8-5-2021

Quality Assurance of Estuarine Water Quality Grab Sampling 2020

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MEMORANDUM

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From: Lara Martin, University of New Hampshire, Great Bay National Estuarine Research Reserve (UNH/GRB NERR)

Date: June 1, 2020

Re: Quality Assurance of the water quality data collected by UNH/GRBNERR April-December 2020 Stations Great Bay (GRBGB), Lamprey River (GRBLR), Oyster River (GRBOR), Squamscott River (GRBSQ), Adams Point (GRBAP), Great Bay East (GRBGBE), Great Bay West (GRBGBW), Hampton Harbor (HHHR), Upper Little Bay (GRBULB), and Upper Piscataqua River (GRBUPR)

PURPOSE

The purpose of this memorandum is to document the results of quality assurance checks on the 2020 water quality data collected by UNH for 6 Jackson Estuarine Laboratory Tidal Water Quality Monitoring stations (JELTWQ), 4 National Estuarine Research Reserve stations (NERRTWQ), and 1 NERR diel sampling site (NERRDIEL). UNH/GRB NERR reviewed these data to ensure that they met data quality objectives for the National Estuarine Research Reserve and its partners. Please see https://scholars.unh.edu/prep/418/ for the Quality Assurance Project Plan (QAPP) for this work.

In addition to the grab samples that are collected at each site once a month, datasondes are deployed at most sites continuously from April-December. These instruments collected pH, specific conductance/ salinity, temperature, turbidity, and dissolved oxygen data every 15 minutes. Please see https://scholars.unh.edu/prep/ for related documents on "Datasonde Monitoring" measurements.

DATA CENSORING

If a result was less than the Long-Term Method Detection Limit (LT-MDL), it was "censored". This means that the data point was flagged with a "<" in the qualifier field and the original result was replaced by the LT-MDL value. For the dataset as a whole, the highest censoring rates were for nitrogen, ammonia as N (18.0% - JELTWQ, 8.3% - NERRTWQ), and nitrogen, nitrate (NO2) + nitrate (NO3) as N (6.7% - JELTWQ). Overall, 4.8% of the 2020 results were censored. The LT-MDL and percentage 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	CARBON, SUSPENDED	0.125	MG/L	1	89	1.1
	NITROGEN, AMMONIA AS N	0.007	MG/L	16	89	18.0
	NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	0.007	MG/L	6	89	6.7

NERRDIEL	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.004	MG/L	1	89	1.1
	NITROGEN, AMMONIA AS N	0.007	MG/L	2	115	1.7
	SOLIDS, SUSPENDED	1	MG/L	2	115	1.7
NERRTWQ	NITROGEN, AMMONIA AS N	0.007	MG/L	4	48	8.3
	NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	0.007	MG/L	1	48	2.1
		GRAND TOTAL		**33**	**682**	**4.8%**

OUTLIER CHECK

The 2020 dataset was checked for outliers by comparing the summary statistics from 2020 against the summary statistics from the same program in 2019. These values were then compared to statistics from a full dataset spanning 1988 – 2019. This check identified 10 anomalous results that were reviewed. (See table below.)

Anomaly	Action
The maximum organic carbon value in the 2020 dataset was 9.251 mg/L (avg = 3.271 mg/L) which was higher than the 2019 maximum value.	The highest organic carbon value in the 2019 dataset was 7.748 mg/L. However, organic carbon values as high as 14.982 mg/L have been observed in the full dataset. No action taken; data confirmed as valid.
The maximum suspended carbon value in the 2020 dataset was 4.152 mg/L (avg = 0.974 mg/L) which was higher than the 2019 maximum value.	The highest suspended carbon value in the 2019 dataset was 3.369 mg/L. However, suspended carbon values as high as 12.170 mg/L have been observed in the full dataset. In addition, this point was part of a triplicate and all suspended carbon values in the set were higher than the 2019 maximum value. No action taken; data confirmed as valid.
The maximum chlorophyll-a value in the 2020 dataset was 48.95 ug/L (avg = 4.34 ug/L) which was higher than the 2019 maximum value.	The highest chlorophyll-a value in the 2019 dataset was 27.13 ug/L. However, chlorophyll-a values as high as 181.01 ug/L have been observed in the full dataset. No action taken; data confirmed as valid.
The maximum Enterococcus value in the 2020 dataset was 1116 #/100ml (avg = 44 #/100ml) which was higher than the 2019 maximum value.	The highest Enterococcus value in the 2019 dataset was 148 #/ml. However, Enterococcus values as high as 1900 #/ml have been observed in the full dataset. In addition, this 2020 data point was collected after heavy rainfall in the preceding days. No action taken; data confirmed as valid.
The maximum Escherichia coli value in the 2020 dataset was 440 #/100ml (avg = 28 #/ml) which was higher than the 2019 maximum value.	The highest Escherichia coli value in the 2019 dataset was 56 #/100ml. However, E. coli values as high as 11,300 #/100ml have been observed in the full dataset. No action taken; data confirmed as valid.
The maximum light attenuation coefficient in the 2020 dataset was 5.33 1/M (avg = 1.41 1/M) which was higher than the 2019 maximum value.	The maximum light attenuation coefficient value in the 2019 dataset was 4.90 1/M. However, light attenuation coefficients as high as 10.92 1/M have been observed in the full dataset. No action taken; data confirmed as valid.
The maximum nitrogen, ammonia as N value in the 2020 dataset was 0.263 mg/L (avg = 0.072 mg/L) which was higher than the 2019 maximum value.	The maximum nitrogen, ammonia as N value in the 2019 dataset was 0.232 mg/L. However, nitrogen, ammonia as N values as high as 0.944 mg/L have been observed in the full dataset. No action taken; data confirmed as valid.
The maximum nitrite (NO2) + nitrate (NO3) as N value in the 2020 dataset was 0.309 mg/L (avg = 0.081 mg/L) which was higher than the 2019 maximum value.	The maximum nitrite (NO2) + nitrate (NO3) as N value in the 2019 dataset was 0.271 mg/L. However, nitrite (NO2) + nitrate (NO3) as N values as high as 0.819 mg/L have been observed in the full dataset. No action taken; data confirmed as valid.

The maximum suspended nitrogen value in the 2020 dataset was 1.168 mg/L (avg = 0.142 mg/L) which was higher than the 2019 maximum value.	The maximum suspended nitrogen value in the 2019 dataset was 0.386 mg/L. However, suspended nitrogen values as high as 1.467 mg/L have been observed in the full dataset. No action taken; data confirmed as valid.
The maximum total fecal coliform value in the 2020 dataset was 496 #/100ml (avg = 31 #/100ml) which was higher than the 2019 maximum value.	The maximum total fecal coliform value in the 2019 dataset was 60 #/100ml. However, fecal coliform values as high as 12,900 #/100ml have been observed in the full dataset. No action taken; data confirmed as valid.

The range of results from the 2020 dataset is shown in the following table.

Parameter	Count (N)	Minimum	Average	Maximum
CARBON, ORGANIC	252	1.039	3.271	9.251
CARBON, SUSPENDED	137	<0.125	0.974	4.152
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	248	0.59	4.34	48.95
DISSOLVED OXYGEN	101	4.05	8.42	14.73
DISSOLVED OXYGEN SATURATION	101	55.1	94.1	132.4
ENTEROCOCCUS	55	1	44	1116
ESCHERICHIA COLI	54	1	28	440
LIGHT ATTENUATION COEFFICIENT	105	0.24	1.41	5.33
NITROGEN, AMMONIA AS N	252	<0.007	0.072	0.263
NITROGEN, DISSOLVED	252	0.055	0.316	0.595
NITROGEN, INORGANIC (AMMONIA, NITRATE AND NITRATE)	252	0.000	0.152	0.344
NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	252	<0.007	0.081	0.309
NITROGEN, ORGANIC	252	0.000	0.163	0.360
NITROGEN, SUSPENDED	137	0.037	0.142	1.168
PHEOPHYTIN-A	248	0.47	2.32	11.09
PHOSPHORUS, ORTHOPHOSPHATE AS P	252	<0.004	0.036	0.101
SALINITY	101	0.1	22.6	31.6
SILICA AS SIO2	32	0.11	0.89	3.73
SOLIDS, SUSPENDED	252	1.0	21.2	97.9
TEMPERATURE WATER	101	2.0	15.4	26.7
TOTAL FECAL COLIFORM	54	1	31	496

FIELD REPLICATE COMPARISON

In 2020, replicates were collected for approximately 25% 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 are two replicates, calculate the absolute difference and the relative percent difference (absolute difference divided by the mean).

    b. If there are 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 277 replicated results (0.4%) 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. Replicate failure was for suspended solids (4.2%).

Parameter	Criteria	Failure Rate	Percent Failure
CARBON, DISSOLVED ORGANIC	1 mg/L, 30%	0 out of 24	0.0%
CARBON, SUSPENDED	1 mg/L, 30%	0 out of 17	0.0%
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	5 ug/L, 30%	0 out of 24	0.0%
NITRITE (NO2) + NITRATE (NO3) AS N	0.1 mg/L, 30%	0 out of 24	0.0%
NITROGEN, AMMONIA AS N	0.05 mg/L, 30%	0 out of 24	0.0%
NITROGEN, DISSOLVED ORGANIC	0.4 mg/l, 30%	0 out of 24	0.0%
NITROGEN, INORGANIC (AMMONIA, NITRATE AND NITRATE)	0.15 mg/l, 30%	0 out of 24	0.0%
NITROGEN, SUSPENDED	0.1 mg/L, 30%	0 out of 17	0.0%
NITROGEN, TOTAL DISSOLVED	0.25 mg/L, 30%	0 out of 24	0.0%
PHEOPHYTIN-A	5 ug/L, 30%	0 out of 24	0.0%
PHOSPHORUS, ORTHOPHOSPHATE AS P	0.025 mg/L, 30%	0 out of 24	0.0%
SILICA AS SI02	2 mg/L, 30%	0 out of 3	0.0%
SOLIDS, SUSPENDED	10 mg/L, 30%	1 out of 24	4.2%
	OVERALL	**1 out of 277**	**0.4%**

TIDE STAGE VALIDATION

Some of the station visits are reported as being associated with a certain tide (e.g., low, high, flood, or ebb). The appropriateness of this designation is checked by comparing the sampling time to the time of high and low tide at the station. The tides at each station are calculated using Portland tide predictions and established tide lags. A sample is 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. If stations fail the tide stage validation, the water quality data for these station visits are retained in the database but the tide stage is flagged as invalid.

All 137 visits met these criteria.

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, Suspended Nitrogen, Suspended 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, UNH removed them from the dataset. Overall, 128 reported values (8 measurements per sampling event) were removed from the dataset.
- All 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.
- Total Fecal Coliform, Escherichia coli, and Enterococcus values less than 4 #/100ml may be below the detection limit.

SUMMARY

The 2020 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 the EMD upon the issuance of this memo.