

## **5.0 VERIFICATION AND VALIDATION OF ANALYTICAL CHEMISTRY DATA**

### **5.1 Purpose**

Data quality verification and validation are essential to ensuring the generation of scientifically sound and legally defensible data. Failure to verify or validate data could lead to wrong decisions and, consequently, to costly errors. This chapter is intended to serve as a data quality verification and validation guide for those performing work for CERP environmental monitoring and research projects. Additional information on this topic may be found in EPA QA/G-8, posted at [www.epa.gov/quality/qs-docs/g8-final.pdf](http://www.epa.gov/quality/qs-docs/g8-final.pdf), and other references provided in **Chapter 12** of this QASR manual.

Data verification is the process of evaluating the completeness, correctness, and conformance/adherence of a specific data set against the method, procedural, or contractual requirements. Data validation is an analyte- and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual conformance to determine the analytical quality of a specific data set (EPA QA/G-8).

Confidence in the data quality will be established through the data verification and validation process. If, during this process, it becomes evident that regulatory or conformance limits have been exceeded, these occurrences should be investigated.

### **5.2 Scope**

For CERP projects, the primary goal of data verification and validation is to ensure that data meet the minimum requirements specified in the QASR and in specific project plans. This ensures that the data used for planning, monitoring, and evaluation purposes are reliable, defensible, and comparable among various sources. Data must satisfy the need for which they were collected, comply with applicable standards, specifications and statutory requirements, and reflect a consideration for cost and economics. Careful project planning with routine project and data review are essential to ensuring that the data collected meet project requirements, in terms of completeness and quality.

### **5.3 Requirements and Regulations**

#### **5.3.1 Federal Requirements and Regulations**

- EPA QA/G-8, Guidance on Environmental Data Verification and Data Validation  
[www.epa.gov/quality/qs-docs/g8-final.pdf](http://www.epa.gov/quality/qs-docs/g8-final.pdf)
- CFR, Title 40  
<http://www.epa.gov/regulations/search/40cfr.html>

### 5.3.2 State Requirements and Regulations

- FDEP: Chapter 62-160, FAC, Quality Assurance  
<http://www.dep.state.fl.us/legal/Rules/general/62-160/62-160.pdf>  
FDEP: A Tiered Approach to Data Quality Assessment (DEP EAS 00/01)  
<ftp://ftp.dep.state.fl.us/pub/labs/assessment/guidance/eas0001.pdf>
- FDEP-QA-002/02, Requirements for Field and Analytical Work  
<ftp://ftp.dep.state.fl.us/pub/labs/assessment/qa/qa00202.doc>

### 5.3.3 Other Requirements and Guidance

- NELAP;
- CGM 23: Water Quality Considerations for the Project Implementation Report Phase;
- CGM 40: Project Level Water Quality and Hydrometeorologic Monitoring and Assessment;
- CGM 41: Agency Responsibility & Coordination for QA, QC and Data Validation for CERP Environmental Monitoring;
- Field Sampling Quality Manual, SFWMD;
- Environmental Resource Assessment Quality Management Plan, SFWMD;
- Chemical Quality Assurance for HTRW Projects; USACE EM 200-1-6;
- Environmental Quality – Guidance for Evaluating Performance Based Chemical Data, USACE EM 200-1-10; and,
- Chemical Data Quality Management for HTRW Remedial Activities, USACE ER 1110-1-263.

## 5.4 Responsibilities

Key personnel involved in each project share responsibility for maintaining consistency and ensuring collection of data of acceptable and verifiable quality through the implementation of a QA/QC program. Responsibilities of key personnel are described in **Chapter 2, Section 2.2**.

Responsibility for data verification and validation rests with both the analyst and analytical laboratory performing the analyses, designated project personnel, and independent third party data validators. If deficiencies in the data are identified, then those deficiencies should be documented for the data user's review and, whenever possible, resolved by corrective action. Data verification and validation apply to activities in the field as well as in the laboratory.

## 5.5 Training

Personnel should have the required experience in performing water quality data verification and validation. Laboratory personnel will meet NELAC requirements for Individual Demonstration of Capabilities (IDCs) and annual Ongoing Demonstration of Capabilities (ODCs).

## 5.6 Project Planning and Review

Refer to **Chapter 2, Sections 2.6-2.7** for guidance and discussion on preparing a MP or a QAPP.

Data review procedures comprise an evaluation of field data, laboratory analytical data, laboratory QC data, and the final laboratory analytical report for each sample delivery group against the data quality objectives and project specific requirements. Manual verification should be performed periodically to ensure that a laboratory's automated laboratory information management system (LIMS) is working properly. Appropriate corrective action should be taken (e.g., re-analysis, data qualification, troubleshooting, or documentation) if any errors or problems are identified by the review procedures.

### **5.6.1 Data Quality Objectives**

Guidelines for formulating project-specific DQOs are presented in QASR **Chapter 2, Section 2.5**.

## **5.7 Procedures**

### **5.7.1 Laboratory Data Verification Checks**

Contract laboratories performing analytical services for CERP are required to implement Automated Data Processing Tools (ADaPT) for data review into their LIMS and provide EDDs (EDD; **QASR, Appendix D**) to the customer. For CERP work, acceptable automated data review tools include: Florida ADaPT, USACE Automated Data Review (ADR), or equivalent.

ADaPT is an FDEP software program that aids data users in an accelerated review and assessment of analytical data. The ADaPT was developed on a Microsoft ACCESS 2000/2002 platform as tools to support technical staff in the evaluation of analytical chemistry data using an expedited and cost effective automated process. EDD provides a standardized format, allowing laboratories to streamline the data deliverable process. USACE developed ADR software and its corresponding database, Environmental Data Management System (EDMS). ADR allows users to do 100% level III summary review on laboratory data packages in a fraction of the time it takes to do the same review manually, leaving ample time to assess the data. After data has been reviewed in ADR, it then can be compiled into EDMS, which contains tools needed to assess overall project goals. This software package is available free of charge to customers working with the USACE.

The laboratory's QM must specify the procedure for data verification before data are released from the laboratory by the analyst and the supervisor. Final verification by the project manager, or QA officer of the raw analytical data and verify that the accuracy and precision goals are met and that the documentation is accurate and complete. Special attention must be made to ensure that any manual data entries are correct.

Laboratory procedures for QC checks and acceptance criteria are described in the laboratory's QM as well as project specific documents (i.e., QAPP, task order, etc.). **Table 5.1** comprises a checklist for laboratory data verification and includes, at the analyst's level, the most common checks necessary to maintain comparable data quality among CERP contract laboratories. Details of the procedures for laboratory QC checks are provided in **Section 5.7.3**.

**Table 5.1 Laboratory Data Verification Checklist**

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                             |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| Analyst/Technician:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Analytical/Prep Method No.: |
| Analysis/Prep Date:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | Test Name:                  |
| Analysis/Prep Time:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                             |
| Supervisor Review:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                             |
| <b>Part A: Chemistry Checklist</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                             |
| <input type="checkbox"/> Sample IDs match on all paperwork<br><input type="checkbox"/> Sample matrix verified and documented<br><input type="checkbox"/> Test method and project requested target analytes verified and documented<br><input type="checkbox"/> Reporting units are correct<br><input type="checkbox"/> Method Detection Limit (MDL) verified with low level Quality Control (QC) standard<br><input type="checkbox"/> Sample preservation verified and documented<br><input type="checkbox"/> Sample preparation holding time met<br><input type="checkbox"/> Sample analysis holding time met<br><input type="checkbox"/> Analytical sensitivity present<br><input type="checkbox"/> Correlation coefficient within limits<br><input type="checkbox"/> Calibration standards within historical limits<br><input type="checkbox"/> Internal standards within limits<br><input type="checkbox"/> Dilution factors and concentration calculations verified<br><input type="checkbox"/> Check for over-range samples performed<br><input type="checkbox"/> Laboratory blanks < MDL, or within method prescribed project specific limits<br><input type="checkbox"/> QC recoveries within project specific limits<br><input type="checkbox"/> Matrix spike (MS) recoveries within project specific limits<br><input type="checkbox"/> Surrogate spike recoveries within limits<br><input type="checkbox"/> Analytical precision within limits<br><input type="checkbox"/> Required number of laboratory QC samples used and sample concentration range bracketed<br><input type="checkbox"/> Required number of laboratory duplicate samples used<br><input type="checkbox"/> Calculations and data reductions correct<br><input type="checkbox"/> Any nonconformance explained and documented<br><input type="checkbox"/> Accuracy of all manual transcriptions of raw data verified |                             |
| <b>Part B: Additional Supervisor or Laboratory Project Manager Checks</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                             |
| <input type="checkbox"/> All required analyses were performed and data were reported.<br><input type="checkbox"/> Electronic Data Deliverables (EDD) format is correct and all required entries are present.<br><input type="checkbox"/> FDEP qualifiers are applied per Chapter 62-160, F.A.C.<br><input type="checkbox"/> Verify correctness of sequence of reported collection, preparation and analysis times.<br><input type="checkbox"/> Project-required MDLs were met and demonstrated through MDL or Practical Quantitation Limit (PQL) checks and method blanks.<br><input type="checkbox"/> Clear case narrative provided with indication of any non-conformance and corrective action taken.<br><input type="checkbox"/> Verify accuracy of all data entries and completeness of document.<br><input type="checkbox"/> Check of reasonable results (e.g., pH not >14)<br><input type="checkbox"/> Conduct comparison checks<br><input type="checkbox"/> Check for reversals and inter-parameter relationships (total > dissolved, results of Conductivity vs. Total Dissolved Solids (TDS))<br><input type="checkbox"/> Ionic balance checks performed and within limits (if permitted by test list)<br><input type="checkbox"/> Check field blanks and field precision recovery, if identified in the batch. Ensure project Data Quality Objectives (DQOs) are met.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                             |

### 5.7.2 CERP Data Validation Checks

The following approach to data validation is based on FDEP's *A Tiered Approach to Data Quality Assessment* (DEP EAS 00/01) and is posted at:

<ftp://ftp.dep.state.fl.us/pub/labs/assessment/guidance/eas0001.pdf>.

The tiered approach is applicable to data in both paper and electronic format, and builds on the tier below it (i.e., a Tier 2 data assessment includes activities in both Tiers 1 and 2). This series of tiered validation checks is included in the ADaPT/ADR software.

**Tier 1 - Basic Electronic Data Review:** This is performed to determine if the EDDs (EDD, **QASR Appendix D**) meet the project-specific DQOs, including:

- Confirm that all stations sampled are included with Laboratory EDD with no additional stations
- Verify that COC forms have been properly signed and dated by laboratory
- If holding times were met
- If the MDLs were reported correctly as per requirement and if blank or MDL check shows that this was achieved
- Case narrative, paying close attention to any non-conformances
- If samples were properly preserved
- Use of data qualifiers
- Evidence of any data reversals (e.g., totals versus dissolved)
- Inter-parameter check (ex. conductivity vs. total dissolved solids, **Section 5.7.3.9**)
- Reasonable range checks (ex. pH).
- Completeness of entries and verify if data were reported in proper format

**Tier 2 - Advanced Electronic Data Review:** This is performed to evaluate the quality of laboratory analyses. This series of checks is included in ADaPT/ADR, except for calibration data.

- Laboratory method blanks
- Field blanks
- Matrix spike recovery
- Precision checks (analytical replicates, field replicates)
- Surrogate recovery
- Calibration data

**Tier 3 - In-depth Review of Paper Records:** Generally, this is performed in conjunction with a field or laboratory audit or when a more extensive data assessment is required; for example, if a significant laboratory quality question arises, when a contract laboratory is to be used for the first time, or if the project is of a particularly sensitive nature.

- Calibration curves
- MDL studies
- Mass spectra, chromatograms, and other instrument outputs

- Bench notes
- Field notes
- COC (laboratory and field)
- Field and laboratory sample IDs

**Table 5.2** comprises a checklist for laboratory data validation. Details of the procedures for laboratory QC checks are provided in **Section 5.7.3**.

**Table 5.2 Data Validation Checklist**

|                                                                                                                                                                                                                                                                       |                      |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|
| QA Staff/Project Manager:                                                                                                                                                                                                                                             | Project:             |
| Review date:                                                                                                                                                                                                                                                          | Contract Laboratory: |
|                                                                                                                                                                                                                                                                       | Report Date/Number:  |
| <input type="checkbox"/> Verify that laboratory performing analysis is identified by name and Florida Department of Health (FDOH) certification number in the Electronic Data Deliverables (EDD), and is certified to perform the specified methods, where applicable |                      |
| <input type="checkbox"/> Verify that copies of internal chain of custody forms are included                                                                                                                                                                           |                      |
| <input type="checkbox"/> Verify that any subcontracted work has been previously approved                                                                                                                                                                              |                      |
| <input type="checkbox"/> Verify that field and laboratory IDs are linked and that information matches (date, time station , etc.) with analytical runs and log-in information                                                                                         |                      |
| <input type="checkbox"/> Check field information data entry for accuracy                                                                                                                                                                                              |                      |
| <input type="checkbox"/> Check that values of field measurements are reasonable                                                                                                                                                                                       |                      |
| <input type="checkbox"/> Verify that calibration requirements for field measurements have been met                                                                                                                                                                    |                      |
| <input type="checkbox"/> Review field notes to determine if data qualifiers need to be applied                                                                                                                                                                        |                      |
| <input type="checkbox"/> Verify that field duplicates are identified and that $(\text{Result} - \text{Duplicate}) / \sqrt{(\text{Original Error}^2 + \text{Duplicate Error}^2)} \leq 1.42$ for radiological analytes                                                  |                      |
| <input type="checkbox"/> Verify preparation batch numbers                                                                                                                                                                                                             |                      |
| <input type="checkbox"/> Review sample discrepancy reports/ comments to determine if data qualifiers need to be applied                                                                                                                                               |                      |
| <input type="checkbox"/> Verify that holding times for sample preparation have been met                                                                                                                                                                               |                      |
| <input type="checkbox"/> Verify that holding times for sample analysis have been met                                                                                                                                                                                  |                      |
| <input type="checkbox"/> Verify that Matrix Spike (MS) recoveries comply with project Data Quality Objectives (DQOs), or are at least within 80-120% or as defined in the methods                                                                                     |                      |
| <input type="checkbox"/> Verify Matrix Spike Duplicates (MSD) comply with project DQOs, or are at least < 20 RPD or as defined in the methods                                                                                                                         |                      |
| <input type="checkbox"/> Verify that laboratory Quality Control (QC) samples are within acceptable range and at correct frequency                                                                                                                                     |                      |
| <input type="checkbox"/> Verify laboratory precision within acceptable range                                                                                                                                                                                          |                      |
| <input type="checkbox"/> Verify method blanks < Method Detection Limit (MDL), or within method prescribed limits                                                                                                                                                      |                      |
| <input type="checkbox"/> Verify MDL achieved per low level QC and blanks                                                                                                                                                                                              |                      |
| <input type="checkbox"/> Verify surrogate recoveries within limits                                                                                                                                                                                                    |                      |
| <input type="checkbox"/> Review trace/ carrier data recoveries for compliance with control limits for radiological analytes                                                                                                                                           |                      |

|                                                                                                                                                                                                                                      |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <input type="checkbox"/> Verify minimum detection activity for radiological analytes                                                                                                                                                 |
| <input type="checkbox"/> Check that analytical sensitivity is present                                                                                                                                                                |
| <input type="checkbox"/> Check for acceptable calibration criteria (correlation coefficient, standard results)                                                                                                                       |
| <input type="checkbox"/> Check that sample results are bracketed by appropriate initial and continuing calibration checks                                                                                                            |
| <input type="checkbox"/> Verify hard copy sample results with EDD                                                                                                                                                                    |
| <input type="checkbox"/> Observe QC recoveries for trends                                                                                                                                                                            |
| <input type="checkbox"/> Observe precision values for trends                                                                                                                                                                         |
| <input type="checkbox"/> Observe blank values for trends                                                                                                                                                                             |
| <input type="checkbox"/> Check that required methods and method numbers are identified                                                                                                                                               |
| <input type="checkbox"/> Check sample results to ensure that they are reasonable                                                                                                                                                     |
| <input type="checkbox"/> Compare sample duplicate results                                                                                                                                                                            |
| <input type="checkbox"/> Check for reversals                                                                                                                                                                                         |
| <input type="checkbox"/> Conduct comparison checks                                                                                                                                                                                   |
| <input type="checkbox"/> Review or conduct ion balance checks                                                                                                                                                                        |
| <input type="checkbox"/> Verify that field and equipment blanks are $< 2 \times \text{MDL}$ or better, if required by DQOs (consult field notes if not acceptable/qualify related samples)                                           |
| <input type="checkbox"/> Verify that field precision is $< 20 \text{ RPD}$ for samples $> \text{Practical Quantitation Limit (PQL)}$ or better, if required by DQOs (consult field notes if not acceptable/ qualify related samples) |
| <input type="checkbox"/> Verify data qualifiers comply with Chapter 62-160 F.A.C.                                                                                                                                                    |
| <input type="checkbox"/> Check that regulatory/ conformance levels are not exceeded (if applicable)                                                                                                                                  |
| <input type="checkbox"/> Verify that QC checks were performed for any extraction clean-up procedures in accordance with the method                                                                                                   |

### 5.7.3 Description of Verification and Validation Checks

The verification and validation measures included in **Tables 5.1** and **5.2** are described in detail below.

#### 5.7.3.1 Analytical Report Review

Laboratory analytical reports must comply with the requirements of NELAC 2003 or most recent update. All QA/QC criteria should be within acceptable limits. Any QC data (e.g., blanks, surrogates, Matrix Spike/ Matrix Spike Duplicates (MS/MSDs), Laboratory Control Sample (LCS)/ LCS duplicates, calibration checks) that do not meet the laboratory or project-specific criteria should be properly documented and adequately explained in the case narrative portion of the analytical report. The number and frequency of QC samples must also meet minimum requirements. Verify that holding times for sample preparation and analysis have been met, that project-required MDLs were met, and that analytical sensitivity was present. Analytical documentation must be complete, accurate, and organized.

### **5.7.3.2 Analytical Range**

Periodically, the numerical magnitude of a sample result may not make sense, and warrants closer examination for data entry or recording errors (e.g., a pH value that is impossible to measure (>14)).

### **5.7.3.3 Blanks Collected in the Field**

Any detection reported for Equipment Blanks (EB) and Field Blanks (FB) should be less than 2x the MDL. Qualify any EB or FB result that does not meet the criteria. Qualify sample results associated with a trip blank, that have sufficiently low concentrations that may have been affected by the positive blank results. Generally, qualify samples with concentration levels that are less than 10x the value of the detection in the blank (unless the sample result is less than the MDL).

### **5.7.3.4 Field Precision**

Verify that field precision is less than 20%, depending on the project DQOs. Consult field notes for any relevant information that may explain poor precision. Qualify associated results if the criteria are not met. Provide feedback to the sampling groups and/or the laboratory so that investigation and corrective action may be initiated.

### **5.7.3.5 Field Parameters and Data Entry**

Review log-in information for correct station IDs and other data entries. Verify that the field parameter values are reasonable and the data entries are correct.

### **5.7.3.6 QC Tracking**

Observe QC recoveries and blank trends. Investigate any bias or outliers. For example, if a method blank detection is greater than the MDL, all associated samples in which the results fall between the MDL and 10x the value detected in the method blank should be flagged with a “V” data qualifier. If spike recoveries are below the laboratory’s acceptance range but are above the rejection point, the associated data must be flagged with a “J” qualifier. If a recovery falls outside of the acceptable criteria, all associated non-detections must be flagged with an “R” qualifier (unusable) and all detections flagged with a “J” qualifier.

### **5.7.3.7 Reworked Values**

Compare multiple results for the same sample and test. If, for example, the original result and reworked result are greater than five times the Practical Quantitation Limit (PQL), and the Relative Percent Difference (RPD) between the two is greater than 20%, both results should be flagged with a “J” (assuming all associated laboratory QC data are acceptable). If possible, determine whether the loss of precision is due to laboratory deficiencies or sample non-homogeneity.

### 5.7.3.8 Data Reversals

The allowable difference for most routine measurements is less than 20% (per FDEP-QA-002/02, posted at <http://www.dep.state.fl.us/labs/qa/index.htm>) for the following analytes:

- Total phosphorus  $\geq$  Total dissolved phosphorus  $>$  Ortho-phosphate
- Total Kjeldahl nitrogen  $\geq$  Total dissolved Kjeldahl nitrogen  $>$  Ammonia
- Total organic carbon  $\geq$  Dissolved organic carbon
- Nitrate + nitrite  $\geq$  Nitrite
- Total suspended solids  $\geq$  Volatile suspended solids
- Total Hg  $\geq$  Dissolved Hg
- Total Hg  $\geq$  or MeHg

### 5.7.3.9 Inter-Parameter Comparisons

The following comparisons must be calculated, as specified in DEP-QA-002/02, when relevant chemical analyses are performed. Any observed failure of the criteria must be investigated by re-analysis of sample aliquots. Only results for samples meeting the criteria will be accepted, unless the laboratory provides a plausible documented explanation.

The total anion charge must be 80–110% of the total cation charge if the measured conductivity is greater than 100  $\mu\text{mhos/cm}$ .

$$(0.8) \times (\text{Total cation charge}) \leq (\text{Total anion charge}) \leq (1.1) \times (\text{Total cation charge})$$

At a minimum, calcium, magnesium, sodium, alkalinity, sulfate, and chloride must be analyzed for the charge balance check to be valid. Potassium and nitrate analyses must be included in the calculation if these analyses were performed. Ion balance checks are an integral component of ADaPT. **Note:** USACE ADR software does not contain this capability. If using ADR and if necessary, the user will need to perform charge balance manually.

The measured specific conductivity ( $\mu\text{mhos/cm}$ ) must be within 80-120% of the conductivity estimated from major cation concentrations (calcium, magnesium, sodium and potassium).

$$(0.8) \times (\text{Measured conductivity}) \leq (\text{Estimated conductivity, cations})$$

$$\leq (1.2) \times (\text{Measured conductivity})$$

The conductivity may be estimated from the major cations by multiplying the sum of the major cation concentration in mg/L by a factor of five. For measured conductivities below 100  $\mu\text{mhos/cm}$ , meeting this criterion is unnecessary. If the initial charge balance calculation passes the criterion, comparison of conductivity with major cation concentrations is not required.

The measured specific conductivity ( $\mu\text{mhos/cm}$ ) must be within 80-120% of the conductivity estimated from major anion concentrations.

$$(0.8) \times (\text{Measured conductivity}) \leq (\text{Estimated conductivity, anions})$$
$$\leq (1.2) \times (\text{Measured conductivity})$$

The conductivity may be estimated from the major anions by multiplying the quantity  $[0.6 \times (\text{alkalinity concentration in mg/L as CaCO}_3) + (\text{chloride concentration in mg/L}) + (\text{sulfate concentration in mg/L})]$  by a factor of three. For measured conductivities below  $100 \mu\text{mhos/cm}$ , meeting this criterion is unnecessary. If the initial charge balance calculation passes the criterion, comparison of conductivity with major anion concentrations is not required.

The measured laboratory conductivity must be within 80-120% of the measured field conductivity.

$$(0.8) \times (\text{Measured lab conductivity}) \leq \text{Measured field conductivity}$$
$$\leq (1.2) \times (\text{Measured lab conductivity})$$

If both measurements are below  $100 \mu\text{mhos/cm}$ , meeting this criterion is unnecessary.

The Total Dissolved Solids (TDS) concentration in mg/L must be within 40-120% of the measured conductivity in  $\mu\text{mhos/cm}$ .

$$(0.4) \times (\text{TDS}) \leq \text{Measured conductivity} \leq (1.2) \times (\text{TDS})$$

If both measurements are below 100 in mg/L or  $\mu\text{mhos/cm}$ , respectively, meeting this criterion is unnecessary.

The measured TDS must be within 80% - 130% of the calculated TDS. If both measurements are below  $100 \mu\text{mhos/cm}$ , meeting this criterion is unnecessary.

The total ammonia concentration must be less than 120% of the Total Kjeldahl Nitrogen (TKN) concentration.

The ortho-phosphate concentration must be less than 120% of the total phosphorus concentration.

The Dissolved Organic Carbon (DOC) must be less than 120% of the Total Organic Carbon (TOC) concentration.

The nitrate concentration must be less than 120% of the total nitrite/nitrate concentration.

The nitrite concentration must be less than 120% of the total nitrite/nitrate concentration.

The nitrite sum of the nitrite and nitrate concentrations must be within 80-120% of the measured total nitrite/nitrate concentration.

All filtered sample results must be less than 120% of the corresponding unfiltered sample results.

### 5.7.3.10 Data Qualifiers

Data qualifiers should be reviewed for compliance with Chapter 62-160.700, FAC (**Table 5.3**). Qualifiers such as “<” or “BDL” rather than “U” are not acceptable.

### 5.7.3.11 Descriptions in Comment Fields

Comment fields contain useful information that may be used to determine the quality of sample results; e.g., “contaminated,” “incorrect preservation,” “thaw,” “over calibration,” and “expired.” Many possible conditions may be indicated in a comments field that may not be captured in fields designated for more specific information and may be associated with the laboratory procedures, field activities, the sample aliquot, the method, or the sample results.

## 5.8 Quality Assurance and Quality Control

Typically, the data validation process results in a summary of the quality of the data and the application of "flags" or "qualifiers" which provide the data user with a qualitative assessment of the data (e.g., "estimated" or "rejected").

### 5.8.1 Data Qualifiers

Data qualifiers should be reviewed for conformance with the provisions of FDEP’s QA rule (Chapter 62-160, FAC). **Table 5.3** comprises the list of FDEP data qualifiers posted at <http://www.dep.state.fl.us/legal/Rules/general/62-160/62-160.pdf>.

**Table 5.3 FDEP Data Qualifiers (Chapter 62-160.700, FAC)**

|          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>A</b> | Value reported is the arithmetic mean (average) of two or more determinations. This code shall be used if the reported value is the average of results for two or more discrete and separate samples. These samples shall have been processed and analyzed independently. Do not use this code if the data are the result of replicate analysis on the same sample aliquot, extract or digestate.                                                                    |
| <b>B</b> | Results based upon colony counts outside the acceptable range. This code applies to microbiological tests and specifically to membrane filter colony counts. The code is to be used if the colony count is generated from a plate in which the total number of coliform colonies is outside the method indicated ideal range. This code is not to be used if a 100 mL sample has been filtered and the colony count is less than the lower value of the ideal range. |
| <b>F</b> | When reporting species: F indicates the female sex.                                                                                                                                                                                                                                                                                                                                                                                                                  |
| <b>H</b> | Value based on field kit determination; results may not be accurate. This code shall be used if a field screening test (i.e., field gas chromatograph data, immunoassay, vendor-supplied field kit, etc.) was used to generate the value and the field kit or method has not been recognized by the Department as equivalent to laboratory methods.                                                                                                                  |
| <b>I</b> | The reported value is greater than or equal to the laboratory method detection limit but less than the laboratory practical quantitation limit.                                                                                                                                                                                                                                                                                                                      |

|          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>J</b> | Estimated value. A “J” value shall be accompanied by a detailed explanation to justify the reason(s) for designating the value as estimated. Where possible, the organization shall report whether the actual value is estimated to be less than or greater than the reported value. A “J” value shall not be used as a substitute for K, L, M, T, V, or Y, however, if additional reasons exist for identifying the value as an estimate (e.g., matrix spiked failed to meet acceptance criteria), the “J” code may be added to a K, L, M, T, V, or Y. Examples of situations in which a “J” code must be reported include: instances where a quality control item associated with the reported value failed to meet the established quality control criteria (the specific failure must be identified); instances when the sample matrix interfered with the ability to make any accurate determination; instances when data are questionable because of improper laboratory or field protocols (e.g., composite sample was collected instead of a grab sample); instances when the analyte was detected at or above the method detection limit in a blank other than the method blank (such as calibration blank or field-generated blanks and the value of 10 times the blank value was equal to or greater than the associated sample value); or instances when the field or laboratory calibrations or calibration verifications did not meet calibration acceptance criteria. |
| <b>K</b> | Off-scale low. Actual value is known to be less than the value given. This code shall be used if:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|          | 1. The value is less than the lowest calibration standard and the calibration curve is known to be non-linear; or                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
|          | 2. The value is known to be less than the reported value based on sample size, dilution.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
|          | This code shall not be used to report values that are less than the laboratory practical quantitation limit or laboratory method detection limit.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| <b>L</b> | Off-scale high. Actual value is known to be greater than value given. To be used when the concentration of the analyte is above the acceptable level for quantitation (exceeds the linear range or highest calibration standard) and the calibration curve is known to exhibit a negative deflection.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
| <b>M</b> | When reporting chemical analyses: presence of material is verified but not quantified; the actual value is less than the value given. The reported value shall be the laboratory practical quantitation limit. This code shall be used if the level is too low to permit accurate quantification, but the estimated concentration is greater than or equal to the method detection limit. If the value is less than the method detection limit use “T” below.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| <b>N</b> | Presumptive evidence of presence of material. This qualifier shall be used if:                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
|          | 1. The component has been tentatively identified based on mass spectral library search; or                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
|          | 2. There is an indication that the analyte is present, but quality control requirements for confirmation were not met (i.e., presence of analyte was not confirmed by alternative procedures).                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| <b>O</b> | Sampled, but analysis lost or not performed.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| <b>Q</b> | Sample held beyond the accepted holding time. This code shall be used if the value is derived from a sample that was prepared or analyzed after the approved holding time restrictions for sample preparation or analysis.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
| <b>T</b> | Value reported is less than the laboratory method detection limit. The value is reported for informational purposes only and shall not be used in statistical analysis.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
| <b>U</b> | Indicates that the compound was analyzed for but not detected. This symbol shall be used to indicate that the specified component was not detected. The value associated with the qualifier shall be the laboratory method detection limit. Unless requested by the client, less than the method detection limit values shall not be reported (see “T” above).                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |

|                                                                                                                                                                                                                                                         |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>V</b>                                                                                                                                                                                                                                                | Indicates that the analyte was detected at or above the method detection limit in both the sample and the associated method blank and the value of 10 times the blank value was equal to or greater than the associated sample value. Note: unless specified by the method, the value in the blank shall not be subtracted from associated samples.                                                                                                                                                                                   |
| <b>X</b>                                                                                                                                                                                                                                                | Indicates, when reporting results from a Stream Condition Index Analysis (LT 7200 and FS 7420), that insufficient individuals were present in the sample to achieve a minimum of 280 organisms for identification (the method calls for two aliquots of 140-160 organisms), suggesting either extreme environmental stress or a sampling error.                                                                                                                                                                                       |
| <b>Y</b>                                                                                                                                                                                                                                                | The laboratory analysis was from an improperly preserved sample. The data may not be accurate.                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| <b>Z</b>                                                                                                                                                                                                                                                | Too many colonies were present for accurate counting. Historically, this condition has been reported as “too numerous to count” (TNTC). The “Z” qualifier code shall be reported when the total number of colonies of all types is more than 200 in all dilutions of the sample. When applicable to the observed test results, a numeric value for the colony count for the microorganism tested shall be estimated from the highest dilution factor (smallest sample volume) used for the test and reported with the qualifier code. |
| <b>?</b>                                                                                                                                                                                                                                                | Data are rejected and should not be used. Some or all of the quality control data for the analyte were outside criteria, and the presence or absence of the analyte cannot be determined from the data.                                                                                                                                                                                                                                                                                                                               |
| <b>*</b>                                                                                                                                                                                                                                                | Not reported due to interference.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| <b><i>The following codes deal with certain aspects of field activities. The codes shall be used if the laboratory has knowledge of the specific sampling event. The codes shall be added by the organization collecting samples if they apply:</i></b> |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| <b>SYMBOL MEANING</b>                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| <b>D</b>                                                                                                                                                                                                                                                | Measurement was made in the field (i.e., in situ). This code applies to any value ( <b>except</b> field measurements of pH, specific conductance, dissolved oxygen, temperature, total residual chlorine, transparency, turbidity or salinity) that was obtained under field conditions using approved analytical methods. If the parameter code specifies a field measurement (e.g., “Field pH”), this code is not required.                                                                                                         |
| <b>E</b>                                                                                                                                                                                                                                                | Indicates that extra samples were taken at composite stations.                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |
| <b>R</b>                                                                                                                                                                                                                                                | Significant rain in the past 48 hours. (Significant rain typically involves rain in excess of 1/2 inch within the past 48 hours.) This code shall be used when the rainfall might contribute to a lower than normal value.                                                                                                                                                                                                                                                                                                            |
| <b>!</b>                                                                                                                                                                                                                                                | Data deviate from historically established concentration ranges.                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |

### 5.8.2 Data Uncertainty

All measured values, whether generated in the field or in the laboratory, are subject to both systematic and random errors. Therefore, no measured value can be stated with absolute certainty. In general, the result of a measurement is only an approximation or estimate of the value of the specific quantity subject to measurement and, thus the result is complete only when accompanied by a quantitative statement of its uncertainty.

Laboratories are required by NELAC, Chapter 5, Section 5.5.4.6 to have a protocol for estimating measurement uncertainty and for reporting uncertainty to clients when requested. Data uncertainty must always be reported with the sample results for radiological measurements. For CERP projects, each laboratory and field contractor must determine the uncertainty of the

measured values they report. Each project work plan or monitoring plan, if required by the DQOs, should specify the calculation method used to determine uncertainty for each field or laboratory activity. Uncertainty in each field or laboratory activity contributes to the total uncertainty of the data and must be described and provided to the end user. Each agency should evaluate and implement measures that may help improve the uncertainty of measured values.

Examples of data uncertainty are listed:

- The parameter may be a standard deviation (or a given multiple of standard deviations) or the half-width of an interval having a stated confidence level.
- Some uncertainty components may be evaluated from the statistical distribution of the results of a series of measurements and can be characterized by the following:
  - Experimental standard deviations
  - Assumed probability distributions based on experience
  - Other information
- All components of uncertainty contribute to dispersion, including those arising from systemic effects such as those associated with corrections and reference standards.
- Potential sources of uncertainty in environmental quality monitoring in both field and laboratory activities, including the following:
  - Non-representative sampling
  - Personal bias
  - Instrument error or limitations
  - Inexact values of measurement standards and reference materials (inaccuracy)
  - Method limitations due to varying matrices
  - Limited repeatability
  - Environmental conditions

Standard uncertainties (standard deviations) should first be determined based on the contribution of an individual factor (e.g., laboratory uncertainty can be determined from the laboratory QC or Round Robin (RR) results). Combined standard uncertainties should then be determined by incorporating uncertainties from independent factors. Last, calculate the combined expanded uncertainty using a chosen coverage factor that encompasses a large fraction of the distribution of values that could reasonably be attributed to the measured value.

Quantitative statements of uncertainty must be determined for each project and made available to the data users so that they can make their own judgments in using and reporting data for research projects and in decision making scenarios.

### **5.8.3 Corrective Actions**

Laboratories must establish a policy and procedure and designate appropriate individuals to implement corrective action when nonconforming work, or departures from the laboratory's acceptance criteria, have been identified. **Table 5.4** comprises laboratory QC samples, their acceptance criteria, and recommended corrective action when QC results fall outside of the acceptance range.

**Table 5.4 Laboratory Quality Control Checks and Corrective Actions**

| QC Activity                                                       | Acceptance Criteria                                                                                                                                                                                                            | Recommended Corrective Action                                                                                                                                                                                                                      |
|-------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Matrix spikes                                                     | 80 – 120 %, (or as specified by the method) recovery at a frequency of w/analytical batch, not to exceed 20 samples<br>Spike level 2-5 times the measured background level and the total concentration within analytical range | Re-make spike and re-analyze. If acceptable, re-analyze affected portions of the analysis. If not acceptable, check for matrix interference. Also check other samples in the sampling group for matrix interference. Qualify samples as necessary. |
| Laboratory fortified blanks (LFB)                                 | 85 – 115 % recovery at the same spiking level as the matrix spike                                                                                                                                                              | Re-make LFB and re-analyze. If acceptable, re-analyze affected portions of the analysis. If not acceptable, check for spiking solution degradation or contamination, dispenser/ pipette calibration, or instrument calibration problems.           |
| Laboratory duplicates/<br>Matrix spike duplicates                 | Precision < 20 (or as specified by the method) Relative Percent Difference (RPD) if concentration over the Practical Quantitation Limit (PQL)                                                                                  | Determine and eliminate cause of problem (baseline drift, carryover, etc.). Re-analyze all affected samples.                                                                                                                                       |
| Field blanks/<br>Equipment blanks                                 | ≤ Method Detection Limit (MDL)                                                                                                                                                                                                 | Re-analyze blanks, if same response, re-digest (if applicable) and re-analyze. If same response, qualify blanks. If different response, re-analyze/ re-digest all samples in the analytical batch.                                                 |
| Field duplicates/<br>Field replicates, if known to the laboratory | Precision < 20 RPD if concentration over the PQL                                                                                                                                                                               | Re-analyze duplicates, if same response, re-digest (if applicable) and re-analyze. If same response qualify samples. If different response, re-digest/re-analyze all samples in the analytical batch.                                              |