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MEMORANDUM: Quality Assurance of 2016 Great Bay Estuary Water Quality Data and 2017 Cocheco River and Bellamy River Water Quality Data collected by UNH

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To: Kalle Matso, PREP
Rachel Rouillard, PREP
Tom Gregory, UNH
Steve Jones, UNH
Matt Wood, NHDES
Dean Peschel, GB Municipal Coalition

From: Lara Martin, *UNH/GRB NERR*

Date: November 25, 2017

Re: Quality Assurance of 2016 Great Bay Estuary Water Quality Data and 2017 Cocheco River and Bellamy River Water Quality Data collected by UNH

PURPOSE

The purpose of this memorandum is to document the results of quality assurance checks on the 2016-2017 water quality data collected by UNH for the Great Bay National Estuarine Research Reserve (GBNERR) System-Wide Monitoring Program, GBNERR Diel Sampling, and UNH Tidal Water Quality Monitoring stations. These programs were previously established in the NHDES Environmental Monitoring Database with project identifiers of "NERRTWQ", "NERRDIEL", and "JELTWQ", respectively. *UNH/GRB NERR* reviewed these data to ensure that they met data quality objectives for the National Estuarine Research Reserve and its partners.

DATA CENSORING

If a result was less than the Reported Detection Limit (RDL), it was flagged with a "<" in the qualifier field and the reported result was replaced by the RDL value. Values reported as "N.D." were assumed to be censored at the RDL. The highest censoring rates were for enterococcus (40.9% for JELTWQ), Escherichia coli (18.2% for JELTWQ), phosphorus, orthophosphate as P (18.0% for NERRDIEL), and total fecal coliform (14.5% for JELTWQ). The RDL and percent of data that were censored for each parameter are shown in the following table. Overall, 8.4% of the 2016 and 2017 GRBCR/GRBBR results were censored.

Lab ID	Parameter	RDL	Units	Censored Samples	Total Samples	Percent Censored
JELTWQ	ENTEROCOCCUS	1	#/100ML	45	110	40.9%
	ESCHERICHIA COLI	1	#/100ML	20	110	18.2%
	NITROGEN, AMMONIA AS N	0.005	MG/L	16	157	10.2%
	NITROGEN, TOTAL DISSOLVED	0.1	MG/L	3	157	1.9%
	NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	0.005	MG/L	2	157	1.3%
	NITROGEN, SUSPENDED	0.025	MG/L	5	154	3.2%

Lab ID	Parameter	RDL	Units	Censored Samples	Total Samples	Percent Censored
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	7	157	4.5%
	TOTAL FECAL COLIFORM	1	#/100ML	16	110	14.5%
	NITROGEN, AMMONIA AS N	0.005	MG/L	4	150	2.7%
NERRDIEL	PHEOPHYTIN-A	0.06	UG/L	4	149	2.7%
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	27	150	18.0%
	SOLIDS, SUSPENDED	1	MG/L	6	149	4.0%
	ENTEROCOCCUS	1	#/100ML	5	47	10.6%
NERRTWQ	NITROGEN, AMMONIA AS N	0.005	MG/L	5	78	6.4%
	NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	0.005	MG/L	1	78	1.3%
	NITROGEN, SUSPENDED	0.025	MG/L	2	78	2.6%
	PHEOPHYTIN-A	0.06	UG/L	2	78	2.6%
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	10	78	12.8%
GRAND TOTAL				180	2147	8.4%

OUTLIER CHECK

The 2016 and 2017 GRBCR and GRBBR datasets were checked for outliers by comparing the summary statistics from 2016 and 2017 against the summary statistics from the same program in 2015. This check identified several anomalous results that were checked (see table below).

Anomaly	Action
The maximum dissolved organic carbon value in the 2016-2017 data was 9.50 mg/l (avg. = 3.81 mg/l), which was higher than the maximum value in 2015.	The highest dissolved organic carbon concentration in the 2015 dataset was 7.11 mg/l (avg = 3.58 mg/l). However, dissolved organic carbon values as high as 10.54 mg/l have been observed in the full dataset (1988-2015). No action taken, confirmed as valid.
The maximum chlorophyll-a, corrected for pheophytin value in the 2016-2017 data was 181.01 µg/l (avg. = 5.18 µg/l), which was higher than the maximum value in 2015.	The highest chlorophyll-a concentration in the 2015 dataset was 37.95 µg/l. However, chlorophyll-a values as high as 160.25 µg/l have been observed in the full dataset (1988-2015). Although this is the maximum value observed within the full dataset (1988-2015) it does not appear to be an invalid result. All other parameters were within typical ranges, suggesting that the sample was representative of the conditions at the time of collection. No action taken, confirmed as valid.
The maximum total dissolved nitrogen value in the 2016-2017 data was 1.405 mg/l (avg. = 0.408 mg/l), which was higher than the maximum value in 2015.	The highest total dissolved nitrogen concentration in the 2015 dataset was 1.087 mg/l. However, total dissolved nitrogen values as high as 1.409 mg/l have been observed in the full dataset (1988-2015). No action taken, confirmed as valid.
The maximum nitrite & nitrate value in the 2016-2017 data was 0.671 mg/l (avg. = 0.136 mg/l), which was higher than the maximum value in 2015.	The highest nitrite & nitrate concentration in the 2015 dataset was 0.506 mg/l. However, nitrite & nitrate values as high as 0.662 mg/l have been observed in the full dataset (1988-2015). Although this is the maximum value observed within the full dataset (1988-2015), it does not appear to be an invalid result. All other parameters were within typical ranges, suggesting that the sample was representative of the conditions at the time of collection. No action taken, confirmed as valid.

Anomaly	Action
The maximum dissolved organic nitrogen value in the 2016-2017 data was 0.702 mg/l (avg. = 0.150 mg/l), which was higher than the maximum value in 2015.	The highest dissolved organic nitrogen concentration in the 2015 dataset was 0.618 mg/l. However, dissolved organic nitrogen values as high as 1.20 mg/l have been observed in the full dataset (1988-2015). No action taken, confirmed as valid.
The maximum silica value in the 2016-2017 data was 5.4 mg/l (avg. = 1.0 mg/l), which was higher than the maximum value in 2015.	The highest silica concentration in the 2015 dataset was 2.6 mg/l. However, silica values as high as 10.69 mg/l have been observed in the full dataset (1988-2015). No action taken, confirmed as valid.
The maximum total suspended solids value in the 2016-2017 data was 391.4 mg/l (avg. = 24.0 mg/l), which was higher than the maximum value in 2015.	The highest total suspended solids concentration in the 2015 dataset was 167.9 mg/l. However, total suspended solids values as high as 378.0 mg/l have been observed in the full dataset (1988-2015). Although this is the maximum value observed within the full dataset (1988-2015), it does not appear to be an invalid result. All other parameters were within typical ranges, suggesting that the sample was representative of the conditions at the time of collection. No action taken, confirmed as valid.
The maximum Enterococcus value in the 2016-2017 data was 248 #/100ml (avg. = 22 #/100ml), which was higher than the maximum value in 2015.	The highest Enterococcus concentration in the 2015 dataset was 84 #/100ml. However, Enterococcus values as high as 1900 #/100ml have been observed in the full dataset (1988-2015). No action taken, confirmed as valid.

After these anomalies were corrected, the range of results from the 2016-2017 dataset is shown in the following tables.

Parameter	N	Min.	Ave.	Max.
CARBON, DISSOLVED ORGANIC	385	1.04	3.81	9.50
CARBON, TOTAL SUSPENDED	232	0.19	0.96	8.61
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	393	0.26	5.18	181.01
DISSOLVED OXYGEN	154	2.5	8.9	13.5
DISSOLVED OXYGEN SATURATION	154	8.8	93.0	173.7
ENTEROCOCCUS	157	<1	22	248
ESCHERICHIA COLI	157	<1	16	178
LIGHT ATTENUATION COEFFICIENT	178	0.35	1.65	6.18
NITROGEN, AMMONIA AS N	385	<0.005	0.122	0.685
NITROGEN, TOTAL DISSOLVED	385	<0.1	0.408	1.405
NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	385	<0.005	0.136	0.671
NITROGEN, DISSOLVED ORGANIC	385	0.000	0.151	0.702
NITROGEN, TOTAL SUSPENDED	232	<0.025	0.129	1.114
PHEOPHYTIN-A	331	<0.06	1.86	23.12
PHOSPHORUS, ORTHOPHOSPHATE AS P	385	<0.005	0.045	0.162
SALINITY	154	0.1	19.3	29.4
SILICA AS SIO2	56	0.1	1.0	5.4
SOLIDS, SUSPENDED	349	<1	24.0	391.4
TEMPERATURE WATER	154	1.1	14.1	27.2
TOTAL FECAL COLIFORM	157	<1	20	230

FIELD REPLICATE COMPARISON

In 2016, replicates were collected on approximately 20 percent 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, nine of 400 replicated results (2.3%) 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 failures were for chlorophyll-a (5.3%), ammonia (2.6%), pheophytin-a (3.1%), and total suspended solids (15.2%).

Parameter	Criteria	Failure Rate	Percent
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	5 µg/L, 30%	2 out of 38	5.3%
DISSOLVED ORGANIC NITROGEN	0.4 mg/l, 30%	0 out of 39	0.0%
AMMONIA	0.05 mg/L, 30%	1 out of 39	2.6%
NITRITE (NO2) + NITRATE (NO3)	0.1 mg/L, 30%	0 out of 39	0.0%
DISSOLVED ORGANIC CARBON	1 mg/L, 30%	0 out of 39	0.0%
PHEOPHYTIN-A	5 µg/L, 30%	1 out of 32	3.1%
ORTHOPHOSPHATE	0.025 mg/L, 30%	0 out of 39	0.0%
TOTAL SUSPENDED CARBON	1 mg/L, 30%	0 out of 28	0.0%
TOTAL SUSPENDED NITROGEN	0.1 mg/L, 30%	0 out of 28	0.0%
SILICA	2 mg/L, 30%	0 out of 7	0.0%
TOTAL DISSOLVED NITROGEN	0.25 mg/L, 30%	0 out of 39	0.0%
TOTAL SUSPENDED SOLIDS	10 mg/L, 30%	5 out of 33	15.2%
	Overall	9 out of 400	2.3%

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. Five of 229 (2.2%) station visits 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)
GRBOR	12/06/2016	08:10:00	LOW	11:18:00	188
GRBLR	12/06/2016	09:14:00	LOW	12:15:00	181
GRBOR	12/06/2016	14:10:00	HIGH	17:26:00	196
GRBLR	12/06/2016	15:05:00	HIGH	18:23:00	198
NH-0057A	12/07/2016	15:07:00	HIGH	18:10:00	183

* 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), Silica (mg/L), Chlorophyll-a (µg/L), Pheophytin (µg/L), Dissolved Oxygen (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 only collected 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/GRB NERR* removed them from the dataset. Overall, 180 (45 for each parameter) reported values were removed form the dataset.
- All of the data collected was recorded using Eastern Standard Time. To facilitate the import of the data to NHDES' 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.
- The UNH Water Quality Analysis Lab reported negative concentrations for dissolved organic nitrogen that were associated with duplicate samples collected at station GRBAP on 06/15/2016 at 09:31:00 and 09:32:00. Discussions with the UNH Water Quality Analysis Lab determined that these concentrations were invalid and caused by the contamination of the ammonia sample. Dissolved organic nitrogen is calculated by taking total dissolved nitrogen and subtracting out nitrate/nitrite and ammonia. Because the UNH Water Quality Analysis Lab does not preserve

duplicate samples, the samples could not be re-analyzed. Therefore, the dissolved organic nitrogen and ammonia samples collected at station GRBAP on 06/15/2016 at 09:31:00 and 09:32:00 were invalidated.

SUMMARY

The 2016-2017 water quality data for projects NERRTWQ, NERRDIEL, and JELTWQ were checked by *UNH/GRB NERR* 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 their Environmental Monitoring Database upon the issuance of this memo.