APPENDIX A. QUALITY ASSURANCE RESULTS

A1. QUALITY ASSURANCE/QUALITY CONTROL METHODS

The section summarizes the methods used to meet the objectives of the San Diego Reference Stream study, including sampling procedures, laboratory analysis, and Quality Assurance/ Quality Control (QA/QC) procedures. Data collected as part of the research study was required to be compatible with the SWAMP quality assurance standards. This required an additional 10 to 15% of samples collected for field and laboratory quality assurance samples.

Field QA/QC samples were used to evaluate potential contamination and sampling error occurring during sample collection. Field QA/QC processes included equipment calibration, field protocols to meet analytical holding times, field duplicates (FD), and field blanks (FB). Laboratory QA/QC samples were used to evaluate the analytical process for contamination, accuracy, and reproducibility. Internal laboratory quality control checks included procedural blanks, blank spikes (BS), matrix spike/matrix spike duplicate (MS/MSDs), and duplicates.

A1.1 Field Equipment Verification and Sampling Procedures

This section discusses the calibration, inspection, and maintenance requirements of the equipment used in the San Diego Reference Stream monitoring effort, as well as the requirements governing sampling procedures for the program.

A1.1.1 Field Equipment Calibration, Inspection, and Maintenance

QA/QC activities for the monitoring equipment included calibration, inspection, and maintenance procedures. Table A1-1 summarizes the equipment used in the San Diego Reference Stream study and the required frequency of calibration, inspection, and/or maintenance of the equipment.

Continuous monitoring of stream flow via a HOBO® Water Quality Data Logger required monthly downloading of 15 min recorded measured data. Calibration activities were conducted monthly, including flow-validation measurements, stream level offset checks, and maintenance activities on an as-needed basis. Data validation or correction activities were conducted to maintain consistent flow measurements.

American Sigma and Marsh-McBirney flow meters, YSI Pro Plus multi-parameter probe (i.e. conductivity, dissolved oxygen, pH, salinity, temperature), and rain gauges used to collect composite and pollutograph samples were required to be calibrated semi-annually or as-needed based on inspections.

Table A1-1: Calibration, Inspection, and Maintenance Schedule of Field Equipment

Equipment	Activity[a]	Responsible Entity	Frequency	SOP Reference
YSI Pro Plus multi-parameter water quality probe	Calibration	SCWRPP Technical Staff	Daily, before use	YSI Pro Plus Series Instruments SOP
Freshwater HOBO Water Level Data Logger (30 ft)	Downloading Data	AMEC Technical Staff	Monthly	HOBO Water Level Manual
American Sigma 950 AVB and Marsh-McBirneyFlowmeters	Inspection,calibration, and maintenance	AMEC and SCCWRP Technical Staff	Semi-annually	American Sigma 950 OM Manual AS009 Marsh-McBirney Manual
American Sigma RainGauge	Inspection,calibration, and maintenance	AMEC Technical Staff	Semi-annually	NA

[a]Activity: Inspection, calibration, or maintenance activity.

A1.1.2 Sampling Procedures

Holding Time Requirements

Holding time requirements were established as part of the analytical methods and required samples to be analyzed within a specified time. Samples were preserved, packaged, and transported within the designated holding times per the method requirements provided in Table A1-2. Specific protocols were required to meet the holding time requirements of the following constituents:

- E. coli, Enterococcus, fecal coliform, and total coliform – Samples were required to be kept in the dark and delivered to the laboratory within six hours (analyzed within eight hours) of the sample collection time.
- Ammonium, dissolved inorganic nitrogen (DIN), dissolved organic carbon (DOC), nitrate+nitrite, nitrite, particulate nitrate (PN), particulate organic carbon (POC), particulate phosphate (PP), total nitrogen (TN), total phosphorus (TP), total dissolved nitrogen (TDN), and total dissolved phosphorus (TDP) – Samples were required to be filtered and frozen within six hours of the sample collection time to provide laboratories with a 28-day holding time.

All measured constituents were analyzed within their holding time requirements except for the following constituents. Five alkalinity and hardness samples, representing 2% of the dry weather collected samples, were analyzed passed their holding time requirements. Six wet weather bacteria and nutrient samples exceeded holding time requirements. In addition six wet weather

filtered nutrient samples (DIN, DOC, TDN/TDP, PN, POC, and PP) were lost in transit (1.5% of filtered samples) after being shipped to the University of Maryland Center for Environmental Science (UMCES) laboratory for analyses and were considered potentially compromised.

Table A1-2: Sample Handling and Custody

Parameter	Container	Volume	Initial Preservation	Holding Time
Alkalinity (Total Alkalinity as $CaCO_3$)	Polyethylene Bottle	(4) 1000 ml	Cool to 6°C and store in the dark	14 days
Chloride				28 days
Hardness (Total Hardness as $CaCO_3$)				6 months
Sulfate				28 days
TDS				7 days
TSS				7 days
Enterococcus	Factory-sealed, pre-sterilized, 125 ml sterile plastic (Pre-sterilized, High density polyethylene or polypropylene container)	1000 ml	Cool to 6°C in the dark[(b)]	8 hours[(a)]
E. coli				
Fecal Coliform				
Total Coliform				
Bacteroides				
M. smithii				
Bacteria community analysis				
Nitrate + Nitrite (as N)	Polyethylene Bottles	(3) 500 ml	Cool to 4°C, store in the dark, filter and freeze at -20°C	48 hours; 28 days if frozen
Ammonia (as N)				48 hours; 28 days frozen
Total Kjeldahl Nitrogen (TKN)			Cool to 4°C and store in the dark. Acidify with H2SO4 to pH<2	7 days or 28 days if acidified or frozen
Total Dissolved Nitrogen	Polyethylene Bottles	(1) 500 ml	Cool to 4°C and store in the dark, filter and freeze at -20°C	28 days if frozen
Orthophosphate (dissolved; Soluble Reactive Phosphorus)	Polyethylene Bottles	(1) 500 ml	Cool to 4°C and store in the dark	48 hours
Total Phosphorus (as P) or TDP				28 days
Particulate Nitrogen and Carbon (PN, POC)	Plastic Petri Dishes	20-60 ml	Keep at 4°C, dark, but must filter within 24 hrs, freeze until dried	12 months after drying at 80°C for 24 hours
Particulate Phosphorus (PP)	Plastic Petri Dishes	20-60 ml	Keep at 4°C, dark, but must filter within 24 hrs, freeze until dried	12 months after drying at 80°C for 24 hours
Dissolved Organic Carbon (DOC)	40-ml glass vial	40 ml	Cool to 6°C and store in the dark	28 days

Table A1-2: (Continued)

Parameter	Container	Volume	Initial Preservation	Holding Time
Cadmium (Total)	Acid-cleaned polyethylene bottle	500 ml	Cool to 6°C in the dark; Acidify to pH<2 with pre-tested HNO_3 within 48 hours	6 months at room temperature following acidification
Chromium (Total)				
Copper (Total)				
Iron (Total)				
Lead (Total)				
Manganese (Total)				
Nickel (Total)				
Selenium (Total)				
Zinc (Total)				
[b]Cadmium (Dissolved)	Acid-cleaned polyethylene bottle	500 ml	Filter within 8 hours of collection[(a)]; Cool to 6°C in the dark; Acidify to pH<2 with pre-tested HNO_3 within 48 hours	6 months at room temperature after filtration and/or acidification
Chromium (Dissolved)				
Copper (Dissolved)				
Iron (Dissolved)				
Lead (Dissolved)				
Manganese (Dissolved)				
Nickel (Dissolved)				
Selenium (Dissolved)				
Zinc (Dissolved)				

(a) Eight hours to analyze fecal indicator bacteria and eight hours to filter for the microbial source testing samples.

(b) Filtration of dissolved metals will be conducted by the laboratory within 8 hours of sample collection.

Broken Sample Containers

Sample handling and delivery protocols were established to make sure samples were received intact by the laboratory for analysis; however, sample containers occasionally break during sample collection, handling, or delivery. To account for the possibility of broken sample containers, a 90% level of completeness requirement was established.

Field Duplicates

Field duplicates were utilized as part of a QA/QC program to assess sampling precision. The project goal for field duplicates was one for every 10 samples collected per sample type per reference stream. Field duplicate collection procedure requirements for the San Diego Reference Stream study were established as being the same as those used for the collection of standard field samples. Duplicates of manual grab samples were collected by filling two grab sample containers at the same time or in rapid sequence. Sample containers for duplicate samples were labeled, but were not identified as duplicates to the laboratories.

Duplicate results were evaluated by calculating the RPD between the two sets of results, which served as a measure of the reproducibility (precision) of the sample results. The acceptable ARPD limits are shown in Table A1-3 below. The RPD was calculated as follows:

Equation 1: RPD = 100 x (sample 1 - sample 2) / ((sample 1 + sample 2)/2) **Eq. 1**

A1.1.2 Laboratory Analysis Quality Control Procedures

Laboratory Duplicates

Laboratory duplicates were utilized as part of a QA/QC program to assess method precision. The project goal for laboratory duplicates was one for every 20 samples collected per event. Duplicate results were evaluated by calculating the RPD between the two sets of results, which served as a measure of the reproducibility (precision) of the sample results. The acceptable ARPD limits are shown in Table A1-3. The RPD was calculated using Equation 1.

Standard Reference Material

Standard reference materials (SRMs) were used to evaluate the relative accuracy of a particular analysis. The project goal for SRMs was one for every 20 samples collected per event or one per batch. An SRM is a homogeneous matrix with a similar concentration as those expected in the samples analyzed. The results should be within 95% of the confidence interval of the mean as stated by the provider of the material.

Laboratory Blank Spikes and Matrix Spikes

Laboratory blank spikes and matrix spikes were used to assess precision and accuracy of the laboratory analytical method, and to evaluate matrix interference. The project goal for matrix spikes was one for every 20 samples collected per event or one per batch. The matrix spike/matrix spike duplicate (MS/MSD) approach was used with the field samples. A matrix spike sample is an aliquot of a field sample into which the laboratory adds a known quantity of an analyte. Reported percent recovery of the known analyte in the sample indicates matrix effects on the analysis. A matrix spike duplicate sample is a duplicate aliquot of the matrix spike sample analyzed separately. Matrix spike duplicate results were compared to the matrix spike results to assess the precision of the laboratory analytical method.

Method Blanks

Laboratory method blanks were run by each analytical laboratory to determine the level of contamination associated with laboratory reagents and equipment. The project goal for method blanks was one for every 20 samples collected per event or one per batch. A method blank is a sample of a known matrix that has been subjected to the same complete analytical procedure as the submitted field samples to determine if contamination has been introduced into the samples

by the laboratory during processing. Results of a method blank analysis should be less than the reporting limit for each analyte.

Field Blanks

Field blanks were used to determine if field sampling activities were a potential source for contamination. The project goal for field blanks was one for every 20 samples collected per event or one per batch. Field blanks were collected by pouring "blank water" (contaminant-free de-ionized or Millipore water) into sampling equipment and containers in the field during a sampling event. The same equipment used for collection of the grab samples was used to transfer the blank water into the blank sample containers.

Table A1-3: Measurement Quality Objectives for Laboratory Data

Group	Parameter	Accuracy	Precision[a]	SWAMP Target Reporting Limit	Completeness (%)
Stream Physiochemical	Total Alkalinity (as $CaCO_3$)	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	1 mg/L	90
Stream Physiochemical	Chloride	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	0.25 mg/L	90
Stream Physiochemical	Total Hardness (as $CaCO_3$)	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	1 mg/L	90
Stream Physiochemical	Sulfate	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	1.0 mg/L	90
Stream Physiochemical	TDS	N/A	Lab Replicate RPD <25%	10 mg/L	90
Stream Physiochemical	TSS	N/A	Lab Replicate RPD <25%	0.5 mg/L	90
Bacteria	Enterococcus	Positive Control and Reference Material = 80-120% Recovery; Negative Control = No growth on filter	Lab Replicate RPD <25%	1 colonies/100 ml	90

Table A1-3: (Continued)

Group	Parameter	Accuracy	Precision[a]	SWAMP Target Reporting Limit	Completeness (%)
Bacteria	*E. coli*	Positive Control and Reference Material = 80-120% Recovery; Negative Control = No growth on filter	Lab Replicate RPD <25%	2 MPN/100 ml	90
Bacteria	Fecal coliform	Positive Control and Reference Material = 80-120% Recovery; Negative Control = No growth on filter	Lab Replicate RPD <25%	2 MPN/100 ml	90
Bacteria	Total coliform	Positive Control and Reference Material = 80-120% Recovery; Negative Control = No growth on filter	Lab Replicate RPD <25%	2 MPN/100 ml	90
Microbial Source Testing	HF183	Positive control amplifies as expected; Negative control = no amplification	Amplification efficiency >85% for Replicates	N/A	90
Nutrients and Carbon	Nitrate + Nitrite (as N)	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	0.01 mg/L	90
Nutrients and Carbon	Ammonia (as N)	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	0.02 mg/L	90
Nutrients and Carbon	Ortho-phosphate (as P)	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	0.01 mg/L	90
Nutrients and Carbon	Total Kjeldahl Nitrogen (TKN)	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	0.5 mg/L	90
Nutrients and Carbon	Total Dissolved Nitrogen	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	0.03 mg/L	90

Table A1-3: (Continued)

Group	Parameter	Accuracy	Precision[a]	SWAMP Target Reporting Limit	Completeness (%)
Nutrients and Carbon	Total Phosphorus (as P)	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	0.014 mg/L	90
Nutrients and Carbon	Particulate or Algal Nitrogen and Carbon	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	165 mg kg^{-1}, 2600 mg kg^{-1} in 10 mg sample	90
Nutrients and Carbon	Particulate or Algal Phosphorus	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	100 mg kg^{-1} in 10 mg sample	90
Nutrients and Carbon	Dissolved Organic Carbon (DOC)	Method Blank Results <RL; MS and MSD Recovery within 80-120%	Lab Replicate and MS/MSD RPD <25%	0.6 mg/L	90
Metals (Total and Dissolved)	Cadmium	Method Blank Results <RL; MS and MSD Recovery within 75-125%	Lab Replicate and MS/MSD RPD <25%	0.01 µg/L	90
Metals (Total and Dissolved)	Chromium	Method Blank Results <RL; MS and MSD Recovery within 75-125%	Lab Replicate and MS/MSD RPD <25%	0.1 µg/L	90
Metals (Total and Dissolved)	Copper	Method Blank Results <RL; MS and MSD Recovery within 75-125%	Lab Replicate and MS/MSD RPD <25%	0.01 µg/L	90
Metals (Total and Dissolved)	Iron	Method Blank Results <RL; MS and MSD Recovery within 75-125%	Lab Replicate and MS/MSD RPD <25%	20 µg/L	90
Metals (Total and Dissolved)	Lead	Method Blank Results <RL; MS and MSD Recovery within 75-125%	Lab Replicate and MS/MSD RPD <25%	0.01 µg/L	90
Metals (Total and Dissolved)	Manganese	Method Blank Results <RL; MS and MSD Recovery within 75-125%	Lab Replicate and MS/MSD RPD <25%	0.01 µg/L	90
Metals (Total and Dissolved)	Nickel	Method Blank Results <RL; MS and MSD Recovery within 75-125%	Lab Replicate and MS/MSD RPD <25%	0.02 µg/L	90
Metals (Total and Dissolved)	Selenium	Method Blank Results <RL; MS and MSD Recovery within 75-125%	Lab Replicate and MS/MSD RPD <25%	0.30 µg/L	90

Table A1-3: (Continued)

Group	Parameter	Accuracy	Precision[a]	SWAMP Target Reporting Limit	Completeness (%)
Metals (Total and Dissolved)	Zinc	Method Blank Results <RL; MS and MSD Recovery within 75-125%	Lab Replicate and MS/MSD RPD<25%	0.10 µg/L	90%
Stream Algae and Physical Habitat	Ash-free Dry Mass	N/A	Lab Replicate RPD<25%	0.01 mg m^{-2}	90%
Water Column Toxicity	Freshwater Acute Toxicity	N/A	90% survival of controls	N/A	90%
Water Column Toxicity	Freshwater Toxicity Identification Evaluation	N/A	N/A	N/A	90%

[a]N/A if native concentration of either sample is less than RL.

A2. QUALITY ASSURANCE/QUALITY CONTROL RESULTS

The Quality Assurance Project Plan (QAPP) was developed to establish activities and procedures to assure both chemical and physical measurements would meet the SWAMP requirements and provide the quality of data needed to validate and calibrate future TMDL models. Field sampling and laboratory quality assurance activities and procedures were implemented to objectives provided in the QAPP.

Quality assurance activities began with field protocols designed to minimize errors introduced during field sampling and measurements. Field procedures included calibration of field equipment as well as sample handling and processing procedures. Field QA/QC samples evaluated potential contamination and sampling error prior to sample delivery to the analytical laboratory. Field QA/QC processes included equipment calibration, field protocols to meet analytical holding times, field duplicates, and field blanks. Laboratory QA/QC samples were used to evaluate the analytical process for contamination, accuracy, and reproducibility.

The primary criteria used to evaluate the quality of data are precision, accuracy, completeness, and representativeness. These criteria are described below:

- Precision describes how well repeated measurements agree. Precision measurements were assessed on both field and laboratory duplicates (i.e., MS1/MS2, BS1/BS2, LCS1/LCS2, LCM1/LCM2, CRM1/CRM2, and surrogate spikes) on a minimum frequency of one per batch. The results of the replicate project sample analysis (R1/R2), were compared to the original samples to estimate a RPD between the two samples.
- Accuracy describes how close the measurement is to its true value using calibration standards, reference samples, and spiked samples. The accuracy of chemical measurements was checked by performing LCS/LCSDs and MS/MSDs during each batch of sample analysis at the laboratory. Accuracy was quantified as the percent recovery of the measured value within established control limits. The recoveries of both LCS/LCSDs and MS/MSDs were evaluated.
- Completeness describes the fraction of collected data that is successfully analyzed in the laboratory. While no specific statistical criteria have been generated as part of this project, it is expected that 90% of all analyses should be completed when sampled. Completeness was quantified by comparing the number of measurements actually collected to the number of measurements planned to be collected.
- Representativeness describes the degree to which the results of analyses represent the samples collected, and the samples in turn represent natural variability and characteristics of the environmental conditions. The monitoring approach was designed to achieve representativeness by sampling at 10, 50, and 90% locations in each reference stream. Sites were chosen to best represent distinctive processes or sections of the reference stream: Monitoring locations were chosen to be representative of the reference stream processes of interest.

Overall, data quality met research study QA/QC objectives. Data were qualified and flagged in the project database with the appropriate SWAMP QA code. Data was required to be reported in a SWAMP compatible format. QA Codes are used in the database to describe any special conditions or situation occurring during the analysis. No data points were rejected based on these qualifiers. Following the review, data results were assigned data qualifiers, as appropriate. Individual sample results were qualified using Result Qualifier Codes and Quality Assurance Codes, which are detailed below:

- **Non-Detect (ND)**: The result was below the MDL
- **Detected Not Quantifiable (DNQ)**: The result was between the MDL and the RL.
- **H: A holding time violation occurred**. Method recommended holding times are the length of time a project sample can be stored under specific conditions after collection and prior to analysis without significantly affecting the analyte's concentration. The majority of the "H" qualifiers were attributable Ato holding-time violations for nutrients and total dissolved solids. These data are flagged in the project database with a QA/QC code of "H".

Any constituent reported as non-detect (Numerical Qualifier "<") received an overall qualification of "ND" in the absence of laboratory quality control qualification. Any constituent that reported a value below the RL but at or above the MDL (with a Numerical Qualifier "<") received an overall qualification of "<" and DNQ to identify that the result was reported as a less than value and was qualified as a DNQ in the absence of laboratory quality control qualification.

The 2012-2014 San Diego Reference Stream monitoring effort has resulted in 18,154 chemical measurements (12,023 dry weather and 6,131 wet weather; total includes both native and replicate samples). Of these native values 1,593 (8.8%) required data qualifications. Of the 1,593 values 1,142 (6.3%) were dry weather results (Table A3-1) and 451 (2.5%) were wet weather results (Table A3-2). Both total and dissolved trace metals comprised the majority of NDs and DNQs. Overall 505 (6.5%) of the reference stream samples collected during dry weather were analyzed as NDs and 907 (11.7%) resulted in DNQs (Table A3-1). During wet weather 527 (12.7%) of the reference stream samples collected were analyzed as NDs and 257 (6.2%) resulted in DNQs (Table A3-2).

Based on a review of the project DQOs and the database data qualifiers, the data collected as part of this study were deemed appropriate for use in the San Diego Reference Stream study as qualified. No data was rejected. The flagged data was applicable as qualified and can be used considering the constraints placed by the qualifiers.

A2.1 Field Duplicates

Field duplicates were analyzed for a minimum of 10% of total samples per constituent. For those samples that did not meet the DQOs, site variations were evaluated by constituent to reflect the sampling strategy.

High RPDs occurred as a result of small absolute differences at low concentrations that tended to amplify RPDs. This occurred for dissolved metals, nutrients, and TSS samples. High RPDs also reflected the heterogeneous nature of environmental samples, and are considered reasonable. Storm water samples routinely have RPDs between 60 and 100%. This is thought to be caused, in many instances by the process of splitting samples (due to the potential for large variations in particle sizes and, therefore, constituent concentrations between primary and duplicate samples).

A2.1.2 Bacteria

Field duplicates were analyzed for 10% of the total bacteria samples collected for this monitoring study. The percent of field duplicates for bacteria (*E. coli*, *Enterococcus,* fecal coliform and total coliform that met the DQO's are provided in Table A2-1. The breakdown by constituent of the field duplicates that met the DQO for precision are as follows:

- *E. coli,* and *Enterococcus:* Total Coliform: Of 50, 49 field duplicates (98%) for each constituent met the DQO for precision.
- Total Coliform: all 50 field duplicates (100%) met the DQO for precision.
- Fecal Coliform*:* all 24 field duplicates (100%) met the DQO for precision.

A2.1.3 Stream Physiochemical Constituents

Field duplicates were analyzed for 10% of the alkalinity, chloride, hardness and sulfate samples collected for this study (Table A2-1). Of 26, 22 field duplicates (85%) analyzed met the DQO for precision.

A2.1.4 Total Suspended Solids (TSS) and Total Dissolved Solids (TDS)

Field duplicates were analyzed for 10% of the total suspended and total dissolved solids samples collected for this study (Table A2-1). Of 26 total field duplicates analyzed for TDS, 100% met the DQO for precision.

A2.1.5 Nutrients

Field duplicates were analyzed for 15% of the total nutrient samples collected during the study. The percentages of field duplicates for each constituent that met the DQOs are provided in Table A2-1. The breakdown by constituent of the field duplicates that met the DQO for precision is as follows:

- Ammonia as N, Nitrate + Nitrite, Total Kjeldahl Nitrogen and Total Phosphorus: Of 41, 39 field duplicates (95.1%) analyzed for ammonia as nitrogen, nitrate + nitrite, TKN and TP met the DQO for precision.
- Orthophosphate: Of 41, 41 field duplicates (100%) analyzed met the DQO for precision.
- Total Dissolved Nitrogen and Total Nitrogen: Of 41, 38 field duplicates (92.7%) analyzed for TDN and TN met the DQO for precision.
- Total Phosphorus, Particulate Nitrogen, Particulate Organic Carbon, Particulate Phosphorus and Dissolved Organic Carbon: Of 41, 40 field duplicates (97.6%) analyzed for TP, PN, POC, PP and DOC met the DQO for precision.

A2.1.6 Total and Dissolved Metals

Field duplicates were analyzed for 10% of the total and dissolved metals samples collected for this study (Table A2-1). Of 26 total and dissolved metals, 21 field duplicates (80.7%) analyzed met the DQO for precision. In some instances, the results for the dissolved fraction were higher than the total fraction for a particular analyte (e.g. total and dissolved copper). This is typically caused by the analytical variation for each result and indicates that the target analyte is primarily in the dissolved phase, within the sample.

A2.1.7 Laboratory Duplicates

Laboratory duplicates serve as an indicator of instrument stability, consistency in laboratory sample preparation and analysis, as well as an estimate of field proficiency. Laboratory duplicates were analyzed for a minimum of 5% of total number of samples analyzed per constituent. The percentage of duplicates meeting the DQOs for individual constituents is presented in Table A2-1.

Bacteria

- *E. coli*, *Enterococcus* and Total Coliform: all 17 laboratory duplicates (100%) for each constituent met the DQO for precision.
- Fecal Coliform*:* all 19 laboratory duplicates (100%) met the DQO for precision.

Stream Physiochemical Constituents

Alkalinity, chloride, hardness and sulfate: Of 11, 10 laboratory duplicates (91%) analyzed met the DQO for precision (Table A2-1).

Total Suspended Solids (TSS) and Total Dissolved Solids (TDS)

All ten laboratory duplicates (100%) for TDS and TSS, met the DQO for precision (Table A2-1).

Nutrients

Approximately 5% of the total number of samples analyzed consisted of laboratory duplicates. For dissolved analytes (i.e., DIN), after a sample was analyzed, the same sample container was placed farther along in the automatic sampler and re-analyzed. The mean of the two values was reported as the concentration for that sample. If a difference of >10% was observed between replicates, then all of the replicates for that particular analytical run are carefully reviewed. If only one of the duplicate pairs was in question, then only that sample was re-analyzed. If all show a similar trend, then instrumentation/reagent problems are suspected and the analytical run was halted until such time as the problem was resolved. This procedure was practiced for all dissolved analytes that were not consumed completely in the analytical procedure. For those that were completely consumed and for particulate analytes, duplicate samples constituted actual duplicate samples collected in the field and analyzed in the same analytical run. In the case of particulate carbon and nitrogen 10% of the total number of samples were analyzed as duplicates. This generated sufficient quality assurance data to compensate for the omission of laboratory spikes for these non-aqueous samples. Thirty-eight (97.7%) of the 39 laboratory duplicates for the individual nutrient constituents met the DQO for precision (Table A2-1).

Total and Dissolved Metals

Total and dissolved metals laboratory duplicates met the DQO for precision 94.7% of the time (Table A2-1).

A2.2 Standard Reference Material

A2.2.1 Nutrients

Particulate Carbon, Nitrogen and Phosphorus: BCSS-1 is a marine sediment reference material prepared by the National Research Council of Canada. It is certified by the Council for carbon content, gives a non-certified range of results for phosphorus, but no information for nitrogen. UMCES has analyzed this sediment for many years and maintains a substantial database for nitrogen and phosphorus, as well as carbon values. UMCES analyzed this sediment quarterly and compared the results to the certified value, non-certified range of values and their historical values. Standard reference materials for ammonium, nitrite + nitrate, nitrite, orthophosphate, dissolved nitrogen, dissolved phosphorus, dissolved organic carbon, sulfate and chloride and hardness are supplied by SPEX, a US EPA certified company. The samples arrived in ampules and UMCES prepared final concentrations to approximate typical estuarine concentrations. The samples were then placed in pre-cleaned poly bottles, frozen and analyzed on a quarterly basis. The analysis of these frozen standard reference materials as a function of time also provides data on the effect of UMCES' preservation technique (freezing) on the integrity of the concentration of samples. The US EPA recommends a holding time of 28 days for many of the parameters UMCES routinely analyzes. Laboratory control samples were analyzed for a minimum of 5% of the total samples collected for all nutrients (i.e., DOC, PP). All results met the DQO (98 - 100%), Table A2-1.

A2.2.2 Trace Metals

Laboratory control samples (LCS) were analyzed for a minimum of 5% of the total samples collected for all total and dissolved metals. All results met the DQO (100%; Table A2-1).

A2.3 Laboratory Blank Spikes and Matrix Spikes

Blank spikes (BS) demonstrates performance of the preparation and analytical methods on a clean matrix void of potential matrix related interferences. The BS is performed in laboratory deionized water, making these recoveries a better indicator of the efficiency of the laboratory method per se.

Matrix spikes (MS)/matrix spike duplicates (MSD) and laboratory blank spikes were analyzed on a minimum of 5% of the total number of samples collected for the following constituents: ammonia as nitrogen, nitrate + nitrite as nitrogen, total nitrogen, total dissolved nitrogen, total phosphorus, total dissolved phosphorus, total and dissolved metals. Nutrient recovery ranged from 97.9% (DOC and nitrate + nitrite) to 100% (ammonia as N, TDN, TN, TP, and orthophosphate), Table A2-1. Total and dissolved metals showed 100% recovery. All results met the DQO (98 - 100%), Table A2-1.

A2.3.1 Nutrients Matrix Spiking Method

A spike was prepared by adding a known volume of standard to a known volume of pre-analyzed sample. University of Maryland Center for Environmental Science (UMCES) added enough concentrated standard to provide a significant response on their instruments that was distinguishable from the original concentration of the sample. This concentrated standard was used to minimize any possible change in sample matrix by the addition of spike.

The spiked sample was analyzed and its expected concentration calculated as the sum of the original concentration and the spike concentration, normalized for the constituent volumes. A comparison was made between the actual value and the expected value. These concentrations (original, expected and actual) were recorded in a separate QA/QC data file along with sample number, sample collection date, analysis date and the amount of spike added. In the case of particulate phosphorus, the volume filtered was not used in the calculation to determine percentage recovery.

If a value of >115% or <85% was observed for percentage recovery of the spike, then all of the spikes for that particular analytical run were carefully reviewed. If only one of the spikes is in question, then only that sample was re-analyzed. If all showed poor recovery, then instrumentation/reagent problems were suspected and the analytical run was halted until such time that the problem was resolved. This procedure was adhered to for all dissolved analytes and for particulate phosphorus.

Table A2-1: Data Quality Objectives and Levels Achieved for Analytical Results

Constituent	Accuracy					Precision			Recovery		Completeness	
	DQO (%)	Percent Achieved (LCS)[1]	DQO	Percent Achieved (FB)[2]	Percent Achieved (LB)[3]	DQO RPD[9] (%)	Percent Achieved (FD)[4]	Percent Achieved (LD)[5]	DQO (%)	Percent Achieved (MS)[6]	DQO (%)	Percent Achieved
Bacteria												
E. coli	NA[7]	NA	<TRL[8]	98.5	100	25	98	100	NA	NA	90	99
Enterococcus	NA[7]	NA	<TRL	98.5	100	25	98	100	NA	NA	90	99
Total Coliform	NA	NA	<TRL	99	100	25	100	100	NA	NA	90	100
Fecal Coliform	NA	NA	<TRL	100	100	25	100	100	NA	NA	90	100
Stream Physiochemical												
Alkalinity (as $CaCO_3$)	80-120	100	<TRL	100	100	25	85	91	NA	NA	90	99
Chloride	80-120	100	<TRL	100	100	25	85	91	NA	NA	90	99
Hardness (as $CaCO_3$)	80-120	100	<TRL	100	100	25	85	91	NA	NA	90	99
Sulfate	80-120	100	<TRL	100	100	25	85	91	NA	NA	90	99
Total Dissolved Solids	80-120	100	<TRL	100	100	25	100	100	NA	NA	90	100
Total Suspended Solids	80-120	100	<TRL	100	100	25	100	100	NA	NA	90	100

Table A2-1: (Continued)

Constituent	Accuracy					Precision			Recovery		Completeness	
	DQO (%)	Percent Achieved (LCS)[1]	DQO	Percent Achieved (FB)[2]	Percent Achieved (LB)[3]	DQO RPD[9] (%)	Percent Achieved (FD)[4]	Percent Achieved (LD)[5]	DQO (%)	Percent Achieved (MS)[6]	DQO (%)	Percent Achieved
Nutrients												
Ammonia-N	80-120	100	<TRL	100	100	25	95.1	97.7	80-120	100	90	99
Dissolved Organic Carbon	80-120	100	<TRL	96.7	100	25	97.6	97.7	80-120	97.9	90	100
Nitrate+Nitrite-N	80-120	100	<TRL	96.7	100	25	95.1	97.7	80-120	97.9	90	100
Particulate Carbon	80-120	100	<TRL	96.7	100	25	97.6	97.7	NA	98.6	90	100
Particulate Nitrogen	80-120	100	<TRL	96.7	100	25	97.6	97.7	NA	98.6	90	100
Particulate Phosphorus	80-120	100	<TRL	96.7	100	25	97.6	97.7	NA	98.6	90	100
Orthophosphate as P	80-120	100	<TRL	100	100	25	97.6	97.7	80-120	100	90	100
Total Kjeldahl Nitrogen (TKN)	80-120	100.0	<TRL	100	100	25	95.1	97.7	80-120	100	90	100
Total Nitrogen (TN)	80-120	98.0	<TRL	100	100	25	92.7	97.7	80-120	100	90	100
Total Dissolved Nitrogen (TDN)	80-120	100.0	<TRL	100	100	25	92.7	97.7	80-120	100	90	100
Total Phosphorus (TP)	80-120	98	<TRL	100	100	25	95.1	97.7	80-120	100	90	100

Table A2-1: (Continued)

Constituent	Accuracy					Precision			Recovery		Completeness	
	DQO (%)	Percent Achieved (LCS)[1]	DQO	Percent Achieved (FB)[2]	Percent Achieved (LB)[3]	DQO RPD[9] (%)	Percent Achieved (FD)[4]	Percent Achieved (LD)[5]	DQO (%)	Percent Achieved (MS)[6]	DQO (%)	Percent Achieved
Heavy and Trace Metals (Total and Dissolved)												
Cadmium	75-125	100	<TRL	100	100	25	80.2	94.7	75-125	100	90	100
Chromium	75-125	100	<TRL	100	100	25	80.2	94.7	75-125	100	90	100
Copper	75-125	100	<TRL	100	100	25	80.2	94.7	75-125	100	90	100
Iron	75-125	100	<TRL	100	100	25	80.2	94.7	75-125	100	90	100
Lead	75-125	100	<TRL	100	100	25	80.2	94.7	75-125	100	90	100
Manganese	75-125	100	<TRL	100	100	25	80.2	94.7	75-125	100	90	100
Nickel	75-125	100	<TRL	100	100	25	80.2	94.7	75-125	100	90	100
Selenium	75-125	100	<TRL	100	100	25	80.2	94.7	75-125	100	90	100
Zinc	75-125	100	<TRL	100	100	25	80.2	94.7	75-125	100	90	100

[1]BS - Laboratory Control Sample

[2]FB - Field Blank

[3]LB - Laboratory Blank

[4]FD - Field Duplicate

[5]LD - Laboratory Duplicate

[6]MSS – Matrix Spike

[7]NA – Not Applicable

[8]TRL – Target Reporting Limit

[9]RPD – Relative Percent Difference

A3. SUMMARY OF DRY AND WET WEATHER QUALIFIED DATA

Table A3-1: Summary of Dry Weather Qualified Data

Constituent	Qualified	%Qualified	ND	% ND	DNQ	%DNQ	Total Result Count
Bacteria							
E. coli	39	10.9	0	0.0	39	9.2	425
Enterococcus	13	3.8	0	0.0	13	3.1	424
Total Coliform	3	0.7	0	0.0	3	0.7	424
Fecal Coliform	61	35.9	0	0.0	61	21.0	291
Stream Physiochemical				0.0			
Alkalinity (as $CaCO_3$)	0	0.0	0	0.0	0	0.0	185
Chloride	0	0.0	0	0.0	0	0.0	164
Hardness (as $CaCO_3$)	0	0.0	0	0.0	0	0.0	318
Sulfate	0	0.0	0	0.0	0	0.0	167
TSS	103	69.6	61	0.0	42	28.4	148
TDS	6	3.8	0	0.0	6	3.8	157
Ammonia-N	10	5.7	0	0.0	10	5.7	176
Dissolved Organic Carbon	0	0.0	0	0.0	0	0.0	185
Nitrate+Nitrite-N	6	4.7	0	0.0	6	4.7	127
Nitrite as N	48	96.0	0	0.0	48	96.0	50
Particulate Nitrogen	14	7.4	0	0.0	14	7.4	188
Particulate Organic Carbon	3	1.6	0	0.0	3	1.6	189
Particulate Phosphate as P	45	24.6	0	0.0	45	24.6	183
Orthophosphate as P; Dissolved Soluble Reactive Phosphorus (SRP)	3	6.0	0	0.0	3	6.0	50
Total Nitrogen (TN)	1	0.6	0	0.0	1	0.6	176
Total Dissolved Nitrogen (TDN)	11	6.3	0	0.0	11	6.3	176
Total Phosphorus (TP)	0	0.0	0	0.0	0	0.0	189
Total Dissolved Phosphorus (TDP)	0	0.0	0	0.0	0	0.0	180

Table A3-1. (Continued)

Constituent	Qualified	Qualified	ND	ND	DNQ	DNQ	Total Result Count
Heavy and Trace Metals (Total and Dissolved)							
Dissolved Cadmium	149	84.7	98	55.7	51	29.0	176
Total Cadmium	141	80.1	97	55.1	44	25.0	176
Dissolved Chromium	91	51.7	29	16.5	62	35.2	176
Total Chromium	87	49.4	16	9.1	71	40.3	176
Dissolved Copper	44	25.0	6	3.4	38	21.6	176
Total Copper	33	18.8	2	1.1	31	17.6	176
Dissolved Iron	35	19.9	1	0.6	34	19.3	176
Total Iron	10	5.7	0	0.0	10	5.7	176
Dissolved Lead	154	87.5	109	61.9	45	25.6	176
Total Lead	108	61.4	35	19.9	73	41.5	176
Dissolved Manganese	2	1.1	1	0.6	1	0.6	176
Total Manganese	2	1.1	2	1.1	0	0.0	176
Dissolved Nickel	39	22.2	11	6.3	28	15.9	176
Total Nickel	35	19.9	7	4.0	28	15.9	176
Dissolved Selenium	55	31.3	14	8.0	41	23.3	176
Total Selenium	50	28.4	9	5.1	41	23.3	176
Dissolved Zinc	7	4.0	6	3.4	1	0.6	176
Total Zinc	4	2.3	1	0.6	3	1.7	176
Total Qualifiers	1412	18.2	505	6.5	907	11.7	7740

Table A3-2. Summary of Wet Weather Qualified Data

Constituent	Qualified	%Qualified	ND	% ND	DNQ	%DNQ	Total Result Count
Bacteria							
E. coli	13	10.9	13	10.7	0	0.0	122
Enterococcus	1	3.8	1	0.8	0	0.0	121
Total Coliform	0	0.0	0	0.0	0	0.0	122
Fecal Coliform	0	35.9	0	0.0	0	0.0	58
Stream Physiochemical							
Alkalinity (as $CaCO_3$)	0	0.0	0	0.0	0	0.0	86
Chloride	0	0.0	0	0.0	0	0.0	86
Hardness (as $CaCO_3$)	0	0.0	0	0.0	0	0.0	86
Sulfate	0	0.0	0	0.0	0	0.0	86
TSS	38	44.2	17	19.8	21	24.4	86
TDS	6	7.0	0	0.0	6	7.0	86
Ammonia-N	48	32.4	48	32.4	0	0.0	148
Dissolved Organic Carbon	47	32.0	47	32.0	0	0.0	147
Nitrate+Nitrite-N	53	35.8	53	35.8	0	0.0	148
Nitrite as N	45	30.4	34	23.0	11	7.4	148
Particulate Nitrogen	53	41.1	46	35.7	7	5.4	129
Particulate Organic Carbon	54	41.5	51	39.2	3	2.3	130
Particulate Phosphate as P	55	42.3	47	36.2	8	6.2	130
Orthophosphate as P; Dissolved Soluble Reactive Phosphorus (SRP)	62	41.9	62	41.9	0	0.0	148
Total Nitrogen (TN)	0	0.0	0	0.0	0	0.0	130
Total Dissolved Nitrogen (TDN)	0	0.0	0	0.0	0	0.0	130
Total Phosphorus (TP)	0	0.0	0	0.0	0	0.0	130
Total Dissolved Phosphorus (TDP)	0	0.0	0	0.0	0	0.0	130

Table A3-1. (Continued)

Constituent	Qualified	%Qualified	ND	% ND	DNQ	%DNQ	Total Result Count
Heavy and Trace Metals (Total and Dissolved)							
Dissolved Cadmium	70	81.4	41	47.7	29	33.7	86
Total Cadmium	74	86.0	46	53.5	28	32.6	86
Dissolved Chromium	16	18.6	13	15.1	3	3.5	86
Total Chromium	19	22.1	7	8.1	12	14.0	86
Dissolved Copper	0	0.0	0	0.0	0	0.0	86
Total Copper	0	0.0	0	0.0	0	0.0	86
Dissolved Iron	11	12.8	0	0.0	11	12.8	86
Total Iron	1	1.2	0	0.0	1	1.2	86
Dissolved Lead	36	41.9	0	0.0	36	41.9	86
Total Lead	15	17.4	0	0.0	15	17.4	86
Dissolved Manganese	0	0.0	0	0.0	0	0.0	86
Total Manganese	0	0.0	0	0.0	0	0.0	86
Dissolved Nickel	8	9.3	0	0.0	8	9.3	86
Total Nickel	6	7.0	0	0.0	6	7.0	86
Dissolved Selenium	26	30.2	0	0.0	26	30.2	86
Total Selenium	27	31.4	1	1.2	26	30.2	86
Dissolved Zinc	0	0.0	0	0.0	0	0.0	86
Total Zinc	0	0.0	0	0.0	0	0.0	86
Total Qualifiers	784	19.0	527	12.7	257	6.2	4135