Appendix D

Data Validation and Usability

USACE New England
Upper Merrimack and Pemigewasset River Water Quality Monitoring

Data Usability and Assessment Review Laboratory Data

December 2012

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Contents

Acronyms

%R	percent recovery
°C	degrees Centigrade
DQI	data quality indicators
DQOs	data quality objectives
EPA	U.S. Environmental Protection Agency
LCS	laboratory control sample
MDL	method detection limit
mg/L	milligrams per liter
MS/MSDs	matrix spike/matrix spike duplicates
NC	not calculable
ND	Nondetect
PARCCS	precision, accuracy, representativeness, comparability, completeness, and sensitivity
QA	quality assurance
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RL	reporting limit
RPD	relative percent difference
SDG	sample delivery group
SOP	standard operating procedures
SQL	sample quantitation limit
SMAST	The School for Marine Science and Technology
UMD	University of Massachusetts Dartmouth

Section 1
Introduction

1.1 Data Usability and Assessment Review

A field sampling program was developed as part of the Upper Merrimack and Pemigewasset River Study. The primary objective of the field sampling program is to provide an accurate and representative picture of the current water quality conditions at specific sampling stations along the mainstem, with particular emphasis on impounded reaches, as well as the mouths of major tributaries. Data collected under this task will be used as input to the existing water quality and hydrologic/hydraulic models which will be extended upstream under subsequent tasks of the Upper Merrimack and Pemigewasset River Study. These models will serve as the basis for future planning and regulatory decisions in the basin.

The purpose of this assessment is to evaluate the data collected and determine whether they meet the quality objectives outlined in the Upper Merrimack River QAPP, Revision 1, 11-20-2008 Quality Assurance Project Plan (QAPP). This report details the quality assurance/quality control (QA/QC) activities conducted, describes the data verification, data validation and data usability review, and summarizes the review results for the first and second low flow events as well as the first high flow event.

Section 2
Usability Summary

Samples were collected and analyzed in accordance with the work plan except for some field changes enacted during the investigations. These changes and deviations did not negatively impact the usability of the data and are discussed in Section 4 of the Upper Merrimack and Pemigewasset River Study Monitoring Report. The sampling deviations did not affect project goals.

The data reported in this draft usability report is usable as reported with the data validation qualifiers added. No sample results were rejected.

Section 3
Quality Assurance Objectives

QA objectives for measuring data are expressed in terms of precision, accuracy, representativeness, comparability, completeness, and sensitivity (PARCCS). The QA objectives provide a mechanism for ongoing control and evaluating and measuring data quality throughout the project.

A review of the collected data is necessary in order to identify if data measurement objectives established in the seven-step data quality objective (DQO) process have been met. In general the following data measurement objectives were considered:

- Specification of particular analytical method and reporting detection limit requirements
- Identification of the appropriate laboratory analytical QC requirements
- Verify if appropriate levels of other PARCCS criteria for the data has been met
- Delineation of specific sample-handling issues or other project-specific issues

The data validation review of the QA objectives verifies if the collected data are of sufficient quality to support their intended use.

Section 4
Summary of Field and Laboratory QA Activities

CDM Smith performed sampling for the 2009 impoundment studies, two low flow events in 2010, and one high flow event in 2012. Specific sampling details are presented in Section 4 of the Upper Merrimack and Pemigewasset River Study Monitoring Report.

CDM Smith completed sampling activities in accordance with the approved QAPP. Samples were collected and shipped to University of Massachusetts University Laboratory, School for Marine Science and Technology at UMASS-Dartmouth, Environmental Protection Agency (EPA) New England Regional Laboratory (SMAST) and Eastern Analytical Laboratory (EAI). The QAPP and associated attachments defined the procedures to be followed and the data quality requirements for the field program.

4.1 Deviations from Field Procedures

Due to conditions encountered in the field, some deviations were made from the QAPP during the fieldwork portion of the sampling events. Specific deviations are discussed in Section 4 of the Upper Merrimack and Pemigewasset River Study Monitoring Report.

None of the deviations compromised the quality of the data.

4.2 Field and Analytical Quality QA/QC

QC samples such as field blanks, equipment rinsate blanks and field duplicates were collected at the frequency described in the QAPP to determine the quality of the field data.

Field QA/QC objectives were accomplished through the use of appropriate sampling techniques and collection of field duplicates and rinsate blanks.

Except for the high flow event, analytical QC data (such as calibrations, method blanks, spike recoveries, etc.) were not provided for independent verification. Method blanks and laboratory duplicates were provided by EAI for the high flow event only. Otherwise, the laboratory indicated if there were any quality issues with the data and those have been addressed in this report.

4.3 Laboratory Methods

Samples were analyzed using the following methods:

Parameter	**Method Description**
Ortho-Phosphate (PO4)	Ascorbic Acid Method (d)
Total Phosphorus (TP)	Persulfate Method (a, c, d)
Ammonia Nitrogen (NH4)	Phenate Method (b)
Dissolved Inorganic Nitrogen (DIN)	Sum of nitrogen ammonia and nitrate + nitrite
Total Suspended Solids (TSS)	gravimetric (g)
Particulate Organic Carbon (POC)	Elemental analysis (e)
Particulate Organic Nitrogen (PON)	Elemental analysis (e)
C/N (Carbon to Nitrogen Ratio)	Ratio: Moles of POC/moles of PON
Chlorophyll a	Cold 90% acetone extract, acid corrected (g)
Phaeophytin	
Total Pigment	Chlorophyll a and Phaeophytin added together
Chlorophyll a + Phaeophytin	Ratio of Chlorophyll a to Phaeophytin
Dissolved Oxygen (DO)	probe method
CBOD5 – 5 day Carbonaceous Biological Oxygen Demand	incubation and DO measurement
CB0D20- 20 day Carbonaceous Biological Oxygen Demand	incubation and DO measurement
Nitrate + Nitrite (NOX)	Automated Cadmium Reduction Method (a)
Total Dissolved Nitrogen (TDN)	Persulfate Digest & Automated Cadmium Reduction Method (a, c,)
Dissolved Organic Nitrogen (DON)	Persulfate Digest & Automated Cadmium Reduction Method (a, c,)
Alkalinity	Titration (f)
Conductivity	Conductivity
DO	Winkler Dissolved Oxygen
DO PERC	Field Dissolved Oxygen Percent
ECOLI	Escherichia coli- 9223B
pH	pH
SP COND	Specific Conductivity
TKN	Total Kjeldhal Nitrogen
TN	Total Nitrogen
TP	Total Phosphorus
TURB	Turbidity

a QuikChem Method 10-107-04-1-J (0-700uM) and 31-107-04-1-C (0-50 and 0-10uM)
Zellweger Analytics, Lachat Instruments Division, Milwaukee, WI USA.
Quik Chem method based upon the following techniques:

Method 4500-NO3- F. Automated Cadmium Reduction Method, Standard Methods
Wood, E., F. Armstrong and F. Richards. 1967. Determination of nitrate in sea water by cadmium copper reduction to nitrite. J. Mar. Biol. Ass. U.K. 47:23-31.
Bendschneider, K. and R. Robinson. 1952. A new spectrophotometric method for the determination of nitrite in sea water. J. Mar. Res. 11: 87-96.

b Ammonia method based upon the following techniques:
Scheiner, D. 1976. Determination of ammonia and Kjeldahl nitrogen by indophenol method. Water Resources 10: 31-36.
Method 4500-NH3 D. Phenate Method, Standard Methods.

c D'Elia, C.F., P.A. Stuedler and N. Corwin. 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. Limnol. Oceanogr. 22: 760-764.

d. Murphy, J. and J.Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Analytical Chimica Acta 27:31-36.
Method 4500-P E. Ascorbic Acid Method, Standard Methods.

e. Perkin-Elmer Model 2400 CHN Elemental Analyzer Technical Manual.

f. Method 2320 Alkalinity, Standard Methods

Hach alkalinity Titration Kit, Digital Titrator Model 16900-01

Not all specific method names were provided by the laboratories. All the methods used for these sampling events met project objectives as specified in the QAPP.

Section 5
Data Review Procedures

Data review was conducted by qualified CDM Smith data validators. Where specific guidance was not available, the data was evaluated in a conservative manner consistent with industry standards using professional experience. To the extent possible the data were reviewed and data qualifiers were added in accordance with the following documents, as applicable for each method.

- U.S. Environmental Protection Agency (EPA), Region 1 Inorganic Data Validation Functional Guidelines, November 2008 – updated guidelines for the 1988 Region 1 Guidelines
- EPA SW 846, Third Edition, Test Methods for Evaluating Solid Waste, update1, July 1992; update IIA, August 1993; update II, September 1994; update IIB, January1995; update III, December 1996; and
- Standard Methods for the Examination of Water and Wastewater, 21st Edition, American Public Health Association 2005.

The data review narratives indicate that the sample analyses generally met the QC criteria cited in the methods. Results associated with QC outliers were qualified by the data validators.

5.1 Qualifier Definitions

The following definitions provide explanations of the qualifiers assigned to results in the data review process.

J Estimated data due to exceeded quality control criteria.

U Analyte was analyzed for but not detected.

UJ Nondetect result is estimated due to exceeded quality control criteria.

R Data is rejected.

ND Non-detect (used by the laboratories for this project)

Section 6
Data Quality Indicators

Data Quality Indicators (DQI) criteria were established to ensure precision, accuracy, representativeness, comparability, completeness, and sensitivity of analysis for the analytical fractions and for the media sampled. Analytical QC procedures are detailed in the most current revisions of SW-846 methodologies and laboratory specific criteria. Analytical precision, accuracy, and sensitivity DQIs required for this project are provided in the laboratory SOWs.

The DQIs provide a mechanism for on-going control, to evaluate and measure data quality throughout the project. These criteria are defined in the sections below. Individual sample delivery group (SDGs) validation reports with specific sample detail are provided in Attachment 1.

6.1 Precision

Precision is a quantitative term that estimates the reproducibility of a set of replicate measurements under a given set of conditions. It is defined as a measurement of mutual agreement between measurements of the same property, and is expressed in terms of relative percent difference (RPD) between duplicate determinations.

RPD is calculated as follows:

RPD = absolute value [(C1-C2)/{(C1+C2)/2)}] x 100%

Where: C1 = Concentration of split sample #1
C2 = Concentration of split sample #2

Laboratory analytical precision for the reported data is determined by review of the laboratory duplicate results. Field duplicate precision is determined by review of field duplicate results. As stated previously, laboratory analytical precision QC was not provided by the laboratories for the low flow or impoundment events.

Six field duplicate samples were collected for the Impoundment 2009 data set; six field duplicate samples were collected for the Low Flow Event #1 2010 – Nutrient data set; six field duplicate samples were collected for the LF2 data set; and four duplicate samples were collected for the high flow data set. Seven laboratory duplicate samples were provided by EAI for the May 2012 High Flow Event.

Analytical precision cannot be determined if the reported value is less than the reporting limit (nondetect). Therefore when an analyte is not detected in either duplicate sample, the RPD result is reported as not calculable (NC).

The field duplicate RPD criterion is 30 percent and the laboratory duplicate RPD criterion is 20 percent. Duplicate results for concentrations close to the detection limits are reviewed based on their absolute differences as compared to their respective

quantitation limit values. When the analyte concentration is less than 5 times the reporting limit in either sample, the criteria used is the absolute difference between the two values which should be less than the reporting limit.

The field duplicate RPD results are as follows:

Impoundment 2009 Data

Two field duplicate pairs analyzed for chlorophyll a (I005-D-4 and I107-D-2) had RPDs above the 30 percent criteria at 41 percent and 66 percent respectively. The chlorophyll a result for the duplicate sample and parent sample were qualified as estimated "J."

Two field duplicate pairs analyzed for phaeophytin (I115-D-3 and I107-D-2) had RPDs above the 30 percent criteria at 42 percent and 67 percent. The phaeophytin result for the duplicate sample and parent sample were qualified as estimated "J."

All other RPD results for this data set were within criteria.

Low Flow Event #1 2010 Data – Nutrients

One field duplicate for TSS (sample M204-D-LF1) had an RPD above the 30 percent criteria at 106 percent. The TSS result for the duplicate sample and parent sample were qualified as estimated "J."

Low Flow Event #1 2010 Data - Bacteria

All RPD results for this data set were within criteria.

The attached data validation report details these results.

Low Flow Event #2 2010 Data

Three field duplicate pairs analyzed for ammonia (M001-G-LF2/M201-DLF2, M009-G-LF2/M209-D-LF2 and M041-G-LF2/M241-D-LF2) had RPDs above the 30 percent criteria at 64 percent, 56 percent and 84 percent respectively. These ammonia results were qualified as estimated "J" for the duplicate sample and parent sample.

Two field duplicate pairs analyzed for dissolved inorganic nitrogen (M001-G-LF2/M201-DLF2 and M041-G-LF2/M241-D-LF2) had RPDs above the criteria at 30 percent and 31 percent respectively.

One field duplicate pair analyzed for Ecoli (M041-G-LF2/M241-D-LF2) had an RPD above the criteria at 136 percent. One sample result was nondetect. The Ecoli results for these two samples was estimated "J."

All other RPD results were within criteria.

High Event #1 2012 Data

One field duplicate pair analyzed for dissolved inorganic nitrogen (T027-G-HF1/ T227-D-HF1) had an RPD above the 30 percent criteria at 129 percent. These results were qualified as estimated "J" for the parent and duplicate sample.

One field duplicate pair analyzed for dissolved organic nitrogen (T027-G-HF1/ T227-D-HF1) had an RPD above the 30 percent criteria at 52 percent. These results were qualified as estimated "J" for the parent and duplicate sample.

Two field duplicate pairs analyzed for ammonia (T027-G-HF1/ T227-D-HF1 and M036-G-HF1/ M236-D-HF1) had RPDs above the 30 percent criteria at 126 percent and 46 percent, respectively. These results were qualified as estimated "J" for the parent and duplicate sample.

One field duplicate pair analyzed for nitrates (T027-G-HF1/ T227-D-HF1) had an RPD above the 30 percent criteria at 130 percent. These results were qualified as estimated "J" for the parent and duplicate sample.

One field duplicate pair analyzed for orthophosphate (M070-G-HF1/ M270-D-HF1) had an RPD above the criteria at 124 percent. One sample result was nondetect and the other result was four times the reporting limit. The detected orthophosphate result was estimated "J" and the nondetect phosphate result was estimated "UJ."

Two field duplicate pairs analyzed for total phosphorous (T027-G-HF1/ T227-D-HF1 and M036-G-HF1/ M236-D-HF1) had RPDs above the 30 percent criteria at 69 percent and 34 percent, respectively. These results were qualified as estimated "J" for the parent and duplicate sample.

One field duplicate pair analyzed for total suspended solids (T027-G-HF1/ T227-D-HF1) had an RPD above the 30 percent criteria at 67 percent. These results were qualified as estimated "J" for the parent and duplicate sample.

It should be noted that one field duplicate pair analyzed for total dissolved nitrogen (M027-G-HF1/ M227-D-HF1) had an RPD above the criteria at 65 percent; however, both results were relatively low. Since the laboratory did not provide a reporting limit, the absolute differences as compared to their respective quantitation limit values cannot be determined. The total dissolved nitrogen results for the parent and duplicate sample were estimated "J" as a conservative measure.

All other RPD results for this data set were within criteria. It should be noted that a $CBOD_{20}$ duplicate sample was submitted for M036; however, the parent sample was not analyzed for $CBOD_{20}$ due to an error on the Chain of Custody.

The laboratory duplicate RPD results are as follows:

High Flow Event #1 2012 Data

All RPD results for this data set were within criteria.

6.2 Accuracy

Accuracy is the degree of agreement of a measurement with an accepted reference or true value, and is a measure of the bias in a system. Accuracy of the data was assessed by comparing LCS recovery, MS recovery, and other applicable laboratory QC. Accuracy is expressed as a percent recovery, which was calculated by:

$$Percent\ Re\ covery = \frac{(Total\ \ Analyte\ \ Found - Analyte\ \ Originally\ \ \ Present) \times 100}{Analyte\ \ Added}$$

The EAI high flow laboratory reports included LCS and LCS duplicate samples. According to the QAPP, the percent recovery criteria range is between 80 and 100 percent, and the RPD between the LCS and LCSD results must be less than 20 percent. The acceptable percent recovery criteria established by the laboratory was slightly different. The LCS/LCSD percent recoveries and RPDs were within all applicable criteria.

Accuracy could not be evaluated based on the analytical data received from the laboratories for the impoundment and low flow data rounds.

Sample Preservation and Holding Times

Sample preservation, handling, and holding times are evaluated during the validation process. All holding times were met for all data sets except for the Low Flow Event #2 2010 Bacteria data set. The laboratory reported that there were samples that did not meet holding time criteria. The bacteria results for the following samples were qualified as estimated due to holding time criteria for the Low Flow Event #2 2010 Bacteria data set:

M001	M016	M017	M024
M032	M047-G	M049-G	M04S-S
M066	M165	T002	T028
T046-G	T064		

For the LF2 sampling event, the laboratory also reported the following samples were outside of holding time criteria for E. Coli analysis:

M020	M042	M053	M054
M060	M062	M066	M165
M034	T002	T059	

The E. Coli results for these samples were qualified as estimated "J."

6.3 Blank Contamination

As stated in the work plan, rinsate blanks were to be prepared and submitted for analysis with primary samples. The field blanks and equipment rinsate blanks consisted of distilled water. Similarly, a laboratory blank is a water sample free of any known contaminants that is used to determine if any contamination occurred during the analytical process. Laboratory blank results were not provided by the laboratories for the impoundment and low flow data sets.

The field blank samples were prepared from distilled water. The individual sample bottles were filled at the sampling location with distilled water. The rinsate blank samples were prepared with distilled water that was passed over the decontaminated sampling equipment and transferred to the appropriate sample bottles.

Field and equipment blanks results are summarized below:

Impoundment 2009 Data

Chlorophyll a and total phosphorus field blank results were all within criteria or sample results were greater than field blank concentrations.

Low Flow Event #1 2010 Data – Nutrients

Numerous field blanks had concentrations greater than sample results. No qualifiers were applied to sample results based on field blank results but the data user should note that some of the field blank samples had minor contamination. Since this is not regulatory sampling, these results will not be used to determine compliance with water quality standards. Thus, for the purposes of the Upper Merrimack and Pemigewasset River Study, blank contamination does not violate the data quality objectives. Specific details of blank concentrations are presented in Attachment 1.

Low Flow Event #1 2010 Data - Bacteria

All field blank results were nondetect.

Low Flow Event #2 Data

Numerous field blanks had concentrations greater than sample results. No qualifiers were applied to sample results based on field blank results but the data user should note that some of the field blank samples had minor contamination. Since this is not regulatory sampling, these results will not be used to determine compliance with water quality standards. Thus, for the purposes of the Upper Merrimack and Pemigewasset River Study, blank contamination does not violate the data quality objectives. Specific details of blank concentrations are presented in Attachment 1.

The Ecoli field blank result for M141 was reported as being 12 mpn/100 mls and the associated sample result was nondetect. This result is suspect.

High Flow Event #1 Data

Numerous field blanks and equipment rinsate blanks had concentrations greater than sample results. No qualifiers were applied to sample results based on these blank results but the data user should note that some of the blank samples had minor contamination. Since this is not regulatory sampling, these results will not be used to determine compliance with water quality standards. Thus, for the purposes of the Upper Merrimack and Pemigewasset River Study, blank contamination does not violate the data quality objectives. Specific details of blank concentrations are presented in Attachment 1.

Section 7
Representativeness, Comparability, and Sensitivity

Representativeness and comparability are achieved by using approved, documented sampling procedures and analytical methodologies. By following the approved QAPP, sampling events should yield results representative of environmental conditions at the time of sampling. Similarly, reasonable comparability of analytical results for this, and future sampling events, can be achieved if the same approved analytical methods and sampling procedures are employed.

A review of reported sample result detection limits compared to the QAPP requirements ensures the collected data meets project objectives for sensitivity.

7.1 Representativeness

Representativeness is a qualitative term that expresses the degree to which the sample data accurately and precisely represent the environmental conditions corresponding to the location and depth interval of sample collection. Requirements and procedures for sample collection are designed to maximize sample representativeness.

Representativeness can be monitored by reviewing field documentation and/or by performing field audits. Chain of custodies and field notes were reviewed by the field team leader for all sampling events. The field team leader also performed audits of the sampling activities including checking paperwork and sampling methods.

Field sampling accuracy was attained through strict adherence to the approved final work plan and by using approved analytical methods for sample analyses. Based on this, the data should represent as near as possible the actual field conditions at the time of the sampling.

By using EPA or applicable approved sampling procedures, analytical methodologies, and written standard operating procedures (SOPs), as presented in the QAPP, this and future sampling events should yield results representative of environmental conditions at the time of sampling.

Deviations to the planned sampling activities were minimal and did not compromise the quality of the data to represent conditions within the project area. Therefore, the data collected are suitable for a representative characterization of the project area.

7.2 Comparability

Comparability is a qualitative term that expresses the confidence with which a data set can be compared with another. Strict adherence to standard sample collection procedures, analytical detection limits, and analytical methods assures that data are

comparable. This comparability is independent of laboratory personnel, data reviewers, or sampling personnel. Comparability criteria are met for the project if, based on data review, the sample collection and analytical procedures are determined to have been followed, or defined to show that variations did not affect the values reported.

To ensure comparability of data generated for the site, standard sample collection procedures and approved analytical methods were utilized by CDM Smith. Sample analyses were performed by the subcontract laboratories using the equivalent methodology. Utilizing such procedures and methods enables the current data to be comparable with the previous data sets generated with similar methods.

For the purposes of this data usability report, comparability has been met.

7.3 Sensitivity

Sensitivity is related to the ability to compare analytical results with project-specific levels of interest, such as delineation levels or action levels. Analytical quantitation limits for the various sample analytes should be below the level of interest to allow an effective comparison.

Detection Limits

Each analytical method used during the monitoring sampling was chosen because it has a reporting limit (RL) at or below the level of concern. For each analyte, the QAPP provided a RL that the laboratory was to achieve to provide analytical results at or below regulatory comparison criteria.

The RL is generally equal to or greater than the method detection limit (MDL). The RLs are set above MDLs to allow for sample matrix interferences and minimize false positives.

Development of the MDL is detailed in 40 CFR part 136 Appendix B as "the minimum concentration of a substance that can be measured and reported with a 99 percent confidence that the analyte concentration is greater than zero…" Generated by statistical analysis of multiple analyses of a low level standard, MDLs represent the best fundamental measurement of instrument sensitivity and the basis for establishing reporting limits.

Reporting limits are a compromise between analytical sensitivity and precision. Setting low RLs can lead to poorly defensible data due to false positive (Type I) and/or false negative (Type II) errors, whereas elevated RLs can hamper site characterization. Laboratory determinations of MDLs are performed on non-typical samples (e.g., distilled water) leading to idealized limits. Confidence in detection limits increases with instrument signal level above the MDL, and higher limits mean better precision.

Laboratory results are reported according to rules that provide established certainty of detection and reporting limits. The laboratory reported nondetect results as "false" or with a "<" sign indicating the result is less than the reporting limit. Qualifying the result as an estimated concentration reflects increased uncertainty in the reported value.

Detection limits were low enough to meet project objectives for all sampling events.

7.4 Data Completeness

Completeness of the field program is defined as the percentage of samples planned for collection as listed in the QAPP versus the actual samples collected during the field program (see equation A).

Completeness for acceptable data is defined as the percentage of acceptable data obtained judged to be valid versus the total quantity of data generated (see equation B.) Acceptable data includes both data which passes all the QC criteria (unqualified data) and data that may not pass all of the QC criteria but had appropriate corrective actions taken (qualified but useable data).

A. $$\%\ \text{Field Completeness} = \text{Cx}\frac{100}{\text{n}}$$

Where: C = actual number of samples collected
n = total number of samples planned

B. $$\%\ \text{Analytical Completeness} = \text{Vx}\frac{100}{\text{n}'}$$

Where: V = number of measurements judged valid
n' = total number of measurements made

Completeness goals for both the number of samples collected in the field and for sample results that are usable for project decisions (not rejected and appropriately qualified if required) have been met for both sampling events.

Section 8
Assessment of Data Usability and Reconciliation with QAPP Goals

For all sampling events, minimal qualifiers were applied due to field QC parameters. No qualifiers were applied to the high flow data set due to laboratory QC parameters. Laboratory QC parameters were not provided by the laboratories for the low flow events and hence were not able to be evaluated. The field QC results were overall within criteria and based on professional judgment the data sets from all sampling events are usable for project decisions.

Section 9
References

CDM Smith Federal Programs. 2008. Upper Merrimack River QAPP Revision 1, 11/20/2008.

EPA (U.S. Environmental Protection Agency). 2008. Region 1 Inorganic Data Validation Functional Guidelines, November 2008 – updated guidelines for the 1988 Region 1 Guidelines

_____. 1996. SW 846, Third Edition, Test Methods for Evaluating Solid Waste, update1, July 1992; update IIA, August 1993; update II, September 1994; update IIB, January1995; update III, December.

Standard Methods for the Examination of Water and Wastewater, 21st Edition, American Public Health Association. 2005.

Attachment 1

Data Validation and Usability Report

Merrimack
Data Validation Worksheet

Sample Delivery Group (SDG) Number: 20100915
Laboratory: School for Marine Science and Technology
EPA New England regional Laboratory

Matrix: Water
Collection date: 7/27/10
Analysis/Methods:

- PO4 - Ortho-Phosphate
- TP - Total Phosphorus (inorganic + organic)
- NH4 - Ammonium Nitrogen
- NOX - Nitrate + Nitrite
- DIN - Dissolved Inorganic Nitrogen (NH4 + NOX) **(calculation)**
- DON - Dissolved Organic Nitrogen
- TSS - Total Suspended Solids
- POC - Particulate Organic Carbon
- PON - Particulate Organic Nitrogen
- C/N - Ratio: Moles of POC/moles of PON **(calculation)**
- CHl-a - Chlorophyll a
- Phaeo - Phaeophytin
- Total Pigment - Chl-a and Phaeophytin added together **(calculation)**
- Chl a/Chl a+Phaeo - Ratio of Chl a to Total Pigments **(calculation)**
- D.O. - Dissolved Oxygen
- CBOD5 - 5 day Carbonaceous Biological Oxygen Demand
- CBOD20 - 20 day Carbonaceous Biological Oxygen Demand
- Ecoli

Samples in SDG:

See Attached Sample Result Tables for the following:
Sampling Event - LF1 Data
Sampling Event - Impoundment Data
Sampling Event - Bacteria Data (Ecoli Defined Substrate Data)

Reference Document Used in Data Validation:

USEPA Region 1 Inorganic Data Validation Functional Guidelines, November 2008 - updated guidelines for the 1988 Region 1 Guidelines

Wet Chemistry Parameters

Precision:	**Yes**	**No**	**N/A**
Are the field duplicate relative percent differences (RPD) ≤ 30% for water or within CRQL criteria?		**No**	
Are the laboratory duplicate RPDs ≤ 20% for water or within CRQL criteria?			**N/A**
Are the matrix spike duplicates RPD ≤ 20%?			**N/A**

Accuracy:	**Yes**	**No**	**N/A**
Was matrix spike criteria met (frequency 20% and % recovery 75-125%)?			**N/A**
Was post digestion spike criteria met (if applicable)?			**N/A**
Was laboratory control sample criteria met?			**N/A**
Was field blanks and rinsate blank criteria met?		**No**	
Was laboratory blank criteria met (within control limits)?			**N/A**
Were ICV/CCV % recoveries within 90-110%?			**N/A**

Comments (note deviations): The field and rinsate blank results for the bacteria data are within control limits. The field and rinsate blank results for the impoundment data are within control limits except for one blank result for Phaeo. One sample result was qualified as nondetect. See associated sample result table. The field and rinsate blank results for the LF1 nutrient data were within control limits or sample results were greater than the blank contamination for numerous analyses. Because the blanks have been evaluated based on the highest observed level and association of the blanks to individual samples is not possible at this time. The blanks that are representative of the parameters that have been calculated from other analyses have not been evaluated in this report. Analyses that had blank concentrations greater than the associated sample results are shown below:

DIN
DON
NH4
NOX
OP
PHAEO
TKN

The field blank samples were prepared from distilled water. The individual sample bottles were filled at the sampling location with distilled water. The rinsate blank samples were prepared with distilled water that was passed over the decontaminated sampling equipment and transferred to the appropriate sample bottles.

No qualifiers were applied to the samples based on field blank contamination but the data user should note that field blank samples had some minor contamination.

Representativeness:	**Yes**	**No**	**N/A**
Were sampling procedures and design criteria met?	**Yes**		
Were holding times met?		**No**	
Was preservation criteria met? (4° C ± 2° C)?	**Yes**		
Were Chain-of-Custody records complete and provided in data package?	**Yes**		

Comments (note deviations): For the bacteria data, the laboratory reported the samples listed below were analyzed outside of the holding time criteria. Sample results were qualified as estimated J. All other holding times were met.

Bacteria Samples

M001	M04S-G
M016	M066
M017	M165
M024	T002
M032	T028
M047-G	T046-G
M049G	T064

Comparability:	**Yes**	**No**	**N/A**
Were analytical procedures and methods follows as defined in the QAPP or field change documentation?	**Yes**		

Comments (note deviations):

Completeness (90%):	**Yes**	**No**	**N/A**
Are all data in this SDG usable?	**Yes**		

Comments (note deviations):

Sensitivity:	**Yes**	**No**	**N/A**
Is a verification report present for method detection limits, interelement correction factors and linear ranges?		**No**	
Are MDLs present and reported?	**Yes**		
Do the reporting limits meet project requirements?	**Yes**		
Are results above the linear range of the instrument?	**Yes**		

Comments (note deviations):

Data Validator: Carrie Madrid/Cherie Zakowski Date: 7-30-10
Data Reviewer: Todd Burgesser Date: 7-30-10

Merrimack
Draft Data Validation Worksheet

Sample Event: LF2
Laboratory: School for Marine Science and Technology at UMASS-Darmouth
EPA New England regional Laboratory
Eastern Analytical Laboratory

Matrix: Water
Collection date: 9/21/2010
Analysis/Methods:
C/N - Carbon to Nitrogen Ratio
CBOD20 - 20 day Carbonaceous Biological Oxygen Demand
CBOD5 - 5 day Carbonaceous Biological Oxygen Demand
CHLA - Chlorophyll a
COND - Conductivity
DIN - Dissolved Inorganic Nitrogen
D.O. - Dissolved Oxygen
D.O. CONC - Field Dissolved Oxygen
D.O. PERC - Field Dissolved Oxygen Percent
DON - Dissolved Organic Nitrogen
Ecoli
NH4 - Ammonium
NOX - Nitrates
OP - Orthophosphates
pH
POC - Particulate Organic Carbon
PON - Particulate Organic Nitrogen
SP COND -Specific Conductivity
Temperature
TKN -Total Kjedhal Nitrogen
TN - Total Nitrogen
TP - Total Phosphorus
TSS - Total Suspended Solids
Turbidity

Samples in SDG:

See Attached Sample Result Tables for the following:
Sampling Event - LF2 Data

Reference Document Used in Data Validation:

USEPA Region 1 Inorganic Data Validation Functional Guidelines, November 2008 - updated guidelines for the 1988 Region 1 Guidelines

Wet Chemistry Parameters

Precision:

	Yes	No	N/A
Are the field duplicate relative percent differences (RPD) ≤ 30% for water or within CRQL criteria?		**No**	
Are the laboratory duplicate RPDs ≤ 20% for water or within CRQL criteria?			**N/A**
Are the matrix spike duplicates RPD ≤ 20%?			**N/A**

Comments (note deviations): All field duplicate RPD results were within criteria except for the analytes listed below. The sample results for the parent sample and the field dupliate sample were qualified as estimated J.

Field Duplicate Pairs	Analyte	RPD	Qualifier	Associated Samples
M001-G-LF2/M201-DLF2	Ammonia	64%	J	M001-G-LF2/M201-DLF2
M001-G-LF2/M201-DLF2	Dissolved Inorganic Nitrogen	30.13%	J	M001-G-LF2/M201-DLF2
M009-G-LF2/M209-D-LF2	Ammonia	55.80%	J	M009-G-LF2/M209-D-LF2
M041-G-LF2/M241-D-LF2	Ammonia	84.40%	J	M041-G-LF2/M241-D-LF2
M041-G-LF2/M241-D-LF2	Dissolved Inorganic Nitrogen	30.70%	J	M041-G-LF2/M241-D-LF2
M041-G-LF2/M241-D-LF2	E. Coli	136%	J	M041-G-LF2/M241-D-LF2

Accuracy:

	Yes	No	N/A
Was matrix spike criteria met (frequency 20% and % recovery 75-125%)?			**N/A**
Was post digestion spike criteria met (if applicable)?			**N/A**
Was laboratory control sample criteria met?			**N/A**

Was field blanks and rinsate blank criteria met? **No**
Was laboratory blank criteria met (within control limits)? **N/A**
Were ICV/CCV % recoveries within 90-110%? **N/A**
Comments (note deviations): Field blanks and field equipment blanks were collected. The majority of the blank concentrations are less than the sample concentrations. Blank results that are greater than some of the sample results are listed below.

Field Blank

Analyte	Blank concentration or Range (approximately 5 field blanks and 5 field equipment blanks were collected for each analyte)	Sample Results
C/N	10-17	All sample results less than 17
DIN	12-17	All sample results greater than 17
DON	65-118	All sample results greater than 118 except for one result
Ecoli	1-12	All sample results greater than 12 except for 20 results
NH4	11-16	All sample results greater than 16 except for 17 results
NOX	0.6-1.209	All sample results greater than 1.209
POC	50-73	All sample results greater than 73
PON	3-6	All sample results greater than 6
TKN	0.08-0.13	All sample results greater than 0.13
TN	0.086-0.138	All sample results greater than 0.138
TP	2-2.3	All sample results greater than 2.3

The field blank concentration for the Ecoli sample M141 is suspect as the associated normal sample is nondetect.

Field Equipment Blanks

Analyte	Blank concentration or Range (approximately 5 field blanks and 5 field equipment blanks were collected for each analyte)	Sample Results
C/N	10-26	All sample results less than 17
DIN	13-36	All sample results greater than 36 except for 4 results
DON	109-291	All sample results greater than 291 except for 49 results
Ecoli	25	All sample results greater than 25 except for 30 results
NH4	13-33	All sample results greater than 33 except for 27 results
NOX	0.7-5.04	All sample results greater than 5.04
POC	49-110	All sample results greater than 110
PON	2-12	All sample results greater than 12 except for 2 results
TKN	0.12-0.24	All sample results greater than 0.24 except for 6 results
TN	0.12-0.33	All sample results greater than 0.33 except for 3 results
TP	1.7-1.9	All sample results greater than 1.9.

The field blank samples were prepared from distilled water. The individual sample bottles were filled at the samplling location with distilled water. The rinsate blank samples were prepared with distilled water that was passed over the decontaminated sampling equipment and transferred to the appropriate sample bottles.

No qualifiers were applied to the samples based on field blank contamination but the data user should note that field blank samples had some minor contamination. Sample concentrations that were less than the blank concentrations have been highlighted.

Representativeness:

	Yes	No	N/A
Were sampling procedures and design criteria met?	**Yes**		
Were holding times met?		**No**	
Was preservation criteria met? (4° C ± 2° C)?			**Not provided**
Were Chain-of-Custody records complete and provided in data package?		**No**	

Comments (note deviations): The laboratory identified the following sample results as being outside of holding time criteria. These results have been estimated J.

Sample Number	Analyte	Qualifier
M020-G-LF2	E. Coli	J
M042-G-LF2	E. Coli	J
M053-G-LF2	E. Coli	J
M054-G-LF2	E. Coli	J
M060-G-LF2	E. Coli	J

M062-G-LF2	E. Coli	J
M066-G-LF2	E. Coli	J
M165-B-LF2	E. Coli	J
M034-G-LF2	E. Coli	J
T002-G-LF2	E. Coli	J
T059-G-LF2	E. Coli	J

Comparability:	**Yes**	**No**	**N/A**
Were analytical procedures and methods follows as defined in the QAPP or field change documentation?	**Yes**		

Comments (note deviations):

Completeness (90%):	**Yes**	**No**	**N/A**
Are all data in this SDG usable?	**Yes**		

Comments (note deviations):

Sensitivity:	**Yes**	**No**	**N/A**
Is a verification report present for method detection limits, interelement correction factors and linear ranges?		**No**	
Are MDLs present and reported?	**Yes**		
Do the reporting limits meet project requirements?	**Yes**		
Are results above the linear range of the instrument?	**Yes**		

Comments (note deviations):

Data Validator: Cherie Zakowski Date: 12-20-11

Data Reviewer: Scott Kirchner Date: 12-29-11

Merrimack
Draft Data Validation Worksheet

Sample Event: HF1
Laboratory: School for Marine Science and Technology at UMASS-Dartmouth
Eastern Analytical Laboratory

Matrix: Water
Collection date: 5/17/2012
Analysis/Methods:

- CBOD20 - 20 day Carbonaceous Biological Oxygen Demand
- CBOD5 - 5 day Carbonaceous Biological Oxygen Demand
- CHLA - Chlorophyll a
- COND - Conductivity
- DIN - Dissolved Inorganic Nitrogen
- D.O. - Dissolved Oxygen
- DON - Dissolved Organic Nitrogen
- E.coli
- NH4 - Ammonium
- NOX - Nitrates
- pH
- PO_4- Orthophosphate
- SP COND -Specific Conductivity
- TDN- Total Dissolved Nitrogen
- Temperature
- TP - Total Phosphorus
- TSS - Total Suspended Solids
- Turbidity

Samples in SDG:

See Attached Sample Result Tables for the following:
Sampling Event - HF1 Data

Reference Document Used in Data Validation:

USEPA Region 1 Inorganic Data Validation Functional Guidelines, November 2008 - updated guidelines for the 1988 Region 1 Guidelines

Wet Chemistry Parameters

Precision:	**Yes**	**No**	**N/A**
Are the field duplicate relative percent differences (RPD) ≤ 30% for water or within CRQL criteria?		**No**	
Are the laboratory duplicate RPDs ≤ 20% for water or within CRQL criteria?	**Yes**		
Are the matrix spike duplicates RPD ≤ 20%?			**N/A**

Comments (note deviations): All field duplicate RPD results were within criteria except for the analytes listed below. The sample results for the parent sample and the field duplicate sample were qualified as estimated J or UJ.

Field Duplicate Pairs	Analyte	RPD	Qualifier	Associated Samples
T027-G-HF1/T227-D-HF1	Dissolved Inorganic Nitrogen	129%	J	T027-G-HF1/T227-D-HF1
T027-G-HF1/T227-D-HF1	Dissolved Organic Nitrogen	52%	J	T027-G-HF1/T227-D-HF1
T027-G-HF1/T227-D-HF1	Ammonia	126%	J	T027-G-HF1/T227-D-HF1
M036-G-HF1/M236-D-HF1	Ammonia	46%	J	M036-G-HF1/M226-D-HF1
T027-G-HF1/T227-D-HF1	Nitrates	130%	J	T027-G-HF1/T227-D-HF1
M070-G-HF1/M270-D-HF1	Orthophosphate	124%	J/ UJ	M070-G-HF1/M270-D-HF1
T027-G-HF1/T227-D-HF1	Total Phosphorous	69%	J	T027-G-HF1/T227-D-HF1
M036-G-HF1/M226-D-HF1	Total Phosphorous	34%	J	M036-G-HF1/M226-D-HF1
T027-G-HF1/T227-D-HF1	Total suspended solids	67%	J	T027-G-HF1/T227-D-HF1
T027-G-HF1/T227-D-HF1	Total Dissolved Nitrogen	65%	J	T027-G-HF1/T227-D-HF1

Accuracy:	**Yes**	**No**	**N/A**
Was matrix spike criteria met (frequency 20% and % recovery 75-125%)?			**N/A**
Was post digestion spike criteria met (if applicable)?			**N/A**
Was laboratory control sample criteria met?	**Yes**		
Was field blanks and rinsate blank criteria met?		**No**	
Was laboratory blank criteria met (within control limits)?	**Yes**		
Were ICV/CCV % recoveries within 90-110%?			**N/A**

Comments (note deviations): Field blanks and field equipment blanks were collected. The majority of the blank concentrations are less than the sample concentrations. Blank results that are greater than some of the sample results are listed below.

Field Blank

Analyte	Blank concentration or Range (approximately 3 field blanks and 3 field equipment blanks were collected for each analyte)	Sample Results
CBOD20	<3	All sample results <3
CBOD5	<3	All sample results <3 or greater
CHLA	<0.5	All sample results <0.5 or greater
DIN	23.202-36.045	All sample results greater than 36.045
DON	67.401-141.946	All sample results greater than 141.946
Ecoli	<1	All sample results <1 or greater
NH4	20.741-30.108	All sample results greater than 30.108 except for 21 results. Associated field sample for each field blank is greater than field blank detection.
NOX	2.461-5.937	All sample results greater than 5.937
PO4	<0.002	All sample results <0.002 or greater
TDN	0.092-0.178	All sample results greater than 0.178
TP	<2-7.282	All sample results greater than 7.282 except for 8 results. Associated field sample for each field blank is greater than field blank detection
TSS	<1	All sample results <1 or greater

Field Equipment Blanks

Analyte	Blank concentration or Range (approximately 3 field blanks and 3 field equipment blanks were collected for each analyte)	Sample Results
CBOD20	<3	All sample results <3
CBOD5	<3	All sample results <3 or greater
CHLA	<0.5	All sample results <0.5 or greater
DIN	31.637-113.456	All sample results greater than 113.456 except for 12 results. Except for T027, associated field sample for each equipment blank is greater than field blank detection.
DON	82.273-918.126	All sample results less than 918.126.
Ecoli	<1	All sample results <1 or greater
NH4	28.859-49.467	All sample results greater than 49.967 except for 32 results. Except for T027, associated field sample for each equipment blank is greater than field blank detection.
NOX	2.475-63.990	All sample results greater than 63.990 except for 6 results. Except for T027, associated field sample for each equipment blank is greater than field blank detection.
PO4	<0.002	All sample results <0.002 or greater
TDN	0.122-0.950	All sample results less than 0.950 except for 1 result.
TP	<2-4.069	All sample results greater than 4.069 except for 5 results. Associated field sample for each equipment blank is greater than field blank detection.
TSS	<1	All sample results <1 or greater

The field blank samples were prepared from distilled water. The individual sample bottles were filled at the sampling location with distilled water. The rinsate blank samples were prepared with distilled water that was passed over the decontaminated sampling equipment and transferred to the appropriate sample bottles.

No qualifiers were applied to the samples based on field blank contamination but the data user should note that field and equipment blank samples had some minor contamination. Sample concentrations that were less than the blank concentrations have been highlighted.

Representativeness:	**Yes**	**No**	**N/A**
Were sampling procedures and design criteria met?	**Yes**		
Were holding times met?	**Yes**		
Was preservation criteria met? (4° C ± 2° C)?	**Yes- As indicated**		
Were Chain-of-Custody records complete and provided in data package?		**No- SMAST**	

Comments (note deviations): COC records were not included with the data package from SMAST.

Comparability:	**Yes**	**No**	**N/A**
Were analytical procedures and methods follows as defined in the QAPP or field change documentation?	**Yes**		

Comments (note deviations):

Completeness (90%):	**Yes**	**No**	**N/A**
Are all data in this SDG usable?	**Yes**		

Comments (note deviations):

Sensitivity:	**Yes**	**No**	**N/A**
Is a verification report present for method detection limits, interelement correction factors and linear ranges?		**No**	
Are MDLs present and reported?	**Yes**		
Do the reporting limits meet project requirements?	**Yes**		
Are results above the linear range of the instrument?	**Yes**		

Comments (note deviations):

Data Validator: Susan Gryszkiewicz Date: 8/28/12