Chesapeake Bay Coordinated
Split Sample Program
Implementation Guidelines

Revision 4

December 2010
BACKGROUND

The Chesapeake Bay Program has operated the Coordinated Split Sample Program (CSSP) since 1989 to validate water quality data generated by the Chesapeake Bay monitoring programs. The CSSP is an interlaboratory testing program that involves the preparation of identical surface water samples for subsequent analysis at participating state, federal and academic water quality laboratories. Testing is conducted four times a year with both saline and fresh water samples. The analytical results are evaluated quarterly to determine if the laboratories are producing comparable data. Comparable data are important to Chesapeake Bay scientists because they often combine data from a variety of sources and time periods to conduct Bay-wide assessments and modeling applications.

PROGRAM OBJECTIVES

The main objective of the CSSP is to establish a measure of comparability of water quality data generated by the tidal and nontidal monitoring organizations within the Chesapeake Bay Program (CBP). The majority of laboratories that submit water quality data to the CBP participate in the applicable component(s) of the CSSP. A second objective of the CSSP is to evaluate the within-lab bias of each parameter using certified standard reference materials of concentration levels similar to the samples.

Continued implementation of the CSSP provides an on-going, long-term data set that is used for several data quality assessment needs:

1. Allows for quantitative estimates of variance and bias among participants;
2. Qualitative comparisons to facilitate timely identification of analytical problems and significant differences in laboratory techniques; and
3. A means to determine if recommended changes resulted in improved comparability.

Even though the laboratories use similar analytical methods, slight differences in instruments, concentration levels, salinities, etc., may bias the results. The CSSP evaluation process allows field and laboratory personnel to communicate their respective techniques, identify problems and formulate corrective actions. As a result, the CSSP has improved the uniformity and reproducibility of field and laboratory methods.

PROGRAM DESIGN CONSIDERATIONS

The original design of the CSSP is documented in the Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines CBP/TRS 58/91, May 1991. Basically, three subsamples were analyzed by each laboratory and the non-parametric Friedman test was used to estimate differences. In 1999, the Analytical Methods and Quality Assurance Workgroup (AMQAW) slightly changed the design so that the day-to-day variance within an individual lab could be compared to the variance between labs using an Analysis of Variance (ANOVA) model. At least three laboratories are needed for a statistical analysis of the results because this is the
minimum number required to run ANOVA tests. If only two laboratories participate, comparable results can be obtained using a paired t-test.

Currently there are two CSSP components: 1) Mainstem Chesapeake Bay and 2) Tributary (Potomac River). For the Mainstem component, a large saline sample is collected at station CB 4.4C, a mesohaline station in the Chesapeake Bay. Four replicates per lab are dispensed and provided to those laboratories who routinely analyze mainstem and tidal tributary samples.

For the Tributary component, a large fresh water sample is collected at station PMS10, a tidal fresh station in the Potomac River. Three replicates per lab are dispensed and provided to those laboratories that routinely analyze Nontidal and River Input samples. A third component covering the River Input Monitoring programs was discontinued in 2004 when it was realized that the same participation of nontidal laboratories could be achieved by adding the Pennsylvania State Laboratory and the USGS National Water Quality Laboratory to the Tributary component.

CSSP field split samples are prepared by taking three or four replicate subsamples from one large whole water sample to eliminate environmental variability. Subsamples are processed (i.e., filtered) by each monitoring agency, and then delivered to each lab for analysis. Individual CSSP sample results includes potential errors from steps performed after the collection of the large whole water sample, including errors associated with the sub-sampling procedure, sample processing, handling, preservation, shipment, storage, analysis and data processing. The order of dispensing the sub-samples permits the detection of a consistent bias between the first and last sets dispensed. Generally, the sub-sampling error is assumed to be negligible and that the replicate CSSP results provide an estimate of each monitoring program’s sample processing and analytical variability. When compared to the results of other laboratories, the split samples provide an estimate of the relative bias among monitoring programs with respect to processing and analytical protocols.

The three or four replicates provide an estimate of the variability within each field/laboratory operation, which may be statistically compared to the variability between other field/laboratory operations. Concurrent laboratory spike analyses are performed to detect interferences that may contribute to the bias between labs. Similarly, analyses of certified standard reference materials are performed to demonstrate that the analytical system was in control and that the analytical system was capable of producing accurate data.

**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 the lead agency are as follows:

1. Maintains contact with all the participating field and lab organizations to coordinate all logistics.
2. Provides for the necessary sampling equipment, sample containers, labels, chain of custody paperwork, etc. at the time of the quarterly split sample collection.

3. Collects the sample and prepare the splits according to the protocol described within this document.

4. Arranges 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, temperature, 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.

**Reporting and Data Management Responsibilities**

The routine submission of split sample data is the responsibility of each individual laboratory or agency. The CBP Water Quality Data Manager is the designated recipient of all data generated through the CSSP. The Data Manager uploads the data into a stand-alone, Microsoft Access® database. S/he is responsible for the processing, routine statistical analysis, report development, and timely distribution of results back to the participating laboratories and agencies.

**Coordinated Split Sample Program Oversight Responsibilities**

The Chesapeake Bay Program Office (CBPO) is responsible for overall coordination of the CSSP. The CBP Quality Assurance (QA) Coordinator ensures that participants report the samples and parameters appropriate for their monitoring program. S/he may assist the participating organizations with logistical and technical problems that cannot be resolved by the coordinating organizations. The CBPO Project Officer or QA Officer may assist in these matters as needed. Quarterly results of the CSSP are posted to the AMQAW web page of the CBP website at the CBPO.

The CBP QA Coordinator reviews and evaluates the results of each split sampling event and consults with the appropriate individuals in each organization to determine the appropriate response to any significant findings.
SPLIT SAMPLE COLLECTION AND PROCESSING PROTOCOLS

The overall goal of preparing replicate sub-samples is to generate samples that are as identical as possible. The sampling crews fill a large vessel such as a carboy with water according to normal sample handling protocol (e.g., submersible pump). They continuously mix the water in the vessel to ensure that the sample is uniformly mixed and that the sub-samples are representative. This may be accomplished with a stir bar arrangement or other form of mechanical mixing as long as a vortex is created. Mixing must continue for the duration of the splitting operation. When 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. Detailed procedures used by the lead CSSP sampling organization for sample collection, stirring and splitting are described below.

Mainstem Split Sample Collection Procedure

Maryland Department of Natural Resources field staff collects a single large sample from station CB4.4C in the Chesapeake Bay. Water is collected with a submersible pump into a 30 gallon Nalgene® carboy. One person continuously stirs the sample with a paint stirrer turned by an electric drill, while a second person dispenses one-gallon subsamples from the bottom spigot into pre-rinsed and labeled containers. Five subsamples are collected for each lab (Lab A, Lab B, etc). A fifth sub-sample is provided as an extra sample in case of accident. Replicate subsamples are collected in the following sequence to permit detection of a consistent bias between the first and last sets dispensed, presumably due to incomplete mixing.

Replicates A1, B1, C1, D1, E1, F1, then
Replicates A2, B2, C2, D2, E2, F2, then
Replicates A3, B3, C3, D3, E3, F3, then
Replicates A4, B4, C4, D4, E4, F4, then
Replicates A5, B5, C5, D5, E5, and F5.

Replicates are immediately placed into ice chests and transported the same day to the laboratories at 4°C. A custody log (Figure 3) is filled out and sent with each group of samples. Replicates are grouped and labeled according to participant as follows:

“A” Replicates (A1 – A5): Extra set of split samples for Virginia labs
“B” Replicates (B1 – B5): Old Dominion University Water Quality Laboratory (ODU)
“C” Replicates (C1 – C5): University of Maryland Chesapeake Biological Lab (CBL)
“D” Replicates (D1 – D5): Virginia Division of Consolidated Laboratory Services (DCLS)
“E” Replicates (E1 – E5): Virginia Institute of Marine Science (VIMS)
**Tributary Split Sample Collection Procedure**

Field staff from the District of Columbia Department of Environment’s Water Quality Division collects and prepares samples for the CSSP Tributary Component. They collect samples at the tidal fresh station PMS-10 (Potomac R., east side of the Key Bridge), by dipping five 5-gallon carboys just below the surface of the water. The carboys are left at Thompson Boathouse ramp where they are retrieved by the split sample preparer and transported to the Blue Plains WWTP facility. Here the grab samples are composited into a 15-gallon cylindrical tank. The water is manually mixed with an 18-inch paddle and subsamples are drawn from a spigot at the bottom of the tank. Three replicates for each laboratory are dispensed in a rotational succession as depicted in Figure 1. Containers are pre-labeled and filled in the following order:

- **MD** (A1; A2; A3) University of Maryland Chesapeake Biological Laboratory (CBL) & Maryland Department of Health and Mental Hygiene (DHMH)
- **VA** (B1; B2; B3) Virginia Department of Consolidated Laboratory Services (DCLS)
- **DC** (C1; C2; C3) District of Columbia Department of Environment
- **FCDPW** (D1; D2; D3) Fairfax County Department of Public Works
- **ODU** (E1; E2; E3) Old Dominion University Water Chemistry Laboratory
- **OL** (F1; F2; F3) Occoquan Watershed Monitoring Lab (VPI-OWML)
- **VIMS** (G1; G2; G3) Virginia Institute of Marine Science
- **USGS** (H1; H2; H3) USGS National Water Quality Laboratory (NWQL)
- **SRBC** (I1; I2; I3) Pennsylvania Department of Environmental Protection Bureau of Laboratories (PADEP)

Samples are placed in an ice chest after each set is finished. Chain of custody sheets for each transfer of samples are prepared and signed. State and federal agencies personnel pick up samples at Blue Plains Wastewater Treatment Plant by 12 pm, using chain of custody procedures.

Samples are delivered as rapidly as possible to permit sample processing by the next day. Normal sample processing, 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.
Figure 1. Example of Sequential Field Split Sample Dispensing Order
(3 replicates per lab depicted)

NOTE: The order of dispensing and the provision for adequate stirring during the split sample preparation are both very important. Be certain to document and follow the procedures used.
LABORATORY HANDLING AND ANALYSIS PROTOCOLS

Samples are analyzed for the parameters listed in Table 1, within the maximum holding times. If there are parameters a lab does not routinely measure, those parameters do not need to be analyzed and reported solely for the purpose of the CSSP unless specific parameters are requested for comparison to results from other laboratories in the component.

Samples are analyzed as soon as possible after arrival at the laboratory to minimize holding time effects. In the mainstem component, participants have agreed to filter the samples on the morning after collection at approximately 8:00 a.m. This may not be possible if samples are delivered by mail. Participants in each component should discuss and agree on when samples will be delivered and analyzed.

Mainstem Split Sample Analysis Procedure

1. Filter all four replicate samples the day after collection, before 8:00 a.m. Prepare and store the split samples exactly the same as routine samples. If two replicates are analyzed the day they are received, freeze the other two.

2. Analyze two of four replicate samples on one day and the remaining two replicates on a different day, within parameter holding times. If a holding time is exceeded, state this as a comment on the data report.

3. For dissolved parameters, spike one of the two replicate samples on one analysis day. If there is sufficient sample volume, analyze a lab duplicate on each day also.

4. Analyze a certified standard reference material (SRM) on each analysis day. It is preferable that the SRM be of similar concentration as the samples. However, if dilution is necessary then deionized water should be used. An additional SRM diluted with artificial seawater may be analyzed if that is the routine standard operating procedure.

A complete schematic of the operational flow of analyses is outlined in Figure 2. Within the laboratory, at least one of the four replicate subsamples is subjected to the normal quality control (QC) routine. If a duplicate and spike sample are analyzed every tenth analysis, the replicate identified for QC may be analyzed as a routine quality control sample. One or more replicates is duplicated and spiked with the appropriate standard. If the laboratory elects to run duplicates and spikes on more than one replicate subsample, all QC results are to be reported.

It is essential that supporting quality control data are available for each laboratory to establish their system’s performance. In the event that significant inter-laboratory differences are found, the QC data will help determine the reason for the discrepancies. Precision and accuracy determined through the analysis of the sub-samples may be compared to the routine precision and accuracy limits of the laboratory. The SRM provides an independent evaluation of laboratory bias and is essential for any diagnostic efforts associated with the Coordinated Split Sample Program.
Figure 2. Operational Flow of Analyses for Coordinated Split Sample Program

3 or 4 Subsamples per Lab

Normal Lab QC Procedures

Lab Duplicates

1-A
Analyze for Routine Parameters

Lab Spike Sample

% Recovery (Interference estimate)

1-B
Analyze for Routine Parameters

SRM

Analyze SRM Parameters (Bias estimate)

2nd Analysis Day
(Mainstem Split only)

Normal Lab QC Procedures

Lab Duplicates

3-A
Analyze for Routine Parameters

Lab Spike Sample

% Recovery

3-B
Analyze SRM Parameters

SRM

Laboratory QC
Table 1. Parameters, Method Codes, Maximum Holding Times & Temperatures

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter Code</th>
<th>Holding Time (days)</th>
<th>Hold Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total phosphorus as P</td>
<td>TP</td>
<td>28</td>
<td>–</td>
</tr>
<tr>
<td>Total dissolved phosphorus as P</td>
<td>TDP</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Particulate phosphorus as P</td>
<td>PP</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Dissolved orthophosphate as P</td>
<td>PO4F</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Total nitrogen as N</td>
<td>TN</td>
<td>28</td>
<td>–</td>
</tr>
<tr>
<td>Total dissolved nitrogen as N</td>
<td>TDN</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Particulate nitrogen as N</td>
<td>PN</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Total Kjeldahl nitrogen as N</td>
<td>TKNW</td>
<td>28</td>
<td>–</td>
</tr>
<tr>
<td>Dissolved Kjeldahl nitrogen as N</td>
<td>TKNF</td>
<td>28</td>
<td>–</td>
</tr>
<tr>
<td>Ammonium as N (filtered)</td>
<td>NH4F</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>NO2 + NO3 as N (filtered)</td>
<td>NO23F</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Nitrite as N (filtered)</td>
<td>NO2F</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Total organic carbon</td>
<td>TOC</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Dissolved organic carbon</td>
<td>DOC</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Particulate carbon</td>
<td>PC</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Silica as Si (filtered)</td>
<td>SI</td>
<td>28</td>
<td>4</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>TSS</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Fixed suspended solids</td>
<td>FSS</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Chlorophyll a (μg/L)</td>
<td>CHLA</td>
<td>28</td>
<td>-20</td>
</tr>
<tr>
<td>Pheophytin (μg/L)</td>
<td>PHEO</td>
<td>28</td>
<td>-20</td>
</tr>
</tbody>
</table>

Table 1 Notes:

1. Laboratories analyze parameters that are routinely measured; only directly-measured parameters are report. If calculations are needed, the WQ Data Manager performs the calculations within the CSSP database.

2. Deviations from maximum holding time or temperature are reported with the data.

3. Samples are processed into particulate and/or dissolved fractions prior to freezing.

4. Several agencies process and freeze the tributary split samples as they do the mainstem samples. (ODU, DCLS, CBL, and DHMH)
Figure 3.

Split Sample Custody Log Example:

MAIN BAY SPLIT SAMPLE CUSTOM LOG

LOCATION: CB4.4

BOTTLE NUMBERS: C1, C2, C3, C4

COLLECTED FOR: CB1

COLLECTION DETAILS: DATE: _______ TIME: _______ DEPTH: 0.5 M SALINITY: _______ PPT

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

SPLITTING DETAILS:

COMPOSITE CONTAINER: sequential bottles

FILLED BY: submersible pump @ 0.5 m into a 30 gallon Nalgene container

<table>
<thead>
<tr>
<th>Splitting Seq.</th>
<th>Bottle #</th>
<th>Splitting Seq.</th>
<th>Bottle #</th>
<th>Splitting Seq.</th>
<th>Bottle #</th>
</tr>
</thead>
<tbody>
<tr>
<td>bottle 1-</td>
<td>A1 EXTRA VA</td>
<td>bottle 9-</td>
<td>C2 CEL</td>
<td>bottle 17-</td>
<td>E3 MSU</td>
</tr>
<tr>
<td>bottle 2-</td>
<td>B1 ODU</td>
<td>bottle 10-</td>
<td>D2 VADCLS</td>
<td>bottle 18-</td>
<td>F3 VIMS</td>
</tr>
<tr>
<td>bottle 3-</td>
<td>C1 CEL</td>
<td>bottle 11-</td>
<td>E2 MSU</td>
<td>bottle 19-</td>
<td>N4 EXTRA VA</td>
</tr>
<tr>
<td>bottle 4-</td>
<td>D1 VADCLS</td>
<td>bottle 12-</td>
<td>F2 VIMS</td>
<td>bottle 20-</td>
<td>B4 ODU</td>
</tr>
<tr>
<td>bottle 5-</td>
<td>E1 MSU</td>
<td>bottle 13-</td>
<td>A3 EXTRA VA</td>
<td>bottle 21-</td>
<td>C4 CEL</td>
</tr>
<tr>
<td>bottle 6-</td>
<td>F1 VIMS</td>
<td>bottle 14-</td>
<td>B3 ODU</td>
<td>bottle 22-</td>
<td>D4 VADCLS</td>
</tr>
<tr>
<td>bottle 7-</td>
<td>A2 EXTRA VA</td>
<td>bottle 15-</td>
<td>C3 CEL</td>
<td>bottle 23-</td>
<td>E4 MSU</td>
</tr>
<tr>
<td>bottle 8-</td>
<td>B2 ODU</td>
<td>bottle 16-</td>
<td>D3 VADCLS</td>
<td>bottle 24-</td>
<td>F4 VIMS</td>
</tr>
</tbody>
</table>

TRANSFER SEQUENCE:

Composite collected
6 split

DATE TIME BY WHOM

TEMP. OF SAMPLE (circle one)

ambient

Subsample picked up

DATE TIME BY WHOM

0°C 4°C ambient

Subsamples delivered to lab

DATE TIME BY WHOM

0°C 4°C ambient

FIELD PROCESSING INFORMATION

BOTTLE # FIELD PROCESSING DONE DATE/TIME BY WHOM

C1 processed sample #

C2 processed sample #

C3 processed sample #

C4 processed sample #

NOTE: PLEASE SEND A COPY OF THIS COMPLETED FORM TO:
Maryland Dept of Natural Resources, TEA/D=2, 580 Taylor Avenue, Annapolis, MD, 21401, (410) 260-8629.
DATA MANAGEMENT AND REPORTING PROTOCOLS

Data Submission

Laboratories are asked to provide the CSSP results to the CBP WQ Data Manager in an Excel spreadsheet with the format displayed in Table 2. It is important to use the exact parameter names from Table 1. Definitions and descriptions of the headers for this spreadsheet are listed in Table 3. Data from all participants are merged into a single Excel spreadsheet file to streamline transfer of the data into the Access database.

Table 2. Sample data set submission format for CSSP data

<table>
<thead>
<tr>
<th>Lab</th>
<th>Cruise Date</th>
<th>Station</th>
<th>Rep Type</th>
<th>Rep Subsamp</th>
<th>Rep No</th>
<th>Parameter</th>
<th>Sample Conc</th>
<th>Spike Conc</th>
<th>Sample + Spike</th>
<th>% Spike Recovery</th>
<th>SRM</th>
<th>SRM DE</th>
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<tbody>
<tr>
<td>ODU</td>
<td>11-Feb-10</td>
<td>MCB4.4</td>
<td>SPLIT</td>
<td>1</td>
<td>1</td>
<td>TDN</td>
<td>0.660</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td>11-Feb-10</td>
<td>MCB4.4</td>
<td>SPLIT</td>
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<td>1</td>
<td>TDN</td>
<td>0.657</td>
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<td></td>
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<td>MCB4.4</td>
<td>SPLIT</td>
<td>3</td>
<td>1</td>
<td>TDN</td>
<td>0.653</td>
<td></td>
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<td>2</td>
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<td>MCB4.4</td>
<td>SPLIT</td>
<td>4</td>
<td>1</td>
<td>TDN</td>
<td>0.646</td>
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<td>SPK</td>
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<td>1</td>
<td>TDN</td>
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<td>0.4</td>
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<td>TDN</td>
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<td>1.027</td>
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Table 3. Header names and definitions

<table>
<thead>
<tr>
<th>Header</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab</td>
<td>The abbreviation for the analytical laboratory (DCLS, CBL, etc.)</td>
</tr>
<tr>
<td>CruiseDate</td>
<td>The sample date in the format MM/DD/YYYY</td>
</tr>
<tr>
<td>Station</td>
<td>The sampling station number (either MCB4.4 or PMS10)</td>
</tr>
<tr>
<td>SDensity</td>
<td>Depth of sample collection: 0.5 m for Mainstem or 1.0 m for Tributary CSSP</td>
</tr>
<tr>
<td>Layer</td>
<td>Water column layer where sample collected; typically “S”</td>
</tr>
<tr>
<td>RepType</td>
<td>Either SPLIT, SPK or SRM</td>
</tr>
<tr>
<td>Subsamp</td>
<td>The field replicate subsample number. Mainstem CSSP replicates are numbered 1, 2, 3 and 4. Tributary replicate subsamples are numbered 1, 2 and 3.</td>
</tr>
<tr>
<td><strong>RepNo</strong></td>
<td>It indicates the <strong>Lab</strong> replicate number (usually 1 or 2) just as it does in other CBP submissions. Report all replicates analyzed.</td>
</tr>
<tr>
<td><strong>Parameter</strong></td>
<td>The abbreviation for the parameter name (see Table 1)</td>
</tr>
<tr>
<td><strong>SampleConc</strong></td>
<td>The concentration for each subsample. Calculate and report the results the way you normally report them to the CBP.</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td>This field is no longer relevant</td>
</tr>
<tr>
<td><strong>SpikeConc</strong></td>
<td>The amount of spike added. This value will be added to the <strong>Sample Conc</strong> in that row to get the theoretical total concentration used for calculation of percent recovery.</td>
</tr>
<tr>
<td><strong>Sample+Spike</strong></td>
<td>The total concentration of the sample, including the spike added.</td>
</tr>
<tr>
<td><strong>% SpikeRecovery</strong></td>
<td>Percentage of calculated spike + sample from measured spike + sample</td>
</tr>
<tr>
<td><strong>SRMEPA</strong></td>
<td>The known certified value for the Standard Reference Material. The SRM results can be put in any row for that parameter. Provide a copy of the supplier’s “Answer Sheet” that comes with each SRM.</td>
</tr>
<tr>
<td><strong>SRMDE</strong></td>
<td>The <strong>Lab</strong> value for the SRM. If dilution was necessary, list the dilution used in the comments section or in the data report.</td>
</tr>
<tr>
<td><strong>Err</strong></td>
<td>Lab or field error reported with the sample</td>
</tr>
</tbody>
</table>

### Data verification

CSSP data are reported quarterly and compiled by the Water Quality Data Manager. S/he contacts data submitters as soon as possible after receipt of the CSSP data if there appear to be any errors, omissions or outliers in the data set. After plotting the data, the Water Quality Data Manager sends the graphical results to the laboratories for a preliminary review so that errors may be investigated prior to meeting with AMQAW.
DATA ANALYSES AND INTERPRETATION

Graphical Analyses

For each parameter, MS Excel formulas are applied to calculate the mean of the three or four replicate subsamples. Within-organization variability is determined by calculating the standard error of the three or four replicate subsamples for each sampling date. The mean concentration for each lab is then plotted on a Date vs. Concentration plot, with error bars based on the standard error. Figure 4 is an example plot for Mainstem TSS results. Note that the Method Limit (calculated as 10 standard deviations from the mean of 7 lab replicates) for each laboratory is shown as a solid bar in the corresponding color. The Method Limit is the number above which the laboratory’s concentrations are expected to have relative precision of ten percent or better. Values below the Method Limit have lower relative precision and are interpreted accordingly.

![Mainstem TSS Split Sample Data](image)

Statistical Analyses

Although statistical analyses are not routinely performed on the split sample results, the following method is recommended if quantitative comparisons are necessary. The statistical analysis employs an Analysis of Variance (ANOVA) that quantifies two levels of innovations that may be present in these data. This approach was developed in 1998 by Dr. Elgin Perry to improve upon the Friedman test. Dr. Perry observed that there are two levels at which random
factors can affect the data. The variance among a laboratory’s subsamples is one level and if there is not a systematic trend from the first to the last of the subsamples, then it is assumed that they differ only by within-lab measurement error. However, this level of measurement error may underestimate the true within-lab variance if all subsamples are processed on the same day or the same run, when some sources of within-lab variance that might be attributed to changes in temperature, humidity, and recalibration would not have an opportunity to differentially affect the subsamples. A better measure of the day-to-day within-lab variance is obtained through the lab*date interaction. As long as each lab always uses the same method, then differences among labs should be constant if they are biased with respect to one another. The degree to which these differences are not constant (measured by lab*date interaction in an ANOVA) reflects the random factors operating day to day within each lab.

This model allows the flexibility to accommodate the Date blocking and the subsample blocking in the same model whereas the non-parametric Friedman test allows for blocking at only one level. In addition, one can compare the differences among labs to the subsampling variance and the day-to-day variance to determine the significance of lab differences. Because of these advantages, the ANOVA procedure was recommended over the Friedman procedure even though the ANOVA requires more checking of distributional assumptions. Dr. Perry developed an ANOVA model using the SAS GLM procedure, and suggested the following interpretations.

1. Type III SS tests are used to assess the variance due to each potential error source vs. the sub-sampling error. If the date*lab term is significant, this implies that there were random factors other than within-day measurement error affecting the results.

2. Least Squares Means using the DATE*LAB error term are used to compare the lab effect to the date*lab interaction. Non-significance here suggests that the long-term averages of differences among labs are not significant when compared to the inconsistency within labs over time.

3. Student-Newman-Keuls tests
   a. Tests for variable means differences vs. the subsampling error (means date rep lab/snk)
   b. Lab differences vs. the interaction error; (means lab/snk e=lab*date)
   c. Looks on a date-by-date basis to see which labs differ (lsmeans lab*date/pdiff) output out=res r=rlnptd
   d. Checks the equal variances assumption, which also shows labs with greatest within-lab variance.

4. Checking Assumptions
   a. Normality assumption is examined using normal probability plots and Shapiro-Wilk test.
   b. Equal variances assumption is checked using Levene's test, which also showed labs with greatest within-lab variance.
Accuracy data from percent recoveries and SRM analyses are reported but are not the subject of statistical tests. These data are used to supplement the split sample results and for diagnostic purposes during investigations of significant inter-organizational differences. SRMs analyzed after dilution are reported as the diluted value, with the expected (diluted) value used.

COORDINATED SPLIT SAMPLE PROGRAM CONTACTS

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Mainstem Component

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REFERENCES


Chesapeake Bay Program. 1989. Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines, Revision 2. EPA Chesapeake Bay Program, Annapolis, MD.
