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QA/QC Results for 2017-2018 Cocheco River and Bellamy River Tidal Water Quality Monitoring: Grab Sampling

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MEMORANDUM
QA/QC Results for 2017-2018 Cocheco River and Bellamy River
Tidal Water Quality Monitoring: Grab Sampling

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 Dean Peschel, GB Municipal Coalition

From: Lara Martin, University of New Hampshire (UNH), Jackson Estuarine Laboratory (JEL)

Date: November 10, 2019

Re: Quality Assurance of the grab-sample water quality data collected October-December 2017 and April-December 2018: Stations Cocheco River (GRBCR) and Bellamy River (GRBBR)

PURPOSE

The purpose of this memorandum is to document the results of quality assurance checks on the 2017-2018 water quality data collected by UNH for 2 Jackson Estuarine Laboratory Tidal Water Quality (JELTWQ) monitoring stations. UNH reviewed these data to ensure that they met data quality objectives for the Great Bay National Estuarine Research Reserve (NERR), as well as for the Piscataqua Region Estuaries Partnership (PREP) and the NH Department of Environmental Services (NHDES). The Quality Assurance Project Plan (QAPP) for this work can be found at: <https://scholars.unh.edu/prep/406/>

DATA CENSORING

If a result was less than the Reported Detection Limit (RDL), it was “censored”—that is, flagged with a “<” in the qualifier field and the reported result was replaced with the RDL value. The highest censoring rates were for Enterococci (62.3%), pheophytin-a (11.4% combined), and nitrogen-ammonia as N (4.3%). Overall, 13.5% of the October-December 2017 and April-December 2018 GRBCR/GRBBR results were below the RDL. The RDL and percent of data that were censored for each parameter are shown in the following table.

Lab ID	Parameter	RDL	Units	Censored Samples	Total Samples	Percent Censored
JELTWQ	ENTEROCOCCUS	1	#/100ML	43	69	62.3
	ESCHERICHIA COLI	1	#/100ML	2	68	2.9
	NITROGEN, AMMONIA AS N	0.005	MG/L	3	70	4.3
	PHEOPHYTIN-A	0.06*	UG/L	5	52	9.6
	PHEOPHYTIN-A	0.28*	UG/L	3	18	16.7

	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	2	70	2.9
	TOTAL FECAL COLIFORM	1	#/100ML	1	68	1.5
Grand Total				56	415	13.5%

*October 2017 - September 2018, the RDL for chlorophyll-a and pheophytin-a was 0.06 mg/L. October – December 2018 the RDL was 0.28 mg/L.

OUTLIER CHECK

The 2017-2018 dataset was checked for outliers by comparing the summary statistics against the summary statistics from the same program in 2016. These values were then compared to statistics from a dataset spanning 1988-2016.

This check identified several anomalous results that were noted (see table below).

Anomaly	Action
The maximum suspended carbon value in the 2017-2018 dataset was 12.170 mg/L (avg = 1.487 mg/L), which was higher than the maximum value in 2016.	The highest suspended carbon concentration in the 1988-2016 dataset was 8.612 mg/L (avg = 0.950 mg/L). Although this observed maximum value does not fall within the full dataset, it does not appear to be an invalid result. The suspended carbon replicates for the site were also high and fell outside of the full dataset range (10.494 mg/L and 10.434 mg/L). Other parameters (chlorophyll-a, pheophytin, Kd, organic carbon, total suspended solids) for these replicates were also on the higher end of their ranges, suggesting that the samples were representative of the conditions at the time of collection. No action taken, confirmed as valid.
The maximum dissolved organic carbon value in the 2017-2018 dataset was 13.65 mg/L (avg = 5.69 mg/L), which was higher than the maximum value in 2016.	The highest dissolved organic carbon concentration in the 1988-2016 dataset was 10.54 mg/L (avg = 3.82 mg/L). Although this observed maximum value does not fall within the full dataset, it does not appear to be an invalid result. The dissolved organic carbon replicates for the site were also high and fell outside of the full dataset range (13.61 mg/L and 13.54 mg/L). In addition, the low tide sample taken 4 hours later at the same site was also out of range (13.08 mg/L). No action taken, confirmed as valid.
The maximum suspended nitrogen value in the 2017-2018 data was 1.176 mg/L (avg. = 0.181 mg/l), which was higher than the maximum value in 2016.	The highest suspended nitrogen concentration in the 2016 dataset was 1.114 mg/L (avg = 0.129 mg/L). However, suspended nitrogen concentrations as high as 1.268 mg/L (avg = 0.111 mg/L) have been observed in the full dataset. No action taken, confirmed as valid.
The maximum total nitrogen value in the 2017-2018 data was 1.254 mg/L (avg = 0.644 mg/L).	The highest total nitrogen concentration in a 1988-September 2019 dataset was 0.901 mg/L (avg = 0.604 mg/L). Although this observed maximum value does not fall within this full dataset, it does not appear to be an invalid result. The sample was collected in very shallow water (<1 meter). One other replicate, collected at the same time, was also elevated (1.015 mg/L). No action taken, confirmed as valid.

Anomaly	Action
The maximum total fecal coliform value in the 2017-2018 data was 710 #/100ml (avg. = 84 #/100ml), which was higher than the maximum value in 2016.	The highest total fecal coliform concentration in the 2016 dataset was 230 #/100ml. However, total fecal coliform values as high as 12,900 #/100ml have been observed in the full dataset. No action taken, confirmed as valid.

After these anomalies were corrected, the result ranges from the 2017-2018 dataset are shown in the following table.

Parameter	Count (N)	Minimum	Maximum	Average
CARBON, DISSOLVED ORGANIC	70	2.35	13.65	5.69
CARBON, SUSPENDED	70	0.326	12.170	1.487
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	70	0.35	86.18	10.20
DISSOLVED OXYGEN	42	4.46	14.02	9.46
DISSOLVED OXYGEN SATURATION	42	56.0	109.5	92.5
ENTEROCOCCUS	69	1	350	25
ESCHERICHIA COLI	68	1	650	64
LIGHT ATTENUATION COEFFICIENT	62	0.90	5.46	2.10
NITROGEN	24	0.313	1.254	0.644
NITROGEN, AMMONIA AS N	70	0.005	0.184	0.045
NITROGEN, TOTAL DISSOLVED	70	0.185	0.604	0.377
NITROGEN, NITRITE (NO₂) + NITRATE (NO₃) AS N	70	0.020	0.407	0.145
NITROGEN, DISSOLVED ORGANIC	70	0.033	0.365	0.187
NITROGEN, SUSPENDED	70	0.038	1.176	0.181
PHEOPHYTIN-A	52	0.06*	21.06	3.22
PHEOPHYTIN-A	18	0.28*	5.89	1.00
PHOSPHORUS AS P	24	0.016	0.147	0.048
PHOSPHORUS, ORTHOPHOSPHATE AS P	70	0.005	0.043	0.022
SALINITY	43	0.08	29.10	11.50
SOLIDS, SUSPENDED	70	2.9	72.5	17.8
TEMPERATURE WATER	46	2.2	26.9	14.4
TOTAL FECAL COLIFORM	68	1	710	76

*October 2017 - September 2018, the RDL for chlorophyll-a and pheophytin-a was 0.06 mg/L. October – December 2018 the RDL was 0.28 mg/L.

FIELD REPLICATE COMPARISON

In 2017-2018, replicates were collected on approximately 25% of the samples. In some cases, three replicates (“triplicates”) were collected during a station visit. The quality assurance methods for analyzing duplicate and triplicate QA samples are listed below:

1. For each replicated result:
 - a. If there were two replicates, calculate the absolute difference and the relative percent difference (absolute difference divided by the mean).
 - b. If there were three replicates, calculate the standard deviation and relative standard deviation (standard deviation divided by the mean).
2. Compare the absolute difference or the standard deviation (for triplicates) to the absolute different criterion for the parameter (see table below).
3. Compare the relative percent difference or the relative standard deviation to the data quality criteria of 30%.
4. If the replicates do not meet both of these checks, then the replicates are considered to have failed the data quality objective test.
5. Summarize the percent of replicates for each parameter that failed the data quality objective test.
 - a. If this percentage is greater than 20%, investigate the possibility of systematic error in the measurements.
 - b. If the percentage is less than 20%, accept all the data as valid.

Overall, one of the 132 replicated results (0.8%) failed the data quality objective test. The failure rate was less than 20% for all parameters. Therefore, all of the data, including the individual replicates that failed the quality assurance analysis were accepted as valid. The only replicate failure was for suspended nitrogen (8.3%).

Parameter	Criteria	Failure Rate	Failure Percent
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	5 ug/L, 30%	0 out of 12	0.0
NITROGEN, DISSOLVED ORGANIC	0.4 mg/l, 30%	0 out of 12	0.0
NITROGEN, AMMONIA AS N	0.05 mg/L, 30%	0 out of 12	0.0
NITRITE (NO₂) + NITRATE (NO₃)	0.1 mg/L, 30%	0 out of 12	0.0
CARBON, DISSOLVED ORGANIC	1 mg/L, 30%	0 out of 12	0.0
PHEOPHYTIN-A	5 ug/L, 30%	0 out of 12	0.0
PHOSPHORUS, ORTHOPHOSPHATE AS P	0.025 mg/L, 30%	0 out of 12	0.0
CARBON, SUSPENDED	1 mg/L, 30%	0 out of 12	0.0
NITROGEN, SUSPENDED	0.1 mg/L, 30%	1 out of 12	8.3
NITROGEN, TOTAL DISSOLVED	0.25 mg/L, 30%	0 out of 12	0.0
SOLIDS, SUSPENDED	10 mg/L, 30%	0 out of 12	0.0
	Overall	1 out of 132	0.8%

TIDE STAGE VALIDATION

Some of the station visits were reported as being associated with a certain tide (e.g., low, high, flood, or ebb). The appropriateness of this designation was checked by comparing the sampling time to the time of high and low tide at the station. The tides at each station were calculated using Portland tide predictions and established tide lags for each station. A sample was considered to be a “high tide” or “low tide” sample if it was collected no more than 3 hours before and no more than 1 hour after the time of high tide or low tide, respectively. The criteria for “flood tide” and “ebb tide” were the same as for “high tide” and “low tide”, respectively. One out of 71 samples (1.4%) did not meet these criteria (see following table). The water quality data for these station visits were retained in the database but the tide stage was flagged as invalid.

Station ID	Sampling Date	Sampling Time (Watch Time)	Tide Stage	Time of High or Low Tide (Watch Time)	Difference (min)
GRBCR	11/1/2017	14:00:00	LOW	17:08:00	188

* A difference of 180 to -60 minutes is acceptable

OTHER ISSUES

The following other issues were identified and addressed as appropriate.

- Numeric results were rounded to the following number of decimal places (if necessary):
 - No decimal place: Escherichia coli, Enterococcus, Total Fecal Coliforms all as #/100 ml
 - One decimal place: Temperature (°C), Salinity (PSS), Dissolved Oxygen Saturation (%), Suspended Solids (mg/L)
 - Two decimal places: Light attenuation coefficient (1/M), Chlorophyll-a (µg/L), Pheophytin (µg/L), Dissolved Oxygen (mg/L), Nitrogen (mg/L), Phosphorus as P (mg/L)
 - Three decimal places: Ammonia, Nitrite+Nitrate, Total Dissolved Nitrogen, Orthophosphate, Particulate Nitrogen, Particulate Carbon, Dissolved Organic Carbon all as mg/L
- Field parameters (dissolved oxygen concentration, dissolved oxygen percent saturation, salinity and water temperature) were collected only once at each site visit but were reported (duplicated) for each instance where a replicate sample was collected for analysis by the laboratory. In order to not mistake these data for true replicate measurements, UNH removed them from the dataset. Overall, 90 (12 for each parameter) reported values were removed from the dataset.
- All of the data collected was recorded using Eastern Standard Time. To facilitate the import of the data to NHDES’ Environmental Monitoring Database (EMD), the times were converted to “watch time”-- i.e., the time that you would see on a watch at that moment, which includes adjustments for Daylight Savings Time.

SUMMARY

The Cocheco River and Bellamy River 2017-2018 water quality data for project JELTWQ were checked by UNH for potential errors. All quality control steps and changes to the dataset have been documented in this memo. The dataset was sent to NHDES for upload to the EMD upon the issuance of this memo.