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Quality Assurance of Estuarine Water Quality Grab Sampling 2019

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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 13, 2020

Re: Quality Assurance of the water quality data collected by UNH/GRBNERR April-December 2019 Stations Great Bay (GRBGB), Lamprey River (GRBLR), Oyster River (GRBOR), Squamscott River (GRBSQ), Adams Point (GRBAP), Great Bay East (GRBGBE), 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 2019 water quality data collected by UNH for 5 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. The Quality Assurance Project Plan (QAPP) for this work can be found at: https://scholars.unh.edu/prep/419/

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, turbidity, and dissolved oxygen data every 15 minutes. See related documents on "Datasonde Monitoring" measurements at https://scholars.unh.edu/prep/

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 by the RDL value. For the dataset as a whole, the highest censoring rates were for nitrogen, ammonia as N (28.2%, 4.4%, 22.2%), phosphorus, orthophosphate as P (20.7%, 1.9%), and pheophytin (12.7%, 8.1% and 11.1%). Overall, 9.8% of the 2019 results were censored. The RDL 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	NITROGEN, AMMONIA AS N	0.005	MG/L	20	71	28.2
	PHEOPHYTIN-A	0.78	UG/L	9	71	12.7

	SILICATE AS SIO2	0.1	MG/L	2	30	6.7
NERRDIEL	**CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN**	0.78	UG/L	3	135	2.2
	NITROGEN, AMMONIA AS N	0.005	MG/L	6	135	4.4
	PHEOPHYTIN-A	0.78	UG/L	11	135	8.1
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	28	135	20.7
	SOLIDS, SUSPENDED	1	MG/L	5	135	3.7
NERRTWQ	**NITROGEN, AMMONIA AS N**	0.005	MG/L	12	54	22.2
	NITROGEN, DISSOLVED	0.1	MG/L	1	54	1.9
	PHEOPHYTIN-A	0.78	UG/L	6	54	11.1
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	1	54	1.9
		GRAND TOTAL		**104**	**1063**	**9.8%**

OUTLIER CHECK

The 2019 dataset was checked for outliers by comparing the summary statistics from 2019 against the summary statistics from the same program in 2018. These values were then compared to statistics from a dataset spanning 1988 – September 19, 2019. This check identified one anomalous result that was reviewed (see table below).

Anomaly	Action
The maximum phosphorus, orthophosphate as P value in the 2019 dataset was 0.141 mg/L (avg = 0.037 mg/L) which was higher than the 2018 maximum value.	The highest phosphorus, orthophosphate as P concentration in the 2018 dataset was 0.110 mg/L. However, orthophosphate values as high as 0.232 mg/L have been observed in the full dataset (1988-2019). No action taken, confirmed as valid.

The range of results from the 2019 dataset is shown in the following table.

Parameter	Count (N)	Minimum	Average	Maximum
CARBON, ORGANIC	260	1.64	4.31	7.75
CARBON, SUSPENDED	125	0.313	1.045	3.369
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	260	<0.78	4.69	27.13
DISSOLVED OXYGEN	89	4.55	8.89	14.60
DISSOLVED OXYGEN SATURATION	89	59.4	96.2	153.7
ENTEROCOCCUS	52	2	13	148
ESCHERICHIA COLI	52	2	14	56
LIGHT ATTENUATION COEFFICIENT	78	0.43	1.66	4.90

NITROGEN, AMMONIA AS N	260	<0.005	0.046	0.232
NITROGEN, DISSOLVED	260	<0.100	0.325	0.681
NITROGEN, INORGANIC (AMMONIA, NITRATE AND NITRATE)	260	0.011	0.143	0.503
NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	260	0.008	0.097	0.271
NITROGEN, ORGANIC	260	0	0.182	0.433
NITROGEN, SUSPENDED	125	0.027	0.131	0.386
PHEOPHYTIN-A	248	<0.78	2.13	19.79
PHOSPHORUS, ORTHOPHOSPHATE AS P	260	<0.005	0.037	0.141
SALINITY	88	0.07	19.8	31.1
SILICA AS SIO2	30	<0.1	1.00	4.75
SOLIDS, SUSPENDED	260	<1.0	17.2	217.9
TEMPERATURE WATER	89	-3.0	14.6	27.5
TOTAL FECAL COLIFORM	52	2	17	60

FIELD REPLICATE COMPARISON

In 2019, 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 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 308 replicated results (0.3%) failed the data quality objective test. The failure rate was less than 20% for all parameters. Therefore, all of the data, including the individual replicate that failed the quality assurance analysis, were accepted as valid. The failure was for nitrite (NO2)+nitrate (NO3) as N (3.7%).

Parameter	Criteria	Failure Rate	Percent Failure
CARBON, DISSOLVED ORGANIC	1 mg/L, 30%	0 out of 27	0.0%
CARBON, SUSPENDED	1 mg/L, 30%	0 out of 18	0.0%
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	5 ug/L, 30%	0 out of 27	0.0%
NITRITE (NO2) + NITRATE (NO3) AS N	0.1 mg/L, 30%	1 out of 27	3.7%
NITROGEN, AMMONIA AS N	0.05 mg/L, 30%	0 out of 27	0.0%
NITROGEN, DISSOLVED ORGANIC	0.4 mg/l, 30%	0 out of 27	0.0%
NITROGEN, INORGANIC (AMMONIA, NITRATE AND NITRATE)	0.15 mg/l, 30%	0 out of 27	0.0%
NITROGEN, SUSPENDED	0.1 mg/L, 30%	0 out of 18	0.0%
NITROGEN, TOTAL DISSOLVED	0.25 mg/L, 30%	0 out of 27	0.0%
PHEOPHYTIN-A	5 ug/L, 30%	0 out of 27	0.0%
PHOSPHORUS, ORTHOPHOSPHATE AS P	0.025 mg/L, 30%	0 out of 27	0.0%
SILICA AS SI02	2 mg/L, 30%	0 out of 3	0.0%
SOLIDS, SUSPENDED	10 mg/L, 30%	0 out of 27	0.0%
	OVERALL	**1 out of 308**	**0.3%**

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 for each station. 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 126 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, 136 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.
- Chlorophyll samples from diel sampling at Station GRBLR on the following dates were run using a fluorometric non-acidification method, rather than an acidified method. The lab was short on needed materials and resorted to the alternative method. As a result, pheophytin-a could not be calculated for these samples. Given the low levels of phytoplankton at this time of the year, the impacts were judged to be negligible and were counted as valid.
  11/12/2019 07:40
  11/12/2019 09:44
  12/09/2019 15:33
  12/09/2019 17:37
  12/09/2019 19:41
  12/09/2019 21:45
  12/10/2019 01:53
  12/10/2019 03:57
  12/10/2019 06:01
  12/10/2019 08:05
  12/10/2019 10:09

SUMMARY

The 2019 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.