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Tidal Water Quality Monitoring: Grab Sampling

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

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Re: Quality Assurance of the water quality data collected by UNH/GRBNERR April-December 2018 Stations Great Bay (GRBGB), Lamprey River (GRBLR), Oyster River (GRBOR), Squamscott River (GRBSQ), Adams Point (GRBAP), Chapman's Landing (GRBCL), 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 2018 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. 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 by the RDL value. For the dataset as a whole, the highest censoring rates were for Enterococcus (69.8%), Escherichia coli (25.6%), total fecal coliform (23.3%), phosphorus, orthophosphate as P (4.9%, 21.6% and 9.3%), and pheophytin-a (2.5%, 28.8%, 7.4%). Overall, 11.1% of the 2018 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	ENTEROCOCCUS	1	#/100ML	30	43	69.8
	ESCHERICHIA COLI	1	#/100ML	11	43	25.6
	NITROGEN, AMMONIA AS N	0.005	MG/L	5	81	6.2
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	4	81	4.9
	SILICA AS SIO2	0.1	MG/L	1	32	3.1

	TOTAL FECAL COLIFORM	1	#/100ML	10	43	23.3
	PHEOPHYTIN-A	0.28	UG/L	2	80	2.5
NERRDIEL	**NITROGEN, AMMONIA AS N**	0.005	MG/L	4	125	3.2
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	27	125	21.6
	SOLIDS, SUSPENDED	1	MG/L	9	125	7.2
	PHEOPHYTIN-A	0.28	UG/L	36	125	28.8
	CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	0.28	UG/L	3	125	2.4
NERRTWQ	**CARBON, SUSPENDED**	0.125	MG/L	1	81	1.2
	NITROGEN, AMMONIA AS N	0.005	MG/L	4	54	7.4
	NITROGEN, SUSPENDED	0.025	MG/L	1	54	1.9
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.005	MG/L	5	54	9.3
	SOLIDS, SUSPENDED	1	MG/L	1	54	1.9
	PHEOPHYTIN-A	0.28	UG/L	4	54	7.4
	CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	0.28	UG/L	1	54	1.9
		GRAND TOTAL		**159**	**1433**	**11.1%**

OUTLIER CHECK

The 2018 dataset was checked for outliers by comparing the summary statistics from 2018 against the summary statistics from the same program in 2017. These values were then compared to statistics from a dataset spanning 1988 – September 19, 2019. This check identified several anomalous results that were checked (see table below).

Anomaly	Action
The maximum light attenuation coefficient in the 2018 dataset was 10.92 1/M which was higher than the maximum value 6.06 1/M in 2017.	The highest light attenuation coefficient in the full dataset is 10.52 1/M. Although this observed maximum value does not fall within the full dataset, it does not appear to be an invalid result. Field logs note that the sample was collected in 1 meter of water and that it had rained ~0.5 inches in the previous 2-3 days. No action taken, confirmed as valid.
The highest organic carbon concentration in the 2018 dataset was 14.98 mg/L which was higher than the maximum value 11.50 mg/L in 2017.	The highest organic carbon concentration in the full dataset is 13.65 mg/L. Although this observed maximum does not fall within the full dataset, it does not appear to be an invalid result. The sample was part of a triplicate set and all organic carbon concentrations were elevated. No action taken, confirmed as valid.

Anomaly	Action
The highest suspended nitrogen concentrations in the 2018 dataset were 1.331, 1.467, 1.390 mg/L. All three of these concentrations were higher than the maximum value 0.800 mg/L in 2017.	The highest suspended nitrogen concentration in the full dataset is 1.268 mg/L. Although these observed maximums do not fall within the full dataset, they do not appear to be invalid results. These 3 values were part of a triplicate set. Field logs note that samples were taken in 0.75 meters of water and that it had rained ~1 inch in the previous week. No action taken, confirmed as valid.

The range of results from the 2018 dataset is shown in the following table.

Parameter	Count (N)	Average	Minimum	Maximum
CARBON, ORGANIC	260	5.79	1.72	14.98
CARBON, SUSPENDED	125	1.542	<0.125	10.180
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	259	5.27	<0.28	63.74
DISSOLVED OXYGEN	93	9.30	3.88	14.10
DISSOLVED OXYGEN SATURATION	93	95.1	52.7	159.0
ENTEROCOCCUS	43	19	<1	272
ESCHERICHIA COLI	43	61	<1	600
LIGHT ATTENUATION COEFFICIENT	105	2.18	0.68	10.92
NITROGEN, AMMONIA AS N	260	0.065	<0.005	0.333
NITROGEN, DISSOLVED	260	0.389	0.126	1.309
NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	260	0.107	0.008	0.587
NITROGEN, ORGANIC	260	0.218	0.037	0.852
NITROGEN, SUSPENDED	125	0.205	<0.025	1.467
PHEOPHYTIN-A	259	3.08	<0.28	26.12
PHOSPHORUS, ORTHOPHOSPHATE AS P	260	0.025	<0.005	0.110
SALINITY	93	14.3	0.0	30.4
SILICA AS SIO2	32	1.88	<0.1	5.20
SOLIDS, SUSPENDED	260	27.6	<1.0	273.2
TEMPERATURE WATER	94	14.33	0.20	28.10
TOTAL FECAL COLIFORM	43	72	<1	760

FIELD REPLICATE COMPARISON

In 2018, replicates were collected on approximately 30% 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, seven of 282 replicated results (2.5%) 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 suspended carbon (11.1%), suspended nitrogen (11.1%), nitrite+nitrate as N (3.7%), pheophytin-a (3.7%), and suspended solids (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%	2 out of 18	11.1%
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, SUSPENDED	0.1 mg/L, 30%	2 out of 18	11.1%
NITROGEN, TOTAL DISSOLVED	0.25 mg/L, 30%	0 out of 27	0.0%
PHEOPHYTIN-A	5 ug/L, 30%	1 out of 27	3.7%
PHOSPHORUS, ORTHOPHOSPHATE AS P	0.025 mg/L, 30%	0 out of 27	0.0%
SILICA AS SIO2	2 mg/L, 30%	0 out of 3	0.0%
SOLIDS, SUSPENDED	10 mg/L, 30%	1 out of 27	3.7%
	OVERALL	**7 out of 282**	**2.5%**

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 153 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 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.
- The majority of the FieldActivityStartTimes for NERRDIEL samples collected 12/20 – 12/21/2018 are unknown. The timestamps for samples collected 12/20/2018 09:40 and 09:42 are correct. Ice formed in the autosampler intake tubing which impeded scheduled collections. In addition, the instrument's battery died which erased all program information, including sample collection times. All data was retained for reference.

SUMMARY

The 2018 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.