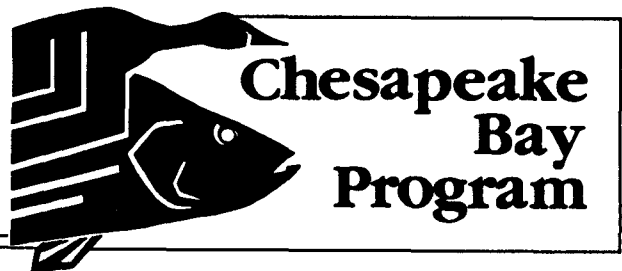


Chesapeake Bay Coordinated Split Sample Program Annual Report, 1989



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by Peter Bergstrom



November 14, 1990

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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 program uses 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 1989, its first full year of operation.

The CSSP has two main objectives: estimating measurement system variability, and identifying parameters with low inter-organization agreement. The variability estimates are most useful to data analysts and modelers who need confidence estimates for monitoring data. 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 document any improvements in inter-organization agreement.

Estimates of measurement system variability based on split sample data show that some parameters have more variable results than others. In some cases these patterns were consistent when different laboratories and sampling stations were compared.

Inter-organization agreement was high for 18 of the 23 comparisons made in two components. Agreement was low enough to recommend investigation for five parameters: Total Phosphorus (TP), Total Dissolved Phosphorus (TDP), Particulate Carbon (PC), Particulate Nitrogen (PN), and Dissolved Organic Carbon (DOC). Recommendations for further investigation were made when there were three or more inter-organization differences that were larger than within-organization precision, and there were statistically significant inter-organization differences at the $P \leq 0.01$ level.

In all five cases of low inter-organization agreement, only one of the four organizations compared had divergent results. In each case, this organization had a different analytical method or instrument type, and in two cases (PC and PN) there was also a difference in filter type. In three cases (TP, TDP, and DOC) method changes have been made to increase inter-organization agreement. The other two cases (PC and PN) are being investigated by the organizations involved to find ways to increase agreement.

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

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TABLE OF CONTENTS

EXECUTIVE SUMMARY	ii
ACKNOWLEDGMENTS	iii
TABLE OF CONTENTS	iv
LIST OF FIGURES	vi
LIST OF TABLES	viii
I. <u>INTRODUCTION</u>	1
II. <u>METHODS</u>	4
A. COMPONENTS AND PARTICIPATING LABORATORIES	4
1. Mainstem and Tidal Tributaries component	4
2. Tidal Potomac component	4
3. Fall Line component	4
B. SAMPLE COLLECTION AND SPLITTING METHODS	4
1. Mainstem and Tidal Tributaries component	4
2. Tidal Potomac component	5
3. Fall Line component	5
C. DATA ENTRY AND REDUCTION	6
1. Mainstem and Tidal Tributaries component	6
2. Tidal Potomac component	6
3. Fall Line component	6
D. DATA ANALYSIS AND GRAPHING	6
1. Preliminary test of splitting randomness	6
2. Precision estimates	7
3. Assessing inter-organization agreement	7
III. <u>RESULTS</u>	9
A. WITHIN-ORGANIZATION PRECISION AND ACCURACY	9
1. Mainstem and Tidal Tributaries component	9
2. Tidal Potomac component	9
3. Fall Line component	15
B. INTER-ORGANIZATION PRECISION	15
1. Mainstem and Tidal Tributaries component	15
2. Tidal Potomac component	15
3. Fall Line component	15
C. INTER-ORGANIZATION AGREEMENT	22
1. Mainstem and Tidal Tributaries component	22
2. Tidal Potomac component	22
3. Fall Line component	22
IV. <u>DISCUSSION</u>	37
A. WITHIN-ORGANIZATION PRECISION AND ACCURACY	37
B. INTER-ORGANIZATION PRECISION	37
C. INTER-ORGANIZATION AGREEMENT	37
1. Mainstem component	37

2. Potomac component	38
3. Fall line component	38
V. <u>SUMMARY AND CONCLUSIONS</u>	38
VI. <u>REFERENCES</u>	39

LIST OF FIGURES

Figure 1.	Chesapeake Bay Coordinated Split Sample Program Components.	2
Figure 2.	Schematic of operational flow of analyses, Coordinated Split Sample Program.	3
Figure 3.	Split sample data for Total Dissolved Phosphorus (TDP), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.23
Figure 4.	Split sample data for Total Phosphorus (TP), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.23
Figure 5.	Split sample data for Particulate Nitrogen (PN), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.24
Figure 6.	Split sample data for Particulate Carbon (PC), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.24
Figure 7.	Split sample data for Silica (SI), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.25
Figure 8.	Split sample data for Nitrite (NO ₂), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.25
Figure 9.	Split sample data for Nitrite + Nitrate (NO ₂ +3), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.26
Figure 10.	Split sample data for Ammonium (NH ₄), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.26
Figure 11.	Split sample data for Particulate Phosphorus (PHOSP), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.27
Figure 12.	Split sample data for Orthophosphate (PO ₄ F), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.27
Figure 13.	Split sample data for Dissolved Organic Carbon (DOC), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.28

Figure 14.	Split sample data for Total Dissolved Nitrogen (TDN), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.28
Figure 15.	Split sample data for Total Nitrogen (TN), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.29
Figure 16.	Split sample data for Total Suspended Solids (TSS), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.29
Figure 17.	Split sample data for Ammonium (NH ₄), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.31
Figure 18.	Split sample data for Nitrite (NO ₂), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.31
Figure 19.	Split sample data for Nitrite + Nitrate (NO ₂ 3), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.32
Figure 20.	Split sample data for Total Kjeldahl Nitrogen Whole (TKNW), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.32
Figure 21.	Split sample data for Orthophosphate (PO ₄), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.33
Figure 22.	Split sample data for Total Phosphorus (TP), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.33
Figure 23.	Split sample data for Total Organic Carbon (TOC), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.34
Figure 24.	Split sample data for Total Suspended Solids (TSS), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.34
Figure 25.	Split sample data for Silica (SI), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.35
Figure 26.	Split sample data for Biological Oxygen Demand 5 day (BOD ₅), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.35

LIST OF TABLES

TABLE 1: Method Detection Limits at Mainstem Component Laboratories, 1989-1990.	10
TABLE 2: Method Detection Limits at Potomac Component Laboratories, 1989-1990.	11
TABLE 3: Method Detection Limits at Fall Line Component Laboratories, 1989-1990.	12
TABLE 4: Within-organization and inter-organization precision estimates, Mainstem Component.	13
TABLE 5: Within-organization and inter-organization precision estimates, Potomac Component.	14
TABLE 6: Within-organization precision estimates, Fall Line Component.	16
TABLE 7: Percent Recovery Data, Mainstem Component, 1989	17
TABLE 8: Percent Recovery Data, Potomac Component, 1989-90.	18
TABLE 9: Percent Recovery Data, Fall Line Component, 1989-90.	19
TABLE 10: Standard Reference Material Results, Mainstem Component, 1989.	20
TABLE 11: Standard Reference Material Results, Potomac Component, 1989-90.	21
TABLE 12: Mainstem Component (Station CB5.3) Split Sample Results using Cruise Means (1987 - 1989).	30
TABLE 13: Potomac Component (Station PMS-10) Split Sample Results using Cruise Means (1989 - 1990).	36

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 estimating measurement system variability and identifying any parameters that have low inter-organization agreement.

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.

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 supervises the water quality monitoring program.

The CSSP has four components, each including three to five laboratories that analyze samples from similar salinity regimes and concentration ranges (Fig. 1). Laboratories in each component analyze triplicate field split samples collected quarterly, following the specified analysis flow (Fig. 2). Laboratory personnel send the analytical results to the EPA Chesapeake Bay Liaison Office (CBLO) in Annapolis for data entry and analysis by Computer Sciences Corporation (CSC/CBLO) staff.

This report summarizes the results of three of the four CSSP components for 1989. These components are 1) the Mainstem and Tidal Tributaries component, which analyzes estuarine samples from the mainstem of the Chesapeake Bay; 2) the Tidal Potomac component, which samples the tidal fresh portion of the river; and, 3) the Fall Line component, which samples the Susquehanna River fall line station. The Virginia Mainstem and Tidal Tributaries component, which samples the tidal fresh portion of the James River, did not operate between January 1989 and February 1990, so it is not included in this report.

This report includes split sample data from September 1987 through March 1990. Early 1990 data were included when there were not enough data through 1989 for statistical analysis.

Figure 1. Chesapeake Bay Coordinated Split Sample Program Components

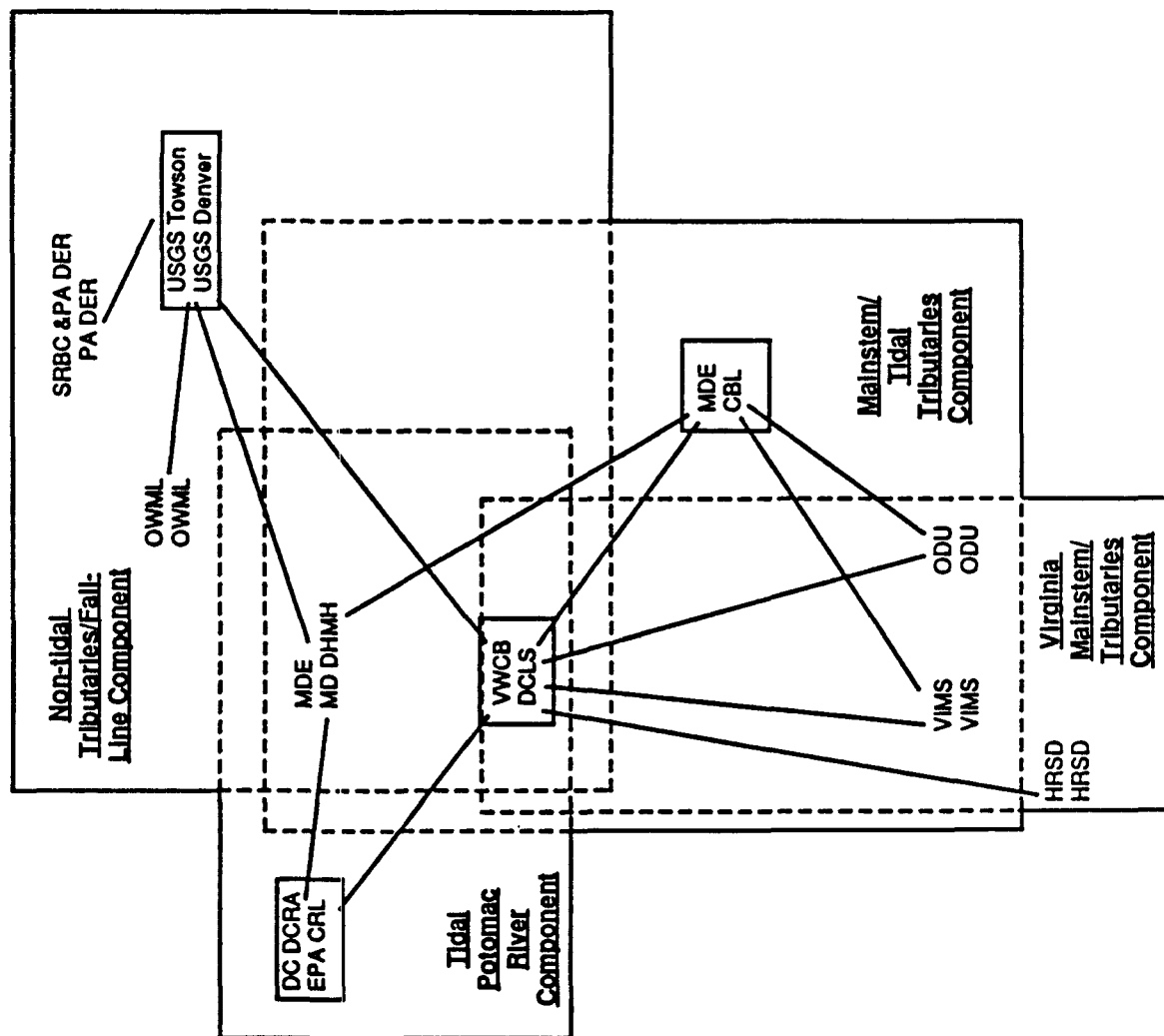
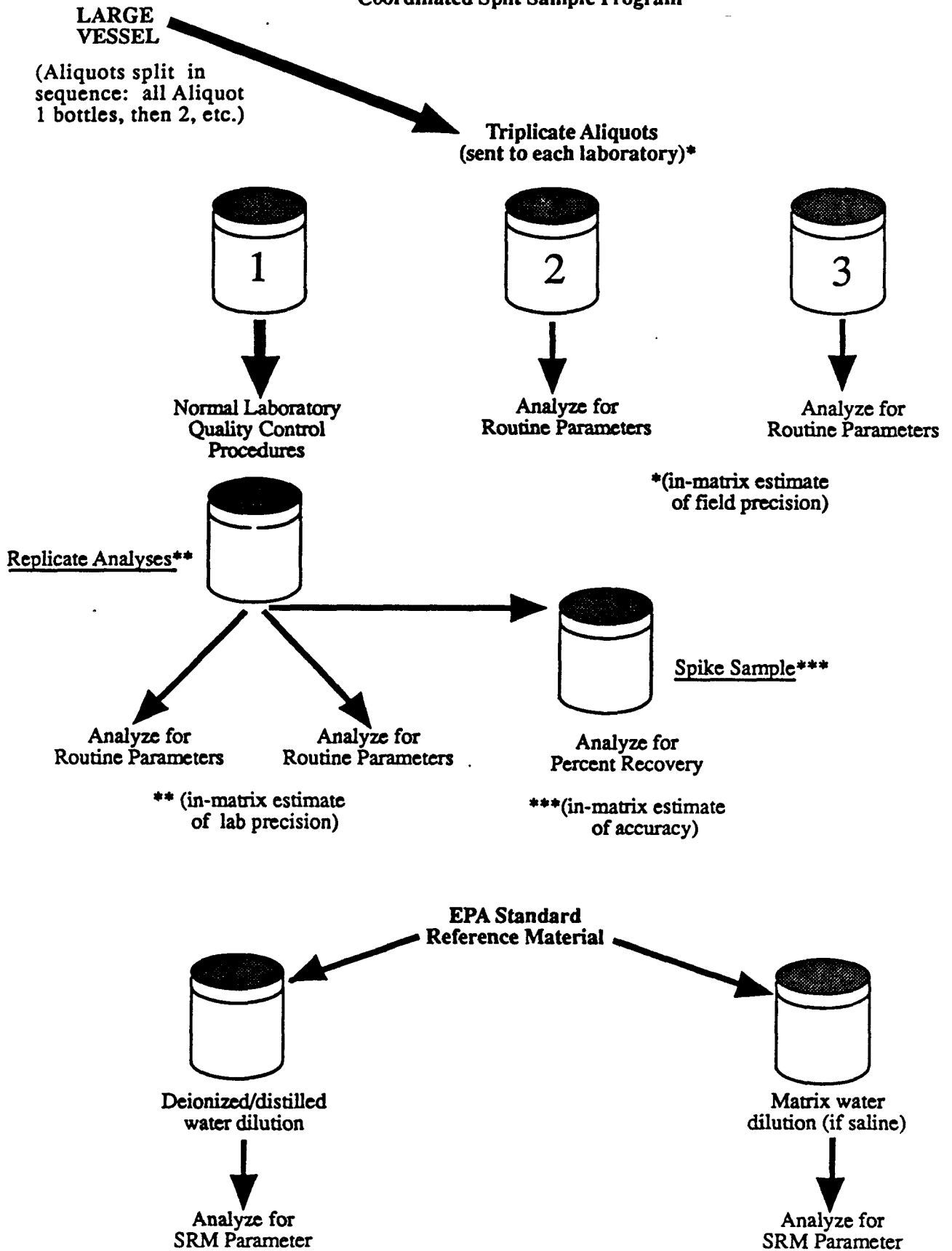


Figure 2. Schematic of the Operational Flow of Analyses,
Coordinated Split Sample Program



II. METHODS

A. COMPONENTS AND PARTICIPATING LABORATORIES

1. Mainstem and Tidal Tributaries component

This component includes the three Chesapeake Bay mainstem analysis laboratories: Chesapeake Biological Laboratory (CBL) in Solomons, MD, Virginia Institute of Marine Science (VIMS) in Gloucester Point, VA, and Old Dominion University (ODU) in Norfolk. It also includes one tributary laboratory, Maryland Department of Health and Mental Hygiene (MDHMH) in Baltimore. Starting in June, 1990, the Virginia tributary laboratory, Division of Consolidated Laboratory Services (DCLS) in Richmond, was added to this component. Split sample results from this component were included in two previous reports (Bergstrom 1989, 1990a).

2. Tidal Potomac component

This component includes three analytical laboratories: MDHMH, DCLS, and the EPA Central Regional Laboratory (CRL) in Annapolis. Analyses at CRL are conducted by District of Columbia Department of Consumer and Regulatory Affairs (DCRA) personnel (referred to as CRL/DCRA). Split sample results from this component were included in two previous reports (Bergstrom 1989, 1990b).

3. Fall Line component

The Fall Line component includes five analytical laboratories: MDHMH, DCLS, 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. DCLS does not currently participate in this component of the CSSP, but they may do so in the future. Split sample results from this component were included in one previous CSSP report (Bergstrom 1990c).

All of these laboratories also participate in two-way split sample programs with USGS. Data from these programs were not included here because the goals and methods of the USGS program are different from those of the CSSP, and many of the two-way split results have been analyzed by others (e.g., Kenney 1990) or will be analyzed in the future.

B. SAMPLE COLLECTION AND SPLITTING METHODS

1. Mainstem and Tidal Tributaries 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 line. The field crew followed the splitting procedures in the CSSP Implementation Guidelines (CBP 1989). The MDE field crew processed and distributed samples to the two Maryland laboratories (CBL and MDHMH), while a VIMS field crew processed and distributed samples to the two Virginia laboratories (VIMS and ODU).

Starting in June 1989, each laboratory analyzed a minimum of four samples per cruise: three aliquots split in the field and a laboratory replicate for one of the aliquots. One exception was CBL, which received four bottles from the field crew. Their "laboratory" replicate was split from Aliquot 1 in the field until March 1990. Some laboratories did more than one laboratory replicate: ODU analyzed all three aliquots in triplicate—nine samples per cruise. Because CSC/CBLO staff received these additional replicate data after data entry was almost complete, they were only included for Cruise 111.

2. Tidal 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 1989) starting in May 1989. The field crew left whole water samples in ice-filled coolers at the designated dock. Personnel from each laboratory retrieved the coolers. The field crew did not filter any samples. MDHMH did laboratory filtration for Total Suspended Solids (TSS) only. In the laboratory, DCLS and CRL/DCRA personnel also filtered samples for Ammonium (NH_4), Nitrite (NO_2), Nitrite + Nitrate ($\text{NO}_2 + \text{NO}_3$), Orthophosphate (PO_4F), Total Dissolved Phosphorus (TDP), Dissolved Organic Carbon (DOC), and Silica (SI). CRL/DCRA and DCLS both used pre-rinsed Gelman cellulose membrane filters with 0.45 micron pore size. 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 May 1989, each laboratory analyzed a minimum of four samples per cruise: three aliquots (field replicates) split in the field and a laboratory replicate for one of the aliquots.

3. Fall Line component

A field crew from USGS-Towson sampled the Susquehanna River fall line station and distributed samples to each laboratory (except DCLS, which did not participate). The field crew used USGS sampling procedures, including flow-weighted cross-sectionally integrated samples. Splitting was done with a churn splitter. Field filtration was done with a 0.45 micron membrane filter and the nutrient samples shipped to USGS and OWML were preserved with mercuric chloride according to USGS standard protocol. All samples were immediately placed and kept on ice. Samples for MDHMH and PADER were delivered to the laboratory the day of collection. Samples for USGS and OWML were sent via priority mail in ice-filled coolers. USGS samples usually arrived in two days. The samples sent to OWML arrived five days later with no ice around them, so their analytical results were not reported.

The Fall Line component generally followed CSSP guidelines (CBP 1989), except each laboratory received less than three aliquots (field replicates) split in the field. The field crew could not split a sufficiently large volume of water accurately to provide three aliquots. Each laboratory received two aliquots in October 1989 and one aliquot in March 1990. Only MDHMH reported a laboratory replicate for one of the aliquots.

C. DATA ENTRY AND REDUCTION

1. Mainstem and Tidal Tributaries component

Laboratory or program personnel submitted raw data on handwritten CSSP Data Submission forms, except VIMS personnel submitted their data on diskette starting in June, 1989. CSC/CBLO staff transcribed and entered the handwritten data, and data originators verified the printouts. Field and laboratory precision and means over the three aliquots were calculated with SAS programs (SAS Institute 1985).

2. Tidal Potomac component

Laboratory or program personnel submitted raw data on handwritten CSSP Data Submission forms. CSC/CBLO staff transcribed and entered the handwritten data. Data submitters verified the printouts through March 1990. Field and laboratory precision and means for the three aliquots were calculated with the SAS procedure MEANS (SAS Institute 1985).

3. Fall Line component

USGS-Towson personnel submitted the Upper Bay data on diskette for October 1989 data and in hard copy for March 1990 data. CSC/CBLO staff transcribed and entered the handwritten data, transferred the diskette data. Data submitters verified printouts of the data. Field precision was calculated with the SAS procedure MEANS (SAS Institute 1985).

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 correctly, the results for one of the aliquots should not be consistently higher or lower than the results for the other aliquots. Since the aliquots are split sequentially, non-random splitting would probably result in higher results for solids and particulates in Aliquot 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 aliquots for each parameter and sampling date. None of the parameters had statistically significant results ($P \geq 0.03$), showing that splitting was done randomly.

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 means 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 means, including all the laboratories or only the mainstem laboratories (see above).

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 author is currently analyzing fall line split sample data to produce precision estimates to use in calibrating the Chesapeake Bay River Input computer model. Preliminary results of this analysis can be sent upon request.

The Method Detection Limit (MDL) was also used to estimate within-organization precision, especially in the graphs of the data (see below). 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

Graphs of the split sample results show which differences were larger than the within-organization precision. Based on a discussion with the Analytical Methods and Quality Assurance Workgroup (AMQAW) on 4/24/90, within-organization precision for CSSP analyses is estimated by the larger of: 1) the Method Detection Limit (MDL, Tables 1-3); or, 2) the standard deviation of the three aliquots for each sample which estimates field precision. Graphs of the cruise means for each laboratory show this estimate as "precision bars." Any laboratory means with non-overlapping

precision bars have differences that are larger than within-organization precision.

Statistical significance was assumed when the significance level (P) ≤ 0.01 , rather than when $P \leq 0.05$ as in the previous report (Bergstrom 1989). 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).

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. The decision is based on graphs with precision bars and the results of statistical tests. Investigation was recommended if:

- 1) three or more sampling dates had inter-organization differences that were larger than within-organization precision; and,
- 2) an appropriate statistical test had a probability (P) ≤ 0.01 that the differences were due to chance alone, equivalent to 99% confidence that the observed difference was real.

The graphs show the magnitude of differences, while the statistical test is more sensitive to consistency of the differences over time. Based on results from the Mainstem component of the CSSP (see below), parameters identified by the combination of these two criteria usually have different field and/or laboratory methods at one of the laboratories involved.

A non-parametric statistical test was used to analyze the split sample data. This test assumes matched (positively correlated) samples, since this is inherent in the split sample design. Comparisons were done with the Friedman two-way, non-parametric, repeated measures analysis of variance (ANOVA), which requires a minimum of 4 complete samples to achieve $P = 0.01$ (Siegel 1956). The $P \leq 0.01$ standard is currently unattainable for most of the parameters in the Potomac component due to small sample sizes. The test was done with the Macintosh software package StatView 512+ (BrainPower, Inc. 1986) using exact P values from Siegel (1956) when sample sizes were small. Below detection limit data were included if they only affected results from one laboratory, but no comparison was made if two or more laboratories had below detection limit data, because this made the rankings of the data ambiguous.

The analyses for the Mainstem component were done on two groups of laboratories, because the four laboratories included in this component differed in analytical methods. The three mainstem laboratories use different analytical methods than the tributary laboratories. Mainstem laboratories measure the dissolved and particulate fractions of nitrogen, carbon, and phosphorus and calculate the total fractions, while tributary laboratories measure the total and dissolved fractions and calculate the particulate fractions (D'Elia et al. 1987). Data analyses and graphs were done for all four laboratories and also for the three mainstem laboratories, because of this difference in analytical methods.

Particulate Carbon (PC) comparisons excluded MDHMH results because their method only measures organic carbon.

Split sample results can also be analyzed by comparing the magnitude of inter-organization CV to the mean within-organization CV of the different organizations. This approach was used with Chesapeake Bay fall line split sample data by Kenney (1990), adapted from a procedure for performance testing given by Taylor (1987). It was not used in this report for three reasons: Taylor's approach does not provide decision rules for identifying parameters which should receive further investigation; CV comparisons could be biased by the dependence of CV on mean concentration, or by a few high CV values; and, this comparison method does not take the consistency of inter-organization differences into account. The evaluation of the consistency of inter-organization differences in this report is designed to facilitate actions by the organizations involved to increase inter-organization agreement.

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 1-3; and the precision of field replicates, the three aliquots split in the field and analyzed by the same laboratory. The Methods section describes how the precision estimates were calculated. Percent recovery data and results from Standard Reference Materials (SRMs) estimated within-organization accuracy.

1. Mainstem and Tidal Tributaries component

Table 4 gives the mean SD and CV of field replicates under "Mean within-organization precision." 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 1% to 45%. In a few cases, the means were inflated by a single high result, and sample sizes varied slightly among organizations.

Percent recovery data (Table 7), although limited, show that most values were near 100%. Results from SRMs (Table 10) from VIMS and ODU also had percent recovery values (SRM results/expected x 100) near 100%. All but three were between 90 and 110%.

2. Tidal Potomac component

Table 5 gives the mean SD and CV of field replicates under "Mean within-organization precision." All CV values were at or below 20%, except for TSS data from MDHMH. Percent recovery data (Table 8) and results from Standard Reference Materials (SRMs, Table 11) estimated within-organization accuracy. Percent recovery data are limited since DCLS did not submit them, but most values were close to 100%. Results from SRMs from CRL/DCRA

TABLE 1: Method Detection Limits at Mainstem Component Laboratories, 1989-1990.

Parameter ¹	Method detection limits (mg/l)				
	CBL ²	DCLS ²	MDHMH ³	ODU ²	VIMS ²
NH4	0.003	0.04	0.008	0.0056	0.01
NO2	0.0002	0.01	0.002	0.001	0.0015
NO23	0.0002	0.04	0.02	0.0025	0.0021
TDN	0.002	-	-	0.05	0.040
PN (PON)	0.0105	-	-	0.05	0.029
PO4F	0.0006	0.01	0.004	0.005	0.0005
TDP	0.001	0.01	0.01	0.005	0.005
PHOSP	0.0012	-	-	0.007	0.003
TP	-	0.01	0.01	-	-
DOC	0.24	1.0	0.5 (0.8, 5/89- 3/90)	0.5	1.0
PC	0.063	-	-	0.24	0.104
TSS	1.5	1	1	2	5
SI	0.01	0.1	0.1	0.023	0.007

- ¹ NH4 = ammonium, NO2 = Nitrite, NO23 = Nitrite + Nitrate, TDN = Total Dissolved Nitrogen, PN = Particulate Nitrogen, PO4F = Orthophosphate filtered, TDP = Total Dissolved Phosphorus, DOC = Dissolved Organic Carbon, PC = Particulate Carbon, TSS = Total Suspended Solids, SI = Silica (as SI).
- ² Calculated from: 3 x standard deviation of 7 replicates of the lowest concentration sample encountered. Limits verified by CBL and ODU.
- ³ Calculated as 2% of full scale, except carbon limits from Method MDL in 40 CFR Pt 113 App. B (7-1-87 Ed.).

TABLE 2: Method Detection Limits at Potomac Component Laboratories, 1989-1990.

Parameter	Method detection limits (mg/l)		
	CRL/DCRA	DCLS	MDHMH
NH4	0.04	0.04	0.008
NO2	0.01	0.01	0.002
NO23	0.04	0.04	0.02
TKNW	0.2	0.1	0.1
PO4	0.007	0.01	0.004
TDP	0.01	0.1 (0.01) ¹	0.01
TP	0.01	0.1 (0.01) ¹	0.01
DOC	1.0	1.0	0.5 (0.8 from 5/89-3/90)
TOC	1.0	1.0	0.5 (0.8 from 5/89-3/90)
TSS	4	1	1
SI	0.2	0.1	0.1
BOD5	1	1	0.5

¹ Their low-level phosphorus system achieves 0.01 mg/l, but this system was not requested by VSWCB, so the high-level system (0.1 mg/l) was used for PMS-10 split sample data.

TABLE 3: Method Detection Limits at Fall Line Component Laboratories, 1989-1990.

Parameter ¹	Method detection limits (mg/l)				
	PADER	DCLS	MDHMH ²	USGS	OWML
NH4	0.02	0.04	0.008	0.01	0.01
NO2	0.004	0.01	0.002	0.001	0.01
NO23	0.04	0.04	0.02	0.10	0.01
TKNW/TKNF	0.2	0.1	0.1	0.20	0.10
PO4F	0.005	0.01	0.004	0.001	0.01
TDP	0.02	0.1	0.01	0.001	-
TP	0.02	0.1	0.01	0.01	0.01
DOC	-	1.0	0.5 (0.8, 5/89- 3/90	-	-
TOC	1.0	1.0	0.5 (0.8, 5/89- 3/90	0.1	-
TSS	1	1	1	1	1
SI	-	0.1	0.1	0.1	0.04
BOD5	-	1	0.5	-	1

- ¹ NH4 = ammonium, NO2 = Nitrite, NO23 = Nitrite + Nitrate, TKNF = Total Kjeldahl Nitrogen Filtered, TKNW = Total Kjeldahl Nitrogen Whole, PO4F = Orthophosphate filtered, TDP = Total Dissolved Phosphorus, TP = Total Phosphorus, TOC = Total Organic Carbon, TSS = Total Suspended Solids, SI = Silica (as SI).
- ² Calculated as 2% of full scale, except carbon limits from Method MDL in 40 CFR Pt 113 App. B (7-1-87 Ed.).

TABLE 4. Within-organization and inter-organization precision estimates, Mainstem Component.

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
NH4	0.010	45.0 ¹	8	0.0071	18.1	8	0.0011	10.6	8	0.0048	30.4 ¹	8	0.014	58.7	0.0069	43.6
NO2	0.0003	19.4	6	0.0001	2.6	6	-	-	-	0.0004	7.6	6	-	-	0.0016	33.2
NO23	0.0036	2.8	3	0.0019	2.2	3	0.0013	1.1	3	0.0051	5.6	3	0.0111	11.1	0.0077	8.4
TDN	0.0450	11.0	7	0.0442	9.5	7	0.0545	15.0	6	0.0258	5.9	7	0.042	10.6	0.042	10.8
PN	0.0032	2.0	7	0.0310	43.2	7	0.0099	12.2	6	0.0115	10.6	7	0.033	29.3	0.028	25.9
TN	0.051	9.4	8	0.165	15.9	8	0.062	13.1	6	0.030	5.7	8	0.098	17.3	0.041	8.2
PO4P	0.0011	28.7	8	-	-	-	-	-	-	-	-	-	-	-	-	-
TDP	0.0015	27.4	8	0.0110	19.0	8	0.0021	13.3	8	0.0019	16.5	8	0.021	106.2	0.0059	51.6
PHOSP	0.004	3.1	7	0.0214	35.4	7	0.0061	22.4	5	0.0010	9.1	7	0.013	67.1	0.0038	23.1
TP	0.0028	12.0	8	0.0281	21.7	8	0.0058	14.3	6	0.0026	10.8	8	0.026	66.2	0.0084	32.6
DOC	0.223	7.6	4	0.045	2.0	4	0.348	9.2	4	-	-	-	-	-	1.28	50.2
PC	0.059	13.8	8	-	-	-	0.045	7.1	6	0.060	10.2	7	-	-	0.14	18.3
TSS	0.739	13.0	4	3.11	29.9	4	4.24	24.1	3	2.12	14.4	4	6.72	52.0	6.80	46.3
SI	0.007	6.2	8	0.043	6.2	8	0.040	20.7	6	0.035	14.5	8	0.079	38.5	0.067	37.1

Notes: Below detection limit data were excluded for NO2, NO23, and PO4P. SD = standard deviation, CV = coefficient of variation (= SD/Mean*100), N = number of cruises over which mean was calculated. Within-organization precision is based on the precision of the results from field triplicate samples; inter-organization precision is based on the precision of means of the triplicate samples for each sampling date.

¹ Means were inflated by high values early in the program (June 1988): without them CBL mean CV was 30%, VIMS mean CV was 23%.

TABLE 5. Within-organization and inter-organization precision estimates, Potomac Component.

Parameter	Mean within-organization precision						Mean inter-organization precision					
	CRL/DCRA			DCLS			MDHH			Three labs		
	SD	CV	N	SD	CV	N	SD	CV	N	SD	CV	N
NH4	0.0068	10.6	3	0.012	15.7	4	0.013	17.9	4	0.0043	5.2	3
NO2	0.0033	20.2	4	0.0	0.0	4	0.00058	4.6	4	0.0033	23.3	4
NO3	0.029	2.4	4	0.0082	0.6	4	0.029	1.7	4	0.14	9.5	4
TKNW	0.043	5.7	3	0.058	12.6	4	0.067	12.5	4	0.18	30.8	3
PO4	0.00072	2.9	3	0.0014	3.9	4	0.0014	4.6	4	0.0068	21.3	3
TP	0.0032	5.0	3	-	-	-	0.0061	7.3	4	-	-	-
TOC	0.92	18.3	4	0.15	4.3	4	0.19	6.0	4	0.90	22.0	4
TSS	2.4	18.0	3	1.7	19.0	4	1.5	40.8	4	3.5	41.3	3
SI	0.017	1.2	3	0.50	19.0	4	0.036	3.3	4	0.11	14.2	3

Notes: Below detection limit data were excluded for TP from DCLS. March 1990 data were not used due to missing data from DCLS. 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 triplicate samples; inter-organization precision is based on the precision of means of the triplicate samples for each sampling date.

show good agreement with the expected results, and all but one result (the last PO4F result) were within the 95% confidence intervals for the SRMs.

3. Fall Line component

Field precision was estimated from the standard deviation of field duplicate aliquots analyzed for the October 11, 1989 Upper Bay sample (Table 6). Although based on results from a single sampling date, the results are generally similar to those from the Potomac component (Table 5). Percent recovery data (Table 9) were only reported by PADER and MDHMH; most values were close to 100%. No SRM results were reported for this component.

B. INTER-ORGANIZATION PRECISION

The tables of inter-organization precision give both the standard deviation (SD) and coefficient of variation (CV) of the mean results from split samples for each sampling date. The data user will have to decide which precision estimate is best for their application (see Methods for a definition and discussion of each estimate).

1. Mainstem and Tidal Tributaries component

Table 4 lists SD and CV estimates under "Mean inter-organization precision." Although parameters with low inter-organization precision tended to have low inter-organization agreement, this correlation was not found in all cases. Three of the five parameters with statistically significant inter-organization differences (TP, TDP, and DOC; see below) had high CV values (> 50%), while the other two parameters in that group (PC and PN) had lower CV values. Three parameters with high agreement (NH4, PHOSP, and TSS) also had mean inter-organization CV values over 50% when four organizations were included.

2. Tidal Potomac component

The mean inter-organization precision estimates for Potomac data (Table 5) varied from CV values of 5% for NH4 to 41% for TSS, and TKNW had the next highest CV value. Due to small sample sizes, more data are needed to determine if there are consistent differences among parameters in CV. The parameter that had the lowest inter-organization agreement based on graphing and ANOVA, NO23 (see below), had one of the lowest CV values.

3. Fall Line component

No estimates were possible due to limited and missing data for 1989.

TABLE 6. Within-organization precision estimates, Fall Line Component.

Parameter	Mean within-organization precision									
	MDHNR			PADER			USGS			
	SD	CV	N	SD	CV	N	SD	CV	N	
NH4	0.0056	6.4	1	0.0	0.0	1	0.0071	10.9	1	
NO2	0.0	0.0	1	-	-	-	0.0028	8.8	1	
NO3	0.071	4.3	1	0.0	0.0	1	0.0	0.0	1	
TKNW	0.11	28.2	1	0.0	0.0	1	0.14	20.2	1	
TKNP	0.035	10.9	1	0.071	20.2	1	0.0	0.0	1	
PO4P	0.0014	28.2	1	0.0	0.0	1	0.0028	35.4	1	
TDP	0.0	0.0	1	0.0	0.0	1	0.0057	40.4	1	
TP	0.014	20.2	1	0.0071	8.3	1	0.0	0.0	1	
TOC	0.22	7.9	1	0.14	4.4	1	0.071	2.2	1	
TSS	2.1	25.0	1	-	-	-	-	-	-	
SI	0.0	0.0	1	-	-	-	0.0	0.0	1	

Notes: OWML and DCIS are not included due to missing data. Inter-organization precision estimates are not included due to missing data. SD = standard deviation, CV = coefficient of variation ($= \text{SD}/\text{Mean} \times 100$), N = number of sampling dates over which mean was calculated. Within-organization precision is based on the precision of the results from field duplicate samples on 10/11/89.

TABLE 7: Percent Recovery Data, Mainstem Component, 1989.

Parameter	Laboratory	Percent Recovery		
		June 89	Sept 89	Dec 89
TDP	CBL	97	102	-
	MDHMH	-	100	102
	VIMS	100	87	87
TP	MDHMH	-	112	100
SI	CBL	-	-	-
	MDHMH	93	95	93
	VIMS	87	-	88
NO2	CBL	99	99	-
	MDHMH	92	100	-
	VIMS	96	100	103
NO23	CBL	96	105	-
	MDHMH	114	116	-
	VIMS	108	91	95
NH4	CBL	107	105	-
	MDHMH	144	102	94
	VIMS	96	101	101
PHOSP	CBL	100	-	-
	VIMS	100	89	-
DOC	CBL	107	-	-
	MDHMH	79	89	122
PO4F	CBL	90	-	-
	MDHMH	120	100	72
	VIMS	98	90	100
TDN	CBL	98	100	-
	VIMS	92	79	85

Note: Percent recovery data are only possible for directly measured parameters. There is no way to spike parameters done in the CHN analyzer (Particulate Carbon, PC and Particulate Nitrogen, PN). ODU did not report any percent recovery data, and CBL did not report percent recovery data after Sept. 89. 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 8: Percent Recovery Data, Potomac Component, 1989-90.

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

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 = Orthophosphate.

TABLE 9: Percent Recovery Data, Fall Line Component, 1989-90.

Parameter	Laboratory	Percent Recovery	
		10/11/89	3/28/90
NH4	PADER	-	100
	MDHMH	-	100
NO2	PADER	-	100
	MDHMH	-	96
NO23	PADER	-	100
	MDHMH	-	101
TKNW	PADER	-	106
	MDHMH	-	100
TKNF	PADER	-	128
	MDHMH	-	100
PO4F	PADER	-	102
	MDHMH	-	-
TDP	PADER	-	97.5
	MDHMH	-	100
TP	PADER	-	100
	MDHMH	-	100
DOC	MDHMH	104	94
	MDHMH	95	-
TOC	PADER	-	100
	MDHMH	92	112
	MDHMH	103	-
SI	PADER	-	-
	MDHMH	-	-

Note: Percent recovery data are not possible for TSS analysis. DCLS, USGS and OWML 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, PO4 = Orthophosphate.

TABLE 10: Standard Reference Material Results, Mainstem Component, 1989.

Parameter	Date	Laboratory	Distilled matrix		Estuarine matrix	
			Results	% Recovery	Results	% Recovery
TDP	6/89	VIMS	0.072	96.0	0.080	106.7
	9/89	VIMS	0.074	98.7	0.074	98.7
	12/89	VIMS	0.074	98.7	0.073	97.3
	12/89	ODU	-	-	0.208	95.9
NO23	6/89	VIMS	0.213	106.5	0.205	102.5
	9/89	VIMS	0.206	103.0	0.189	94.5
	12/89	VIMS	0.203	101.5	0.189	94.5
	12/89	ODU	0.0397	99.3	-	-
NH4	6/89	VIMS	0.164	82.0	0.196	98.0
	9/89	VIMS	0.183	91.5	0.201	100.5
	12/89	VIMS	0.181	90.5	0.218	109.0
	12/89	ODU	0.041	102.5	-	-
PHOSP	12/89	ODU	0.37	94.9	-	-
DOC	12/89	ODU	4.07	93.3	-	-
PO4F	6/89	VIMS	0.050	100.0	0.050	100.0
	9/89	VIMS	0.047	94.0	0.048	96.0
	12/89	VIMS	0.051	102.0	0.053	106.0
TDN	6/89	VIMS	0.253	101.2	0.266	106.2
	9/89	VIMS	0.217	86.6	0.287	114.8
	12/89	VIMS	0.323	129.2	0.231	92.2
	12/89	ODU	0.343	107.2	-	-

Note: CBL and MDHMH have not reported any SRM results. Results are given for diluted samples, diluted either with distilled/deionized or estuarine water. Confidence intervals are not given due to the dilution. ODU results for PHOSP are for a PO4F standard diluted with 1N HCl. TDP = Total Dissolved Phosphorus, NO23 = Nitrite + Nitrate, NH4 = ammonium, PHOSP = Particulate Phosphorus, DOC = Dissolved Organic Carbon, PO4F = Orthophosphate filtered, TDN = Total Dissolved Nitrogen.

TABLE 11: Standard Reference Material Results, Potomac Component, 1989-90.

Parameter	Date	Laboratory	Results (mg/l)		95% CI ¹
			Expected	Distilled	
NH4	6/89	CRL/DCRA	1.90	1.88	1.68 - 2.12
	9/89	CRL/DCRA	1.90	1.80	1.68 - 2.12
	1/90	CRL/DCRA	1.90	1.84	1.68 - 2.12
	3/90	CRL/DCRA	1.90	1.93	1.68 - 2.12
NO23	5/89	CRL/DCRA	1.43	1.32	1.28 - 1.56
	6/89	CRL/DCRA	1.43	1.32	1.28 - 1.56
	9/89	CRL/DCRA	1.43	1.38	1.28 - 1.56
	1/90	CRL/DCRA	1.43	1.35	1.28 - 1.56
	3/90	CRL/DCRA	1.43	1.29	1.28 - 1.56
TKNW	9/89	CRL/DCRA	5.00	5.70	3.88 - 6.02
	1/90	CRL/DCRA	4.78	5.05	3.70 - 5.77
	3/90	CRL/DCRA	4.78	4.90	3.70 - 5.77
PO4F	5/89	CRL/DCRA	0.35	0.327	0.33 - 0.37
	6/89	CRL/DCRA	0.35	0.331	0.33 - 0.37
	9/89	CRL/DCRA	0.35	0.326	0.33 - 0.37
	3/90	CRL/DCRA	0.35	0.401	0.33 - 0.37
TDP	1/90	CRL/DCRA	1.00	1.00	0.89 - 1.21
	3/90	CRL/DCRA	1.03	0.924	0.89 - 1.21
TP	6/89	CRL/DCRA	1.50	1.53	1.30 - 1.76
	9/89	CRL/DCRA	1.50	1.60	1.30 - 1.76
TOC	5/89	CRL/DCRA	6.1	9.2	3.50 - 9.32
	6/89	CRL/DCRA	6.1	7.3	3.50 - 9.32
	9/89	CRL/DCRA	6.1	7.1	3.50 - 9.32
	1/90	CRL/DCRA	6.1	7.5	3.50 - 9.32
	3/90	CRL/DCRA	6.1	6.9	3.50 - 9.32

¹ Provided by EPA Environmental Monitoring and Support Laboratory (EMSL) Cincinnati.

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.

C. INTER-ORGANIZATION AGREEMENT

1. Mainstem and Tidal Tributaries component

Cruise means with precision bars for each parameter are shown in Figs. 3-16. Five parameters out of 14 analyzed had three or more cruises with non-overlapping error bars: Total Dissolved Phosphorus (TDP), Total Phosphorus (TP), Particulate Nitrogen (PN), Particulate Carbon (PC), and Dissolved Organic Carbon (DOC).

Friedman ANOVA performed on cruise means assessed inter-organization agreement and determined which parameters had statistically significant inter-organization differences. The Friedman ANOVA results (Table 12) showed that the same five parameters (TDP, TP, PN, PC, and DOC) had statistically significant inter-organization differences ($P < 0.01$). The first two parameters had significantly higher results from MDHMH, while the two particulate parameters had significantly higher results from CBL. DOC results were significantly lower at MDHMH, due to a series of below detection limit values starting in June 1989 (Fig. 13) after they started using a new DOC instrument.

2. Tidal Potomac component

Cruise means with precision bars for each parameter plotted against time show inter-organization agreement (Figures 17-26). Two parameters out of 10 graphed, NO₂₃ and TP, had three or more sampling dates with non-overlapping precision bars. NO₂₃ samples (Fig. 19) were from unfiltered samples at MDHMH and filtered samples at the other two laboratories. TP results had non-overlapping precision bars between MDHMH and CRL/DCRA results on three dates (Fig. 22). The other parameters had inter-organization differences that tended to be smaller than within-organization precision. Two parameters are not shown due to missing data: TDP and DOC.

The Friedman ANOVA results (Table 13) showed that none of the nine parameters analyzed had statistically significant inter-organization differences at the $P < 0.01$ level, although this significance level was only possible when $N = 4$. NO₂₃ results were the closest to statistical significance ($P = 0.042$). Below detection limit values at DCLS prevented the analysis of TP results, and missing data ruled out analysis of BOD₅ results.

3. Fall Line component

No analyses were possible due to limited and missing data for 1989.

FIGURE 3. Split sample data for Total Dissolved Phosphorus (TDP), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

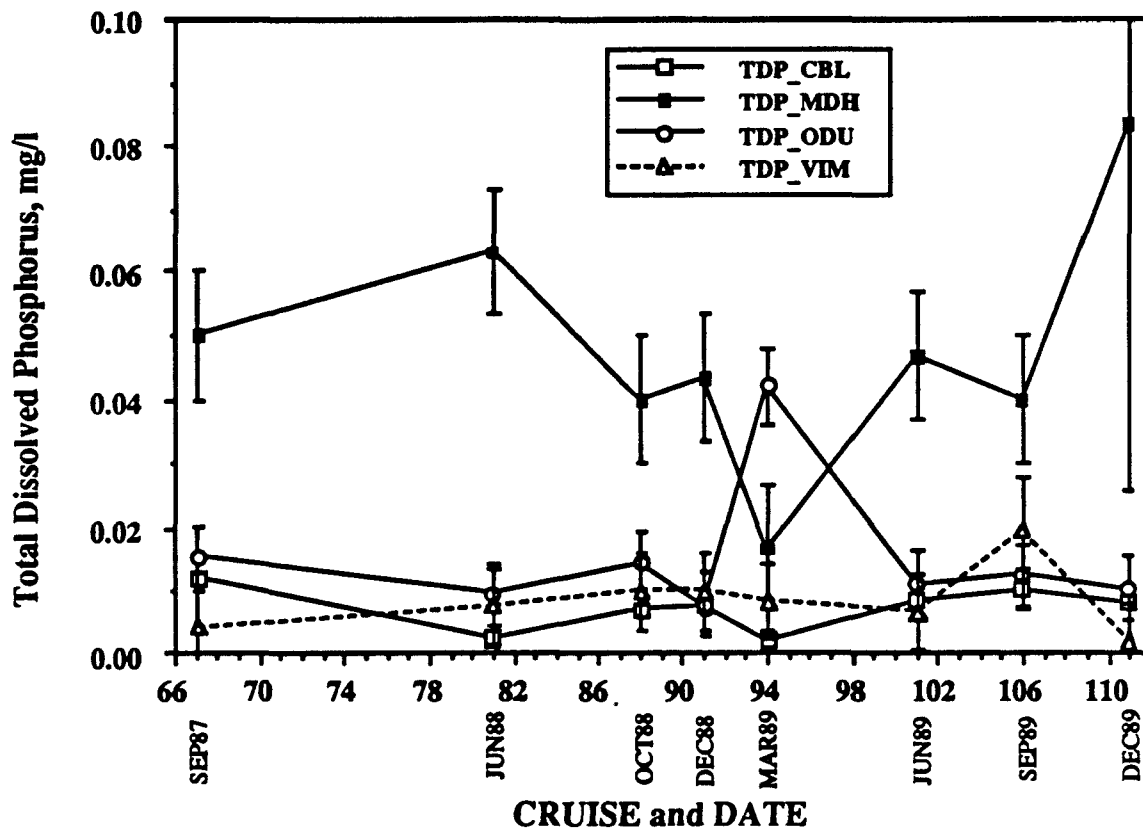


FIGURE 4. Split sample data for Total Phosphorus (TP), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

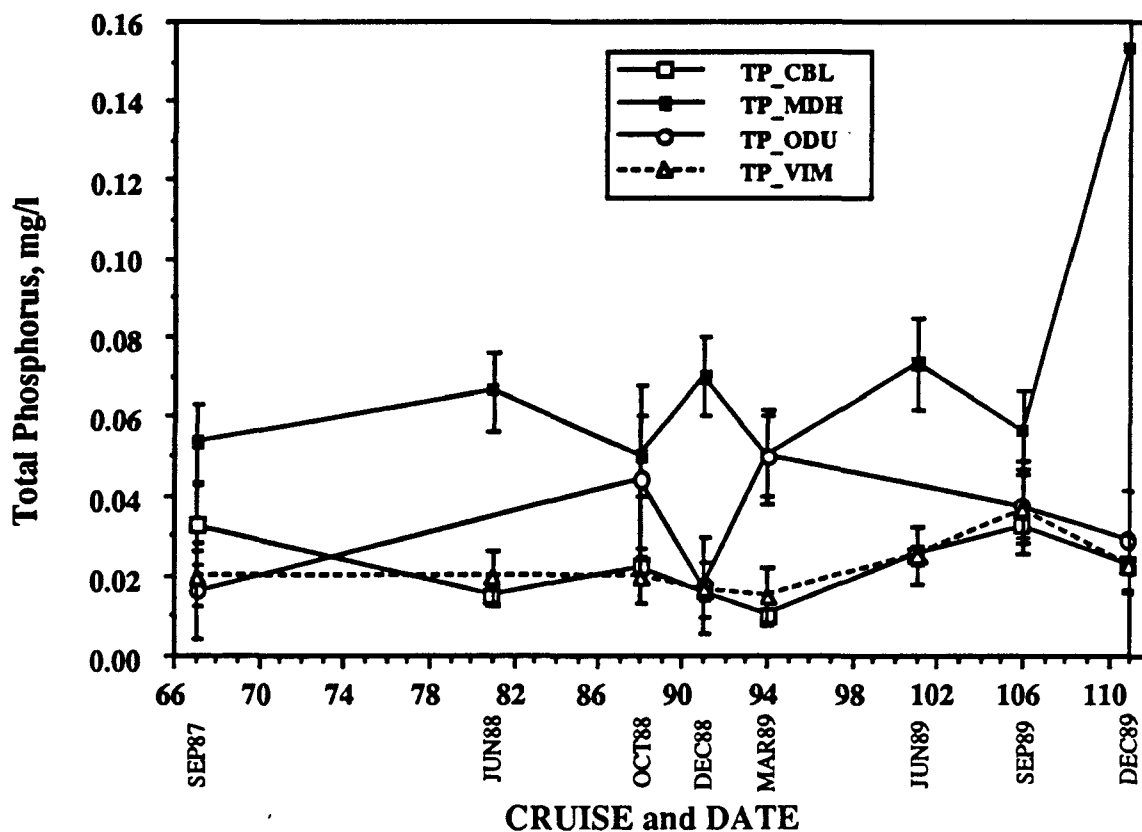


FIGURE 5. Split sample data for Particulate Nitrogen (PN), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

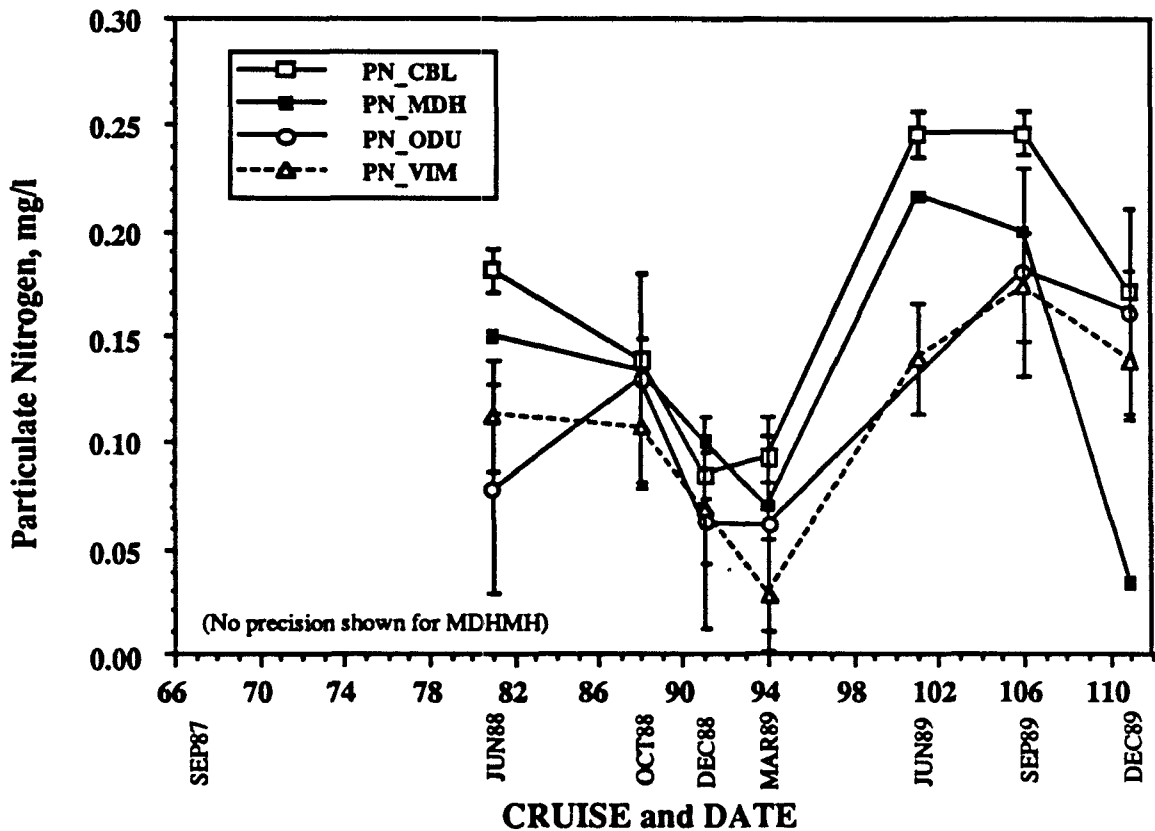


FIGURE 6. Split sample data for Particulate Carbon (PC), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

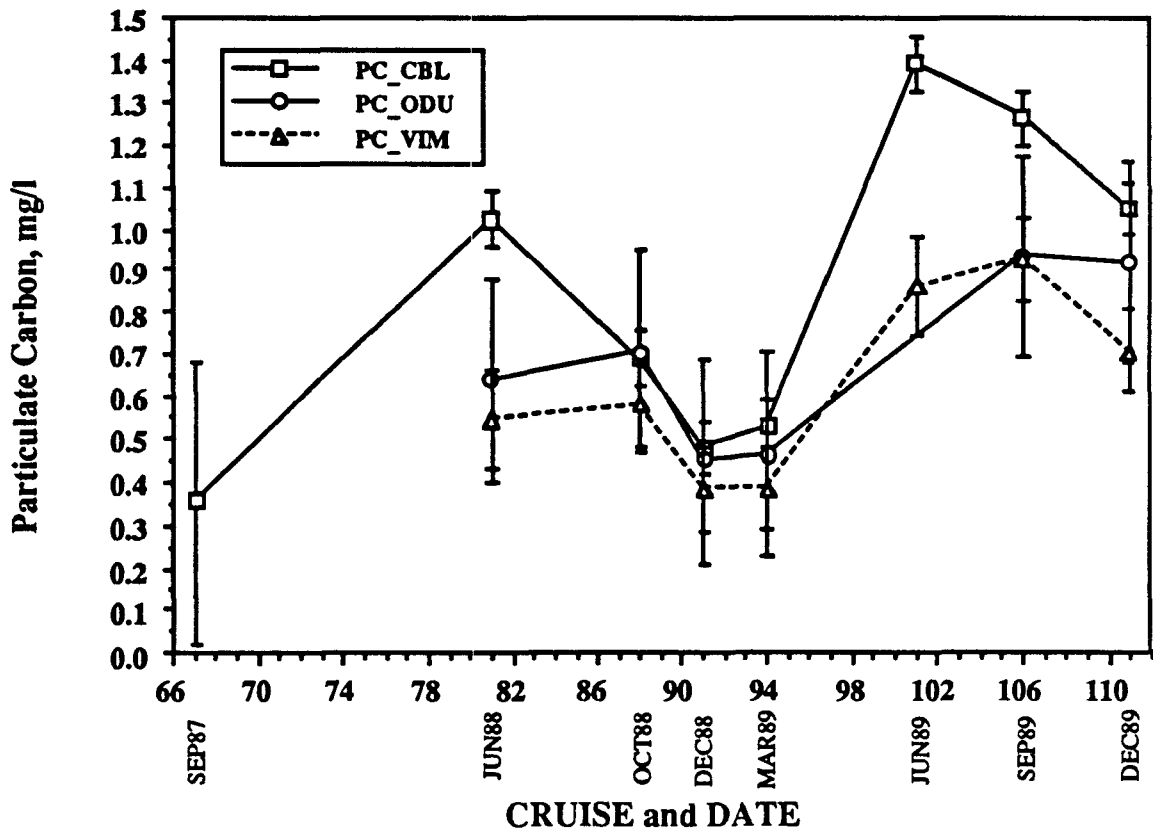


FIGURE 7. Split sample data for Silica (SI), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

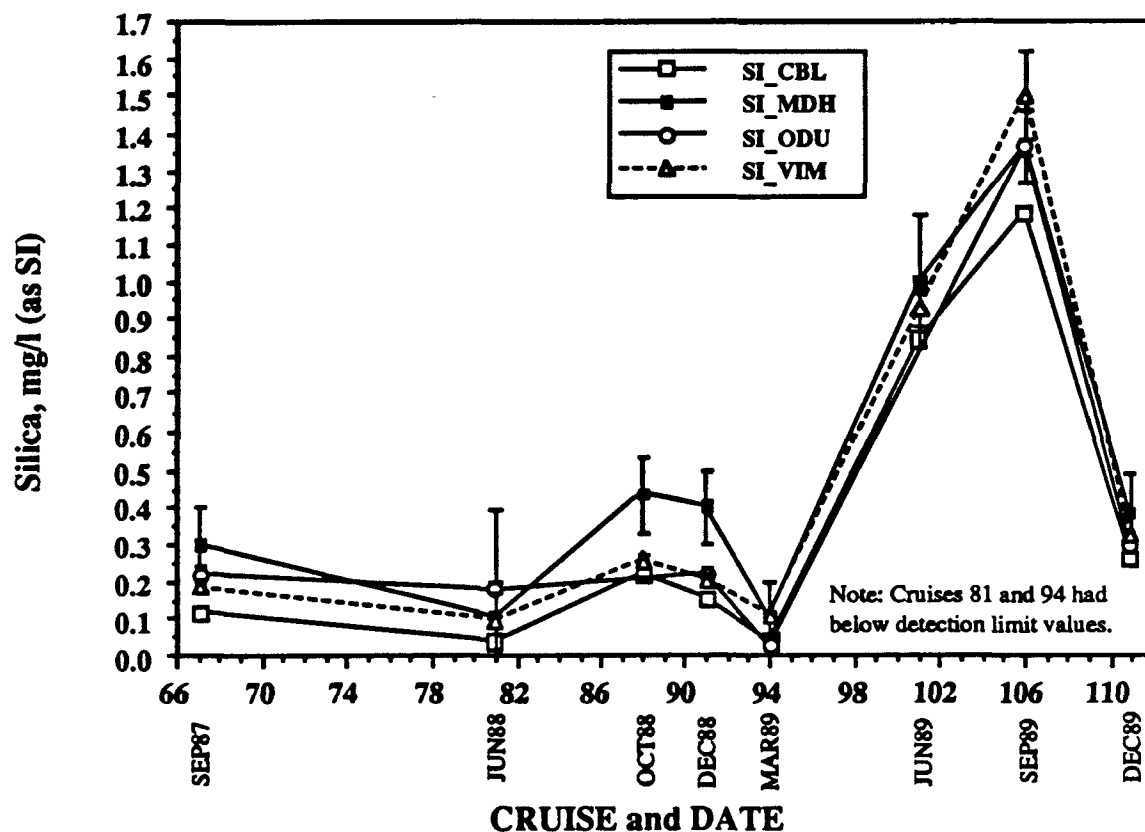


FIGURE 8. Split sample data for Nitrite (NO₂), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

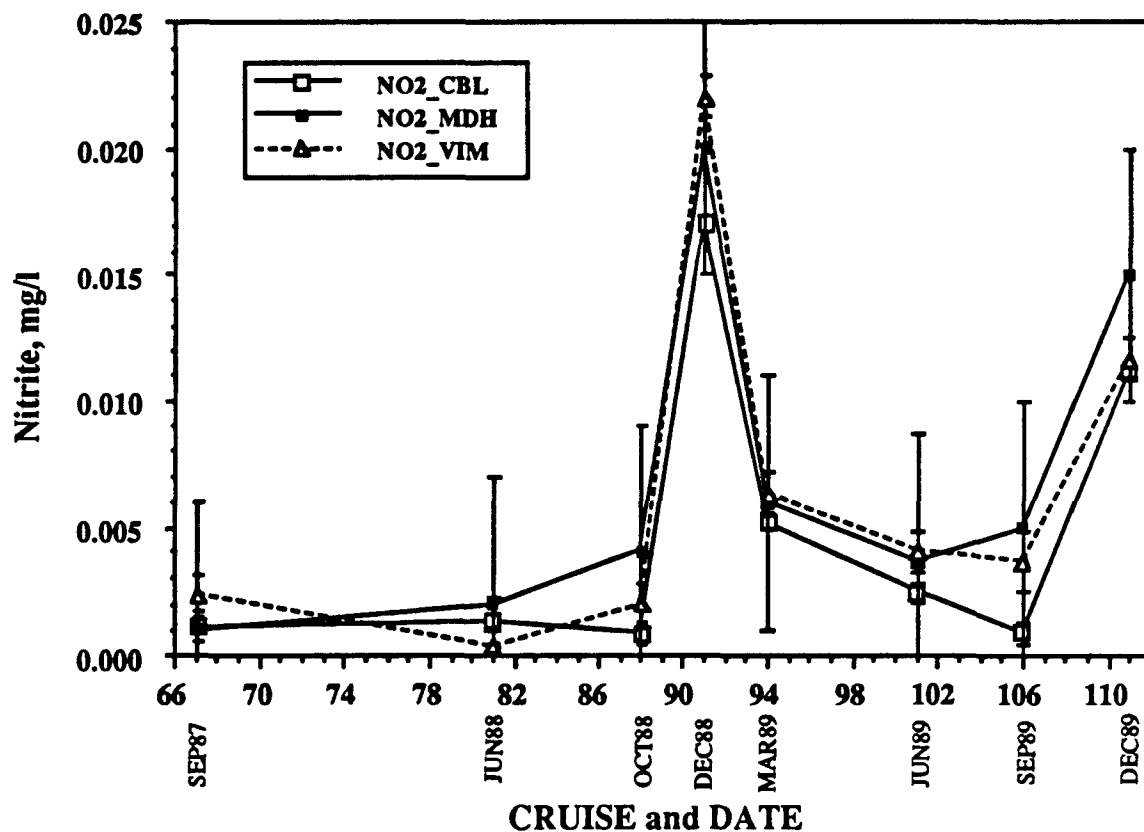


FIGURE 9. Split sample data for Nitrite + Nitrate (NO₂₃), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

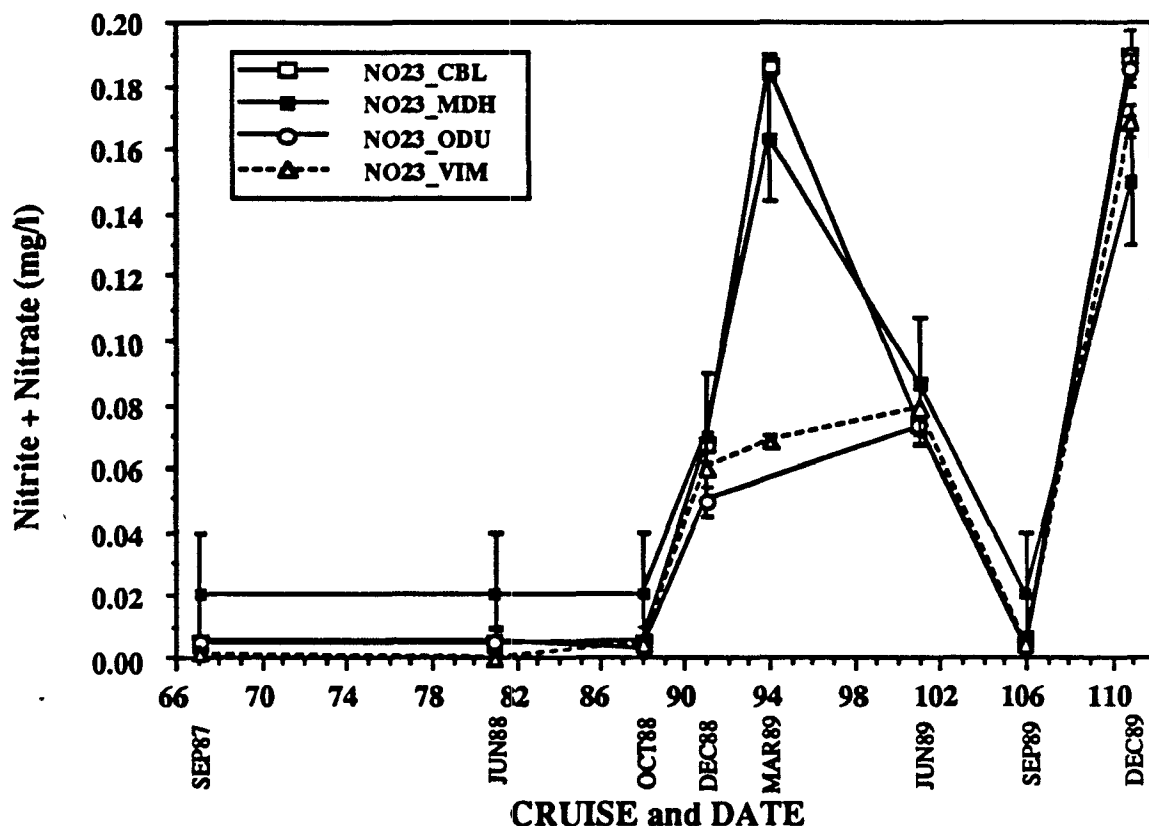


FIGURE 10. Split sample data for Ammonium (NH₄), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

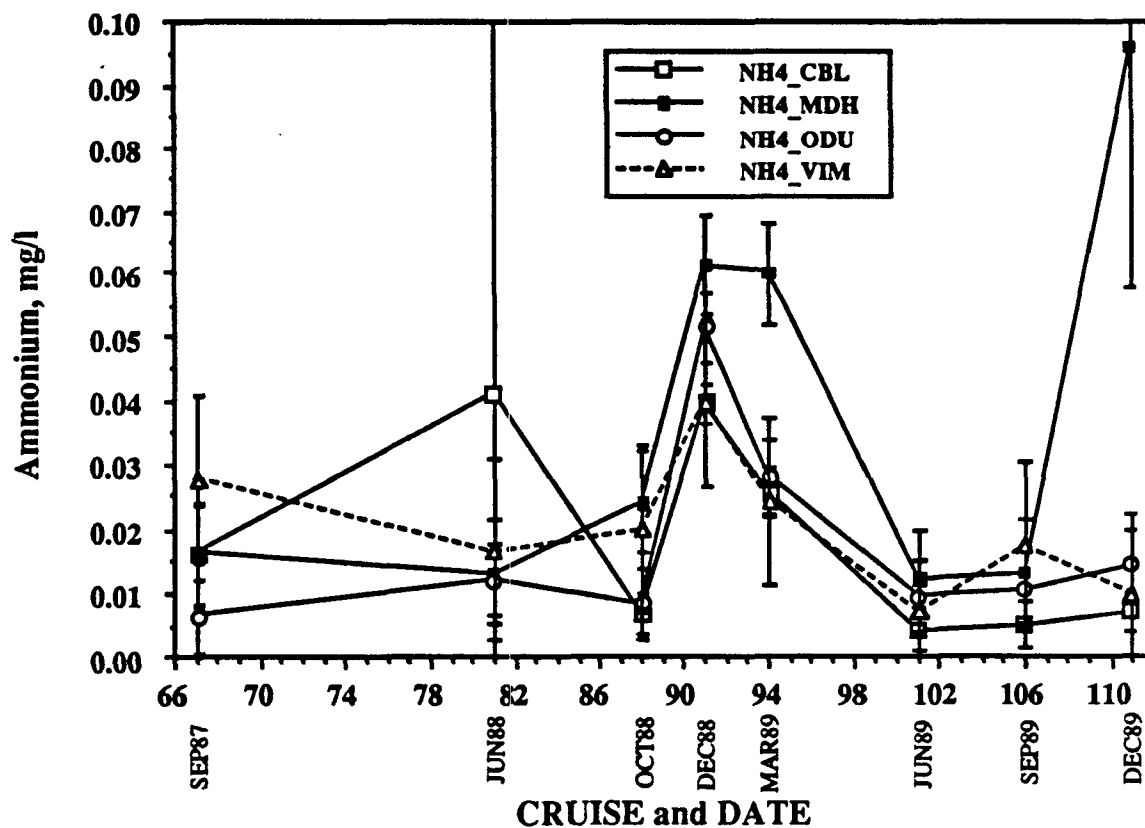


FIGURE 11. Split sample data for Particulate Phosphorus (PHOSP), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

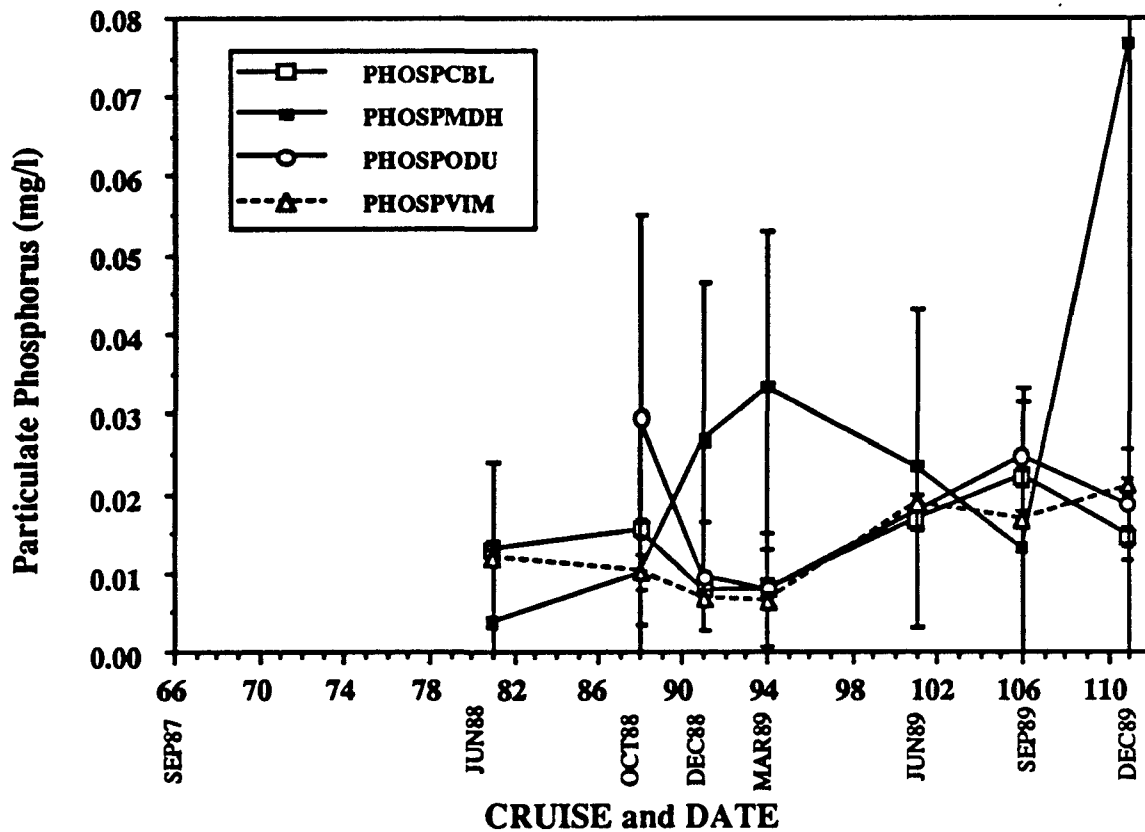


FIGURE 12. Split sample data for Orthophosphate (PO₄F), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

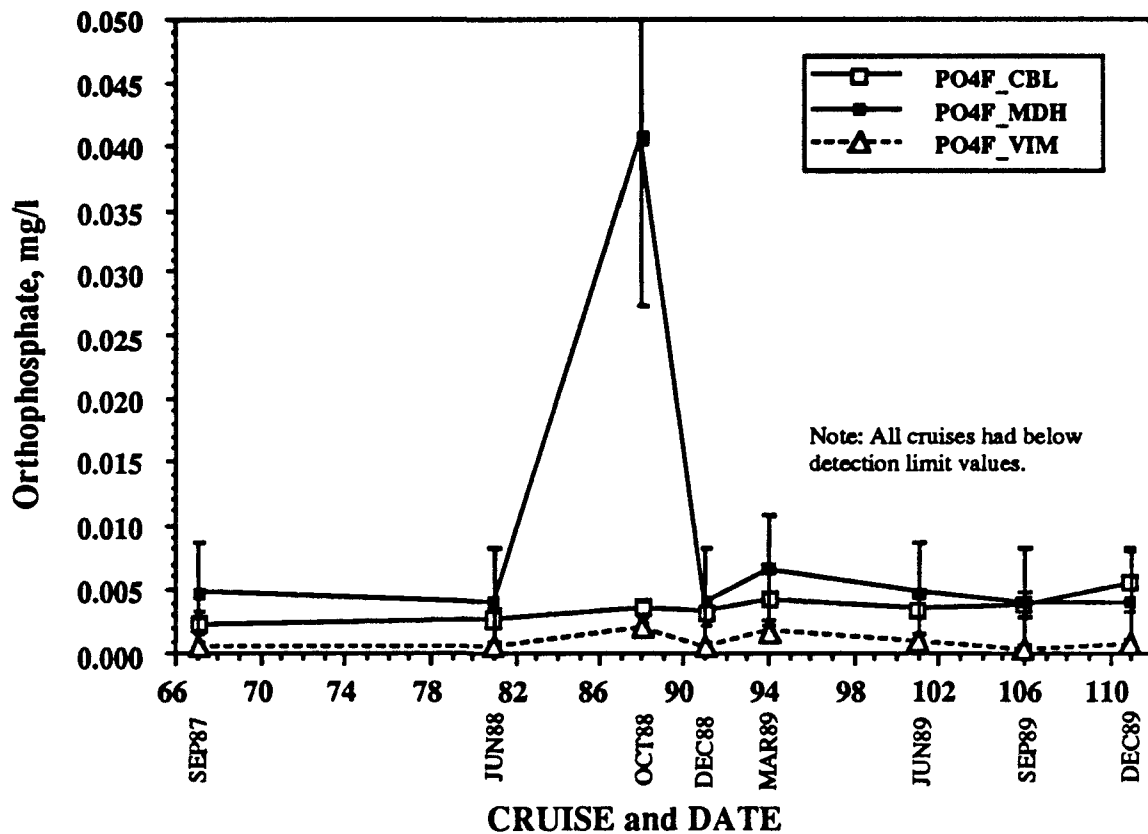


FIGURE 13. Split sample data for Dissolved Organic Carbon (DOC), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

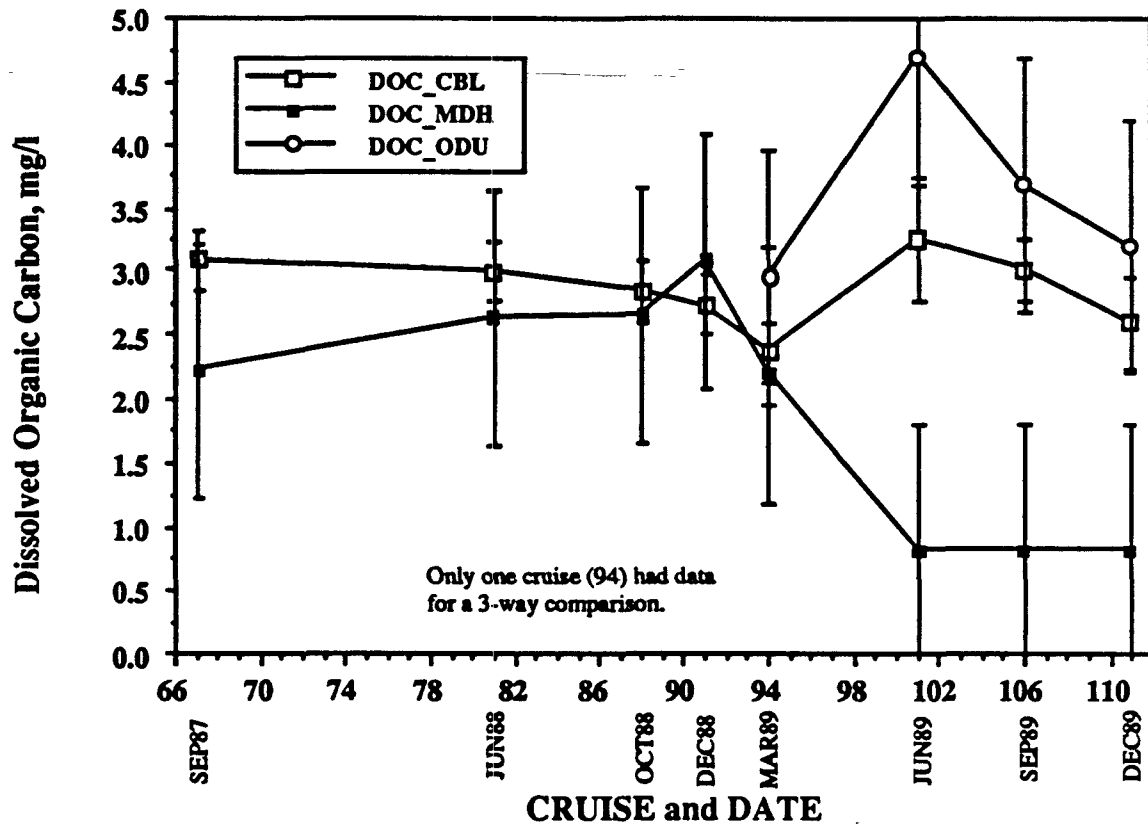


FIGURE 14. Split sample data for Total Dissolved Nitrogen (TDN), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

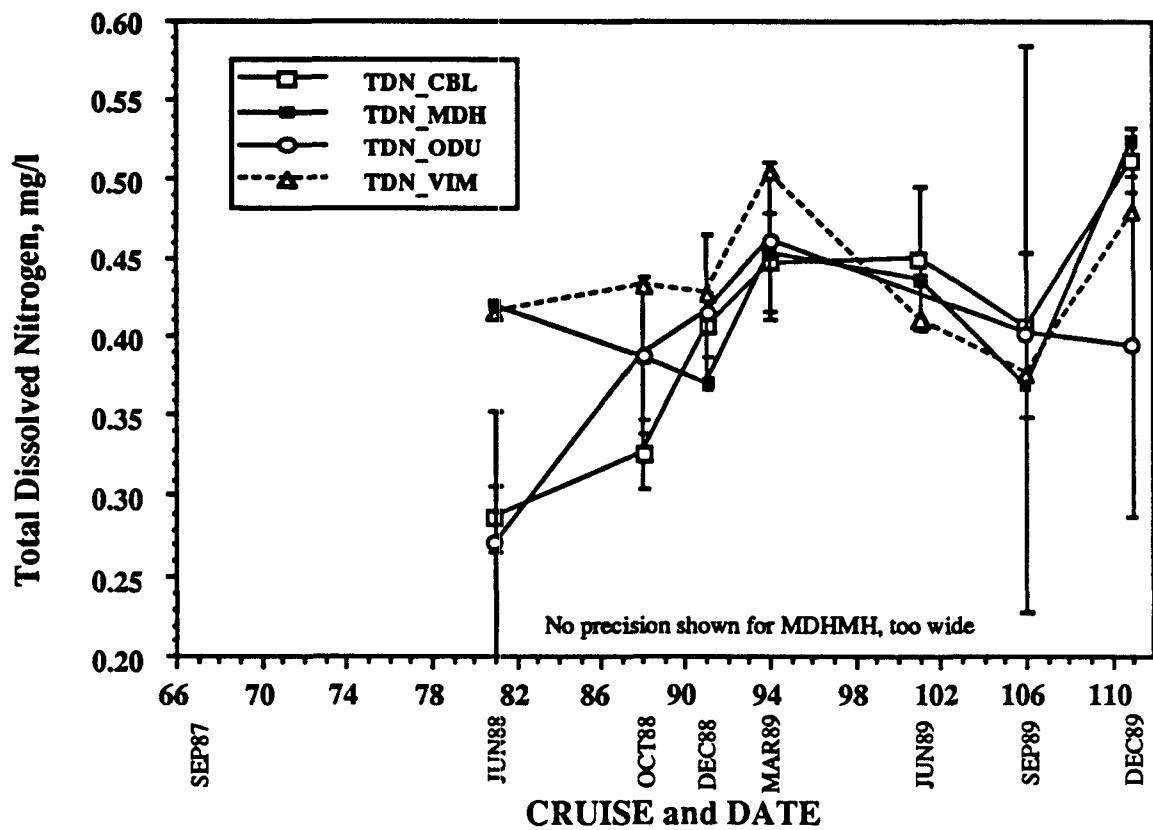


FIGURE 15. Split sample data for Total Nitrogen (TN), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

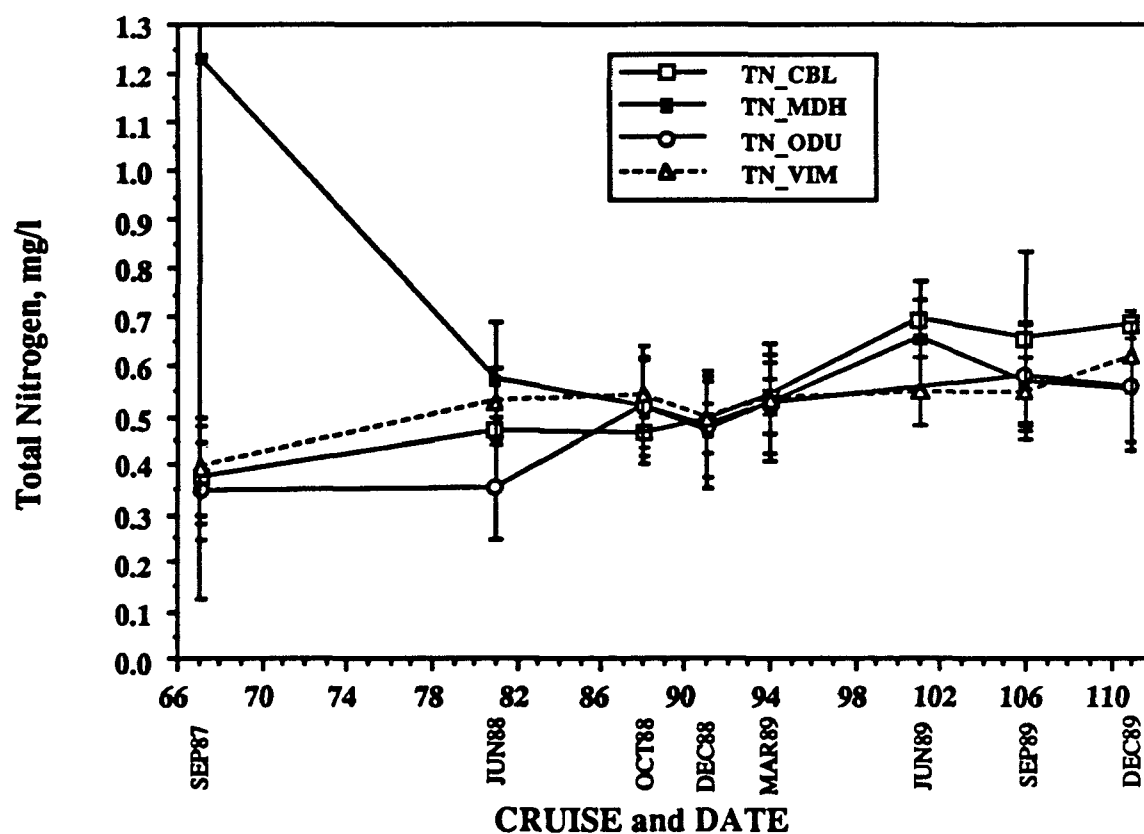


FIGURE 16. Split sample data for Total Suspended Solids (TSS), from samples collected at Station CB5.3 (Mainstem), showing cruise means with precision bars.

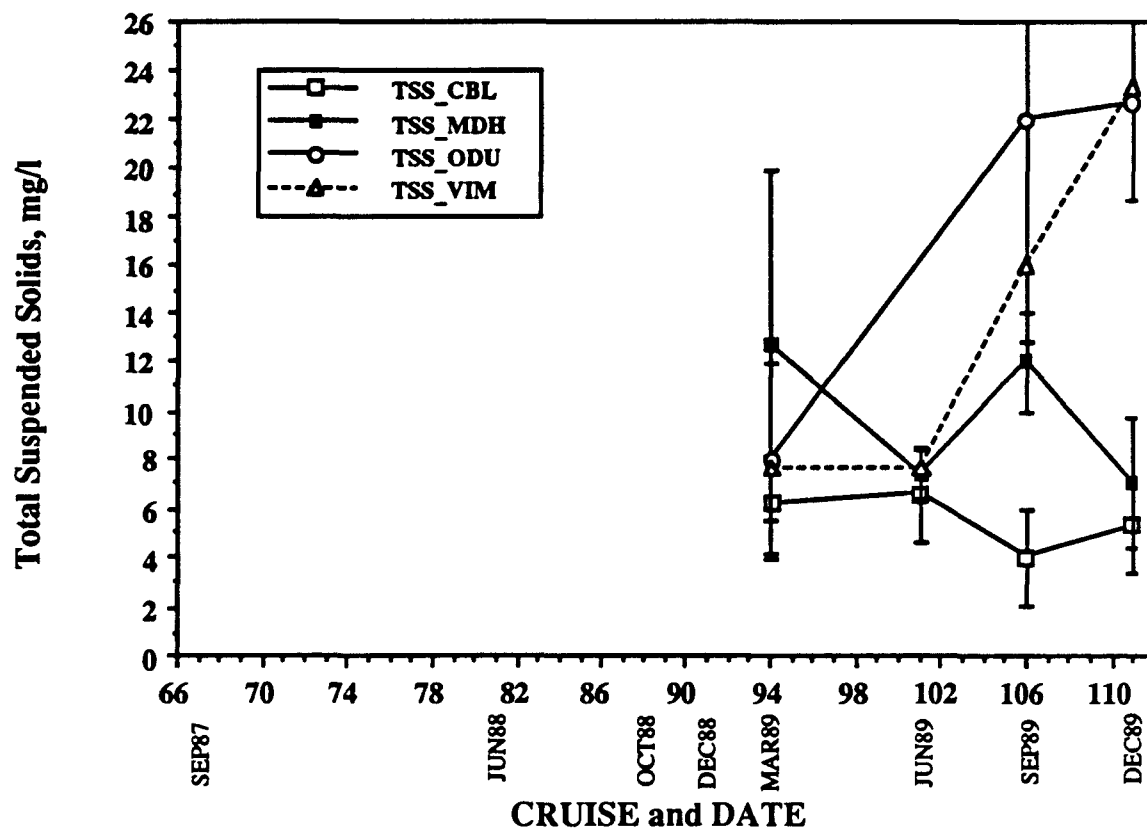


TABLE 12: Mainstem Component (Station CB5.3) Split Sample Results using Cruise Means (1987 - 1989).

Parameter	N	Laboratory Means (mg/l)				P values ¹ 4 way / 3 way
		CBL	MDHMH	ODU	VIMS	
NH4	8	0.0181	0.0370	0.0176	0.0203	0.051/0.285
NO2	6 ²	0.00756	0.0089	-	0.00828	- /0.184
NO23	3 ²	0.110	0.102	0.102	0.102	0.608/0.36
TDN	6	0.398	0.421	0.388	0.439	0.532/0.43
PN	6	0.152 A	0.114	0.112	0.105 B	<u>0.0074/0.0055</u>
TN	7	0.525	0.633	0.479	0.523	0.28 /0.085
PO4F	8 ³	0.0036	0.0091	-	0.00071	- /MDL ³
TDP	8	0.0071 A	0.048 B	0.015 B	0.0084 A	<u>0.0011/0.079</u>
PHOSP	5	0.0138	0.0320	0.0181	0.0124	0.47 /0.17
TP	6	0.0227 A	0.0722 B	0.0322	0.0218	<u>0.0055/0.142</u>
DOC	4	2.81	1.15 ⁴ A	3.63 B	-	- / <u>0.0046</u>
PC	6	0.840 A	- ⁵	0.686	0.588 B	- / <u>0.0017</u>
TSS	3	5.1	10.6	17.5	15.6	0.148/0.194
SI	6	0.297	0.442	0.382	0.404	0.016/0.052

- ¹ Underlined P values were statistically significant ($P < 0.01$, Friedman 2-way ANOVA on cruise means, using exact probabilities for 3-way comparisons. Laboratory means with different letters below them had statistically significant pairwise differences (experimentwise $P < 0.01$), otherwise they did not differ. When there were data from four labs, 3-way comparisons omitted MDHMH data.
- ² Only using data from cruises that had values above detection limits.
- ³ Too many values were below the MDL to make a comparison.
- ⁴ MDHMH data were mostly below detection due to a faulty instrument.
- ⁵ MDHMH data were excluded because they included only organic carbon.

FIGURE 17. Split sample data for Ammonium (NH₄), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.

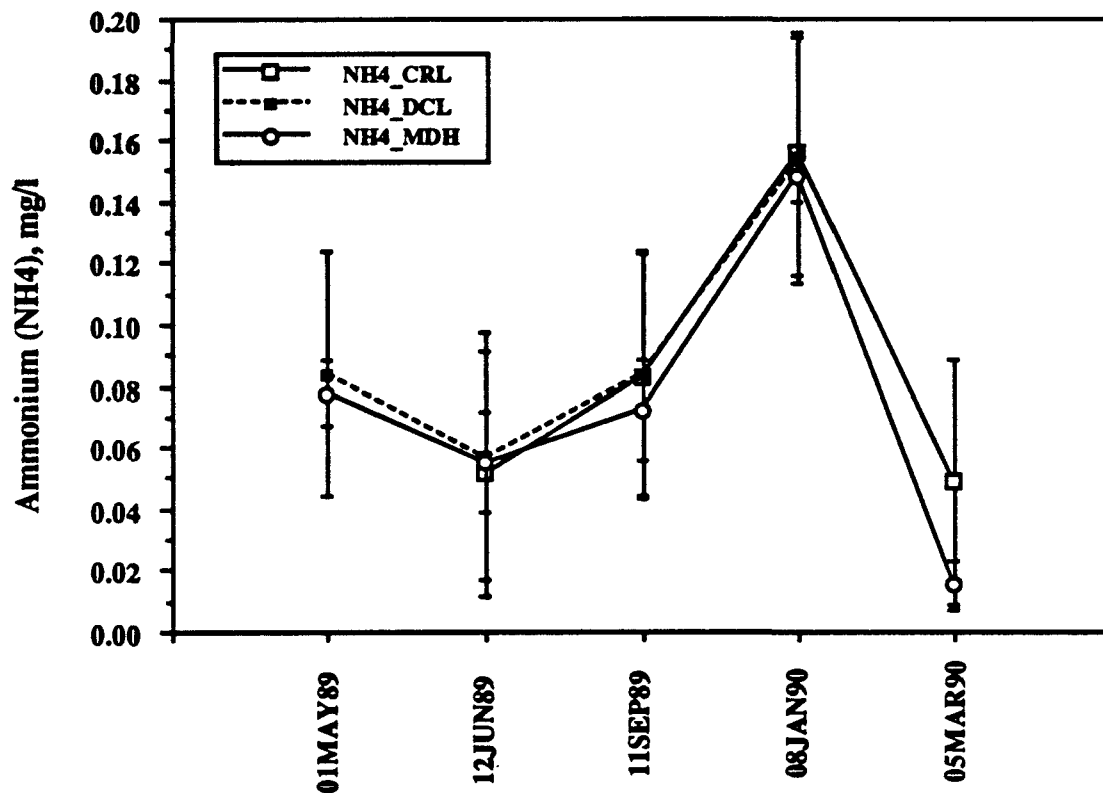


FIGURE 18. Split sample data for Nitrite (NO₂), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.

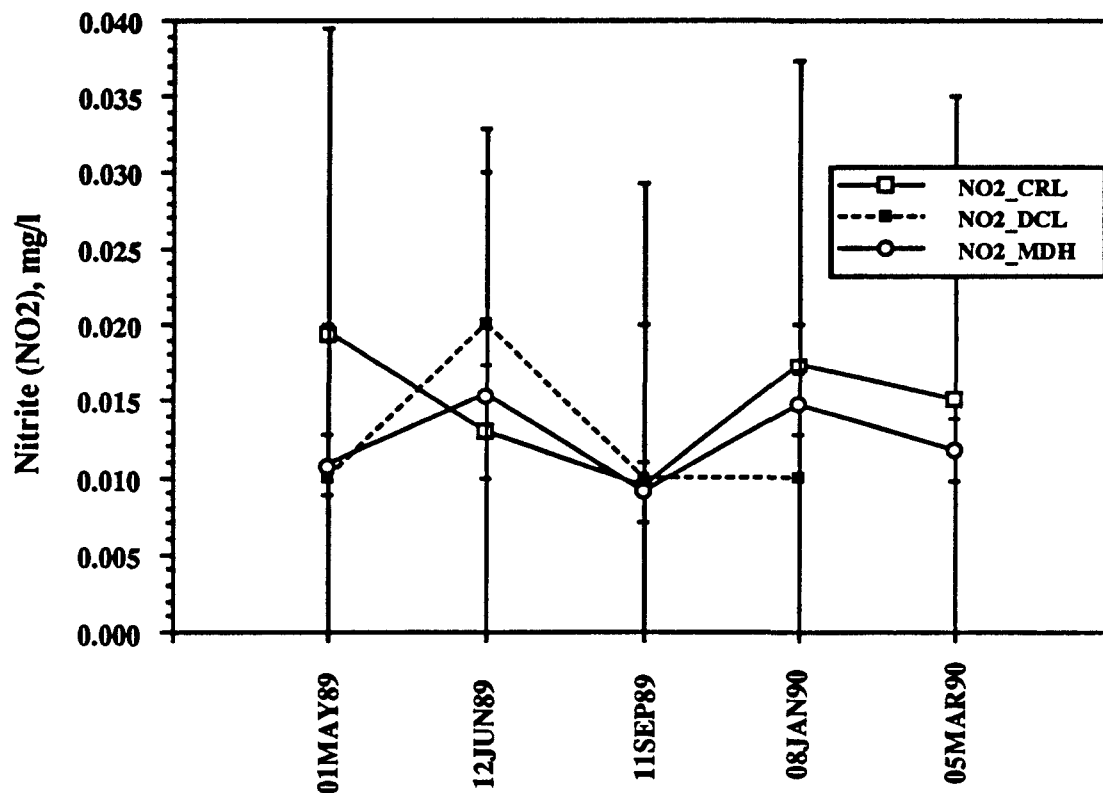


FIGURE 19. Split sample data for Nitrite + Nitrate (NO₂₃), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars. MDHMH samples were unfiltered, other samples were filtered (see text).

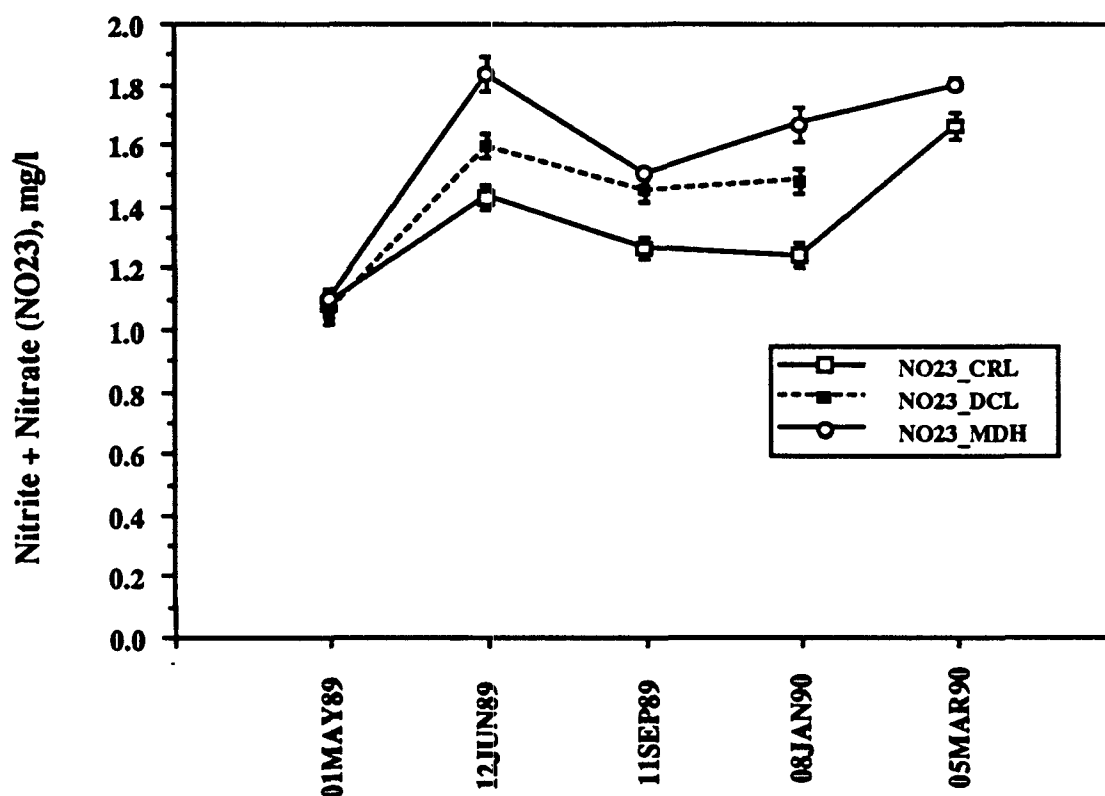


FIGURE 20. Split sample data for Total Kjeldahl Nitrogen Whole (TKNW), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision

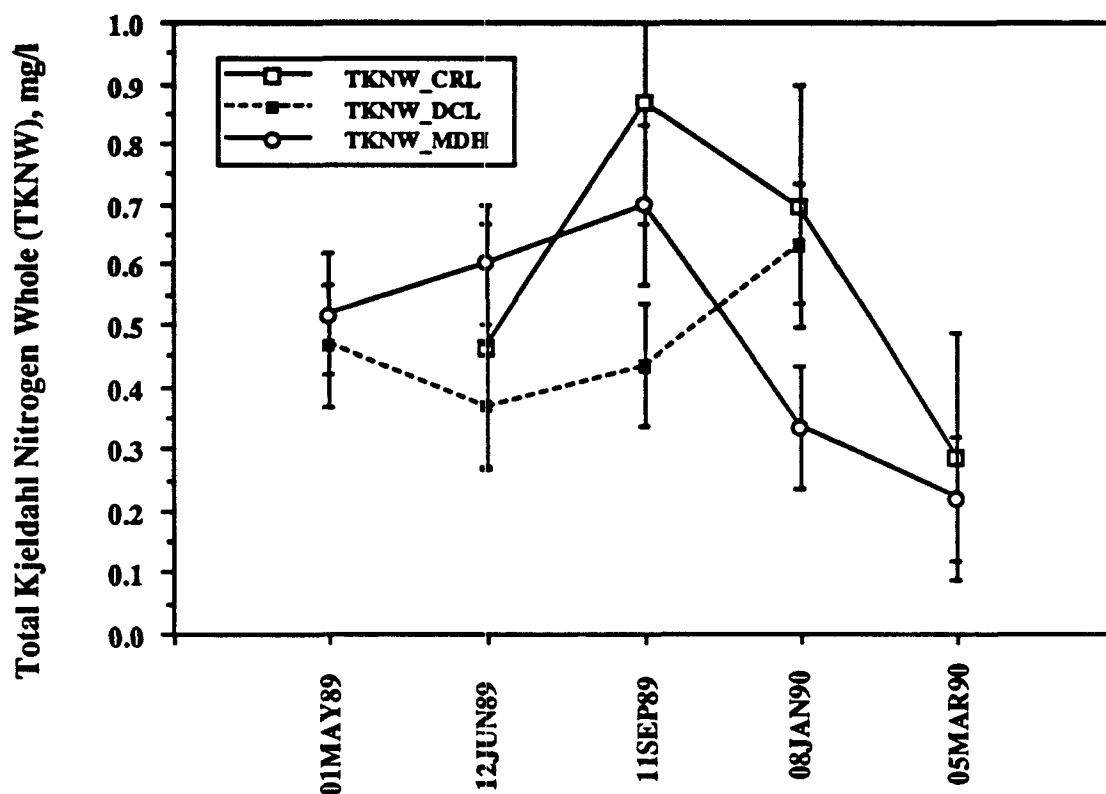


FIGURE 21. Split sample data for Orthophosphate (PO₄), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.

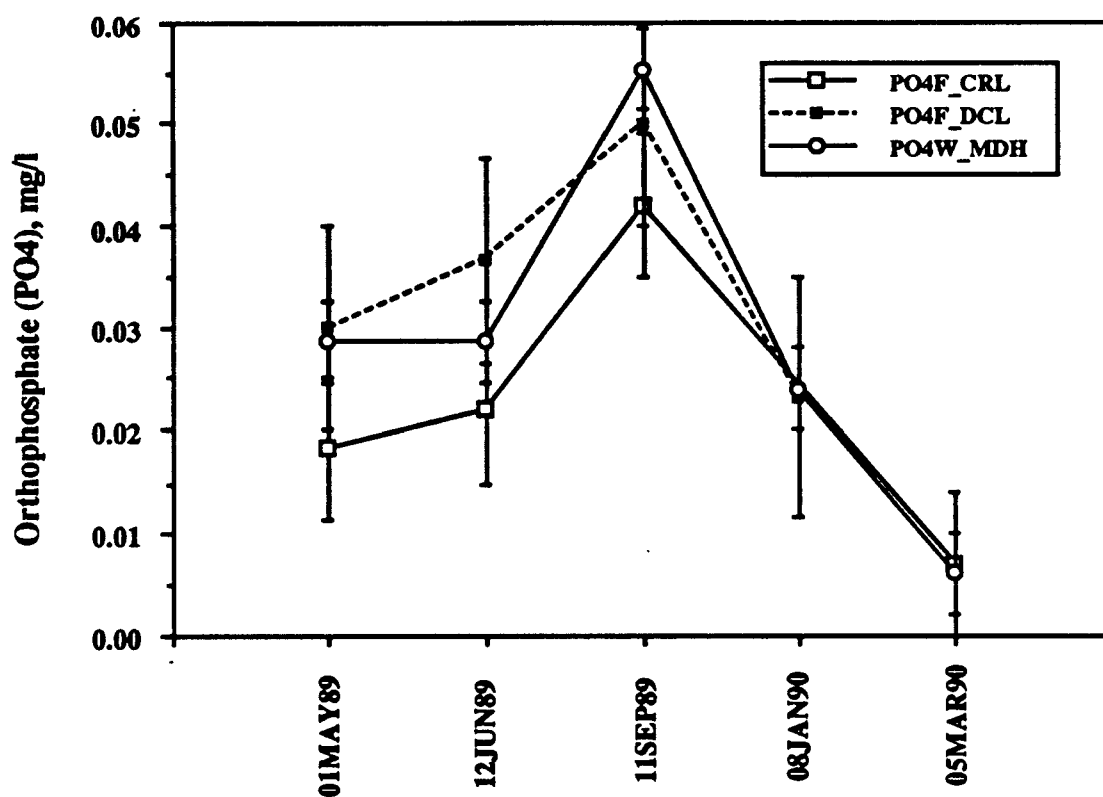


FIGURE 22. Split sample data for Total Phosphorus (TP), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.

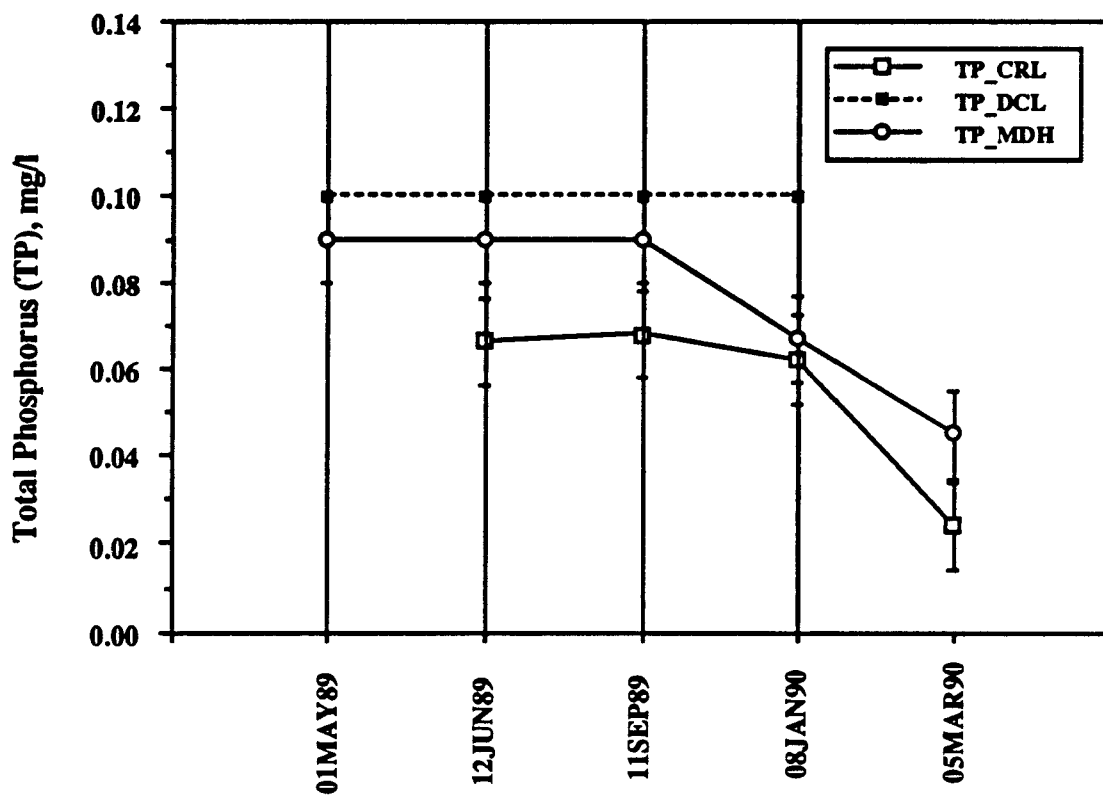


FIGURE 23. Split sample data for Total Organic Carbon (TOC), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.

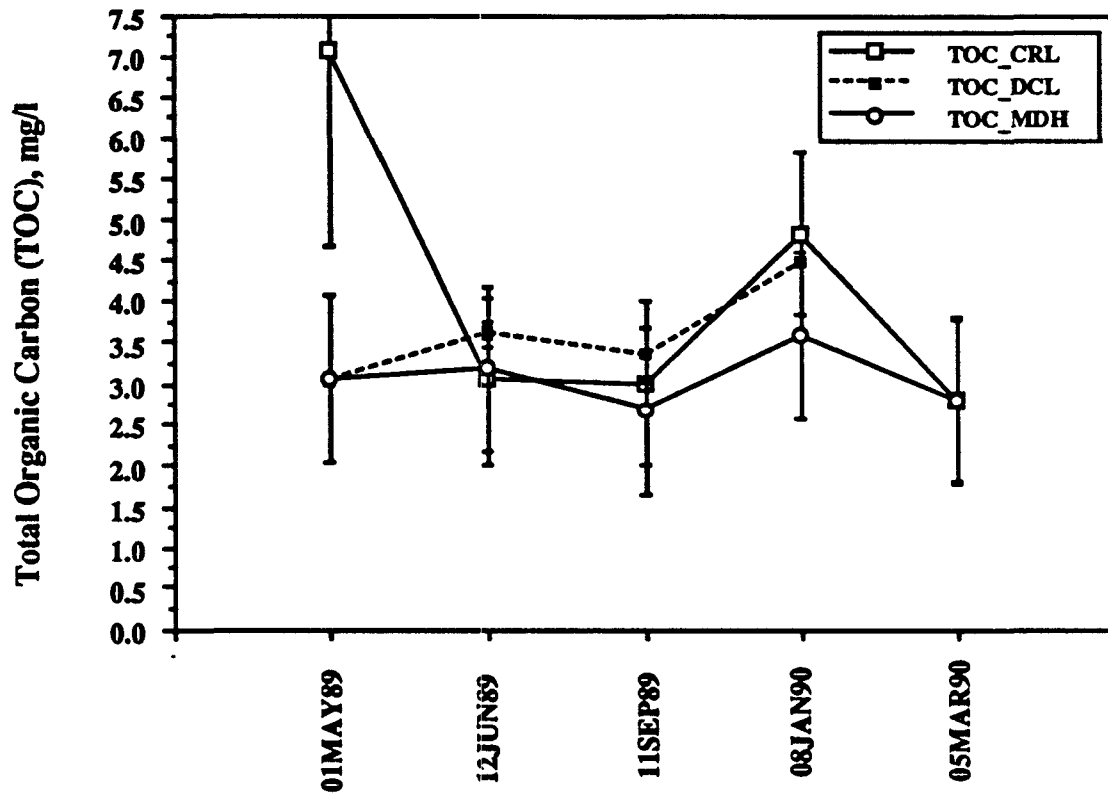


FIGURE 24. Split sample data for Total Suspended Solids (TSS), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.

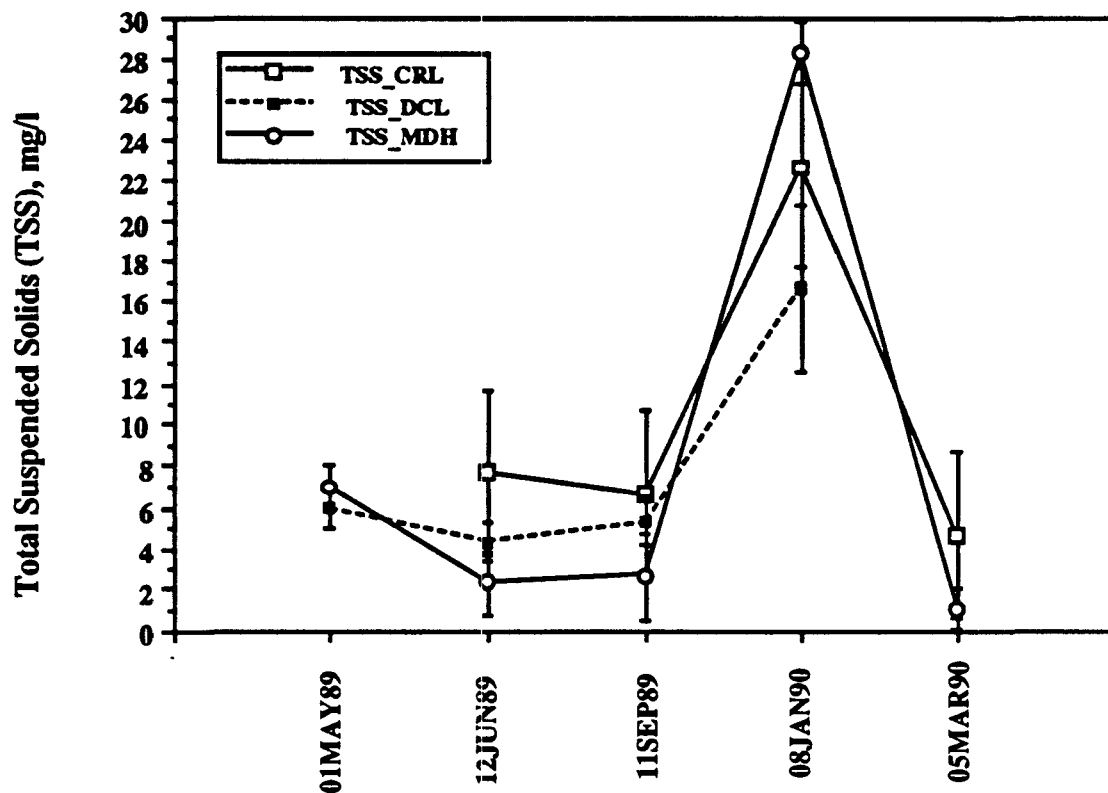


FIGURE 25. Split sample data for Silica (SI), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars.

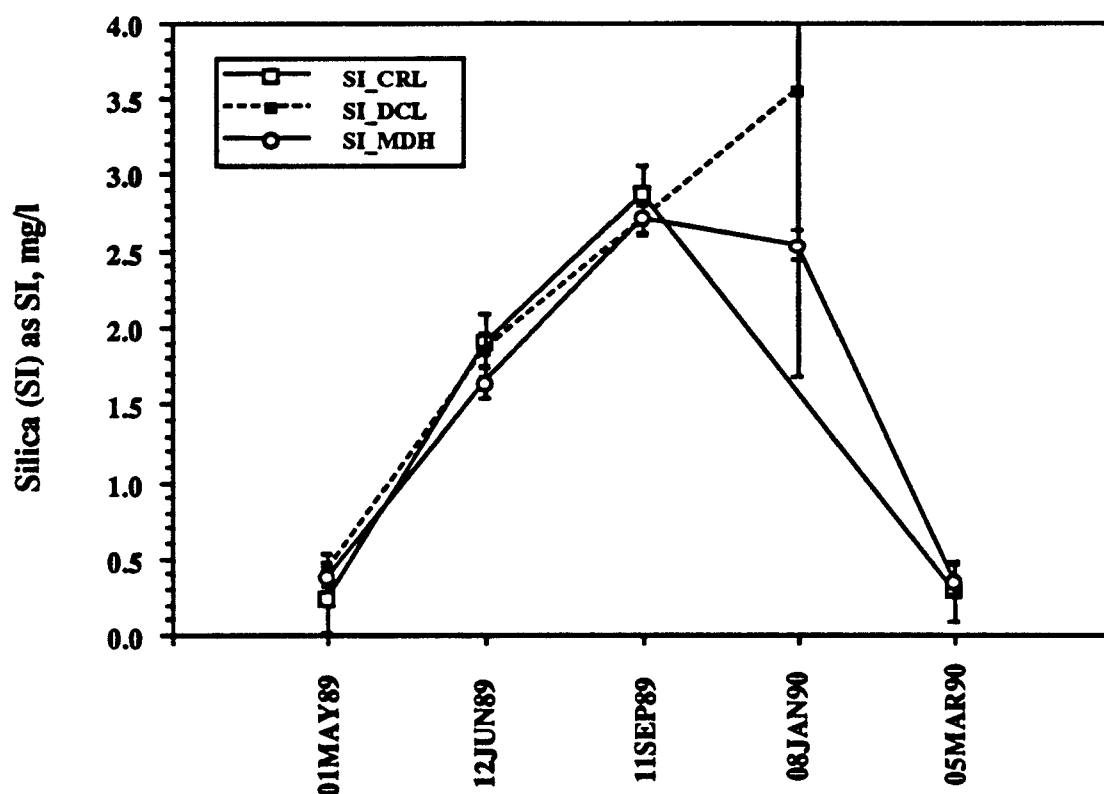


FIGURE 26. Split sample data for Biological Oxygen Demand 5 day (BOD5), from samples collected at Station PMS-10 (Potomac), showing cruise means with precision bars. CRL/DCRA data from 05MAR90 were added to the figure.

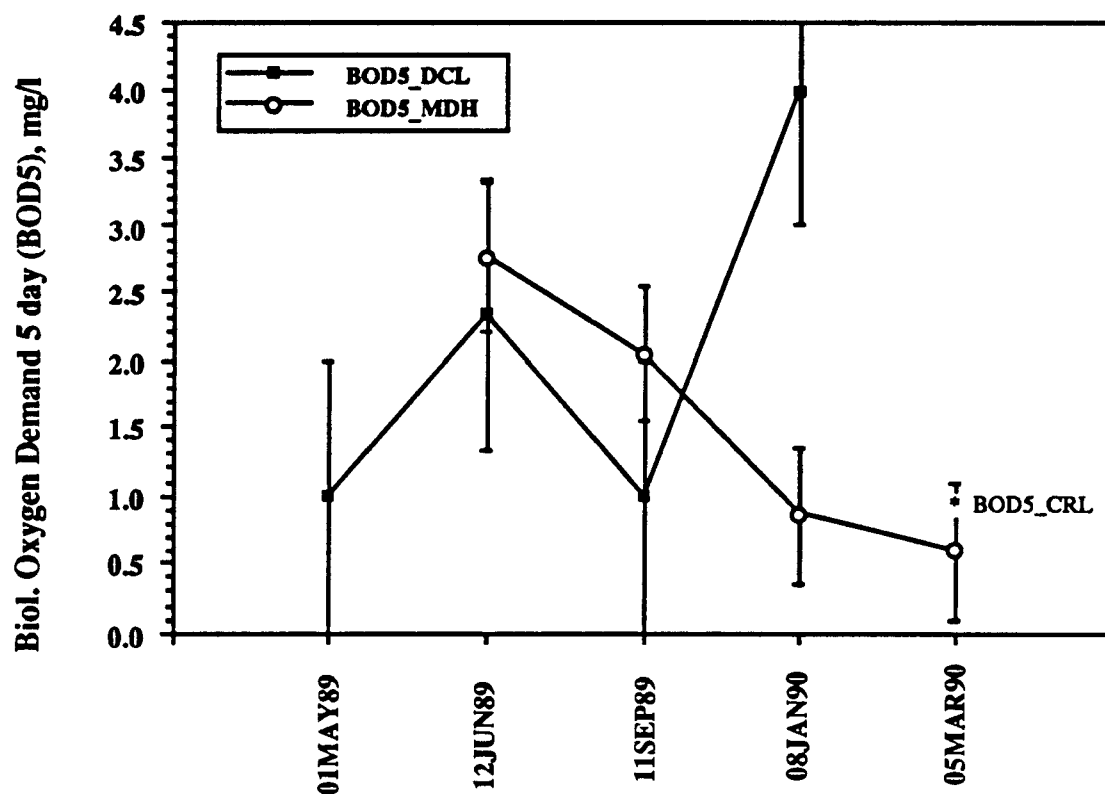


TABLE 13: Potomac Component (Station PMS-10) Split Sample Results using Cruise Means (1989 - 1990).

Parameter ¹	N	Laboratory Means (mg/l)			P value ²
		CRL/DCRA	DCLS	MDHMH	
NH4	3	0.097	0.098	0.092	0.36
NO2	4	0.015	0.013	0.012	0.93
NO23	4	1.255	1.395	1.525	0.042
TKNW	3	0.676	0.478	0.544	0.36
PO4	3	0.027	0.039	0.038	0.19
TP	3	0.065	0.10	0.082	MDL ³
TOC	4	4.48	3.62	3.12	0.65
TSS	3	12.3	8.8	11.1	0.53
SI	3	1.66	1.66	1.57	0.53

¹ Total Dissolved Phosphorus (TDP), Dissolved Organic Carbon (DOC), and Biological Oxygen Demand 5 day (BOD5) could not be analyzed due to missing data.

² No P values were statistically significant ($P < 0.01$, Friedman 2-way ANOVA on cruise means using exact probabilities).

³ Too many values were below the MDL to make a comparison.

IV. DISCUSSION

All of these results are preliminary, due to small sample sizes and start-up problems inherent in any new sampling program. The results are not necessarily or exclusively a reflection of laboratory performance. They may suggest that CSSP design features, specific parameters, or field or laboratory methods should receive extra attention in future quality assurance work.

Readers should also keep in mind that all the components include state 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. Some of the laboratories have also had difficulty obtaining and paying for the Standard Reference Material samples that are included in some CSSP results.

A. WITHIN-ORGANIZATION PRECISION AND ACCURACY

The estimates of within-organization precision and accuracy 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 4). These 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. One parameter, TDN, was calculated by addition in the MDHMH data and directly by the other organizations. It had similar precision among the four organizations.

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. They should not be used to assess inter-organization agreement. Unless there are consistent inter-organization differences over several sampling dates, larger SD and/or CV values may not indicate any problem with inter-organization agreement. For example, some tests may be more sensitive to variations in splitting procedures than others; this variability may not be under the laboratory's control. The SD and CV results will be more useful when sample sizes are larger.

C. INTER-ORGANIZATION AGREEMENT

1. Mainstem component

In the Mainstem component, five parameters (of 14 compared) showed statistically significant inter-organization differences that were larger than within-organization precision. All involve a method difference at the laboratory that had divergent results. MDHMH uses a different method for TP and TDP from the three mainstem laboratories. The MDHMH method does not

appear sufficiently sensitive to measure the low TP and TDP concentrations at Station CB5.3. Recent digestion method changes should increase sensitivity to low TP and TDP concentrations. CBL uses a different CHN analyzer (used for PC and PN) and a different filter (25 mm diameter Whatman GF/F) than ODU or VIMS. ODU and VIMS both use identical CHN analyzers and 13 mm diameter Gelman AE filters. Experiments are being planned to study the possible effects of these different instruments and filters on PC and PN results. The problem with DOC analyses at MDHMH was caused by a new DOC instrument that did not work with estuarine samples. It has now been remedied by using their old DOC instrument, which works better with estuarine samples.

2. Potomac component

In the Potomac component, none of the nine parameters analyzed met the criteria for recommending further investigation. Two of the parameters, NO23 and TP, had inter-organization differences that were larger than within-organization precision on three or more sampling dates. However, none of them had statistically significant differences. Unfiltered samples at MDHMH may have accounted for the NO23 differences, since MDHMH had higher results than the other two laboratories. MDHMH will receive filtered samples starting in late 1990. The DCLS results for TP were all below their detection limit because their low-level phosphorus system was not requested for these samples.

3. Fall line component

No analyses were done due to the limited data for 1989. The sample distribution problems were solved in 1990, and each laboratory should start receiving triplicate aliquots once a cone splitter is obtained.

V. SUMMARY AND CONCLUSIONS

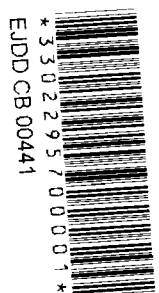
Estimates of within-organization and inter-organization precision were presented which may be useful in statistical analyses and computer modeling of Chesapeake Bay water quality. In three cases, parameters that showed low inter-organization precision also had low inter-organization agreement, but the two were not always correlated. Other parameters such as TKNW and TSS usually had fairly low inter-organization precision but generally high inter-organization agreement. Estimates of within-organization accuracy, including percent recovery results and Standard Reference materials (SRMs), showed high accuracy.

Assessments of inter-organization agreement found high agreement for 18 of the 23 comparisons made in two components. Agreement was low enough to recommend investigation for five parameters (TP, TDP, PC, PN, and DOC). In all five cases, the organization with divergent results had a different analytical method or instrument type, and in two cases (PC and PN) there was also a difference in filter type. In three cases (TP, TDP, and DOC), method changes have been made to increase inter-organization agreement, and

the other two cases are being investigated by the organizations involved to find ways to increase agreement.

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