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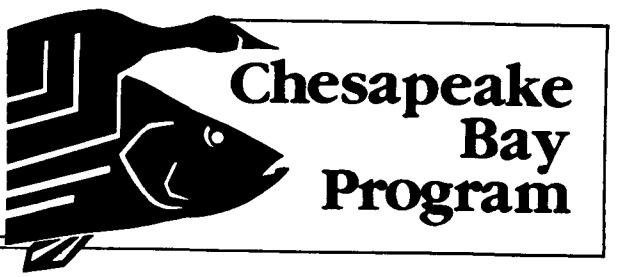
Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines

Revision 3



Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines

Revision 3

Prepared By:

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

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

BACKGROUND

In 1988, the Chesapeake Bay Program's Monitoring Subcommittee identified the need to assess the comparability of the water quality data produced by the many agencies participating in the basinwide data collection programs. The Monitoring Subcommittee's Analytical Methods and Quality Assurance Workgroup recommended the implementation of a basinwide coordinated split sample program to address this programmatic need. Although individual laboratories can evaluate the performance of their own analytical operations against standard reference materials, the most complete mechanism for the evaluation of total sampling and analysis system variability is through the use of field split samples. These include both field and laboratory sources of variability. The Coordinated Split Sample Program (CSSP) was started in June 1989, following the earlier revision of these guidelines (CBP 1989). This revision incorporates changes and refinements based on the first two years of CSSP operation.

PROGRAM OBJECTIVES

The major objective of the Coordinated Split Sample Program is to establish a measure of comparability between sampling and analytical operations for water quality monitoring basinwide. A secondary objective is to evaluate the in-matrix dilution of standard EPA reference materials. These standard reference materials are analyzed in appropriate matrix, fresh to saline, and concentration level to match the sample.

Continued implementation of the Coordinated Split Sample Program provides the institutional structure to address three important program coordination needs:

- o implemention of a valid statistical approach for the evaluation of split sample results to assure the use of these data in data quality assessment;
- o facilitation of efforts to identify problems and achieve solutions in individual programs as revealed through the comparability evaluation; and
- o improvement of communication of split sample analytical findings among organizations through a central computerized data base for split sample results.

The CSSP provides the forum and information necessary to promote an on-going refinement of the field and laboratory techniques rather than assuming that the system is static and never changing. The statistical assessment of the data allows the field and laboratory personnel to improve their respective techniques. In addition, the description of the data quality provides the necessary information for assessment and application of the data by the intended user.

PROGRAM DESIGN CONSIDERATIONS

The Analytical Methods and Quality Assurance Workgroup determined through a series of surveys that a limited number of split sampling programs were in place. There was considerable diversity in the objectives of these split sampling operations and, therefore, their designs varied accordingly. Prior to the implementation of the Coordinated Split Sample Program, few programs were able to work out a well organized method of data submission, compilation, analysis and timely distribution to participating laboratories and agencies. Most of the other programs use only two-way split samples and therefore do not provide the multiple comparisons that are part of the CSSP results.

Because of the difficulties associated with measurements of waters of varying salinities and the Monitoring Subcommittee's desire to link tidal and nontidal monitoring programs, linkages were created between laboratories routinely analyzing samples of comparable salinities. Through common "third party" laboratories, those laboratories analyzing only estuarine samples are linked with laboratories whose analytical responsibilities are limited to freshwater tidal/nontidal samples.

The Coordinated Split Sample Program's field split samples and laboratory duplicate and spike samples provide an estimate of overall sampling and analytical precision and accuracy. Since field split samples are defined as samples divided into portions following sampling, they provide precision and accuracy information about all steps <u>after</u> sample acquisition including effects of sample splitting procedures, sample processing, storage, shipment, analysis, and data processing. CSSP field split samples are divided from one large sample rather than consecutive co-located samples. Therefore, they provide an estimate of overall sampling and analytical precision and accuracy assuming analytical comparability. Combined with routine analysis of standard reference materials such as EPA certified materials, results from the Coordinated Split Sample Program can be used to verify analytical comparability and provide an independent measure of accuracy.

The actual structural design of the Coordinated Split Sample Program is based on a series of interconnected and interrelated split sample component programs organized around common geographical areas and similar sample salinitiy ranges. The four component programs are the Mainstem/Tidal Tributaries Component, the Virginia Mainstem/Tributaries Component, the Tidal Potomac River Component, and the Non-tidal Tributaries/Fall-line Component.

The Mainstem/Tidal Tributaries Component and Virginia Mainstem/Tributaries Component form the central core of the Coordinated Split Sample Program, interrelating laboratory and field operations working the Bay mainstem and tidal tributaries. The other components build upon this network of laboratories, linking directly with a laboratory or group of laboratories associated with monitoring the mainstem of the Chesapeake Bay.

SPLIT SAMPLE PROGRAM RESPONSIBILITIES

Component Program Responsibilities

For each component of the Coordinated Split Sampling Program, one agency has been assigned the coordination responsibility for that component's operation. The responsibilities of that lead agency are as follows:

A. Maintain contact with all the participating field and lab organizations to coordinate all logistics.

B. Provide for the necessary sampling equipment, sample containers, labels, chain of custody paperwork, etc. at the time of the quarterly split sample collection.

C. Collect the sample and prepare the splits according to the protocol described within this document.

D. Arrange for the direct exchange, transfer or shipment of the individual split samples to each participating laboratory within the component program. This may be accomplished by meeting the other organizations' crew at some mutually satisfactory point, personal delivery or by common courier. The goal should be the most rapid, feasible means of sample delivery. Every attempt should be made to adhere to normal holding times, temperatures, preservatives and filtration arrangements followed routinely by each organization. Records should be maintained of all handling conditions and practices so that data evaluations may be facilitated.

Data Management and Reporting Responsibilities

The routine submission of split sample data is the responsibility of each individual laboratory/agency and its in-house data management organization. The Chesapeake Bay Liaison Office contractor for the management and operation of the Chesapeake Bay Program Computer Center, Computer Sciences Corporation (CSC), is the designated recipient of all data generated through the Coordinated Split Sample Program. CSC is responsible for the processing, routine statistical analysis, report development, and timely distribution of results back to the participating laboratories and agencies within their respective component programs when all the data are received from all agencies within the individual component program.

The Chesapeake Bay Program's Monitoring Coordinator and Quality Assurance Officer both review and evaluate the results of each split sampling component program and consult with the appropriate individuals in each organization to determine the appropriate response to any significant findings.

Coordinated Split Sample Program Oversight Responsibilities

The Chesapeake Bay Liaison Office is responsible for overall coordination of the Coordinated Split Sample Program. The Chesapeake Bay Program's Monitoring Coordinator assists organizations in working out any logistical problems which cannot be resolved by the participating organizations. The Chesapeake Bay Quality Assurance Officer helps resolve any technical concerns which arise concerning the sampling and analysis of the split samples. The Analytical Methods and Quality Assurance Workgroup reports regularly to the Monitoring Subcommittee on the Program's results and any blockages to the full implementation of the Program which are based on resource constraints.

SPLIT SAMPLE COLLECTION AND PROCESSING PROTOCOLS

For each sample collected, the sampling crew fills a single large vessel such as a large carboy according to normal sample handling protocol. For instance, if a submersible pump is normally used this would be employed; if a cubitainer is normally dipped manually, this would be done. If multiple grabs are required to collect adequate volume for the splitting, these multiple grabs should be composited in a larger vessel prior to splitting. Field triplicate sub-samples obtained from a "single sample" potentially reduces additional sources of variability caused by sampling sequentially.

It is imperative that a strong mixing be applied to the large vessel to ensure that the sample is uniformly mixed and the sub-samples will be representative. This may be accomplished with a stir bar arrangement or other form of mechanical mixing as long as a vortex is created. This mixing must continue for the duration of the splitting operation. When more particulates are present in the sample, the splitting operation will be more difficult to accomplish a representative sample therefore, more effort must be applied to provide a good mix. As of March 1991, the sample collection, stirring and splitting methods used by each sampling organization (defined in the Split Sample Component Program section) were:

MDE (Mainstem Component, at CB4.4)--Samples are collected by submersible pump into a 15 gallon carboy; sub-samples are split on the boat from the carboy agitated with paint stirrer turned by electric drill.

VWCB (Virginia Component, at TF5.5)--Samples are collected by submersible pump into three 9-liter churn splitters, filled in sequential sections (a few liters at a time in sequence 1-2-3-1-2-3, etc.) until all are filled. Sub-samples are split on the boat from the churn splitters, one used for sub-sample 1, one for 2, and one for 3. This deviates from the recommended single large vessel.

DCRA (Potomac Component, at PMS-10)--Samples are collected in three 5-gallon carboys by dipping. In the lab, these are composited into one 15-gallon carboy, and the sub-samples are split from the large carboy via a spigot, while the carboy is agitated manually with a paddle.

USGS Towson (Fall Line Component, at CB1.0)--They have used a large churn splitter, but did not have enough water to split three sub-samples for each laboratory. They may get a cone splitter.

From the single large vessel of continuously well mixed sample, all four organizations draw three sub-samples for each laboratory in rotational succession (see Figure 1). These sub-samples were previously called "aliquots" (CBP 1989), and the name was changed to indicate that they are split in the field, not in the laboratory.

For example, if there are three laboratories receiving the split samples, the sample in the large vessel would be divided into nine sub-samples in nine bottles, three bottles for each laboratory. The first bottle for each laboratory would be filled first, then the second and the third, resulting in the first laboratory receiving bottles #1, #4 and #7. Data from this type of sample collection would indicate if there was any type of bias caused by non-uniform mixing resulting in samples that are not representative. Splitting effectiveness is checked statistically in CSSP reports (see Data Analysis).

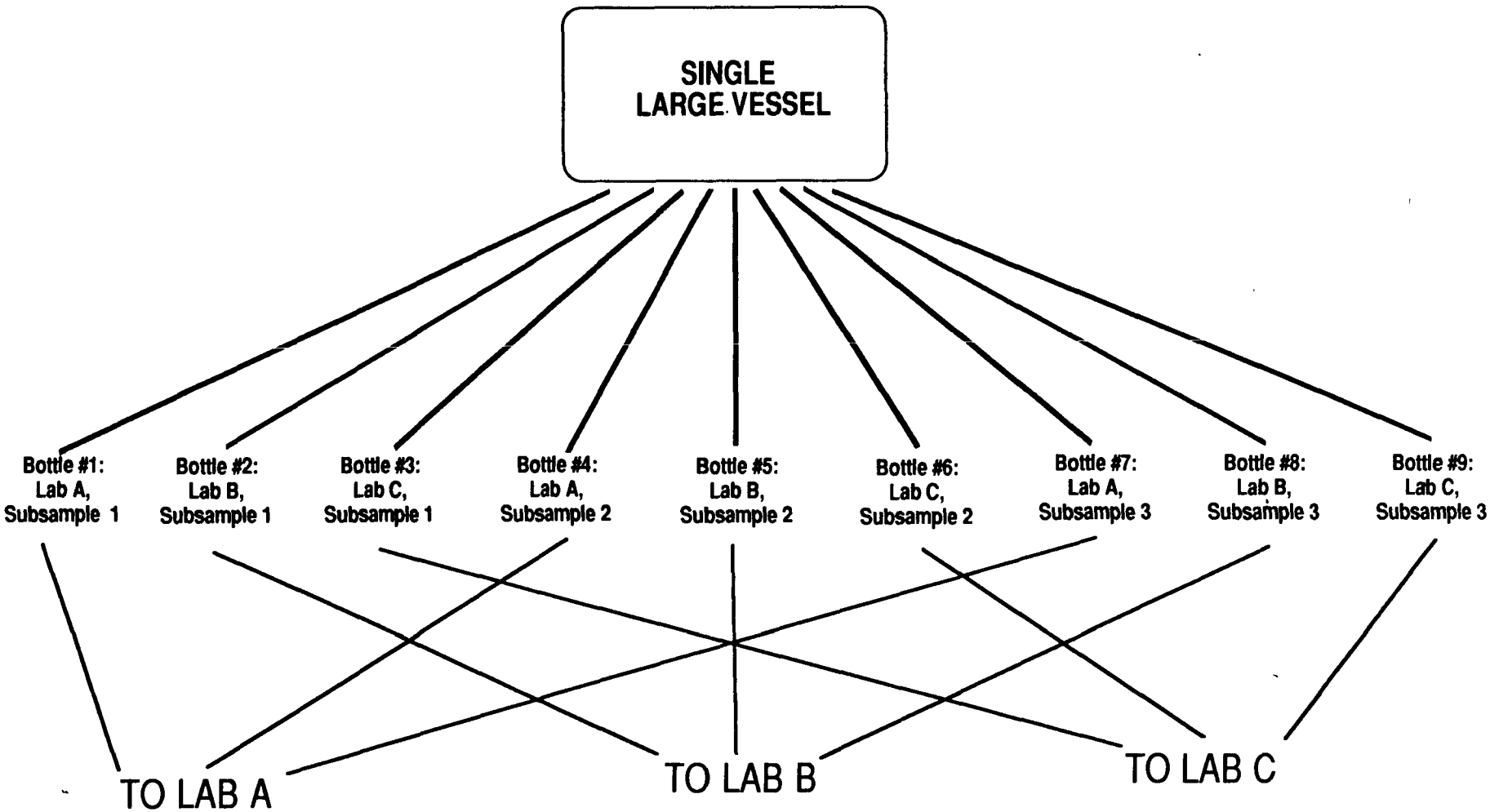
Each laboratory evaluates these three sub-samples as discrete samples. This approach provides an estimate of the variability of the material in the composite container which must be established to provide assurance that any inter-organization variability observed is not a function of a poorly mixed initial sample. Three sub-samples are statistically the minimum number required to permit an effective analysis of variance. For similar reasons, the minimum number of laboratories involved in any split sampling operation should be three wherever possible.

Once the splitting is completed, the sampling organization processes their three sub-samples through their normal handling and preservation procedures. The remaining sub-samples for the other organizations are iced down until they are delivered to the appropriate organization. Samples are delivered to the participating laboratories as rapidly as possible. The chain of custody form is sent with the samples (see Data Submission). Normal sample handling and preservation methods and holding times for CBP samples are adhered to as closely as possible. Any deviations from normal procedures should be noted on the chain of custody form and sent to CSC.

LABORATORY SAMPLE HANDLING AND ANALYSIS PROTOCOLS

Samples should be analyzed as soon as possible after arrival at the laboratory to minimize holding time effects. In some components (e.g., Virginia Component), participants have agreed to filter the samples the morning after collection, so that all are analyzed at approximately the same time. This would not be possible when some samples are delivered by mail (in the Fall Line Component). Participants in each component should discuss and agree on when samples will be delivered and analyzed.

Figure 1. Sequential Field Split Sample Dispensing Order



NOTE: The order of dispensing and the provision for adequate stirring during the split sample preparation are both very important. Be certain to provide complete documentation of the procedures used.

All samples are analyzed for the parameters listed in Table 1 within the recommended Chesapeake Bay Monitoring Program holding times. If there are parameters in Table 1 which are not routinely measured in CBP samples by a participating laboratory, these parameters do not need to be analyzed and reported solely for the purposes of the CSSP, unless specific parameters are requested for comparison to results from other laboratories in the component. CSC computes any calculated parameters used in the reports, using the methods outlined in D'Elia et al. (1987). Currently the calculated parameters include Total Nitrogen (TN) for all laboratories, and Total Phosphorus (TP), Particulate Phosphorus (PHOSP), Total Dissolved Nitrogen (TDN), and Particulate Nitrogen (PN) for those laboratories that do not calculate them directly.

A complete schematic of the operational flow of analyses is outlined in Figure 2. Within the laboratory, at least one of the three sub-samples is subjected to the normal quality control (QC) routine. If a duplicate and spike sample are analyzed every tenth analysis, the sub-sample identified for QC should be analyzed as a routine quality control sample. This lab QC sample is divided into a duplicate and spiked with the appropriate standard. Additional QC samples from any source can be analyzed to fit the lab QC sample frequency. If the laboratory elects to run more than one sub-sample for additional quality control, these data are to be submitted for evaluation as well.

To perform adequate diagnostics in the event that significant inter-organization differences are found, it is essential that quality control data are available for each laboratory on their system's performance with the specific matrix under consideration in this program. It will be useful to compare the precision and accuracy during analysis of the sub-samples (and their matrix) against the routine precision and accuracy limits of the laboratory over all matrices.

To supplement the analyses of the three sub-samples and the respective QC sample, EPA standard reference material for each parameter are analyzed where available. The analysis of standard reference materials provides a strong measure of comparability between all laboratories and within one laboratory's analytical system over time. Quarterly analysis of standard reference materials is the most independent evaluation of laboratory performance available at this time. It is a critical element of any diagnostic efforts associated with the Coordinated Sample Split Program.

The standard reference material (SRM) should be diluted with deionized/distilled water in all components. In the Mainstem Component, an additional standard diluted in the appropriate concentration saline matrix should be analyzed. The concentration of the estuarine dilution water should be subtracted as a blank value.

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

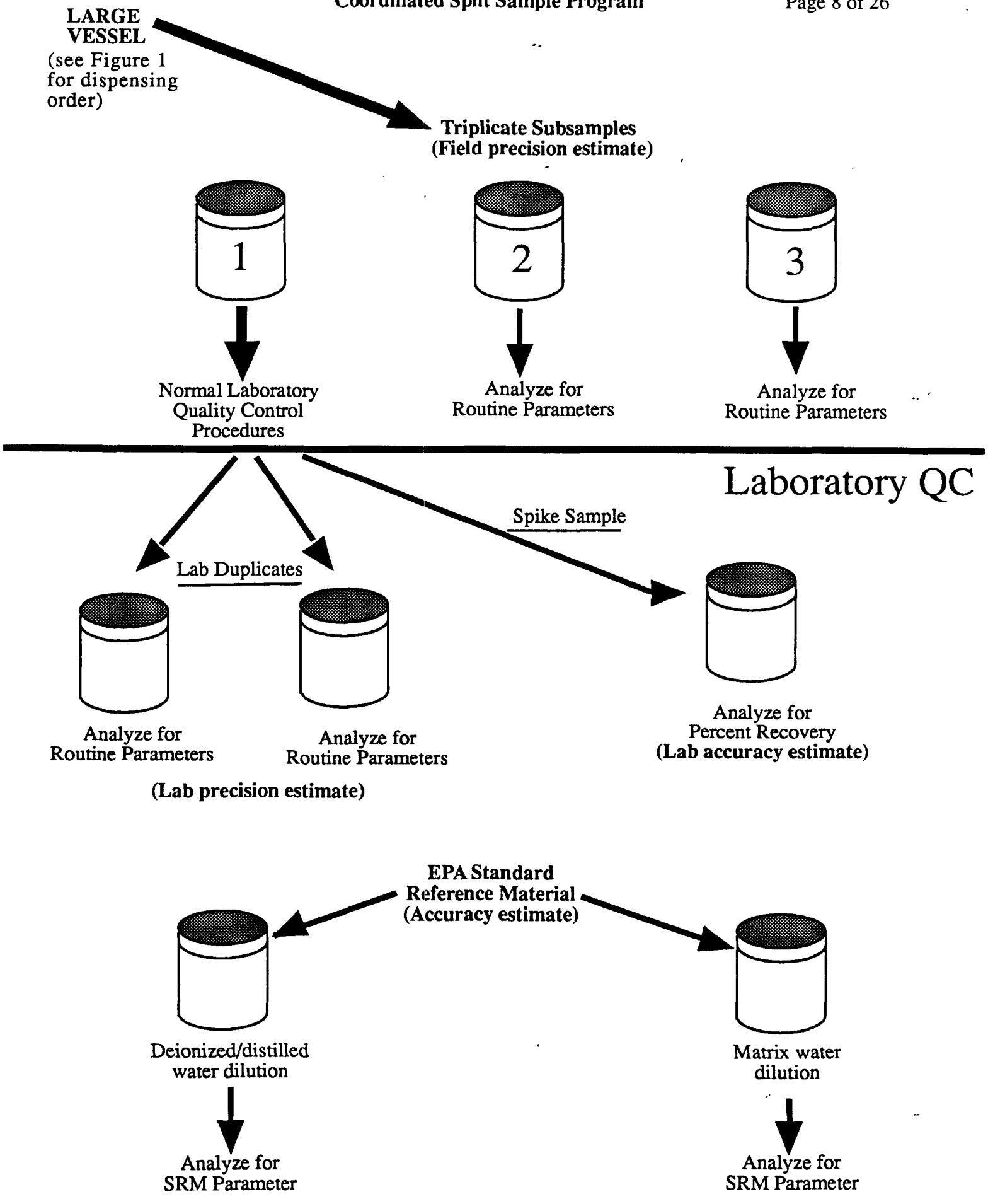


Table 1. Parameters and their CBP code, holding times and temperatures

Parameter (mg/l except CHLA)	CODE	HOLDING TIME (days)	TEMPERATURE (°C)
Total phosphorus as P	TP	28	-20
Total dissolved phosphorus as P	TDP	28	-20
Particulate phosphorus as P	PHOSP	28	-20
Dissolved orthophosphate as P	PO4F	28	-20
Total nitrogen as N	TN	N/A	N/A
Total dissolved nitrogen as N	TDN	28	-20
Particulate nitrogen as N	PN	28	-20
Total Kjeldahl nitrogen as N	TKNW	28	-20
Dissolved Kjeldahl nitrogen as N	TKNF	28	-20
Ammonium as N (filtered)	NH4	28	-20
NO2 + NO3 as N (filtered)	NO23	28	-20
Nitrite as N (filtered)	NO2	28	-20
Nitrate as N (filtered)	NO3	28	-20
Total organic carbon	TOC	28	-20
Dissolved organic carbon	DOC	28	-20
Particulate organic carbon	POC	28	-20
Particulate carbon	PC	28	-20
Silica as Si (filtered)	SI	28	4
Total suspended solids	TSS	7	4
Chlorophyll a (ug/l)	CHLA	30	-20
Pheaophytin	PHEA	30	-20
Biological Oxygen Demand 5 day	BOD5	N/A	N/A

Notes:

1. Report all parameters that are measured directly. Calculated parameters will be calculated by CSC using the outline in D'Elia et al. 1987.

2. If there are parameters noted above which are not routinely measured by a participating laboratory, these parameters do not need to be analyzed and reported solely for the purposes of the Coordinated Split Sample Program. In some cases, laboratories may be requested to analyze parameters performed by other laboratories in the component. Please report all of the parameters listed that you routinely analyze.

3. Please report any deviations from these maximum holding times in a narrative accompanying the submitted data.

4. Parameters without holding times and temperature were determined by calculating the concentration from parameters that were measured directly (per D'Elia et al. 1987).

EPA standard reference materials are available through the Cooperative Research and Development Agreement (CRADA) of the U.S. EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. These EPA certified materials are obtained from the company awarded the specific contract by EPA. Standards are or will be available for organic compounds, toxic and hazardous compounds, pesticides and inorganic compounds. Any questions in regards to the EPA standard reference materials should be directed to Claudia Walters, CBP Quality Assurance Officer, CBLO, at (301) 267-0061 or (800) 523-2281.

DATA MANAGEMENT REQUIREMENTS AND PROTOCOLS

Chain-of-custody form

Upon sampling, the chain of custody form is filled out completely by the sampling agency to convey the necessary information to the other participants regarding the sampling site, time of collection, handling and any special observations which might affect the results. A sample chain of custody form for the Mainstem Component (Fig. 3) should be adapted for other components if not already in use. This form should be sent with the split samples to the laboratories, and sent to CSC with the data submission. Each laboratory should perform the requisite analyses and report concentration values for each determination on each sub-sample of the split sample, with the associated QC and SRM data.

Diskette submission

Data sets are submitted to CSC as an ASCII text file on an IBM diskette, unless other arrangements have been made with CSC. CSC has no keypunching staff, since virtually all of the data they receive are on diskettes or tapes. The provided Data Submission form (Fig. 4) is optional (see below), and may be used to prepare the data for keypunching. If questions arise concerning data submission, please contact Peter Bergstrom, CSC, at (301) 267-0061 or (800) 523-2281.

A. Data format and parameter names

The preferred data format is standard columnar text (ASCII), with each variable in a separate column, and columns separated by spaces. This can be created and edited with a word processor if it is saved as an ASCII or text file. If you use LOTUS or dBASE please send an ASCII file (.PRN from Lotus). Include all the variables listed above, in the same order; values for PARAM are in Table 1. Please report values that are below detection limits as you normally report them, and be sure they get the '<' flag. Report missing values for numeric variables as a period. The data received to date will fit in a 132 column width. If you cannot fit your data into a 132 column width, please submit them as two files, each less than 132 columns wide, on the same diskette. A sample format with hypothetical data is in Table 2. This format is available on diskette from CSC to facilitate data entry.

Figure 3.

COLLECTED FOR: ODU

BOTTLE NUMBER: D1, D2, D3

MAIN BAY SPLIT SAMPLE CUSTODY LOG

COLLECTION DETAILS: DATE: 12-10-90 TIME: 1416 DEPTH: 0.5

LOCATION: MCB4.4 SALINITY: 11.9 E

COMMENTS: (unusual conditions, problems, floating algae, high solids, etc.)

SPLITTING DETAILS:

COMPOSITE CONTAINER FILLED BY:
multiple grabs ___
pump ✓
other ___

COMPOSITE SUBSPLIT BY:
sequential bottles ✓
cone splitter ___
other ___

SPLITTING SEQUENCE	BOTTLE LABELLED
bottle 1	MDE - A1
bottle 2	VIMS - B1
bottle 3	CBL - C1
bottle 4	(ODU - D1)
bottle 5	VWCB - E1
bottle 6	MDE - A2
bottle 7	VIMS - B2
bottle 8	CBL - C2
bottle 9	(ODU - D2)
bottle 10	VWCB - E2
bottle 11	MDE - A3
bottle 12	VIMS - B3
bottle 13	CBL - C3
bottle 14	(ODU - D3)
bottle 15	VWCB - E3

TRANSFER SEQUENCE:	DATE	TIME	BY WHOM?	TEMP. OF SAMP (circle one)
Composite collected & split	12-10-90	1416	MDE	0°C 4°C ambie
Subsamples picked up	12-10-90	1730		0°C (4°C) ambie
Subsamples delivered to lab	12-10-90	20:30	VKD	0°C (4°C) ambie

FIELD PROCESSING INFORMATION

BOTTLE #	FIELD PROCESSING DONE ON SAMPLE	DATE/TIME	BY
D1	Filtered for TSS/NO3/NUTS/chl	11DEC90 9:05	LD/DG
D2	"	"	LD/DG
D3	"	"	LD/DG

NOTE: PLEASE SEND A COPY OF THIS COMPLETED FORM TO: PETER BERGSTROM, CSC, SEVERN AVENUE, SUITE 110, ANNAPOLIS, MD, 21403, (800) 523-2281

Table 2. Sample data set submission format for Coordinated Split Sample data

STATION	DATE	LAB	PARAM	APC	MDL	SUBSAMP	REP_NUM	RESULTS	PCRECOV	SPIKE	SRM_EPA	SRM_DE	SRM_MA
CB5.3	890515	DCLS	PHOSP		<	1	1	0.010	106	0.023	0.016	0.024	0.019
CB5.3	890515	DCLS	PHOSP			1	2	0.011	.	.	.	.	.
CB5.3	890515	DCLS	PHOSP	QQ	<	2	1	0.009	.	.	.	.	.
CB5.3	890515	DCLS	PHOSP			3	1	0.013	.	.	.	.	.
CB5.3	890515	DCLS	TKNW			1	1	0.754	92	1.11	0.645	0.623	0.554
CB5.3	890515	DCLS	TKNW			1	2	0.712	105	1.56	.	.	.
CB5.3	890515	DCLS	TKNW			2	1	0.657	.	.	.	.	.
CB5.3	890515	DCLS	TKNW	AA		3	1	0.774	.	.	.	.	.
CB5.3	890515	DCLS	SI			1	1	2.42	.	.	.	.	.
CB5.3	890515	DCLS	SI			1	2	2.44	111	3.45	1.65	1.54	1.62
CB5.3	890515	DCLS	SI			2	1	2.17	.	.	.	.	.
CB5.3	890515	DCLS	SI			3	1	2.39	.	.	.	.	.

The parameter names to use and their meanings are:

STATION is the **sampling station number** (CB5.3, PMS-10, etc.)

DATE is the sampling date, as **YYMMDD**

LAB is the abbreviation for the **analysis laboratory** (DCLS, OWML, etc.), not the collecting agency

PARAM is the **CBP abbreviation** for the parameter (see revised Table 1). Please do not use other abbreviations.

APC (Analysis problem code): One or two letters, from Table 20 of the CBP Data Management Plan for Water Quality Data (latest version is Revision 2, July 1990).

MDL (Method Detection Limit): For values below the Method Detection limit record '<'. For samples requiring a dilution record '>' (list the dilution factor in the comments section or narrative). Otherwise leave this blank.

SUBSAMP is the sub-sample number (1, 2, or 3). Previously this variable was called 'ALQ' and included the lab replicate designation, but the codes used by different submitters have been so diverse that identification of the replicates was uncertain. In the future, indicate ONLY the field replicate or sub-sample number here, and show the lab replicate number with the following new variable:

REP_NUM is being requested for the first time in CSSP submissions. It indicates the **LAB** replicate number (usually 1 or 2, sometimes 3, 4, or 5) just as it does in other CBP submissions. This needs to be a separate number for data analysis.

RESULTS is the concentration for that sub-sample. Report the results the way you normally report them to the CBP (corrected for dilution if necessary).

PCRECOV is the percent recovery from the spiked sample. List it in the row of the sub-sample that was spiked. This can be done for more than one sub-sample if desired; please report all spikes run.

SPIKE is the amount of spike added. This value will be added to the RESULTS in that row to get the theoretical total concentration used for calculation of percent recovery.

SRM_EPA is the EPA value for the Standard Reference Material. The SRM results can be put in any row for that parameter. Please attach a copy of the "Answer Sheet" that came from the EPA with each standard.

SRM_DE is the lab value for that SRM, diluted in deionized water. Please list the dilution used in the Comments section, or in your narrative.

SRM_MA is the lab value (if done) for the SRM diluted in lowest concentration saline matrix.

B. Diskette formats

CSC/CBLO staff are currently able to read the following diskette formats:

IBM: 5.25", 360KB (PC/XT) and 1.2MB (AT); OR 3.5", 720KB and 1.44MB

Macintosh: 3.5", 800KB

C. Diskette labeling

All diskettes submitted must be labeled in the following manner (based on page 4-4 of the Chesapeake Bay Program's Data Management Plan for Water Quality Data):

a. Data format used and the software and version number used for data storage
b. Creation date
c. Submitting individual, organization, and telephone number
d. Names and a brief description of all files on the diskette

Please contact Peter Bergstrom of CSC at (301) 267-0061 (or toll free (800) 523-2281 or FTS 691-6873) if you have any questions about data submission.

Hardcopy submission

A hardcopy submission is optional. Use the data submission form provided (Fig. 4). Data entry errors will be minimized if each laboratory puts their own data on the standard form. Please double check all decimal points and all numbers for clarity, and put decimal points in a separate box.

Accompanying narrative

Please attach to the data sheets a narrative detailing the methods and procedures followed in each step of the analysis process. Describe how the sample was handled before and after you received it and any sample preparations including any digestions, preservatives added or filters used. Give details of each analytical method used (include method code if known), any dilutions used, and any unusual conditions or problems. This information will be very useful if differences are found in the results. This narrative can be included on the diskette (if used) as an ASCII text file if desired.

Once the narrative has been sent, future submissions only need to include any changes in procedures. Please indicate whether the changes are temporary or permanent.

Please attach copies of the original lab sheets if there are any ambiguous parameters or other features of the data that may need clarification. These are currently received from MDHMH, and have been requested from DCLS.

Data verification

CSC/CBLO staff will upload the submitted data to the VAX computer and combine the data for each component into a single data set. Since errors can be introduced in this process, each laboratory should verify that their data are correct in the combined data set. Normally a printout with a Data Set Checklist will be sent with each Interim Report, requesting verification of the new data in the report. The graphs and analyses in the report will help identify any outliers in the data. The data should be checked against the original lab sheets, and any changes sent to CSC before the Annual Report is produced. Any data submitted between the Interim Report and the Annual Report will have to be verified before the Annual Report is finalized. Although data verification is tedious work, the use of the data requires that the numbers be as correct as possible.

STATISTICAL DATA ANALYSIS AND REPORTING

The data analysis and reporting scheme was developed by Peter Bergstrom in consultation with members of the Analytical Methods and Quality Assurance Workgroup (AMQAW) during 1990. The current approach uses two main tools: graphs of the data with "precision bars," and two-way analysis of variance.

Figure 4.

CHESAPEAKE BAY PROGRAM
COORDINATED SPLIT SAMPLE PROGRAM
DATA SUBMISSION FORM

VERSION 2 2/26/91

SAMPLING STATION: _____

CONTACT PERSON: _____

SAMPLING DATE: _____

LAB (analytical laboratory): _____

TELEPHONE NUMBER: ( )

DATE SAMPLE REC'D by LAB: _____

PARAM (CBP Code)	Problem Code	MDL	ALQ	REPNUM	RESULTS (mg/l) Please code decimal	PCRECOV	SPIKE	SRM_EPA (expected value)	SRM_DE (distilled dilution)	SRM_MA (matrix dilution) (Mainstem only)
			1	1						
			1	2						
			2	1						
			2	2						
			3	1						
			3	2						

COMMENTS:

			1	1						
			1	2						
			2	1						
			2	2						
			3	1						
			3	2						

COMMENTS:

			1	1						
			1	2						
			2	1						
			2	2						
			3	1						
			3	2						

COMMENTS:

Graphs of the split sample results show which differences were larger than the within-laboratory precision. Based on a discussion with AMQAW members on 4/24/90, within-laboratory precision for the graphs is estimated by the larger of: 1) the Method Detection Limit (MDL); or, 2) the standard deviation of the three sub-samples for each sample, which estimates analytical and field precision. In most cases, the MDL is larger than the field precision so the MDL usually sets the precision limit. 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-laboratory precision.

The Friedman two-way non-parametric repeated measures analysis of variance (ANOVA) with replication within blocks (Marascuilo and McSweeney 1977) is used to test statistically for differences among results from different organizations. In this design, the organizations are treatments, the sampling dates are blocks, and the three sub-samples are replicates within blocks. The null hypothesis is that there are no consistent differences among the concentrations measured by the different organizations. The ANOVA design is shown in Table 3.

Table 3. Analysis of variance design for testing inter-organization differences, Coordinated Split Sample Program.

TREATMENTS (Organizations)
(Potomac Component shown)

BLOCKS (Sampling dates)	CRL/DCRA	DCLS	MDHMH
March	1 2 3*	1 2 3	1 2 3
June	1 2 3	1 2 3	1 2 3
September	1 2 3	1 2 3	1 2 3
December	1 2 3	1 2 3	1 2 3

*Replicates within blocks (sub-samples)

The Friedman program used before (Bergstrom 1990) did not allow for replicates, so cruise means had to be used in previous reports. This change to using replicate data uses more information in the data and increases the power of the test, or its ability to detect real differences. The test is done with a computer program written by Peter Bergstrom in SAS 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).

The Friedman test is also used for a preliminary test of splitting effectiveness. This is done to check whether the results from one sub-sample were consistently higher or lower than the results from other sub-samples. This would most likely occur if the later sub-samples, drawn from lower in the carboy, had more sediment in them or if some of the sample bottles are contaminated. This test is done separately for each parameter and sampling date, using the three sub-samples as treatments and the organizations as blocks. The null hypothesis is that there are no consistent differences among the concentrations of the three sub-samples. The ANOVA design is shown in Table 4. If the results do not show any differences caused by splitting, the analysis for inter-organization differences is done. If there are significant effects of splitting, the data must be examined to see if these effects will bias the tests of inter-organization differences.

Table 4. Analysis of variance design for testing splitting effectiveness, Coordinated Split Sample Program.

		TREATMENTS (Sub-samples)		
		1	2	3
Blocks (Organizations)	DCLS	1	2	3
	HRSD	1	2	3
	ODU	1	2	3
	VIMS	1	2	3

(Note: No replicates within blocks.)

Statistical significance is assumed when $P \leq 0.01$ (Bergstrom 1990). 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 $P \leq 0.01$ standard is now attainable for most of the parameters most components, due to larger sample sizes and the use of replicates in the Friedman test.

Accuracy data, from percent recoveries and Standard Reference Material (SRM) analysis, are included in tables for each report, but are not the subject of statistical tests. These data are used to supplement the split sample results, and for diagnostic purposes if the split sample results show inter-organization differences that should be investigated. Confidence limits for SRMs (provided by EPA) are included only when the standards were analyzed

without dilution, since the confidence limits do not apply to diluted samples. SRMs analyzed after dilution are reported as the diluted value, with the expected value based on the dilution used.

Variability data are reported for within-organization and inter-organization variability, as the standard deviations and coefficients of variation (CV). Within-organization variability comes from the variability of the triplicate sub-samples (field replicates) for each sampling date, using REP_NUM=1 if there were laboratory replicates done, using the MEANS procedure in SAS. Variability of laboratory replicates is used for diagnostic purposes only, since it includes fewer sources of variability than the field replicates (sub-samples). Inter-organization variability is calculated among the mean concentrations of the three sub-samples reported by each laboratory for each sampling date, using the MEAN and CV functions is SAS. All the variability estimates are reported in one table to facilitate comparisons.

Each quarterly meeting of AMQAW includes an update on the latest CSSP results by CSC/CBLO staff. In addition, CSC/CBLO staff contact data submitters as soon as possible after receipt of the CSSP data if there appear to be any errors or outliers in the data or other problems with the data.

Written results of the statistical analysis of the split sample data are routinely distributed to agencies and laboratories within the individual program components. These are called Interim Reports. The original quarterly reporting schedule has proved impractical due to slow submission of data and the time needed for report preparation. The current schedule is one Interim Report per year per component, including data from two or three sampling dates from that year. It may be possible to prepare two Interim Reports a year per component if data submission and reporting are streamlined. An Annual Report is prepared summarizing the results of all components and any responses to the Interim Reports (Bergstrom 1990). The Annual Report is approved by AMQAW, distributed to all participating agencies and laboratories, and formally presented to the Monitoring Subcommittee.

COORDINATED SPLIT SAMPLE PROGRAM IMPLEMENTATION

Implementation of the Coordinated Split Sample Program is an ongoing process, and the program requirements change slightly over time. Since the program's inception in June 1989, most organizations have made changes in their protocols to achieve full implementation. The few remaining gaps in full implementation are the result of problems with obtaining splitting equipment or Standard Reference Materials. Hopefully these will be remedied in the near future.

Samples are split quarterly. Discussions of CSSP implementation and statistical analysis of the data occur during the quarterly AMQAW meetings attended by the coordinating agency, field members and lab representatives for each component and the CBP Quality Assurance Officer and the CBP Monitoring Coordinator.

SPLIT SAMPLE COMPONENT PROGRAMS

Chesapeake Bay Coordinated Split Sample Program (See Figure 5)

Coordinating Agency: U.S. EPA Chesapeake Bay Liaison Office
Coordinated Split Sample Program Coordinator: Joe Macknis (800) 523-2281
Technical Program Coordinator: Claudia Walters (800) 523-2281
Data Management Coordinator: Peter Bergstrom, CSC (800) 523-2281
Statistical Analysis Coordinator: Peter Bergstrom, CSC (800) 523-2281

The overall Coordinated Split Sample Program will be coordinated through the Chesapeake Bay Liaison Office (CBLO). Computer Sciences Corporation (CSC) staff at CBLO will have the major responsibility for centralized data management, statistical analysis and reporting on behalf of all the participating agencies and laboratories.

Mainstem/Tidal Tributaries Component (See Figure 6)

Coordinating and Field Sampling Agency: Maryland Department of the Environment
Component Program Coordinator: Bruce Michael

Contact Persons:
Robert Magnien, MDE (301) 631-3680 (MD MONITORING PROGRAMS)
Bruce Michael, MDE (301) 631-3680 (MD MAINSTEM FIELD)
Carolyn Keefe, CBL (301) 326-4281 (MD MAINSTEM LAB)
Sally Bowen, MDE (301) 974-3238 (MD TRIBUTARY FIELD)
Alvin Bober, MD DHMH (301) 225-6200 (MD TRIBUTARY LAB)
Frederick Hoffman, VWCB (804) 367-6683 (VA MONITORING PROGRAMS/VA TRIB FIELD)
Betty Salley, VIMS (804) 642-7213 (VA UPPER MAINSTEM FIELD AND LAB)
Steve Sokolowski, ODU (804) 683-4524 (VA LOWER MAINSTEM FIELD AND LAB)
Norma Roadcap, DCLS (804) 786-4853 (VA TRIBUTARY NUTRIENT LAB)
Robert Potts, DCLS (804) 786-4826 (VA TRIBUTARY CARBON/TSS/BOD LAB)

The Mainstem/Tidal Tributaries Component forms the central core of the Coordinated Split Sample Program, interrelating laboratory and field operations working the Bay tidal mainstem and tributaries. It is the only component that analyzes saline samples. Sampling is performed by a field crew from MDE, currently at Station CB4.4, and before June 1990 at Station CB5.3.

Virginia Mainstem/Tributaries Component (Figure 7)

Coordinating and Field Sampling Agency: Virginia Water Control Board
Component program Coordinator: Frederick Hoffman

Frederick Hoffman, VWCB (804) 367-6683 (VA MONITORING PROGRAMS/VA TRIB FIELD)
Betty Salley, VIMS (804) 642-7213 (VA UPPER MAINSTEM FIELD AND LAB)
Steve Sokolowski, ODU (804) 683-4524 (VA LOWER MAINSTEM FIELD AND LAB)

Figure 5. Chesapeake Bay Coordinated Split Sample Program Components

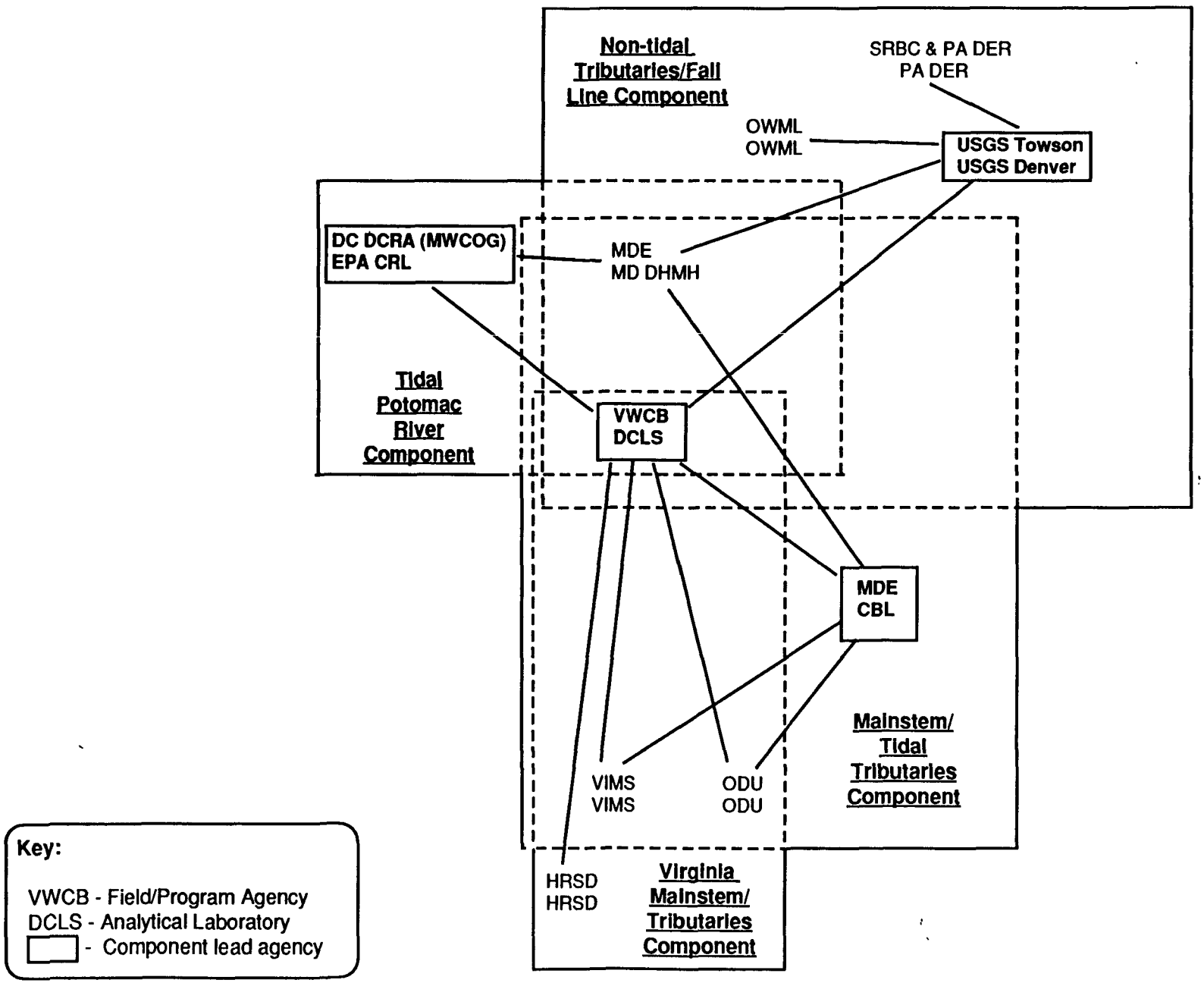
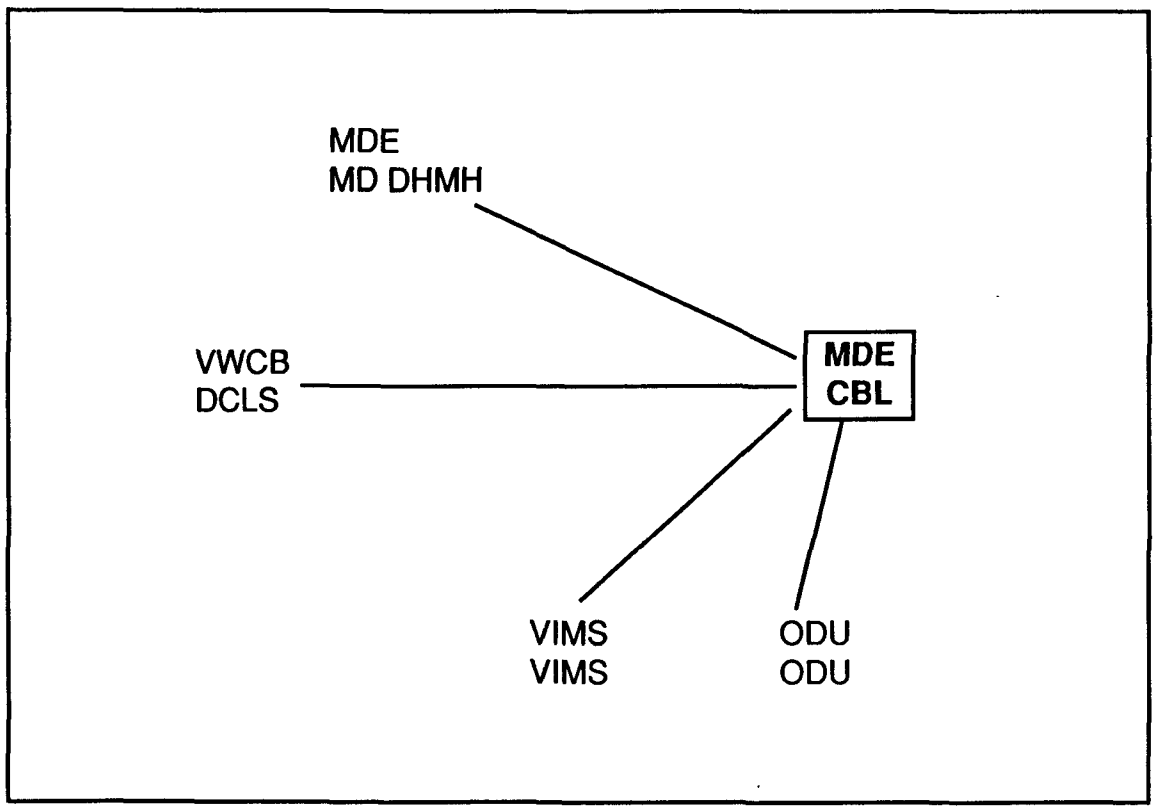


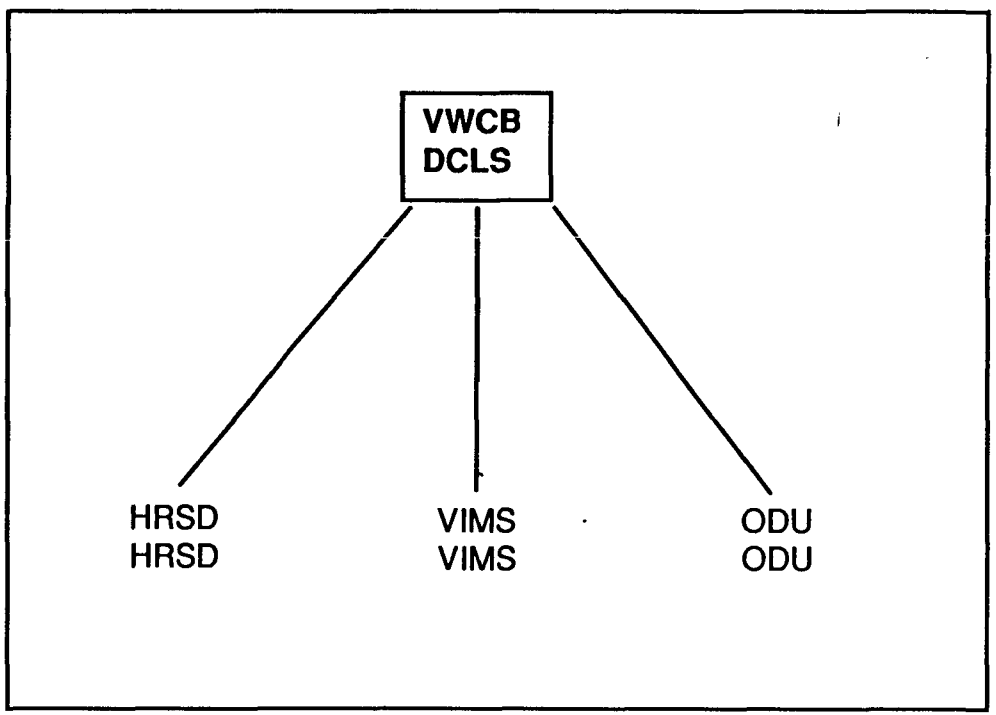
Figure 6. Chesapeake Bay Coordinated Split Sample Program: Mainstem/Tidal Tributaries Component



Key:

MDE - Field/Program Agency
CBL - Analytical Laboratory
□ - Component lead agency

Figure 7. Chesapeake Bay Coordinated Split Sample Program: Virginia Mainstem/Tributaries Component



Key:

HRSD - Field/Program Agency
HRSD - Analytical Laboratory
☐ - Component lead agency

Norma Roadcap, DCLS (804) 786-4853 (VA TRIBUTARY NUTRIENT LAB)
Robert Potts, DCLS (804) 786-4826 (VA TRIBUTARY CARBON/TSS/BOD LAB)
Drew Francis, HRSD (804) 460-2261 (HRSD FIELD AND LAB)

The Virginia Mainstem/Tributaries Component links the field agencies and laboratories involved in sampling the Virginia Chesapeake Bay mainstem and tributaries, building on the existing, routine split sampling program between the Virginia Institute of Marine Science and the Old Dominion University. Sampling is done by a field crew from VWCB at Station TF5.5, in the James River at Hopewell, VA.

Tidal Potomac River Component (Figure 8)

Coordinating Agency: Metropolitan Washington Council of Governments
Component Program Coordinator: Tom An
Field Sampling Agency: DC Department of Consumer and Regulatory Affairs

Contact Persons:
Tom An, MWCOG (202) 962-3366 (POTOMAC COORDINATED MONITORING PROGRAM)
Morris Hennesy, MDE (301) 974-3677 (MD TRIBUTARY PROGRAM)
Sally Bowen, MDE (301) 974-3677 (MD TRIBUTARY FIELD)
Alvin Bober, MD DHMH (301) 225-6200 (MD TRIBUTARY LAB)
Hamid Karimi, DC DCRA (202) 404-1120 (DC MONITORING PROGRAMS)
Sheila Besse, DC DCRA (202) 404-1120 (DC FIELD)
Al Robertson, DC DCRA/CRL (301) 266-9180 (DC LAB)
Frederick Hoffman, VWCB (804) 367-6683 (VA MONITORING PROGRAMS)
Jeff Talbott, VWCB/NRO (703) 490-7352 (VA TRIBUTARY FIELD)
Norma Roadcap, DCLS (804) 786-4853 (VA TRIBUTARY NUTRIENT LAB)
Robert Potts, DCLS (804) 786-4826 (VA TRIBUTARY CARBON/TSS/BOD LAB)

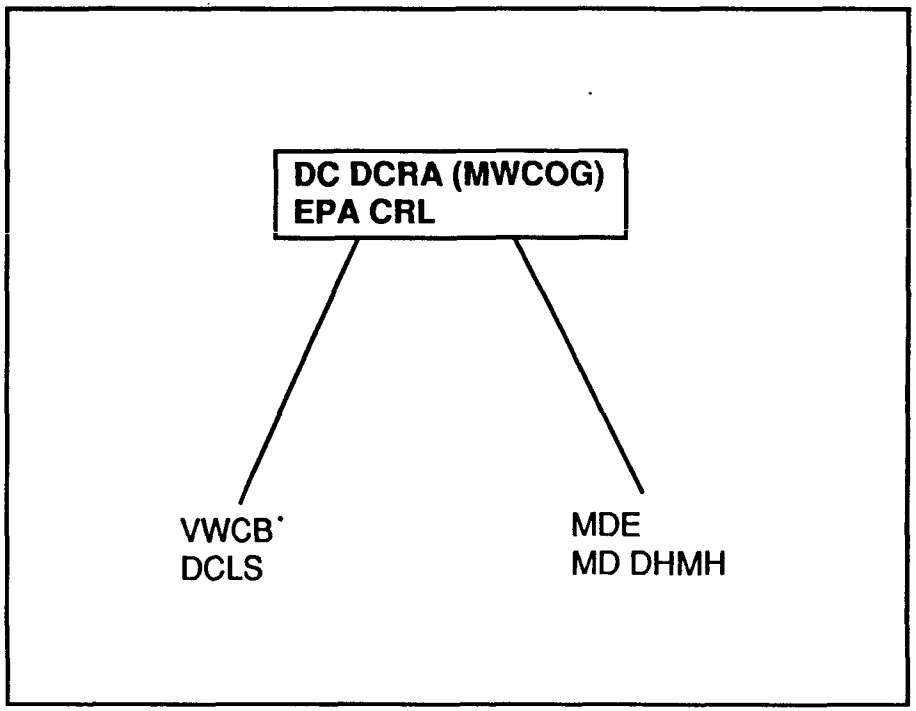
Building upon the existing Potomac Regional Monitoring Program's co-located split sampling program, the laboratories and field agencies involved in sampling the Potomac River are incorporated into the Baywide split sample program through the Tidal Potomac River Component. The samples are collected by a field crew from DCRA at Station PMS-10, at Key Bridge.

Non-tidal Tributaries/Fall-line Component (Figure 9)

Coordinating and Field Sampling Agency: USGS Mid-Atlantic Regional Office
Component Program Coordinator: Joel Blomquist

Contact Persons:
Dwayne Womer, PA DER (717) 787-9637 (PA PROGRAM)
Ken Walizer, PA DER (717) 787-8184 (PA FIELD)
Lynn Schaffer, PA DER (717) 783-1998 (PA LAB)
Bruce Michael, MDE (301) 631-3680 (MD FALL-LINE PROGRAM)
Linda Zynjuk, USGS Towson (301) 828-1535 (MD FALL-LINE FIELD)
Joel Blomquist, USGS Towson (301) 828-1535 (MD FALL-LINE LAB)

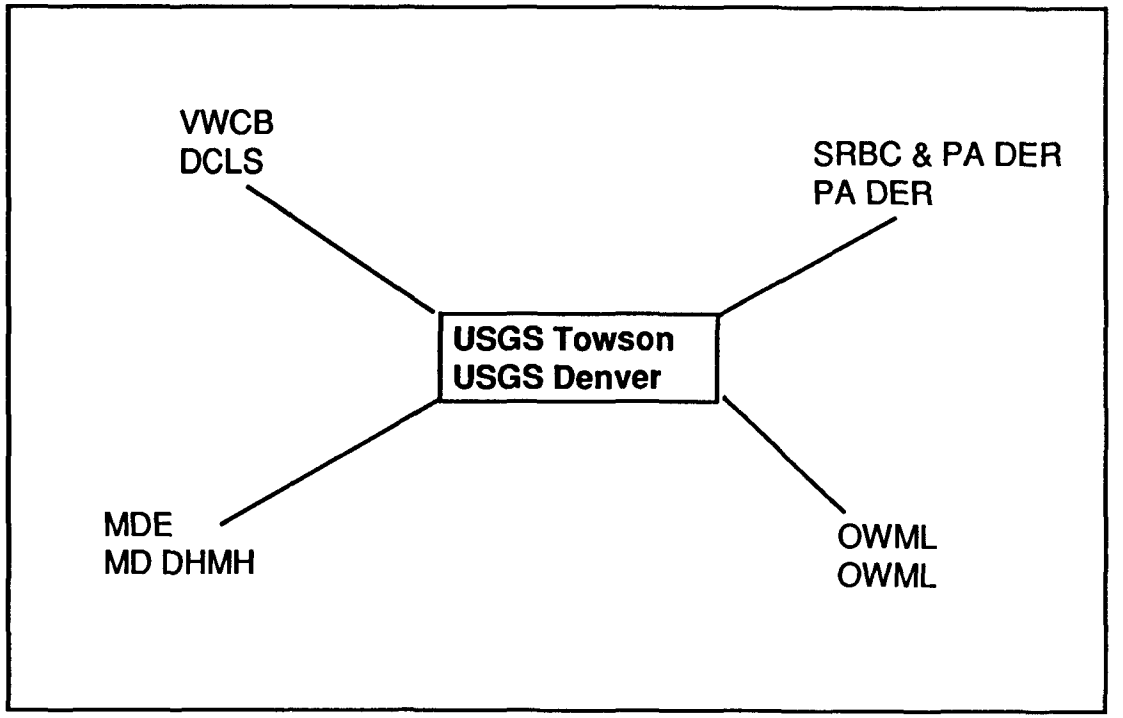
Figure 8. Chesapeake Bay Coordinated Split Sample Program: Tidal Potomac River Component



Key:

VWCB - Field/Program Agency
DCLS - Analytical Laboratory
- Component lead agency

Figure 9. Chesapeake Bay Coordinated Split Sample Program: Non-tidal Tributaries/Fall Line Component



Key:

USGS Towson - Field/Program Agency
USGS Denver - Analytical Laboratory
- Component lead agency

Alvin Bober, MD DHMH (301) 225-6200 (MD TRIBUTARY LAB)
Tom Grizzard, OWML (703) 361-5606 (MD POTOMAC FALL-LINE PROGRAM)
Harold Post, OWML (703) 361-5606 (MD POTOMAC FALL-LINE FIELD)
David Sirois, OWML (703) 361-5606 (MD POTOMAC FALL-LINE LAB)
Frederick Hoffman, VWCB (804) 367-6683 (VA MONITORING PROGRAMS/TRIB FIELD)
Norma Roadcap, DCLS (804) 786-4853 (VA TRIBUTARY NUTRIENT LAB)
Robert Potts, DCLS (804) 786-4826 (VA TRIBUTARY CARBON/TSS/BOD LAB)
Donna Belval, USGS Richmond (804) 771-2427 (VA FALL-LINE FIELD/LAB)

The Non-tidal Tributaries/Fall-line Component links those field agencies and laboratories involved in sampling the fall line stations of all the Chesapeake Bay tributaries. The Susquehanna River Basin Commission's monitoring programs are also linked to this component via the Pennsylvania Department of Environmental Resources laboratory. All samples are collected by a field crew from USGS Towson at the Susquehanna River fall line station (CB1.0) at Conowingo, MD.

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