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Chesapeake Bay Coordinated Split Sample Program Annual Report, 1990-1991

Chesapeake Bay Program

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Analytical Methods and Quality Assurance Workgroup
of the Chesapeake Bay Program Monitoring Subcommittee

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EXECUTIVE SUMMARY

The Chesapeake Bay Program is a federal-state partnership with a goal of restoring the Chesapeake Bay. Its ambient water quality monitoring programs, started in 1984, sample over 150 monitoring stations once or twice a month. Due to the size of the Bay watershed (64,000 square miles) and the cooperative nature of the CBP, these monitoring programs involve 10 different analytical laboratories. The Chesapeake Bay Coordinated Split Sample Program (CSSP), initiated in 1988, assesses the comparability of the water quality results from these laboratories. This report summarizes CSSP results for 1990 and 1991, its second and third full years of operation.

The CSSP has two main objectives: identifying parameters with low inter-organization agreement, and estimating measurement system variability. The identification of parameters with low agreement is used as part of the overall Quality Assurance program. Laboratory and program personnel use this information to investigate possible causes of the differences, and take action to increase agreement if possible. Later CSSP results will document any improvements in inter-organization agreement. The variability estimates are most useful to data analysts and modelers who need confidence estimates for monitoring data.

The CSSP has four components, each including three to five laboratories that analyze samples from similar salinity regimes and concentration ranges (CBP 1991). Laboratories in each component analyze triplicate field split samples that are usually collected quarterly. The Mainstem Component is the only component that analyzes saline water samples. The five laboratories in this component analyze samples from the mainstem of the Chesapeake Bay, originally from near the mouth of the Potomac River, and later from near the mouth of the Patuxent River. The three laboratories in the Potomac Component analyze samples from near Key Bridge on the Potomac River. The four laboratories in the Virginia Component analyze samples from near Hopewell, VA on the James River. The four laboratories in the Fall Line Component analyze samples from the Susquehanna River fall line station at Conowingo, MD.

In the Mainstem Component, inter-organization agreement was high for 11 of the 17 parameters compared, but was low enough for the remaining 6 parameters to recommend investigation. Further investigation was recommended when more than half of the inter-organization differences were larger than within-organization precision, and there were statistically significant inter-organization differences at the $\underline{P} \leq 0.01$ level. Three of the 6 parameters that met those criteria had already been identified and studied (Bergstrom 1990, Zimmermann et al. 1992). Two of these parameters, particulate carbon (PC) and particulate nitrogen (PN) had method changes made in 1992, which should lead to higher inter-organization agreement. The results for the third parameter, dissolved organic carbon (DOC), appear to depend on the instrument used. The three parameters recommended for further investigation were ammonium (NH4), total suspended solids (TSS), and silica (SI). Two parameters previously identified as having low agreement, total dissolved phosphorus (TDP)

and total phosphorus (TP) (Bergstrom 1990), now have high agreement since a blank adjustment factor at one laboratory was corrected.

In the Potomac Component, inter-organization agreement was high for 9 of the 11 comparisons made. Two of the 11 parameters studied, nitrite + nitrate (NO23) and Total Organic Carbon (TOC), had inter-organization differences that were larger than within-laboratory precision on more than half of the sampling dates. Both parameters also had statistically significant results from the Friedman test. Unfiltered samples at one laboratory probably accounted for the NO23 differences, since that laboratory had higher results than the other laboratories when they were analyzing unfiltered samples. Thus, no investigation is recommended for NO23, since agreement improved when all three laboratories analyzed filtered samples. The differences in TOC were probably due to different instruments at the three laboratories.

In the Virginia Component, inter-organization agreement was high for 9 of the 13 parameters compared, but was low enough for the remaining four parameters to recommend investigation. The four parameters identified were Orthophosphate (PO4F), Silica (SI), Total Organic Carbon (TOC) and Particulate Phosphorus (PHOSP). In all four cases, different analytical methods at one of the tributary laboratories probably accounted for the inter-organization differences.

In the Fall Line Component, inter-organization agreement was high for all 9 comparisons made. However, sample sizes were small, and the power of the statistical test used was reduced by not being able to use replicate data.

Estimates of measurement system variability based on split sample data show that some parameters have more variable results than others. Within-organization coefficients of variation (CV) were generally below 20%, while inter-organization CV values were somewhat higher, usually less than 40 to 60% depending on the component. In some cases these patterns were consistent when results from different laboratories and sampling stations were compared.

The results from the second and third years of operation show that the CSSP is successful at achieving its goals. The communication and cooperation among participants that occurred was essential for getting the split sample results translated into actions that have increased inter-organization agreement.

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GLOSSARY

accuracy	Closeness of an analytical result to a "true" value. Usually assessed with laboratory spike samples or by analysis of SRMs.
agreement	Tendency for different organizations (laboratories) to have similar analytical results over time. Low inter-organization agreement results from consistent differences with magnitudes greater than the within-organization precision.
AMQAW	Analytical Methods and Quality Assurance Workgroup (part of the CBP Monitoring Subcommittee)
ANOVA	Analysis of Variance
BOD5	Biological Oxygen Demand 5 day
CBL	Chesapeake Biological Laboratory (Solomons, MD)
CBP	Chesapeake Bay Program
CBPO	Chesapeake Bay Program Office (Annapolis, MD)
CHLA	Chlorophyll a
CRL	Central Regional Laboratory (EPA, Annapolis, MD)
CSC	Computer Sciences Corporation (contractor at CBPO)
CSSP	Coordinated Split Sample Program
CV	Coefficient of Variation (SD/mean x 100)
decision rule	Used to decide which parameters have inter-organization differences that should be investigated. Those recommended have statistically significant differences at $P < 0.01$ and have more than half of the sample dates with inter-organization differences larger than within-organization precision.
DCLS	Division of Consolidated Laboratory Services (Richmond, VA)
DCRA	Department of Consumer and Regulatory Affairs (Washington, DC)
DCRA/CRL	DCRA staff who perform laboratory analyses at CRL
DOC	Dissolved Organic Carbon
EPA	Environmental Protection Agency
Friedman ANOVA	Nonparametric statistical test used as part of the assessment of inter-organization agreement. Assumes matched (positively correlated) samples. Results are affected by the consistency of differences over time.
HRSD	Hampton Roads Sanitation District (Virginia Beach, VA)
MDE	Maryland Department of the Environment (Baltimore & Annapolis, MD)
MDHMH	Maryland Department of Health and Mental Hygiene (Baltimore, MD)
MDL	Method Detection Limit; usually based on within-organization precision, calculated from 3 times the SD of 7 low-level replicates.
NH4	ammonium
NO2	nitrite
NO23	nitrite + nitrate
ODU	Old Dominion University (Norfolk, VA)
OWML	Occoquan Watershed Monitoring Laboratory (Manassas, VA)

PADER	Pennsylvania Department of Environmental Resources (Harrisburg, PA)
PC (POC)	Particulate Carbon (Particulate Organic Carbon); the former is measured directly (mainstem labs); the latter is calculated from TOC - DOC (tributary labs).
PHEA	Phaeophytin
PHOSP	Particulate Phosphorus
PN (PON)	Particulate Nitrogen (Particulate Organic Nitrogen); the former is measured directly (mainstem labs); the latter is calculated from TKNW - TKNF (tributary labs).
PO4F	Orthophosphate filtered
PO4W	Orthophosphate unfiltered (whole water)
precision	Repeatability of analytical measurements. Precision is high if successive measurements are very similar, resulting in low SD and CV values. Within-organization precision is estimated in the CSSP from the variability among field replicates (subsamples), and inter-organization precision is estimated from the variability among the medians over the three subsample results from each organization. For graphing and use in the decision rule, within-organization precision is estimated from the larger of the MDL, or the SD of the results from the three subsamples.
QA	Quality Assurance
SAS	Statistical Analysis System
SD	Standard Deviation
SI	Silica
SRM	Standard Reference Material
subsample	Replicates split in the field, soon after sample collection, either on the sampling boat, on a dock, or in a laboratory. Each laboratory should receive three subsamples per split sample. Subsamples were called "aliquots" in some previous CSSP reports.
TDN	Total Dissolved Nitrogen; measured directly (mainstem labs) or calculated from TKNF + NO23 (tributary labs).
TDP	Total Dissolved Phosphorus
TKNW	Total Kjeldahl Nitrogen Whole
TKNF	Total Kjeldahl Nitrogen Filtered
TN	Total Nitrogen; calculated from either TKNW + NO23 (tributary labs) or TDN + PN (mainstem labs).
TOC	Total Organic Carbon; measured directly (tributary labs) or calculated from PC + DOC (mainstem labs).
TP	Total Phosphorus; measured directly (tributary labs) or calculated from TDP + PHOSP (mainstem labs)
TSS	Total Suspended Solids
USGS	United States Geological Survey (Towson, MD and other offices)
VIMS	Virginia Institute of Marine Science (Gloucester Point, VA)
VWCB	Virginia Water Control Board (Glen Allen, VA)

I. INTRODUCTION

The Monitoring Subcommittee of the Chesapeake Bay Program initiated the Chesapeake Bay Coordinated Split Sample Program (CSSP) in 1988. Its goal is to assess the comparability of water quality results from the 10 analytical laboratories that participate in the Chesapeake Bay Monitoring Program (Chesapeake Bay Program 1989). This goal is being achieved by identifying any parameters that have low inter-organization agreement and estimating measurement system variability .

Identifying parameters with low agreement enables the organizations involved to investigate any significant differences and take actions to raise inter-organization agreement. This might involve changing field methods, laboratory methods, or both. Because results of field split samples are affected by both field and laboratory variability, the terms "inter-organization" and "within-organization" are used rather than "inter-laboratory" and "within-laboratory." The organization includes all the elements of the measurement system: field sampling, sample handling, laboratory analysis, data handling, and the state or municipal agency that supervise water quality monitoring program.

Estimates of measurement system variability are useful to data users such as statisticians and modelers who need confidence bounds for monitoring data. Although split sample results do not include sampling variability, they are the best estimate available of total system variability for Chesapeake Bay water quality monitoring data.

The CSSP has four components, each including three to five laboratories that analyze samples from similar salinity regimes and concentration ranges (CBP 1991). Laboratories in each component analyze triplicate field split samples that are usually collected quarterly. Laboratory personnel send the analytical results to the EPA Chesapeake Bay Program Office (CBPO) in Annapolis for data transfer (or entry) and analysis by Computer Sciences Corporation (CSC/CBPO) staff.

This report summarizes the 1990-1991 results from the four CSSP components:

1. The Mainstem and Tidal Tributaries Component is the only component that analyzes saline water samples. This component includes three mainstem laboratories: Chesapeake Biological Laboratory (CBL), Virginia Institute of Marine Science (VIMS), and Old Dominion University (ODU). It also includes a Maryland tributary laboratory, Maryland Department of Health and Mental Hygiene (MDHMH), and a Virginia tributary laboratory, Division of Consolidated Laboratory Services (DCLS).

2. The Tidal Potomac River component includes three analytical laboratories: the Maryland Department of Health and Mental Hygiene (MDHMH) in Baltimore, the Virginia Division of Consolidated Laboratory Services (DCLS) in Richmond, and the EPA Central Regional Laboratory (CRL) in Annapolis. DC Department of Consumer and Regulatory Affairs (DCRA) personnel (referred to as DCRA/CRL) conduct the analyses at CRL.

3. The Virginia Mainstem and Tidal Tributaries component of the CSSP includes four analytical laboratories: the Virginia Institute of Marine Science (VIMS), Old Dominion University (ODU), Division of Consolidated Laboratory Services (DCLS), and Hampton Roads Sanitation District (HRSD).

4. The Fall Line component includes four analytical laboratories: the Maryland Department of Health and Mental Hygiene (MDHMH) in Baltimore, the United States Geological Survey (USGS) in Denver, the Pennsylvania Department of Environmental Resources (PADER) in Harrisburg, and the Occoquan Watershed Monitoring Laboratory (OWML) in Manassas, VA. The component was planned to include the Virginia Division of Consolidated Laboratory Services (DCLS) in Richmond (CBP 1991), but logistical problems with sample splitting and distribution have prevented this.

Communication is a key element of the CSSP, enabling the staff of the participating laboratories and program agencies to study the results and take action when appropriate. Interim reports on each component are issued regularly by CSC/CBPO staff to the laboratory and program personnel involved in each component. CSC/CBPO staff combine the interim reports in a public annual report, which can include comments or discussion from the laboratory or program personnel. The previous Annual Report (Bergstrom 1990) included CSSP results through December 1989.

II. METHODS

A. SAMPLE COLLECTION AND SPLITTING

1. Mainstem Component

A field crew from the Maryland Department of the Environment (MDE) collected quarterly water samples from the surface layer at Station CB5.3, near Smith Point on the Maryland-Virginia state line. The sampling station was changed to CB4.4 in June 1990 to facilitate getting the samples to participating laboratories. The field crew followed the splitting procedures in the CSSP Implementation Guidelines (CBP 1991) starting in June 1989. One large sample was stirred on the boat in a 15 gallon carboy with a paint stirrer connected to an electric drill. Subsamples were drawn sequentially from a spigot at the bottom of the carboy.

The bottles for Subsample 1 were split in the sequence MDHMH-VIMS-CBL-ODU-DCLS, followed by the bottles for subsamples 2 and 3 in the same sequence.

Before June 1990, samples were transferred from the MDE to the VIMS boat at station CB5.3, and MDE staff filtered and distributed Maryland samples, and VIMS staff filtered and distributed Virginia samples. As of June 1990, the MDE field crew filtered and distributed samples to the two Maryland laboratories (CBL and MDHMH). VIMS personnel picked up the samples in Port Royal, VA and distributed unfiltered samples to the three Virginia laboratories (VIMS, ODU, and DCLS). Each Virginia laboratory filtered their own samples. DCLS started analyzing Mainstem Component samples in June 1990.

Beginning in June 1989, each laboratory analyzed a minimum of four samples per sample date: three subsamples split in the field and a laboratory replicate for one of the subsamples. Some laboratories did more replicates. Two estimates of within-laboratory precision were calculated from subsample (field replicate) and lab replicate data: field precision and laboratory precision. Only field precision is reported here, because it generally includes laboratory precision.

2. Potomac Component

A field crew from DCRA collected quarterly water samples from the surface layer at Station PMS-10, at Key Bridge on the Potomac River. The field crew followed the splitting procedures in the CSSP Implementation Guidelines (CBP 1991) starting in June 1989. One large sample was stirred at the dock in a 15 gallon carboy with boat paddle. Subsamples were drawn sequentially from a spigot at the bottom of the carboy, in the sequence MDHMH-DCLS-DCRA/CRL. The field crew left whole water samples in ice-filled coolers at the designated dock. Personnel from each laboratory retrieved the coolers. The DCRA field crew did not filter any samples. Starting in December 1990, the MDE crew that picks up samples for MDHMH began filtering samples for nutrient analysis, usually when they picked up the samples at Blue Plains. The MDE crew used Whatman GF/F filters with a 0.7 micron pore size.

In the laboratory, DCLS and DCRA/CRL personnel filtered samples for Ammonium (NH4), Nitrite (NO2), Nitrite + Nitrate (NO23), Orthophosphate (PO4F), Silica (SI), and Total Suspended Solids (TSS). DCRA/CRL and DCLS both used pre-rinsed Gelman cellulose membrane filters with 0.45 micron pore size, smaller than the pores in the filters used by MDE. MDHMH did laboratory filtration for TSS only. Samples were received by the laboratories either the same day they were collected or the following day. The March 1990 samples were not picked up for DCLS, so there are no DCLS results for that split sample.

Starting in June 1989, each laboratory analyzed a minimum of four samples per sampling date. These come from three subsamples (field replicates) split in the field and a laboratory replicate for one of the subsamples.

3. Virginia Component

A field crew from the Virginia Water Control Board (VWCB) collected quarterly water samples from the bottom layer at Station TF5.5, near Hopewell on the James River. The field crew followed the splitting procedures in the CSSP Implementation Guidelines (CBP 1991) starting in February 1990, filling the subsamples in the sequence HRSD-VIMS-ODU-DCLS. The three subsamples sent to each laboratory came from three separate churn splitters, which were filled in rotation from the sampling hose (CBP 1991). This is not the standard splitting protocol, which calls for starting from a single well-mixed sample. The use of three separate splitters appeared to affect the results from the May 1990 sample, which had very high suspended solids (see below). VWCB staff switched to splitting from a single large churn splitter in June 1992.

The field crew delivered iced whole water samples to each laboratory. Samples were received by the laboratories either the same day they were collected or the following day, and were usually filtered the morning after they were collected. DCLS and HRSD used pre-rinsed Gelman cellulose membrane filters with 0.45 micron pore size, while ODU and VIMS used Whatman GF/F glass fiber filters with 0.7 micron nominal pore size, and Gelman AE filters for PC/PN analyses.

Starting in February 1990, each laboratory analyzed a minimum of four samples per sampling date. These come from three subsamples (field replicates) split in the field and a laboratory replicate for one of the subsamples. In the data collected during 1988-89 the three analytical results did not always come from three separate subsamples, but sometimes were split in the laboratory. For this reason, the 1988-89 data were not included in the graphs or the statistical tests.

4. Fall Line Component

A field crew from USGS-Towson sampled the Susquehanna River fall line station at Conowingo, MD (CB1.0), and distributed samples to each laboratory. The field crew used USGS sampling procedures, including flow-weighted cross-sectionally integrated samples collected at 5 sections along the well-mixed turbine outflow. Splitting was done with a single churn splitter. Field filtration was done with a 0.45 micron membrane filter and the nutrient samples shipped to USGS were preserved with mercuric chloride and sodium chloride according to USGS standard protocol. Samples sent to OWML, MDHMH and PADER were not preserved. All samples were immediately placed and kept in ice-filled coolers with a 6:1 ratio of ice to sample. Samples for MDHMH and PADER were delivered to the laboratory on the day of collection. Samples for USGS and OWML were sent via priority mail. USGS samples usually arrived in two days.

There were several deviations from the recommended procedures in the CSSP guidelines (CBP 1991). Samples were not split quarterly, each laboratory received less than three

subsamples (field replicates) split in the field, Standard Reference Material (SRM) results were not reported, and laboratory replicates and spikes were not performed routinely. Samples were collected twice in 1990 and once in 1991; they could not be split quarterly due to budget constraints at USGS. The field crew could not split enough water to provide three subsamples due to the size of the churn splitter. Each laboratory received two subsamples in October 1989 and July 1991, and one subsample on other dates. This reduced the power of the statistical test used, and limited the within-organization variability estimates that could be calculated. USGS will try using three churn splitters in future samples, one for each subsample. Only MDHMH and OWML reported any laboratory replicates for the subsamples, and percent recovery results were incomplete: USGS did not submit any, and PADER and MDHMH only reported them for one sample.

B. DATA ENTRY AND REDUCTION

Laboratory or program personnel submitted their data on diskette or computer tape, or they submitted raw data on handwritten CSSP Data Submission forms. CSC/CBPO staff entered the handwritten data, and uploaded the digital data and converted it to SAS data sets. Data were adjusted up to the method detection limit (MDL) if they were below it because most labs did this to their data before submission. Field and laboratory precision and medians of the three subsamples were calculated with the SAS procedure UNIVARIATE (SAS Institute 1990). These medians of the three subsamples for each sampling date were then used to calculate inter-organization standard deviations and coefficients of variation using the SAS functions STD and CV respectively.

C. ANALYTICAL CHEMISTRY METHODS

1. Mainstem Component

The three mainstem laboratories in this component use different analytical methods than the two tributary laboratories. Mainstem laboratories measure the dissolved and particulate fractions of most nutrients and calculate the total fractions, while tributary laboratories measure the total and dissolved fractions and calculate the particulate fractions (D'Elia et al. 1987). To account for this difference in analytical methods, data analyses were done for four and five laboratories and also for the three mainstem laboratories. Comparisons among four laboratories were done using MDHMH data, because DCLS started analyzing samples later, which reduced the sample size for five-way comparisons.

2. Potomac Component

Because the three laboratories included in the Potomac component use similar analytical methods, data analyses treated them as a single group without any subgroups. All three

laboratories used a single acid sulfate (not persulfate) block digestion for Total Kjeldahl Nitrogen Whole (TKNW) and Total Phosphorus (TP) analyses.

3. Virginia Component

The four laboratories included in the Virginia component used two different groups of analytical chemistry methods. DCLS and HRSD laboratories analyze tributary samples and perform whole water and dissolved nutrient analyses, and calculate any particulate parameters. Both use a single acid sulfate block digestion for Total Kjeldahl Nitrogen Whole (TKNW) and Total Phosphorus (TP) analyses. VIMS and ODU analyze primarily mainstem Bay samples and perform dissolved and particulate nutrient analyses, and calculate any total parameters. Both use separate alkaline persulfate digestions for nitrogen and phosphorus parameters (TDN and TDP), except ODU uses acid persulfate for TDP. The Friedman test used for statistical analysis requires a minimum of three laboratories, so data from the tributary and mainstem laboratories could not be analyzed separately. The method differences among the four laboratories should be taken into account when interpreting the split sample results.

There was one method change at HRSD during the time period covered by this report. They changed from an automated (EPA method 365.1) to a manual technique (EPA method 365.3) for Orthophosphate (PO4F) in August, 1990. This reduced their method detection limit for PO4F from 0.05 mg/l to 0.01 mg/l (Table 2). ODU also uses the manual procedure, while DCLS and VIMS use the automated procedure (see Tables 1 & 2 for method detection limits).

4. Fall Line Component

In general, three of the laboratories (MDHMH, OWML, and PADER) followed EPA standard methods, and USGS followed USGS standard methods. All four laboratories reported the same parameters, with a few exceptions: PADER did not report NO2, SI, or TSS data, and USGS did not report TSS data.

D. DATA ANALYSIS AND GRAPHING

1. Preliminary test of splitting randomness

Data were checked for the randomness of the splitting procedures. If splitting was done uniformly, the results for one of the subsamples should not be consistently higher or lower than the results for the other subsamples. Since the subsamples are split sequentially, non-random splitting would probably result in higher results for solids and particulates in Subsample 3, which is drawn from the lower part of the splitting vessel. Splitting randomness was checked with the Friedman two-way non-parametric analysis of variance, comparing the results for the three subsamples for each parameter and sampling date, using $P < 0.05$ to indicate significance.

In the Mainstem Component, sixty-one of the 63 parameter-date combinations tested did not have statistically significant differences ($\underline{P} \geq 0.05$). For the two parameters and dates with significant differences (PHOSP, P = 0.042, and TOC, P = 0.0046, on one date each), the magnitudes of the differences were less than the method detection limit. This shows that splitting was done randomly.

In the Potomac Component, 97 of the 101 parameter-date combinations tested did not have statistically significant differences ($\underline{P} \geq 0.05$). The four significant differences ($\chi^2 = 6.0$, P = 0.028) were all for NH4, and all involved the same pattern: the subsample results were ranked from low to high, 1 < 2 < 3. The four dates affected included three in June (1989, 1990, and 1991) and one in September 1989. Since none of the particulate or whole-water parameters were affected, and NH4 is filtered, these differences for NH4 could not be due to inadequate stirring during sample splitting. They might be due to some sort of contamination, but the regular pattern of the differences seems to make that unlikely. The magnitudes of the differences were relatively large, and were consistent across laboratories. For example, in June 1989, DCRA/CRL reported 0.04, 0.051, and 0.063 mg/l; MDHMH reported 0.036, 0.060, and 0.068 mg/l; and DCLS reported 0.04, 0.06, and 0.07 mg/l. These differences did not lead to significant results in tests for inter-organization differences in NH4 (see Results), probably because they were consistent across laboratories.

In the Virginia Component, the subsamples were not split sequentially from a single vessel, but from three separate churn splitters. Thus, non-random splitting could result in higher results for solids and particulates in any subsample, not just in Subsample 3.

In the Virginia Component, the results for PHOSP and TP on May 31, 1990 show a significant effect of non-random splitting. The test for both parameters in May had $\underline{P} = 0.042$ ($\chi^2 = 6.5$), and for both parameters, all four laboratories had the highest results for Subsample 2. The difference between subsamples was as large as 0.603 to 0.831 mg/l, a 38% difference. All laboratories except ODU had the lowest results for Subsample 1. TSS data could not be tested because HRSD did not analyze TSS in May, but it showed the same consistent differences in subsample results in ODU and VIMS data. The maximum TSS difference between subsamples for TSS was 514 and 702 mg/l, a 36% difference. TSS values in this range are an extreme test of splitting effectiveness, but since they occur at TF5.5, the splitting procedure should not be affected by them. The splitting method was recently changed to one using a single vessel, as recommended in the CSSP Implementation Guidelines (CBP 1991). Although there was a probable effect of splitting order on the May 1990 PHOSP and TP data, this had no apparent effect on the tests for inter-organization agreement (see Results). Non-random splitting could accentuate inter-organization differences if it occurred consistently over several sample dates.

The test for splitting randomness could not be done on Fall Line data, because three subsamples were not analyzed.

2. Precision estimates

The standard deviation (SD) and coefficient of variation (CV, standard deviation/mean x 100) of field triplicate results estimated within-organization precision. Since the field replicates are usually split by a different organization from the one doing the laboratory analysis, they do not measure only "within-organization" field and laboratory precision, but they are considered to approximate it for the purposes of this report. The CSSP results also include laboratory replicates, split in the laboratory just before analysis. These were not used to estimate within-organization precision because they do not include field variability, and are almost always less variable than the field replicates.

The medians of the field triplicate results were then used to calculate the SD and CV of the results from different organizations for each sampling date, which estimated inter-organization precision. For the Mainstem component, precision estimates were calculated separately for groups of four and three laboratory medians, including all the laboratories or only the mainstem laboratories (see above). Results from DCLS were excluded for now because they started analyzing mainstem samples at a later date.

The SD was positively correlated with the mean for several parameters, and usually the CV was not affected by the mean. However, the CV was sometimes affected by concentration as well. It was positively correlated with the mean in a few cases, and negatively correlated with the mean in a few other cases. The negative correlation usually occurred when the mean concentrations were low. Thus, neither precision estimate should be used in other analyses without checking for concentration effects. Because the primary purpose of the CSSP is to assess inter-organization agreement, a detailed analysis of precision estimates is beyond the scope of this report.

The Method Detection Limit (MDL) was also used to estimate within-organization precision, especially in the graphs of the data (see next section). At many of the laboratories, the MDL is calculated from three times the standard deviation of seven replicates of a low-level sample, so it estimates within-organization precision.

3. Assessing inter-organization agreement

Inter-organization agreement is the tendency for split sample analytical results from different organizations to be consistently similar over time. Thus, any pair of laboratories with large and consistent inter-organization differences are considered to have low agreement. A decision rule was developed to identify which parameters had inter-organization differences that were large and consistent enough to warrant investigation by the organizations involved. Based on discussions by the Analytical Methods and Quality Assurance Workgroup (AMQAW) on 4/24/90 and 1/26/93, the decision was based on graphs of the data with precision bars, and the results of statistical tests. Graphs with precision bars show the magnitude of differences, while

the statistical test is more sensitive to consistency of the differences over time. Investigation was recommended if:

1) more than half of the sampling dates had pairwise inter-organization differences that were larger than within-organization precision; and,

2) an appropriate statistical test had a probability (P) $\leq$ 0.01 that the differences were due to chance alone, equivalent to 99% confidence that the observed difference was real.

Parameters identified by the combination of these two criteria usually have different field and/or laboratory methods at one or more of the laboratories involved.

Graphs of the split sample results show which differences were larger than the within-organization precision. Within-organization precision for CSSP analyses is estimated by the larger of: 1) the Method Detection Limit (MDL, Tables 1 and 2); or, 2) the standard deviation of the three subsamples for each sample which estimates field precision. Graphs of the medians for each sample date for each laboratory show this estimate as "precision bars." Any pair of laboratory medians with non-overlapping precision bars have differences that are larger than within-organization precision. Because the overlap was sometimes difficult to assess graphically, it was also checked with a SAS program.

A non-parametric statistical test was used to assess inter-organization agreement using the split sample data. This test assumes matched (positively correlated) samples, since this is inherent in the split sample design. Below detection limit data were included if they were lower than any other results, but no comparison was made if two or more laboratories had below detection limit data, unless the data from one laboratory could be adjusted to remove the bias. In the Potomac data this occurred with TSS, since MDHMH and DCLS have a lower detection limit (1 mg/l) than DCRA/CRL (4 mg/l). The bias was avoided by adjusting TSS data that were below 4 mg/l up to 4 mg/l before running the Friedman test. Statistical significance was assumed when the significance level (P) $\leq$ 0.01. Standard quality control procedures use the P = 0.01 level as the "control" or action level for precision and accuracy charts (e.g., Montgomery 1985).

The Friedman two-way non-parametric repeated measures analysis of variance (ANOVA) with replication within blocks (Marascuilo and McSweeney 1977) was used to test statistically for differences among laboratory results. The Friedman program used before (Bergstrom 1990) did not allow for replicates, so means for each sample date were used in the previous report. This change uses more information in the data and increases the power of the test, or its ability to detect real differences. This test was run with a SAS computer program written by CSC/CBPO staff using the formula in Marascuilo and McSweeney (1977), including their formula for post hoc pairwise comparisons. The program was tested with the example in Marascuilo and McSweeney (1977). Exact P values (for N $<$ 10) are from Siegel (1956).

III. RESULTS

A. WITHIN-ORGANIZATION PRECISION AND ACCURACY

Two estimates of within-organization precision were used in this analysis: the Method Detection Limits (MDLs), listed in Tables 1 and 2; and the precision of field replicates, the three subsamples split in the field and analyzed by the same laboratory. Percent recovery data and results from Standard Reference Materials (SRMs) estimated within-organization accuracy.

1. Mainstem Component

Table 3 lists the mean Standard Deviation (SD) and Coefficient of Variation (CV) of field replicates. These within-organization precision estimates varied among parameters in data from the same organization, as well as among organizations for the same parameter, with CV values ranging from 0.8% to 114%. Over all organizations, the parameters with the highest CVs were TSS, PHEA, PO4F, and NH4. There was a negative CV for PN from MDHMH because the mean PN was negative, calculated from TKNW - TKNF.

Percent recovery data from spiked samples (Table 4) show that most values were near 100%. Only 3 of 260 values fell outside the range of 80-120%. Results from SRMs (Table 5) from all laboratories except MDHMH also had percent recovery values (SRM results/expected x 100) near 100%. All but 41 of 229 recoveries were between 90 and 110%, and all but 18 of 229 recoveries were between 80 and 120%.

2. Potomac Component

Table 6 lists the mean Standard Deviation (SD) and Coefficient of Variation (CV) of the three field replicates as "Within-organization precision." For parameters affected by the change to filtered samples at MDHMH, medians were calculated before and after the method change. The change to filtered samples had little effect on within-organization precision in MDHMH data, although variability went down in NO23 results. Precision also changed over time for some parameters at the other laboratories, presumably due to random variations.

These precision estimates varied among parameters in data from the same organization, as well as among organizations for the same parameter, with CV values ranging from 0% to 25%. Over all organizations, the parameters with the highest CVs were TKNW, TSS, and NH4.

Percent recovery data (Table 7) and results from Standard Reference Materials (SRMs, Table 8) estimated within-laboratory accuracy. Percent recovery data are limited since DCLS did not submit them, but most values were close to 100%. Results from SRMs from DCRA/CRL show good agreement with the expected results, and all but three results (for PO4F and TOC) were within the 95% confidence intervals for the SRMs.

TABLE 1. Lower Detection Limits of Water Quality Parameters, Chesapeake Bay Mainstem Monitoring Program, 1984-1992.

PARAMETER	MD/OEP-MDE (CRL then CBL)	VA/VWCB (ODU)	VA/VWCB (VIMS)
TN	.240+ (6/84-2/85)	.11+ (6/84-3/15/86)	.11*+ (6/84-9/87)
(Calc.	.2009+(3/85-5/15/85)	.105+ (3/16/86-4/15/86)	.124*+(10/87-4/88)
TKNW +	.031+ (5/16/85-9/86)	.11+ (4/16/86-4/30/86)	.071+ (5/88-5/89)
NO23,or	.2009+(10/86-9/87)	.105+ (5/86-9/87)	.069+ (6/89-6/90)
TDN+	.0305+(10/87-)	.10+ (10/87-8/90)	.045+ (7/90-6/91)
PON)		.075+ (9/90-10/90)	.081+ (7/91-1/92)
		.061+ (11/90-)	.045+ (2/92-)
TDN	.240+ (6/84-2/85)	.11+ (6/84-3/15/86)	.12*+(6/84-10/15/86)
(Calcu-	.2009+(3/85-5/15/85)	.105+ (3/16/86-4/15/86)	.11*+(10/16/86-9/87)
lated,	.03 (5/16/85-9/86)	.11+ (4/16/86-4/30/86)	.1*(.05-.462)
then	.02 (10/87-)	.105+ (5/86-9/87)	(10/87-4/88)
direct)		.05 (10/87-8/90)	.045 (5/88-5/89)
		.025 (9/90-)	.040 (6/89-6/90)
			.026 (7/90-6/91)
			.075 (7/91-1/92)
			.026 (2/92-)
PON	.40+ (6/84-5/15/85)	.20+ (6/84-9/87)	.20*+ (6/84-9/87)
(Calcu-	.001 (5/16/85-9/86)	.05 (10/87-10/90)	.024*(.023-.026)
lated,	.40+ (10/86-9/87)	.036 (11/90-)	(10/87-4/88)
then	.0105 (10/87-)		.026 (5/88-5/89)
direct)			.029 (6/89-6/90)
			.019 (7/90-6/91)
			.006 (7/91-1/92)
			.019 (2/92-)
NH4	.020 (6/84-1/85)	.01 (6/84-5/15/85)	.01*(.002-.051)
	.040 (2/85)	.0056 (5/16/85-)	(6/84-4/88)
	.003 (3/85-4/15/88)		.013 (5/88-5/89)
	.005 (4/16/88-7/88)		.006 (6/89-6/90)
	.003 (8/88-)		.004 (7/90-6/91)
			.002 (7/91-1/92)
			.004 (2/92-)
NO23	.040 (6/84-2/85)	.01 (6/84-3/15/86)	.01*(.001-.025)
	.0009 (3/85-9/87)	.005 (3/16/86-4/15/86)	(6/84-4/88)
	.00015 (10/87-8/88)	.01 (4/16/86-4/30/86)	.0014 (5/88-5/89)
	.0002 (9/88-)	.005 (5/86-6/88)	.0021 (6/89-6/90)
		.0025 (7/88-)	.0024 (7/90-1/92)
			.0008 (2/92-)
NO2	.01 (6/84-2/85)	.001 (6/84-)	.004*(.001-.007)
	.0005 (3/85-9/87)		(6/84-4/88)
	.00015 (10/87-8/88)		.0008 (5/88-5/89)
	.0002 (9/88-)		.0015 (6/89-6/90)
			.0006 (7/90-6/91)
			.0005 (7/91-1/92)
			.0002 (2/92-)

* VIMS had variable detection limits during this period, within range shown.

+ Parameter calculated during this period; MDL shown is the sum of the detection limits of the components.

All concentrations on this page are in mg/l.

TABLE 1 (continued). Lower Detection Limits of Water Quality Parameters, Chesapeake Bay Mainstem Monitoring Program, 1984-1992.

PARAMETER	MD/OEP-MDE (CRL then CBL)		VA/VWCB (ODU)		VA/VWCB (VIMS)	
TP (Direct, then calc.)	.012	(6/84-1/85)	.01	(6/84-12/86)	.01*(.009-.01)	(6/84-10/87)
	.01	(2/85)	.005	(1/87-9/87)		
	.005	(3/85-5/15/85)	.012+	(10/87-)	.02*+	(11/87-4/88)
	.0063+	(5/16/85-9/86)			.007+	(5/88-5/89)
	.012	(10/86-9/87)			.008+	(6/89-6/90)
	.0022+	(10/87-)			.005+	(7/90-5/92)
					.0022+	(6/92-)
TDP	.012	(6/84-1/85)	.01	(6/84-11/86)	.01*(.009-.012)	(6/84-4/88)
	.01	(2/85)	.005	(12/86-)		
	.005	(3/85-9/86)			.006	(5/88-5/89)
	.012	(10/86-9/87)			.005	(6/89-6/90)
	.001	(10/87-)			.002	(7/90-)
PHOSP (Calc., then direct)	.024+	(6/84-1/85)	.02+	(6/84-11/86)	.02*+	(6/84-10/87)
	.02+	(2/85)	.015+	(12/86)	.01*(.009-.01)	(11/87-4/88)
	.010+	(3/85-5/15/85)	.01+	(1/87-9/87)		
	.0013	(5/16/85-9/86)	.007	(10/87-)	.001	(5/88-5/89)
	.024+	(10/86-9/87)			.003	(6/89-5/92)
	.0012	(10/87-)			.0002	(6/92-)
PO4F	.012	(6/84)	.01	(6/84-11/86)	.01*(.009-.013)	(6/84-7/87)
	.007	(7/84-2/85)	.005	(12/86-)		
	.0016	(3/85-9/87)			.002*(.001-.004)	(8/87-4/88)
	.0006	(10/87-)			.0005	(5/88-5/89)
					.003	(6/89-6/90)
					.0006	(7/90-6/91)
					.0008	(7/91-1/92)
					.0006	(2/92-)
TOC (Direct, then calc.)	1.0	(6/84-5/15/85)	1.0	(6/84-9/87)	1.0	(ODU**,6/84-9/87)
	.501+	(5/16/85-9/86)	1.24+	(10/87-8/88)	1.581*+	(10/87-4/88)
	1.0	(10/86-9/87)	.74+	(9/88-10/90)	1.099+	(5/88-8/88)
	.501+	(10/87-8/88)	.63+	(11/90-)	.599+	(9/88-5/89)
	.303+	(9/88-)			.604+	(6/89-6/90)
					.457+	(7/90-6/91)
					.234+	(7/91-1/92)
					.597+	(2/92-)
DOC	1.0	(6/84-5/15/85)	1.0	(6/84-8/88)	1.0	(ODU**,6/84-8/88)
	.50	(5/16/85-8/88)	.50	(9/88-)	.50	(ODU**,9/88-6/90)
	.24	(9/88-)			.36	(VIMS, 7/90-6/91)
					.15	(VIMS, 7/91-1/92)
					.50	(VIMS, 2/92-)

* VIMS had variable detection limits during this period, within range shown.

** ODU did TOC and DOC analyses for VIMS stations until 7/90.

\+ Parameter calculated during this period; MDL shown is the sum of the detection limits of the components.

All concentrations on this page are in mg/l.

TABLE 1 (continued). Lower Detection Limits of Water Quality Parameters, Chesapeake Bay Mainstem Monitoring Program, 1984-1992.

PARAMETER	MD/OEP-MDE (CRL then CBL)		VA/VWCB (ODU)		VA/VWCB (VIMS)	
POC	2.0+	(6/84-5/15/85)	2.0+	(6/84-9/87)	2.0+	(6/84-9/87)
(Calc.,	.001	(5/16/85-9/86)	.24	(10/87-10/90)	.581*	(.581-.581)
then	1.5+	(10/86-9/87)	.13	(11/90-)		(10/87-4/88)
direct)	.001	(10/87-8/88)			.099	(5/88-5/89)
	.063	(9/88-)			.104	(6/89-6/90)
					.097	(7/90-6/91)
					.084	(7/91-1/92)
					.097	(2/92-)
SI	.1	(6/84-2/85)	.028	(6/84-5/86)	.056*	(.009-.1)
(as SI)	.012	(3/85-3/87)	.023	(6/86-12/90)		(6/84-4/88)
	.01	(4/87-)	.0281	(1/91-4/91)	.009	(5/88-5/89)
			.0234	(5/91-)	.007	(6/89-6/90)
					.013	(7/90-6/91)
					.006	(7/91-1/92)
					.013	(2/92-)
TSS	4.0	(6/84-5/15/85)	4.0	(6/84-8/88)	4.0	(6/84-4/88)
	1.0	(5/16/85-9/87)	2.0	(9/88-)	5.0	(5/88-6/91)
	1.98	(10/87-8/88)			1.4	(7/91-1/92)
	1.5	(9/88-)			2.0	(2/92-)
CHLA	1+	(6/84-5/15/85)	0.2+	(6/84-1/91)	1.0+	(6/84-5/89)
(ug/l)	0.2+	(MDHMH,5/16/85-)	1.1+	(2/91-)	3.2+	(6/89-6/90)
					1.32+	(7/90-6/91)
					1.95+	(7/91-1/92)
					0.95+	(2/92-)
PHEA	1+	(6/84-5/15/85)	0.2+	(6/84-1/91)	1.0+	(6/84-5/89)
(ug/l)	0.2+	(MDHMH,5/16/85-)	0.8+	(2/91-)	3.2+	(6/89-6/90)
					1.91+	(7/90-6/91)
					3.43+	(7/91-1/92)
					1.34+	(2/92-)

* VIMS had variable detection limits during this period, within range shown.

\+ Parameter calculated during this period; MDL shown is the sum of the detection limits of the components. All concentrations are in mg/l except CHLA and PHEA.

Abbreviations: TN = Total Nitrogen, TDN = Total Dissolved Nitrogen, PON = Particulate (Organic) Nitrogen, NH4 = ammonium, NO23 = Nitrite + Nitrate, NO2 = Nitrite, TP = Total Phosphorus, TDP = Total Dissolved Phosphorus, PHOSP = Particulate Phosphorus, PO4F = Orthophosphate filtered, TOC = Total Organic Carbon, DOC = Dissolved Organic Carbon, POC = Particulate (Organic) Carbon, SI = Silica (as SI), TSS = Total Suspended Solids, CHLA = Chlorophyll a, PHEA = Phaeophytin.

Current limits at CBL & VIMS calculated from: 3 x standard deviation of 7 replicates of the lowest concentration sample encountered. ODU calculates this also, but uses a higher MDL equivalent to 1-2% of full scale if the calculated value is below 1-2% of full scale. MDHMH limits shown are calculated as 2% of full scale.

Calculation methods (used when a + follows the MDL) are: TN = TKNW + NO23 or TDN + PON, TDN = TKNF + NO23, PON = TKNW - TKNF, PHOSP = TP - TDP, POC = TOC - DOC, TOC = DOC + POC.

TABLE 2. Lower detection limits of water quality parameters, Chesapeake Bay Fall Line and Tributary Water Quality Monitoring Programs, 1984-1992.

PARAMETER	SRBC (PADER)	USGS (USGS)	OWML (OWML)	HRSD (HRSD)	VA/VWCB (DCLS)	MD/OEP-MDE (MDHMH)	DC/DCRA (CRL)
TOC	1.0	0.1/ 1.0	.05	-	1.0	1.0 0.5 (4/90-)	1.0
DOC	-	-	.05	-	1.0	1.0 0.8 (5/89-3/90) 0.5 (4/90-)	1.0
NH4	.008? .002?	.002/ .01	.01	.05	.05 .04 (2/88-)	.02 .008 (6/86 -)	.04
NO23	.04	.01/ .10	.01	.01	.05 .04 (2/88-)	.02	.04
NO2	.004	.001/ .01	.01	.01	.01	.002	.01
TKNW/ TKNF	.20/ 1.0	.20	.10 .05 (9/90)	.05	.10	.10	.20
TP	.02	.001/ .01	.01	.05	.01/ .10	.01	.01
TDP	.02	.001/ .01	.01	.05	.01/ .10	.01	.01
PO4F	.005? .002?	.001/ .01	.01	.05 .01 (8/90-)	.01	.01 .004 (6/86-)	.007
SI	-	.1	.04 .03 9/90	-	.1	.1	.2
TSS	1	1	1	1	5 1 (7/88-)	1	4
CHLA (ug/l)	?	?	1.0	-	3.1	1	?
BOD5	?	?	1	-	1	0.5	1

All concentrations are in mg/l except CHLA. USGS and DCLS have low and high limits for some parameters depending on what is requested. Where the second or third limit has a date after it, the first limit applied until that date.

TABLE 3. Within-organization and inter-organization precision estimates, Mainstem Component, June 1989 - December 1991.

Parameter	Mean within-organization precision												Mean inter-organization precision				
	CBL			MDHMH			ODU			VIMS			Four labs		Three labs		
	SD	CV	N	SD	CV	N	SD	CV	N	SD	CV	N	SD	CV	SD	CV	N
NH4	0.0045	46.4	7	0.0067	13.8	7	0.0012	11.3	7	0.0014	25.5	7	0.016	86.5	0.0047	54.1	7
NO2	0.0006	20.0	6	0.0005	6.0	6	0.0003	5.7	6	0.0002	6.0	6	0.0013	31.5	0.0015	35.1	6
NO23	0.0086	20.8	9	0.0019	0.8	9	0.0026	4.5	9	0.0041	12.4	9	0.0139	54.9	0.0075	24.4	9
TDN	0.0604	13.1	9	0.0652	16.0	9	0.0288	6.9	9	0.0230	5.6	9	0.079	17.5	0.050	12.6	9
PN	0.0044	2.3	9	0.0858	-52.5	9	0.0089	6.9	9	0.0092	6.3	9	0.058	38.3	0.029	19.2	9
TN	0.0607	9.0	9	0.0665	11.3	9	0.0305	5.6	9	0.0219	4.0	9	0.103	16.3	0.060	10.7	9
PO4F	0.0008	19.5	4	0.0038	29.6	4	0.0019	20.1	4	0.0001	10.8	4	0.0033	64.6	0.0021	57.3	4
TDP	0.0006	7.4	6	0.0115	38.0	6	0.0014	15.0	6	0.0021	16.9	6	0.012	63.1	0.0036	29.6	6
PHOSP	0.0008	6.0	9	0.0076	26.6	9	0.0011	6.1	9	0.0009	5.8	9	0.0074	61.8	0.0019	10.7	9
TP	0.0016	6.2	9	0.0052	11.9	9	0.0017	6.6	9	0.0034	11.9	9	0.012	40.9	0.0043	16.3	9
DOC	0.1508	5.3	8	-	-	-	0.1887	6.3	8	0.1724	4.6	8	-	-	0.412	13.2	8
PC	0.0538	4.8	9	-	-	-	0.0587	7.1	9	0.0479	5.1	9	-	-	0.166	17.1	9
TOC	0.1480	3.6	8	-	-	-	0.2246	5.7	8	0.1934	4.2	8	-	-	0.372	9.2	8
TSS	0.8100	17.5	9	1.491	15.3	9	3.014	27.9	9	1.713	13.3	9	5.16	48.6	5.79	54.4	9
CHLA	-	-	-	0.8562	11.7	8	1.182	14.6	8	0.7560	9.2	8	-	-	1.460	18.3	8
PHEA	-	-	-	0.4583	114.4	6	0.9149	39.0	6	0.6526	66.0	6	-	-	0.685	76.8	6
SI	0.0054	4.6	9	0.0257	7.9	9	0.0098	3.8	9	0.0218	4.3	9	0.068	18.4	0.059	11.4	9

Notes: DCLS data were excluded because they started later. Sample dates with below detection limit and missing data were excluded. SD = standard deviation, CV = coefficient of variation (= SD/Mean*100), N = number of sample dates over which mean was calculated. Within-organization precision is based on the precision of the results from field triplicate subsamples; inter-organization precision is based on the precision of medians of the triplicate subsamples for each organization and sampling date.

TABLE 4. Percent Recovery Data from Spiked Mainstem Component Split Samples.

Parameter	Laboratory	Percent Recovery							
		3/90	6/90	9/90	12/90	4/91	6/91	9/91	12/91
NH4	CBL	-	-	97	89	98	97	95	100
	DCLS	-	100	105	-	-	100	105	81
	MDHMH	88	100	116	84	124	112	96	-
	ODU	109	-	-	100	101	-	102	96
	VIMS	92	97	89	104	96	91	91	101
NO2	CBL	-	-	103	91	98	96	100	98
	DCLS	-	100	100	-	-	103	100	-
	MDHMH	100	98	-	96	104	-	96	-
	ODU	-	104	85	100	103	-	100	100
	VIMS	105	107	-	98	100	98	95	100
NO23	CBL	-	-	100	95	100	96	97	95
	DCLS	-	100	103	-	-	-	-	-
	MDHMH	110	106	110	106	-	-	-	-
	ODU	-	99	101	98	95	-	-	103
	VIMS	95	101	109	100	105	94	100	113
TDN	CBL	99	-	101	100	98	98	99	104
	ODU	-	103	104	125	110	106	102	102
	VIMS	101	98	93	90	93	92	121	99
TKNW	DCLS	-	93	93	-	-	100	107	100
	MDHMH	100	106	100	80	-	86	102	96
TKNF	MDHMH	-	100	108	86	-	84	-	112
PO4F	CBL	-	-	93	94	100	96	99	102
	DCLS	-	100	90	-	-	100	100	100
	MDHMH	120	84	88	92	-	84	-	-
	ODU	-	100	98	100	95	-	100	94
	VIMS	96	100	100	99	97	103	102	103
TDP	CBL	100	-	100	99	103	94	93	100
	DCLS	-	100	91	-	-	100	100	100
	MDHMH	-	-	104	86	-	84	-	107
	ODU	-	101	102	100	101	102	103	-
	VIMS	100	100	105	96	91	95	111	108
PHOSP	CBL	100	-	101	-	100	99	85	-
	ODU	-	103	87	82	100	91	90	-
	VIMS	92	100	110	102	102	98	100	102

TABLE 4 continued. Percent Recovery Data from Spiked Mainstem Component Split Samples.

Parameter	Laboratory	Percent Recovery 3/90	6/90	9/90	12/90	4/91	6/91	9/91	12/91
TP	DCLS	-	100	91	-	-	100	100	100
	MDHMH	96	-	104	80	-	111	-	109
DOC	CBL	-	-	108	101	100	109	104	-
	MDHMH	-	112	106	-	-	-	-	107
	ODU	-	91	115	100	90	105	98	-
	VIMS	102	94	97	99	105	106	98	98
TOC	DCLS	-	-	-	-	-	-	-	-
	MDHMH	-	113	106	-	-	-	-	108
SI	CBL	83	100	98	100	93	94	92	90
	DCLS	-	100	102	-	-	-	100	100
	MDHMH	-	-	140	100	117	88	102	-
	ODU	-	98	106	96	-	103	99	97
	VIMS	98	103	90	88	97	96	94	101

Note: Percent recovery data are only possible for directly measured parameters. There is no way to spike parameters analyzed directly from filters (PC, PN, CHLA or TSS). Percent recovery was not calculated when the sample concentration was censored at the detection limit. TDP = Total Dissolved Phosphorus, TP = Total Phosphorus, SI = Silica, NO2 = nitrite, NO23 = nitrite + nitrate, NH4 = ammonium, PHOSP = Particulate Phosphorus, DOC = dissolved Organic Carbon, PO4F = Orthophosphate filtered, TDN = Total Dissolved Nitrogen.

TABLE 5. Standard Reference Material Percent Recovery Results from Mainstem Component Laboratories.

Parameter	Date	CBL Dist.[1] (EPA)[2]	DCLS Dist. (EPA)	ODU Dist./Est.[3] (EPA)	VIMS Dist./Est. (EPA)
NH4	3/90	-	-	102/ - (0.04)	79/ 88 (2.0)
	6/90	104 (0.2)	95 (1.9)	72/ 68 (0.056)	75/100 (2.0)
	9/90	97 (0.2)	100 (2.0)	110/107 (0.04)	73/ 85 (0.2)
	12/90	95 (0.2)	-	97/ 99 (0.04)	85/107 (0.2)
	4/91	-	-	95/ 95 (0.04)	99/107 (0.2)
	6/91	99 (0.2)	103 (1.0)	96/ 86 (0.04)	86/ - (0.2)
	9/91	101 (0.2)	100 (1.0)	96/ 94 (0.04)	81/ 77 (0.2)
	12/91	99 (0.2)	100 (1.0)	96/ 94 (0.04)	90/ 77 (0.2)
NO23	3/90	-	-	101/ - (0.04)	102/ 94 (2.0)
	6/90	103 (0.2)	97 (1.42)	101/ 94 (0.04)	107/103 (2.0)
	9/90	102 (0.2)	100 (2.0)	101/ 98 (0.04)	103/ 99 (0.2)
	12/90	105 (0.2)	-	101/ 96 (0.04)	112/112 (0.2)
	4/91	105 (0.2)	-	100/ 94 (0.04)	106/ 99 (0.2)
	6/91	104 (0.2)	100 (1.0)	100/104 (0.04)	93/ - (0.2)
	9/91	103 (0.2)	100 (1.0)	100/ 97 (0.04)	100/105 (0.2)
	12/91	-	100 (1.0)	107/ 97 (0.04)	96/105 (0.2)
TDN	3/90	-	-[4]	100/ - (0.5)	-
	6/90	-	-	101/ 99 (0.5)	100/107 (5.0)
	9/90	99 (0.5)	-	103/104 (0.5)	71/ 66 (0.25)
	12/90	96 (0.5)	-	99/ 86 (0.5)	103/ 89 (0.25)
	4/91	-	-	104/100 (0.25)	113/ 89 (0.25)
	6/91	106 (0.5)	-	109/ 97 (0.25)	119/122 (0.25)
	9/91	116 (0.5)	-	94/ 99 (0.25)	143/ 62 (0.25)
	12/91	-	-	97/105 (0.5)	114/ 62 (0.25)
TKNW	3/90	-[4]	-	-[4]	-[4]
	6/90	-	100 (1.6)	-	-
	9/90	-	96 (5.0)	-	-
	12/90	-	-	-	-
	4/91	-	-	-	-
	6/91	-	100 (2.5)	-	-
	9/91	-	100 (2.5)	-	-
	12/91	-	100 (2.5)	-	-
PO4F	3/90	-	-	-	100/ 96 (0.5)
	6/90	108 (0.05)	100 (0.35)	97/100 (0.039)	100/ 96 (0.5)
	9/90	104 (0.05)	100 (0.39)	97/ 95 (0.039)	123/118 (0.039)
	12/90	102 (0.05)	-	105/103 (0.039)	95/100 (0.039)
	4/91	101 (0.05)	-	103/103 (0.039)	100/100 (0.039)
	6/91	109 (0.05)	100 (0.25)	105/ 95 (0.039)	103/ - (0.039)
	9/91	102 (0.05)	95 (0.2)	110/100 (0.039)	105/ 87 (0.039)
	12/91	-	95 (0.2)	100/102 (0.039)	87/ 87 (0.039)

TABLE 5 (continued). Standard Reference Material Percent Recovery Results from Mainstem Component Laboratories.

Parameter	Date	CBL Dist.[1] (EPA)[2]	DCLS Dist. (EPA)	ODU Dist./Est.[3] (EPA)	VIMS Dist./Est. (EPA)
TDP	3/90	-	-	-	-
	6/90	-	96 (0.5)	105/104 (0.075)	107/ 99 (1.5)
	9/90	102 (0.15)	87 (1.5)	103/ 99 (0.15)	112/ 87 (0.075)
	12/90	101 (0.15)	-	105/ 99 (0.15)	85/ 72 (0.075)
	4/91	-	-	99/ 98 (0.15)	100/ 72 (0.075)
	6/91	99 (0.15)	100 (0.75)	101/ 97 (0.15)	104/120 (0.075)
	9/91	107 (0.15)	-	103/ 95 (0.15)	95/ 91 (0.075)
	12/91	-	-	100/ 95 (0.15)	97/ 91 (0.075)
PHOSP	3/90	-[5]	-[4]	-	-[5]
	6/90	-	-	95/ - (0.78)	-
	9/90	-	-	96/ - (0.98)	-
	12/90	-	-	91/ - (0.78)	-
	4/91	-	-	96/ - (0.78)	-
	6/91	-	-	91/ - (0.78)	-
	9/91	-	-	96/ - (0.78)	-
	12/91	-	-	96/ - (0.78)	-
DOC	3/90	-[5]	-[4]	112/ - (4.10)	-
	6/90	-	-	98/ - (6.12)	105/107 (4.10)
	9/90	-	-	111/ 84 (9.18)	95/112 (4.1/2.05)
	12/90	-	-	103/ 73 (9.18)	98/109 (2.05)
	4/91	-	-	108/ 72 (3.01)	102/106 (4.20)
	6/91	-	-	105/ 79 (3.06)	109/102 (4.20)
	9/91	-	-	92/ 81 (3.06)	88/104 (2.05)
	12/91	-	-	97/ 82 (3.67)	100/ 99 (3.08)
TSS	3/90	-[5]	-[5]	-	-[5]
	6/90	-	-	106/ - (31.2)	-
	9/90	-	-	103/ - (278)	-
	9/90	-	-	90/ - (36.1)	-
	12/90	-	-	-	-
	4/91	-	-	-	-
	6/91	-	-	-	-
	9/91	-	-	-	-
	12/91	-	-	-	-

[1] SRM diluted before analysis in distilled/deionized water matrix.
[2] SRM diluted before analysis in estuarine (saline) water matrix.
[3] Expected (EPA) value for SRM, in mg/l.
[4] Analysis not performed by this laboratory.
[5] Analysis performed by this laboratory, but SRM results not reported.

TABLE 6. Within-organization and inter-organization precision estimates, Potomac Component, May 1989- December 1991.

Parameter	Period[1]	Within-organization precision									Inter-organization precision		
		DCRA/CRL			DCLS			MDHMH			Three labs		
		SD	CV	N	SD	CV	N	SD	CV	N	SD	CV	N
NH4	U	0.0068	9.8	5	0.0114	16.5	5	0.0114	16.5	5	0.0076	8.5	5
NH4	F	0.0184	23.0	5	0.0102	14.6	5	0.0098	17.1	5	0.0111	19.4	5
NO2	U	0.0028	17.2	5	0.0	0.0	5	0.00088	6.1	5	0.0030	21.1	5
NO2	F	0.00058	4.4	5	0.0012	4.9	5	0.00058	6.4	5	0.0017	15.0	5
NO23	U	0.024	1.9	6	0.014	0.98	6	0.038	2.3	6	0.12	8.0	6
NO23	F	0.035	2.8	5	0.019	1.5	5	0.013	0.75	5	0.052	4.0	5
TKNW	A	0.056	10.7	10	0.023	5.6	10	0.115	24.9	10	0.097	19.6	10
TN	A	0.061	3.4	10	0.038	2.0	10	0.127	7.8	10	0.116	6.3	10
PO4F	U	0.0014	4.1	4	0.0087	16.7	4	0.0030	5.7	4	0.0087	23.3	4
PO4F	F	0.0018	4.3	5	0.0023	6.4	5	0.0013	4.7	5	0.0040	13.0	5
TP	F	0.0075	12.1	5	0.0051	11.0	5	0.0110	14.3	5	0.0064	10.2	5
TDP	F	0.0042	8.6	4	0.0039	6.9	4	0.0077	15.4	4	0.0091	28.6	4
TOC	A	0.61	12.1	11	0.14	4.6	11	0.43	9.1	11	1.38	30.8	11
TSS	A	2.0	13.4	9	1.9	15.0	9	1.3	23.5	9	3.6	38.6	9
SI	U	0.013	0.81	5	0.055	5.6	5	0.029	2.6	5	0.11	10.1	5
SI	F	0.045	1.7	5	0.0097	0.76	5	0.0058	0.24	5	0.17	7.4	5
BOD5	A	0.105	7.0	3	0.236	15.7	3	0.283	19.8	3	0.43	34.5	3

[1] U = MDHMH unfiltered (before Dec. 1990), F = MDHMH filtered (starting Dec. 1990), A = all available data. TP used data from F period only, because DCLS lowered their MDL in December 1990.

Notes: March 1990 and DOC data were not used due to missing data.

SD= standard deviation, CV = coefficient of variation (= SD/Mean*100), N = number of sampling dates over which mean precision was calculated.

Within-organization precision is based on the precision of three subsamples; inter-organization precision is based on the precision of medians of the subsamples for each sampling date.

TABLE 7. Percent Recovery Data from Spiked Potomac Component Samples, 1989-91.

Parameter	Laboratory	Percent Recovery						
		5/1/89	6/12/89	9/11/89	1/8/90	3/5/90	6/11/90	9/11/90
NH4	DCRA/CRL	-	107	93	102	86	101	104
	MDHMH	140	108	102	110	76	108	72
NO2	DCRA/CRL	110	108	116	102	96	110	-
	MDHMH	98	100	100	100	-	104	96
NO23	DCRA/CRL	105	85	106	85	95	95	120
	MDHMH	-	95	108	102	-	100	104
TKNW	DCRA/CRL	-	117	67	109	98	91	73
	MDHMH	102	98	100	98	104	112	100
PO4	DCRA/CRL	100	96	96	-	98	113	-
	MDHMH	144	106	112	136	-	160	-
TDP	DCRA/CRL	-	-	95	100	94	106	113
TP	DCRA/CRL	-	115	83	100	102	99	86
	MDHMH	116	104	76	100	100	108	100
DOC	DCRA/CRL	82	-	86	108	105	96	94
TOC	DCRA/CRL	-	91	92	115	104	100	98
	MDHMH	103	99	92	93	103	108	106
SI	DCRA/CRL	136	111	75	-	138	87	78
	MDHMH	-	-	-	95	-	100	85

Parameter	Laboratory	Percent Recovery				
		12/10/90	4/22/91	6/3/91	9/3/91	12/2/91
NH4	DCRA/CRL	115	104	101	104	110
	MDHMH	107	-	100	-	100
NO2	DCRA/CRL	110	110	106	108	106
	MDHMH	98	-	100	98	-
NO23	DCRA/CRL	90	121	96	116	98
	MDHMH	96	-	104	-	-
TKNW	DCRA/CRL	107	107	124	98	-
	MDHMH	118	98	92	82	106
PO4F	DCRA/CRL	97	97	101	110	103
	MDHMH	96	-	116	100	108
TDP	DCRA/CRL	93	106	108	109	-
	MDHMH	88	-	78	-	99
TP	DCRA/CRL	93	89	108	95	-
	MDHMH	100	97	94	76	113
DOC	DCRA/CRL	85	99	-	92	-
	MDHMH	84	-	99	-	-
TOC	DCRA/CRL	100	100	-	95	-
	MDHMH	96	-	91	99	-
SI	DCRA/CRL	112	104	-	100	116
	MDHMH	100	-	-	105	-

Note: Percent recovery data are not possible for TSS analysis. DCLS did not report any percent recovery data. TDP = Total Dissolved Phosphorus, TP = Total Phosphorus, SI = Silica, NO2 = Nitrite, NO23 = Nitrite + Nitrate, TKNW = Total Kjeldahl Nitrogen Whole, NH4 = Ammonium, DOC = Dissolved Organic Carbon, TOC = Total Organic Carbon, PO4/PO4F = Orthophosphate.

TABLE 8. Standard Reference Material Results, Potomac Component, 1990-1991.

Parameter	Date	Laboratory	Results (mg/l) Expected	Distilled	95% CI*
NH4	1/90	DCRA/CRL	1.90	1.84	1.68 - 2.12
	3/90	DCRA/CRL	1.90	1.93	1.68 - 2.12
	6/90	DCRA/CRL	1.90	1.92	1.68 - 2.12
	9/90	DCRA/CRL	1.90	1.78	1.68 - 2.12
	12/90	DCRA/CRL	1.90	1.85	1.68 - 2.12
	4/91	DCRA/CRL	1.90	1.84	1.68 - 2.12
	6/91	DCRA/CRL	1.90	1.73	1.68 - 2.12
	9/91	DCRA/CRL	1.90	1.80	1.68 - 2.12
	12/91	DCRA/CRL	1.90	2.02	1.68 - 2.12
NO23	1/90	DCRA/CRL	1.43	1.35	1.28 - 1.56
	3/90	DCRA/CRL	1.43	1.29	1.28 - 1.56
	6/90	DCRA/CRL	1.43	1.50	1.28 - 1.56
	9/90	DCRA/CRL	1.43	1.51	1.28 - 1.56
	12/90	DCRA/CRL	1.43	1.46	1.28 - 1.56
	4/91	DCRA/CRL	1.43	1.35	1.28 - 1.56
	6/91	DCRA/CRL	1.43	1.35	1.28 - 1.56
	9/91	DCRA/CRL	1.43	1.40	1.28 - 1.56
	12/91	DCRA/CRL	2.00	1.98	1.68 - 2.32
TKNW	1/90	DCRA/CRL	4.78	5.05	3.70 - 5.77
	3/90	DCRA/CRL	4.78	4.90	3.70 - 5.77
	6/90	DCRA/CRL	4.78	4.72	3.70 - 5.77
	9/90	DCRA/CRL	4.78	4.68	3.70 - 5.77
	12/90	DCRA/CRL	0.40	0.411	0.089- 0.836
	4/91	DCRA/CRL	0.40	0.330	0.089- 0.836
	9/91	DCRA/CRL	0.40	0.460	0.089- 0.836
	12/91	DCRA/CRL	0.40	0.340	0.089- 0.836
PO4F	3/90	DCRA/CRL	0.35	0.401**	0.33 - 0.37
	6/90	DCRA/CRL	0.35	0.347	0.33 - 0.37
	12/90	DCRA/CRL	0.35	0.333	0.33 - 0.37
	4/91	DCRA/CRL	0.35	0.342	0.33 - 0.37
	6/91	DCRA/CRL	0.35	0.337	0.33 - 0.37
	9/91	DCRA/CRL	0.35	0.357	0.33 - 0.37
	12/91	DCRA/CRL	0.500	0.514	0.43 - 0.57
TDP	1/90	DCRA/CRL	1.00	1.00	0.89 - 1.21
	3/90	DCRA/CRL	1.03	0.924	0.89 - 1.21
	9/90	DCRA/CRL	1.03	1.06	0.89 - 1.21
TP	6/90	DCRA/CRL	1.03	0.896	0.89 - 1.21
	9/90	DCRA/CRL	1.03	1.06	0.89 - 1.21
	12/90	DCRA/CRL	0.120	0.127	0.087- 0.169
	4/91	DCRA/CRL	0.130	0.120	0.096- 0.180
	6/91	DCRA/CRL	0.130	0.120	0.096- 0.180
	9/91	DCRA/CRL	0.120	0.130	0.087- 0.169

TABLE 8 (continued). Standard Reference Material Results, Potomac Component, 1990-1991.

Parameter	Date	Laboratory	Results (mg/l) Expected	Distilled	95% CI*
TOC	1/90	DCRA/CRL	6.1	7.5	3.50 - 9.32
	3/90	DCRA/CRL	6.1	6.9	3.50 - 9.32
	6/90	DCRA/CRL	17.2	17.7	15.4 - 19.8
	9/90	DCRA/CRL	10.0	10.2	9.0 - 11.8
	12/90	DCRA/CRL	10.0	11.9**	9.0 - 11.8
	4/91	DCRA/CRL	6.12	5.91	5.31 - 7.60
	6/91	DCRA/CRL	6.1	6.0	3.50 - 9.32
	9/91	DCRA/CRL	6.1	7.5	3.50 - 9.32
	12/91	DCRA/CRL	12.2	16.5**	10.83 - 14.13

* Provided by EPA Environmental Monitoring and Support Laboratory (EMSL) Cincinnati.

** Measured value was outside the 95% confidence interval.

Note: DCLS and MDHMH have not reported any SRM results. NH4 = ammonium, NO23 = Nitrite + Nitrate, TKNW = Total Kjeldahl Nitrogen Whole, PO4F = Orthophosphate filtered, TDP = Total Dissolved Phosphorus, TP = Total Phosphorus, TOC = Total Organic Carbon.

3. Virginia Component

Means of within-organization precision, based on field replicates, are listed in Table 9. The mean CV values were generally low (less than 16%) except for PN at HRSD, which had CV= 26%.

Percent recovery data from laboratory spikes (Table 10) and results from Standard Reference Materials (SRMs, Table 11) estimated within-laboratory accuracy. VIMS and ODU also diluted SRMs in the sample matrix, although the salinity at TF5.5 is usually zero. Percent recovery values (Table 10) were almost all (96%, 219/227 values) within the range 80-120% recovery. Results from SRMs (Table 11) generally show good agreement with the expected results; percent recoveries were within the 80-120% range for 90% of the reported values (139/155).

4. Fall Line Component

Within-organization precision was estimated from the standard deviation and coefficient of variation of field replicates (Table 12). Within-organization coefficients of variation ranged from 0% for several parameters to 52% for total dissolved phosphorus (TDP) results from USGS.

Percent recovery data and results from Standard Reference Materials (SRMs) are used to estimate within-organization accuracy in the CSSP. Percent recovery data (Table 13) were only reported by PADER, MDHMH, and OWML; most values were close to 100%. None of the laboratories reported SRM results.

TABLE 9. Within-organization and inter-organization precision estimates, Virginia Component, 1990-1991.

Parameter	Mean within-organization precision												Mean inter-organization precision				
	DCLS			HRSD			ODU			VIMS			Four labs		Three labs		
	SD	CV	N	SD	CV	N	SD	CV	N	SD	CV	N	SD	CV	SD	CV	N
NH4	0.0056	6.3	8	0.0034	2.7	8	0.0034	4.7	8	0.0069	7.7	8	0.0137	16.3	-	-	8
NO2	0.0019	11.5	3	0.0	0.0	3	0.00064	1.8	3	0.00069	1.9	3	0.0117	29.9	-	-	3
NO23	0.0046	1.5	8	0.0083	2.4	8	0.00422	1.2	8	0.0089	3.0	8	0.0111	3.5	-	-	8
TDN	-	-	-	0.0459	8.6	4	0.0276	3.4	4	0.0548	5.6	4	-	-	0.1043	17.7	4
PN	-	-	-	0.0566	26.2	3	0.0233	8.9	3	0.0113	4.2	3	-	-	0.0806	33.1	3
TN	0.0293	2.3	5	0.0297	4.2	5	0.0374	3.6	5	0.0402	3.4	5	0.051	12.1	-	-	5
PO4F	0.0	0.0	7	0.00738	10.9	7	0.00173	4.3	7	0.00209	7.2	7	0.0154	39.8	-	-	7
TDP	0.0016	4.5	7	0.0078	15.6	7	0.0025	6.2	7	0.0063	15.0	7	0.0176	40.2	-	-	7
PHOSP	0.0087	4.3	7	0.0226	15.9	7	0.0089	4.0	7	0.0202	8.7	7	0.0450	27.9	-	-	7
TP	0.0093	3.7	7	0.0210	11.4	7	0.0098	3.7	7	0.0257	8.9	7	0.0467	16.2	-	-	7
TOC	0.460	9.5	5	-	-	-	0.219	3.1	5	0.173	2.5	5	-	-	1.987	32.8	5
TSS	1.63	5.0	5	1.60	4.1	5	1.86	4.3	5	1.28	3.3	5	3.206	7.4	-	-	5
SI	0.0313	1.9	8	-	-	-	0.0450	1.4	8	0.1088	3.1	8	-	-	0.180	5.3	8

Notes: SD = standard deviation, CV = coefficient of variation (= SD/Mean*100), N = number of sample dates over which mean was calculated. Within-organization precision is based on the precision of the results from triplicate sub-samples; inter-organization precision is based on the precision of medians of the triplicate sub-samples for each sampling date.

TABLE 10. Percent Recovery Data from Spiked Virginia Component Samples, 1990-1991.

Parameter	Laboratory	Percent Recovery from Laboratory Spikes							
		2/90	5/90	9/90	1/91	5/91	6/91	9/91	12/91
NH4	DCLS	97	104	100	-	107	94	96	85
	HRSD	99	-	100	80	93	90	89	85
	ODU	98	101	92	105	99	99	-	-
	VIMS	96	-	103	94	95	88	91	77
NO2	DCLS	100	100	100	-	100	100	100	100
	HRSD	98	-	100	105	95	90	105	105
	ODU	96	-	99	99	104	102	-	-
	VIMS	105	-	98	102	98	95	91	102
NO23	DCLS	92	107	92	-	122	117	105	108
	HRSD	98	-	98	90	103	90	100	99
	ODU	95	99	102	101	100	98	-	-
	VIMS	-	-	104	101	98	95	103	109
TKNW	DCLS	92	100	93	-	93	100	100	100
	HRSD	100	-	60	104	99	52	99	107
TKNF	HRSD	101	-	60	100	100	121	101	111
TDN	ODU	102	103	100	102	102	100	-	-
	VIMS	101	81	97	90	94	100	112	115
PO4F	DCLS	100	100	100	-	100	100	100	92
	HRSD	100	-	100	110	100	100	93	98
	ODU	95	99	98	95	97	-	-	-
	VIMS	98	-	104	102	97	106	95	105
TDP	DCLS	100	93	100	-	100	100	100	92
	HRSD	98	-	100	58	92	97	102	95
	ODU	102	101	105	101	102	103	-	-
	VIMS	97	105	105	100	111	-	74	118
PHOSP	ODU	101	97	97	95	96	97	-	-
	VIMS	96	-	95	100	113	94	84	97
TP	DCLS	91	100	100	-	92	100	100	92
	HRSD	94	-	120	93	99	92	86	86
DOC	ODU	98	96	104	99	94	96	-	-
	VIMS	-	103	97	105	94	94	100	104
SI	DCLS	98	102	100	-	103	100	100	102
	ODU	100	103	101	101	101	101	-	-
	VIMS	96	-	94	90	92	90	95	94

Note: Percent recovery is not possible for TSS, PC or PN. TDP = Total Dissolved Phosphorus, TP = Total Phosphorus, SI = Silica, NO2 = Nitrite, NO23 = Nitrite + Nitrate, TKNW = Total Kjeldahl Nitrogen Whole, TDN = Total Dissolved Nitrogen, NH4 = Ammonium, DOC = Dissolved Organic Carbon, PO4F = Orthophosphate. When percent recovery was done on more than one subsample, the first value for that date is listed.

TABLE 11. Standard Reference Material Percent Recovery Results from Virginia Component laboratories, 1990-1991.

Parameter	Date	DCLS Dist.[1] (EPA)[2]	HRSD Dist. (EPA)	ODU Dist./Est.[3] (EPA)	VIMS Dist./Est. (EPA)
NH4	2/90	96 (0.28)	92 (2.35)	98/ 95 (0.04)	79/ 88 (2.0)
	5/90	95 (1.9)	85 (0.48)	95/ 90 (0.04)	79/ 91 (2.0)
	9/90	100 (2.0)	100 (0.2)	109/105 (0.04)	83/ 76 (0.2)
	1/91	-	96 (0.5)	96/ 98 (0.04)	81/ 83 (0.2)
	5/91	93 (11.0)	102 (0.5)	101/ - (0.04)	85/ 90 (0.2)
	6/91	98 (1.0)	103 (0.89)	101/103 (0.04)	86/ 83 (0.2)
	9/91	98 (1.0)	108 (0.201)	96/ 94 (0.04)	81/ 77 (0.2)
	12/91	98 (1.0)	-	104/ 96 (0.04)	81/ 90 (0.2)
NO23	2/90	100 (0.14)	103 (5.34)	102/102 (0.04)	102/ 94 (2.0)
	5/90	101 (1.43)	100 (0.38)	101/103 (0.04)	100/100 (2.0)
	9/90	90 (2.0)	97 (0.33)	111/107 (0.04)	103/ 99 (0.2)
	1/91	-	92 (0.5)	100/101 (0.04)	97/ 75 (0.2)
	5/91	96 (1.3)	102 (0.5)	103/ 94 (0.04)	92/105 (0.2)
	6/91	92 (1.0)	98 (0.55)	104/ 99 (0.04)	93/ - (0.2)
	9/91	102 (1.0)	91 (0.268)	99/ - (0.04)	100/105 (0.2)
	12/91	-	-	98/104 (0.04)	109/ 96 (0.2)
TDN	2/90	-[4]	-[4]	98/103 (0.5)	-
	5/90	-	-	84/106 (0.25)	-
	9/90	-	-	103/102 (0.5)	133/104 (0.25)
	1/91	-	-	98/100 (0.5)	123/108 (0.25)
	5/91	-	-	112/102 (0.25)	79/100 (0.25)
	6/91	-	-	109/ 99 (0.25)	119/122 (0.25)
	9/91	-	-	94/ 99 (0.25)	143/ 62 (0.25)
	12/91	-	-	97/105 (0.5)	84/114 (0.25)
TKNW	2/90	94 (0.32)	100 (5.0)	-[4]	-[4]
	5/90	94 (0.32)	105 (1.02)	-	-
	9/90	96 (5.0)	112 (0.76)	-	-
	1/91	-	56 (0.5)	-	-
	5/91	104 (2.5)	111 (1.0)	-	-
	6/91	100 (1.0)	98 (1.0)	-	-
	9/91	104 (2.5)	91 (0.99)	-	-
	12/91	96 (2.5)	-	-	-
PO4F	2/90	100 (0.05)	112 (1.1)	103/100 (0.04)	100/ 96 (0.5)
	5/90	100 (0.035)	110 (0.46)	97/100 (0.04)	100/ 92 (0.5)
	9/90	100 (0.39)	103 (0.039)	97/ 96 (0.039)	123/ 97 (0.039)
	1/91	-	113 (0.039)	103/ 95 (0.039)	100/ 87 (0.039)
	5/91	88 (0.48)	103 (0.039)	92/ 98 (0.039)	121/ 90 (0.039)
	6/91	92 (0.25)	105 (0.058)	-	103/ - (0.039)
	9/91	100 (0.2)	102 (0.055)	100/ 98 (0.039)	105/ 87 (0.039)
	12/91	100 (0.2)	-	97/ 97 (0.039)	105/ 87 (0.039)

TABLE 11 (continued). Standard Reference Material Percent Recovery Results from Virginia Component Laboratories, 1990-1991.

Parameter	Date	DCLS Dist.[1] (EPA)[2]	HRSD Dist. (EPA)	ODU Dist./Est.[3] (EPA)	VIMS Dist./Est. (EPA)
TDP	2/90	110 (0.1)	-[5]	105/ 98 (0.15)	-
	5/90	100 (0.1)	-	105/104 (0.075)	-
	9/90	100 (1.5)	-	102/ 99 (0.15)	104/ 95 (0.075)
	1/91	-	-	105/ 99 (0.15)	96/ 96 (0.075)
	5/91	96 (0.75)	-	100/ 96 (0.15)	101/101 (0.075)
	6/91	100 (0.3)	-	100/ 96 (0.15)	104/120 (0.075)
	9/91	-	-	97/ 98 (0.15)	95/ 91 (0.075)
	12/91	-	-	105/102 (0.15)	105/ 97 (0.075)
PHOSP	2/90	-[4]	-[4]	87/ - (0.39)	-[5]
	9/90	-	-	96/ - (0.98)	-
	1/91	-	-	95/ - (0.98)	-
	5/91	-	-	99/ - (0.78)	-
	6/91	-	-	91/ - (0.78)	-
	9/91	-	-	96/ - (0.78)	-
	12/91	-	-	96/ - (0.78)	-
TP	2/90	110 (0.1)	87 (1.8)	-[4]	-[4]
	5/90	100 (0.1)	96 (0.98)	-	-
	9/90	100 (1.5)	96 (0.5)	-	-
	5/91	101 (0.75)	-	-	-
	6/91	100 (0.3)	93 (0.3)	-	-
	9/91	-	88 (0.765)	-	-
DOC	2/90	-[4]	-[4]	103/ 86 (4.5)	-
	5/90	-	-	96/ 81 (6.12)	105/107 (4.1)
	9/90	-	-	104/ 88 (9.79)	100/111 (8.2)
	1/91	-	-	91/ 89 (9.18)	99/109 (2.05)
	5/91	-	-	92/ 74 (3.06)	101/ 96 (4.1)
	6/91	-	-	98/ 91 (3.06)	101/ 96 (4.1)
	9/91	-	-	99/ 78 (3.06)	109/102 (4.2)
	12/91	-	-	97/ 87 (0.19)	100/ 99 (3.08)
TSS	9/90	-[5]	-[5]	94/ 97 (31.5)	-[5]
	5/91	-	-	103/ - (113.0)	-
	12/91	-	-	-	-

[1] SRM diluted before analysis in distilled/deionized water matrix.

[2] SRM diluted before analysis in estuarine (saline) water matrix.

[3] Expected (EPA) value for SRM, in mg/l. When the EPA values for the distilled and estuarine dilutions were different, the value for the distilled dilution is shown.

[4] Analysis not performed by this laboratory.

[5] Analysis performed by this laboratory, but SRM results not reported.

TABLE 12. Within-organization field and laboratory precision estimates, Fall Line Component, July 1991.

Parameter	Mean within-organization field precision												Mean inter-organization Precision, Four labs		
	PADER			USGS			MDHMH			OWML					
	SD	CV	N	SD	CV	N	SD	CV	N	SD	CV	N	SD	CV	N
NH4	0.0071	5.1	2	0.0035	4.7	2	0.0042	5.4	2	0.0	0.0	2	0.028	25.7	2
NO2	no data		0	0.0018	4.7	2	0.0	0.0	2	0.0	0.0	2	0.0034[1]	11.7[1]	2
NO23	0.0	0.0	2	0.0	0.0	2	0.0035	2.1	2	0.0035	0.3	2	0.067	7.0	2
TKNW	0.0141	2.7	2	0.141	18.9	2	0.0884	18.9	2	0.0071	1.7	2	0.163	27.7	2
TKNF	0.0636	15.8	2	0.0	0.0	2	0.159	29.0	2	0.0177	5.8	2	0.110	35.9	2
TN	0.0141	0.9	2	0.141	7.3	2	0.124	6.3	2	0.0106	0.7	2	0.145	9.0	2
PO4F	0.0	0.0	2	0.0014	17.7	2	below MDL		0	below MDL		0	below MDL		0
TDP	0.0	0.0	2	0.0057	51.6	2	0.0064	10.1	2	below MDL		0	0.023[1]	88.1[1]	2
TP	0.0035	4.2	2	0.0	0.0	2	0.0092	16.5	2	0.0	0.0	2	0.013	40.3	2
TOC	0.141	4.5	2	0.707	2.5	2	0.113	4.1	2	0.283	8.2	2	0.764	25.2	2
TSS	no data		0	no data		0	1.41	36.0	2	no data		0	no data		0
SI	no data		0	0.0	0.0	1	0.0	0.0	2	0.0	0.0	2	0.066[1]	4.7[1]	2

Notes: Sampling dates with below detection limit and missing data were excluded. SD = standard deviation, CV = coefficient of variation (= SD/Mean*100), N = number of sampling dates over which mean was calculated. Within-organization precision is based on the precision of the results from field duplicate subsamples; inter-organization precision is based on the precision of results from the first subsample for each sampling date across all four organizations.

[1] Based on data from three laboratories due to missing or below detection limit data.

TABLE 13. Percent Recovery Data from Spiked Fall Line Component Samples, 1990-91.

Parameter	Laboratory	Percent Recovery		
		3/28/90	8/1/90	7/24/91
NH4	PADER	100	-	-
	MDHMH	100	-	-
	OWML	-	101	107.9
NO2	PADER	100	-	-
	MDHMH	96	-	-
	OWML	-	99	100.5
NO23	PADER	100	-	-
	MDHMH	101	-	-
	OWML	-	86	104.9
TKNW	PADER	106	-	-
	MDHMH	100	-	-
	OWML	-	112	97.0
TKNF	PADER	128	-	-
	MDHMH	100	-	-
	OWML	-	104	102.0
PO4F	PADER	102	-	-
	OWML	-	79	104.0
TDP	PADER	97.5	-	-
	MDHMH	100	-	-
	OWML	-	104	103.6
TP	PADER	100	-	-
	MDHMH	100	-	-
	OWML	-	100	90.4
DOC	MDHMH	94	103	-
	OWML	-	117	90.8
TOC	PADER	100	-	-
	MDHMH	112	102	-
	OWML	-	101	120.5
SI	OWML	-	101	104.4

Note: Spiked samples, and thus percent recovery data, are not possible for TSS analysis. DCLS and USGS did not report any percent recovery data. TDP = Total Dissolved Phosphorus, TP = Total Phosphorus, SI = Silica, NO2 = Nitrite, NO23 = Nitrite + Nitrate, TKNW = Total Kjeldahl Nitrogen Whole, TKNF = Total Kjeldahl Nitrogen Filtered, NH4 = Ammonium, DOC = Dissolved Organic Carbon, TOC = Total Organic Carbon, PO4F = Orthophosphate.

B. INTER-ORGANIZATION PRECISION

1. Mainstem Component

Table 3 lists the standard deviation (SD) and coefficient of variation (CV) of the mean results from split samples for each organization on each sampling date, under "Mean inter-organization precision." For example, in three-way comparisons, these estimates represent the mean variability among results from CBL, VIMS, and ODU. The data user should decide which precision estimate is best for a particular application (see Methods for a definition and discussion of each estimate).

Although parameters with low inter-organization precision might be expected to have low inter-organization agreement, this correspondence was not found. Three parameters had high inter-organization CV means (over 50% for four-way and three-way comparisons): NH4, PO4F, and PHEA (although there were no four-way comparisons for PHEA). Only one of these, NH4, was identified as having low inter-organization agreement (see next section). These three parameters (NH4, PO4F, and PHEA) also had among the highest within-organization CV means (see previous section).

2. Potomac Component

The coefficient of variation (CV) of laboratory medians for each sampling date estimated inter-organization precision (Table 6). The mean CV over 3-10 sample dates ranged from 4% for NO23 to 39% for TSS, but more data are needed to determine if there are consistent differences among parameters in CV. TP data were excluded when DCLS data were below detection limits (before December 1990). The parameter that had the lowest inter-organization agreement based on graphing and ANOVA, NO23, did not have the highest inter-organization CV values.

3. Virginia Component

The coefficient of variation (CV) of laboratory medians for each sampling date estimated inter-organization precision (Table 9). The mean CV over 3-8 sample dates ranged from 4% for NO23 to 40% for TDP and PO4F.

4. Fall Line Component

The standard deviation (SD) and coefficient of variation (CV) of results from three or four organizations for each sampling date estimated inter-organization precision (Table 12). The inter-organization CV ranged from 88% for TDP to 4.7% for SI, based on August 1990 and July 1991 results. In almost all cases, inter-organization SD and CV means were higher than any of the within-organization precision estimates for the same parameters. More data are needed to determine if consistent differences exist among parameters in CV.

C. INTER-ORGANIZATION AGREEMENT

1. Mainstem Component

Friedman ANOVA was used to assess inter-organization agreement and determine which parameters had statistically significant inter-organization differences. The ANOVA results (Table 14) show that 16 out of 17 parameters had statistically significant inter-organization differences ($P < 0.01$) for at least one comparison. The medians over all sample dates are shown for comparison purposes only, and are not used in the statistical test. Comparing the three mainstem laboratories only, there were significant differences in 11 of the 15 parameters compared. In the last CSSP report (Bergstrom 1990), only 4 out of 14 parameters had statistically significant differences in the Mainstem Component, 2 of which were among the three mainstem laboratories (PN and PC). This increase in the number of parameters with significant differences probably reflects the increased power of the Friedman test used in this report. The current Friedman test uses data from three subsamples per sample date rather than the means used before, effectively tripling the sample size compared to the test used before. The number of sample dates included was similar in both reports, since the earlier report covered 1987-1989 data, and this report includes 1989-1991 data.

Because the Friedman test does not consider the magnitudes of inter-organization differences, time plots of the data with precision bars were used to see if the differences were larger than within-organization precision. Figures 1-17 show the medians for each sample date with precision bars for each parameter. These graphs show that 6 of the 17 parameters graphed had more than half of the sample dates with non-overlapping error bars, showing that the differences were larger than within-organization precision for those parameters. These 6 parameters were ammonia (NH4), particulate nitrogen (PN), dissolved organic carbon (DOC), particulate carbon (PC), total suspended solids (TSS), and silica (SI).

TABLE 14. Mainstem Component (CB5.3 & CB4.4) Split Sample Results, June 1989-Dec. 1991. Medians over all dates with complete data are shown.

Parameter	N[1]	Medians over all dates (mg/l except CHLA & PHEA) CBL	ODU	VIMS	MDHMH	DCLS	Friedman results[2] χ^2	P
NH4	7	0.0070	0.0098	0.0090	.	.	4.0	<0.20
NH4	7	0.0070 B	0.0098	0.0090	0.0400 A	.	35.2	<0.001
NH4	4	0.0150	0.0080	0.0057	0.0400	0.0450	-	MDL[3]
NO2	8	0.0064 A	0.0065 A	0.0055 B	.	.	17.7	<0.001
NO2	6	0.0064	0.0065	0.0055 B	0.0075 A	.	48.4	<0.001
NO2	4	0.0050	0.0040	0.0031	0.0060	0.0100	-	MDL
NO23	11	0.0970 A	0.0881 B	0.0950	.	.	25.9	<0.001
NO23	9	0.0970 AB	0.0881 C	0.0950 BC	0.1000 A	.	48.9	<0.001
NO23	5	0.0970	0.0881	0.0950	0.1000	0.0400	-	MDL
TDN	10	0.440 A	0.372 B	0.412 A	.	.	22.4	<0.001
TDN	7	0.430	0.364	0.409	0.370	.	19.4	<0.001
PN	10	0.178 A	0.143 B	0.138 B	.	.	47.3	<0.001
PN	9	0.185 A	0.126 B	0.140 B	0.150	.	31.5	<0.001
TN	10	0.610 A	0.506 B	0.556 A	.	.	35.7	<0.001
TN	8	0.607 A	0.526 B	0.556	0.550	.	20.5	<0.001
TN	5	0.599 A	0.461 B	0.508	0.500	0.540 A	25.4	<0.001
PO4F	4	0.0037	0.0075 A	0.0017 B	.	.	26.6	<0.001
PO4F	4	0.0037	0.0075	0.0017	0.0040	.	-	MDL
PO4F	4	0.0037	0.0075	0.0017	0.0040	0.0100	-	MDL
TDP	10	0.0086	0.0085	0.0100	.	.	3.1	<0.30
TDP	6	0.0127	0.0070 B	0.0130	0.0190 A	.	39.5	<0.001
TDP	6	0.0127	0.0070	0.0130	0.0170	0.0100	-	MDL

TABLE 14 (continued). Mainstem Component Split Sample Results.

Parameter	N[1]	Medians over all dates (mg/l except CHLA & PHEA) CBL	ODU	VIMS	MDHMH	DCLS	Friedman results[2] χ^2	P
PHOSP	9	0.0150	0.0140	0.0160	.	.	6.4	<0.048
PHOSP	9	0.0150	0.0140	0.0160	0.0155	.	6.5	<0.10
PHOSP	6	0.0146 B	0.0140 B	0.0146	0.0175	0.0200 A	23.4	<0.001
TP	9	0.0244	0.0220	0.0275	.	.	2.1	<0.40
TP	9	0.0244	0.0220	0.0275	0.0440	.	6.5	<0.10
TP	6	0.0262	0.0215 B	0.0241	0.0450 A	0.0350 A	32.7	<0.001
DOC	8	2.81 B	2.84 B	3.52 A	.	.	36.9	<0.001
PC	10	1.19 A	0.920 B	0.964 B	.	.	45.4	<0.001
TOC	8	3.92	3.75 B	4.52 A	.	.	28.1	<0.001
TOC	5	3.76	3.43 B	4.43 A	.	3.06 B	20.2	<0.001
TSS	9	4.80 B	9.30 A	12.7 A	.	.	31.5	<0.001
TSS	9	4.80 B	9.30 A	12.7 A	10.0 A	.	42.1	<0.001
TSS	6	4.70 B	8.35	8.80 A	10.5 A	4.50	28.8	<0.001
CHLA[4]	8	.	8.37	8.44	8.61	.	6.8	<0.038
PHEA[4]	6	.	1.30 A	0.985	0.150 B	.	14.0	<0.001
SI	9	0.260 B	0.293 A	0.323 A	.	.	30.0	<0.001
SI	9	0.260 B	0.293 A	0.323 A	0.350 A	.	40.6	<0.001
SI	5	0.730 B	0.906 A	0.821	0.950 A	0.794	40.5	<0.001

1 Number of sample dates with complete data. For parameters with more than one line of results, the first line is usually three-way comparisons among CBL, VIMS, and ODU (except for CHLA and PHEA), the second line is four-way comparisons adding MDHMH (except for TOC), and the third line is five-way comparisons adding DCLS. The sample sizes may vary depending on which laboratories were included.

2 Underlined values were statistically significant ($P < 0.01$), Friedman two-way ANOVA. Pairs of medians that have different letters below them also had statistically significant pairwise differences ($A > B > C$, $P < 0.01$). Medians that have no letter below them, or have a letter in common, did not differ significantly.

3 Too many values were below the method detection limit to analyze.

4 Units are ug/l, not mg/l, for CHLA and PHEA.

FIGURE 1. Split sample data for ammonium (NH4), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

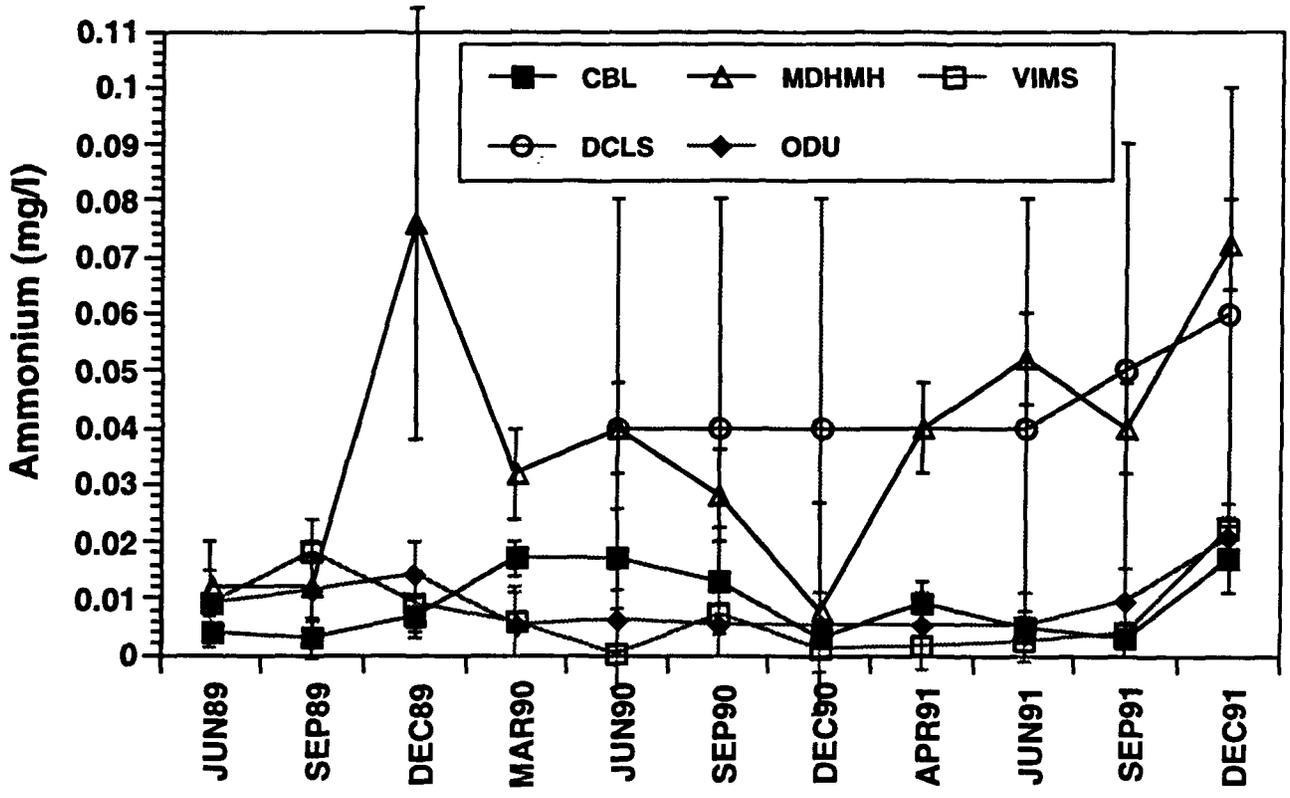


FIGURE 2. Split sample data for nitrite (NO2), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

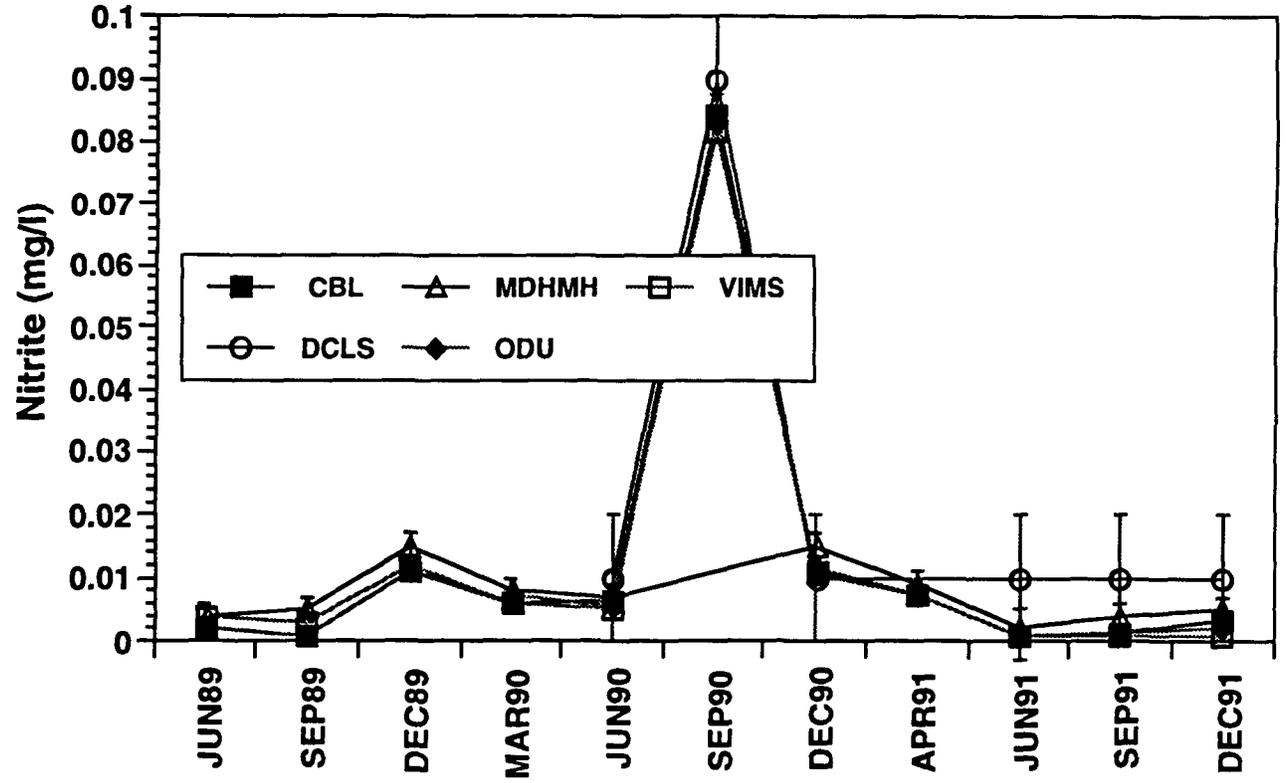


FIGURE 3. Split sample data for nitrite + nitrate (NO23), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

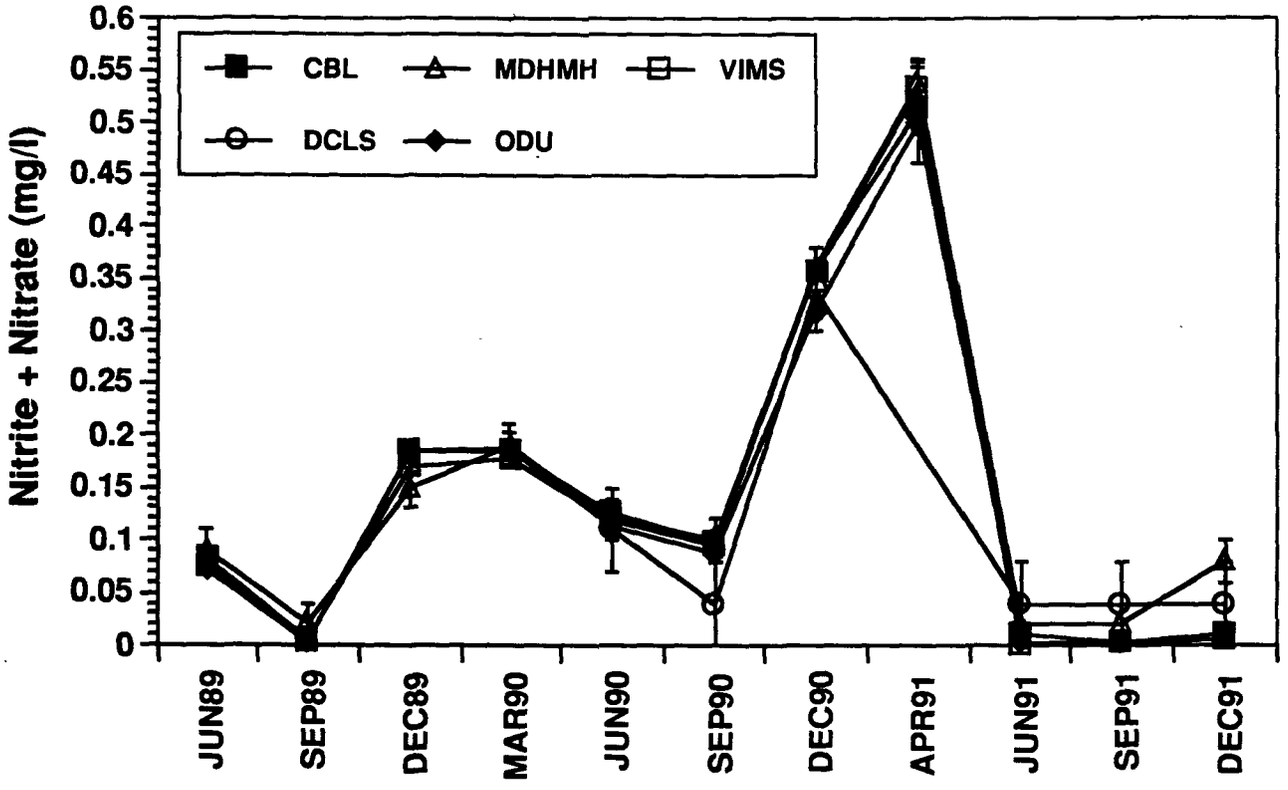


FIGURE 4. Split sample data for total dissolved nitrogen (TDN), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

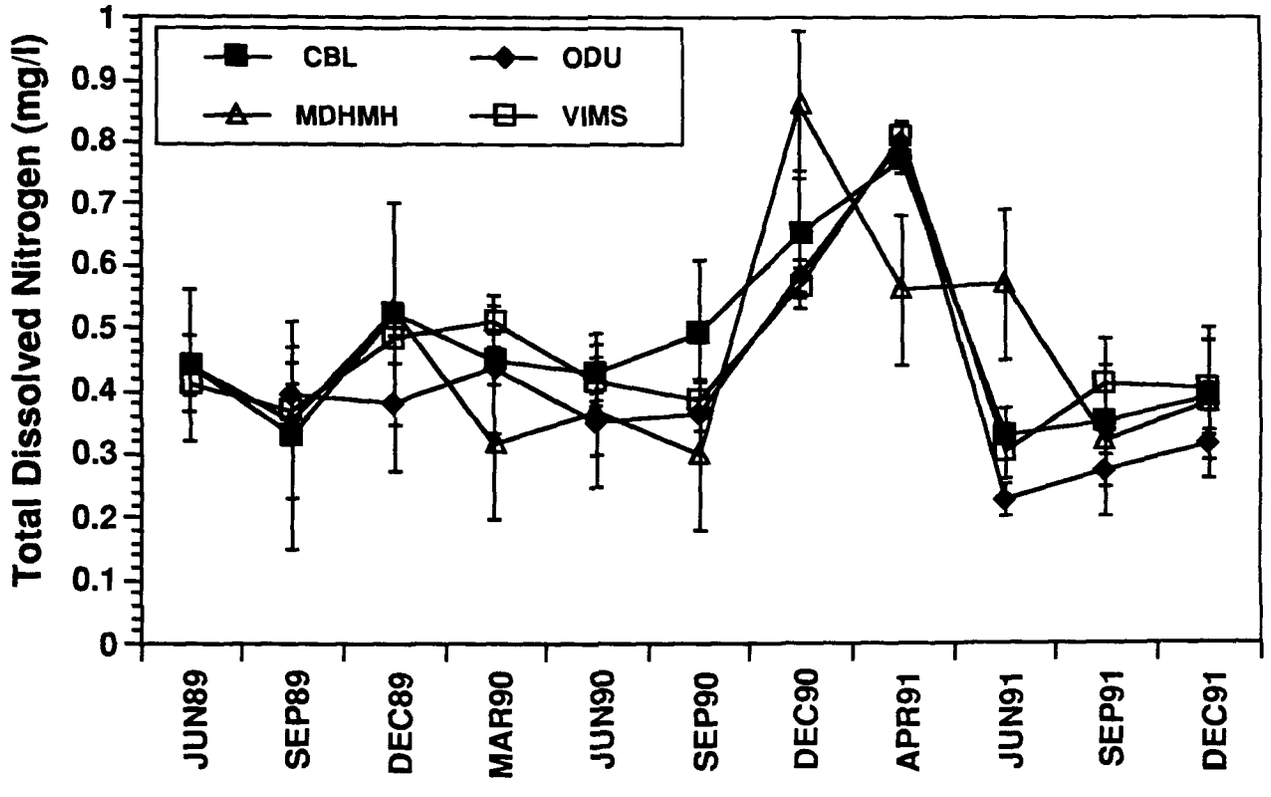


FIGURE 5. Split sample data for particulate nitrogen (PN), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars. Precision bars for MDHMH are not shown since they were large (0.2 mg/l).

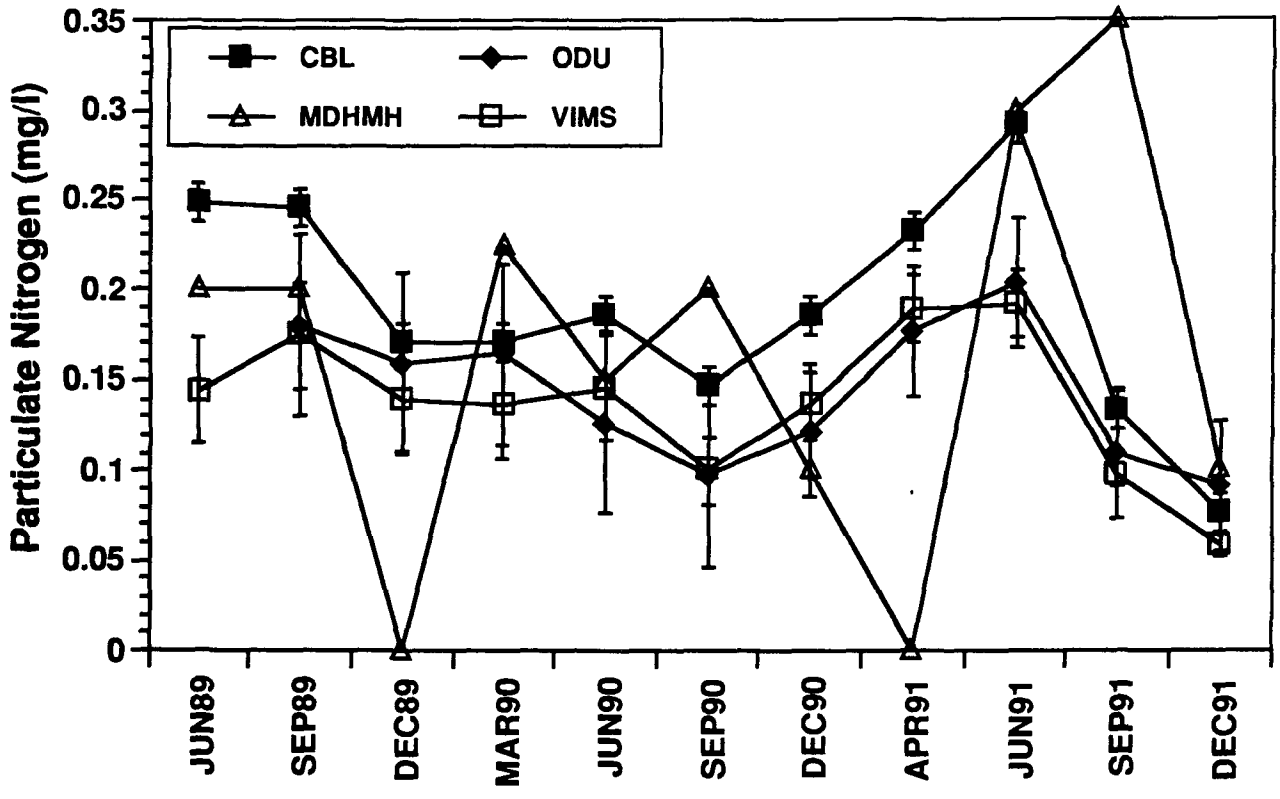


FIGURE 6. Split sample data for total nitrogen (TN), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

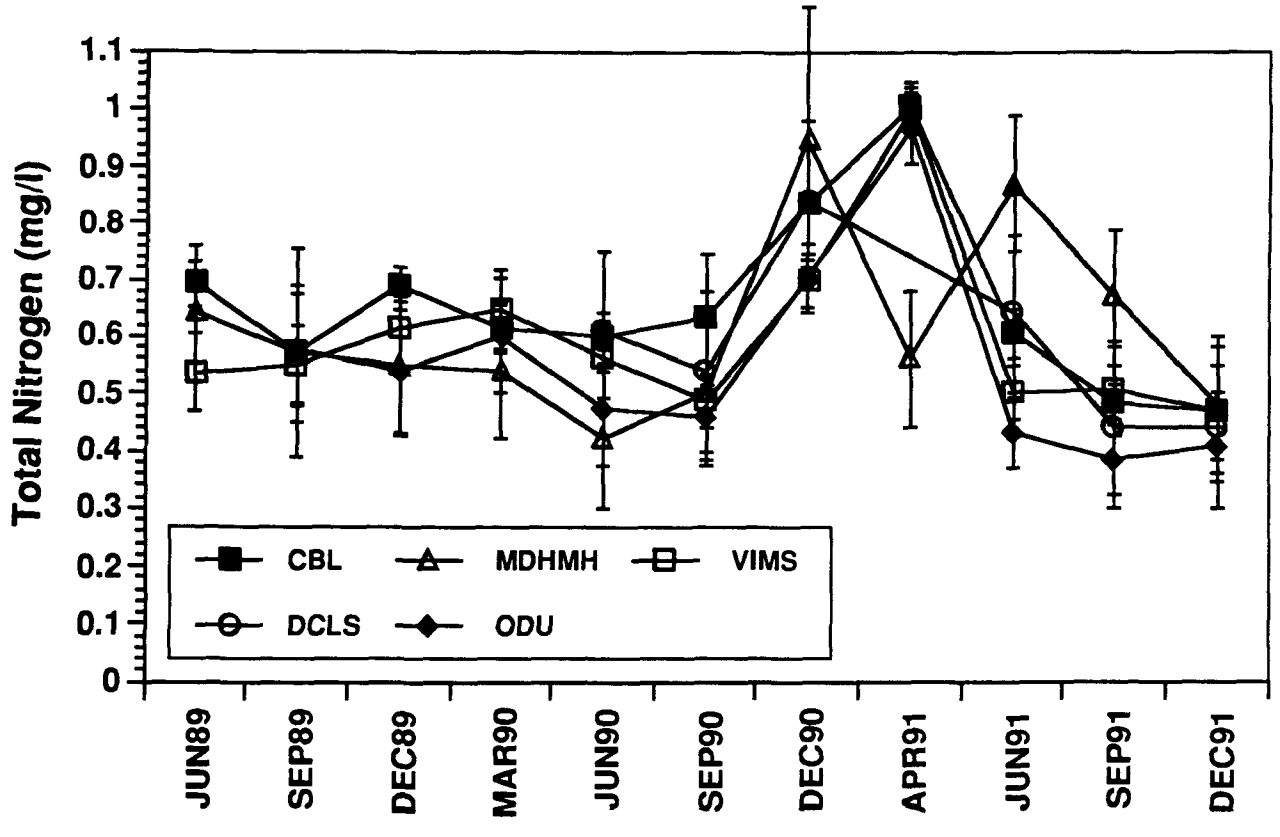


FIGURE 7. Split sample data for orthophosphate (PO4F), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

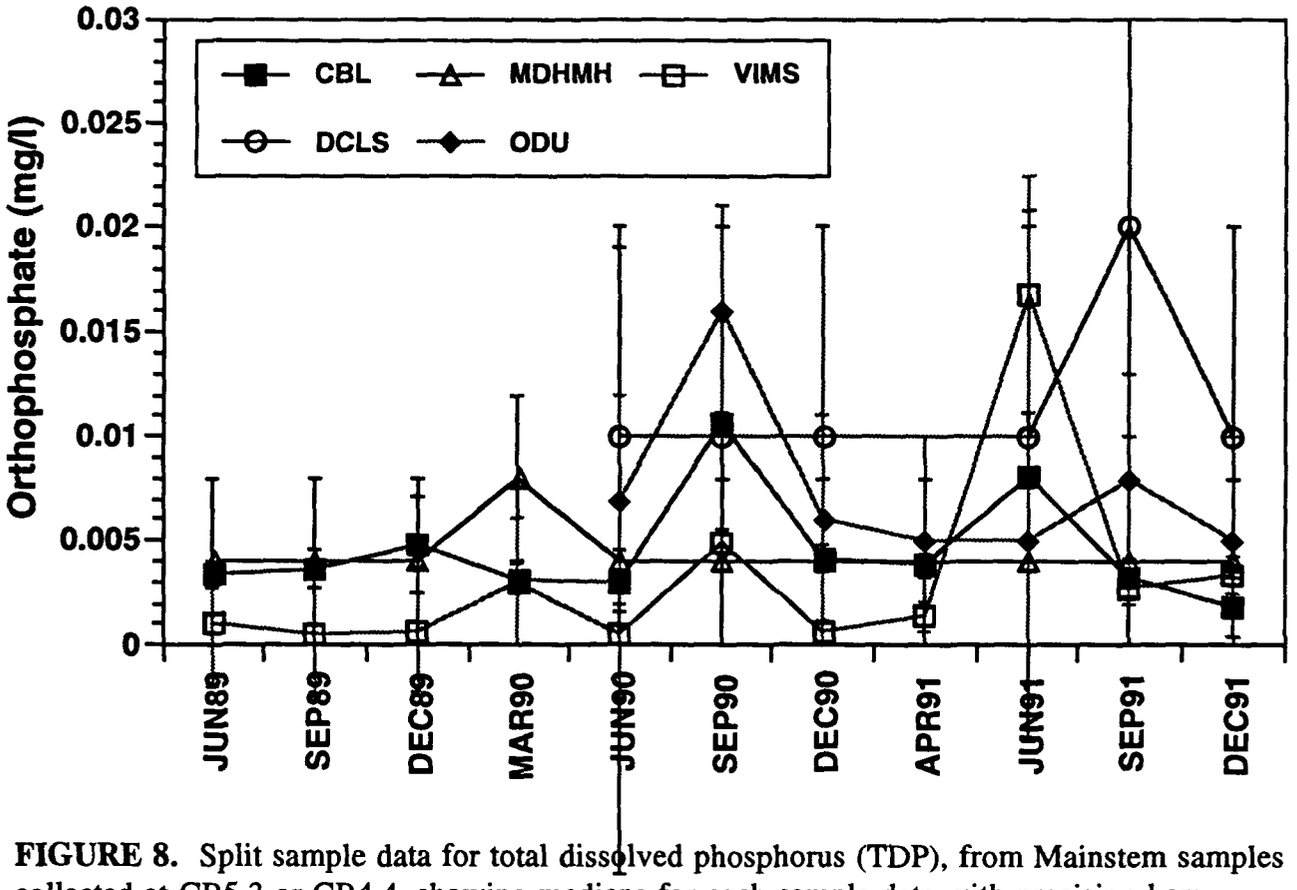


FIGURE 8. Split sample data for total dissolved phosphorus (TDP), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

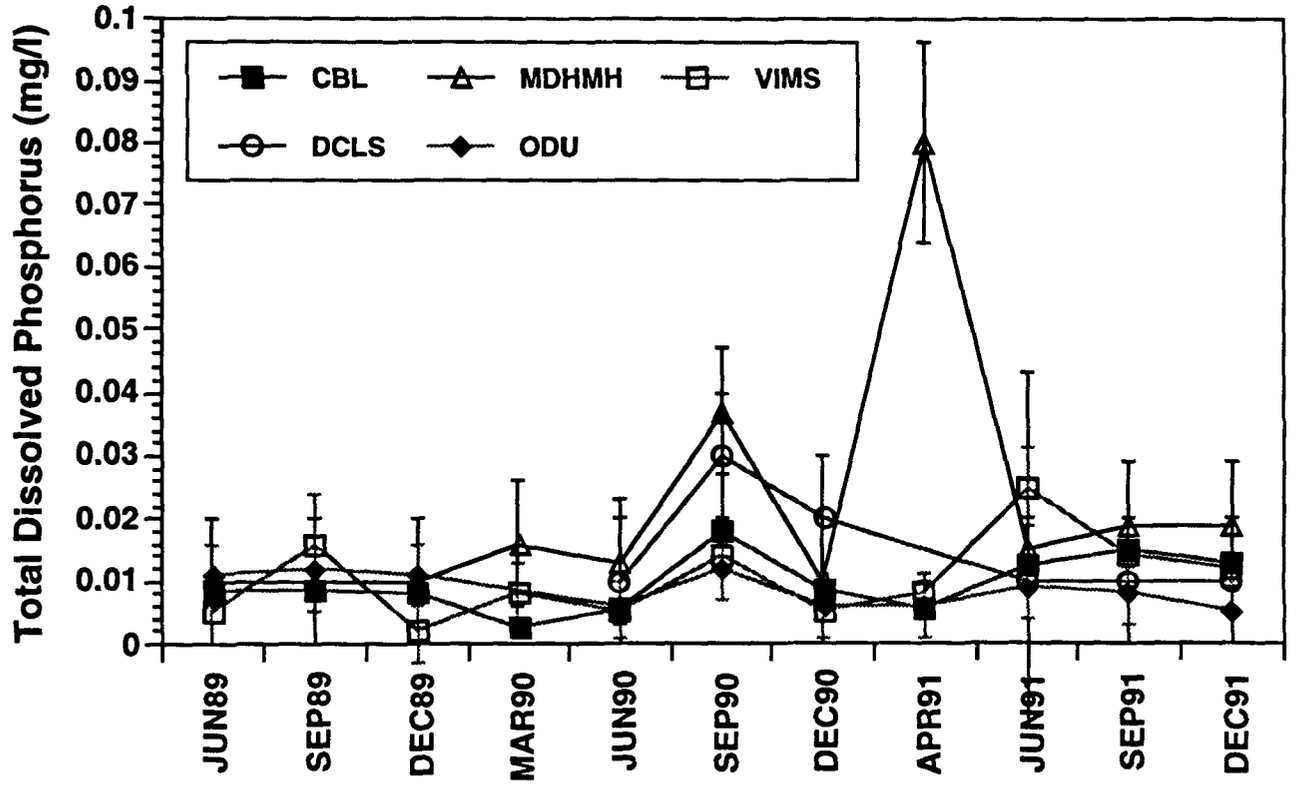


FIGURE 9. Split sample data for particulate phosphorus (PHOSP), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars. Precision bars for MDHMH are not shown since they were large (0.02 mg/l).

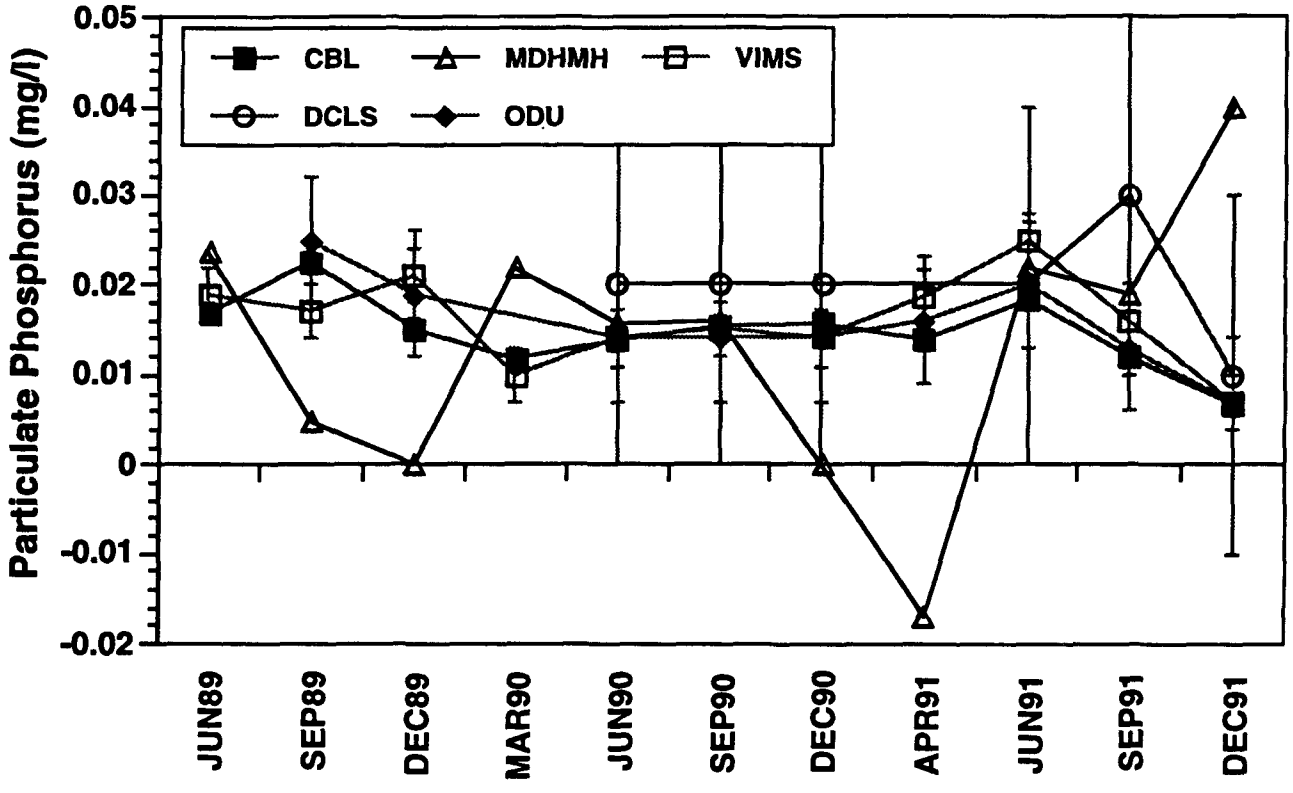


FIGURE 10. Split sample data for total phosphorus (TP), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

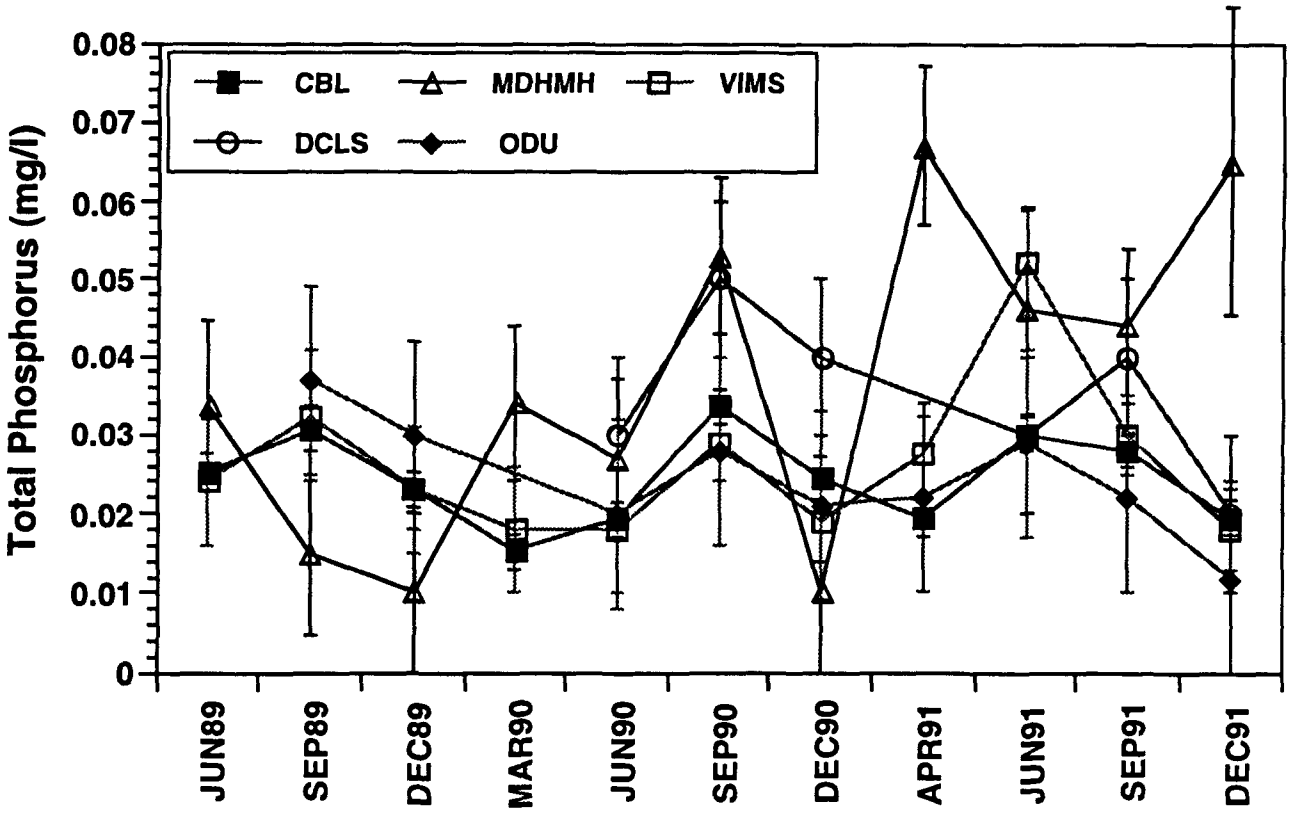


FIGURE 11. Split sample data for dissolved organic carbon (DOC), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars. There was only one date with data from MDHMH (December 1991).

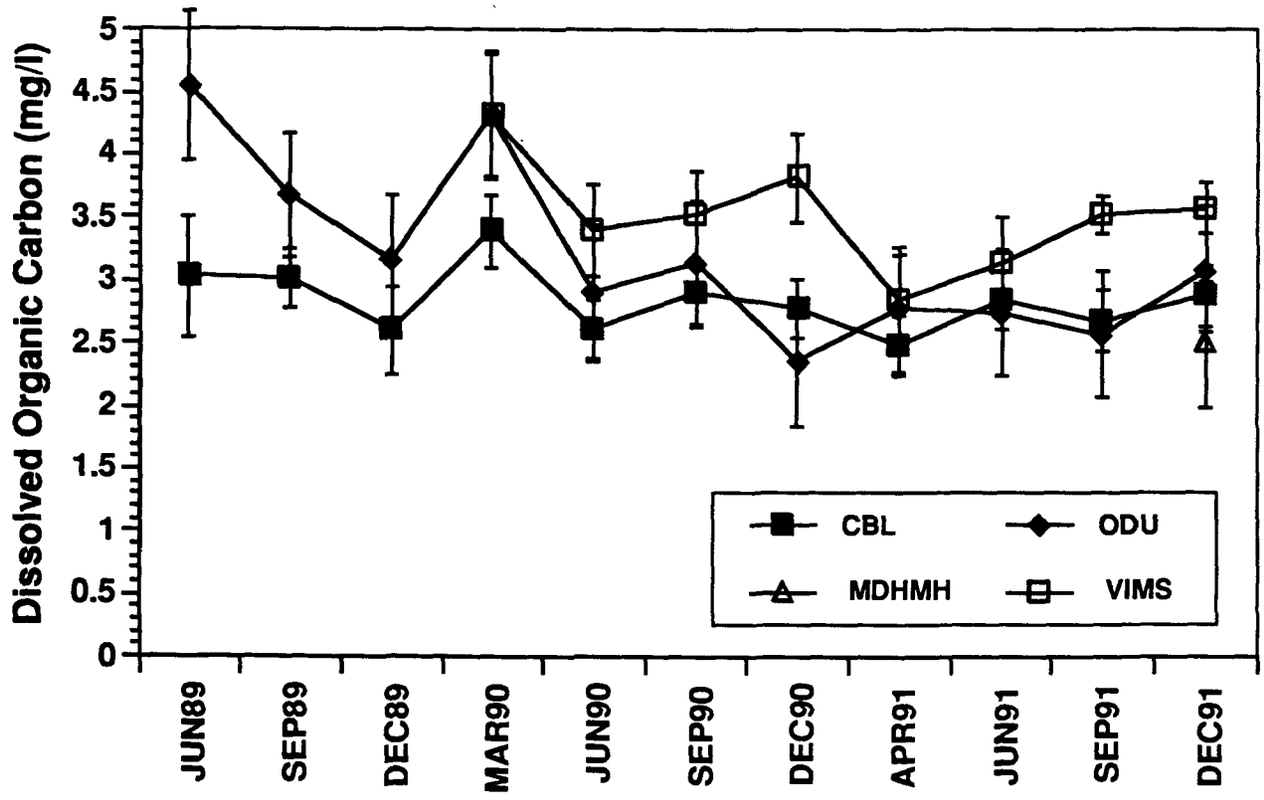


FIGURE 12. Split sample data for particulate carbon (PC), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

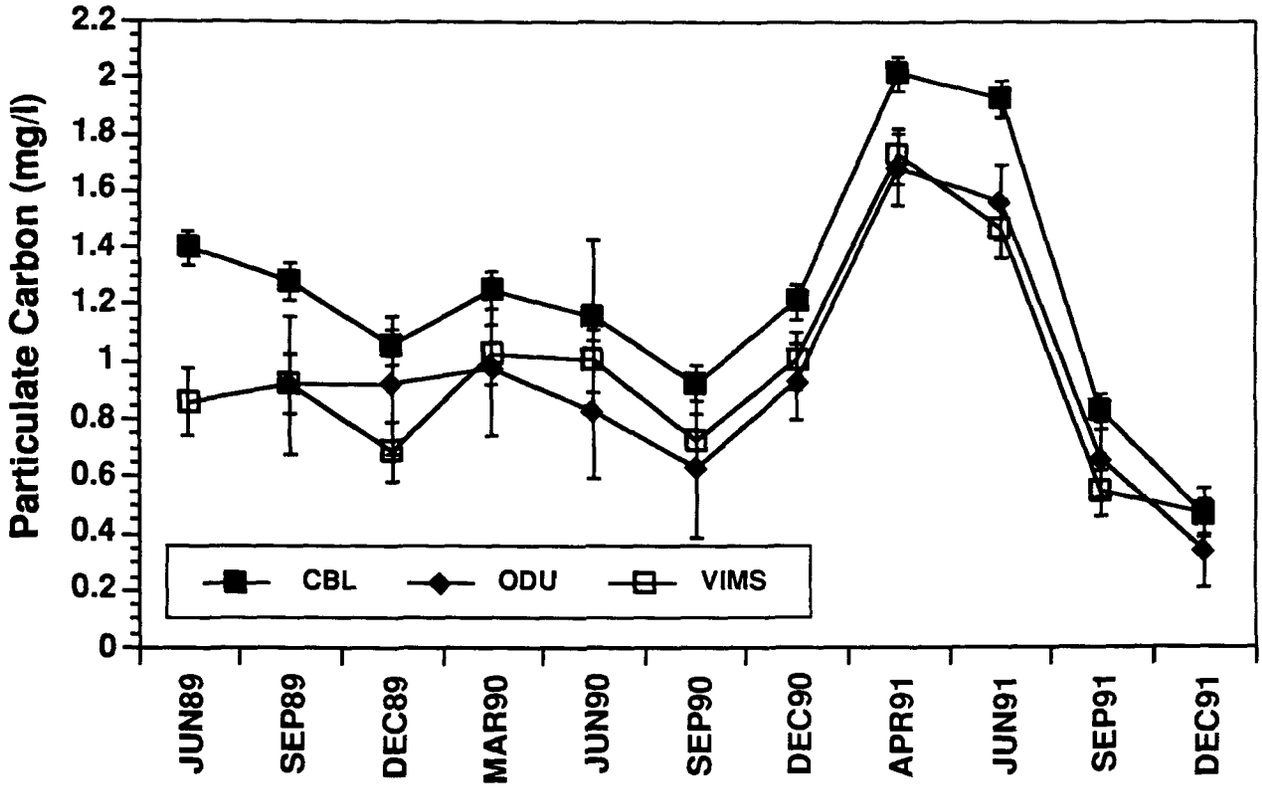


FIGURE 13. Split sample data for total organic carbon (TOC), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

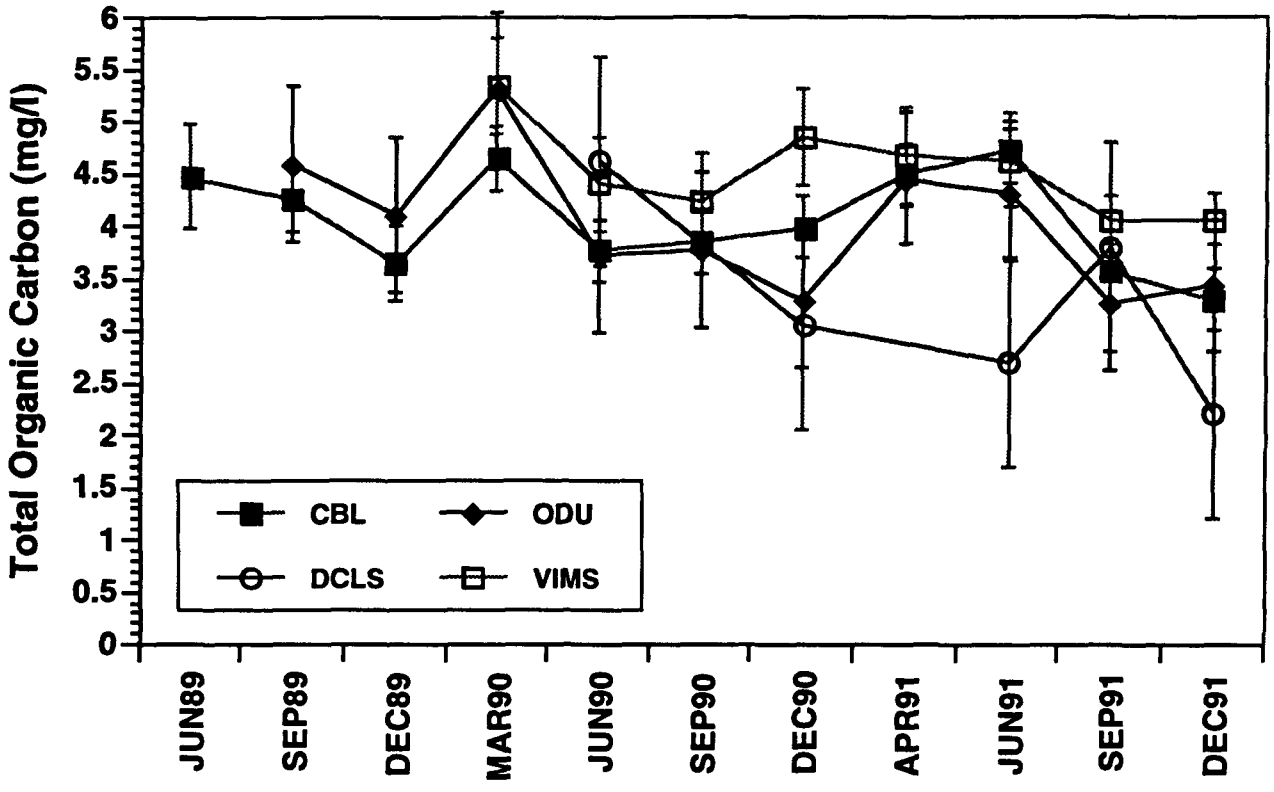


FIGURE 14. Split sample data for total suspended solids (TSS), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

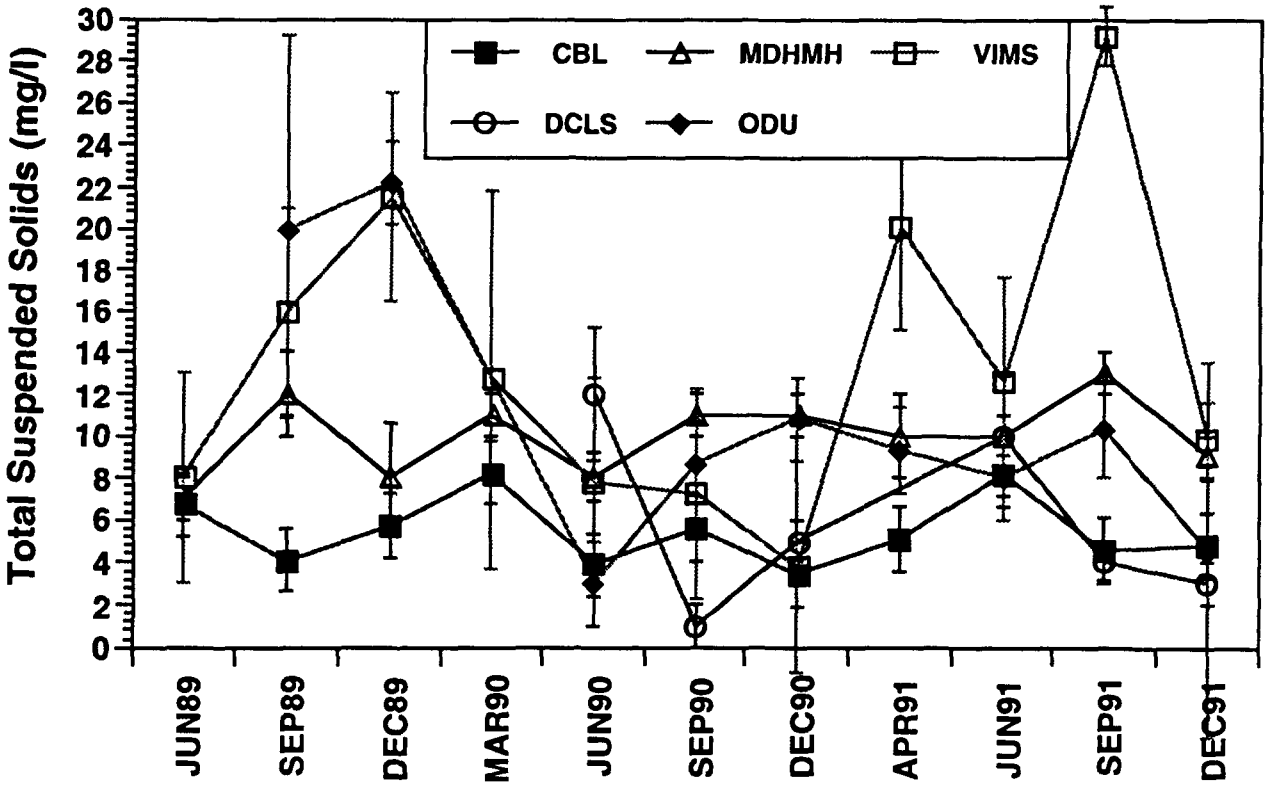


FIGURE 15. Split sample data for chlorophyll *a* (CHLA), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.

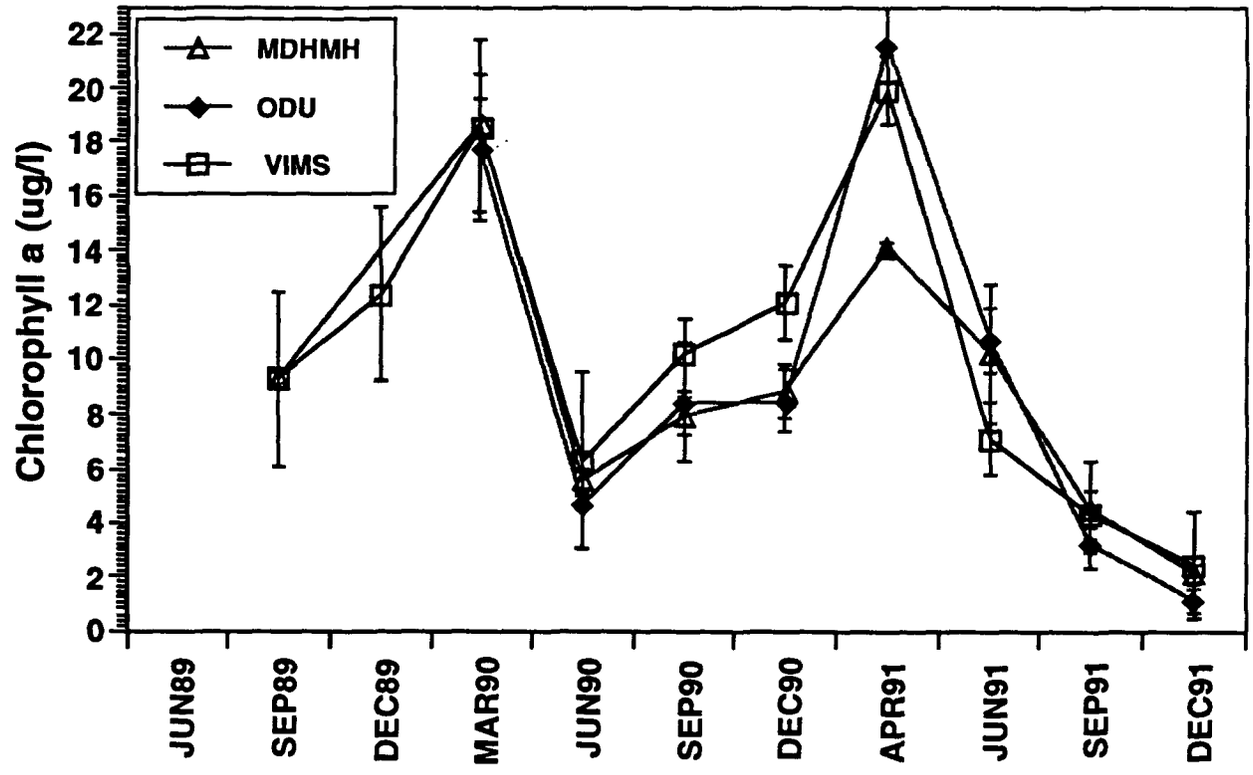


FIGURE 16. Split sample data for phaeophytin (PHEA), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars. Only positive precision bars are shown for VIMS data since they were large.

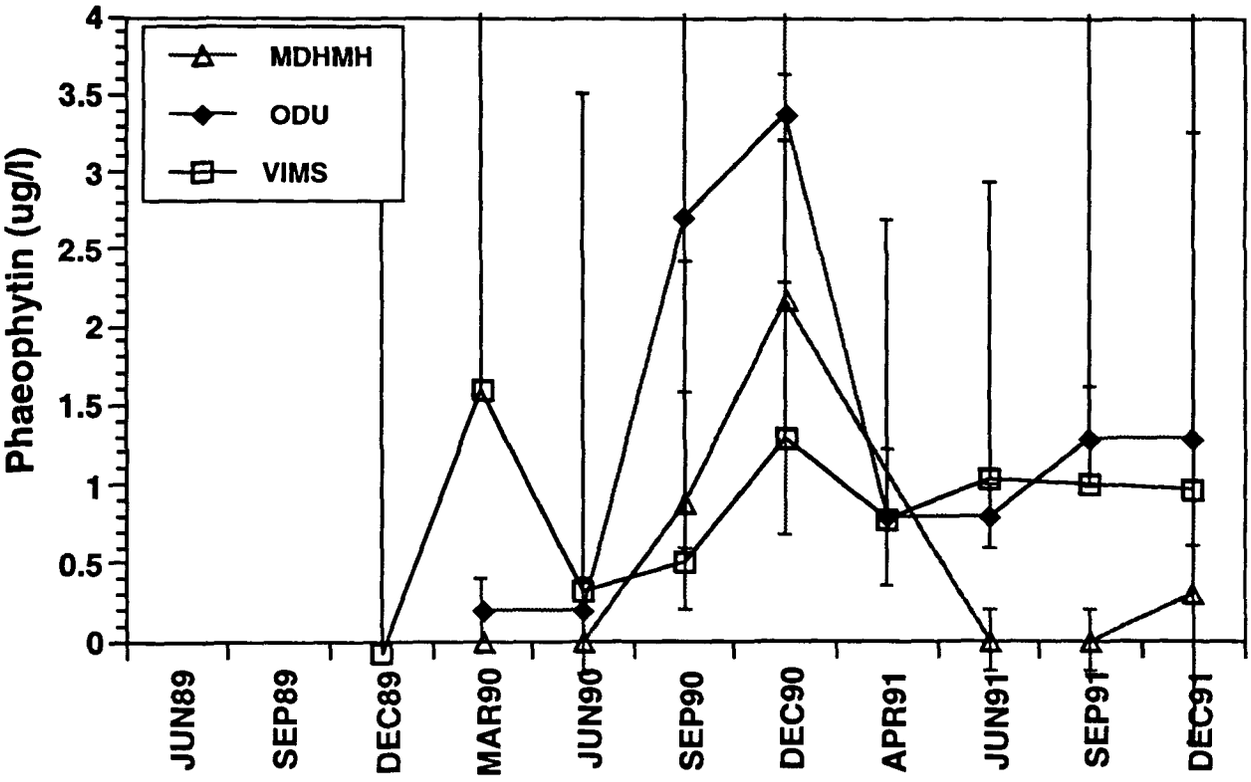
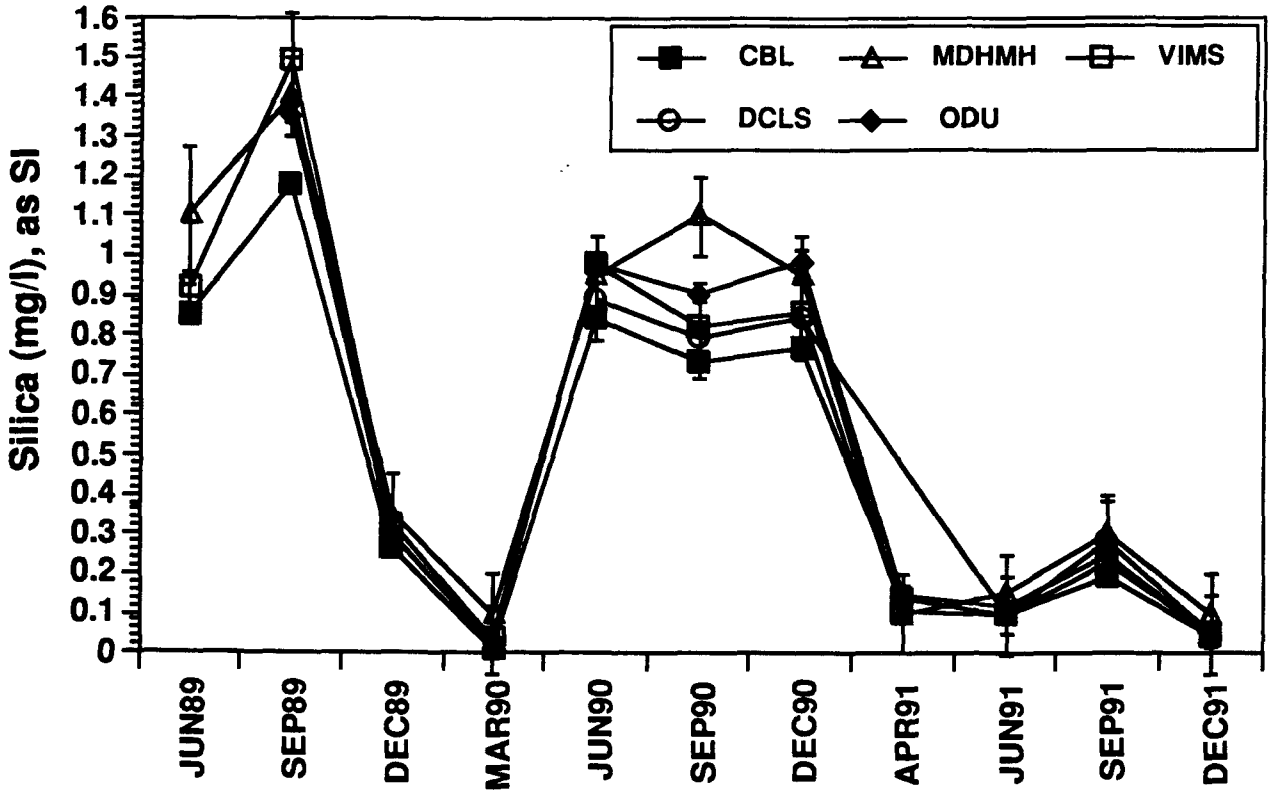


FIGURE 17. Split sample data for silica (SI), from Mainstem samples collected at CB5.3 or CB4.4, showing medians for each sample date with precision bars.



2. Potomac Component

Friedman ANOVA performed on results from the three subsamples assessed inter-organization agreement and determined which parameters had statistically significant inter-organization differences. The results (Table 15) show that 7 of the 11 parameters analyzed (NO23, TKNW, PO4, TDP, TOC, TSS, and SI) had statistically significant inter-organization differences at the $P < 0.01$ level. Three of these, NO23, PO4 and SI, could have been affected by the change to filtered samples in MDHMH data in December 1990. NO23 results were significant only in early data (before December 1990), SI results were significant only in late data, and PO4 results were significant in both time periods. Three other parameters, TKNW, TOC, and TSS, had large enough sample sizes to test 1991 data separately, to see if the differences persisted. Only TOC still had statistically significant differences in 1991 data (Table 15). Missing data ruled out analysis of DOC results.

Medians for each sample date with precision bars for each parameter plotted against time show inter-organization agreement (Figures 18-30). The length of the precision bars are the MDL (Tables 1 & 2) or the standard deviation of three field subsamples for that sample, whichever was greater. On sample dates with non-overlapping precision bars, the inter-organization differences were larger than the within-organization precision.

Four parameters, nitrate + nitrite (NO23), orthophosphate (PO4F/PO4W), Total Organic Carbon (TOC), and Total Phosphorus (TP), had more than half of the sampling dates with non-overlapping precision bars. NO23 samples (Fig. 20) and PO4 samples (Fig. 23) were from unfiltered samples at MDHMH (until December 1990) and filtered samples at the other two laboratories. For NO23, there were eight sampling dates with non-overlapping precision bars, and all but two, December 1990 and June 1991, were during the period when MDHMH received unfiltered samples. PO4 had three sample dates with non-overlapping precision bars, all before December 1990. TOC results had non-overlapping precision bars between DCLS and DCRA/CRL results on six dates (Fig. 26). Total Phosphorus (TP, Fig. 24) had several non-overlapping precision bars due to high detection limits in early DCLS data. The other 9 parameters had inter-organization differences that tended to be smaller than within-laboratory precision.

TABLE 15. Potomac Component (PMS-10) Split Sample Results (May 1989 - December 1991).

Parameter	N	Laboratory Medians (mg/l)*			Friedman Results+	
		DCRA/CRL	DCLS	MDHMH	χ^2	P
NH4 (W)**	5	0.081	0.090	0.072	4.4	>0.10
NH4 (F)	4	0.075	0.070	0.074	1.0	>0.70
NO2 (W)**	5	0.013	0.010	0.015	0.84	>0.70
NO2 (F)	5	0.011	0.010	0.010	0.52	>0.70
NO23 (W)**	6	1.26 B	1.46 B	1.60 A	29.5	<0.001
NO23 (F)	5	1.38	1.39	1.40	3.5	>0.18
TKNW	10	0.536 A	0.500 B	0.425 B	12.3	<0.01
TKNW++	4	0.490	0.450	0.400	0.69	>0.70
TN	10	1.915	1.925	2.015	5.08	>0.05
PO4 (W)**	4	0.032 B	0.040 A	0.042 A	15.0	<0.001
PO4 (F)	5	0.032	0.030	0.024	8.9	<0.01
TP***	5	0.059	0.060	0.062	2.1	>0.3
TDP	4	0.048	0.035	0.048	8.87	<0.01
TOC	11	4.30 A	3.30 B	3.44	17.0	<0.001
TOC++	4	5.25 A	3.30 B	3.95	13.4	<0.01
TSS	9	11.0 A	12.0	7.0 B	12.5	<0.001
TSS++	3	8.0	4.0	6.0	3.6	>0.20
SI (W)**	5	2.89	2.71	2.70	2.5	>0.20
SI (F)	5	2.54	2.38	2.40	8.4	<0.01
BOD5	3	1.4	1.0	1.2	1.8	>0.50

* Medians over the number of sample dates shown (N). Pairs of medians that have different letters below them also differed significantly ($P < 0.01$, A > B).

\+ Probability associated with Chi-square value with 2 df, testing for consistent differences among the three organizations with Friedman ANOVA. Statistically significant values ($P < 0.01$) are underlined.

** (W) used data through September 1990 only, when MDHMH analyzed unfiltered samples, and (F) includes data from December 1990 on, when MDHMH analyzed filtered samples. CRL and DCLS always analyzed filtered samples.

++ Using 1991 data only, to see if significant differences persisted.

*** Using TP data from December 1990 onward, after the MDL was lowered for DCLS analyses.

FIGURE 18. Split sample data for ammonium (NH4), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars. MDHMH samples were filtered starting in December 1990.

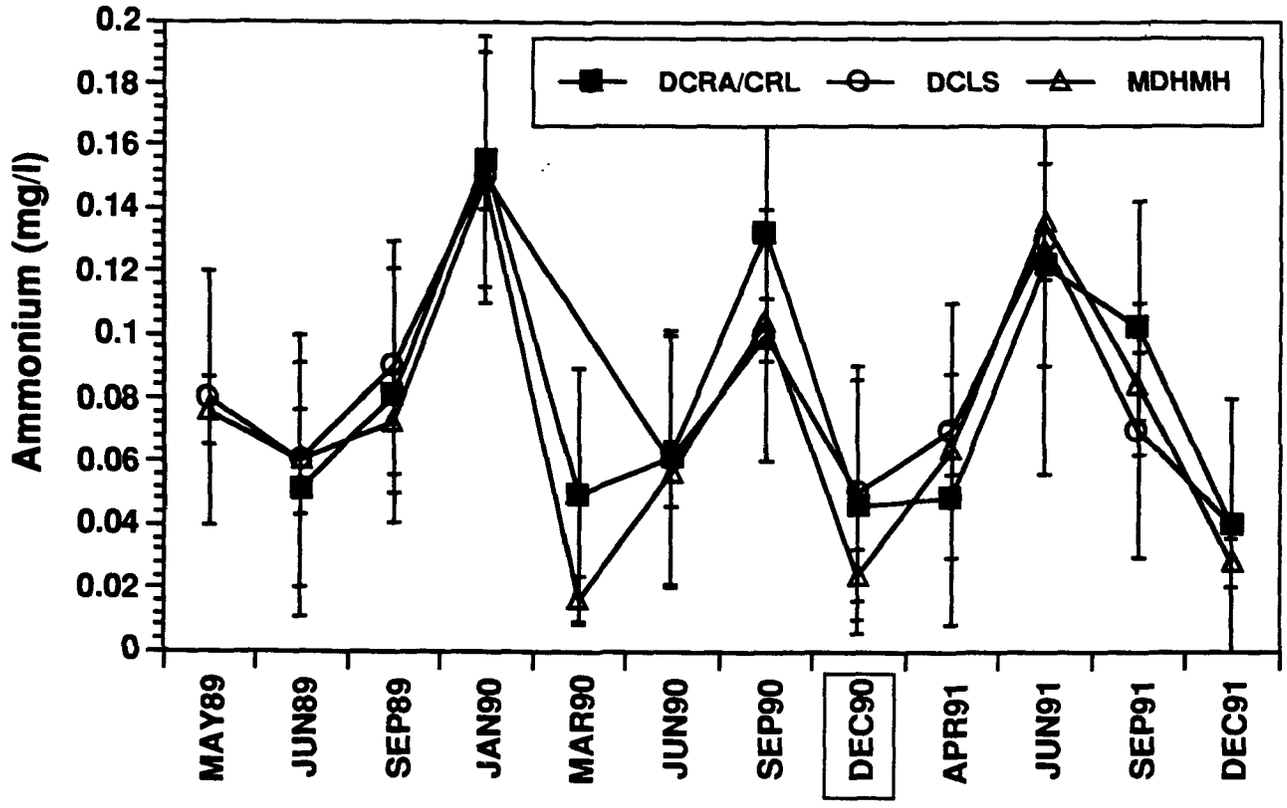


FIGURE 19. Split sample data for nitrite (NO2), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars. MDHMH samples were filtered starting in December 1990. Negative error bars were omitted for clarity.

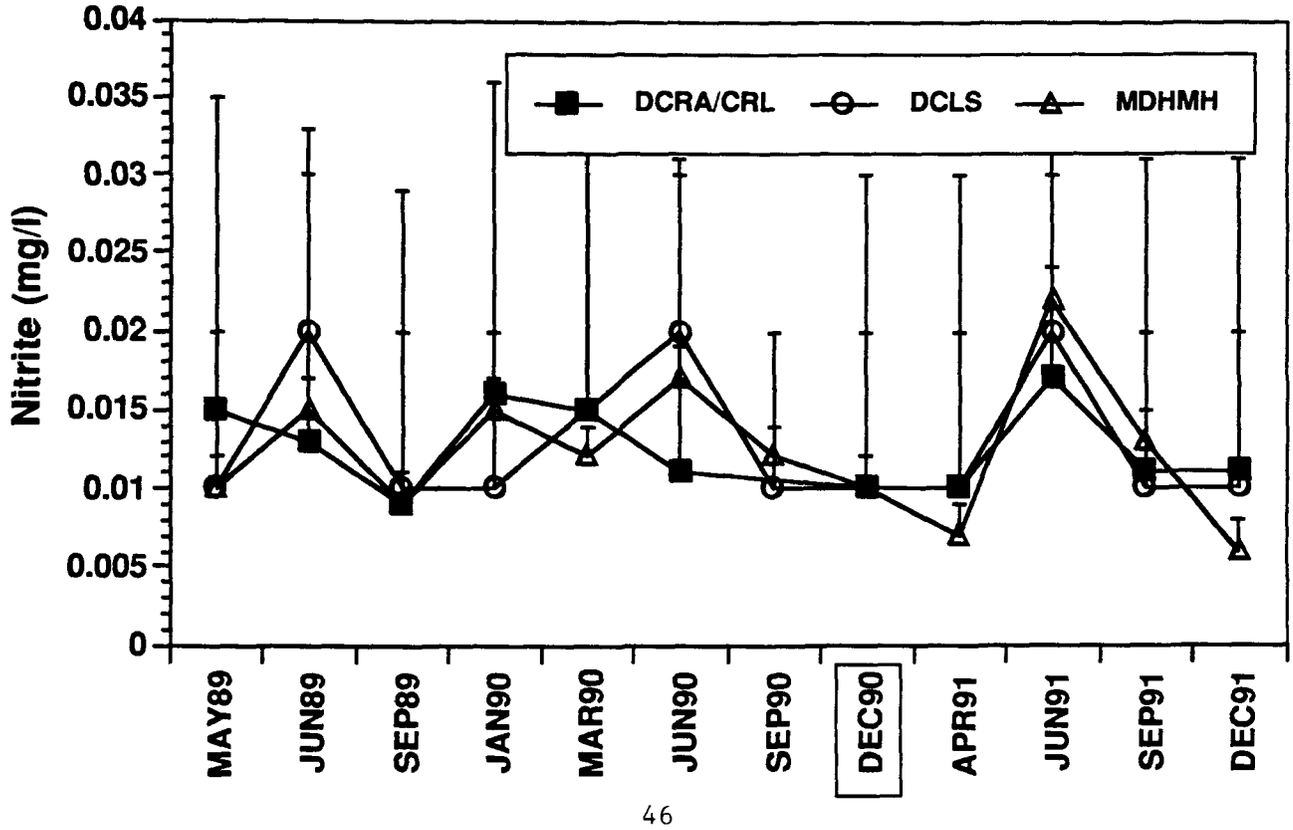


FIGURE 20. Split sample data for nitrite + nitrate (NO23), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars. MDHMH samples were filtered starting in December 1990.

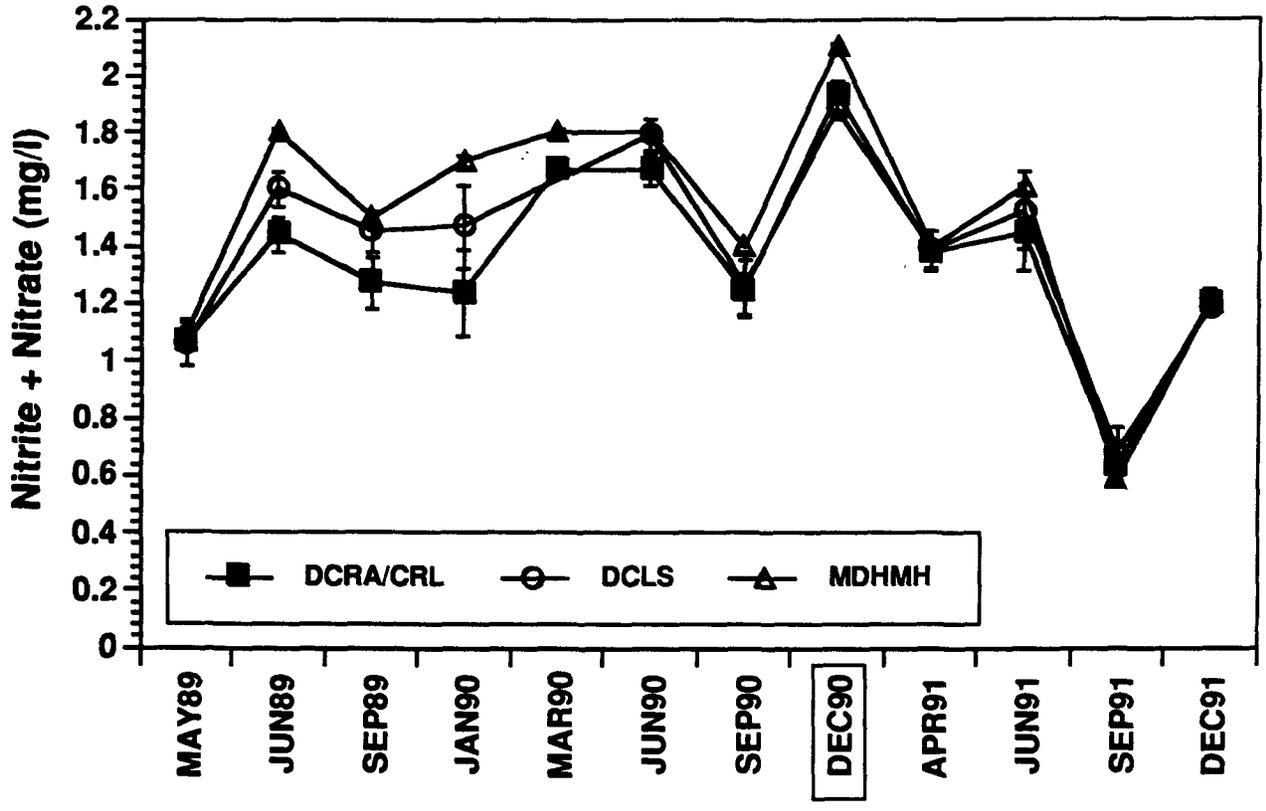


FIGURE 21. Split sample data for total Kjeldahl nitrogen whole (TKNW), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars.

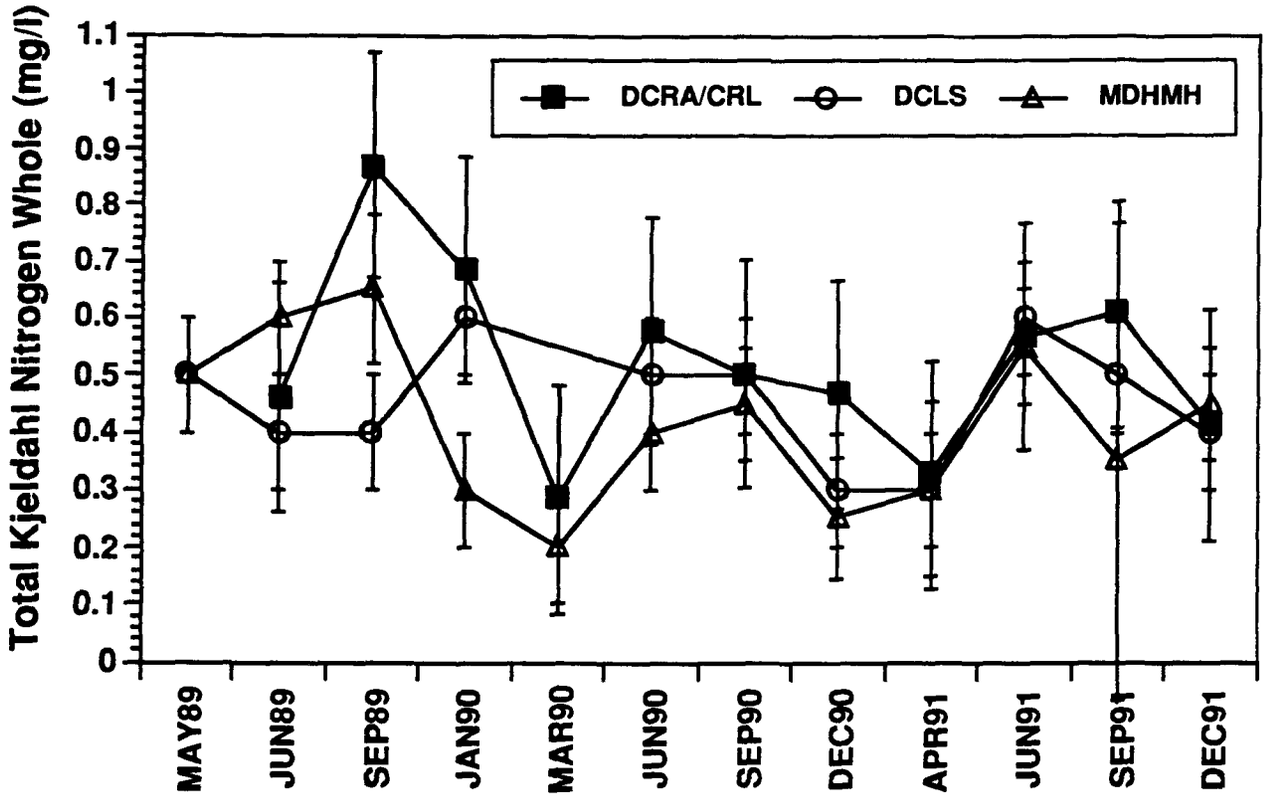


FIGURE 22. Split sample data for total nitrogen (TN), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars. MDHMH samples for NO23, one of the components of TN, were filtered starting in December 1990.

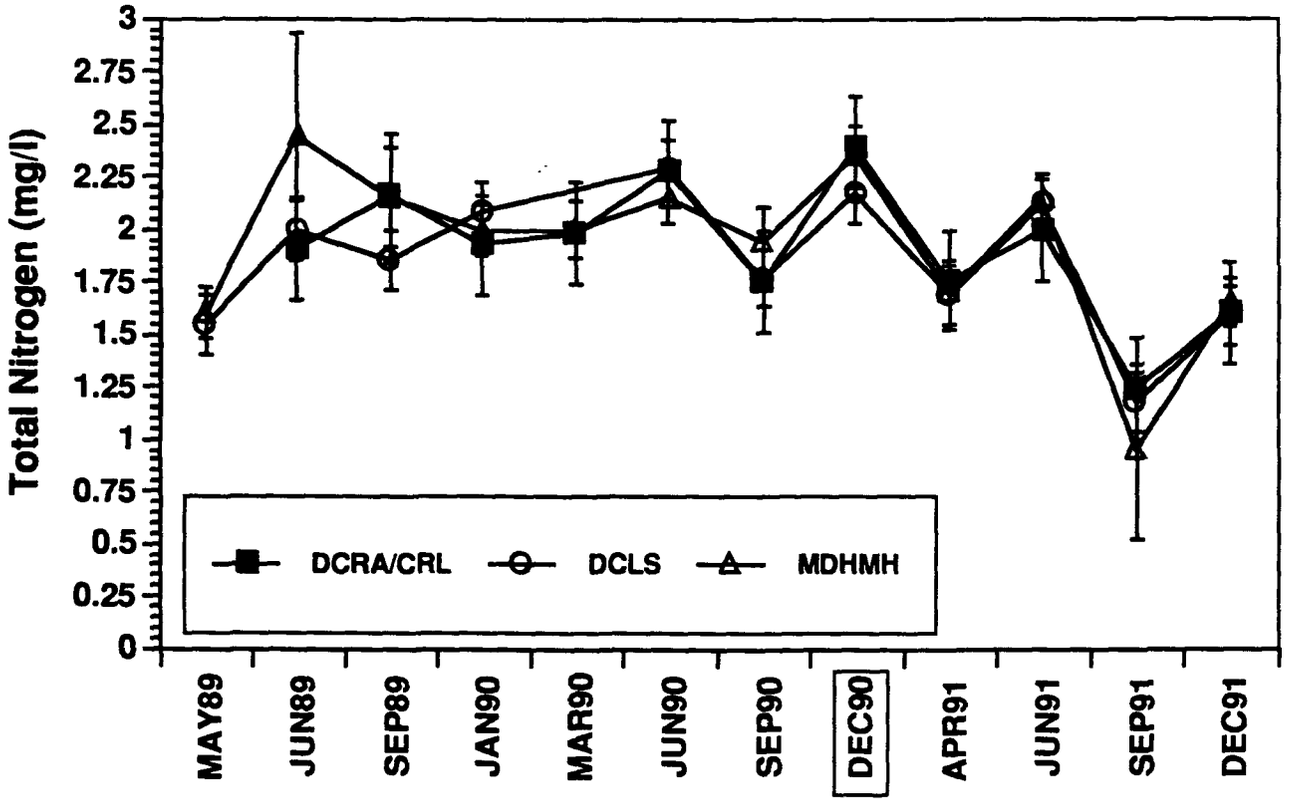


FIGURE 23. Split sample data for orthophosphate (PO4F), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars. MDHMH samples were filtered starting in December 1990.

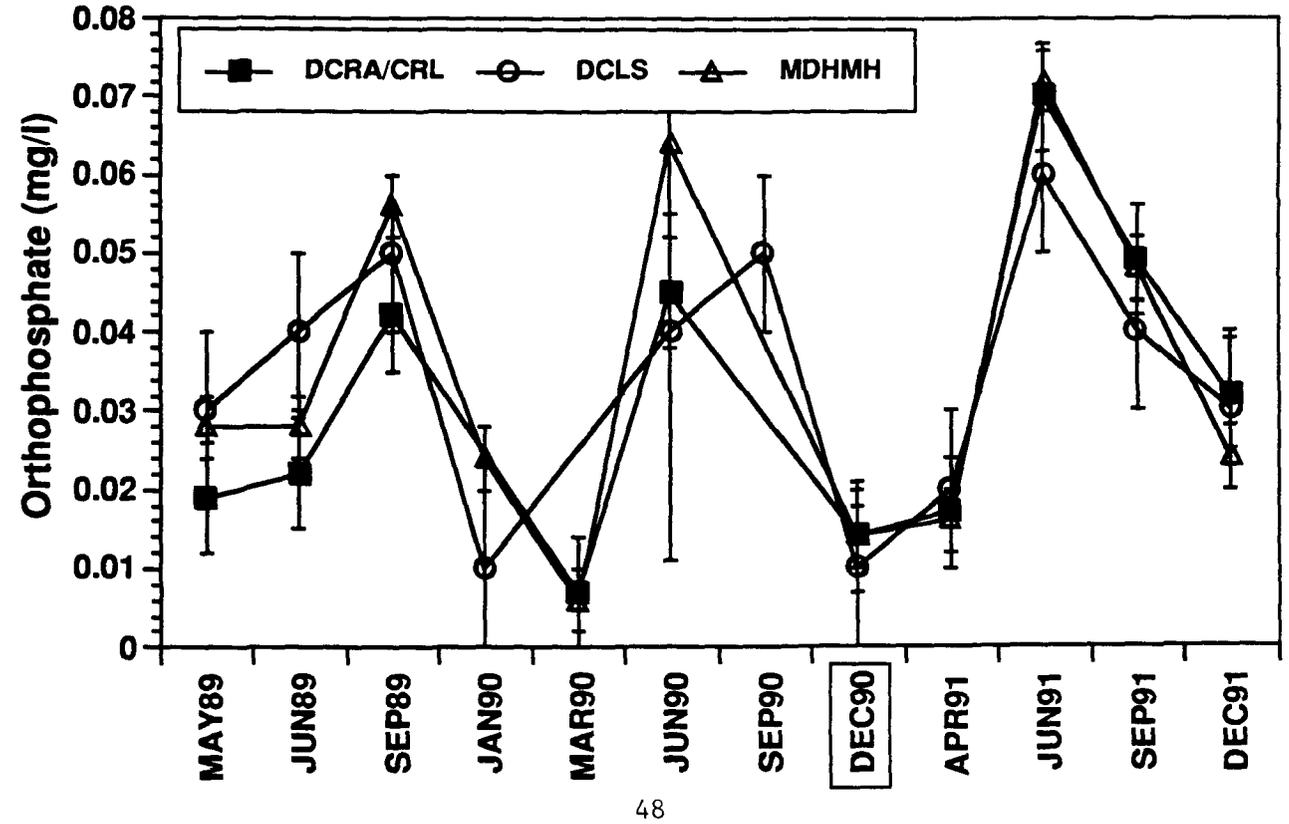


FIGURE 24. Split sample data for total phosphorus (TP), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars.

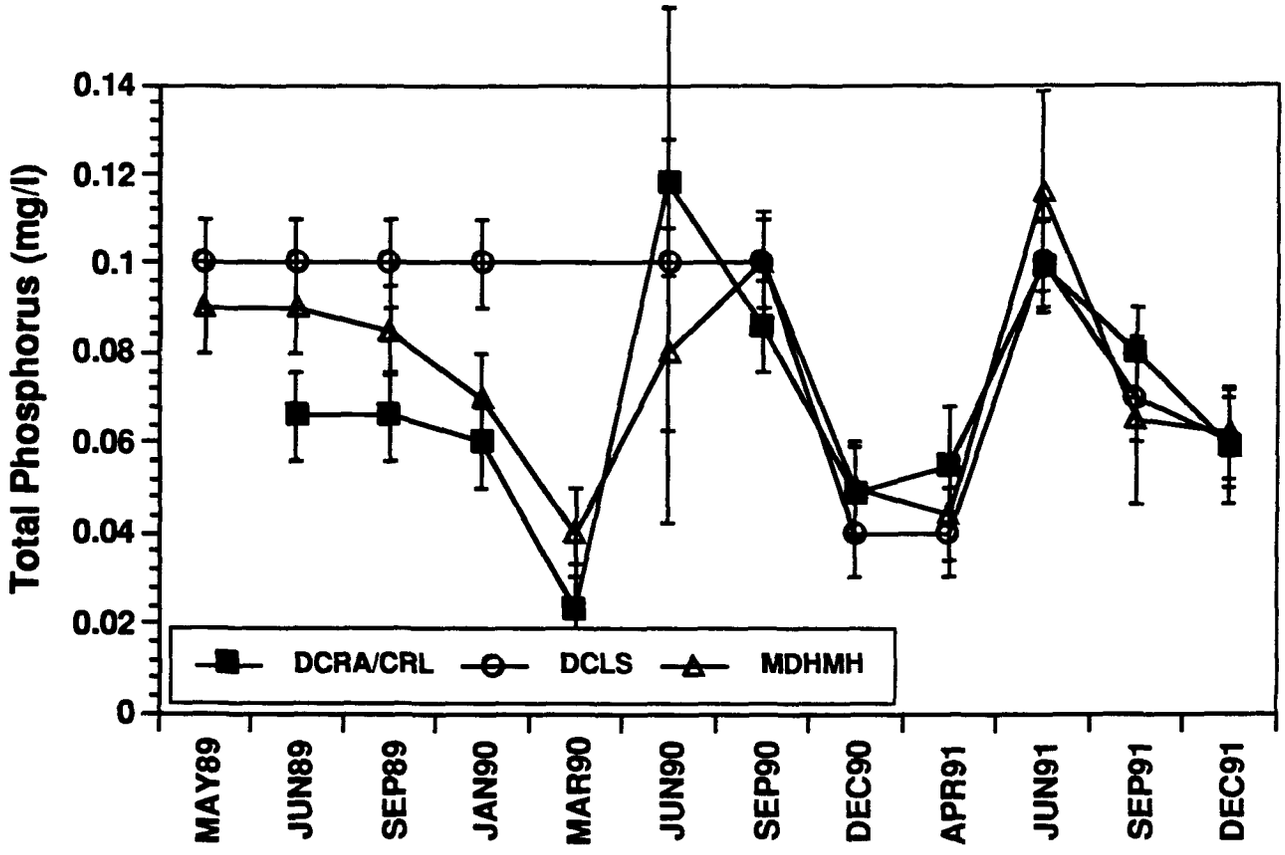


FIGURE 25. Split sample data for total dissolved phosphorus (TDP), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars.

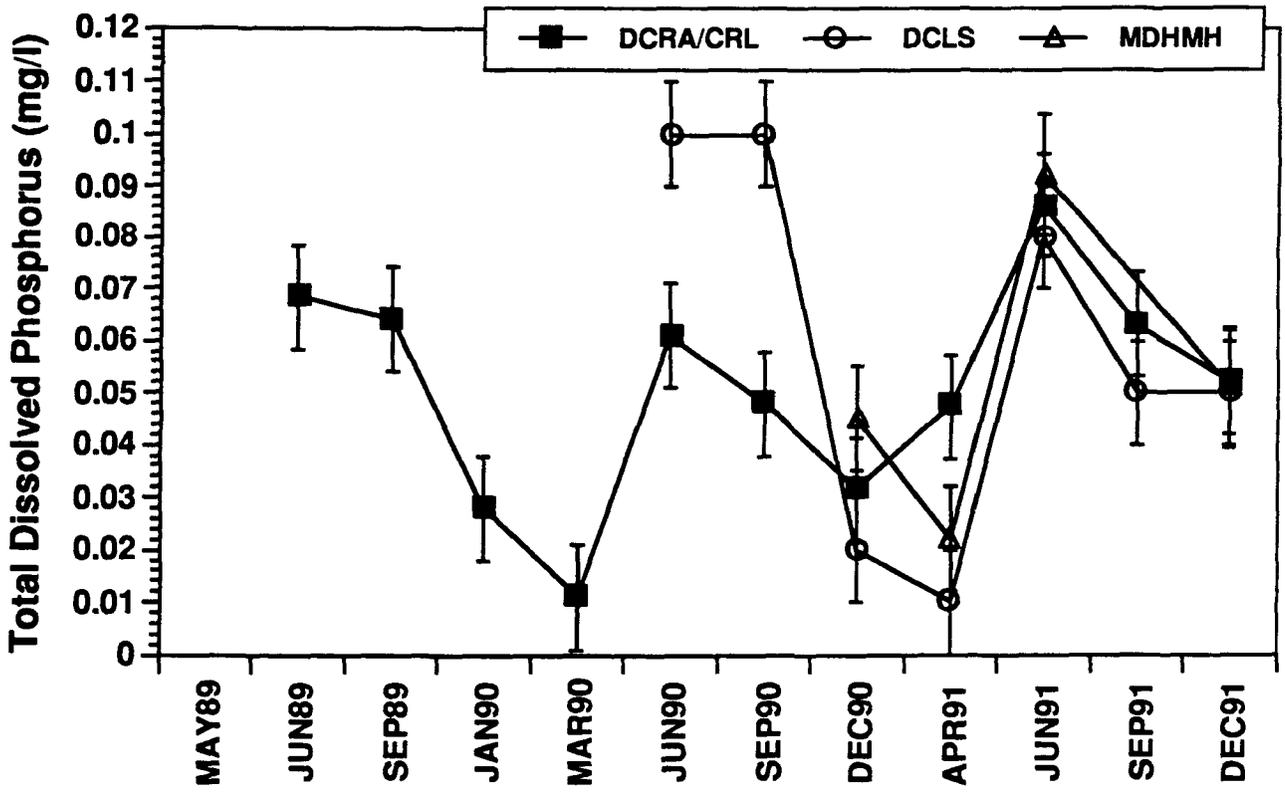


FIGURE 26. Split sample data for total organic carbon (TOC), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars.

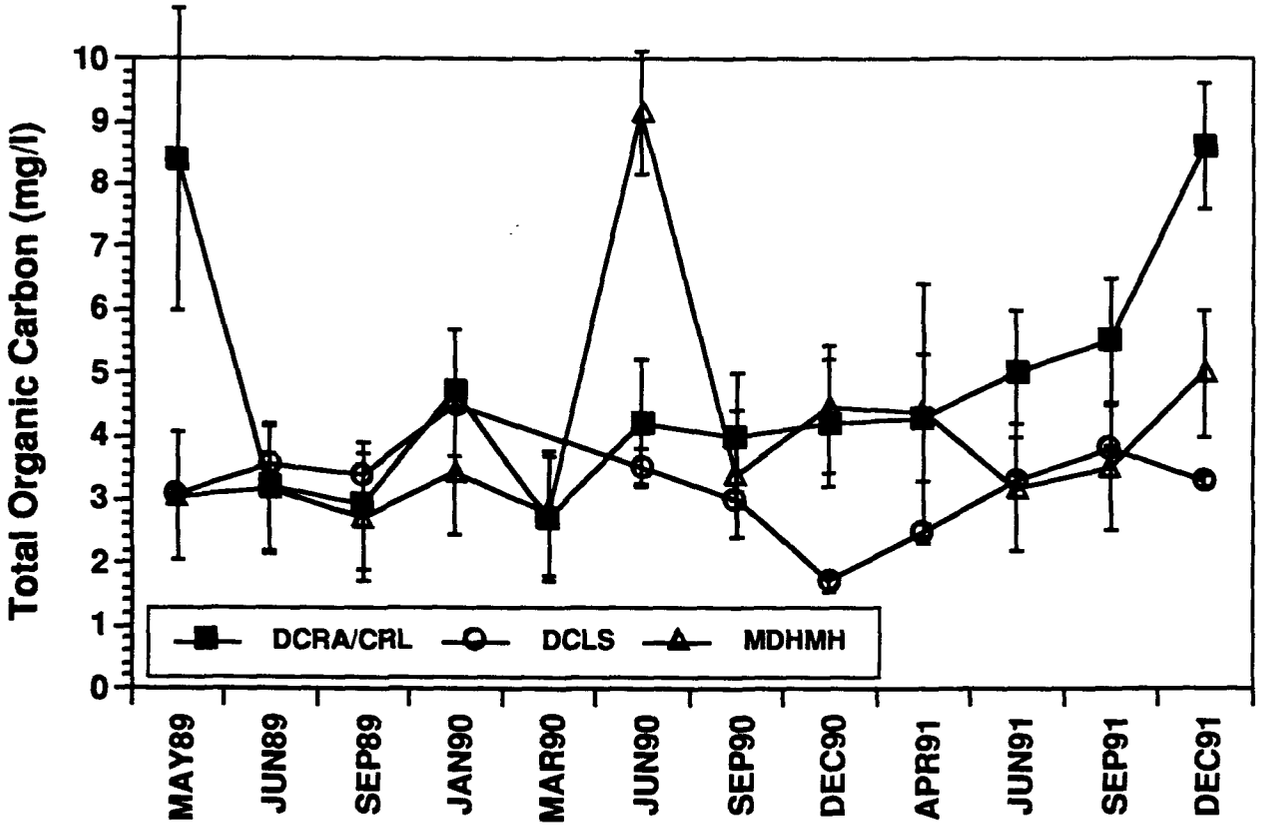


FIGURE 27. Split sample data for dissolved organic carbon (DOC), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars.

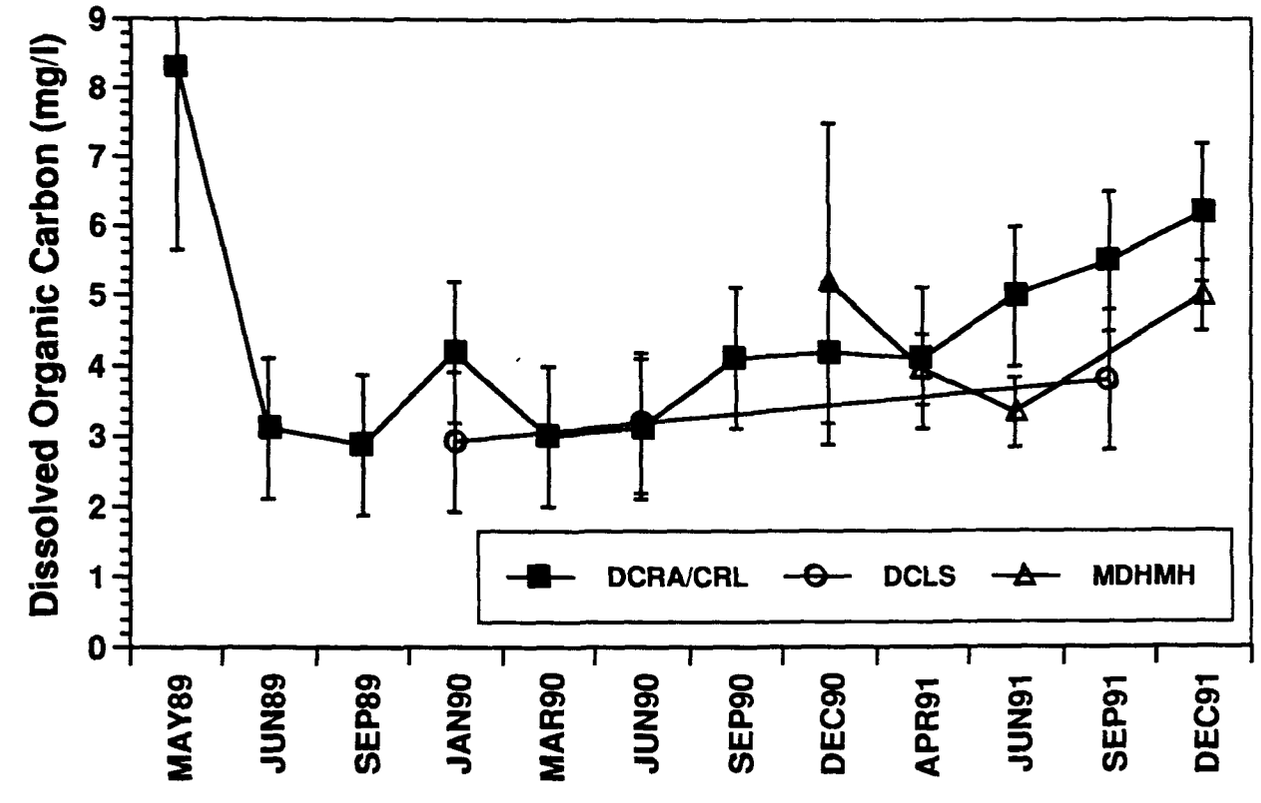


FIGURE 28. Split sample data for total suspended solids (TSS), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars.

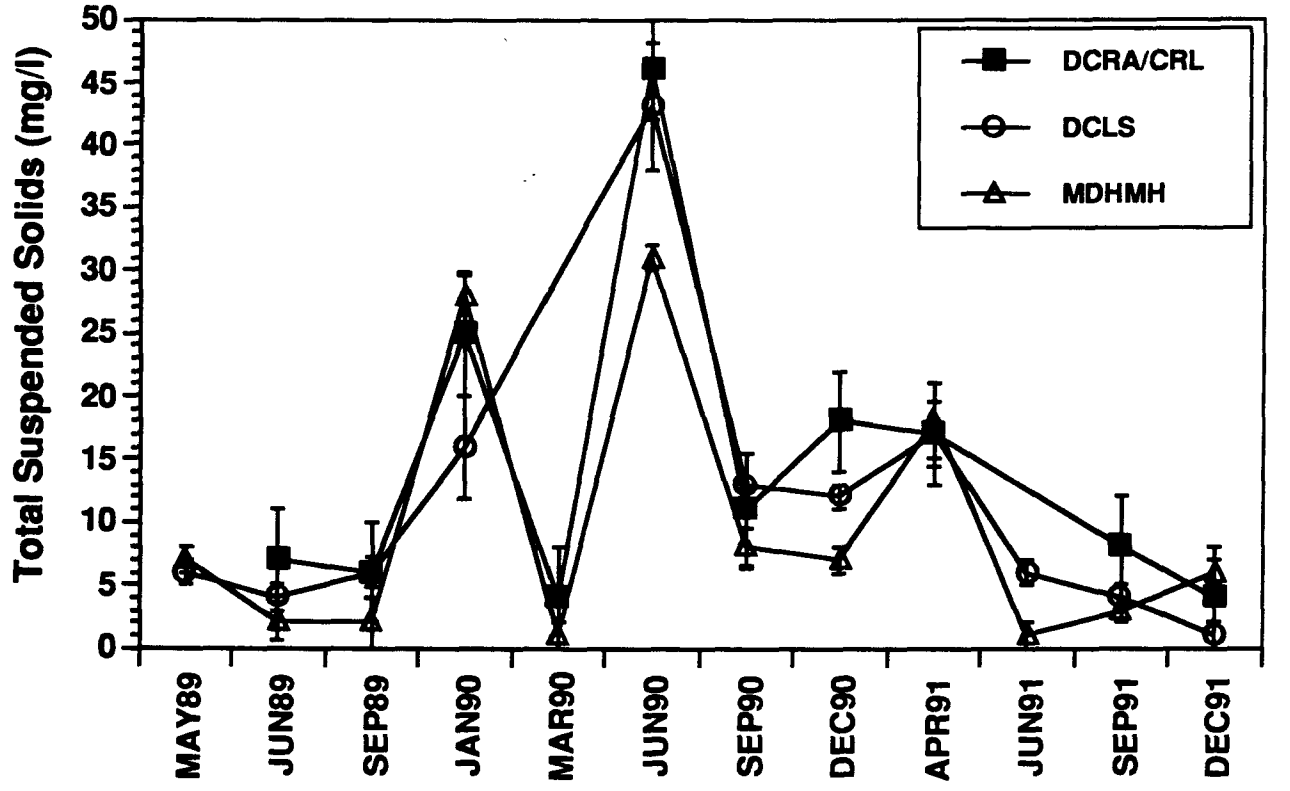


FIGURE 29. Split sample data for silica (SI), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars. MDHMH samples were filtered starting in December 1990.

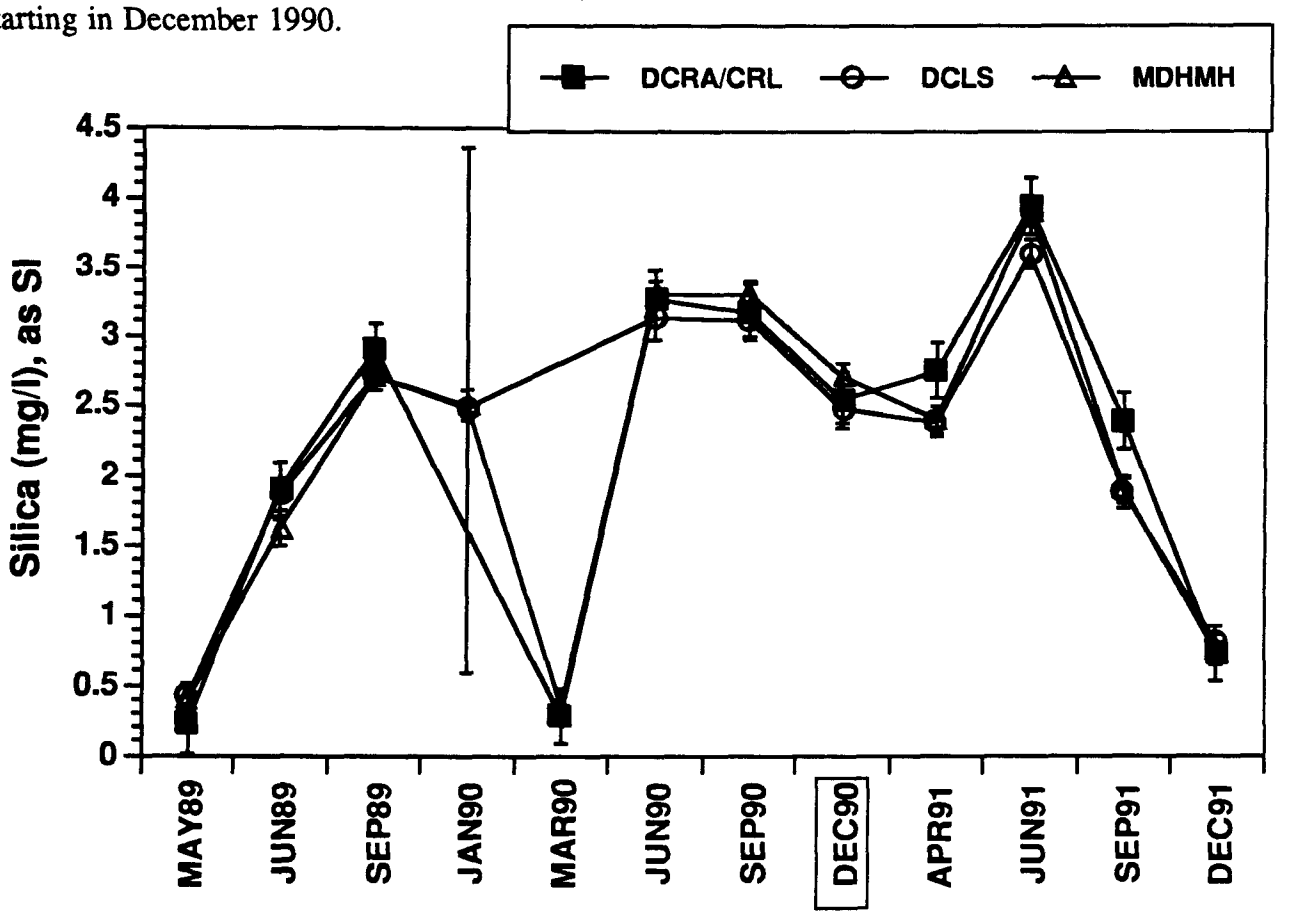
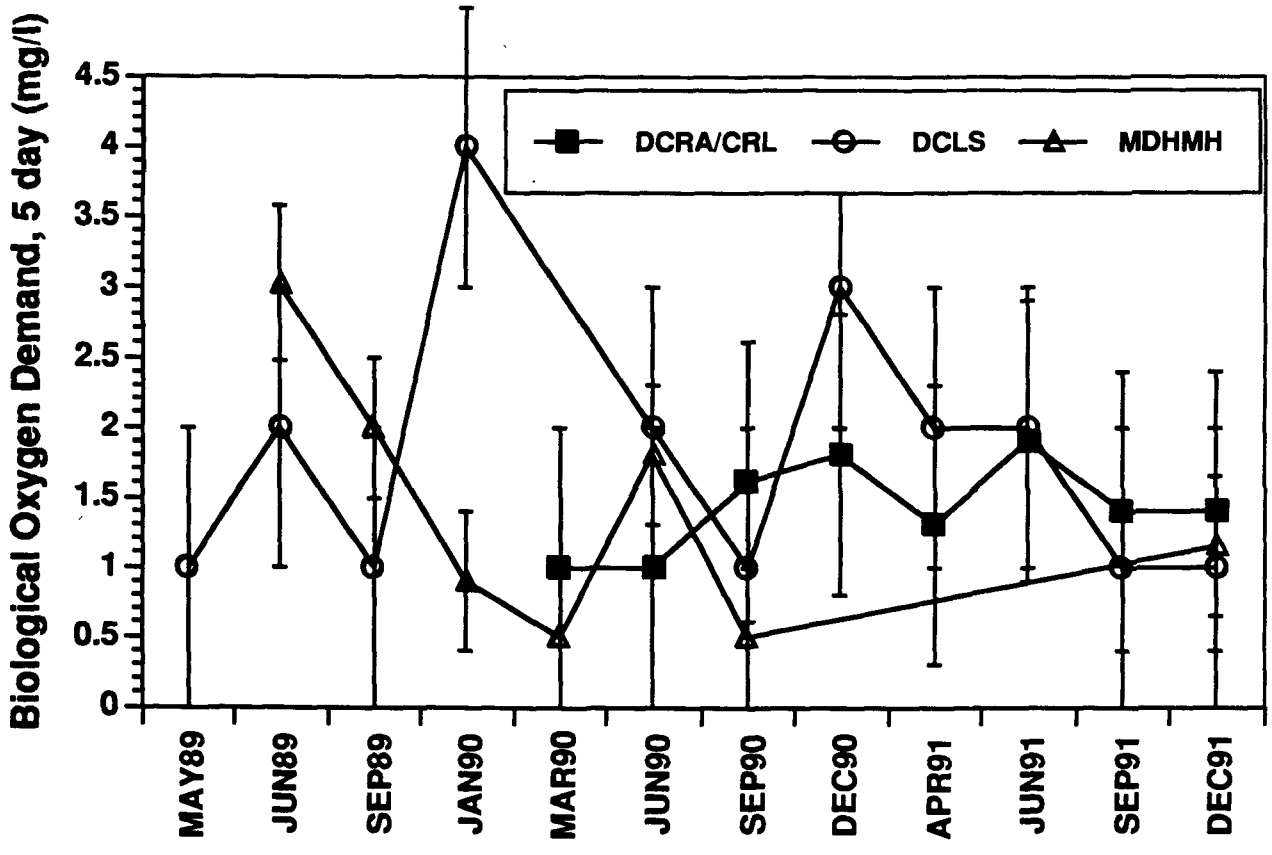


FIGURE 30. Split sample data for biological oxygen demand 5 day (BOD5), from Potomac samples collected at PMS10, showing medians for each sample date with precision bars.



3. Virginia Component

Friedman ANOVA performed on results from the three subsamples assessed inter-organization agreement and determined which parameters had statistically significant inter-organization differences. The results (Table 16) show that 9 of the 13 parameters analyzed had statistically significant inter-organization differences at the $\underline{P} < 0.01$ level over the 1990-1991 period. Analyses were also done using 1991 data only, when 8 of the 13 parameters had statistically significant differences. Three parameters, NO23, PN, and TSS, had no significant differences over both time periods.

Medians for each sample date with precision bars plotted against time show inter-organization agreement (Figures 31-47). Four parameters were graphed that were not analyzed statistically because data were reported by only two laboratories (PC, DOC, CHLA, and PHEA).

Four of the 17 parameters graphed, PO4F, PHOSP, TOC, and SI, had inter-organization differences that were larger than within-organization precision on more than half of the sampling dates. The other parameters had inter-organization differences that tended to be smaller than within-organization precision.

4. Fall Line Component

The results from the Friedman ANOVA are shown in Table 17, with medians for each laboratory over all sampling dates analyzed. The results show that none of the 9 parameters had statistically significant differences.

Graphs of the results with precision bars (Figures 48-59) also show that most of the parameters had high inter-organization agreement. One parameter, nitrite + nitrate (NO23), had three samples with non-overlapping precision bars, due to higher results from MDHMH.

TABLE 16. Virginia Component (TF5.5) split sample medians with Friedman analysis results, 1990-1991 data. Data from 1991 were analyzed separately where applicable.

Parameter[1]	N[2]	Laboratory Medians (mg/l)				Friedman results[3]	
		DCLS	HRSD	ODU	VIMS	χ^2	P
NH4	8	0.0750	0.0950 A	0.0728 B	0.0760	18.2	<0.001
NH4	5	0.0800	0.1000	0.0739	0.0800	6.1	<0.20
NO2	3	0.050	0.080 A	0.046 B	0.052	15.6	<0.01
NO2	2	0.035	0.055	0.027	0.032	12.7	<0.01
NO23	8	0.365	0.385	0.374	0.385	1.1	>0.70
NO23	5	0.400	0.420	0.421	0.410	7.8	<0.10
TDN	4	-	0.623 B	0.737	0.878 A	11.2	<0.01
PN	3	-	0.450	0.258	0.315	1.4	>0.30
TN	5	0.800	0.710 B	0.799 B	0.933 A	26.8	<0.001
TN	4	1.150	1.070 B	1.072 B	1.158 A	21.1	<0.001
PO4F	7	0.020 C	0.030 AB	0.037 A	0.025 BC	39.4	<0.001
PO4F	4	0.020 B	0.028	0.036 A	0.025 B	30.0	<0.001
TDP	7	0.030 B	0.060 A	0.036	0.033	24.5	<0.001
TDP	4	0.030	0.056	0.032	0.033	5.3	<0.20
PHOSP	7	0.090 A	0.090	0.078	0.064 B	15.1	<0.01
PHOSP	4	0.110 A	0.101	0.097	0.083 B	15.9	<0.01
TP	7	0.160	0.169	0.127	0.136	8.7	<0.05
TP	4	0.165	0.169	0.138	0.138	13.1	<0.01
TOC	5	3.87 B	-	7.18 A	7.43 A	21.3	<0.001

TABLE 16 (continued): Virginia Component (TF5.5) split sample medians with Friedman analysis results, 1990-1991 data. Data from 1991 were analyzed separately where applicable.

Parameter[1]	N[2]	Laboratory Medians (mg/l)				Friedman results[3]	
		DCLS	HRSD	ODU	VIMS	χ^2	P
TSS	5	43.0	49.0	48.7	49.3	4.4	>0.20
TSS	4	45.0	53.5	49.1	50.7	6.3	<0.10
SI	8	3.28 B	-	3.56 A	3.48 A	35.7	<0.001
SI	5	2.90 B	-	3.28 A	3.16 A	17.4	<0.001

1 Dissolved Organic Carbon (DOC), Particulate Carbon (PC), Chlorophyll (CHLA), and Phaeophytin (PHEA) could not be analyzed due to missing data. Where two lines of results are shown for a parameter, the first includes all complete data, and the second includes only 1991 data. Where there is only one line, the complete data were all from 1991.

2 Number of sampling dates with complete data. In one case (NO2), dates were excluded due to below detection limit data.

3 Underlined P values were statistically significant ($P < 0.01$, Friedman 2-way ANOVA on three replicates per sample date). Laboratory medians with different letters below them had statistically significant pairwise differences ($P < 0.01$, A>B>C), otherwise they did not differ significantly.

FIGURE 31. Split sample data for ammonium (NH4), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

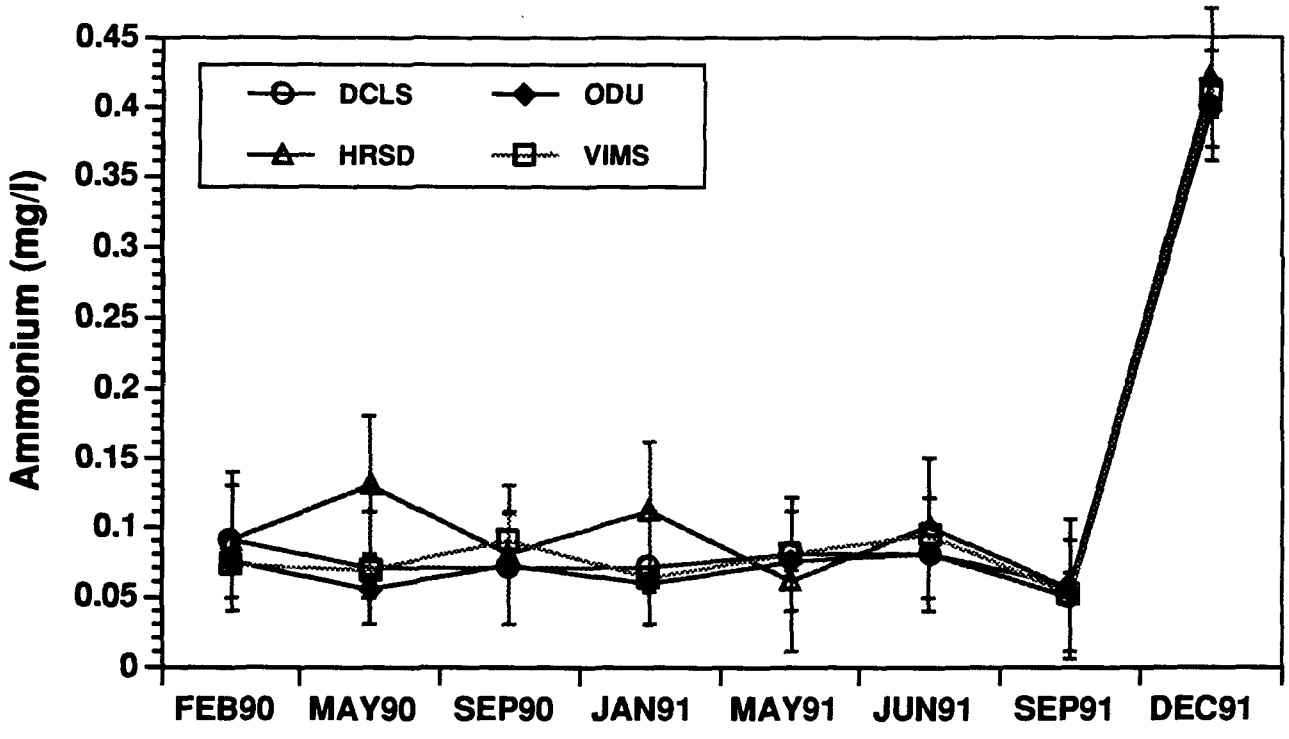


FIGURE 32. Split sample data for nitrite (NO2), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

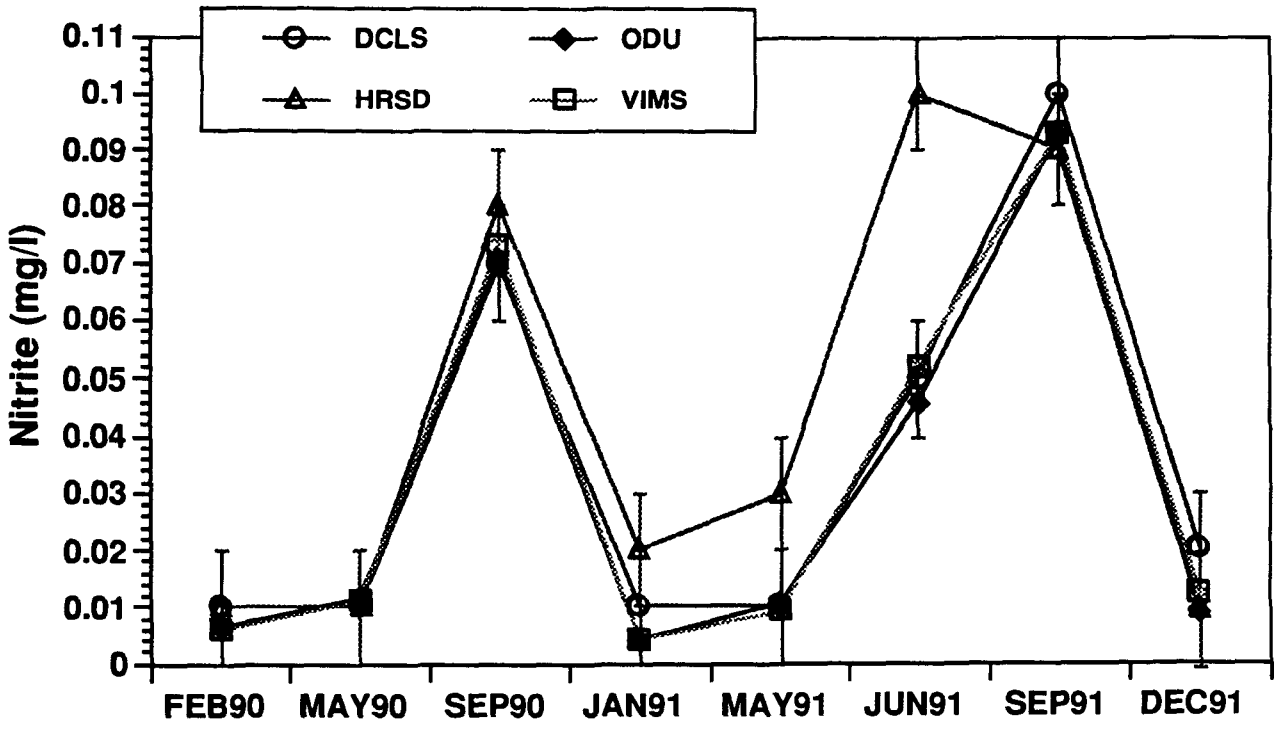


FIGURE 33. Split sample data for nitrite + nitrate (NO23), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

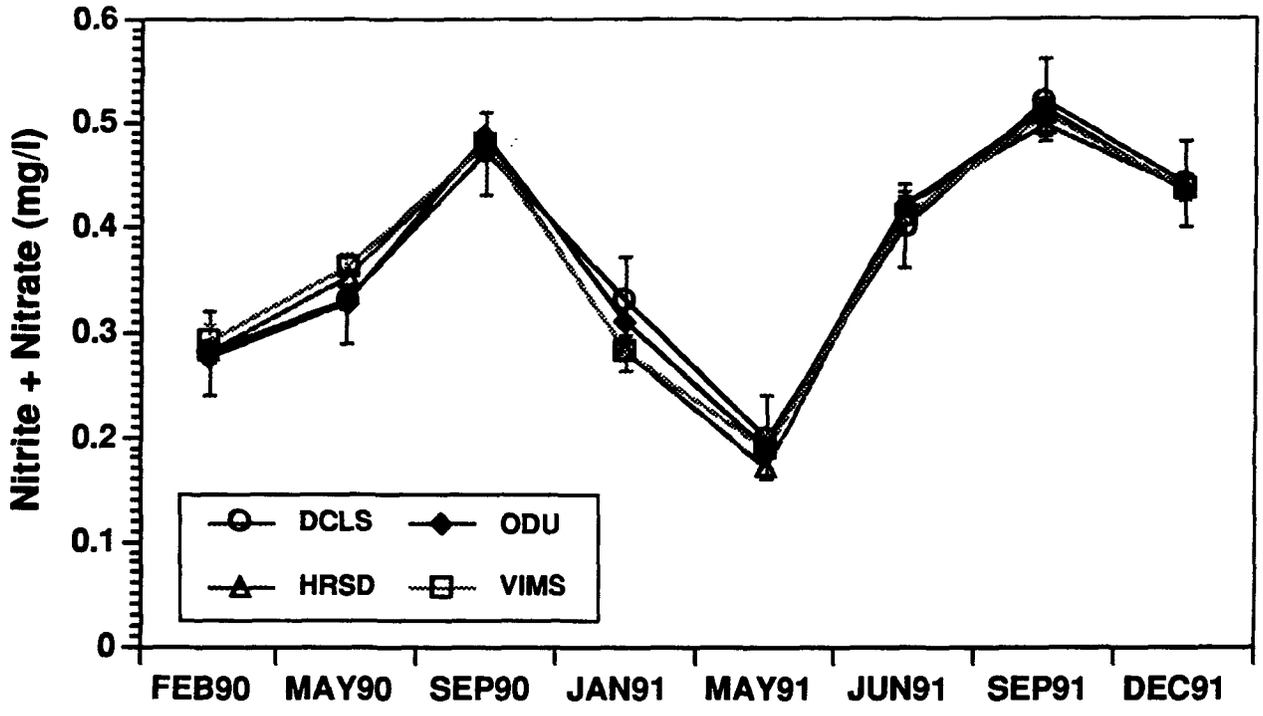


FIGURE 34. Split sample data for total dissolved nitrogen (TDN), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

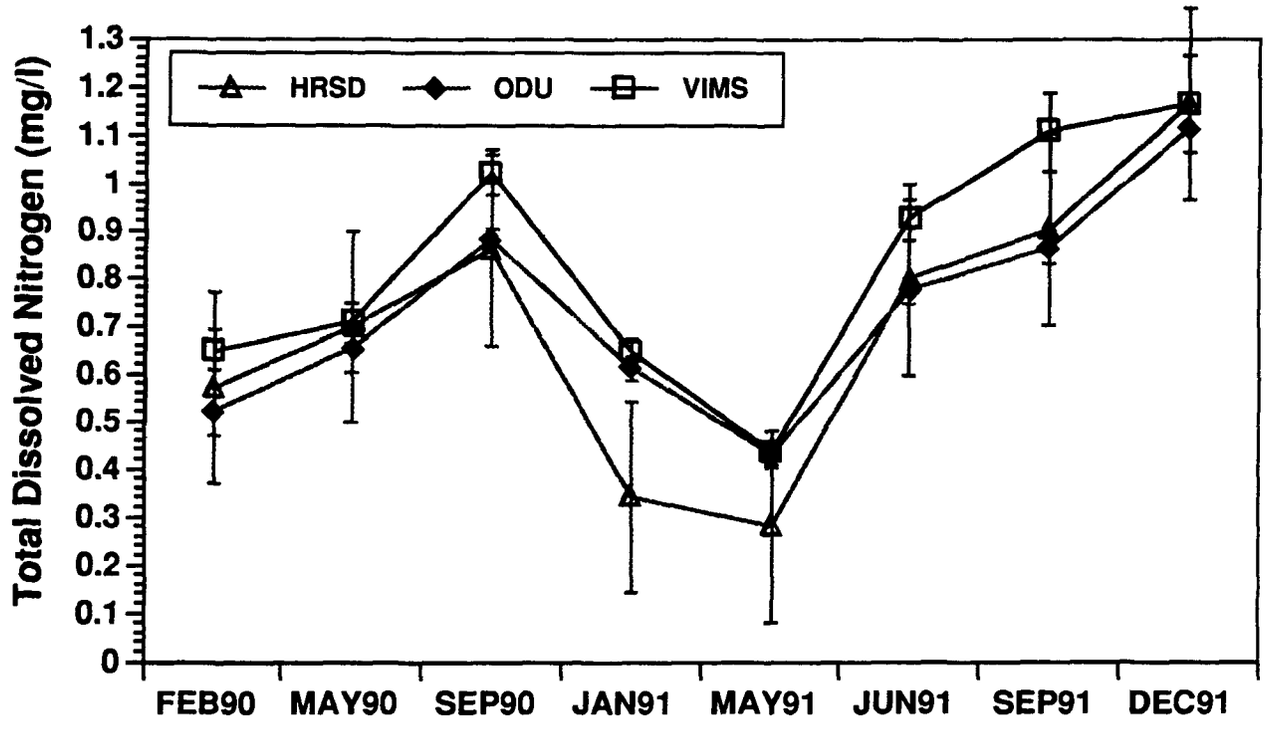


FIGURE 35. Split sample data for particulate nitrogen (PN), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

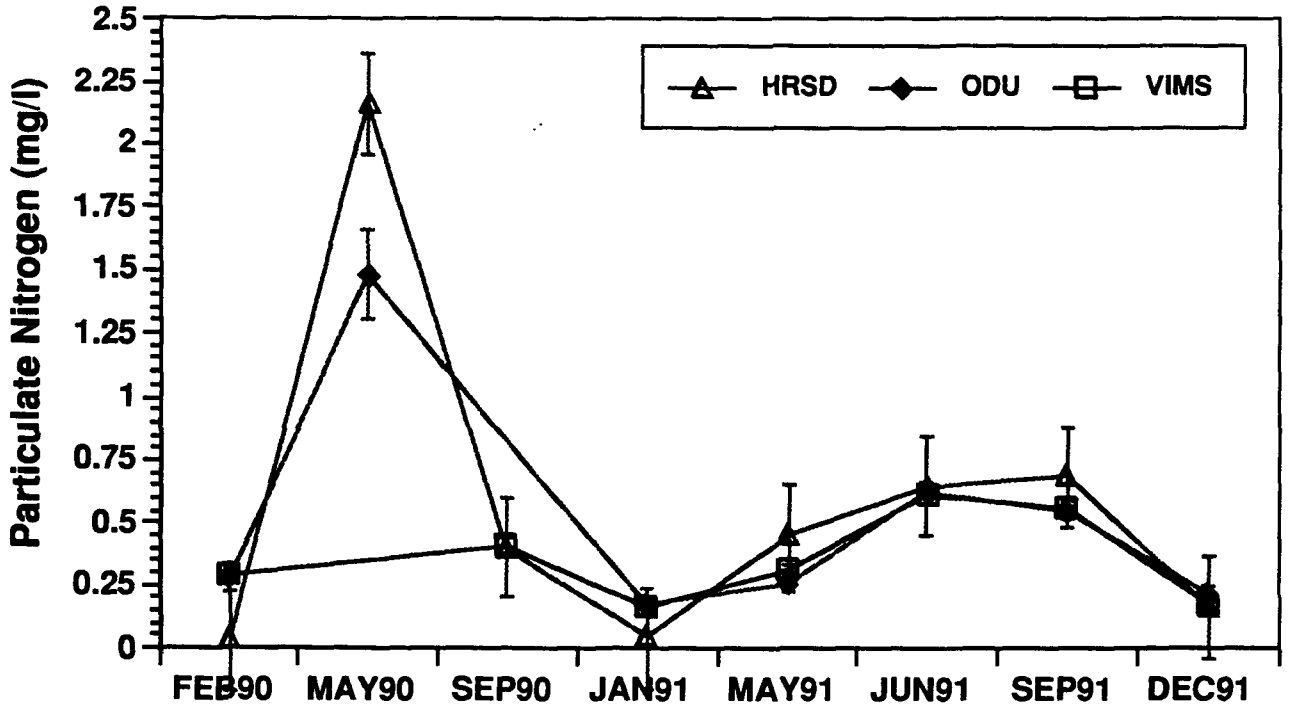


FIGURE 36. Split sample data for total nitrogen (TN), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

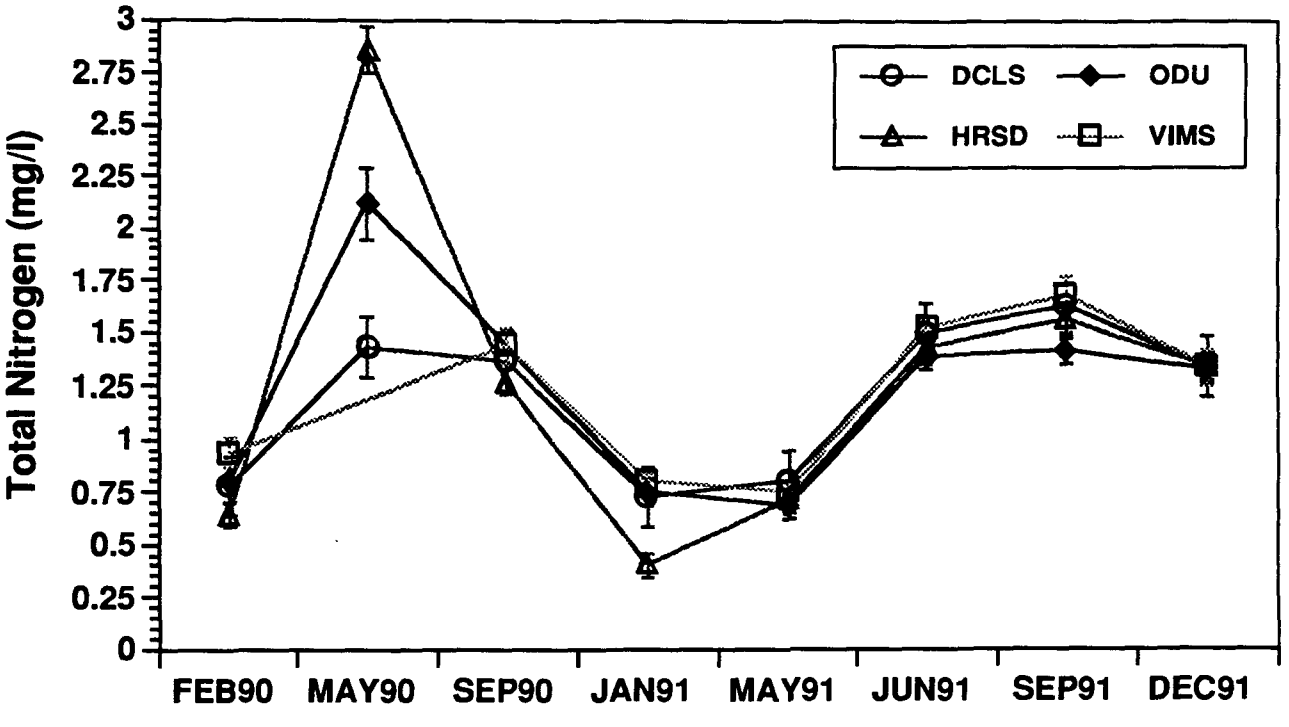


FIGURE 37. Split sample data for orthophosphate (PO4F), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

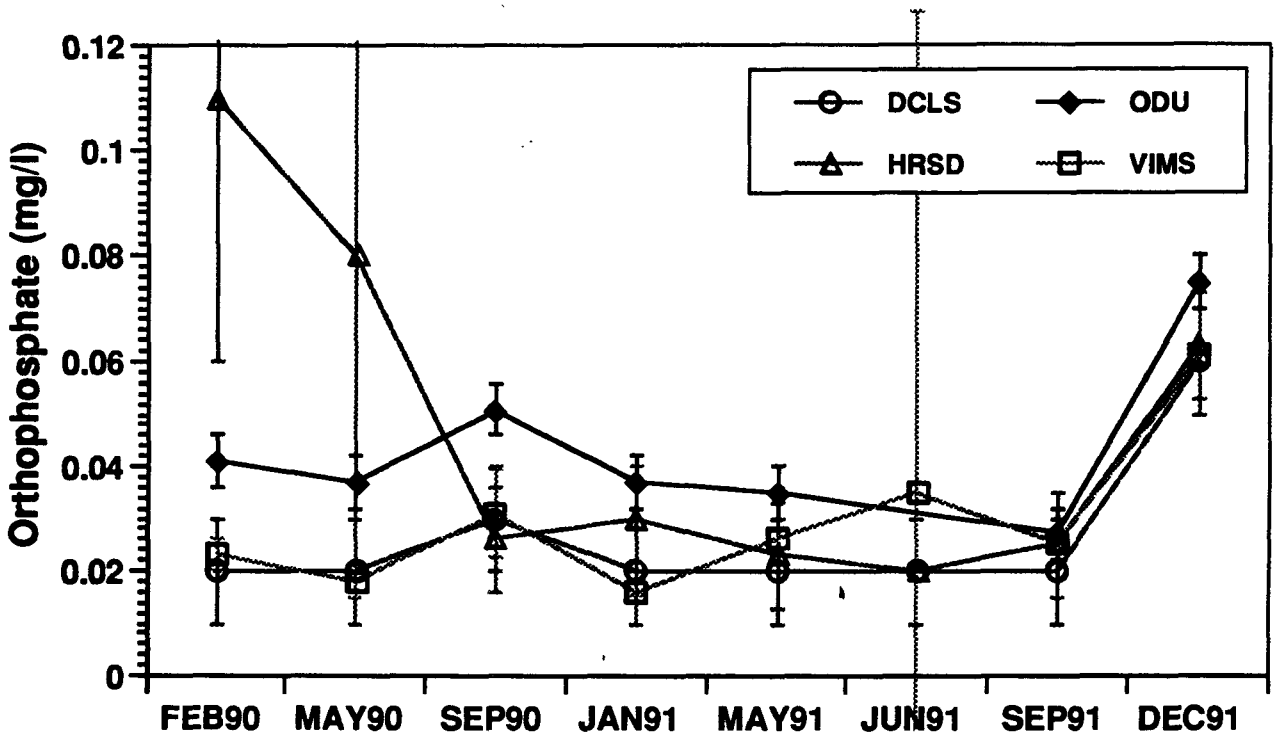


FIGURE 38. Split sample data for total dissolved phosphorus (TDP), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

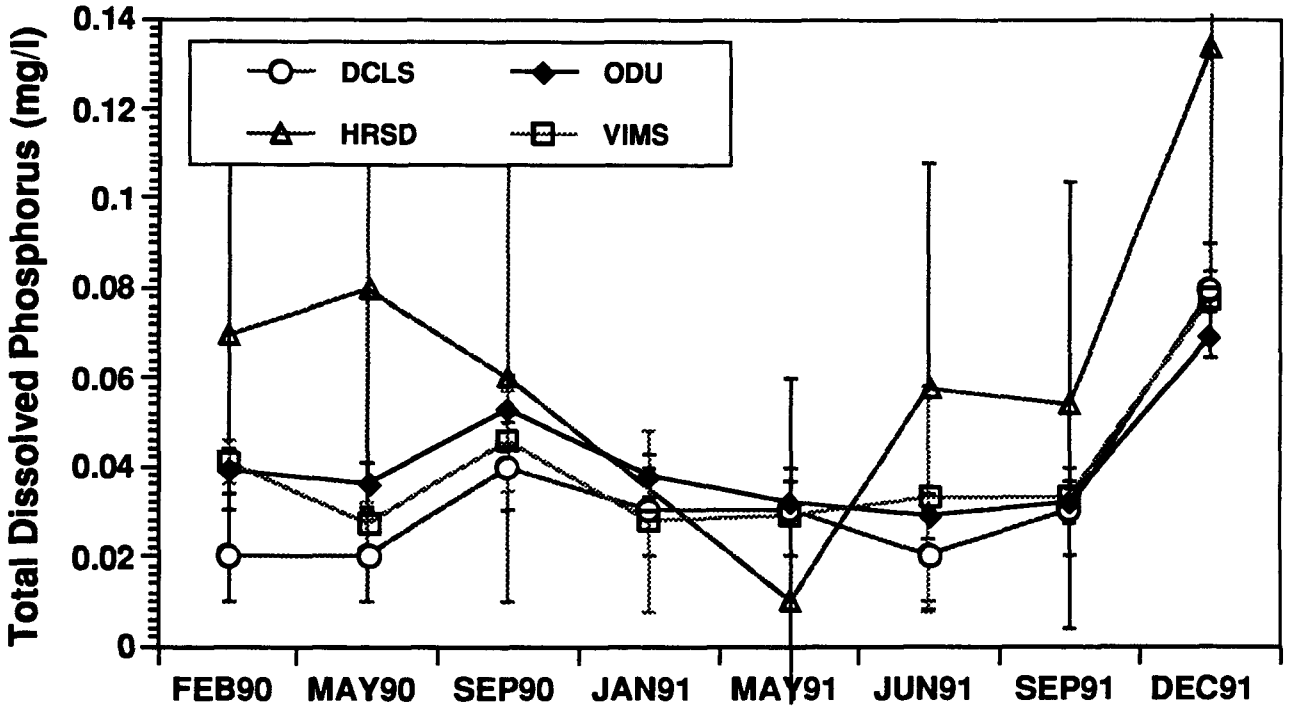


FIGURE 39. Split sample data for particulate phosphorus (PHOSP), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

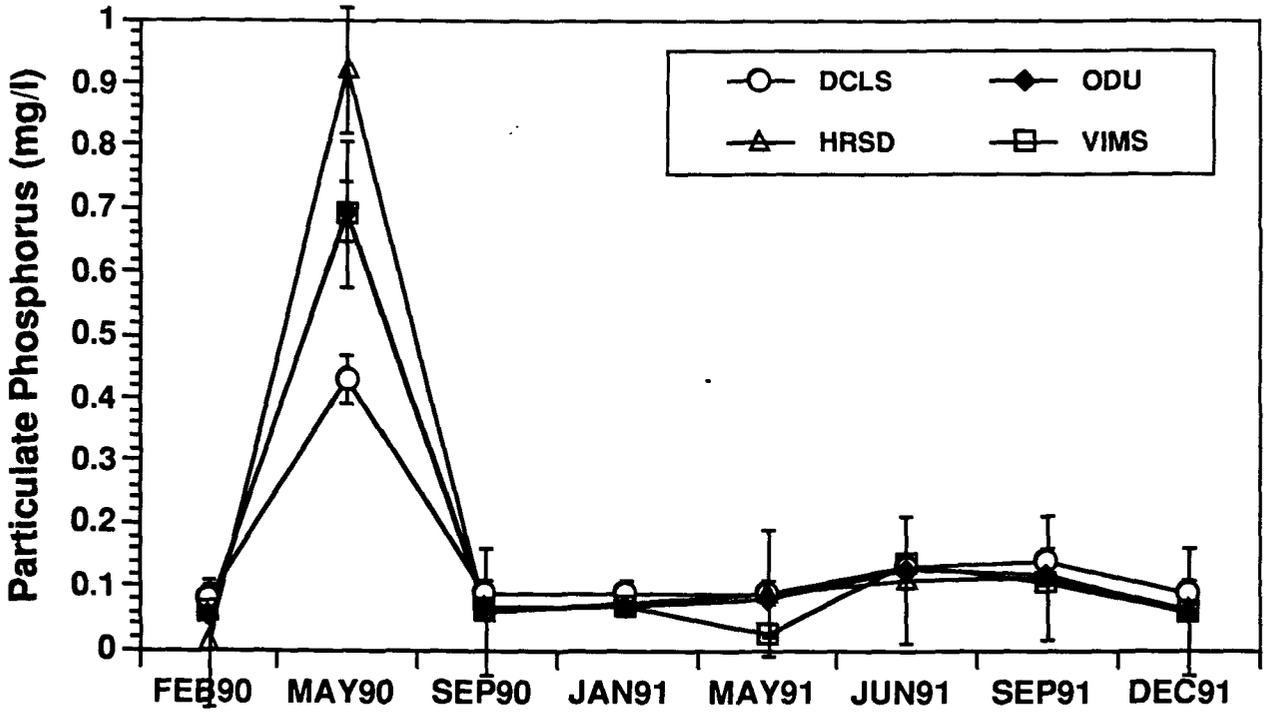


FIGURE 40. Split sample data for total phosphorus (TP), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

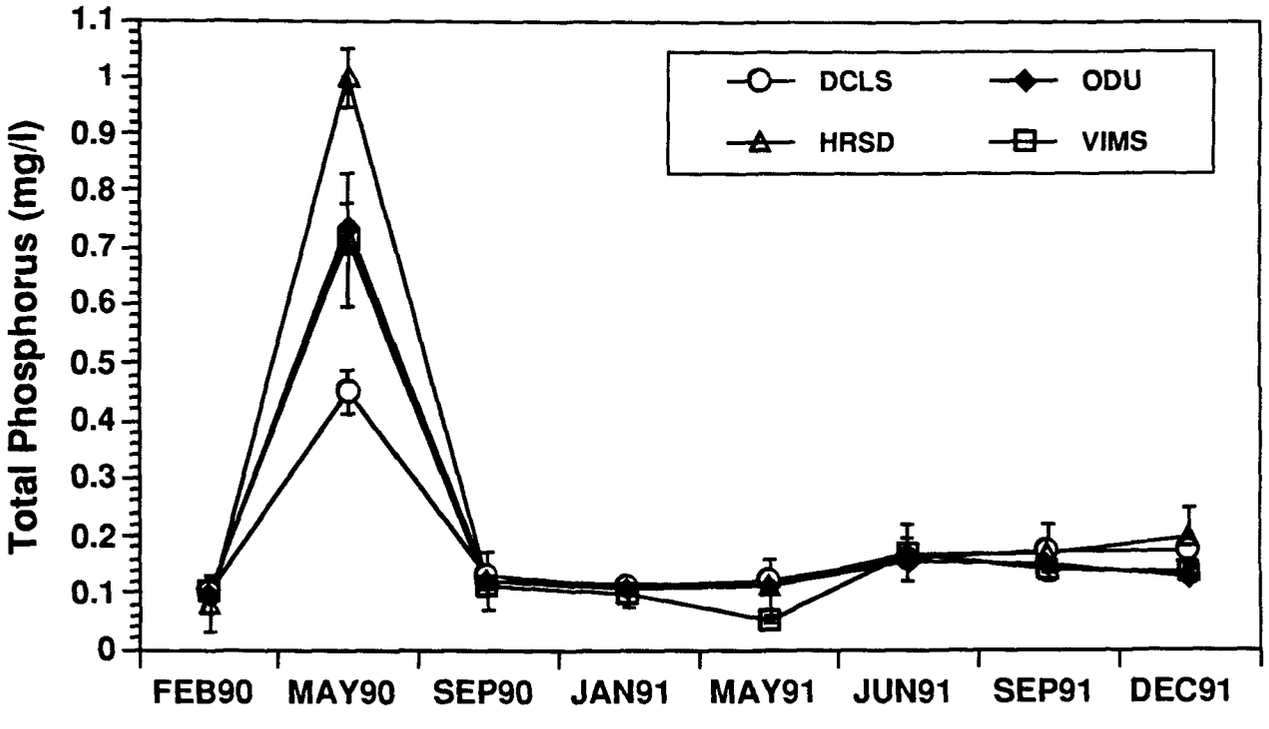


FIGURE 41. Split sample data for dissolved organic carbon (DOC), from Virginia samples collected at TF5.5 showing medians for each sample date with precision bars.

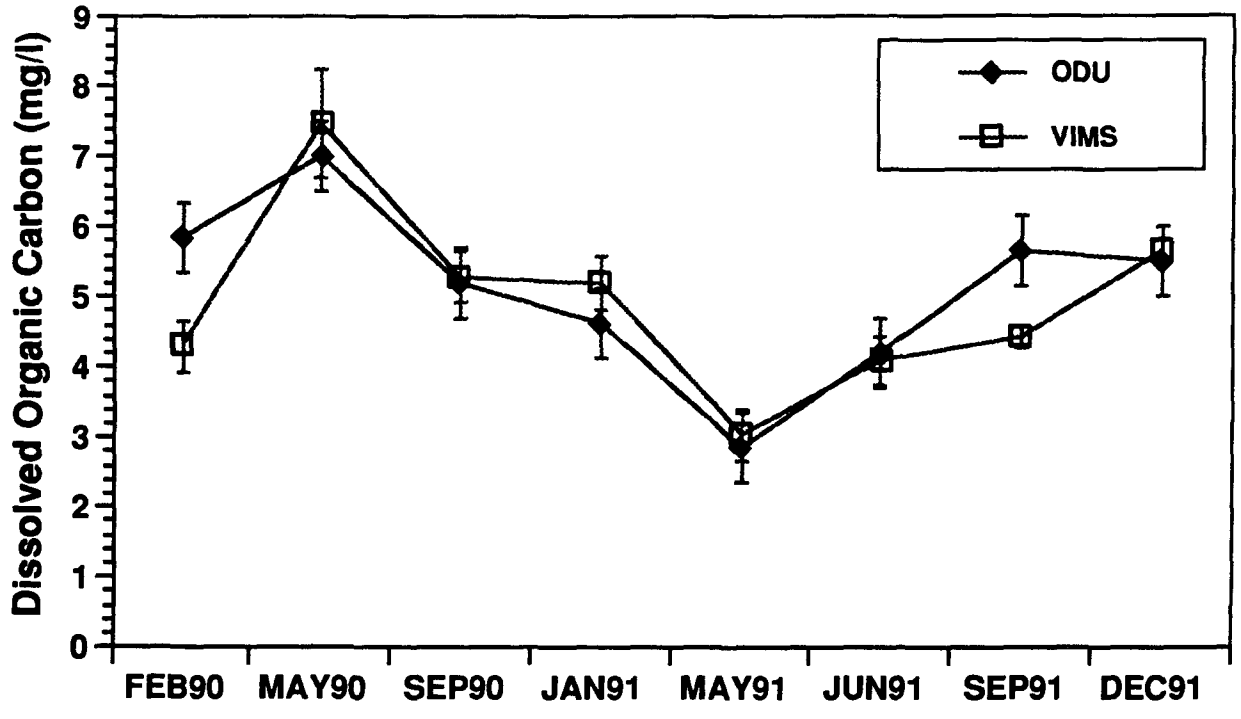


FIGURE 42. Split sample data for particulate carbon (PC), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

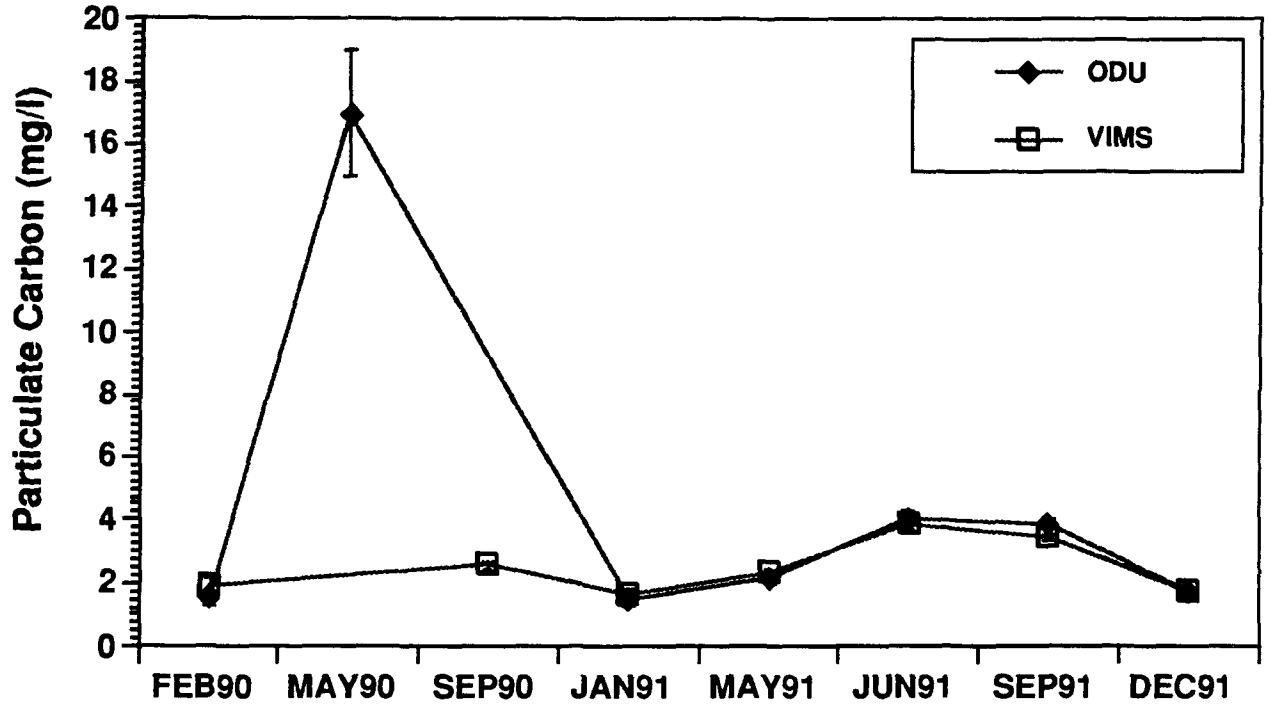


FIGURE 43. Split sample data for total organic carbon (TOC), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

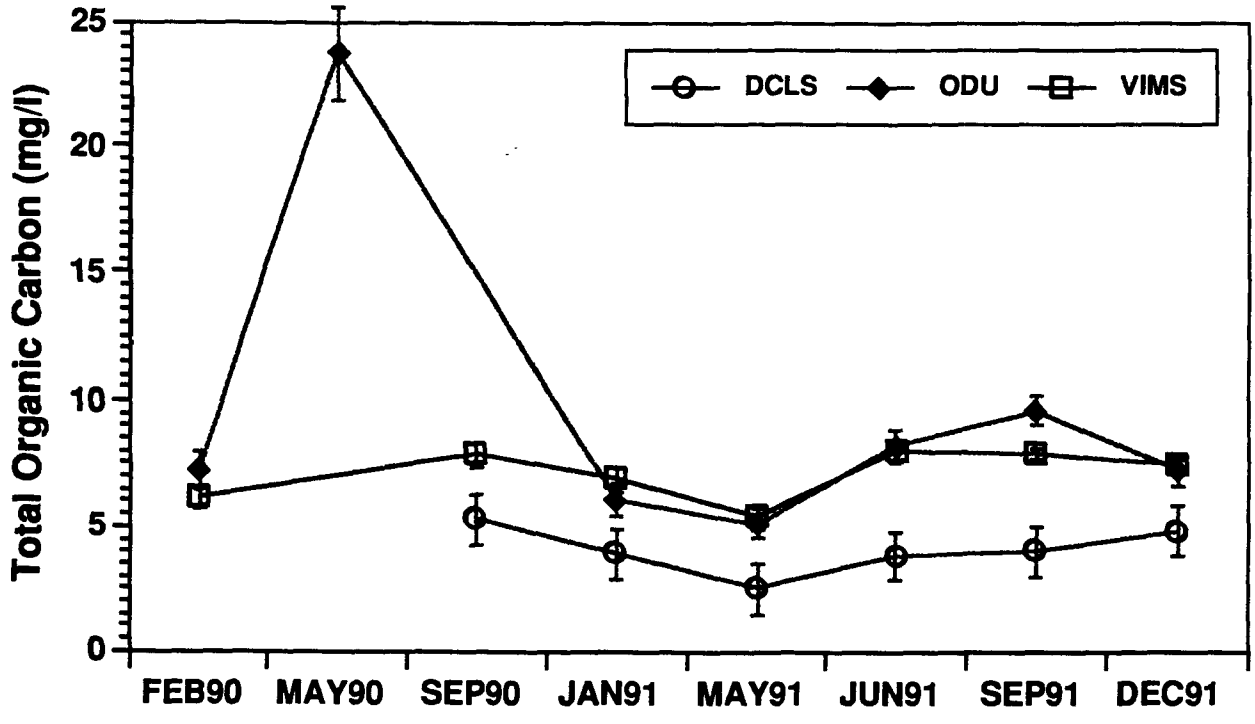


FIGURE 44. Split sample data for total suspended solids (TSS), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

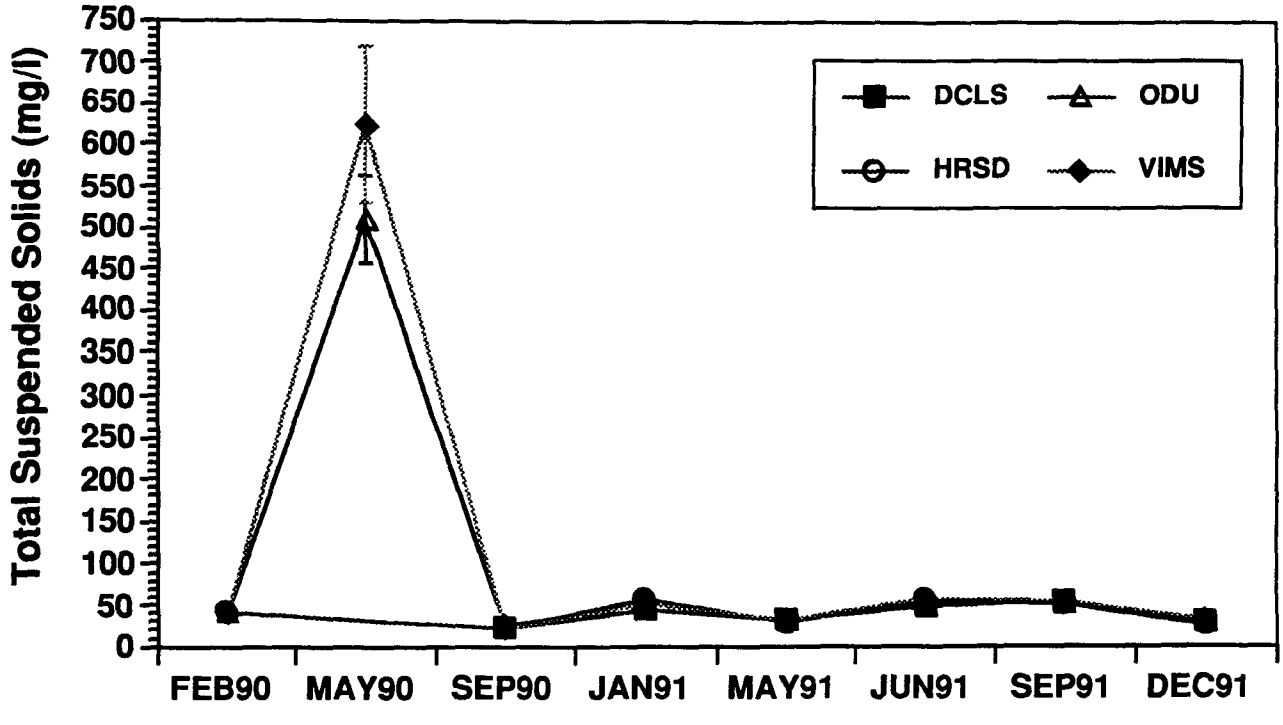


FIGURE 45. Split sample data for chlorophyll *a* (CHLA), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

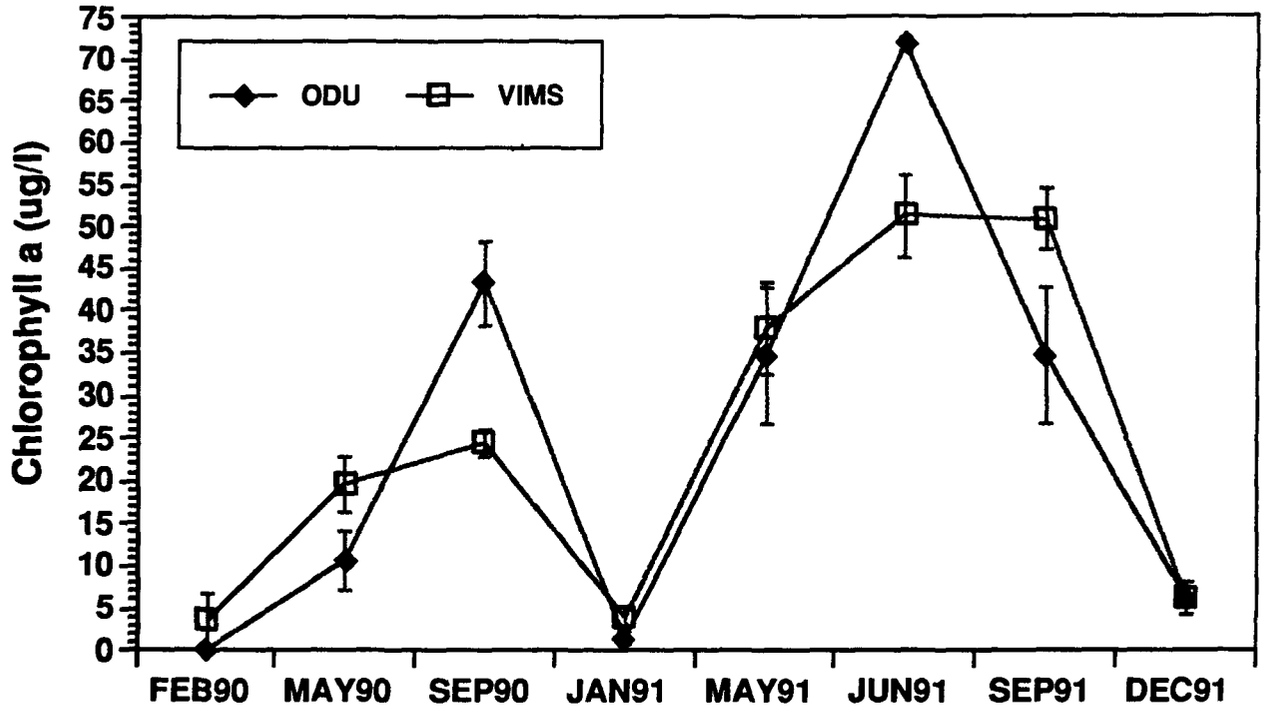


FIGURE 46. Split sample data for phaeophytin (PHEA), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

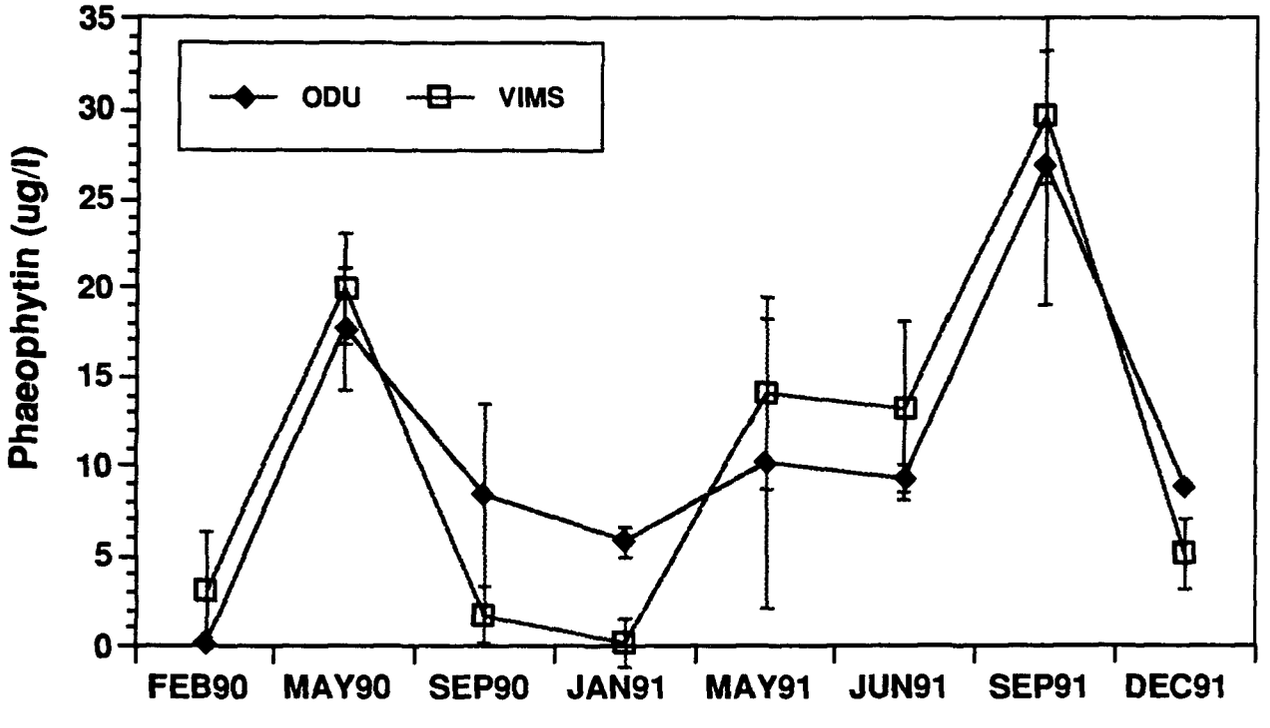


FIGURE 47. Split sample data for silica (SI), from Virginia samples collected at TF5.5, showing medians for each sample date with precision bars.

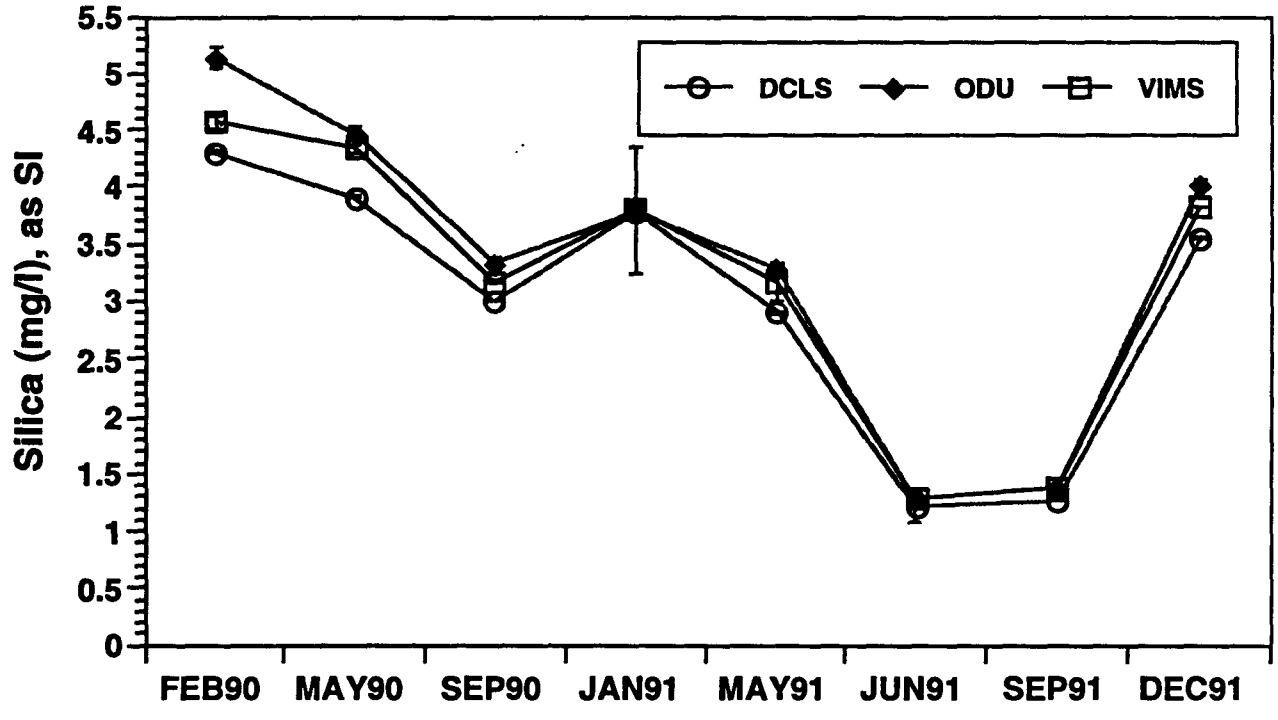


TABLE 17. Fall Line (CB1.0) Split Sample Results using one subsample per sample date, October 1989-July 1991.

Parameter[1]	N[2]	Laboratory Medians, Subsample 1 (mg/l) PADER	USGS	MDHMH	OWML	Friedman results[3] χ^2	P
NH4	4	0.0900	0.0650	0.096	.	1.5	0.65
NH4	2	0.1250	0.0850	0.134	0.105	4.2	0.38
NO2	0	.	.	.	.	-	-
NO23	4	1.225	1.150	1.300	.	5.4	>0.069
NO23	2	0.995	0.950	1.050	0.970	1.1	>0.83
TKNW	4	0.470	0.600	0.450	.	0.4	>0.93
TKNW	2	0.470	0.650	0.625	0.430	0.6	0.96
TKNF	4	0.380	0.350	0.325	.	1.5	0.65
TKNF	2	0.360	0.350	0.250	0.355	1.1	0.83
TN	4	1.73	1.80	1.90	.	1.5	0.65
TN	2	1.47	1.60	1.68	1.40	3.6	0.46
PO4F	4	0.0020	0.0050	0.0040	.	0.5	0.93
PO4F	2	0.0020	0.0025	0.0040	0.0150	4.7	>0.21
TDP	4	0.025	0.0060	0.038	.	6.0	0.069
TDP	2	0.025	0.0060	0.044	0.015	4.2	0.38
TP	4	0.055	0.035	0.038	.	4.9	>0.069
TP	2	0.050	0.035	0.028	0.025	4.1	>0.38
TOC	4	3.05	2.70	2.68	.	1.6	0.65
TOC	2	3.10	2.70	3.14	3.15	0.6	0.96
TSS	0	.	.	.	.	-	-
SI	0	.	.	.	.	-	-

[1] NH4 = ammonium, NO2 = Nitrite, NO23 = Nitrite + Nitrate, TKNW = Total Kjeldahl Nitrogen Whole, TKNF = Total Kjeldahl Nitrogen Filtered, TN = Total Nitrogen (= TKNW + NO23), PO4F = Orthophosphate filtered, TDP = Total Dissolved Phosphorus, TP = Total Phosphorus, TOC = Total Organic Carbon, TSS = Total Suspended Solids, SI = Silica (as SI). Missing data prevented running the Friedman test for NO2, TSS, and SI. The first line for each parameter shows three-way comparisons (without OWML) and the second line shows four-way comparisons.

[2] Number of sample dates with complete data.

[3] Probability that the observed differences were due to chance (accepting the null hypothesis), based on Friedman 2-way ANOVA (Siegel 1956).

FIGURE 48. Split sample data for Ammonium (NH4), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

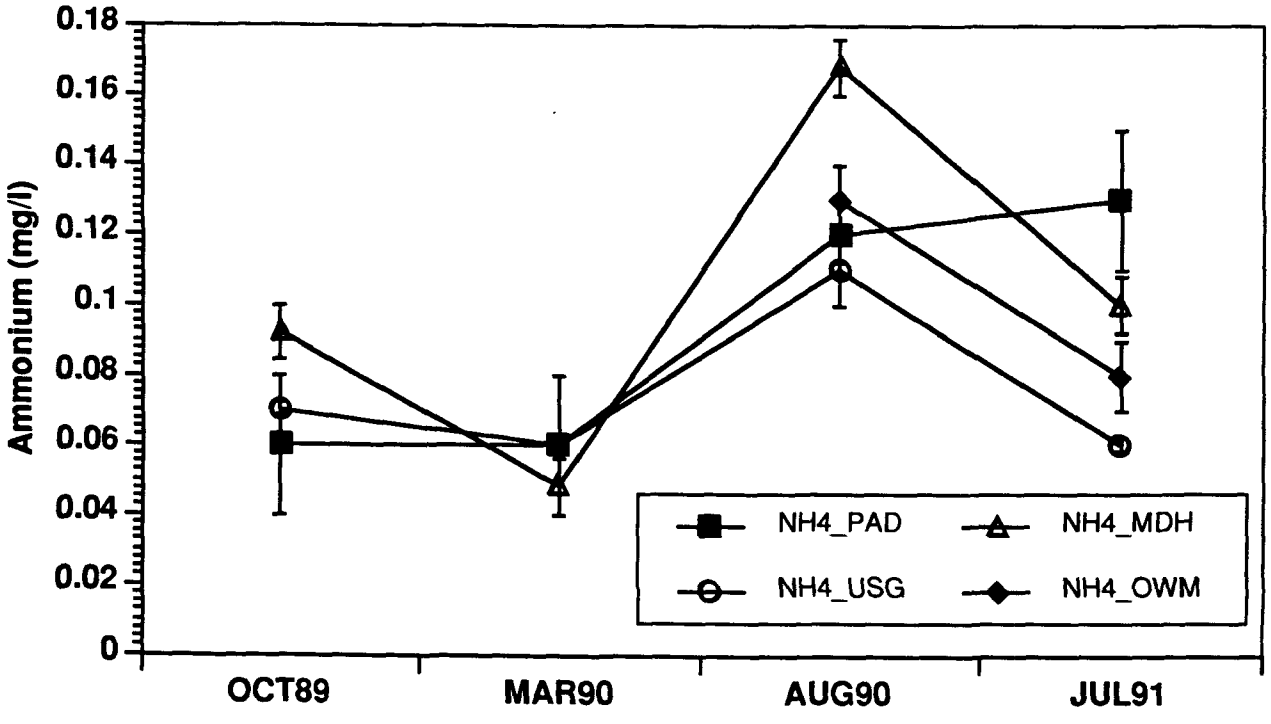


FIGURE 49. Split sample data for Nitrite (NO2), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

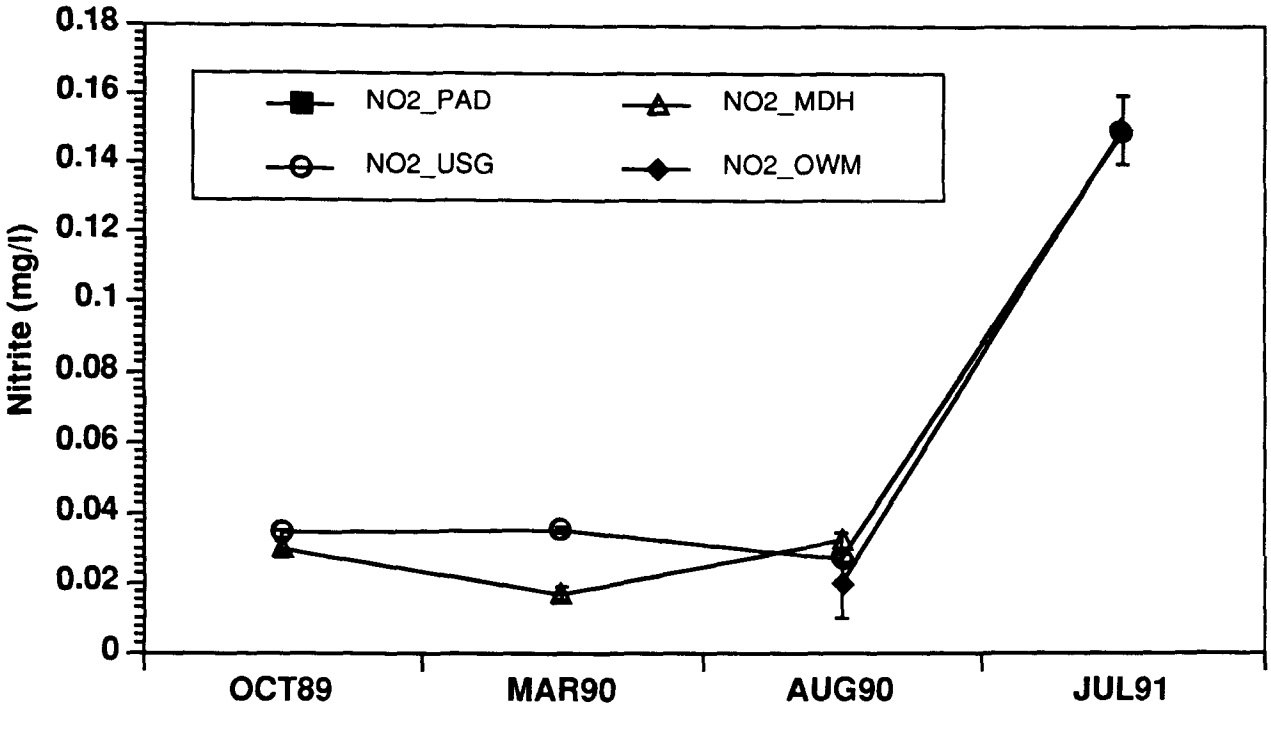


FIGURE 50. Split sample data for Nitrite + Nitrate (NO23), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

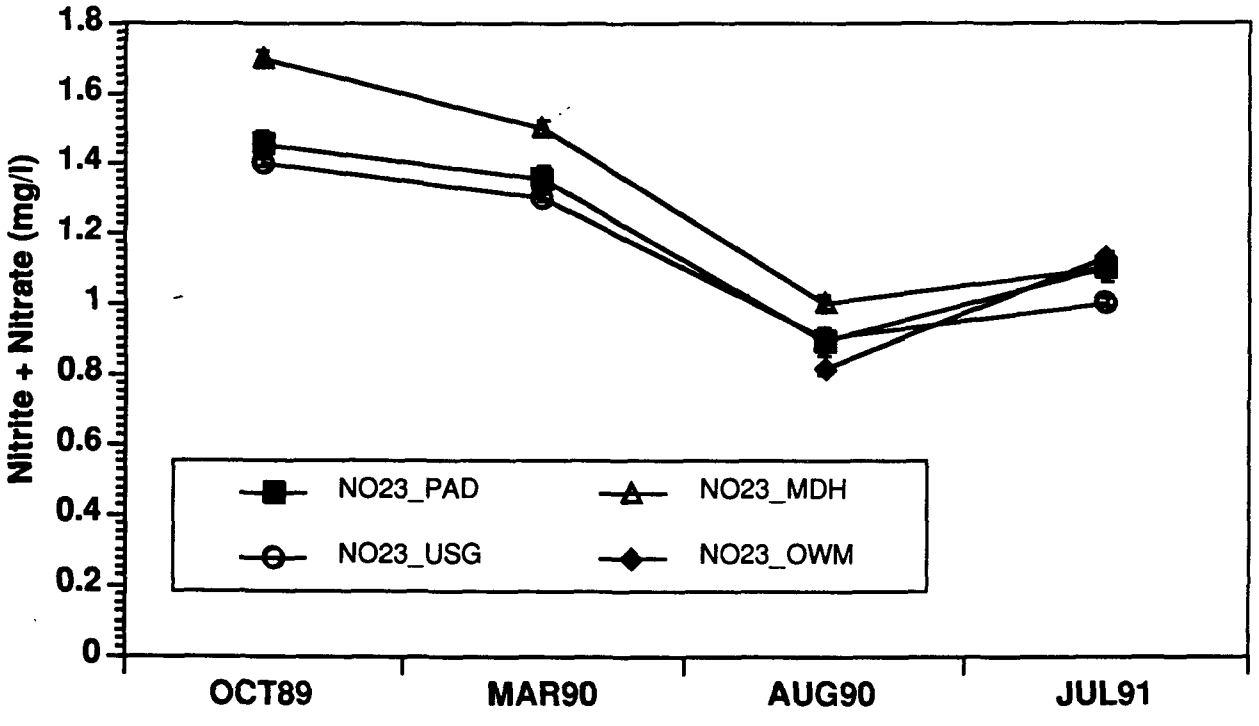


FIGURE 51. Split sample data for Total Kjeldahl Nitrogen Whole (TKNW), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

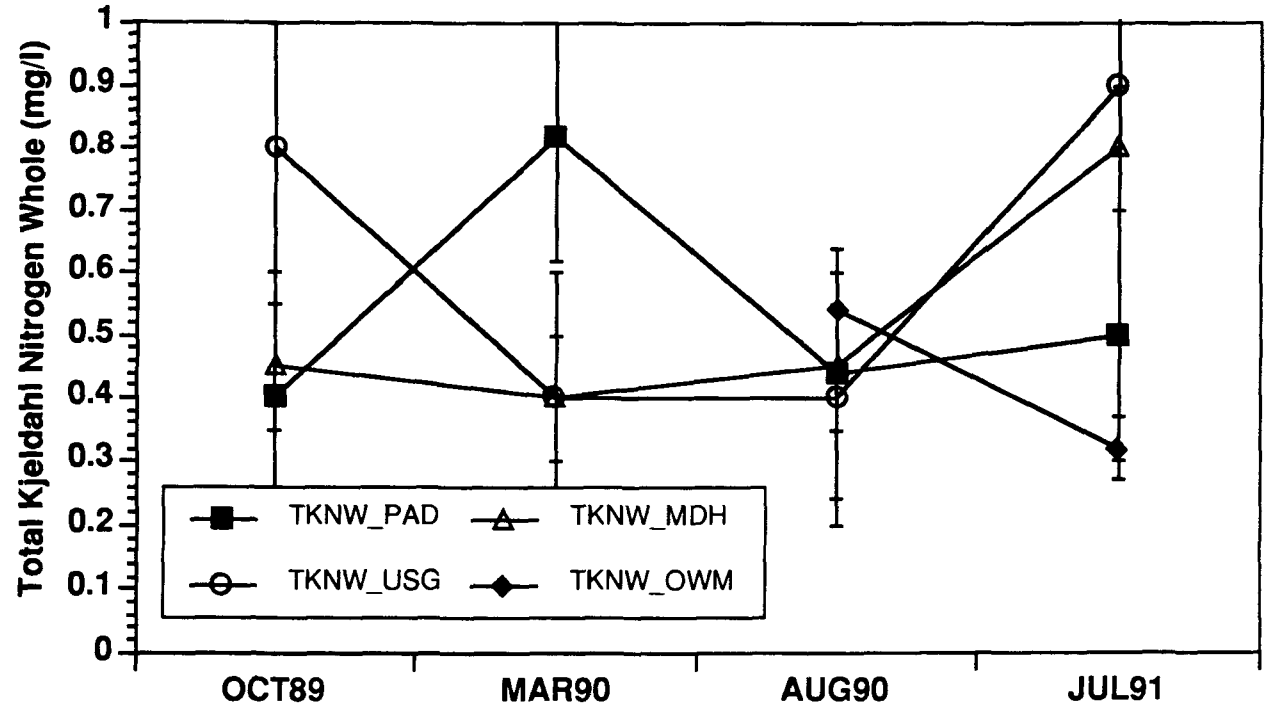


FIGURE 52. Split sample data for Total Kjeldahl Nitrogen Filtered (TKNF), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

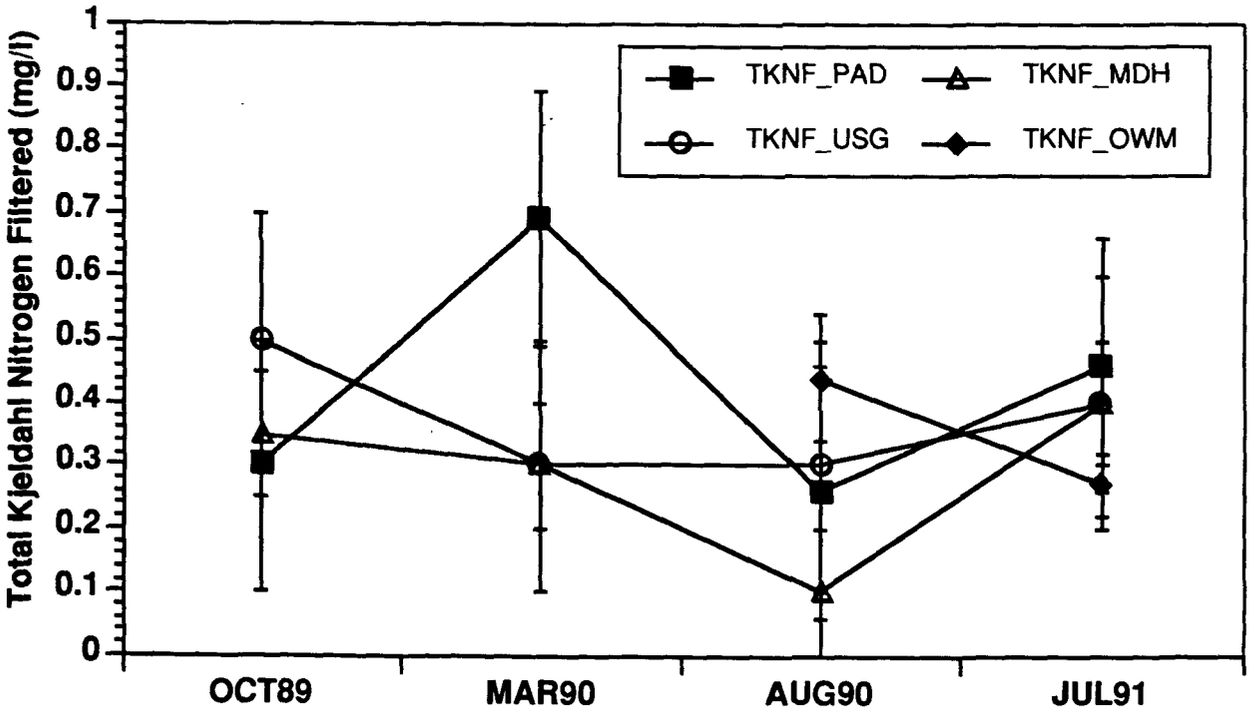


FIGURE 53. Split sample data for Total Nitrogen (TN), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

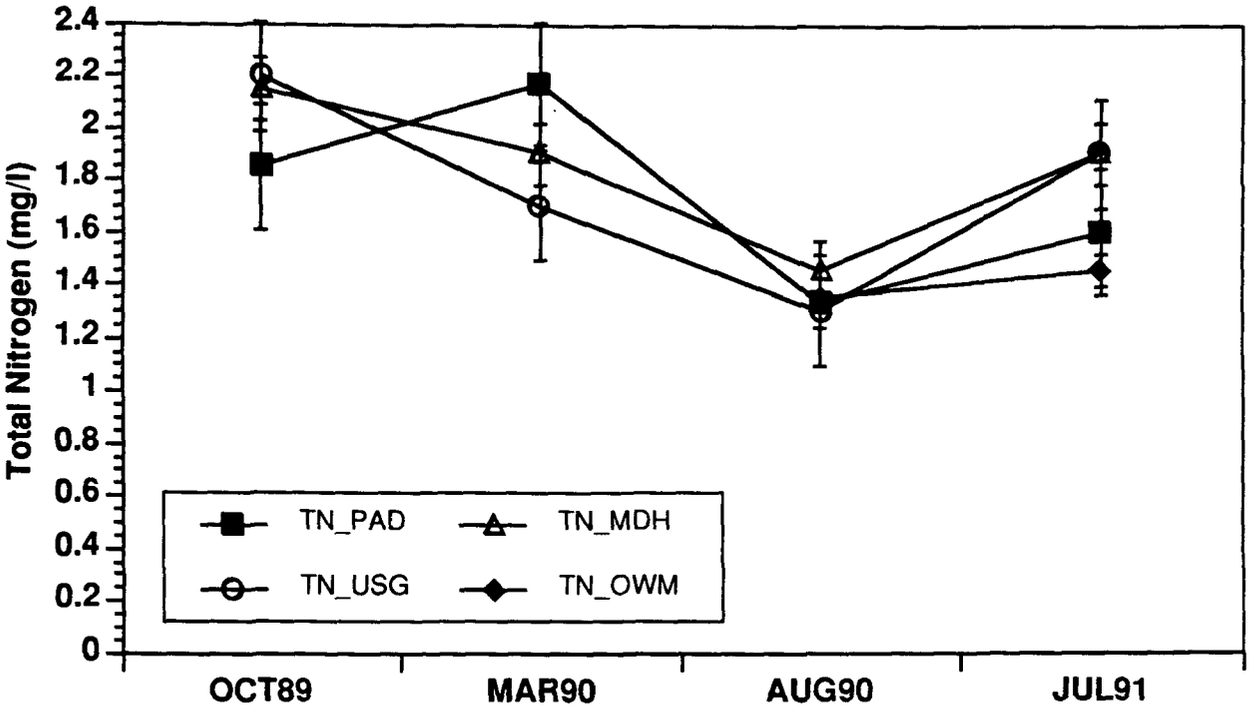


FIGURE 54. Split sample data for Orthophosphate (PO4F), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

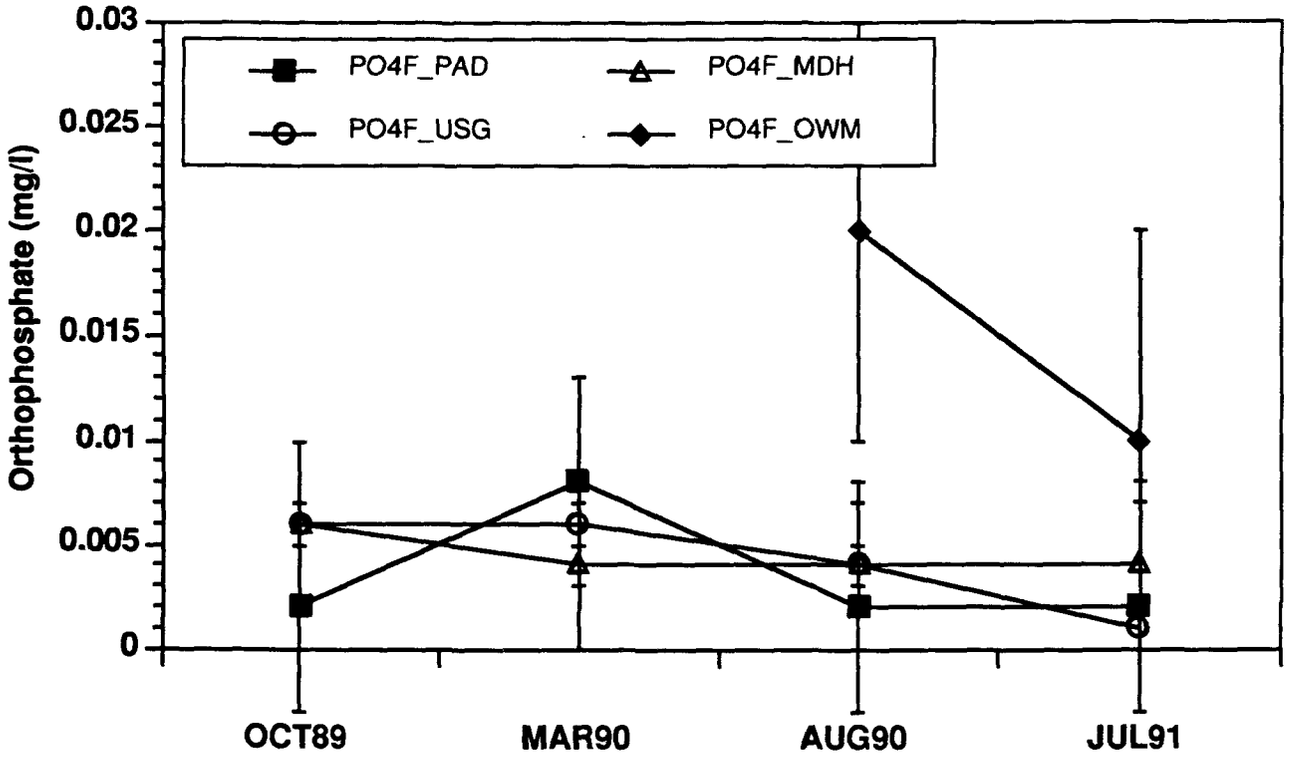


FIGURE 55. Split sample data for Total Dissolved Phosphorus (TDP), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

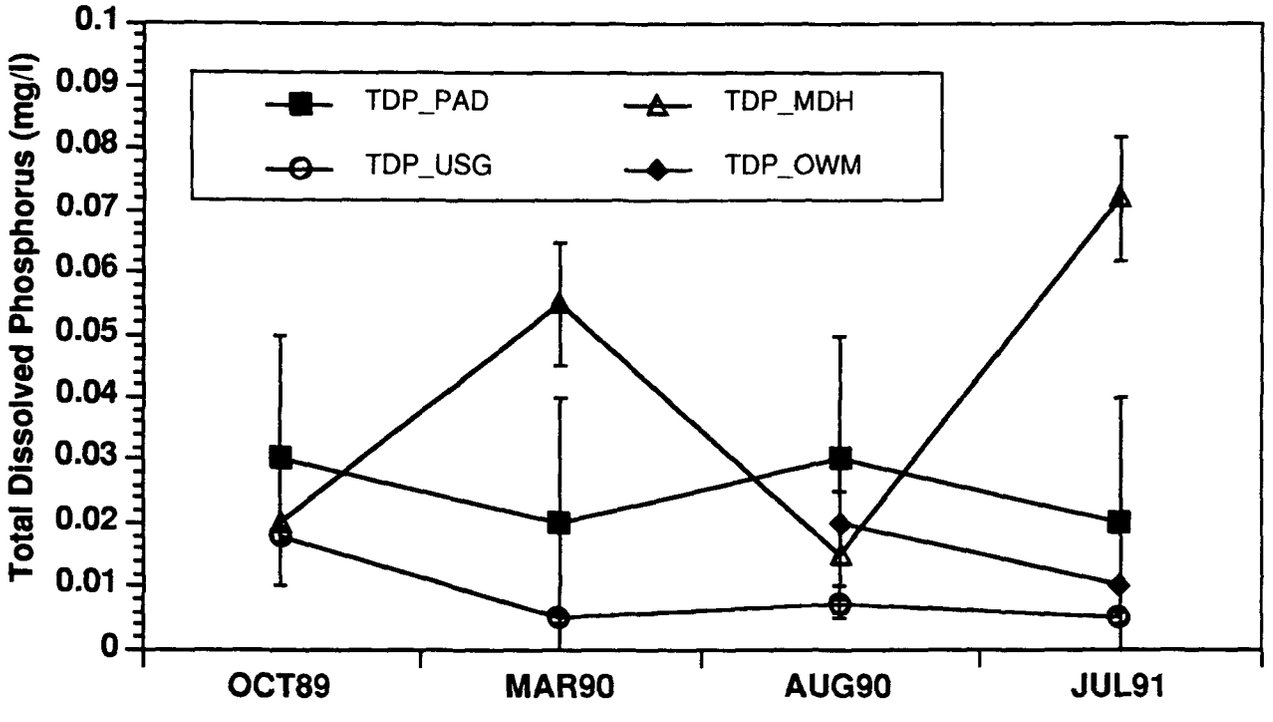


FIGURE 56. Split sample data for Total Phosphorus (TP), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

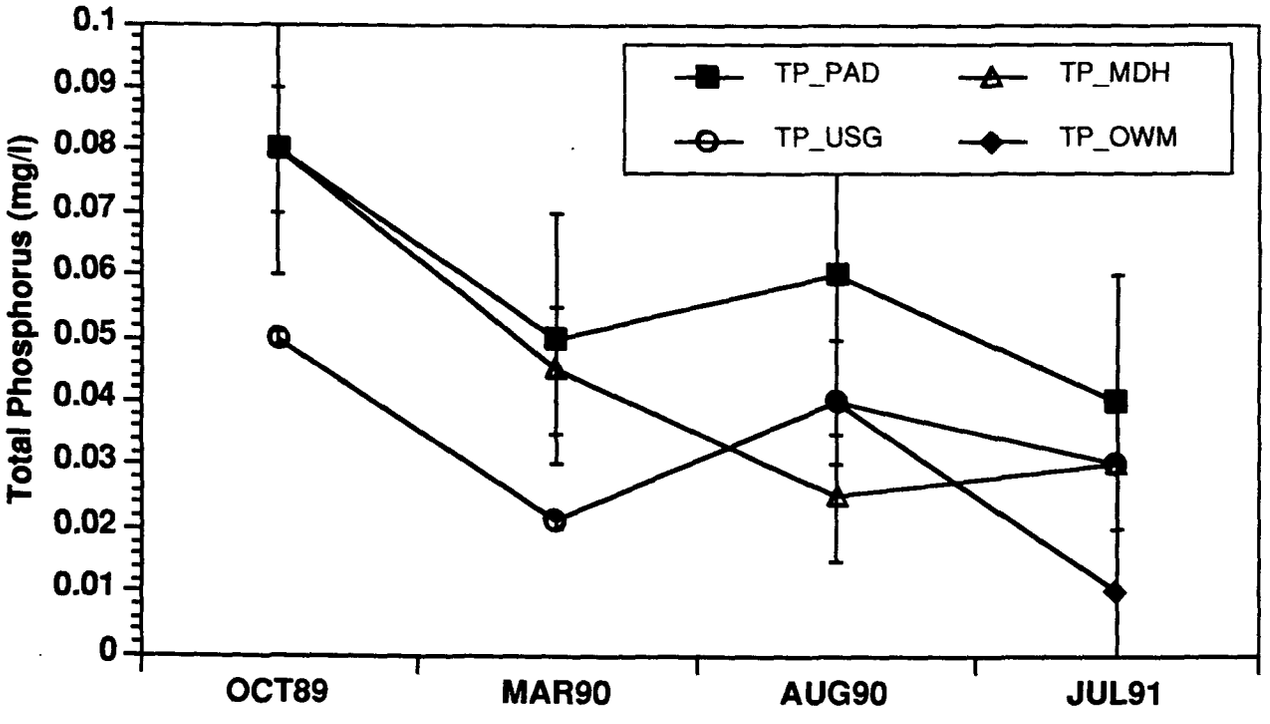


FIGURE 57. Split sample data for Total Organic Carbon (TOC), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

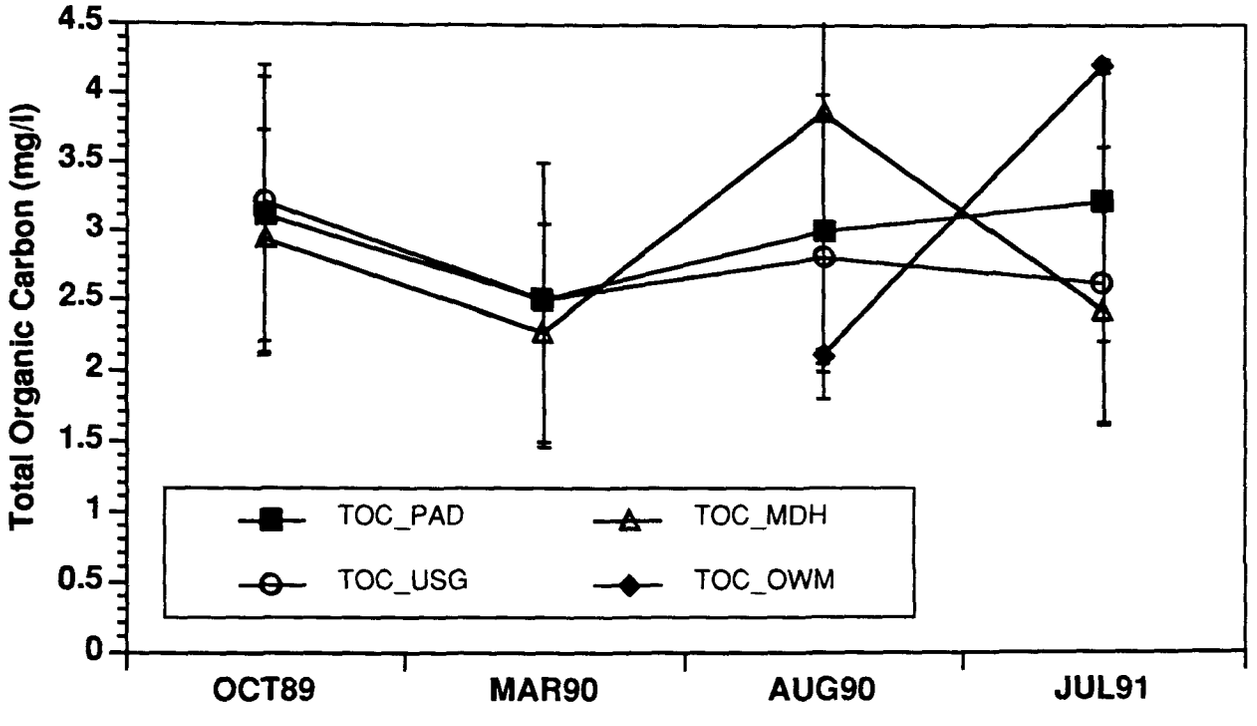


FIGURE 58. Split sample data for Total Suspended Solids (TSS), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.

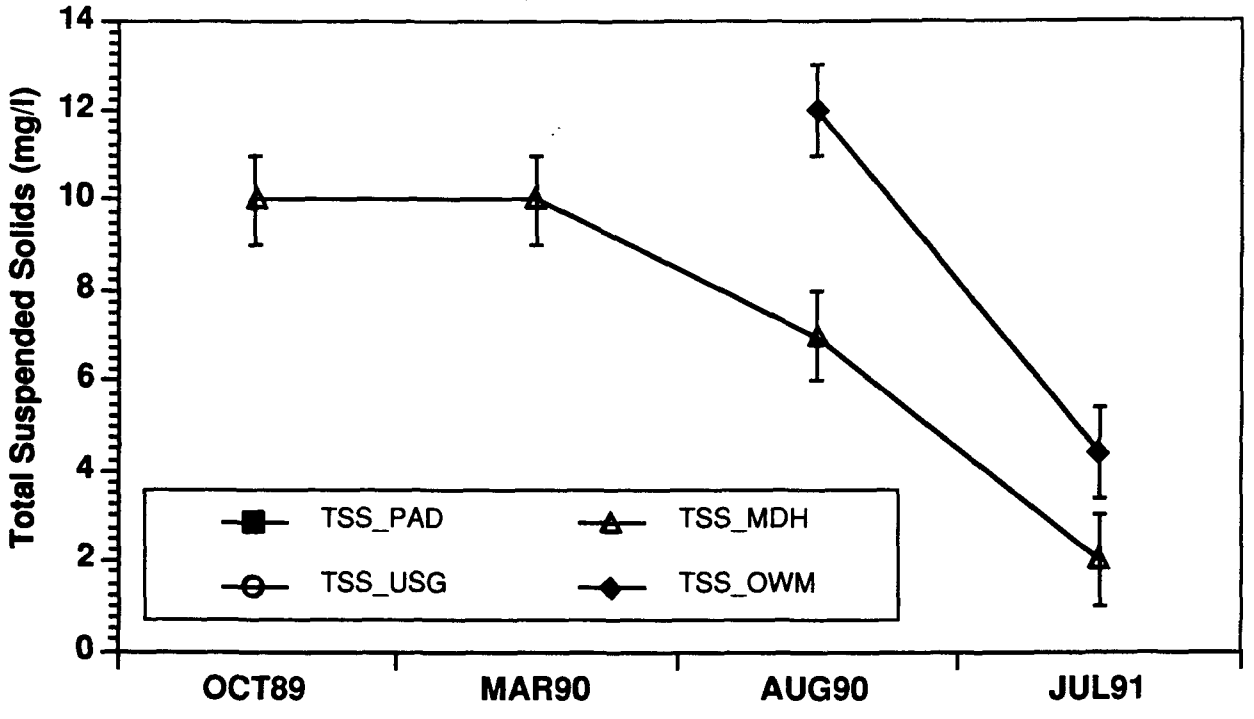
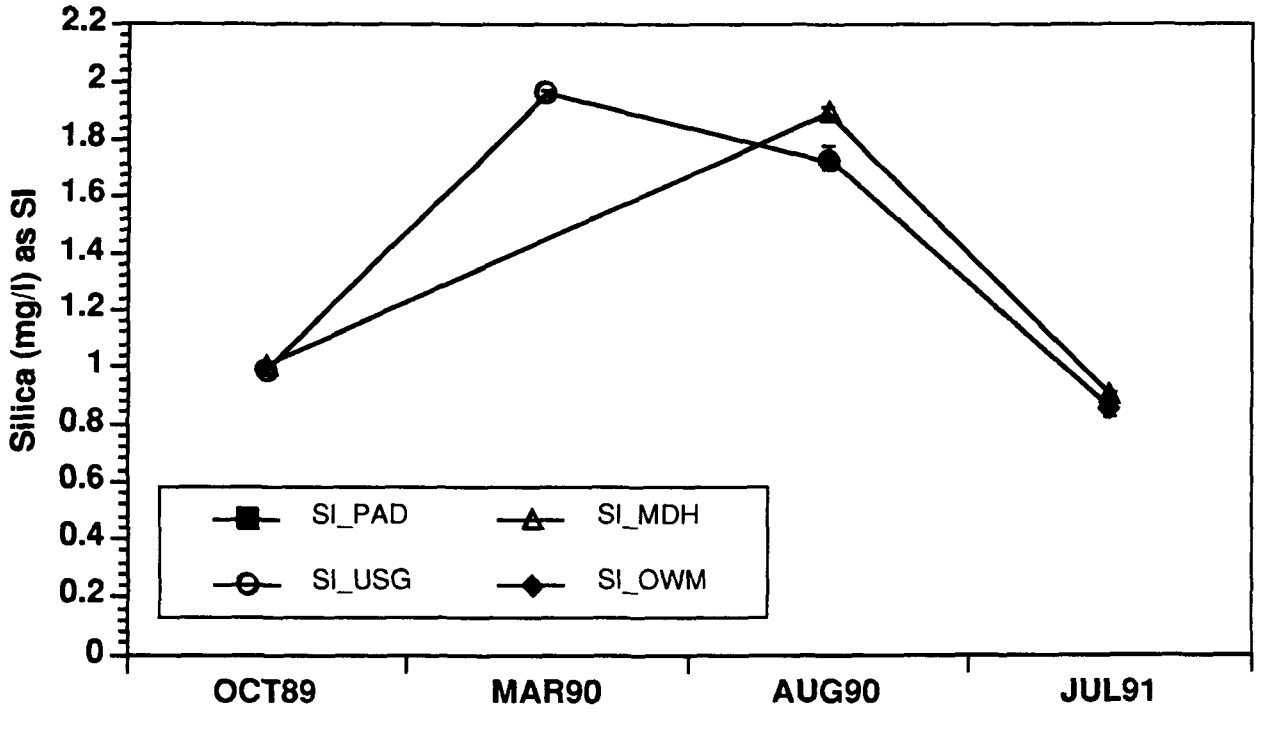


FIGURE 59. Split sample data for Silica (SI), from samples collected at CB1.0 (Fall Line), showing first subsample results with precision bars.



IV. DISCUSSION

Readers should keep in mind that all the components include some laboratories that analyze a large number of samples per day comprising a wide range of sample concentrations--from estuarine samples to wastewater treatment plant samples. The number of samples they analyze reduces the time available for researching advanced techniques and equipment.

In addition, in some components the concentrations encountered are much higher or lower than those usually encountered by some of the laboratories in their Chesapeake Bay sampling. This occurred in the Virginia Component with ODU and VIMS, so their samples from TF5.5 often required considerable dilution. Laboratories encountering samples below their usual range of concentrations may find they are near or below their detection limit. This introduces additional sources of variability not encountered in their routine sampling.

A. WITHIN-ORGANIZATION PRECISION AND ACCURACY

1. Mainstem Component

The estimates of within-organization precision generally show similar results from the different organizations involved. One exception is the two parameters calculated by subtraction in the Mainstem component, PN and PHOSP results from MDHMH (Table 3). These parameters were more variable than the PN and PHOSP results calculated directly by the other three organizations. The same pattern was noted by D'Elia et al. (1987) and used as an argument for using the direct methods. On the other hand, one parameter, TDN, was calculated by addition in the MDHMH data and directly by the other organizations, and it had similar precision among the four organizations that reported it.

The estimates of within-organization accuracy generally showed similar results from the different organizations involved for spike recovery (Table 4), but there were a few differences among organizations for Standard Reference Material (SRM) recovery (Table 5). VIMS had more variable SRM recoveries for TDN than those reported by CBL or ODU, but all the VIMS values were within the confidence limits (+/- 1 SD) supplied by EPA, which correspond to TDN SRM recoveries between 53% and 184%. ODU showed slightly lower recoveries of DOC SRMs diluted in saline matrix than VIMS, but this is consistent with the known differences between the DOC instruments used.

2. Potomac Component

The estimates of within-organization precision (Table 6) generally show similar results from the different organizations involved.

The estimates of within-organization accuracy generally showed similar results from the different organizations involved for spike recovery (Table 7). Standard Reference Material (SRM) results (Table 8) could not be compared because only DCRA/CRL reported them.

3. Virginia Component

Particulate Nitrogen (PN) data at HRSD was probably more variable because it is calculated by subtraction (TKNW-TKNF). Parameters calculated by subtraction tend to be more variable than directly measured parameters (D'Elia et al. 1987).

As in the Mainstem Component, VIMS had more variable SRM results for TDN than ODU, but all the VIMS results were within the +/- 1 SD limits provided by EPA (53-184% recovery). Another pattern seen in Mainstem SRM results, lower DOC results from ODU in estuarine matrix, was also found in the Virginia Component data (mean SRM recoveries were 86% from ODU and 103% from VIMS). This is consistent with the known tendency for the Shimadzu analyzer used by VIMS to achieve higher DOC recoveries.

4. Fall Line Component

The within-organization precision estimates are quite tentative, since they are based on duplicates of only two samples. The one high CV value, from TDP results from USGS, resulted from divergent values for two low-concentration samples, which tends to inflate the CV. These estimates will be more reliable when sample sizes are larger.

B. INTER-ORGANIZATION PRECISION

The estimates of inter-organization precision are designed to assess the measurement system variability in each component after sampling has occurred. They should be used with caution for that purpose, since both SD and CV values can be affected by concentration.

The estimates of inter-organization precision should not be used to assess inter-organization agreement. Unless there are consistent inter-organization differences over several sampling dates, larger CV values may not indicate any problem with inter-organization agreement. Some tests give more variable results than others, and this variability may not be under the laboratory's control. In the discussion that follows, the parameters with the highest inter-organization CV values are identified, and this list is compared to the list of parameters with high within-organization CV values, and the list of parameters with low inter-organization agreement.

1. Mainstem Component

The highest inter-organization CV means were over 50% (Table 3): NH4, PO4F, and PHEA. These three parameters also had among the highest within-organization CV means (see previous section). Only one of these three, NH4, was identified as having low inter-organization agreement (see next section).

2. Potomac Component

The highest inter-organization CV means were over 30% (Table 6): TOC, TSS, and BOD5. Contrary to the results in the Mainstem Component, these three parameters did not have the highest within-organization CV means (see previous section). Only one of these, TOC, was identified as having low inter-organization agreement (see next section).

3. Virginia Component

The highest inter-organization CV means were over 30% (Table 9): PN, PO4F, TDP, and TOC. Contrary to the results in the Mainstem Component, these three parameters did not have the highest within-organization CV means (see previous section), except for PN (PON) at HRSD. Only two of these, PO4F and TOC, were identified as having low inter-organization agreement (see next section).

4. Fall Line Component

The inter-organization CV results (Table 12) will be more useful when they can be compared to past data from the same program. Current results are similar to inter-organization variation estimates from the Mainstem Component, but sample sizes are too limited to draw any conclusions.

C. INTER-ORGANIZATION AGREEMENT

1. Mainstem Component

The results in Table 14 and Figures 1-17 are summarized in Table 18, showing what actions are recommended based on these results. Eleven parameters (NO2, NO23, TDN, TN, PO4F, TDP, PHOSP, TP, TOC, CHLA, and PHEA) had inter-organization agreement that was high enough that no action is recommended. Two of these, TP and TDP, were investigated following the last CSSP report (Bergstrom 1990), and the differences were reduced by using a more accurate blank correction.

Two parameters (PN and PC) currently show inter-organization differences, but should show higher inter-organization agreement in 1992 data, after field method changes were

implemented in January 1992. One parameter (DOC) is the subject of an extensive comparison study by VIMS, documenting the magnitudes of differences caused by the use of different instruments.

Three parameters (NH4, TSS, and SI) are recommended for initial study to determine possible cause(s) of the inter-organization differences found. The higher NH4 results from MDHMH were probably related to the autoanalyzer used there; agreement should improve in 1993 after a new autoanalyzer was obtained. For SI, the inter-organization differences mainly occurred when concentrations were high. The five dates with non-overlapping error bars were September 1989, June through December 1990, and September 1991. These dates all had SI concentrations over 0.8 mg/l, except September 1991.

2. Potomac Component

The results from graphing (Figures 18-30) and the Friedman test (Table 15) are combined in Table 19. Two of the 11 parameters graphed, NO23 and TOC, had inter-organization differences that were larger than within-laboratory precision on more than half of the sampling dates. Both parameters also had statistically significant results from the Friedman test.

Unfiltered samples at MDHMH probably accounted for the NO23 differences, since MDHMH had higher results than the other laboratories during the early period. Thus, no investigation is recommended for NO23, since agreement improved after December 1990.

The differences in TOC involved higher results from DCRA/CRL, lower results from DCLS, and intermediate results from MDHMH. Different instruments at the three laboratories may account for these differences. DOC results showed a similar pattern, but missing data prevented any statistical analysis. Which results are more accurate cannot be estimated, because only DCRA/CRL reported SRM results for TOC. The differences are continuing, since some of the larger differences were in 1991 data. Investigation of possible causes of the differences in TOC results is recommended.

The other five parameters that had statistically significant results from the Friedman test (TKNW, PO4F, TDP, TSS, and SI) did not meet the criteria for recommending action, because the magnitude of the differences was smaller than within-organization precision (Table 19). Agreement of TKNW, PO4F, and TSS results appears to be improving over time, based on graphing and Friedman results. More data are needed to determine whether the small differences in TDP and SI results will persist.

3. Virginia Component

Four of the 13 parameters that were analyzed statistically, PO4F, PHOSP, TOC, and SI, had inter-organization differences that were larger than within-organization precision on

TABLE 18. Summary of Friedman ANOVA results (Table 14) and plots of medians for each sample date (Figs. 1-17), Mainstem Component, 1989-1991.

Parameter	Friedman ANOVA significant[1] 3-way	4-way	5-way	More than half of Differences > than MDL	Recommended Action
Ammonium (NH4)	no	yes	MDL[2]	Yes (MDHMH > CBL), 7/7 dates	study[3]
Nitrite (NO2)	yes	yes	MDL	No	none
Nitrite + Nitrate (NO23)	yes	yes	MDL	No	none
Total Dissolved Nitrogen (TDN)	yes	yes	-	No	none
Particulate Nitrogen (PN)	yes	yes	-	Yes (CBL > others), 7/10 dates	method changes[4]
Total Nitrogen (TN)	yes	yes	yes	No	none
Orthophosphate (PO4F)	yes	MDL	MDL	No	none
Total Dissolved Phosphorus (TDP)	no	yes	MDL	No	none[5]
Particulate Phosphorus (PHOSP)	no	no	yes	No	none
Total Phosphorus (TP)	no	no	yes	No	none[5]
Dissolved Organic Carbon (DOC)	yes	-	-	Yes (VIMS > others), 6/8 dates	comparison study[6]
Particulate Carbon (PC)	yes	-	-	Yes (CBL > others), 8/10 dates	method changes[4]
Total Organic Carbon (TOC)	yes	yes	-	No	none

TABLE 18 (continued). Summary of Friedman ANOVA results (Table 14) and plots of medians for each sample date (Figs. 1-17), Mainstem Component, 1989-1991.

Parameter	Friedman ANOVA significant[1] 3-way	4-way	5-way	More than half of Differences > than MDL	Recommended Action
Total Suspended Solids (TSS)	yes	yes	yes	Yes (Others > CBL), 8/9 dates	study[3]
Chlorophyll a (CHLA)	no	-	-	No	none
Phaeophytin (PHEA)	yes	-	-	No	none
Silica (SI)	yes	yes	yes	Yes (Others > CBL), 5/9 dates	study[3]

[1] Three-way comparisons include CBL, ODU, and VIMS; four-way add MDHMH; and five-way add DCLS. Sample sizes were usually smaller for five-way comparisons, because DCLS data started in June 1990.

[2] Too many values were below the Method Detection Limit (MDL) for a comparison.

[3] Study begins with a comparison of MDLs and field and laboratory methods to look for possible cause(s) of differences, and may later include a method comparison study if needed.

[4] Method changes were implemented in January 1992 to make field methods more consistent and to reduce or eliminate these differences, which were caused by different filtration methods.

[5] After the 1989 CSSP Mainstem report showed that MDHMH results were high for these two parameters, a more accurate blank correction was found, and MDHMH data were corrected for this report.

[6] Study done by VIMS documents the magnitude of these differences, which are apparently due to the use of different instruments.

TABLE 19. Summary of Friedman ANOVA results (Table 15) and plots of medians for each sample date (Figs. 18-30), Potomac Component, 1989-1991.

A. Parameters affected by the change to filtered samples at MDHMH in December 1990

Parameter	Friedman ANOVA significant[1] unfiltered	filtered	More than half of Differences > than MDL	Recommended Action
Ammonium (NH4)	no	no	no	none
Nitrite (NO2)	no	no	no	none
Nitrite + Nitrate (NO23)	yes	no	yes[2], 8/11 dates	none
Orthophosphate (PO4F, PO4W)	yes	yes	no	none
Silica (SI)	no	yes	no	none

B. Parameters not affected by the change to filtered samples at MDHMH

Parameter	Friedman ANOVA significant[1] all data	1991 data	More than half of Differences > than MDL	Recommended Action
Total Kjeldahl Nitrogen Whole (TKNW)	yes	no	no	none
Total Nitrogen (TN)	no	-	no	none
Total Phosphorus[3] (TP)	no	-	no	none
Total Dissolved Phosphorus (TDP)	yes	-	no	none
Total Organic Carbon (TOC)	yes	yes	yes, 6/11 dates	study[4]
Dissolved Organic Carbon (DOC)	-[5]	-	-	none

TABLE 19 (continued). Summary of Friedman ANOVA results (Table 15) and plots of medians for each sample date (Figs. 18-30), Potomac Component, 1989-1991.

B. (continued). Parameters not affected by the change to filtered samples at MDHMH.

Parameter	Friedman ANOVA significant[1] all data	1991 data	More than half of Differences > than MDL	Recommended Action
Total Suspended Solids (TSS)	yes	no	no	none
Biological Oxygen Demand 5 day (BOD5)	-[5]	-	-	none

[1] $P < 0.01$.

[2] All, or almost all, of the differences larger than the MDLs were before December 1990, when MDHMH analyzed unfiltered samples. Thus, no action is recommended.

[3] Using data from December 1990 onward, after the MDL was lowered for DCLS analyses.

[4] Study begins with a comparison of MDLs and field and laboratory methods to look for possible cause(s) of differences, and may later include a method comparison study if needed.

[5] Missing data prevented statistical analysis for DOC and BOD5.

more than half of the sampling dates (Table 20). All of these parameters also had statistically significant results ($P < 0.01$) from the Friedman test (Table 16), so they meet the criteria for recommending investigation.

The PO4F differences appear to have been caused by higher results from ODU, where PO4F calibrations are by standard additions. ODU also had higher PO4F results in Mainstem Component samples (Table 14), although the magnitudes of the differences were small (Table 18). The different matrix and higher PO4F concentrations at Hopewell (TF5.5) may contribute to the higher results from ODU in the Virginia Component. HRSD changed methods and lowered their method detection limit (MDL) in August, 1990.

The PHOSP differences appear to be due to higher results from DCLS, and to a lesser extent from HRSD. Since both DCLS and HRSD calculate PHOSP by subtraction, from TP - TDP, and VIMS and ODU measure it directly, no further investigation appears to be necessary.

The TOC results from DCLS averaged about 3.5 mg/l lower than results from VIMS or ODU. The lower results were probably due to the use of a different digestion method at DCLS. Until 1992, DCLS used a Dorman DC-180 TOC analyzer with UV persulfate digestion, which tends to provide less complete digestion when particulates are present compared to other TOC methods (R. Potts pers. comm.). They started using a Dorman DC-190 with high-temperature digestion (680 °C) in March 1992, which should increase agreement in 1992 data. The differences in SI results might be due to different methods at DCLS; DCLS results averaged about 0.3 mg/l lower than results from ODU or VIMS. However, SI agreement appears to have increased slightly during 1991 (Table 16, Fig. 47).

The other parameters that had statistically significant results from the Friedman test did not meet the criteria for recommending investigation, because the magnitude of the differences was smaller than within-organization precision. Additional data are needed to determine whether the agreement of these parameters warrants further study.

4. Fall Line Component

Inter-organization agreement was high for all 9 parameters analyzed (Table 21). The one parameter with more than half of the sample dates with non-overlapping precision bars (NO23) did not have statistically significant differences. However, the small sample sizes, and resulting low power of the test used, mean that there may be some significant differences when sample sizes are larger. Also, the higher MDLs in this component, compared to the Mainstem Component, make it more likely that the precision bars will be overlapping in this component. The differences among laboratories in sample preservation, detection limits, and analytical methods did not cause any detectable differences in results. These differences include preserved samples at OWML and USGS, but not at MDHMH or PADER; and USGS analytical methods at USGS, and EPA methods at the other three laboratories.

TABLE 20. Summary of Friedman ANOVA results (Table 16) and plots of medians for each sample date (Figs. 31-47), Virginia Component, 1990-1991.

Parameter	Friedman ANOVA significant[1] all data	1991 data	More than half of Differences > than MDL	Recommended Action
Ammonium (NH4)	Yes	No	No	none
Nitrite (NO2)	Yes	Yes	No	none
Nitrite + Nitrate (NO23)	No	No	No	none
Total Dissolved Nitrogen (TDN)	Yes	Yes	No	none
Particulate Nitrogen (PN)	No	No	No	none
Total Nitrogen (TN)	Yes	Yes	No	none
Orthophosphate (PO4F)	Yes	Yes	Yes (ODU>VIMS, 6/7 dates, + ODU>DCLS, 4/7 dates)	study[2]
Total Dissolved Phosphorus (TDP)	Yes	No	No	none
Particulate Phosphorus (PHOSP)	Yes	Yes	Yes (DCLS>VIMS, 4/7 dates)	none[3]
Total Phosphorus (TP)	No	Yes	No	none
Total Organic Carbon (TOC)	Yes	Yes	Yes (Others > DCLS, 5/5 dates)	study[2]
Total Suspended Solids (TSS)	No	No	No	none
Silica (SI)	Yes	Yes	Yes (Others > DCLS, 6/8 dates)	study[2]

[1] Data for 1991 were analyzed separately to see if differences persisted.

[2] Study begins with a comparison of MDLs and field and laboratory methods to look for possible cause(s) of differences, and may later include a method comparison study if needed.

[3] Higher PHOSP results from DCLS are probably due to determination by subtraction by TP - TDP; HRSD also used this method and had high results.

TABLE 21. Summary of Friedman ANOVA results (Table 17) and plots of medians for each sample date (Figs. 48-59), Fall Line Component, 1989-1991.

Parameter	Friedman ANOVA significant[1]	More than half of Differences > than MDL	Recommended Action
Ammonium (NH4)	No	No	none
Nitrite (NO2)	No	No	none
Nitrite + Nitrate (NO23)	No	Yes, 3/4 dates	none
Total Kjeldahl Nitrogen Whole (TKNW)	No	No	none
Total Kjeldahl Nitrogen Filtered (TKNF)	No	No	none
Total Nitrogen (TN)	No	No	none
Orthophosphate (PO4F)	No	No	none
Total Dissolved Phosphorus (TDP)	No	No	none
Total Phosphorus (TP)	No	No	none
Total Organic Carbon (TOC)	No	No	none
Total Suspended Solids (TSS)	No	No	none
Silica (SI)	No	No	none

[1] $P < 0.01$.

5. Parameters recommended for investigation in two or more components

Two parameters, Total Organic Carbon (TOC) and Silica (SI), were recommended for investigation in two components each. The patterns of their differences were compared to see if the same laboratories were involved.

Investigation was recommended for TOC in the Potomac and Virginia components. TOC also showed significant differences in the Mainstem Component, although most of the differences were smaller than the precision estimates. In all three components, TOC results from the Division of Consolidated Laboratory Services (DCLS) in Richmond tended to be lower than results from other laboratories. This tendency was probably due to the use of the Dorman DC-180 TOC instrument used at DCLS, which used UV persulfate digestion. TOC agreement should increase in 1992 data after DCLS started using a Dorman DC-190 with high-temperature digestion.

Investigation was recommended for SI in the Mainstem and Virginia components. In the Mainstem Component, Chesapeake Biological Laboratory (CBL) tended to have lower results, and in the Virginia Component, DCLS tended to have lower results. CBL did not participate in the Virginia Component, but DCLS results were close to CBL results in the Mainstem Component (see Table 14). The SI methods and instruments used should be studied to see if they could be a cause of these patterns.

D. FUTURE DIRECTIONS FOR THE CSSP

1. Changes in Splitting Methods

Two changes in splitting methods have been made or will be made soon, although they did not affect 1990-1991 data. The Virginia Component changed from using three separate churn splitters to a single large churn splitter (30 liters, about 8 gallons) in June 1992. The Fall Line Component will change from using a single churn splitter, which was not large enough to provide the subsamples needed, to using three separate churn splitters.

Although these changes appear inconsistent, each is suited to the logistics and the concentrations encountered in each component. The Virginia Component encounters much higher TSS concentrations, and data analyzed in this report showed that the three separate splitters did not split evenly under those conditions. The Fall Line Component encounters lower TSS concentrations, so the three splitters should be adequate there. The change to using three churn splitters, and thus providing three subsamples to each Fall Line laboratory, will increase the power of the Friedman test, making it easier to detect any differences that are present. Especially if sampling cannot be done quarterly, providing three subsamples is very important. Also, the Fall Line Component uses USGS field procedures, which include using churn splitters, but do not include splitting from a large carboy. USGS staff have been

unable to obtain a single churn splitter that was large enough to provide the required number of subsamples.

2. Ensuring adequate ranges of split sample concentrations

Low ambient concentrations may be a problem in any split sample program. They can lead to two data problems: the occurrence of below detection limit results, and a lack of data on inter-organization agreement at higher concentrations. Both are a problem in the Mainstem Component, and to a lesser extent for certain parameters in other components.

Below detection limit values tend to limit the usefulness of the split sample results: they may rule out assessing inter-organization agreement, and they usually prevent calculation of percent recovery from spiked samples. Also, the low concentrations of some parameters such as TSS in Mainstem samples (30 mg/l or less, Figure 14) limits our knowledge of inter-organization agreement at higher concentrations.

The simplest way to expand the concentration range of Mainstem Component split samples would be to start using bottom samples from CB4.4. Mainstem splits have always used surface samples, but the VIMS-ODU two-way split samples used bottom samples. Higher TSS values in bottom samples might make it more difficult to split samples accurately, but extremely high concentrations do not occur at CB4.4. The maximum TSS concentrations during 1984-1990 were less than 93 mg/l at CB4.4 (Table 22).

TABLE 22. Concentrations of selected parameters in surface and bottom layers at Station CB4.4, 1984 - 1990.

	SURFACE			BOTTOM		
Parameter	Mean	Min.	Max.	Mean	Min.	Max.
SALIN (Salinity)	13.6	6.6	18.9	20.2	15.9	24.2
TSS	5.2	2.5	18.2	14.9	2.0	92.6
CHLA	10.7	1.8	33.0	8.1	0.4	59.8
PO4F	0.0043	0.0015	0.011	0.019	0.0018	0.084
NH4	0.024	0.003	0.14	0.15	0.003	0.48
NO23	0.21	0.0009	0.96	0.064	0.001	0.32

Using bottom samples would expand the concentration range of most of the parameters that have a limited range in CB4.4 surface samples (Table 22): TSS, CHLA, PO4F, and NH4. The range might be slightly reduced for NO23, but there are no agreement problems for NO23. The salinity would be increased, but would still be within the range encountered by the two tributary laboratories at the mouths of rivers. Higher concentrations might increase the number of samples that required dilution before analysis by some of the mainstem laboratories, however. Bottom samples could be used for every split sample, or surface and bottom samples could be used in alternation or chosen at random (e.g., with a coin toss). Bottom sample data from CB4.4 would increase the usefulness of mainstem CSSP results with little or no increase in effort or cost.

V. REFERENCES

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