IMPLEMENTATION OF A QA/QC PROGRAM FOR SURFACE WATER QUALITY MONITORING ACTIVITIES IN MISSISSIPPI: QUEST FOR RELIABLE DATA.

M.B. Hicks, D.D. Loch, K.R. Pigott
Mississippi Department of Environmental Quality, Water Quality Assessment Branch, P. O. Box 10385, Jackson, Mississippi 39289.

ABSTRACT

The Mississippi Department of Environmental Quality (MDEQ) has developed a comprehensive Quality Assurance/Quality Control (QA/QC) program for all components of its surface water monitoring programs. A statewide project to monitor and assess Clean Water Act Section 303(d) listed streams and develop an Index of Biological Integrity (IBI) was used as a springboard for this program. The following QA/QC procedures were developed and implemented during the 303(d)/IBI project: preparation of a Quality Assurance Project Plan (QAPP), inclusion of Quality Control activities and Corrective Actions, and procedures for developing and evaluating method performance characteristics. The QA/QC program is generally structured to isolate, identify and correct problems in either process or design that produce error and increase variability. Quality Control activities are focused upon each step of the assessment process. Several QC activities used to evaluate either particular methods or results for this project included the following: field and laboratory audits, duplicate and repeat sampling, calculation of percent sorting efficiency, pickate re-checks, taxonomic re-identifications, 100% re-checks of data entries, and re-calculation of metrics. The end result will ensure that the discrimination efficiency of the index for the 303(d)/IBI project is acceptable for any waterbody or region in the state of Mississippi. MDEQ intends to continue to utilize and further develop this QA/QC program during future surface water monitoring activities. Consistently following QA/QC procedures will produce reliable data that will be used to make sound biological assessments.

KEYWORDS

Methods, Water Quality, Management and Planning, Quality Assurance, Quality Control

INTRODUCTION

Any water quality monitoring program is only as good as the data that it generates. The quality of data generated from a monitoring program is essential to the success of meeting program objectives (EPA 2001). Therefore, a good monitoring program must have as one of its goals to produce data of the highest quality possible. In reality, however, no monitoring program will ever be capable of producing data of absolute certainty. No matter how well a monitoring program is designed and implemented, there will always be a particular amount of uncertainty associated with the data generated.

Considering both of these ideas, MDEQ is committed to developing a QA/QC Program to complement all Surface Water Monitoring Program (SWMP) activities. Identified objectives of the QA/QC Program are:

- Structure the framework and design of SWMP activities so that MDEQ can minimize, isolate, identify and correct problems in either process or design that produce error and increase data variability.
- Evaluate and report the quality of all data as well as the type and amount of uncertainty associated with all data.

The purpose of this paper is to describe in detail MDEQ's QA/QC Program with respect to biological data and to briefly discuss how this program was implemented during a statewide project to develop biological reference conditions and an Index of Biological Integrity. The quality of chemical and physical data is also monitored in MDEQ's QA/QC Program, however that aspect is not discussed here.

STRUCTURE AND DESIGN OF SWMP ACTIVITIES

The first step to ensure collection and use of high quality data is performed during the design of the monitoring program structure and framework. This involves:

- Development of standardized operating procedures (SOPs) for all data collection and analysis activities.

- Designing the program so that the characteristics of data quality are optimized (i.e., accuracy, precision, representativeness, completeness and comparability).

- Development and implementation of a Quality Assurance Project Plan (QAPP). This includes clearly defining project objectives, project organization, work to be performed to collect and analyze the data, the standards to be met, and the procedures that will be used to ensure that the data are scientifically valid and defensible and that uncertainty has been reduced to a known and acceptable level.

- Development and implementation of a routine training program for all monitoring activities.

- Designing and implementing performance and system audits of all procedures.

EVALUATION OF DATA QUALITY

Evaluation of data quality involves three steps: (1) establishing scientific data quality objectives (DQOs), (2) evaluating program design to determine whether the objectives can be met, and (3) establishing assessment and measurement quality objectives that can be used to evaluate the appropriateness of the methods being used in the program. The process of establishing DQOs involves identifying the allowable uncertainty of a dataset, which may lead to two types of error:

- *false positives* (Type I error: a problem is found to exist when in fact it does not); and,

- *false negatives* (Type II error: a problem is not found when in fact it does exist).

The acceptance probabilities of those errors as established by the data users are the DQOs. The DQO process entails establishing action-triggering values and selecting rates of *false positives* and *false negatives* that are acceptable to the data user.

Therefore, to assess whether or not DQOs have been met, one must be able to measure the types and amount of error associated with the data. Sources of error or uncertainty associated with variables and indicators include the following (Diamond, Barbour, and Stribling 1996):

- Sampling error: The difference between sample values and in-situ "true" values from unknown biases due to sampling design. Sampling error includes natural variability (spatial heterogeneity and temporal variability in population abundance and distribution) not specifically accounted for in a design, and variability associated with model parameters or incorrect model specification.

- Measurement error: The difference between sample values and in-situ "true" values associated with the measurement process. Measurement error includes bias and imprecision associated with sampling methodology, specification of the sampling unit, sample handling, storage, preservation, identification, instrumentation, etc.

To establish DQOs, MDEQ employed the use of data quality indicators (DQIs). Conventional DQIs include the following:

- Precision
- Accuracy
- Representativeness
- Completeness
- Comparability

<u>Precision</u>

Precision is a measure of the nearness of two values and can be used as an indicator of internal method consistency (Diamond, Barbour, and Stribling 1996). Consistency is demonstrated by the degree of mutual agreement between individual measurements or enumerated values of the same property of a sample, usually under demonstrated similar conditions. Precision of sampling methods is estimated by collecting duplicate samples at the same or immediately adjacent sampling site.

Precision also addresses uncertainty due to natural variation and sampling error.

Precision is calculated from two duplicate samples using relative percent difference (RPD) as follows:

$$RPD = \frac{|C_1 - C_2|}{(C_1 + C_2)/2} \times 100$$

where C_1 and C_2 = the two values. If it is to be calculated from three or more replicate samples (as is often the case in analytical laboratory work), the relative standard deviation (RSD) will be used and is calculated as

$$RSD = \frac{s}{\bar{X}} \times 100$$

where s = standard deviation and $\bar{X}$ = mean of repeated samples. Precision can also be expressed using coefficient of variability (CV) and is calculated as:

$$CV = \frac{SD}{\bar{X}}$$

where SD = standard deviation and $\bar{X}$ = mean of repeated sample measurements.

Precision of taxonomic identifications is calculated as percent taxonomic disagreement (PTD), and is calculated as:

$$PTD = \left(1 - \frac{\text{No. agreements}}{\text{Total no. organisms}}\right) \times 100$$

To measure the precision of field sampling, repeat samples are collected. As a general rule for all projects, repeated samples are collected from at least 10 percent of the total number of stations and are chosen randomly. At least three repeated samples are collected for projects that consist of ≤30 sites, if possible. Two types of duplicate sampling may be employed:

1. Duplicate sampling – sample collected from 100-meter stream reaches, adjacent to the primary sampling reaches, and by the same field team.
2. Repeat sampling – samples collected from the same 100-meter stream reach by separate sampling teams. This type is to be used when a project involves multiple sampling teams.

Estimates of precision for field sampling are calculated mainly using RPD between index scores of duplicate samples. These values are used to identify duplicate pairs that are abnormally different, when compared to other values. This allows for exploration of potential field sampling aspects that may be adding variability to the dataset. By identifying specific error sources, MDEQ is able to implement corrective actions to decrease variability and improve overall confidence in data and assessment.

Estimates for precision of the assessment tool (biotic index called the Mississippi Benthic Index of Stream Quality [M-BISQ]) used to determine stream condition are calculated using CVs for the duplicate samples taken during the development of the M-BISQ. The precision estimate is reported and implemented as the 90 percent confidence interval (CI) for the overall M-BISQ. This CI is a range around any point that is expressed as ± X number of index points. For any index score obtained at any site, MDEQ is 90 percent confident that the score is that value ± X number of points. For example, for assessment and reporting purposes, we use a box and whisker plot to display the range of reference scores obtained in a specific region. If we decide that the 25th percentile of that range is the cutoff between the assessment ratings of good and fair, this would also be reported in the context of the 25th percentile value ± the 90 percent CI. Therefore, if a score for a stream falls within the CI, then we cannot say with 90 percent confidence, whether the site is assessed as good or fair. Figure 1 displays an example of a box plot showing the CI around the 25th percentile.

To measure the precision of laboratory sorting of biological samples, two types of measures are performed:

1. Intra-laboratory check – A co-worker checks 10 percent of the primary samplers sorted samples (real-time), missed specimens are removed and counted.

2. Inter-laboratory check – An independent laboratory checks 10 percent of the sorted samples, missed specimens are removed and counted.

To measure the precision of taxonomic identification, three checks are performed:

1. Use of reference collection – Specimens verified by taxonomic experts are archived and available for reference when a taxonomist is unsure of an identification or wants to verify an identification.

2. Intra-laboratory taxonomic verification – A separate taxonomist within MDEQ's laboratory checks 10 percent of the primary taxonomist's identifications.

3. Inter-laboratory taxonomic verification – An independent taxonomist checks 10 percent of all samples identified during a project.

Estimates of precision for taxonomic identifications are made by calculating percent taxonomic disagreement (PTD). Failure to meet the DQO for PTD involves discussions between the two taxonomists. If agreement cannot be reached, then the PTD is reported as the taxonomic precision associated with that dataset. PTD values are also used to identify specific taxa that may need to be focused upon in the future to improve the precision of taxonomic identification of those taxa. Improving taxonomic precision may involve consulting taxonomic experts, revising taxonomic list of keys, lumping taxa to the next highest taxonomic level where consistent agreement can be reached, improving resources used for identification, allowing staff to attend taxonomic workshops, and increasing the frequency of training exercises.

Accuracy

Accuracy is defined as the degree of agreement between an observed value and an accepted reference or true value (Diamond, Barbour, and Stribling 1996). Accuracy is a combination of random error (precision) and systematic error (bias), which are due to sampling and analytical operations. Bias is the systematic distortion of a measurement process that causes errors in one direction so that the expected sample measurement is always greater or lesser to the same degree than the sample's true value. The U.S. Environmental Protection Agency (EPA) now recommends that the term *accuracy* not be used and that *precision* and *bias* be used instead (USEPA 1998). Since accuracy is the measurement of a parameter and comparison with a "truth," and the true values of biological characteristics cannot be known, use of a surrogate is required (i.e. bias).

Standard operating procedures (SOPs) for biological sample collection and processing were intentionally structured to reduce bias and improve precision and representativeness. Where possible, SOPs were structured to reduce the amount of operator choice. An example of reducing bias or operator choice is the standardization of equipment or techniques used, such as, standardized fixed count subsampling rather than field picking of organisms or the use of a standardized list of taxonomic literature or keys.

Estimates of accuracy for laboratory sorting are made by calculating percent sorting efficiency (PSE), and is calculated as:

$$PSE = \frac{T1}{T2} \times 100$$

Where T1 = total number of organisms sorted by primary sorter and T2 = total number of organisms sorted by primary sorter + total number of missed organisms found by a second sorter. Any sorter or laboratory that fails the DQO for sorting efficiency must have all of their samples rechecked for missed organisms.

Representativeness

Data representativeness is defined as the degree to which data accurately and precisely represent a characteristic of a population, parameter, variations at a sampling point, a process condition, or an environmental condition (Diamond, Barbour, and Stribling 1996). Therefore, representativeness addresses the natural variation or the spatial and temporal heterogeneity of a population.

The benthic macroinvertebrate field sampling SOP is designed to ensure collection of benthic macroinvertebrate samples that are representative of the overall assemblage the existing stream habitat is capable of supporting. For biological monitoring, the sampling approach developed by MDEQ is designed to take benthic

macroinvertebrate samples from 100 meter assessment reach (AR). The AR is delineated by the sampling team and is chosen based on the objectives of the program/project. Most of MDEQ programs/projects are designed to monitor watershed scale water quality, as opposed to small scale and local water quality and potential stresses. For watershed scale programs/projects, the AR is intended to represent a typical reach of the stream minus rare and local abnormalities (i.e. bridge crossing, isolated rip-rap). However, if the abnormalities are common or dominant features both locally and throughout the watershed and the field team expects that they would potentially have a broad scale effect, then they would not be considered rare, and would be incorporated in the AR. For projects other than watershed scale projects, the AR is delineated according to project objectives.

The biological sampling procedure involves collecting from multiple habitats, including bottom substrates, undercut banks, snags (including leaf packs), and submerged and floating aquatic vegetation. A pre-determined number of jabs (20) are applied in each sample location. Five jabs (25 percent of the total sampling effort) are placed in bottom areas of substrate particle fines (defined as very coarse sand, coarse sand, sand, and silt). The remaining 75 percent (or 15 jabs) are allocated among the following productive habitats in proportion to their frequency of occurrence within each 100-meter stream reach:

- Riffle/run: Bottom areas defined as having relatively fast water flowing over substrate particles of gravel or larger size.

- Undercut banks: Lower submerged banks having associated roots and emergent plants.

- Snags/woody debris: Sticks, large woody debris and leaves that have been submerged for a relatively long period of time (not recent deadfall). If leaves are not present in snags, one handful of leaves is taken from another location in the stream and added to that jab.

- Aquatic vegetation: Submerged, floating, and emergent macrophytes, sometimes seasonal in occurrence.

If there is not enough productive habitat available to satisfy the fifteen (15) jab requirment, the remaining jabs are applied to the bottom areas of substrate particle fines. This ensures representativeness by allotting effort for sampling the macroinvertebrate habitats in proportion to the occurrence of the habitat.

An increase in standardization of laboratory procedures (i.e., random fixed-count sub-sampling using a Caton gridded screen [Caton 1991]) has been shown to result in higher data quality and confidence in inferences made on biological data (Barbour and Gerritsen 1996, Vinson and Hawkins 1996). When making broad-scale spatial statements on biological data (as with the M-BISQ development study) the standardization of laboratory methods increases the likelihood that the data used to make these statements are of high quality (Gurtz and Muir 1994). The standardization of laboratory sorting procedures increases representativeness, comparability and precision, three key data quality indicators.

Thus, the subsampling method used by MDEQ involves randomly choosing a fraction or “grid” within a pan and sorting all organisms within the grid, regardless of size, color, or morphology. The random selection and complete sorting of grids continues until the target number of organisms (200) is exceeded with the final grid being picked to completion. If the upper range of the target number (240) is exceeded, then the rarefaction formula (Heck, Belle, and Simberloff 1975) is used and the result is all data used for analyses and assessment are based on samples that contain 160 – 240 organisms.

Completeness

Completeness is defined as the percentage of measurements made that are judged to be valid according to specific criteria and entered into the data management system (Diamond, Barbour, and Stribling 1996). To achieve this objective, in part, every effort is made to avoid accidental or inadvertent sample and/or data loss. Accidents during sample transport or lab activities that cause the loss of the original samples will result in irreparable loss of data. Incomplete data entry will compromise the ability to perform data analyses, integrate results, and prepare reports.

To ensure completeness, field personnel maintain strict record keeping by assigning a set

of continuous identifiers to a batch of samples. Samples are stored and transported in unbreakable (plastic) containers. All sample processing (i.e., subsampling, sorting, identification, and enumeration) occurs in a controlled laboratory environment. The assignment of a set of continuous (serial) laboratory numbers to a batch of samples that have undergone chain-of-custody inspections makes it less likely for the technician or taxonomist to overlook samples when preparing them for processing and identifications. The laboratory serial (or log) numbers also make it easy during the data compilation to recognize whether some samples have not been analyzed.

To measure completeness, percent completeness (*%C*) is calculated as follows:

$$\%C = \frac{V}{T} \times 100$$

where *V* = the number of measurements judged valid and *T* = the total number of measurements.

Comparability

Two data sets are considered to be comparable when there is confidence that the two sets are equivalent with respect to the measurement of a specific variable or group of variables. Measurement data collected by MDEQ follow established SOPs to permit comparisons of water quality, benthic assemblages, and physical characteristics. Comparability is dependent on the proper design of the sampling program and adherence to accepted sampling techniques, SOPs, and QA guidelines. For the development of the M-BISQ values, comparability of data was ensured by similarity in sampling methods, parameter measurement protocols, and by uniform training and experience of field sampling and laboratory personnel. It was also ensured by similarity in geographic, seasonal, and method characteristics. Guidelines followed in order to ensure comparability of data collected for MDEQ's SWMP are:

- Samples collected in Mississippi will be compared only with reference conditions developed from streams of the same type, that is, of a similar size or order and occurring within the same bio-region.
- All sampling will be conducted within a single index period from the first week in January, until the end of March.
- All benthic macroinvertebrate samples will be collected using MDEQ standard protocols including documentation of required data quality characteristics (metadata).
- All field personnel conducting sampling will have adequate training and appropriate experience.

DATA QUALITY OBJECTIVES FOR THE STATEWIDE PROJECT TO DEVELOP AN INDEX OF BIOLOGICAL INTEGRITY (M-BISQ)

A project to monitor and assess wadeable 303(d) Listed waterbodies and develop an Index of Biological Integrity (IBI) was initiated in December 2000 and is nearly complete. The final index, called Mississippi Benthic Index of Stream Quality (M-BISQ) will be used to assess waters as to their water quality status and whether or not they should remain on the 303(d) List. A QAPP was developed for this project and was approved and signed by MDEQ Project Management and USEPA Region 4 personnel (MDEQ 2001).

Data quality is addressed, in part, by consistent performance of valid procedures documented in the SOPs and is enhanced by the training and experience of project staff and documentation of project activities. A training session was held prior to the start of sampling. A QC Officer (one member of each Field Team) ensured that samples were taken according to the established protocols and that all forms, check lists, and measurements were recorded and completed correctly during the sampling event. Staff performance was reviewed throughout the sampling and analysis phases to ensure adherence to project protocols. Two official field and laboratory audits were performed during the project. Observed deviations from SOP or any actions that were believed to potentially compromise data quality were recorded by the reviewers and were relayed to all field and laboratory personnel in the form of a report. Observations by the auditors that were considered major were reported as needing corrective actions and were immediately addressed with the Project Managers and field and/or laboratory personnel. Also, corrective

actions were implemented to ensure compliance.

Duplicate samples were collected and analyzed to measure the repeatability of the results obtained by a single set of field investigators. Independent revisits were performed to measure sampling team bias.

Summary statistics used for this project were:

- Precision of field sampling using duplicate and repeat sampling data
  - relative percent difference
  - coefficient of variability
- Accuracy of laboratory sample sorting
  - percent sorting efficiency
- Precision of taxonomic identifications between two independent taxonomists
  - percent taxonomic disagreement
- Precision of field chemical sampling
  - relative percent difference of duplicate samples
- Accuracy of data entry
  - number of errors/corrective actions
- Completeness
  - percent of valid data points obtained compared to those projected

Table 1 presents a summary of the measurement performance criteria targeted for all parameters included in this study.

All data entries were re-checked against the original handwritten field and laboratory data sheets. A minimum of 10 percent of randomly selected metric values was recalculated by hand to verify the computer-generated values.

Data Quality Report

The Data Quality Report will describe the analysis of all QA/QC data as well as any anecdotal information. This report will summarize the results of the QA/QC procedures used throughout the project with associated data and/or documentation. The preparation of the data quality report will involve a collaborative effort between all Project QA Managers.

The data quality report will include the following:

- An introduction summarizing the general nature of the project, DQOs and measurement performance criteria, QC procedures, and all reviewed project forms and documentation (*e.g.*, Chain of Custody Records, Sample Request Forms, Bench Sheets, etc.).
- Statistical results of QA/QC data analyses with qualifiers and summary of conclusions for project QA adherence.
- Legible copies of all raw data sheets, calibration logs, Chain of Custody Records, taxonomic bench sheets, subsampling bench sheets and all other project records.

SUMMARY

Reducing data uncertainty is of the highest priority to MDEQ. Because data collected and reported by MDEQ will be used for water resources management and regulatory purposes, it is important to reduce uncertainty using appropriate QA/QC protocols.

MDEQ is in the process of developing a comprehensive QA/QC Program for all components of its surface water monitoring programs. The following QA/QC Program components were developed and have been implemented: QAPP preparation, QC activities and corrective action procedures, procedures for developing and evaluating method performance characteristics, procedures to evaluate and report the quality of all data as well as the type and amount of uncertainty associated with all data. The QA/QC Program is generally structured to isolate, identify and correct problems in either process or design that produce error and increase variability. Quality control activities are focused upon each step of the assessment process. Several QC activities used to evaluate either particular methods or results for this project included the following: field and laboratory audits, duplicate and repeat sampling, calculation of percent sorting efficiencies, sorted sample re-checks, taxonomic re-identifications, 100% checks of data entries, and re-calculations of metrics. The end result will objectively define the capacity of the M-BISQ to correctly identify the water quality status of sampling reaches. It will also ensure that all monitoring data and decisions based on the data are of known and documented data quality.

MDEQ intends to continue to utilize and further develop these QA/QC procedures for conducting future surface water monitoring projects.

ACKNOWLEDGEMENTS

We thank Jeff Thomas, David Felder, James Stribling, David Bressler, Randy Reed, Phil Bass, Henry Folmar, Mike Beiser and Chip Bray for reviewing and providing comments on this paper. There are many MDEQ personnel who have been instrumental in developing and implementing MDEQ's Surface Water QA/QC Program. For their contribution, we thank them. In addition, James "Sam" Stribling is thanked for countless hours of conversation, sharing his experiences and ideas, providing suggestions and feedback and for encouraging us to continue this long and arduous process in spite of obstacles and difficulties encountered. Also, Sam is thanked for allowing us to borrow much of the information and concepts presented here from his and his staff's previous work. His mentorship is greatly and most definitely under-appreciated.

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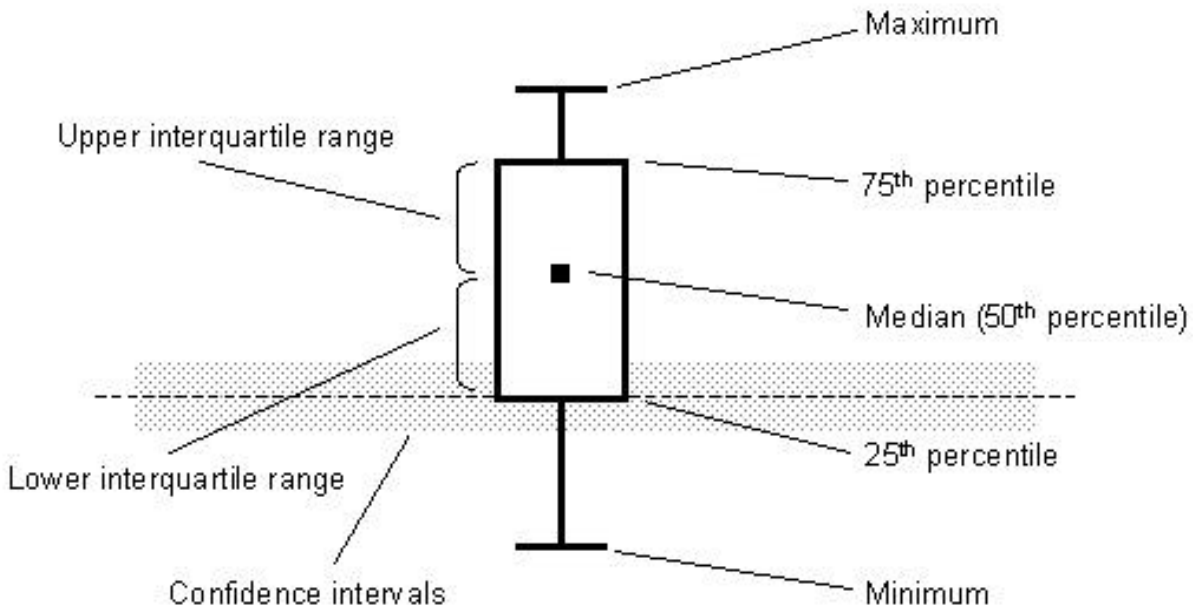

Figure 1. Example Box and Whisker Plot showing the use of the 90 percent Confidence Interval.

Table 1. Measurement Performance Criteria to measure data quality during the statewide 303(d) assessment and IBI Development Project.

Measurement Parameter	Precision	Accuracy	Completeness
GPS		± 15 m	≥95
Dissolved oxygen		The greater value of ± 2% of reading[a] or ± 0.2 mg/L for 0-20 mg/L[b]	
PH		± 0.2 standard units[b]	
Temperature		± 0.15 °C[a] or ± 0.10 °C[c]	
Specific Conductance		± 0.5% + 1µS/cm[a] or the greater value of ± 1% of reading or ± 1µS/cm[c]	
Turbidity		± 2 %[d]	
Total dissolved solids		± 0.5% + 1 mg/L[a] or the greater value of ± 1% of reading or + 1 mg/L[c]	
COD	± 17 mg/L	90-110%	
TOC	± 1 mg/L	90-110%	
TP	± 0.04 mg/L @ (<1.0 mg/L) ± 0.10 mg/L @ (1.0 mg/L)	80-120%	
TKN	± 0.25 mg/L	80-120%	
Ammonia	± 0.12 mg/L	90-110%	
Nitrate/nitrite	± 0.02 mg/L @ (<1.0 mg/L) ± 0.10 mg/L @ (>1.0 mg/L)	90-110%	
Total alkalinity	± 1.8 mg/L	90-110%	
Total chlorides	±0.9 mg/L	90-110%	
Physical habitat assessment	RPD ≤ 20%		
Water surface elevation	NA	NA	
Pebble Count	RPD ≤ 20%		
Taxonomic Precision	PTD ≤ 15%		
Taxa counts	RPD ≤ 20%		
Metric values	RPD ≤ 20%		
Metric scores	RPD ≤ 5%		
Bioassessment scores	RPD ≤ 5%, RMSE ≤ 8.0, CV ≤ 12		

NA = Not available

[a] Dependent upon range of measurement used on the YSI multiprobe.

[b] Dependent upon range of measurement used on both the YSI and Hydrolab multiprobe.

[c] Dependent upon range of measurement used on the Hydrolab multiprobe.

[d] Dependent upon range of measurement used on the Hach Portable Turbidimeter

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