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QA/QC Results for 2017 Tidal Water Quality Monitoring: Grab Sampling

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MEMORANDUM
QA/QC Results for 2017 Tidal Water Quality Monitoring: Grab Sampling

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Re: Quality Assurance of the grab-sample water quality data collected January-December 2017 Stations Great Bay (GRBGB), Lamprey River (GRBLR), Oyster River (GRBOR), Squamscott River (GRBSQ), Adams Point (GRBAP), Chapman's Landing (GRBCL), Coastal Marine Laboratory (GRBCML), Upper Piscataqua River (GRBUPR).

PURPOSE

The purpose of this memorandum is to document the results of quality assurance checks on the 2017 water quality data collected by UNH for four JEL Tidal Water Quality Monitoring stations (JELTWQ), four National Estuarine Research Reserve (NERR) stations (NERRTWQ), and one NERR diel sampling site (NERRDIEL). UNH reviewed these data to ensure that they met data quality objectives for the NERR, as well as for the Piscataqua Region Estuaries Partnership (PREP) and the NH Department of Environmental Services (NHDES).

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 non-detect "N.D." were changed to the RDL. For the dataset as a whole, the highest "N.D." rates were for Enterococci (56.4%), phosphorus/orthophosphate as P (37.0%), *Escherichia coli* (29.7%), and pheophytin-a (29.2%). The RDL and percent of data that were changed to the RDL for each parameter are shown in the following table. Overall, 19.3% of the 2017 results were below the RDL. Negative organic nitrogen values were invalidated.

Lab ID	Parameter	RDL	Units	Censored Samples	Total Samples	Percent Censored
	ENTEROCOCCi	1	#/100ML	57	101	56.4
	ESCHERICHIA COLI	1	#/100ML	30	101	29.7
	NITROGEN, AMMONIA AS N	0.005	MG/L	22	101	21.8
	NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	0.005	MG/L	2	101	2.0

JELTWQ	**NITROGEN, SUSPENDED**	0.025	MG/L	5	101	5.0
	PHEOPHYTIN-A	0.06	UG/L	28	101	27.7
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	14	101	13.9
	SILICA AS SIO2	0.1	MG/L	7	60	11.7
	TOTAL FECAL COLIFORM	1	#/100ML	22	101	21.8
NERRDIEL	**NITROGEN, AMMONIA AS N**	0.005	MG/L	15	135	11.1
	PHEOPHYTIN-A	0.06	UG/L	14	134	10.4
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	50	135	37.0
NERRTWQ	**ENTEROCOCCI**	1	#/100ML	18	54	33.3
	ESCHERICHIA COLI	1	#/100ML	6	56	10.7
	NITROGEN, AMMONIA AS N	0.005	MG/L	11	72	15.3
	NITROGEN, SUSPENDED	0.025	MG/L	1	72	1.4
	PHEOPHYTIN-A	0.06	UG/L	21	72	29.2
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	20	72	27.8
	SOLIDS, SUSPENDED	1.0	MG/L	2	72	2.8
	TOTAL FECAL COLIFORM	1	#/100ML	1	53	1.9
		Grand Total		**346**	**1795**	**19.3%**

OUTLIER CHECK

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

Anomaly	Action
The maximum dissolved organic carbon value in the 2017 dataset was 11.5 mg/L (avg = 4.62 mg/L), which was higher than the maximum value in 2016.	The highest dissolved organic carbon concentration in the full dataset (1988-2016) was 10.5 mg/L (avg = 3.94 mg/L). Although this observed maximum value exceeds all values in the full dataset, it does not appear to be an invalid result. The dissolved organic carbon value for a low tide sample taken at this site later in the day was also unusually high (11.2 mg/L). In addition, there were field notes for both samples indicating that water at the site was a dark tea color. No action taken, confirmed as valid.
The maximum nitrogen/nitrite (NO2) + nitrate (NO3) value in the 2017 dataset was 0.819 mg/L (avg = 0.158 mg/L), which was higher than the maximum value in 2016.	The highest nitrogen/nitrite (NO2) + nitrate (NO3) concentration in the full dataset was 0.671 mg/L (avg = 0.136 mg/L). Although this observed maximum value does not fall within the full dataset, it does not appear to be an invalid result. The sample was taken at low tide, when concentrations can be highest. In addition, all other nutrient measurements are within range. No action taken, confirmed as valid.
The maximum total fecal coliform value in the 2017 data was 1030 #/100ml (avg = 46 #/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 12900 #/100ml have been observed in the full dataset (1988-2016). No action taken, confirmed as valid.
The maximum *Escherichia coli* value in the 2017 dataset was 780 #/100ml (avg = 31 #/100ml), which was higher than the maximum value in 2016.	The highest *Escherichia coli* concentration in the 2016 dataset was 178 #/100ml. However, *Escherichia coli* values as high as 11300 #/100ml have been observed in the full dataset (1988-2016). No action taken, confirmed as valid.

Anomaly	Action
The maximum Enterococci value in the 2017 data was 590 #/100ml (avg = 14 #/100ml), which was higher than the maximum value in 2016.	The highest Enterococci concentration in the 2016 dataset was 248 #/100ml. However, Enterococci values as high as 1900 #/100ml have been observed in the full dataset (1988-2016). No action taken, confirmed as valid.

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

Parameter	Count (N)	Average	Minimum	Maximum
CARBON, DISSOLVED ORGANIC	308	4.62	1.21	11.5
CARBON, SUSPENDED	173	1.013	0.147	6.56
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	306	4.0	0.21	66.9
DISSOLVED OXYGEN	123	9.03	3.97	13.3
DISSOLVED OXYGEN SATURATION	123	95.4	51.5	162.1
ENTEROCOCCI	155	14	<1	590
ESCHERICHIA COLI	157	31	<1	780
LIGHT ATTENUATION COEFFICIENT	95	1.8	0.34	6.06
NITROGEN, AMMONIA AS N	308	0.0743	<0.005	0.817
NITROGEN, TOTAL DISSOLVED	308	0.403	0.116	1.33
NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	308	0.158	<0.005	0.819
NITROGEN, DISSOLVED ORGANIC	303	0.158	0.000	0.399
NITROGEN, SUSPENDED	173	0.133	<0.025	0.800
PHEOPHYTIN-A	307	0.95	<0.06	17.0
PHOSPHORUS, ORTHOPHOSPHATE AS P	307	0.0292	<0.005	0.131
SALINITY	123	15.8	0.10	28.9
SILICA AS SIO2	60	1.049	<0.10	4.68
SOLIDS, SUSPENDED	226	24.0	<1.0	195.4
TEMPERATURE WATER	123	14.4	-0.9	25.2
TOTAL FECAL COLIFORM	154	46	<1	1030

FIELD REPLICATE COMPARISON

In 2017, replicates were collected on approximately 20% of the samples. In most 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, three of 321 replicated results (0.9%) 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 failures were for phosphorus, orthophosphate as P (3.3%) and suspended solids (6.7%).

Parameter	Criteria	Failure Rate	Failure Percent
CARBON, DISSOLVED ORGANIC	1 mg/L, 30%	0 out of 30	0.0
CARBON, SUSPENDED	1 mg/L, 30%	0 out of 21	0.0
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	5 ug/L, 30%	0 out of 30	0.0
NITRITE (NO2) + NITRATE (NO3) AS N	0.1 mg/L, 30%	0 out of 30	0.0
NITROGEN, AMMONIA AS N	0.05 mg/L, 30%	0 out of 30	0.0
NITROGEN, DISSOLVED ORGANIC	0.4 mg/l, 30%	0 out of 30	0.0
NITROGEN, SUSPENDED	0.1 mg/L, 30%	0 out of 21	0.0
NITROGEN, TOTAL DISSOLVED	0.25 mg/L, 30%	0 out of 30	0.0
PHEOPHYTIN-A	5 ug/L, 30%	0 out of 30	0.0
PHOSPHORUS, ORTHOPHOSPHATE AS P	0.025 mg/L, 30%	1 out of 30	3.3
SILICA AS SIO2	2 mg/L, 30%	0 out of 9	0.0
SOLIDS, SUSPENDED	10 mg/L, 30%	2 out of 30	6.7
	Overall	**3 out of 321**	**0.9%**

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 of 179 (0.6%) 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)

GRBUP	05/02/2017	15:25:00	HIGH	18:34:00	189

*A difference of 180 to -60 minutes is acceptable

OTHER ISSUES

The following other issues were identified and addressed as described.

- Numeric results were rounded to the following number of decimal places (if necessary):
  - No decimal place: *Escherichia coli*, Enterococci, 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) in each instance where a replicate sample was collected for analysis by the laboratory. In order to not mistake these data for true replicate measurements, these data were removed from the dataset. Overall, 160 reported values (8 measurements per sampling event) 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' 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 2017 water quality data for projects JELTWQ, NERRTWQ, and NERRDIEL 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 their Environmental Monitoring Database upon the issuance of this memo.