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Quality Assurance Memorandum for Year 2021 Estuarine Grab Data

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

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Re: Quality Assurance of the water quality data collected by UNH/GRBNERR April-December 2021 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 2021 water quality grab 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. 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, dissolved oxygen, depth, and chlorophyll 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, the highest censoring rates were for nitrogen, ammonia as N (10.0% - JELTWQ), phosphorus, orthophosphate as P (5.7% - JELTWQ, 11.9% - NERRDIEL, 1.9% - NERRTWQ) and suspended solids (7.4% - NERRDIEL and NERRTWQ). Overall, 6.5% of the 2021 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	NITROGEN, AMMONIA AS N	0.007	MG/L	7	70	10.0
	NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	0.007	MG/L	4	70	5.7
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.004	MG/L	4	70	5.7

	SILICA AS SIO2	0.02	MG/L	2	33	6.1
NERRDIEL	**NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N**	0.007	MG/L	1	135	0.7
	PHOSPHORUS, ORTHOPHOSPHATE AS P	0.004	MG/L	16	135	11.9
	SOLIDS, SUSPENDED	1	MG/L	10	135	7.4
NERRTWQ	**PHOSPHORUS, ORTHOPHOSPHATE AS P**	0.004	MG/L	1	54	1.9
	SOLIDS, SUSPENDED	1	MG/L	4	54	7.4
		GRAND TOTAL		**49**	**756**	**6.5%**

OUTLIER CHECK

The 2021 dataset was checked for outliers by comparing the summary statistics from 2021 against the summary statistics from the same program in 2020. These values were then compared to statistics from a full dataset spanning 1988 – 2020. This check identified 7 anomalous results that were reviewed. (See table below.)

Anomaly	Action
The maximum organic carbon value in the 2021 dataset was 13.650 mg/L (avg = 5.645 mg/L) which was higher than the 2020 maximum value.	The highest organic carbon value in the 2020 dataset was 9.251 mg/L. However, organic carbon values as high as 14.982 mg/L have been observed in the full dataset. This sample was collected 3 days after a significant rainfall (5 inches over the span of a week). Two other grab samples collected the same day had values exceeding that of 2020 (10.796 and 10.539 mg/L). No action taken; data confirmed as valid.
The maximum dissolved nitrogen value in the 2021 dataset was 0.723 mg/L (avg = 0.361 mg/L) which was higher than the 2020 maximum value.	The highest dissolved nitrogen value in the 2020 dataset was 0.595 mg/L. However, dissolved nitrogen values as high as 1.409 mg/L have been observed in the full dataset. This sample was collected 3 days after a significant rainfall (5 inches over the span of a week). No action taken; data confirmed as valid.
The maximum organic nitrogen values in the 2021 dataset were 0.483 and 0.456 mg/L (avg = 0.209 mg/L) which were higher than the 2020 maximum value.	The highest organic nitrogen value in the 2020 dataset was 0.360 mg/L. However, organic nitrogen values as high as 1.2 mg/L have been observed in the full dataset. These samples were collected 3 days after a significant rainfall (5 inches over the span of a week). No action taken; data confirmed as valid.
The maximum suspended carbon values in the 2021 dataset were 12.950 and 12.587 mg/L (avg = 1.700 mg/L) which were higher than the 2020 maximum value.	The highest suspended carbon value in the 2020 dataset was 4.152 mg/L. The maximum suspended carbon value in the full dataset is 12.170 mg/L and the 2021 values exceed that. These samples were collected in December at absolute low tide at Squamscott River. It had rained 0.25 inches the previous day and there had been wind gusts up to 40 mph. No action taken; data confirmed as valid.
The maximum total suspended solids values in the 2021 dataset were 247.1 and 223.6 mg/L (avg = 19.5 mg/L) which were higher than the 2020 maximum value.	The highest total suspended solids value in the 2020 dataset was 97.9 mg/L. However, total suspended solids values as high as 391.4 mg/L have been observed in the full dataset. These samples were collected in December at absolute low tide at Squamscott River. It had rained 0.25 inches the previous day and there had been wind gusts up to 40 mph. No action taken; data confirmed as valid.
The maximum light attenuation coefficients in the 2021 dataset were 14.54, 14.01, 14.08 1/M (avg = 2.43 1/M) which were higher than the 2020 maximum value.	The maximum light attenuation coefficient in the 2020 dataset was 5.33 1/M. The maximum light attenuation coefficient in the full dataset is 10.92 1/M and the 2021 values exceed that. These samples were

Anomaly	Action
	collected in December at absolute low tide at Squamscott River. It had rained 0.25 inches the previous day and there had been wind gusts up to 40 mph. The water was extremely turbid. No action taken; data confirmed as valid.
The maximum total nitrogen values in the 2021 dataset were 1.707 and 1.697 mg/L (avg = 0.488 mg/L) which were higher than the 2020 maximum.	The highest total nitrogen value in the 2020 dataset was 1.412 mg/L. The maximum total nitrogen value in the full dataset is 1.25 mg/L and the 2021 values exceed that. These samples were collected in December at absolute low tide at Squamscott River. It had rained 0.25 inches the previous day and there had been wind gusts up to 40 mph. No action taken; data confirmed as valid.

The range of results from the 2021 dataset is shown in the following table.

Parameter	Count (N)	Minimum	Average	Maximum
CARBON, ORGANIC	259	1.713	5.645	13.650
CARBON, SUSPENDED	123	0.299	1.700	12.950
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	258	0.27	4.56	41.51
DISSOLVED OXYGEN	87	3.41	8.37	14.06
DISSOLVED OXYGEN SATURATION	87	44.3	92.2	146.3
ENTEROCOCCUS	35	1	13	140
ESCHERICHIA COLI	40	1	39	360
LIGHT ATTENUATION COEFFICIENT	99	0.47	2.43	14.54
NITROGEN	123	0.087	0.488	1.707
NITROGEN, AMMONIA AS N	259	0.007	0.056	0.220
NITROGEN, DISSOLVED	259	0.121	0.361	0.723
NITROGEN, INORGANIC (AMMONIA, NITRATE AND NITRATE)	259	0.008	0.152	0.362
NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	259	0.007	0.096	0.214
NITROGEN, ORGANIC	259	0.016	0.209	0.483
NITROGEN, SUSPENDED	123	0.035	0.167	1.260
PHOSPHORUS, ORTHOPHOSPHATE AS P	259	0.004	0.031	0.144
SALINITY	87	0.1	17.4	29.7
SILICA AS SIO2	33	0.02	1.68	3.49
SOLIDS, SUSPENDED	259	1.0	19.5	247.1
TEMPERATURE WATER	87	2.1	15.9	25.5
TOTAL FECAL COLIFORM	40	1	44	360

FIELD REPLICATE COMPARISON

In 2021, replicates were collected for 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 checks, then the replicates are considered to have failed the data quality objective test.
5. Summarize the percentage 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, five of 282 replicated results (1.8%) failed the data quality objective test. The failure rate was less than 20% for all parameters. Therefore, all the data, including the individual replicates that failed the quality assurance analysis can be accepted as valid. Replicate failures were for suspended solids (11.1% and suspended carbon and nitrogen 5.6%).

Three of the failed replicates (suspended carbon, suspended nitrogen, total suspended solids) were from the same sample collected at Squamscott River (GRBSQ) 12/08/2021 08:51 as part of a triplicate. The values for these parameters differed dramatically from the 2 other replicates. This triplicate was collected at absolute low tide. It had rained 0.25 inches the previous day and there had been wind gusts up to 40 mph. The water was extremely turbid. Because this sample's values were so anomalous, they were rejected. Total nitrogen, which is a calculated value that includes suspended nitrogen, was also rejected.

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%	1 out of 18	5.6%
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%	0 out of 27	0.0%
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%	1 out of 18	5.6%
NITROGEN, TOTAL DISSOLVED	0.25 mg/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%	3 out of 27	11.1%
	OVERALL	**5 out of 282**	**1.8%**

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 labeled "high tide" or "low tide" sample if it was collected no more than 3 hours before and no more than 15 minutes 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 124 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), Dissolved Oxygen (mg/L)
    - Three decimal places: Ammonia, Nitrite+Nitrate, Nitrogen, Total Dissolved Nitrogen, Suspended Nitrogen, Orthophosphate, 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. So as not to 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.
- Light casts were not completed at the Oyster River site as the water is too shallow at the collection location.

SUMMARY

The 2021 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.