate concentrations. A 5% increase in mean concentrations between time 0 (0.491 mg N/l) and 48 hours (0.517 mg N/l) was noted in the Upper James River data set. This increase appeared to correspond well with sampling times, i.e., there was a slight upward trend in concentration over time. Within sampling variability was slight (CV < 2%). The 1-way ANOVA for subsampling period revealed significant ($P<0.00001$) differences over time in mean NO_2+NO_3-N concentration. Tukey's pairwise comparison of means showed that mean NO_2+NO_3-N concentrations at times 24 and 48 hours were significantly greater than at all other times. Mean NO_2+NO_3-N concentration at time 12 hours was significantly greater than earlier subsampling periods. There were no significant differences in mean NO_2+NO_3-N concentrations among times 0 through 4 hours.

No trend was observed in the Mid Chesapeake Bay site's NO_2+NO_3-N data. Concentrations were approximately three times less than (~0.145 mg N/l) those reported for the Upper James River. Within sampling variability was less than 5%. The

Figure 2. Ammonium in the upper James River and mid and lower Chesapeake Bay.

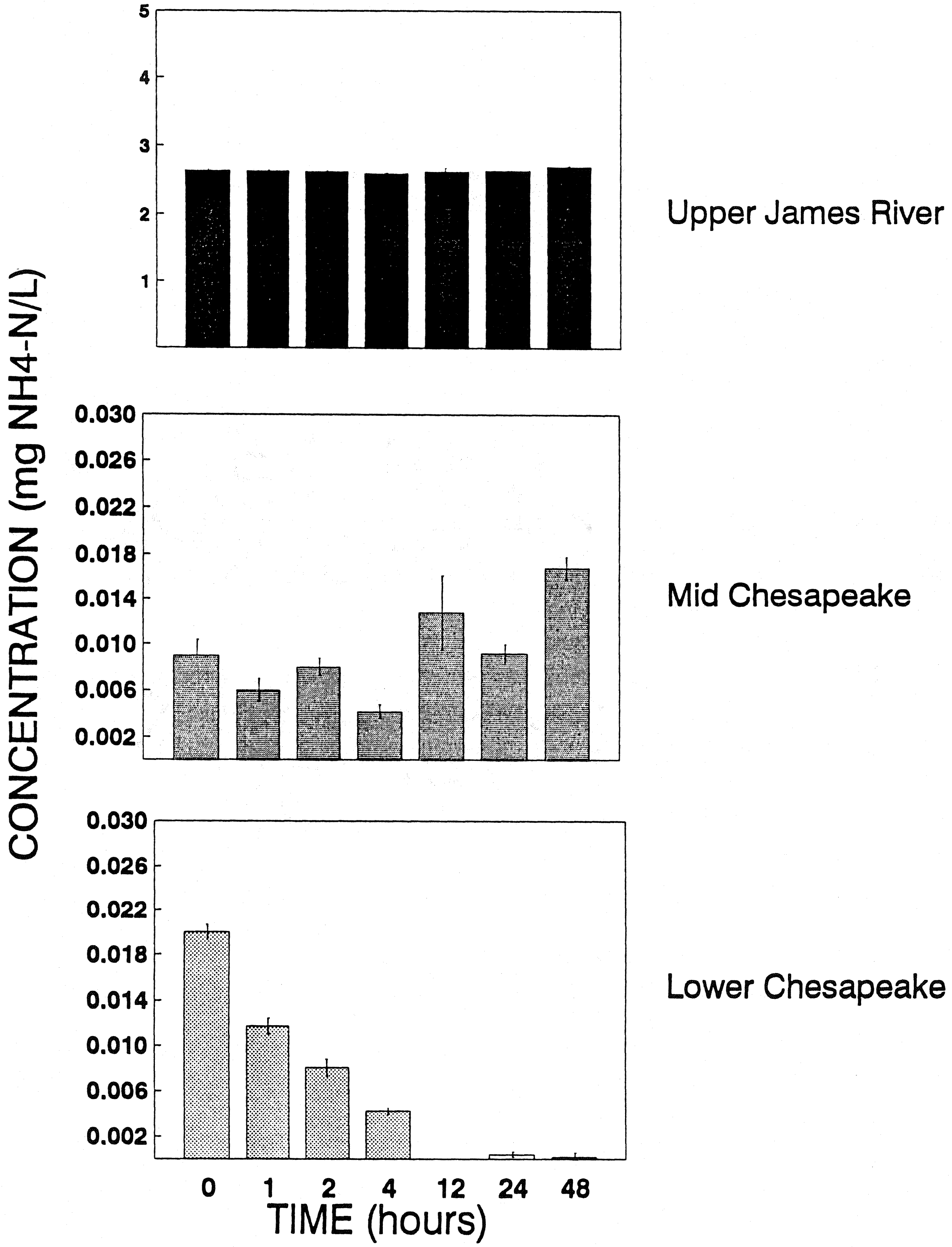
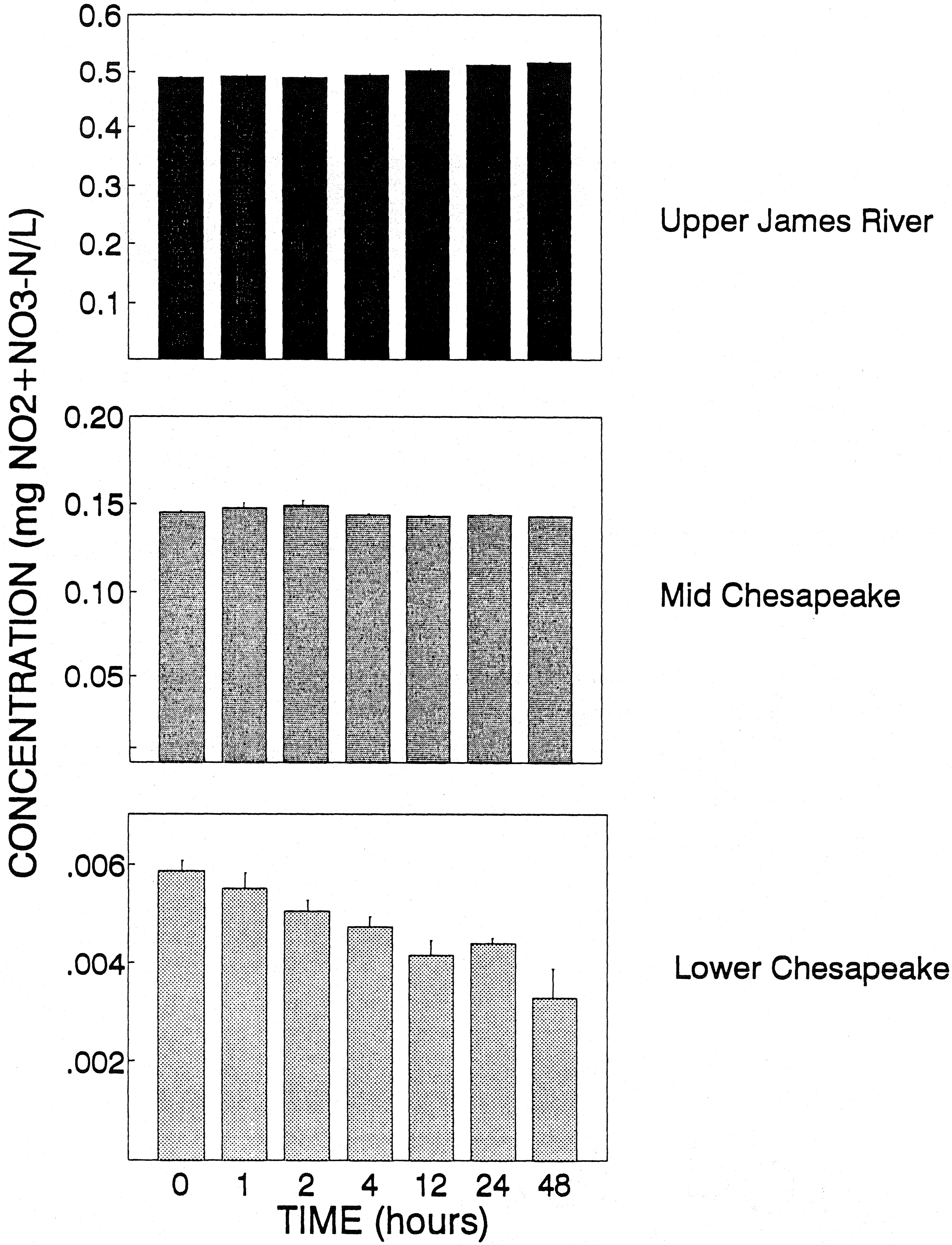


Figure 3. Nitrite+nitrate in the upper James River and mid and lower Chesapeake Bay.



1-way ANOVA for subsampling period showed no significant (P=0.1289) changes with time in mean NO_2+NO_3-N concentration.

Concentrations of NO_2+NO_3-N reported for the Lower Chesapeale Bay site were nearly 100 times less (~0.0050 mg N/l) than those from the Upper James River. A continuous decrease in concentration with time was also noted. The percent change in concentration from time 0 to 48 hours was nearly 50%. The 1-way ANOVA for subsampling period showed significant ($P<0.00001$) differences in mean NO_2+NO_3-N concentration over time. Tukey's pairwise comparison of means revealed mean NO_2+NO_3-N concentration at time 0 hour was significantly greater than at times 12 through 48 hours. Mean NO_2+NO_3-N concentration at 48 hours was significantly lower than at times 0 through 4 hours. There was no significant difference, however, in mean NO_2+NO_3-N concentrations among times 2 through 24 hours.

Nitrite (Figure 4): For the Upper James River sample, 1-way ANOVA for subsampling period revealed significant ($P<0.00001$) differences in mean nitrite concentration over time. Tukey's pairwise comparison of means showed mean nitrite concentration at time 48 hours was significantly lower than at any other subsampling period. Mean nitrite concentration at time 0 hour was significantly greater than all periods. There was no significant difference among subsampling periods 1 through 24 hours in mean nitrite concentration.

For the Mid Chesapeake Bay sample, 1-way ANOVA for subsampling period revealed no significant (P=0.5607) differences in mean nitrite concentration over time.

For the Lower Chesapeake Bay sample, the 1-way ANOVA for subsampling period showed significant ($P<0.00001$) differences in mean nitrite concentration over time. Tukey's pairwise comparison of means showed mean nitrite concentrations at times 12 through 48 hours were significantly greater than at periods 0 through 4 hours. There were no significant differences in mean nitrite concentration among times 0 through 4 hours.

Total Dissolved Nitrogen (TDN): TDN concentrations followed the same pattern as all the dissolved nitrogen species; the highest concentrations were reported in the Upper James River (>3 mg N/l) and the lowest in the Lower Chesapeake Bay (~0.25 mg N/l) [Figure 5]. TDN results from the Upper James River showed low coefficients of variation (<5%) for within sampling variation. The 1-way ANOVA for subsampling period showed no significant (P=0.1905) differences among subsampling periods in mean TDN concentration.

Mid Chesapeake Bay TDN data showed no clear trends as a function of time. Within sampling variability was generally close. One errant replicate brought the percent CV for the 24 hour sampling to 20%. Given the high standard deviation, there is effectively

Figure 4. Nitrite in the upper James River and mid and lower Chesapeake Bay.

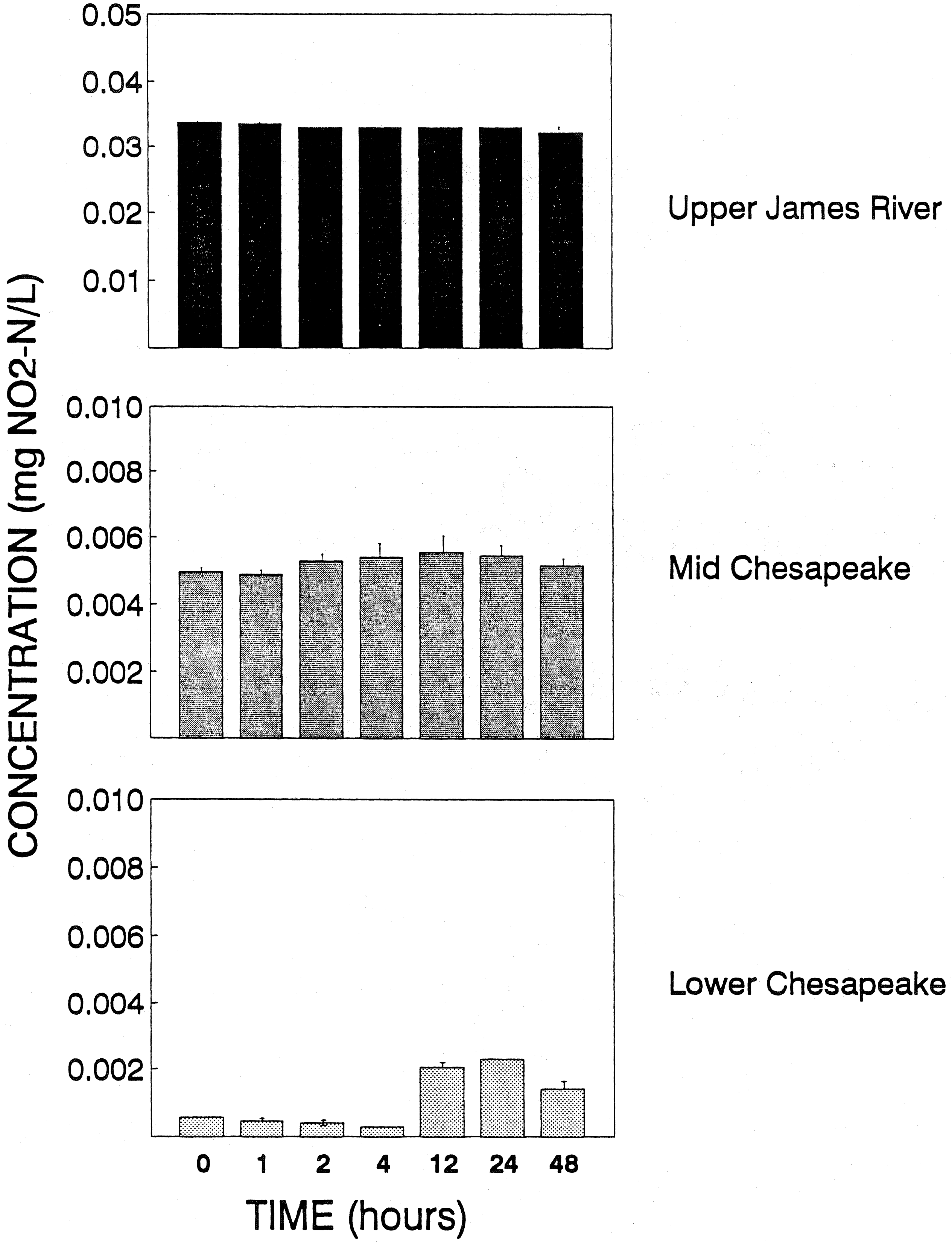
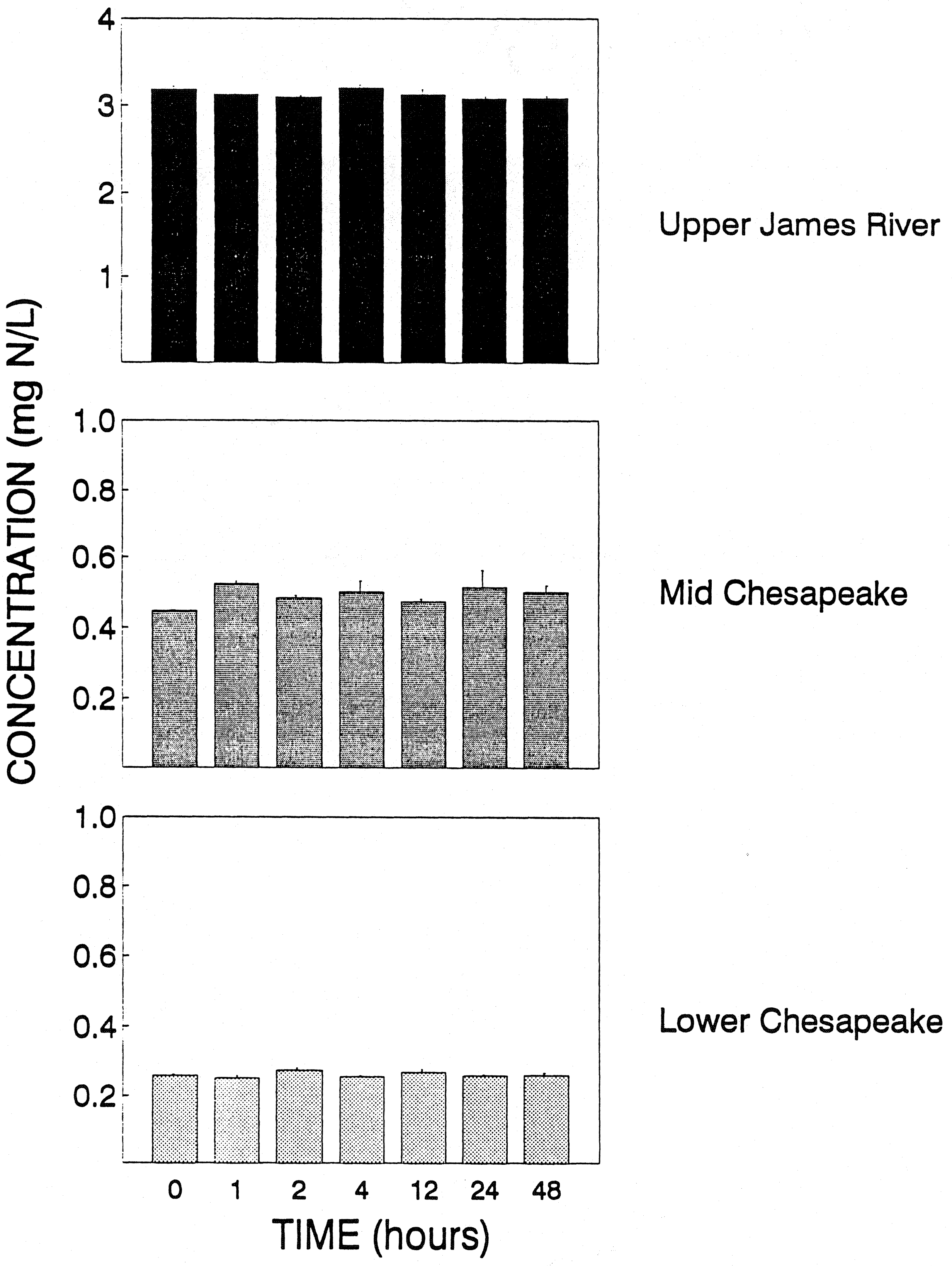


Figure 5. Total dissolved nitrogen in the upper James River and mid and lower Chesapeake Bay.



no change between the beginning concentrations and those values obtained after 48 hours. The 1-way ANOVA for subsampling period showed no significant ($P=0.3200$) differences among subsampling periods in mean TDN concentration.

Essentially no change in mean concentration between 0 and 48 hour samplings was noted for the Lower Chesapeake Bay TDN data. Coefficients of variation for within sampling reproducibility were less than 10%. The 1-way ANOVA for subsampling period showed no significant ($P=0.2208$) differences among subsampling periods in mean TDN concentration.

Dissolved Organic Nitrogen (DON): DON was calculated by subtracting the sum of the mean ammonium and nitrite+nitrate concentrations for each sampling period from the mean TDN concentration for that same sampling period. The resulting dissolved organic nitrogen concentrations reveal the considerable differences in the concentrations of this nutrient between the sampling sites (Figure 6).

The sample collected in the Upper James River contained essentially no dissolved organic nitrogen. More than 80% of the TDN fraction was comprised of ammonium plus 15% was NO_2+NO_3-N. In some cases the mean concentration of ammonium and nitrite and nitrate exceeded the corresponding mean TDN concentration.

In contrast, nitrite+nitrate accounted for only 32% of the TDN and DON comprised 60% of the Mid Chesapeake Bay sample. Ninety percent of the Lower Chesapeake Bay dissolved nitrogen samples was DON.

Small changes as a function of time with no observed trends in the mean DON values indicated stable conditions in the Mid and Lower Chesapeake Bay samples. No statistical analyses could be conducted on these data.

Silicate(Si): Concentrations of dissolved silicate at Upper James River location averaged nearly 3 mg Si/l. A very slight decrease (4%) with time was noted and coefficients of variation for within sampling variability were less than 2%. The 1-way ANOVA for subsampling period showed significant ($P<0.00001$) changes in Si concentration with time. Tukey's pairwise comparison of means revealed mean Si concentration at time 0 hour to be significantly greater than at all times after 1 hour. There was no significant difference among times 2 through 48 hours in mean Si concentration.

The Mid Chesapeake Bay concentrations were approximately one sixth of the Upper James River concentrations and no change over time was seen, as depicted in Figure 7. The 1-way ANOVA for subsampling period revealed no significant ($P=0.5439$) difference in Si concentration over time.

Figure 6. Dissolved organic nitrogen in the upper James River and mid and lower Chesapeake Bay.

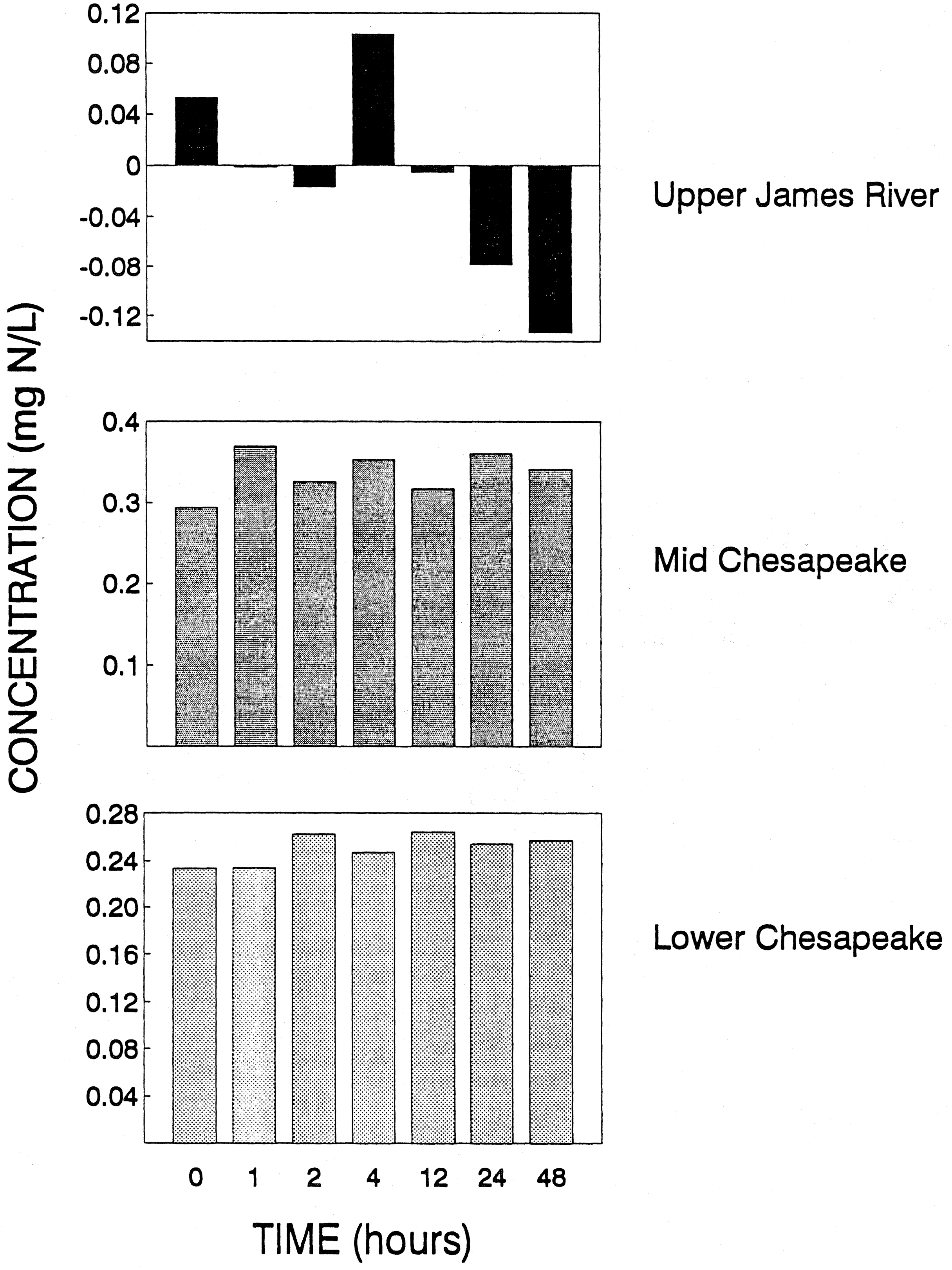
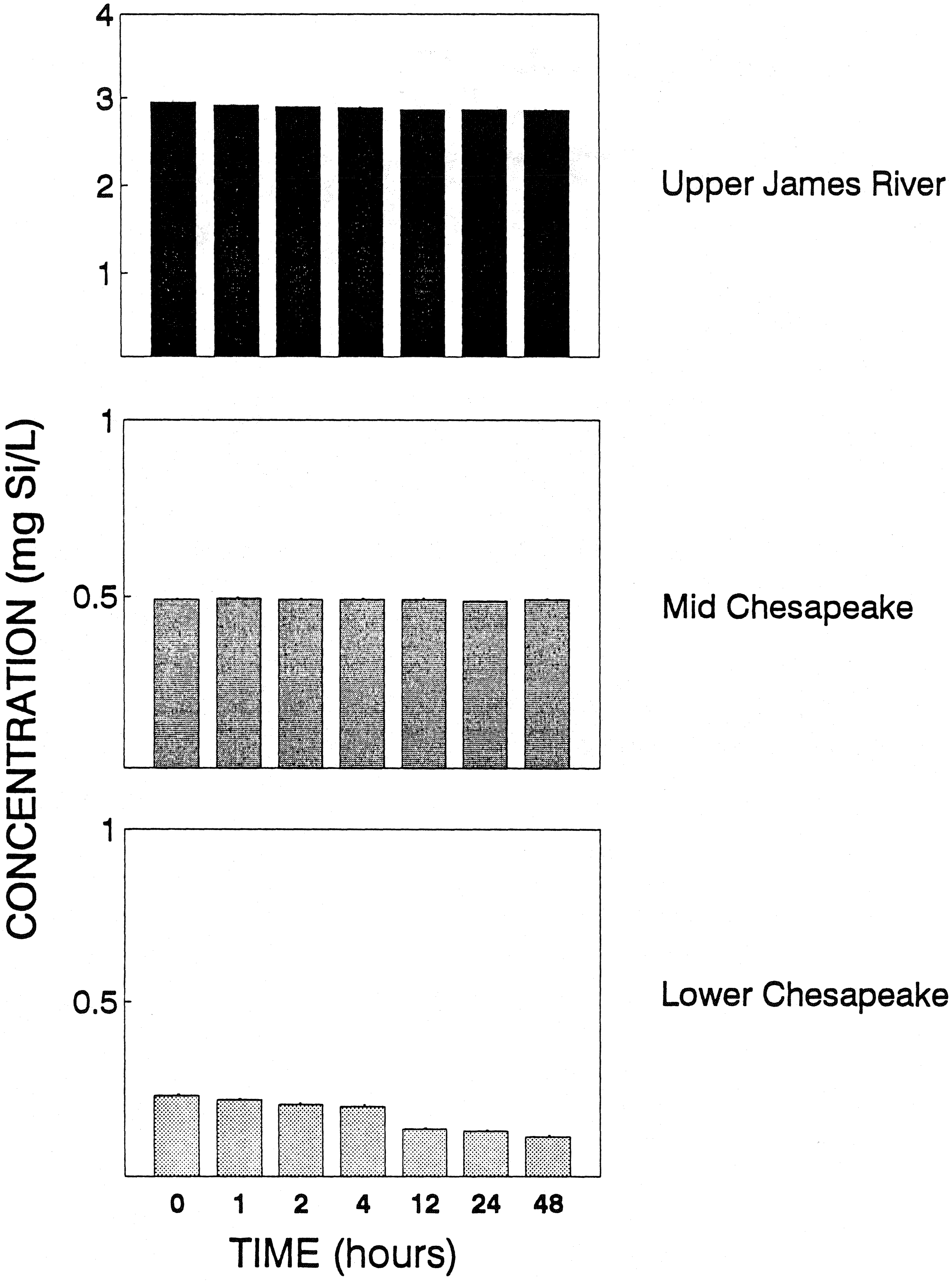


Figure 7. Dissolved silicate in the upper James River and mid and lower Chesapeake Bay.



Mean silicate concentration from the Lower Chesapeake Bay sample was 0.23 mg Si/l at time 0, but by 48 hours decreased to 0.11 mg Si/l. This represents a 50% decline during 48 hours. The 1-way ANOVA for subsampling period showed significant ($P<0.00001$) differences among subsampling periods in mean Si concentration. Tukey's pairwise comparison of means revealed consistent significant decreases in Si concentration over time.

Total Dissolved Phosphorus (TDP): A modest 18% decline in mean TDP values was noted between 0 and 48 hours for the Upper James River sample (Figure 8). Coefficients of variation of 1-9% were noted in comparing within sample period reproducibility. The 1-way ANOVA for subsampling period revealed significant ($P=0.0003$) differences in mean TDP concentration over time. Tukey's pairwise comparison of means revealed TDP concentration at time 48 hours were significantly lower than at times 0 through 4 hours. There were no significant differences among mean TDP concentrations measured at times 0 through 24 hours.

Concentrations of TDP from the sample collected in Mid Chesapeake Bay were an order of magnitude lower than those from the other two sites with correspondingly high percent coefficients of variation. Concentrations increased between 0 and 1 hour, but no trends were observed after that time. A 16% increase in concentration occurred between the mean concentrations at times 0 and 48 hours. The 1-way ANOVA for subsampling period revealed significant ($P=0.0461$) differences over time in mean TDP concentration. Tukey's pairwise comparison of means showed TDP concentration at time 0 hour was significantly lower than at time 1 hour. There were no significant differences among all other subsampling periods in mean TDP concentration.

There was very little change during the study period in TDP concentrations from the sample collected in the Lower Chesapeake Bay. Within sampling variability was small (<5%) and only a 4% decrease in concentration was found between time 0 and 48 hour mean concentrations. The 1-way ANOVA for subsampling period showed significant ($P<0.00001$) differences with time in mean TDP concentration. Tukey's pairwise comparison of means revealed mean TDP concentrations significantly greater ($P<0.05$) during 1, 2, 4, 12 and 24 hours than at time 0 and hour 48.

Phosphate: Mean phosphate concentrations declined by nearly 15% between time 0 and 48 hours for the sample collected in the Upper James River. Within sampling variation was always less than 5%. The 1-way ANOVA for subsampling period showed significant ($P<0.00001$) differences over time in mean phosphate concentration. Tukey's pairwise comparison of means revealed a consistent significant decline in mean phosphate concentration with time.

Concentrations reported for the Mid Chesapeake Bay were an order of magnitude lower than those from the Upper James River. Within sampling variability was

Figure 8. Total dissolved phosphorus in the upper James River and mid and lower Chesapeake Bay.

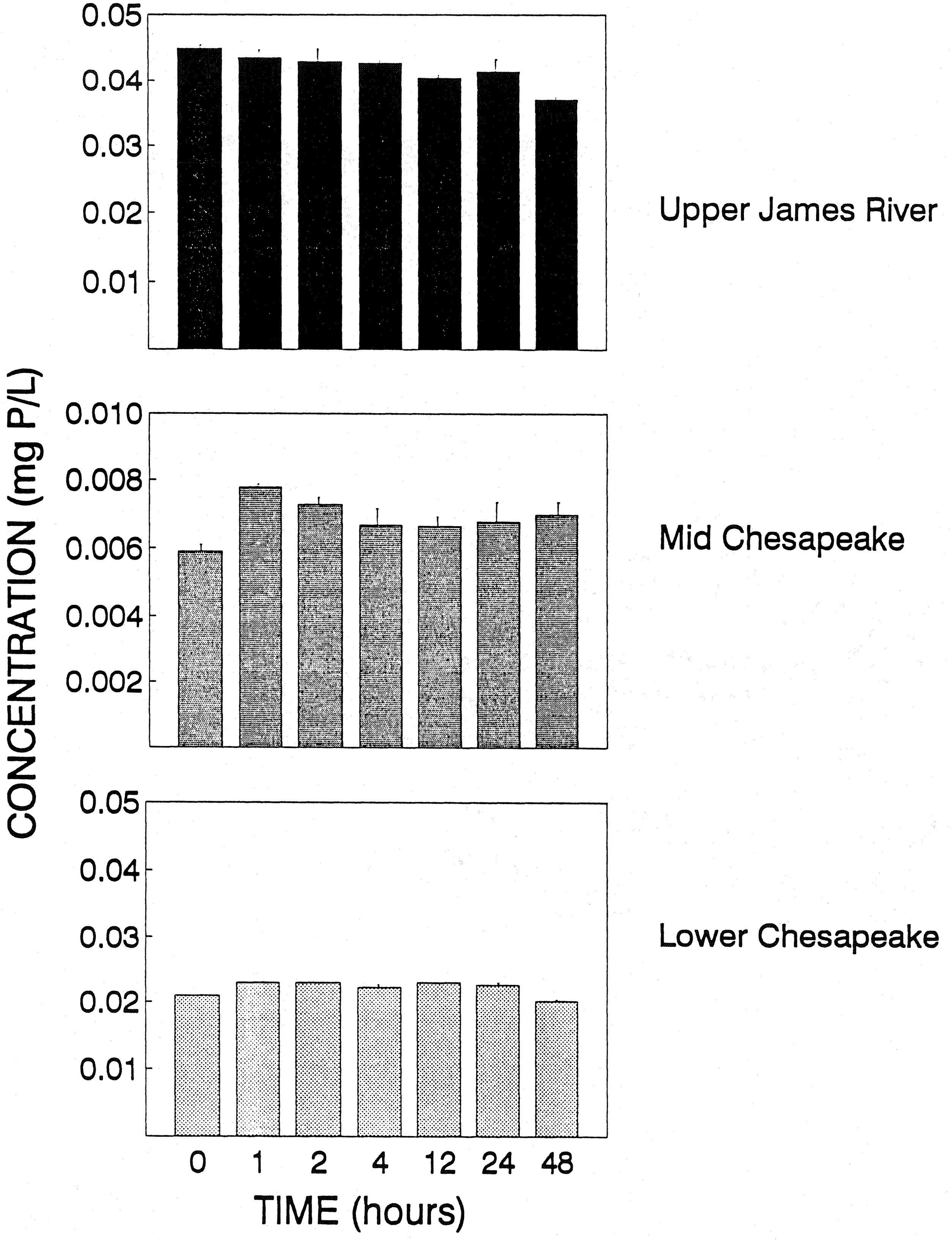
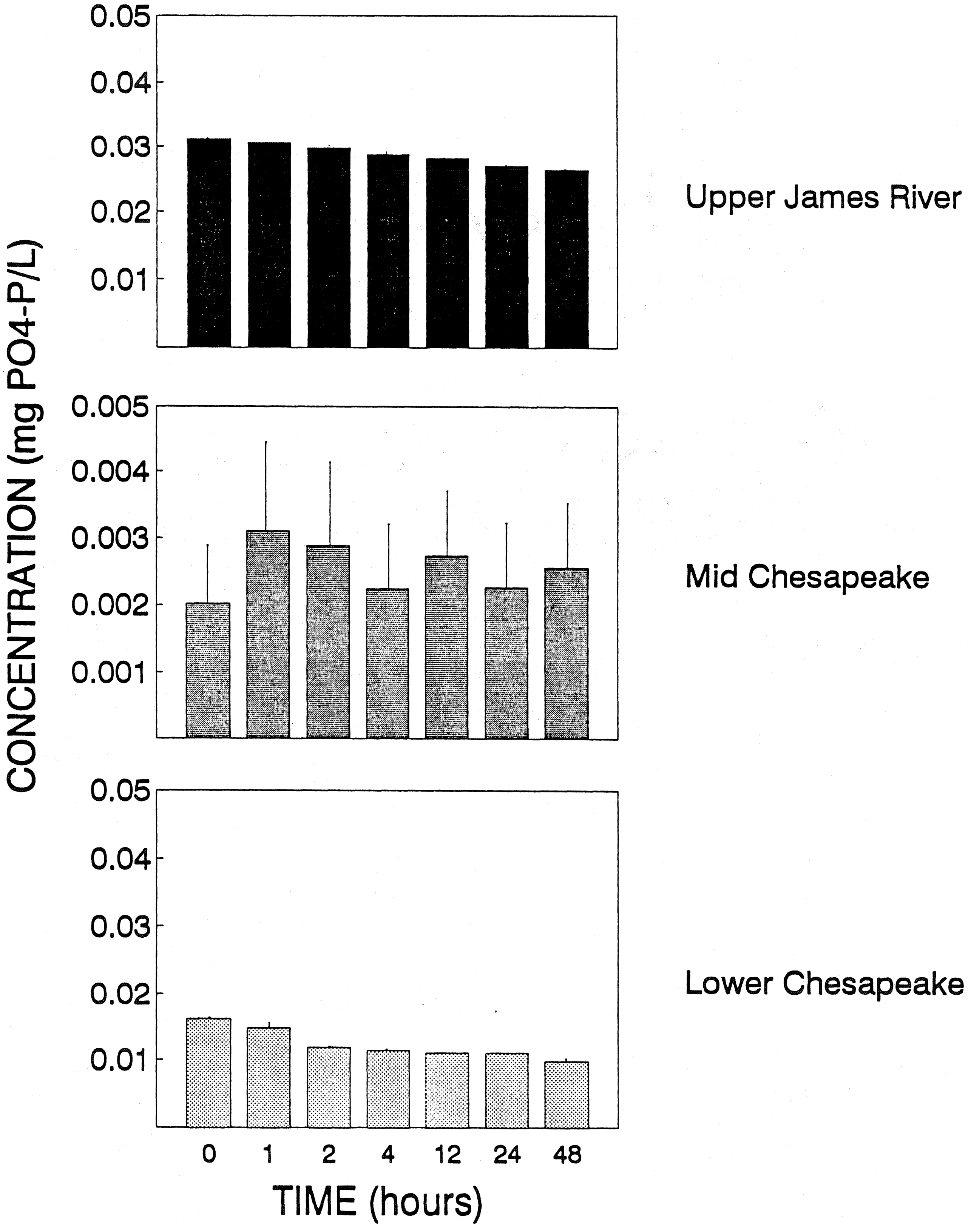


Figure 9. Dissolved phosphate in the upper James River and mid and lower Chesapeake Bay.



substantially higher (6-40%) but with no clearly defined trends. Because of large within sampling variability, the actual percent change, if any, was difficult to determine. The 1-way ANOVA for subsampling period showed no significant (P=0.1138) differences among subsampling periods in mean phosphate concentration.

Phosphate concentrations in the Lower Chesapeake Bay sample continually declined as a function of time (Figure 9). A 40% decline in mean phosphate values was noted from beginning to end of the experiment. The 1-way ANOVA for subsampling period showed significant (P<0.00001) differences in mean phosphate concentration over time. Tukey's pairwise comparison of means showed mean phosphate concentrations at times 0 and 1 hours were significantly greater than at all other subsampling periods. There was no significant difference among times 2 through 24 hours or times 4 through 48 hours in mean phosphate concentration.

PARTICULATE PARAMETERS

Particulate Phosphorus: Concentrations of particulate phosphorus were approximately three times higher for the Upper James River sample than those reported for the Lower Chesapeake Bay site and more than four times greater than the Mid Chesapeake Bay sample (Figure 10). The Upper James River sample's replicate analyses provided very low percent coefficients of variation (<6%) and the concentration from the first sample collected at time 0 was only 4% lower than the mean concentration reported at time 48 hours (0.073 vs 0.076 mg P/l, respectively).

For the Upper James River site, 1-way ANOVA for subsampling period showed significant (P=0.0258) differences in mean particulate phosphorus concentration with time. Tukey's pairwise comparison of means showed mean particulate phosphorus concentrations at time 0 hour were significantly lower than at times 1 and 24 hours. There were no significant differences among mean particulate phosphorus concentrations measured at times 1 through 48 hours.

For the sample collected in Mid Chesapeake Bay, the 1-way ANOVA for subsampling period revealed no significant (P= 0.2746) differences among subsampling periods in mean particulate phosphorus concentration. Coefficients of variation among sample sets were generaly less than 5%.

A three percent change in concentraions was found for time 0 versus time 48 hours (0.0216 vs 0.0222 mg P/l, respectively) in the Lower Chesapeake Bay sample. Percent coefficients of variation were also quite small (<6%). The Lower Chesapeake Bay sample's 1-way ANOVA for subsampling period showed significant (P=0.0007) differences in mean particulate phoshphorus concentration over time. Tukey's pairwise comparison of means showed mean particulate phosphorus concentration at time 0 hour was significantly lower than at times 4 and 24 hours. At time 4 hours, mean

Figure 10. Particulate phosphorus in the upper James River and mid and lower Chesapeake Bay.

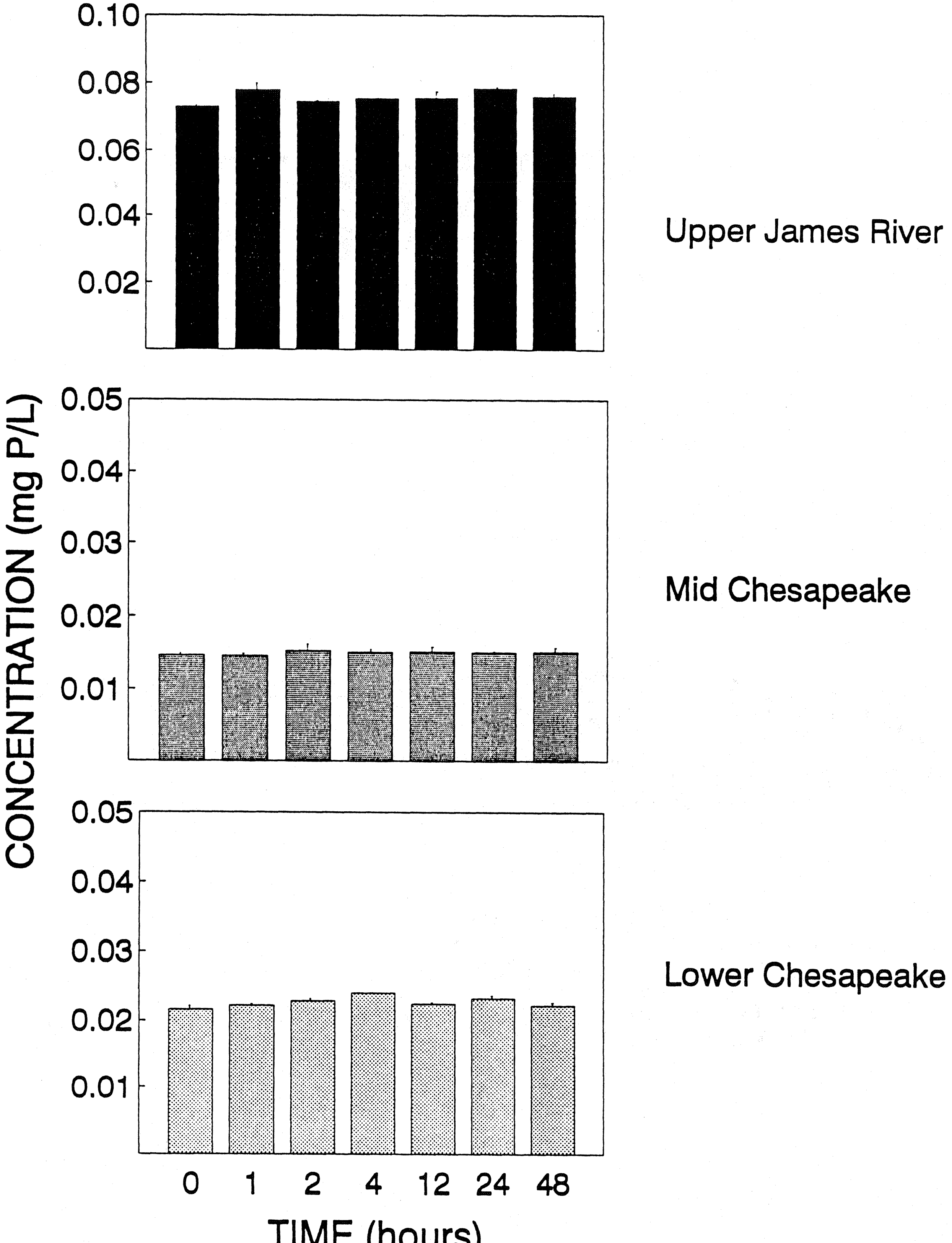


Figure 11. Particulate carbon in the upper James River and mid and lower Chesapeake Bay.

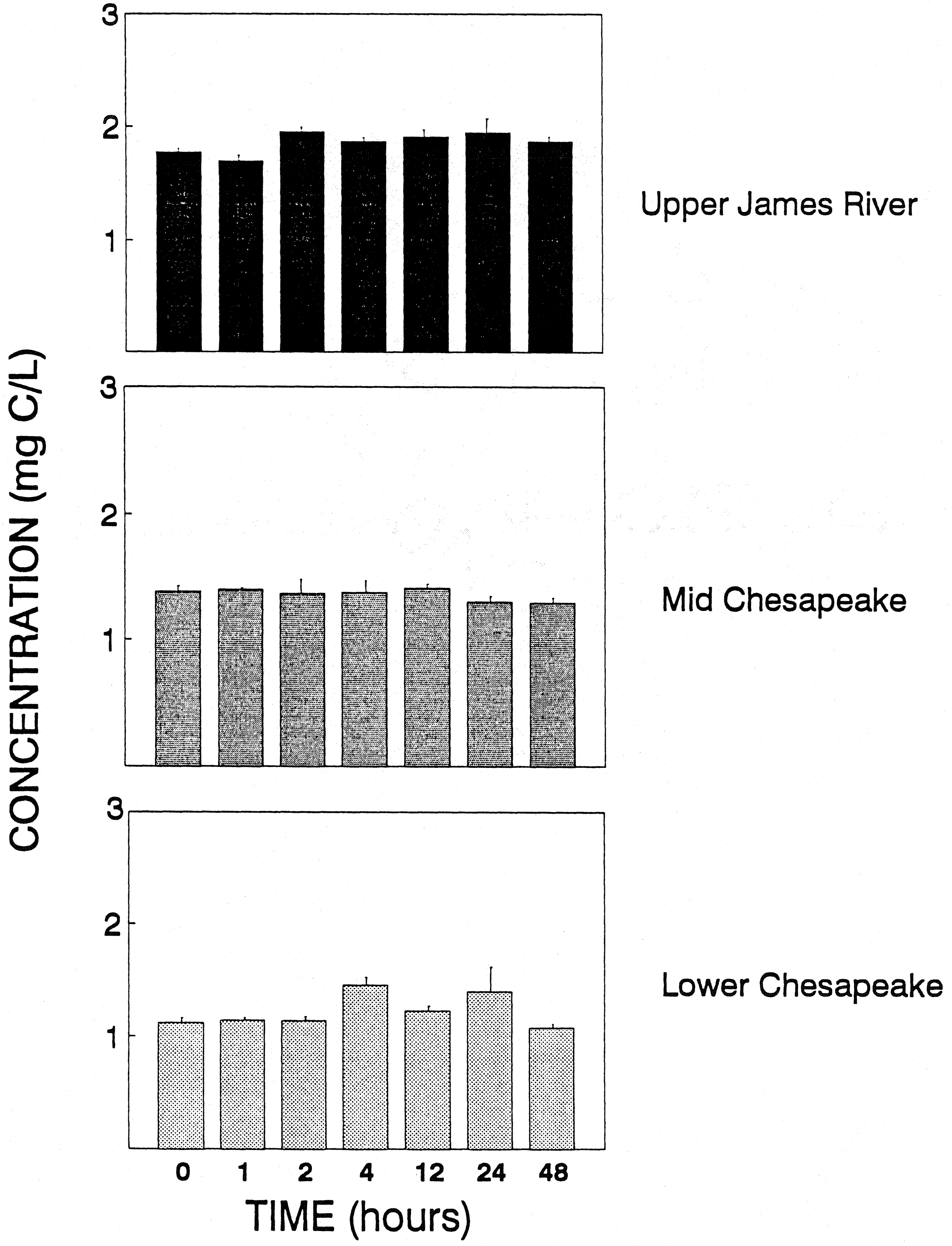
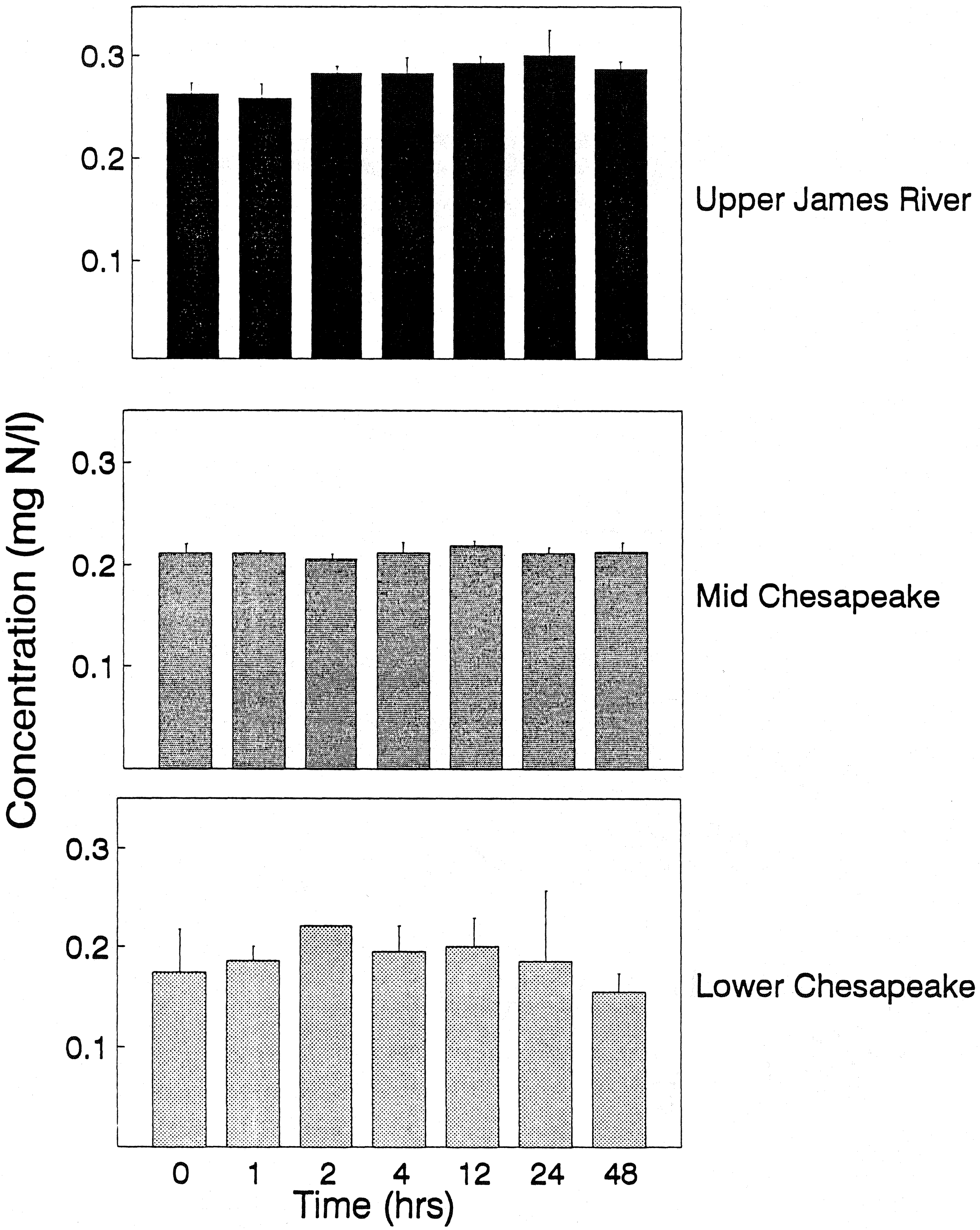


Figure 12. Particulate nitrogen in the upper James River and mid and lower Chesapeake Bay.



particulate phosphorus concentration was significantly greater than at times 0, 1, 12 and 48 hours. There was no significant difference among subsampling periods time 1, 2, 12, 24 and 48 hours in mean particulate phosphorus concentration.

<u>Particulate Carbon (Figure 11)</u>: Upper James River: The 1-way ANOVA for subsampling period showed no significant (P=0.0537) difference between subsampling periods in mean particulate carbon concentration.

Mid Chesapeake Bay: A one way ANOVA revealed that there was a significant (P=0.0380) change in particulate carbon concentrations as a function of time; however, follow up analysis using Tukey's pairwise comparison of means showed no significant differences among time periods for particulate carbon concentrations.

Lower Chesapeake Bay: The 1-way ANOVA for subsampling period showed no significant (P=0.0935) difference in particulate carbon concentration with time. In some instances, incomplete data sets were used to compile mean and standard deviations of ODUs particulate C and N data.

<u>Particulate Nitrogen (Figure 12)</u>: Upper James River: The 1-way ANOVA for subsampling period showed significant differences over time in mean particulate nitrogen concentrations. Tukey's pairwise comparison of means showed mean particulate nitrogen concentration at time 1 hour was significantly lower than at times after 4 hours and concentration at time 0 hour was significantly lower than at times 12 and 24 hours. There were no significant differences among mean particulate nitrogen concentrations measured at times 2 through 48 hours or among concentrations measured at times 0 through 4 hours.

Mid Chesapeake Bay: The 1-way ANOVA for subsampling period showed no significant (P=0.0543) differences among particulate nitrogen concentrations during the length of this experiment. Mean particulate nitrogen concentrations ranged from 0.212 mg N/l at time zero to 0.218 mg N/l at hour 48. Within sampling period reproducibility was also very close, with coefficients of variation 5% or less.

Lower Chesapeake Bay: The 1-way ANOVA for subsampling period showed no significant (P=0.8116) differences among subsampling periods in mean particulate nitrogen concentration. Relatively high percent coefficients of variation (>10%) coupled with incomplete data sets in five of the seven sampling periods make interpretation difficult for this ODU data set.

<u>Total Suspended Solids (TSS)</u>: Upper James River: The 1-way ANOVA for subsampling period showed significant (P=0.0001) differences in mean TSS concentration with time. The mean TSS concentration at time 1 hour was significantly greater than at all other subsampling periods which apparently caused the Tukey's

pairwise comparison of means to show a significant difference with time. There was no significant difference among times 0, 2, 4, 12, 24 and 48 hours in mean TSS concentration.

Mid Chesapeake Bay: There was no significant change (P=0.9673) in total suspended solids concentrations with time.

Lower Chesapeake Bay: The 1-way ANOVA for subsampling period showed significant (P<0.00001) differences in mean TSS concentration with time. Tukey's pairwise comparison of means showed no significant differences in mean TSS concentration measured at times 0, 1, 2, 4 and 24 hours. Mean TSS concentrations at times 24 and 48 hours were significantly lower than at times 1 through 12 hours.

Results for the three stations are presented in Figure 13. With the exception of one time period (1 hour), the Upper James River data indicated no obvious trends as a function of time. Percent coefficients of variation were generally less than 10%

The suspiciously high TSS value from the upper James River may have been a sample and/or sample partitioning artifact.

TSS concentrations from the lower Chesapeake station demonstrated a decreasing trend from 12-48 hours. While not as pronounced, this same trend was noted in the chlorophyll data for this same station. This could also be a sampling artifact where senescing phytoplankton (lower chlorophyll levels) sank to the bottom and were not adequately resuspended when sampling at 24 and 48 hours.

<u>Chlorophyll-a:</u> Upper James River: The 1-way ANOVA for subsampling period showed significant (P=0.0021) differences in mean chlorophyll-a concentration with time. Tukey's pairwise comparison of means revealed that the mean chlorophyll-a concentration at time 0 hour was significantly lower than at times 2 through 24 hours. There was no significant difference among subsampling periods 1 through 48 hours in mean chlorophyll-a concentration.

Mid Chesapeake Bay: The 1-way ANOVA for subsampling period showed no significant (P=0.1008) difference in mean chlorophyll-a concentration over time.

Lower Chesapeake Bay: The 1-way ANOVA for subsampling period showed significant (P=0.0001) differences in mean chlorophyll-a concentration with time. Tukey's pairwise comparison of means revealed no significant difference in mean chlorophyll-a concentration among subsampling periods 1, 2, 4, 24 and 48 hours. Mean chlorophyll-a concentration at time 0 hour was significantly lower than at times 4 through 48 hours.

Chlorophyll data for all sites can be found in Figure 14. High coefficients of variation

Figure 13. Total suspended solids in the upper James River and mid and lower Chesapeake Bay.

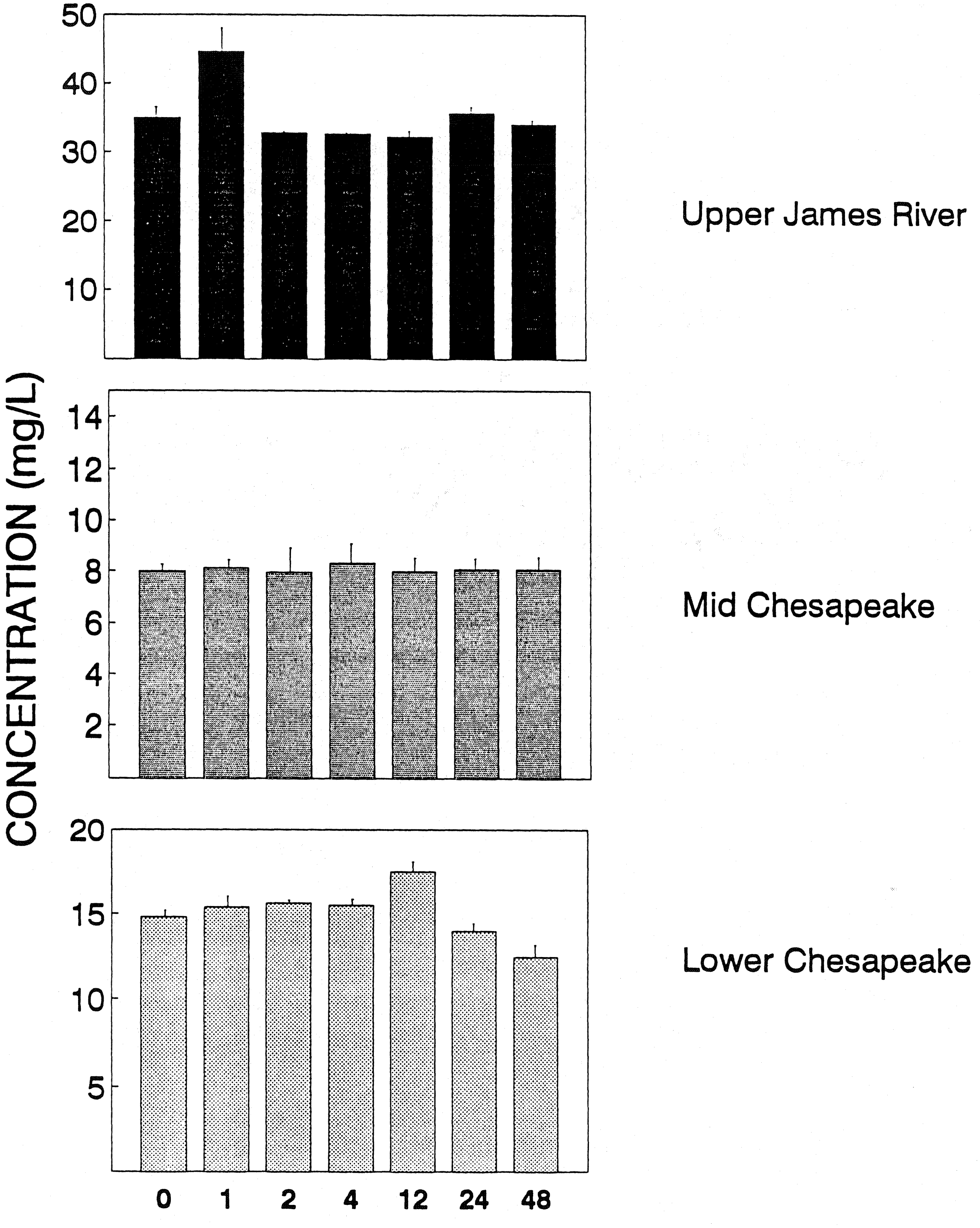
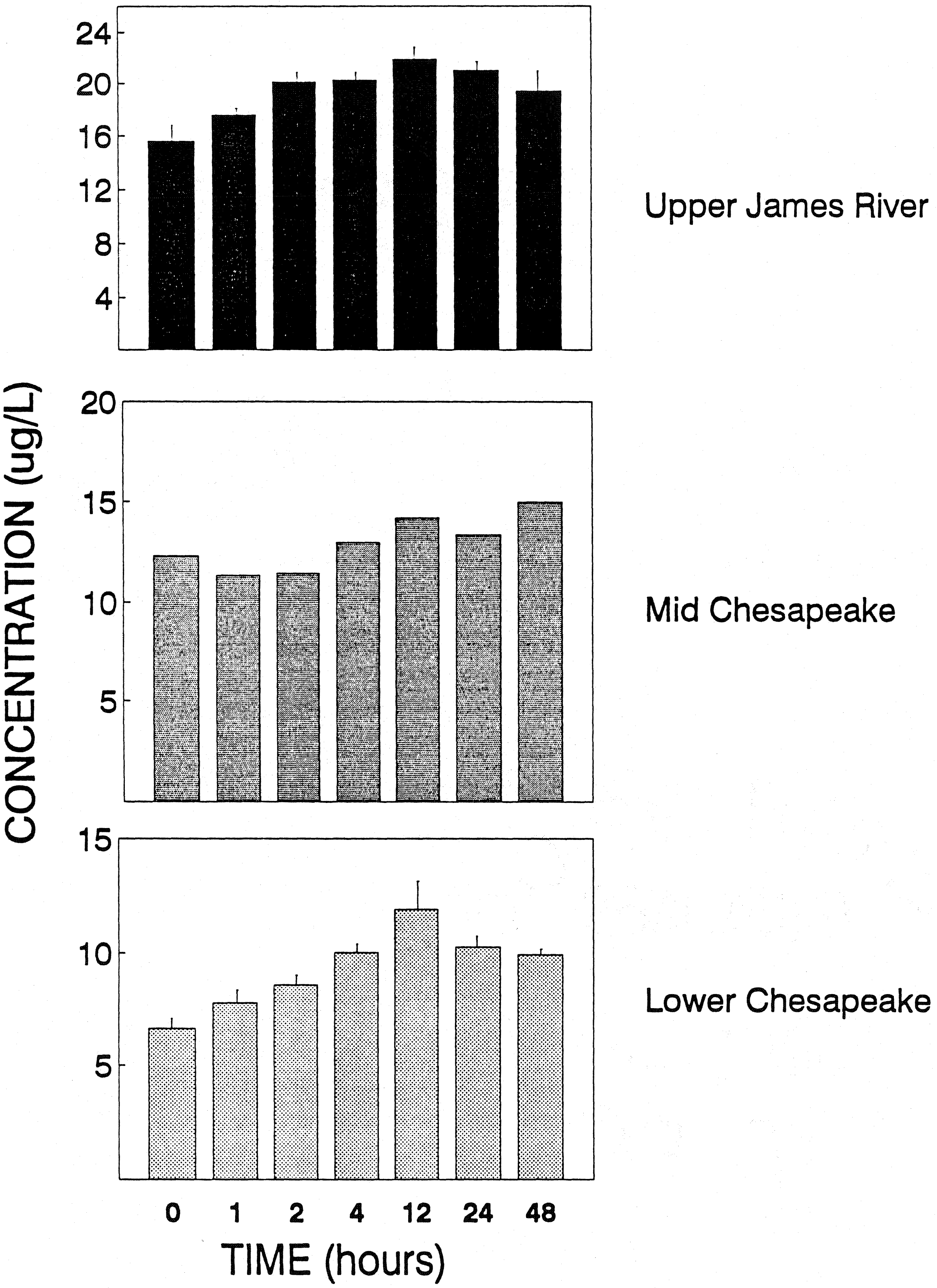


Figure 14. Chlorophyll-a in the upper James River and mid and lower Chesapeake Bay.



(>10%) are present in many of the subsets of all three laboratories. The Upper James River data yielded mean concentrations ranging from 15.6-21.9 ug/l. The Mid Chesapeake Bay data yielded mean concentrations renging from 4.24-5.41 ug/l. The Lower Chesapeake Bay data yielded mean concentrations ranging from 6.64-11.94 ug/l. Given the high degree of field, sampling and analytical variation associated with this method, the resulting upward trends in chlorophyll concnetration are surprisingly consistent within each site.

DISCUSSION AND CONCLUSIONS

The results presented in this study provide necessary data for helping to determine the critical holding time of samples before they require filtration. These data have also substantiated that the sampling procedures currently in place in the mainstem and in many of the tributaries are appropriate. The importance of immediate filtration of these samples is exemplified in the clear downward trend in concentration shown in the ammonium data from the Lower Chesapeake Bay. Had this sample not been filtered immediately, that concentration would have been quickly altered and the actual concentration significantly underestimated. It is also noteworthy that a comparison of chlorophyll and ammonium results show the distinct inverse relationship between these two analytes. As ammonium concentrations decreased, chlorophyll a concentrations (an indicator of algal biomass) increased. It is likely that algal biomass increased as a result of phytoplanktonic uptake of ammonium.

At least four factors must be considered in attempting to determine how long a sample can be held before being partitioned into particulate and dissolved fractions:

- The plankton population present in the water column at that point in time.
- The expected nutrient concentrations (high, low, etc.).
- The expected turnover time.
- The data quality objectives of the study.

There are at least two possible scenarios involving the first three factors. First, If nutrient concentrations are high and uptake rates are low, the turnover time is long, indicating a large supply of nutrients relative to demand. These conditions would be indicative of a situation where samples could be held chilled and in the dark for several hours before being processed.

Alternatively, often when nutrient concentrations are low, phytoplankton uptake rates are elevated and nutrient turnover times are short, due to the small supply relative to demand (Fisher, et al, 1992). This type of situation would dictate immediate filtration of the sample.

The ultimate decision concerning how long filtration of a whole water sample can be delayed before being processed resides with the individuals designing the program. Their data quality objectives must address certain questions pertaining to the amount of variability that would be acceptable in their nutrient data. For example, do the data quality objectives prohibit the occurrence of a 10% change in concentration of a particular analyte while the sample is waiting 36 hours to be filtered?
If so, then the samples need to be filtered prior to that time to ensure a <10% difference.

It also seems logical that data quality objective decisions should be based on the biological population present in the water column, the expected nutrient concentrations and the expected turnover times of those nutrients. The sample from the Upper James River frequently typifies the type of water which would be collected as part of a watershed water quality monitoring program. It probably depicts a scenario where the nutrient supply is high and the demand is low. These conditions suggest a long turnover time. These data indicate, with one exception (phosphate), that whole water samples from high nutrient freshwater can be kept chilled and in the dark for up to 48 hours without appreciable change in nutrient concentration. However, the data cannot describe what conditions will be like at other times of the year or at other locations on the river. Do the concentrations of nutients change seasonally and/or spatially to such a degree that turnover times are much shorter? We know this occurs throughout the mainstem (Glibert, et al, 1995). Does it also occur in upland creeks within a watershed? For example, a review of Maryland Dept. of Natural Resources Watershed Restoration nutrient data for the Pocomoke River indicates extreme variations in nitrate concentrations from the seven stations sampled as part of this project. Concentrations in late October, 1996 ranged from 0.008-14.56 mg NO3-N/l. This concentration range would dictate immediate filtration of all samples- which is the sampling procedure. The low nitrate concentrations found at one site closely approximate concentrations found at the Lower Chesapeake station. Nitrite+nitrate concentrations at the lower Chesapeake station declined substantially during the 48 hours of this experiment.

Ten months (January-October, 1996) of ammonium data at one station located on German Branch (a freshwater creek located on Maryland's Eastern Shore), yielded concentrations ranging from barely detectable (0.003 mg NH4-N/l) to 0.512 mg NH4-N/l. Data from our present study indicate that ammonium concentrations less than approximately 0.02 mg N/l require immediate filtration. Data from German Branch show a more than two order of magnitude difference in concentration at one station during a 10 month period. Obviously, field sample partitioning at German Branch has been a wisely executed part of the sampling protocol.

The immediacy of partitioning a sample depends on the ambient concentrations and turnover time at the season of the year when nutrient concentrations are lowest and their turnover times shortest. Field sampling and sample partitioning protocols should remain constant throughout the study to avoid the possibility of changes in protocols that are instituted too tardily or unanticipated changes in the phytoplankton population.

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Chlorophyll-a

VIMS

Time Period

	0	1	2	4	12	24	48
	14.658	19.09	21.146	20.345	20.506	18.944	13.884
	17.622	18.022	18.423	18.65	24.297	22.562	20.853
	12.896	16.02	22.561	22.428	24.297	20.118	23.95
	13.423	18.023	20.118	19.384	20.706	20.826	19.091
	19.384	16.687	18.423	20.559	19.825	22.748	19.358
Mean	15.60	17.57	20.13	20.27	21.93	21.04	19.43
Std. Dev.	2.7993	1.2147	1.7867	1.4279	2.1887	1.6219	3.6515
%CV	17.95	6.91	8.87	7.04	9.98	7.71	18.80
N	5	5	5	5	5	5	5
Std. Error	1.2519	0.5432	0.7991	0.6386	0.9788	0.7254	1.6330

CBL (Feb.96)

Time Period

	0	1	2	4	12	24	48
	12.03	9.67	10.14	11.88	12.59	12.9	16.85
	11.57	12.16	13.93	12.56	15.76	11.81	13.06
	13	11.85	12.87	15.73	13.15	15.39	17.41
	11.85	14.89	8.61	9.51	14.43	9.7	12.84
	13.12	8.15	11.72	15.27	15.14	17.04	14.83
Mean	12.31	11.34	11.45	12.99	14.21	13.37	15.00
Std. Dev.	0.7017	2.5739	2.1226	2.5609	1.3289	2.9014	2.1029
%CV	5.70	22.69	18.53	19.71	9.35	21.70	14.02
N	5	5	5	5	5	5	5
Std. Error	0.3138	1.1511	0.9492	1.1453	0.5943	1.2975	0.9404

ODU

Time Period

	0	1	2	4	12	24	48
	6.6	8	7.2	10.7	17	12.2	9.6
	6.7	7	7.8	8.9	10.5	10.4	9.9
	7.7	6.2	9.4	10.8	10.7	9.1	9.4
	5	9.7	9.1	9.4	10.5	9.9	10.1
	7.2	8	9.4	10.4	11	9.8	10.8
Mean	6.64	7.78	8.58	10.04	11.94	10.28	9.96
Std. Dev.	1.0164	1.3122	1.0159	0.8444	2.8360	1.1692	0.5413
%CV	15.31	16.87	11.84	8.41	23.75	11.37	5.43
N	5	5	5	5	5	5	5
Std. Error	0.4545	0.5869	0.4543	0.3776	1.2683	0.5229	0.2421

APPENDIX A. Addresses of Participating Laboratories

Applied Marine Research Laboratory
Old Dominion University
1034 West 45th Street
Norfolk, VA 23529

Contact: Mr. Steve Sokolowski
(757)-664-1043

Virginia Institute of Marine Science
Nutrient Laboratory
Gloucester Point, VA 23062

Contact: Ms. Carol Pollard
(804)-642-7213

Chesapeake Biological Laboratory
Nutrient Analytical Services Laboratory
Solomons, MD 20688-0038

Contact: Mr. Carl Zimmermann
(410)-326-7252

Appendix B. Nutrient data provided by the three laboratories.

Ammonium

VIMS
Time Period

	0	1	2	4	12	24	48
	2.636	2.645	2.581	2.607	2.452	2.609	2.672
	2.625	2.661	2.615	2.613	2.677	2.624	2.694
	2.648	2.619	2.614	2.586	2.628	2.659	2.69
	2.597	2.618	2.669	2.591	2.629	2.645	2.709
	2.674	2.602	2.618	2.577	2.732	2.659	2.704
Mean	2.64	2.63	2.62	2.59	2.62	2.64	2.69
Std. Dev.	0.0284	0.0236	0.0316	0.0149	0.1050	0.0221	0.0144
%CV	1.08	0.90	1.21	0.57	4.00	0.84	0.53
N	5	5	5	5	5	5	5
Std. Error	0.0127	0.0106	0.0141	0.0067	0.0470	0.0099	0.0064

CBL

Time Period

	0	1	2	4	12	24	48
	0.007	0.01	0.007	0.003	0.011	0.011	0.014
	0.01	0.004	0.008	0.005	0.008	0.007	0.017
	0.007	0.005	0.008	0.006	0.007	0.011	0.02
	0.014	0.005	0.011	0.003	0.026	0.009	0.016
	0.007	0.006	0.006	0.004	0.012	0.008	0.017
Mean	0.009	0.006	0.008	0.004	0.013	0.009	0.017
Std. Dev.	0.0031	0.0023	0.0019	0.0013	0.0077	0.0018	0.0022
%CV	34.25	39.09	23.39	31.04	59.86	19.44	12.90
N	5	5	5	5	5	5	5
Std. Error	0.0014	0.0010	0.0008	0.0006	0.0034	0.0008	0.0010

ODU

Time Period

	0	1	2	4	12	24	48
	0.02	0.0128	0.0073	0.0041	ND	0.0001	0.0009
	0.0192	0.012	0.0112	0.0049	ND	0.0009	ND
	0.0224	0.0136	0.0065	0.0041	ND	0.0001	0.0001
	0.02	0.0105	0.0081	0.0049	ND	0.0001	0.0001
	0.0184	0.0097	0.0073	0.0033	ND	0.0009	
Mean	0.020	0.012	0.008	0.004	0.000	0.000	0.000
Std. Dev.	0.0015	0.0016	0.0018	0.0007	0.0000	0.0004	0.0005
%CV	7.48	13.72	22.69	15.71	ERR	104.33	125.97
N	5	5	5	5	5	5	3
Std. Error	0.0007	0.0007	0.0008	0.0003	0.0000	0.0002	0.0003

Dissolved Organic Carbon

VIMS

Time Period

	0	1	2	4	12	24	48
	4.85	4.56	4.5	4.36	4.26	4.745	4.37
	4.68	4.365	4.4	4.48	4.57	4.57	4.38
	4.69	4.63	4.47	4.51	4.53	4.73	4.5
	4.67	4.43	4.66	4.595	4.48	4.57	4.54
	4.55	4.4	4.57	4.46	4.7	4.68	4.66
Mean	4.69	4.48	4.52	4.48	4.51	4.66	4.49
Std. Dev.	0.1069	0.1129	0.0992	0.0850	0.1608	0.0847	0.1204
%CV	2.28	2.52	2.20	1.90	3.57	1.82	2.68
N	5	5	5	5	5	5	5
Std. Error	0.0478	0.0505	0.0444	0.0380	0.0719	0.0379	0.0539

CBL

Time Period

	0	1	2	4	12	24	48
	2.53	2.59	2.54	2.44	2.44	2.5	2.42
	2.48	2.57	2.48	2.56	2.51	2.47	2.49
	2.54	2.61	2.58	2.47	2.63	2.48	2.4
	2.51	2.54	2.52	2.44	2.53	2.4	2.43
	2.52	2.56	2.49	2.44	2.55	2.44	2.45
Mean	2.52	2.57	2.52	2.47	2.53	2.46	2.44
Std. Dev.	0.0230	0.0270	0.0402	0.0520	0.0687	0.0390	0.0342
%CV	0.92	1.05	1.60	2.10	2.71	1.59	1.40
N	5	5	5	5	5	5	5
Std. Error	0.0103	0.0121	0.0180	0.0232	0.0307	0.0174	0.0153

ODU

Time Period

	0	1	2	4	12	24	48
	2.74	2.47	2.32		1.58	2.62	2.5
	2.51	2.55	2.86	2.39	2.71	2.47	2.46
	2.47	2.53	2.44	2.27		2.47	2.69
	2.57	2.71	2.62	4.25		2.55	2.39
	2.85	2.43	2.68	2.88			2.39
Mean	2.63	2.54	2.58	2.95	2.15	2.53	2.49
Std. Dev.	0.1613	0.1073	0.2104	0.9075	0.7990	0.0723	0.1234
%CV	6.14	4.23	8.14	30.79	37.25	2.86	4.96
N	5	5	5	4	2	4	5
Std. Error	0.0721	0.0480	0.0941	0.4538	0.5650	0.0361	0.0552

Silicate

VIMS

Time Period

	0	1	2	4	12	24	48
	2.949	2.914	2.9	2.869	2.859	2.869	2.874
	3.053	2.923	2.919	2.884	2.861	2.861	2.839
	2.93	2.924	2.883	2.896	2.864	2.856	2.865
	2.947	2.923	2.903	2.902	2.872	2.874	2.882
	2.913	2.932	2.911	2.913	2.883	2.88	2.871
Mean	2.96	2.92	2.90	2.89	2.87	2.87	2.87
Std. Dev.	0.0549	0.0064	0.0135	0.0169	0.0098	0.0097	0.0164
%CV	1.85	0.22	0.46	0.59	0.34	0.34	0.57
N	5	5	5	5	5	5	5
Std. Error	0.0245	0.0029	0.0060	0.0076	0.0044	0.0043	0.0073

CBL

Time Period

	0	1	2	4	12	24	48
	0.5	0.5	0.5	0.49	0.51	0.49	0.49
	0.5	0.5	0.5	0.49	0.49	0.49	0.5
	0.49	0.5	0.49	0.5	0.49	0.49	0.5
	0.49	0.5	0.49	0.5	0.49	0.49	0.49
	0.49	0.49	0.49	0.49	0.49	0.49	0.49
Mean	0.49	0.50	0.49	0.49	0.49	0.49	0.49
Std. Dev.	0.0055	0.0045	0.0055	0.0055	0.0089	ERR	0.0055
%CV	1.11	0.90	1.11	1.11	1.81	0.00	1.11
N	5	5	5	5	5	5	5
Std. Error	0.0024	0.0020	0.0024	0.0024	0.0040	ERR	0.0024

ODU

Time Period

	0	1	2	4	12	24	48
	0.2242	0.2126	0.1952	0.1894	0.1371	0.1313	0.1139
	0.2358	0.2184	0.2184	0.2068	0.1371	0.1313	0.1197
	0.2358	0.2242	0.2068	0.2126	0.1313	0.1371	0.1139
	0.2242	0.2184	0.201	0.1836	0.1371	0.1255	0.1081
	0.23	0.2126	0.201	0.201	0.1371	0.1255	
Mean	0.23	0.22	0.20	0.20	0.14	0.13	0.11
Std. Dev.	0.0058	0.0049	0.0088	0.0120	0.0026	0.0049	0.0047
%CV	2.52	2.23	4.30	6.05	1.91	3.73	4.16
N	5	5	5	5	5	5	4
Std. Error	0.0026	0.0022	0.0039	0.0054	0.0012	0.0022	0.0024

TDP

VIMS

Time Period

	0	1	2	4	12	24	48
	0.046	0.042	0.042	0.044	0.042	0.047	0.037
	0.044	0.048	0.042	0.042	0.04	0.041	0.036
	0.043	0.041	0.038	0.043	0.04	0.039	0.038
	0.046	0.045	0.045	0.043	0.039	0.041	0.038
	0.046	0.042	0.048	0.042	0.041	0.039	0.036
Mean	0.045	0.044	0.043	0.043	0.040	0.041	0.037
Std. Dev.	0.0014	0.0029	0.0037	0.0008	0.0011	0.0033	0.0010
%CV	3.14	6.61	8.70	1.95	2.82	7.94	2.70
N	5	5	5	5	5	5	5
Std. Error	0.0006	0.0013	0.0017	0.0004	0.0005	0.0015	0.0004

CBL

Time Period

	0	1	2	4	12	24	48
	0.0065	0.0076	0.007	0.006	0.0067	0.0072	0.0084
	0.0062	0.0077	0.0069	0.0086	0.0061	0.0062	0.0072
	0.0056	0.0075	0.0069	0.0062	0.0067	0.0089	0.0058
	0.0056	0.008	0.0077	0.0061	0.006	0.0058	0.007
	0.0056	0.0081	0.0079	0.0065	0.0077	0.0058	0.0065
Mean	0.0059	0.0078	0.0073	0.0067	0.0066	0.0068	0.0070
Std. Dev.	0.0004	0.0003	0.0005	0.0011	0.0007	0.0013	0.0010
%CV	7.19	3.33	6.62	16.31	10.19	19.41	13.76
N	5	5	5	5	5	5	5
Std. Error	0.0002	0.0001	0.0002	0.0005	0.0003	0.0006	0.0004

ODU

Time Period

	0	1	2	4	12	24	48
	0.021	0.023	0.023	0.023	0.023	0.023	0.021
	0.021	0.023	0.023	0.023	0.023	0.023	0.02
	0.021	0.023	0.023	0.023	0.023	0.023	0.02
	0.021	0.023	0.023	0.021	0.023	0.021	0.02
	0.021	0.023	0.023	0.021	0.023	0.023	0.02
Mean	0.0210	0.0230	0.0230	0.0222	0.0230	0.0226	0.0202
Std. Dev.	ERR	ERR	ERR	0.0011	ERR	0.0009	0.0004
%CV	ERR	ERR	ERR	4.93	ERR	3.96	2.21
N	5	5	5	5	5	5	5
Std. Error	ERR	ERR	ERR	0.0005	ERR	0.0004	0.0002

PHOSPHATE

VIMS

Time Period

	0	1	2	4	12	24	48
	0.031	0.03	0.031	0.029	0.029	0.028	0.026
	0.031	0.031	0.03	0.029	0.028	0.027	0.026
	0.032	0.03	0.028	0.03	0.028	0.027	0.027
	0.031	0.031	0.03	0.029	0.028	0.027	0.026
	0.031	0.031	0.03	0.0269	0.028	0.026	0.027
Mean	0.031	0.031	0.030	0.029	0.028	0.027	0.026
Std. Dev.	0.0004	0.0005	0.0011	0.0011	0.0004	0.0007	0.0005
%CV	1.43	1.79	3.68	3.95	1.59	2.62	2.07
N	5	5	5	5	5	5	5
Std. Error	0.0002	0.0002	0.0005	0.0005	0.0002	0.0003	0.0002

CBL

Time Period; not salinity corrected

	0	1	2	4	12	24	48
	0.0022	0.0031	0.0025	0.0025	0.002	0.0021	0.0022
	0.0019	0.0028	0.0039	0.0021	0.0046	0.0021	0.0025
	0.0019	0.0047	0.0026	0.0022	0.0026	0.0026	0.0021
	0.0019	0.0023	0.0027	0.0022	0.0019	0.0024	0.0034
	0.0022	0.0026	0.0027	0.0022	0.0026	0.0021	0.0026
Mean	0.0020	0.0031	0.0029	0.0022	0.0027	0.0023	0.0026
Std. Dev.	0.0002	0.0009	0.0006	0.0002	0.0011	0.0002	0.0005
%CV	8.13	30.35	20.01	6.77	39.78	10.19	20.03
N	5	5	5	5	5	5	5
Std. Error	0.0009	0.0014	0.0013	0.0010	0.0012	0.0010	0.0011

ODU

Time Period

	0	1	2	4	12	24	48
	0.016	0.016	0.012	0.012	0.011	0.011	0.009
	0.016	0.016	0.012	0.011	0.011	0.011	0.011
	0.017	0.012	0.012	0.011	0.011	0.011	0.009
	0.016	0.016	0.011	0.012	0.011	0.011	0.009
	0.016	0.014	0.012	0.011	0.011	0.011	0.011
Mean	0.0162	0.0148	0.0118	0.0114	0.0110	0.0110	0.0098
Std. Dev.	0.0004	0.0018	0.0004	0.0005	ERR	ERR	0.0010
%CV	2.76	12.09	3.79	4.80	ERR	ERR	10.20
N	5	5	5	5	5	5	5
Std. Error	0.0002	0.0008	0.0002	0.0002	ERR	ERR	0.0004

Particulate Phosphorus

VIMS

Time Period

	0	1	2	4	12	24	48
	0.072	0.076	0.074	0.076	0.070	0.077	0.075
	0.071	0.086	0.075	0.075	0.080	0.079	0.077
	0.074	0.075	0.075	0.075	0.076	0.078	0.078
	0.074	0.076	0.075	0.076	0.078	0.079	0.073
	0.074	0.077	0.074	0.075	0.074	0.079	0.077
Mean	0.073	0.078	0.075	0.075	0.076	0.078	0.076
Std. Dev.	0.0014	0.0045	0.0005	0.0005	0.0038	0.0009	0.0020
%CV	1.94	5.80	0.73	0.73	5.09	1.14	2.63
N	5	5	5	5	5	5	5
Std. Error	0.0006	0.0020	0.0002	0.0002	0.0017	0.0004	0.0009

CBL (FEB.1996)

Time Period

	0	1	2	4	12	24	48
	0.0148	0.0146	0.0166	0.0154	0.0162	0.0151	0.0153
	0.0141	0.0147	0.0148	0.0144	0.0153	0.0152	0.0161
	0.0148	0.0142	0.0158	0.0152	0.0149	0.0150	0.0148
	0.0146	0.0149	0.0145	0.0152	0.0142	0.0150	0.0153
	0.0150	0.0146	0.0148	0.0152	0.0153	0.0152	0.0145
Mean	0.0147	0.0146	0.0153	0.0151	0.0152	0.0151	0.0152
Std. Dev.	0.0003	0.0003	0.0009	0.0004	0.0007	0.0001	0.0006
%CV	2.34	1.75	5.74	2.59	4.78	0.66	4.00
N	5	5	5	5	5	5	5
Std. Error	0.0002	0.0001	0.0004	0.0002	0.0003	0.0000	0.0003

ODU

Time Period

	0	1	2	4	12	24	48
	0.022	0.022	0.022	0.024	0.022	0.023	0.023
	0.02	0.022	0.022	0.024	0.023	0.022	0.022
	0.021	0.022	0.023	0.024	0.022	0.024	0.023
	0.022	0.023	0.023	0.024	0.022	0.023	0.022
	0.023	0.022	0.024	0.024	0.023	0.024	0.021
Mean	0.0216	0.0222	0.0228	0.0240	0.0224	0.0232	0.0222
Std. Dev.	0.0011	0.0004	0.0008	ERR	0.0005	0.0008	0.0008
%CV	5.28	2.01	3.67	ERR	2.45	3.61	3.77
N	5	5	5	5	5	5	5
Std. Error	0.0005	0.0002	0.0004	ERR	0.0002	0.0004	0.0004

Particulate Carbon

VIMS

Time Period

	0	1	2	4	12	24	48
	1.735	1.657	1.866	1.929	1.793	2.423	1.882
	1.898	1.635	1.949	1.961	1.94	1.842	1.845
	1.749	1.842	1.886	1.821	2.123	1.781	2.021
	1.789	1.797	2.074	1.802	1.862	1.827	1.766
	1.756	1.616	2.011	1.885	1.871	1.899	1.876
Mean	1.79	1.71	1.96	1.88	1.92	1.95	1.88
Std. Dev.	0.0660	0.1028	0.0866	0.0681	0.1260	0.2653	0.0923
%CV	3.70	6.01	4.42	3.62	6.57	13.58	4.92
N	5	5	5	5	5	5	5
Std. Error	0.0295	0.0460	0.0387	0.0305	0.0563	0.1187	0.0413

CBL (FEB.96)

Time Period

	0	1	2	4	12	24	48
	1.39	1.4	1.33	1.46	1.41	1.35	1.31
	1.38	1.41	1.55	1.45	1.4	1.33	1.24
	1.42	1.4	1.37	1.32	1.45	1.3	1.26
	1.31	1.38	1.28	1.25	1.36	1.23	1.29
	1.4	1.38	1.29	1.38	1.41	1.3	1.35
Mean	1.38	1.39	1.36	1.37	1.41	1.30	1.29
Std. Dev.	0.0418	0.0134	0.1099	0.0887	0.0321	0.0455	0.0430
%CV	3.03	0.96	8.06	6.47	2.28	3.49	3.33
N	5	5	5	5	5	5	5
Std. Error	0.0187	0.0060	0.0492	0.0397	0.0144	0.0203	0.0192

ODU

Time Period

	0	1	2	4	12	24	48
	1.08	1.1	1.21	1.74	1.27	2.28	1.11
	1.17	1.23	1.23	1.43	1.16	1.32	1.11
	1.1	1.18	1.14	1.39	1.27	1.15	1.03
	1.05	1.1	1.07	1.4		1.08	
	1.25	1.14	1.09	1.35		1.2	
Mean	1.13	1.15	1.15	1.46	1.23	1.41	1.08
Std. Dev.	0.0803	0.0557	0.0709	0.1580	0.0635	0.4964	0.0462
%CV	7.11	4.84	6.17	10.81	5.15	35.30	4.26
N	5	5	5	5	3	5	3
Std. Error	0.0359	0.0249	0.0317	0.0707	0.0367	0.2220	0.0267

Particulate Nitrogen

VIMS

Time Period

	0	1	2	4	12	24	48
	0.269	0.253	0.283	0.296	0.285	0.347	0.279
	0.276	0.248	0.275	0.294	0.3	0.288	0.294
	0.259	0.283	0.279	0.262	0.3	0.284	0.295
	0.26	0.257	0.285	0.27	0.288	0.29	0.279
	0.247	0.249	0.293	0.293	0.294	0.295	0.288
Mean	0.262	0.258	0.283	0.283	0.293	0.301	0.287
Std. Dev.	0.0110	0.0144	0.0068	0.0158	0.0068	0.0261	0.0078
%CV	4.19	5.59	2.40	5.59	2.33	8.69	2.71
N	5	5	5	5	5	5	5
Std. Error	0.0049	0.0064	0.0030	0.0071	0.0031	0.0117	0.0035

CBL (FEB.96)

Time Period

	0	1	2	4	12	24	48
	0.210	0.215	0.208	0.224	0.220	0.219	0.220
	0.211	0.214	0.212	0.222	0.218	0.214	0.211
	0.227	0.212	0.210	0.204	0.226	0.213	0.214
	0.203	0.211	0.201	0.202	0.215	0.203	0.220
	0.210	0.209	0.200	0.211	0.221	0.211	0.224
Mean	0.212	0.212	0.206	0.213	0.220	0.212	0.218
Std. Dev.	0.0089	0.0024	0.0054	0.0101	0.0041	0.0058	0.0052
%CV	4.18	1.13	2.62	4.75	1.85	2.75	2.39
N	5	5	5	5	5	5	5
Std. Error	0.0040	0.0011	0.0024	0.0045	0.0018	0.0026	0.0023

ODU

Time Period

	0	1	2	4	12	24	48
	0.186	0.195	0.221	0.223	0.223	0.309	0.173
	0.22	0.168		0.192	0.168	0.131	0.136
	0.116	0.175		0.171	0.211	0.159	0.159
	0.179	0.199				0.143	
		0.196				0.189	
Mean	0.18	0.19	0.22	0.20	0.20	0.19	0.16
Std. Dev.	0.0434	0.0141		0.0262	0.0289	0.0720	0.0187
%CV	24.75	7.55	0.00	13.39	14.41	38.67	11.98
N	4	5	1	3	3	5	3
Std. Error	0.0217	0.0063	0.0000	0.0151	0.0167	0.0322	0.0108

Total Suspended Solids

VIMS

Time Period

	0	1	2	4	12	24	48
	30.5	39.75	32.5	33.25	31.5	34.25	35.75
	32.75	58.25	32.5	32	30.75	34.5	34
	39.75	45.5	33.25	32.25	32.25	39.25	34.75
	37	41	33	33.25	35.5	35.5	32.75
	35	39	33	32.5	31.25	34.75	33.25
Mean	35.00	44.70	32.85	32.65	32.25	35.65	34.10
Std. Dev.	3.6012	7.9832	0.3354	0.5755	1.8957	2.0661	1.1937
%CV	10.29	17.86	1.02	1.76	5.88	5.80	3.50
N	5	5	5	5	5	5	5
Std. Error	1.6105	3.5702	0.1500	0.2574	0.8478	0.9240	0.5339

CBL (FEB.96)

Time Period

	0	1	2	4	12	24	48
	8	8.2	7.6	9.2	7.4	8.6	8.4
	8	8	8	7.6	8.4	8	8.4
	7.8	7.8	9.4	9	8.6	7.8	8.2
	7.8	8	6.8	8.2	8	8.4	7.2
	8.4	8.6	8	7.6	7.6	7.6	8.2
Mean	8.00	8.12	7.96	8.32	8.00	8.08	8.08
Std. Dev.	0.2449	0.3033	0.9423	0.7563	0.5099	0.4147	0.5020
%CV	3.06	3.74	11.84	9.09	6.37	5.13	6.21
N	5	5	5	5	5	5	5
Std. Error	0.1095	0.1356	0.4214	0.3382	0.2280	0.1855	0.2245

ODU

Time Period

	0	1	2	4	12	24	48
	14.9	14.4	16	16.5	18.1	15.1	12.6
	15.5	13.7	15.3	14.9	19	14.3	14.5
	13.6	16.6	15.9	15.8	15.6	14.3	11.3
	14.6	16.6	15.2	15	17.7	12.4	11.7
	15.7	15.8	15.8	15.5	17	14	
Mean	14.86	15.42	15.64	15.54	17.48	14.02	12.53
Std. Dev.	0.8325	1.3161	0.3647	0.6504	1.2755	0.9935	1.4245
%CV	5.60	8.53	2.33	4.19	7.30	7.09	11.37
N	5	5	5	5	5	5	4
Std. Error	0.3723	0.5886	0.1631	0.2909	0.5704	0.4443	0.7122

NO2+NO3

VIMS

Time Period

	0	1	2	4	12	24	48
	0.49	0.493	0.493	0.491	0.505	0.51	0.52
	0.49	0.496	0.496	0.49	0.508	0.515	0.519
	0.49	0.496	0.49	0.503	0.5	0.51	0.518
	0.495	0.493	0.488	0.495	0.497	0.514	0.513
	0.488	0.488	0.483	0.495	0.507	0.517	0.515
Mean	0.491	0.493	0.490	0.495	0.503	0.513	0.517
Std. Dev.	0.0026	0.0033	0.0049	0.0051	0.0047	0.0031	0.0029
%CV	0.53	0.66	1.01	1.03	0.94	0.61	0.56
N	5	5	5	5	5	5	5
Std. Error	0.0012	0.0015	0.0022	0.0023	0.0021	0.0014	0.0013

CBL

Time Period

	0	1	2	4	12	24	48
	0.15	0.144	0.143	0.145	0.142	0.142	0.143
	0.143	0.148	0.155	0.143	0.144	0.145	0.143
	0.145	0.159	0.159	0.143	0.144	0.143	0.143
	0.143	0.144	0.143	0.143	0.143	0.146	0.144
	0.145	0.144	0.147	0.146	0.144	0.143	0.144
Mean	0.1452	0.1478	0.1494	0.1440	0.1434	0.1438	0.1434
Std. Dev.	0.0029	0.0065	0.0073	0.0014	0.0009	0.0016	0.0005
%CV	1.97	4.40	4.86	0.98	0.62	1.14	0.38
N	5	5	5	5	5	5	5
Std. Error	0.0013	0.0029	0.0032	0.0006	0.0004	0.0007	0.0002

ODU

Time Period

	0	1	2	4	12	24	48
	0.0054	0.006	0.0054	0.0054	0.0037	0.0043	0.0043
	0.006	0.0043	0.0054	0.0049	0.0037	0.0043	0.0043
	0.0066	0.006	0.0054	0.0049	0.0037	0.0043	0.0026
	0.0054	0.006	0.0049	0.0043	0.0049	0.0043	0.002
	0.006	0.0054	0.0043	0.0043	0.0049	0.0049	
Mean	0.0059	0.0055	0.0051	0.0048	0.0042	0.0044	0.0033
Std. Dev.	0.0005	0.0007	0.0005	0.0005	0.0007	0.0003	0.0012
%CV	8.54	13.36	9.58	9.81	15.72	6.07	35.77
N	5	5	5	5	5	5	4
Std. Error	0.0002	0.0003	0.0002	0.0002	0.0003	0.0001	0.0006

NITRITE

VIMS
Time Period

	0	1	2	4	12	24	48
	0.034	0.033	0.033	0.033	0.033	0.033	0.032
	0.034	0.034	0.033	0.033	0.033	0.033	0.032
	0.034	0.034	0.033	0.033	0.033	0.033	0.032
	0.034	0.033	0.033	0.033	0.033	0.033	0.032
	0.033	0.034	0.033	0.033	0.033	0.033	0.033
Mean	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Std. Dev.	0.0004	0.0005	ERR	ERR	ERR	ERR	0.0004
%CV	1.32	1.63	ERR	ERR	ERR	ERR	1.39
N	5	5	5	5	5	5	5
Std. Error	0.0002	0.0002	ERR	ERR	ERR	ERR	0.0002

CBL

Time Period

	0	1	2	4	12	24	48
	0.0049	0.0052	0.0049	0.0049	0.0049	0.0065	0.0058
	0.0052	0.0048	0.0055	0.0049	0.0047	0.005	0.0051
	0.0049	0.0048	0.0049	0.0067	0.0048	0.0056	0.0054
	0.0048	0.0048	0.006	0.0049	0.0069	0.0054	0.0047
	0.0051	0.0049	0.0052	0.0057	0.0065	0.0048	0.0048
Mean	0.0050	0.0049	0.0053	0.0054	0.0056	0.0055	0.0052
Std. Dev.	0.0002	0.0002	0.0005	0.0008	0.0011	0.0007	0.0005
%CV	3.30	3.53	8.75	14.67	18.93	12.12	8.73
N	5	5	5	5	5	5	5
Std. Error	0.0001	0.0001	0.0002	0.0004	0.0005	0.0003	0.0002

Note: Doesn't look like biological changes in concentration.

ODU

Time Period

	0	1	2	4	12	24	48
	0.0006	0.0003	0.0006	0.0003	0.0023	0.0023	0.0017
	0.0006	0.0006	0.0003	0.0003	0.002	0.0023	0.0017
	0.0006	0.0003	0.0003	0.0003	0.002	0.0023	0.0014
	0.0006	0.0006	0.0003	0.0003	0.002	0.0023	0.0017
	0.0006	0.0006	0.0006	0.0003	0.002	0.0023	0.0006
Mean	0.0006	0.0005	0.0004	0.0003	0.0021	0.0023	0.0014
Std. Dev.	0.0000	0.0002	0.0002	0.0000	0.0001	ERR	0.0005
%CV	0.00	34.23	39.12	0.00	6.51	ERR	33.55
N	5	5	5	5	5	5	5
Std. Error	0.0000	0.0001	0.0001	0.0000	0.0001	ERR	0.0002

TDN

VIMS
Time Period

	0	1	2	4	12	24	48
	3.242	3.108	3.103	3.306	3	3.12	3.082
	3.264	3.064	3.098	3.277	3.04	2.976	3.131
	3.123	3.096	3.032	3.16	3.106	3.075	2.961
	3.075	3.185	3.073	3.156	3.368	3.094	3.061
	3.194	3.152	3.158	3.067	3.095	3.104	3.154
Mean	3.180	3.121	3.093	3.193	3.122	3.074	3.078
Std. Dev.	0.0796	0.0477	0.0460	0.0977	0.1441	0.0571	0.0751
%CV	2.50	1.53	1.49	3.06	4.62	1.86	2.44
N	5	5	5	5	5	5	5
Std. Error	0.0356	0.0213	0.0206	0.0437	0.0645	0.0255	0.0336

CBL

Time Period

	0	1	2	4	12	24	48
	0.44	0.52	0.49	0.48	0.49	0.49	0.55
	0.45	0.51	0.46	0.62	0.45	0.49	0.52
	0.45	0.53	0.47	0.47	0.48	0.7	0.46
	0.45	0.51	0.5	0.43	0.46	0.45	0.46
	0.45	0.55	0.5	0.51	0.49	0.44	0.52
Mean	0.4480	0.5240	0.4840	0.5020	0.4740	0.5140	0.5020
Std. Dev.	0.0045	0.0167	0.0182	0.0719	0.0182	0.1064	0.0402
%CV	1.00	3.19	3.75	14.32	3.83	20.71	8.02
N	5	5	5	5	5	5	5
Std. Error	0.0020	0.0075	0.0081	0.0322	0.0081	0.0476	0.0180

ODU

Time Period

	0	1	2	4	12	24	48
	0.252	0.242	0.268	0.263	0.31	0.257	0.263
	0.263	0.257	0.304	0.247	0.263	0.263	0.278
	0.263	0.223	0.278	0.252	0.263	0.252	0.263
	0.252	0.268	0.268	0.268	0.257	0.263	0.268
	0.268	0.268	0.263	0.252	0.252	0.263	0.236
Mean	0.2596	0.2516	0.2762	0.2564	0.2690	0.2596	0.2616
Std. Dev.	0.0072	0.0192	0.0165	0.0087	0.0234	0.0050	0.0156
%CV	2.79	7.64	5.96	3.41	8.69	1.92	5.95
N	5	5	5	5	5	5	5
Std. Error	0.0032	0.0086	0.0074	0.0039	0.0105	0.0022	0.0070