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## New Hampshire Estuaries Probabilistic Monitoring Program in 2008

Phil Trowbridge  
*PREP/NHDES*

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**MEMORANDUM**

To: Jennifer Hunter, PREP Director

From: Phil Trowbridge, PREP/NHDES Coastal Scientist

Date: April 30, 2009

**Re: Quality Assurance Memo, New Hampshire Estuaries Probabilistic Monitoring Program, 2008**

The New Hampshire Department of Environmental Services (NHDES), the U.S. Environmental Protection Agency (EPA) and the University of New Hampshire (UNH) partnered in 2008 to implement the National Coastal Assessment in NH’s estuarine waters. USEPA provided the study design and field protocols. UNH collected the samples and field data at the designated sites in the estuary. Funding for this sampling effort was provided by the Piscataqua Region Estuaries Partnership, NHDES, and the New Hampshire Coastal Program.

The purpose of this memo is to document the quality assurance checks that were performed by NHDES. The data were not collected as part of a national survey; therefore, the data have not been transmitted to USEPA.

A. Task Completeness Check

*Determine how many samples were collected by media based on the field sheets and document reasons why samples were missed, if necessary.*

- The samples collected in 2008 are listed in the following table by media. The actual station visits are compared to the expected visits from the 2008 workplan. There are no major data gaps for the NCA design stations.

Station Visits For 2008 Sampling Season

| Medium          | Date Range      | Planned | Actual | Comments   |
|-----------------|-----------------|---------|--------|--|
| Sediment        | NA              | 0       | 0      | No sediment samples collected in 2008                                |
| Water           | 6/30/08-8/13/08 | 25      | 25     | 36 water samples collected including depth duplicates and QC samples |
| Fish Trawls     | NA              | 0       | 0      | No fish trawls in 2008   |
| Fish Tissue     | NA              | 0       | 0      | No fish samples collected in 2008                                    |
| Monthly Water   | NA              | 0       | 0      | Monthly trend sample were collected by the GBNERR/UNH Program        |
| Summer bacteria | 7/9/08-8/18/08  | 15      | 15     | 18 water samples collected including depth duplicates and QC samples |

B. Field Data File Check

*Check station names on field sheets and databases for consistency with study design*

- All station names were consistent with the design. Nutrient results listed for “NH08-505-“ were assigned to station visit NH08-0504 on 7/8/08. This was the only station visit that was missing nutrient data.

*Check station locations from field sheets for consistency with study design*

- Station visits were within 0.13 minutes of design sites (<0.5 minutes is acceptable). The field records for stations NH08-0501 and NH08-0517 needed to be changed because the crew recorded decimal degrees instead of degrees and minutes.

*Check and edit, as needed, the “Event Purpose” field for all station visits.*

- Typographic errors corrected and text standardized.

*Check sample ID numbers for water, sediment, and fish tissue samples.*

- No sediment or fish tissue samples were collected. All water samples were analyzed in house.

*Check that all physicochemical and fish trawl entries are accurate and complete.*

- No transcription errors detected for spot checked entries. Fish trawls were not conducted. Transcription errors in water physicochemistry should be detected by range and replicate analyses.

*Calculate range and box plots for each field parameter to identify outliers*

- Temperature measurements from the datasonde at the surface and bottom of casts fell between 15 and 26 deg C, which matches observations from previous years. For 2 of the 40 surface observations, there was a difference of >1 deg C between the sonde measurement and the measurement with an independently calibrated YSI-85 meter. These discrepancies are not important. The temperature measurements from the sonde will be used.
- Salinity measurements from the datasonde at the surface and bottom of casts fell between 3 and 55 ppt, which does not match observations from previous years. For 36 of the 40 surface observations, there was a difference of >1 ppt between the sonde measurement and the measurement with an independently calibrated YSI-85 meter. The range of salinities from the YSI-85 measurements was 2-31 ppt, which matches previous observations. Therefore, the salinity data from the YSI-85 will be used for this dataset.
- Dissolved oxygen measurements from the datasonde at the surface and bottom of casts fell between 5.2 and 10.2 mg/L, which matches observations from previous years. For 1 of the 40 surface observations, there was a difference of >0.5 mg/L between the sonde measurement and the measurement with an independently calibrated YSI-85 meter. This discrepancy was attributed to a malfunction of the YSI-85 in the field notes. The dissolved oxygen measurements from the sonde will be used.
- pH measurements from the datasonde at the surface and bottom of casts fell between 7.2 and 8.7, which matches observations from previous years. pH values were not checked with an independently calibrated YSI-85 meter. The pH measurements from the sonde will be used.
- Only one bottom water measurement was recorded in the database. Therefore, only surface measurements will be incorporated into the EMD.

### C. CTD File Check

*Check that file names for CTD casts match station IDs*

- Ecowatch files are available for 39 of the 40 water station visits. The Ecowatch file names were edited to match station names. The only station visit without a Ecowatch file was for station NH-0057A on 8/20/08. Water samples for bacteria were collected during this station visit. These samples were collected by Jeremy LeClair during a routine visit for the JEL Tidal Water Quality Monitoring Program. The field parameters for the station visit were recorded with the JELTWQ activity.

*Extract physicochemical data from Ecowatch files (e.g., Bottom DO, Attenuation Coefficient)*

- No data were extracted from the ecowatch CTD files. The surface PAR sensor was not connected to the sonde. The surface PAR and the water PAR readings were recorded on the field hydrograph forms. Therefore, to calculate light attenuation coefficients, the data from the field hydrograph sheet were compiled into a spreadsheet and analyzed.
- There were only 11 station visits with 3 or more paired results for surface and water PAR on the down cast. The Kd values for these station visits ranged from 0.3 to 1.62 m<sup>-1</sup>, which is within the expected range for NH's estuaries. The r-squared for the regressions were between 0.76 and 0.99.

*Calculate range and box plots for each CTD parameter to identify outliers*

- The temperature, salinity, dissolved oxygen and pH data from the field sheets will be used in the water quality database. The only CTD data that will be used is the Kd values, which were within the expected range.

### D. Laboratory Data Check

*Check that station IDs and dates match field data sheets*

- StationIDs and dates in coastl08.dbf and the UNH laboratory database match the field sheets for the base NCA station visits.

*Check that data tables contain all data submitted to laboratory*

- Water: Results were reported for most of the waters samples submitted to the laboratory for the base NCA design. One of 25 samples was missing for particulate nitrogen, particulate carbon, and particulate phosphorus (Station NH08-0509). One of 25 samples for CDOM was missing (ME08-0506). Bacteria results were provided for all of the summer bacteria samples.
- Sediment: No sediment samples were collected.
- Fish Tissue: No fish tissue samples were collected.

*Check that data has appropriate metadata (methods, units, name of laboratory)*

- For water samples, UNH provided a QA report which details the analytical methods and method detection limits.

*Check that appropriate QA procedures were completed by the laboratory*

- For water samples for nutrients, UNH ran several quality assurance tests: lab replicates, spikes, QC samples and “standards run as unknowns”. The results of the tests were within data quality objectives for 50 of 50 replicates, 18 of 18 spikes, 47 of 47 QC samples, and 80 of 80 standards run as unknowns.
- No quality control tests with standard reference materials were performed for chlorophyll-a or suspended solids.
- Bacteria: All quality control tests for bacteria parameters were within acceptable limits.

*Calculate range and box plots for each laboratory parameter to identify outliers*

- Summary statistics were calculated for the 2008 water chemistry data and compared to statistics for the 2007 dataset (see table below). Elevated values relative to the 2007 dataset were also compared to summary statistics for each parameter from the water quality database for the estuary from all programs and all years. This analysis identified that there were unusually high concentrations of most analytes at station NH08-0537. The field crew reported that the samples at this station were collected during heavy rain when the water was turbid, which explains the results. The results for this station were retained in the database. The only other unexplained anomaly was for total dissolved nitrogen at station NH08-0515. The TDN value at this station was 2.6 mg/L. This value is not credible because the DIN concentration in this sample was only 0.09 mg/L and the dissolved organic carbon concentration was close to the average for the estuary. The highest TDN concentration that had been observed in the estuary through 2007 was 1.4 mg/L. Therefore, the reported concentration of 2.6 mg/L TDN at station NH08-0515 was not credible and was invalidated.

| AnalyteName                                  | FractionType | 2007 |        |         | 2008 |          |           |
|--|--------------|------|--------|---------|------|----------|-----------|
|  |              | N    | Ave    | Max     | N    | Ave      | Max       |
| CARBON, ORGANIC                              | DISSOLVED    | 36   | 2.438  | 6.790   | 34   | 3.978    | 7.969     |
| CARBON, SUSPENDED                            | TOTAL        | 32   | 0.402  | 3.113   | 33   | 0.971    | 5.117     |
| CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN      |              | 34   | 4.768  | 60.900  | 35   | 2.343    | 22.400    |
| COLORED DISSOLVED ORGANIC MATTER (CDOM)      |              | 28   | 0.622  | 2.130   | 29   | 1.146    | 2.477     |
| DISSOLVED OXYGEN                             |              | 49   | 8.153  | 9.800   | 40   | 6.713    | 10.200    |
| ENTEROCOCCUS                                 |              | 32   | 54.391 | 555.000 | 51   | 1009.690 | 41200.000 |
| ESCHERICHIA COLI                             |              | 39   | 33.705 | 280.000 | 51   | 204.847  | 8800.000  |
| LIGHT ATTENUATION COEFFICIENT                |              | 7    | 0.6124 | 0.9455  | 11   | 0.937    | 1.613     |
| NITROGEN, AMMONIA AS N                       | DISSOLVED    | 22   | 0.024  | 0.169   | 34   | 0.146    | 0.397     |
| NITROGEN, DISSOLVED                          | TOTAL        | 34   | 0.180  | 0.390   | 34   | 0.431    | 2.589     |
| NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N | DISSOLVED    | 30   | 0.017  | 0.039   | 34   | 0.072    | 0.426     |
| NITROGEN, SUSPENDED                          | TOTAL        | 29   | 0.077  | 0.529   | 33   | 0.129    | 0.526     |
| PH   |              | 49   | 7.853  | 8.100   | 40   | 7.778    | 8.700     |
| PHOSPHORUS AS P                              | DISSOLVED    | 36   | 0.040  | 0.066   | 34   | 0.039    | 0.127     |
| PHOSPHORUS AS P                              | SUSPENDED    | 28   | 0.010  | 0.063   | 32   | 0.020    | 0.153     |
| PHOSPHORUS, ORTHOPHOSPHATE AS P              | DISSOLVED    | 34   | 0.026  | 0.045   | 34   | 0.028    | 0.118     |
| SALINITY                                     |              | 49   | 29.557 | 33.500  | 40   | 24.800   | 30.900    |
| SECCHI DISK TRANSPARENCY                     |              | 9    | 1.611  | 4.200   | 15   | 1.313    | 1.800     |
| SILICA AS SIO2                               | DISSOLVED    | 27   | 0.407  | 1.280   | 34   | 1.189    | 6.940     |
| SOLIDS, SUSPENDED                            | TOTAL        | 36   | 14.023 | 52.000  | 35   | 25.190   | 122.000   |
| TEMPERATURE WATER                            |              | 49   | 19.371 | 25.100  | 40   | 20.453   | 25.500    |
| TOTAL FECAL COLIFORM                         |              | 39   | 34.410 | 280.000 | 51   | 997.022  | 47200.000 |

### *Evaluate field replicate samples for systematic errors*

Three pairs of field duplicate samples were analyzed by the laboratory, resulting in 39 parameter comparisons. Seven of the 39 parameter comparisons failed the acceptance criteria established by DES (30% RPD or less than a trivially small difference). Most of the failures were for nutrient parameters for station NH08-0502. The two duplicate samples had extremely different concentrations for nutrients. After consulting with the laboratory, it was determined that something must have happened (e.g., broken filter) to the duplicate sample and that it should be deleted from the database. The only other failure was for ammonia at NH08-0512. This parameter missed the data quality objectives by a small margin. Because there was only one documented failure, there is no evidence of systematic sampling errors. The field duplicate results for all nitrogen, phosphorus, and carbon parameters from station NH08-0502 were deleted from the database. The field duplicate result for ammonia at NH08-0512 was retained in the database.

### E. Summary

NHDES has completed a quality assurance review of the 2008 field and water quality data for the NH National Coastal Assessment. There were only two major deviations from the NCA QAPP:

- Chlorophyll-a was measured by a spectrophotometric method, rather than a fluorometric method. This deviation does not present at problem. Chlorophyll-a has been traditionally measured in Great Bay using the spectrophotometric method.
- No QC samples of a standard reference material were run for chlorophyll-a or TSS to validate these results. Given the long record of monitoring chlorophyll-a and TSS in the estuary using these same methods, this deviation is not considered to be critical for the data quality.

Despite these issues, NHDES considers the results in the data files uploaded to the EMD to be valid for use in national and regional assessments.