

I. Data Set and Research Descriptors

1) Principal investigator(s) and contact persons –

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2) Research objectives –

a) Monthly Grab Sampling Program-

The monthly grab samples provide data for 5 additional water quality variables to supplement the 15-minute interval data stream from the YSI 6600's. Grabs are collected from a similar depth stratum as the YSI datalogger (within 1 m of the depth of the probes) at each site. These variables (nitrate, NO₃, ammonium, orthophosphate, silicate and chlorophyll a), are important indicators of estuarine trophic status and point and non-point sources of nutrient enrichment. Although limited, these data enable estimation of average trophic status, and may demonstrate seasonal patterns. Our datalogger monitoring design allows for gradient analysis from head of tide to inlet in the Webhannet estuary, allowing comparison of the Little River and Webhannet River estuaries at their inlets, where they exchange water directly with the Atlantic Ocean. Monthly grab data provide the basis for investigation of questions regarding watershed and marine inputs of nutrients in Wells NERR estuaries, and nutrient influence on trophic status as indicated by chlorophyll a.

b) Diel Sampling Program-

At the Webhannet Inlet site, the monthly grab samples are augmented with a 24-hour sampling series (at 2 hr 15 min intervals for a total of 12 samples – 1 sample per 2 hr 15 min interval). These data can provide estimates of temporal variation in nutrients and chlorophyll on the scale of hours, providing a context for interpretation of data collected less frequently. This finer scale information will also inform interpretation SWMP grab sample data. These data can be used to investigate the relationship between nutrients, chlorophyll, and dissolved oxygen, an integrator of water column metabolism.

3) Research methods –

a) Monthly Grab Sampling Program

Monthly grab samples are collected at 2 sites in the Webhannet River Estuary and 2 sites in the Little River Estuary. These sites coincide with the four datasonde sites: Head of Tide (HT), Skinner Mill (SM), and Inlet (IN) in the Webhannet River; and the Mouth (LM) in the Little River. All grab samples are taken within a 24-hour period, and efforts are made to sample between +/- 3 hours slack low tide. Efforts are also made to allow for a previous dry period of 72 hours prior to sampling, however, this was not always possible due to lengthy periods of inclement weather. Replicate (N=2) 1-liter samples are collected at a depth of 0.5 meters below the water surface at the HT, SM, and LM sites. Replicate (N=2) samples at the IN site are taken by pumping the sample up through the ISCO sampler. All samples are collected in 1-liter wide-mouth amber Nalgene bottles that were previously washed with Fisher brand Versa-Clean and water, acid washed (10% HCl), rinsed (3x) with distilled-deionized water, dried, and rinsed (3x) with ambient water prior to collection of the sample. Samples are immediately placed on ice in a dark cooler, and returned to the laboratory for immediate processing.

b) Diel Sampling Program

Diel samples are collected once a month, during the same 24-hour period as our grab sample collection, at the Webhannet River Inlet (IN) datalogger site. An ISCO 6700 automated sampler is deployed on a floating dock at the Wells Harbor pier. As with the grab samples, efforts are made to begin the automated sampling between +/- 3 hours around slack-low tide. Efforts are also made to allow for a previous dry period of 72 hours prior to sampling, however this was not always possible due to lengthy periods of inclement weather. Sampling events are staggered each month at the optimal low tide, given constraints of Reserve personnel scheduling. A 1-liter sample is taken every 2-hours and 15 minutes over the complete tidal cycle (just over 24 hrs) for a total of 24 samples. All samples are pumped into ISCO 1-liter polypropylene wedge sample bottles that were previously washed with Fisherbrand Versa-Clean and water, acid washed (10% HCl), rinsed (3x) with distilled-deionized water and dried prior to collection of the sample. The ISCO sampler is filled with ice and/or frozen gel packs prior to deployment, and at the end of the 24-hour period the sample bottles are immediately capped, kept in the dark, and returned to the laboratory for immediate processing.

Once back in the Wells NERR laboratory, samples are shaken and processed for nutrient and Chlorophyll-a analysis. All samples are filtered at the Wells NERR. The Chl-a analysis is completed on-site at the Wells NERR laboratory with a Turner Designs 10-AU field fluorometer, and the nutrient analysis takes place at the Virginia Institute of Marine Science (VIMS).

The nutrient processing methodology includes filtering 50 mL of a sample through 25 mm, 0.45 µm HV Millipore Durapore® membrane filters using a Becton, Dickinson and Co. (BD) 60 mL polyethylene syringe with Luer-Lok® tip locked to a Millipore Swinnex 25 mm polypropylene filter holder. If a sample is particularly turbid, a 25 mm PALL A/E Glass Fiber Filter is used to filter the sample prior to filtering through the 0.45 µm Millipore filter, although this happens very rarely. The liquid volume of the filtered sample is collected into a Fisherbrand 50 ml polypropylene centrifuge tube (after rinsing collection tube (3x) with sample) and placed in the freezer and mailed overnight delivery to VIMS for analysis.

The Chl-a processing methodology here at the Wells NERR Research Laboratory follows the non-acidification method, “A Procedure For Measuring Extracted Chlorophyll a Free From The Errors Associated With Chlorophyll b and Pheopigments”, adapted from the EPA Method 445.0: “In Vitro Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluorescence.” This methodology involves filtering 200-1000 mL of a sample through 47 mm Whatman® GF/F

filters using a vacuum pump and filter flask apparatus, and to determine the Chl-a concentration we use a Turner Designs 10-AU Field Fluorometer. Chlorophyll filters are held at -20°C until analysis.

All laboratory glassware, centrifuge tubes, syringes, filter holders, 1-liter graduated cylinders, and forceps were previously washed with Fisherbrand Versa-Clean and water, rinsed (3x) with distilled-deionized water and dried prior to filtration of the sample; and rinsed (3x) between samples with distilled-deionized water to avoid any contamination.

4) Site location and character –

The Wells National Estuarine Research Reserve is located in York County, within the Town of Wells, on the coast of southern Maine and faces the Atlantic Ocean. The Wells NERR is approximately 31 km (20 miles) south of Portland, Maine and 110 km (70 miles) north of Boston, Massachusetts. The Reserve encompasses 1,690 acres along the Gulf of Maine coastline of tidally-flushed wetlands, riparian and transitional upland fields and forests within the Little River Estuary and the larger Webhannet River Estuary. Both estuaries arise in the sandy glacial outwash plain about eight miles inland. Both rivers empty into Wells Bay, a sandy basin stretching for approximately ten miles along the Atlantic coast. Bordering each river's inlet are double spit barrier beaches attached to the mainland. The backbarrier system in the Webhannet River Estuary is approximately 5 sq. km and is composed of large intertidal marshes (predominantly *S. patens* and *S. alterniflora*), intertidal sand and mud flats, and tidal channels. The watershed for the Webhannet River estuary covers an area of 35 sq. km and has a total of 6 streams, brooks or creeks, which enter the estuary. These tributaries flow across sand and gravel deposits near the headwaters and the impermeable sandy muds of the Presumpscot Formation in the lower reaches.

The watershed for the Little River estuary covers an area of 84 sq. km and has a total of 2 tributaries. The backbarrier system in the Little River Estuary is approximately 2.51 sq. km and is composed of large intertidal marshes (predominantly *S. patens* and *S. alterniflora*), intertidal sand and mud flats, and tidal channels. The Webhannet River is connected to the ocean via Wells Inlet, which has a spring tidal prism of 28,200,000 cubic m (Ward 1993). The Little River is connected to the ocean by an unstructured, double spit system and is one of the few tidal inlets along the southern Maine coast that is not stabilized by either natural outcrops or artificial jetties. The force and volume of tidal action affect the salinity level of both rivers. In the Wells region, the annual mean wave height is almost 20 inches. These estuarine systems are dominated by semi-diurnal tides having a range of 8.5 to 9.8 feet. The volume of freshwater influx into both estuaries is moderate to low (on the order of 0.5 cubic meters/second), especially in the summer, because of the rivers' relatively small drainage areas and the presence of deep glacial deposits. The relatively low flows from these two rivers taken in with the 20 inch per year average runoff of the area surrounding the estuaries combine to form a fresh water flow, which is dwarfed by tidal flushing. Twelve-foot tides dwarf the freshwater flow into the Webhannet estuary, which has a drainage area of 14.1 square miles. The Merrilland River and Branch Brook meet south of Route 9 to form the Little River, which drains an area of 10.75 sq. miles. The Webhannet estuary, fed by both Blacksmith and Depot Brooks, is adjacent to the harbor and greatly developed land. It offers a valuable opportunity for comparison with the relatively pristine Little River estuary. The land use of the Webhannet estuary include a total of 15% for wetland, fresh water, and tidal marsh; a total of 63.7 % for woodland; and a total of 18.6% for developed land compared to a total of 5.7% development in the Little River estuary (WNERR RMA 1996; Holden 1997).

The following information regarding annual weather patterns in the area was supplied by Maine State Climatologist Professor Gregory A. Zielinski extracted from "Monthly Station Normals of Temperature, Precipitation, Heating and Cooling Degree Days 1971-2000", Climatology of the United States No. 81, National Oceanic and Atmospheric Administration, National Climatic Data Center, Asheville, NC. and "Daily Normals of Temperature, Precipitation, and Heating and

Cooling Degree Days, 1971-2000", Climatology of the United States No. 84: "Average monthly temperatures range from 21.6F in January to 66.7F in July with daily highs averaging just below freezing in January and lows around 11F. Daily highs in July average around 76F and daily lows around 57F. The sea breeze often keeps daily highs lower during the summer than areas inland. Annual average temperature is 44.6F. Annual precipitation is 47.07 inches, including the water equivalent of snowfall, with monthly averages ranging from 3.01 inches in July to 4.77 inches in October. August receives just 3.02 inches on average. Annual snowfall is around 66 inches." According to Zielinski, "cool ocean temperatures keep down the number of afternoon showers and especially thunderstorms resulting in low summer precipitation amounts."

There are two sampling sites in the Webhannet River estuary. These are located at the Head of Tide (HT), and at the Inlet (IN). The tidal range at each of these sites is 2.6-2.9 meters. There are two sampling sites in the Little River estuary, the Little River Mouth (LM) and Skinner Mill (SM). The tidal range of the Little River estuary is 2.6-3.0 meters (Mariano and FitzGerald, 1988).

The Head of Tide (HT) site is located 4 miles south of the Wells Reserve, just downstream of the Webhannet Falls (freshwater) and 10 feet east of Route One (43° 17' 54.05 N Latitude, 70° 35' 13.54 W Longitude). Route One is used heavily with traffic all year, especially during the summer tourist months. This site has soft mud, sand, and a rocky substrate, and the low and high tide depth is relatively shallow. The salinity range here is 0-31 psu, with a mean of 3.6 psu. Depth at MHW for the sample site is approximately 1.5 meters. These headwaters of the Webhannet are relatively undeveloped. This site is located just 10 feet east of the Route One bridge, and is our roving site.

The Skinner Mill (SM) site is located approximately 100 meters downstream from the intersection of the Merriland River (tributary to Merriland/Branch/Little River estuary) and Skinner Mill Road (at 43° 20' 40.96" N Latitude, 70° 32' 57.18" W Longitude). This site is approximately 70 meters downstream from the Watershed Evaluation Team (Educational water quality program at Wells NERR) site L5. Substrate is mud/sand bottom, salinities range from 0 psu on low or outgoing tides and as high as 27 psu on high tides. Depth at MHW for the sample site is approximately 1.9 meters. Data prior to 5/30/2006 is from the original SM site located approximately 70 meters upstream from the current site, which is approximately 20-30 meters beyond the head of the estuary where mixing between fresh and marine waters occur. Please see the 2006 Water quality metadata for a better description of the original site.

The Inlet site (IN) is located 1.5 miles south of the Wells Reserve, at the Wells Harbor pier (43° 19' 12.32 N, 70° 33' 48.39 W). The mouth of the Webhannet estuary forms an extensive wetland/salt marsh area, which is surrounded by development. Wells Harbor, which was most recently dredged in 1971, has moorings for approximately 200 commercial fishing and recreational boats. The mouth of the river flows between two jetties to the Atlantic Ocean. This channel was dredged in 1974. This site has a predominately sand substrate and is characterized by strong current during incoming and outgoing tides. The maximum depth of the Inlet site is 3 meters. The salinity range here is 7-35 psu, with a mean of 31 psu. The Inlet site is heavily impacted at the Wells Harbor dock and is our long-term monitoring site.

The Little River Mouth (LM) site is located 1,270.78 meters upstream from the mouth of the estuary, and 813.94 meters direct from the Wells NERR Coastal Ecology Center (43° 20' 24.55" Latitude, 70° 32' 26.17" Longitude). The tidal range of the Little River estuary is 2.6-3.0 meters (Mariano and FitzGerald, 1988). The Little River sites existed in a shallow and relatively pristine system with a sandy to mud bottom and a salinity range of 0-32 psu. Depth at MHW for the sample site is approximately 2.6 meters. There are two major freshwater inputs, the Merriland and Branch Brook Rivers, which converge to form the Little River. The Little River Mouth site is our comparative system site.

Note: Both original Little River Mouth sites were abandoned in prior years due to problems with heavy sediment movement in the inlet of the Little River. We were forced to relocate the site twice. The first location (N 43° 20.176 Latitude, W 70° 32.497 Longitude) was located in the main channel of the river, just inland of a spit, beside a bank. The second location (N 43° 20.083 Latitude, W 70° 32.585 Longitude) was located 1/8 mi. southwest of the first site, within an inlet, just inland of a spit. The second site was located in an area of much lower current than the first site and often drains completely during low tides. It was also placed within a pool next to incipient low marsh peat that retains calm water during low tides.

All Wells NERR historical nutrient/pigment monitoring stations:

Station Code	SWMP Status	Station Name	Location	Active Dates	Reason Decommissioned	Notes
welinnut	P	Inlet	Wells Harbor-Mouth of the Webhannet River	05/01/2002 - current	NA	NA
welhtnut	P	Head of Tide	Head of tide of Webhannet River	05/01/2002 - current	NA	NA
wellmnut	P	Little River Mouth	Mouth of the Little River Estuary	05/01/2002 – current	NA	NA
welsmnut	P	Skinner Mill	Head of Tide of Little River Estuary	01/01/2004 – current	NA	NA
welmlnut	D	Mile Road	Middle of Webhannet River	01/01/2002 – 12/31/2003	Unknown	none

5) Coded variable definitions –

Reserve code:
wel = Wells NERR

Station codes:
in = Webhannet River Inlet
sm = Skinner Mill (on Merriland R.)
ht = Head of Tide at Webhannet R.
lm = Little River Mouth

Program code:
nut = nutrient sampling program

These abbreviations are combined to form the sample name as follows:
welinnut = sample taken from Webhannet River Inlet as part of the Wells NERR nutrient sampling program

The monitoring codes are set as “1” to indicate grab samples and “2” to indicate diel samples. Replicates are also given specific codes. Grab samples in which a duplicate sample is collected are indicated by “1” for first sample and a “2” for second sample. Diel samples are always labeled with a “1” since only one sample is taken at each 2 hr 15 min interval.

6) Data collection period –

Year in which monitoring started at each station:

welinnut: 2002

welhtnut: 2002

wellmnut: 2002

welsmnut: 2004

Diel Sampling, every 2 hours, 15 minutes as follows:

welinwq	1/29/2018 8:30	1/30/2018 9:15
welinwq	2/27/2018 10:15	2/28/2018 11:00
welinwq	3/20/2018 10:30	3/21/2018 11:15
welinwq	4/23/2018 8:30	4/24/2018 9:15
welinwq	5/15/2018 9:00	5/16/2018 9:45
welinwq	6/18/2018 10:30	6/19/2018 11:15
welinwq	7/16/2018 8:45	7/17/2018 9:30
welinwq	8/20/2018 8:45	8/21/2018 9:30
welinwq	9/23/2018 8:45	9/24/2018 9:30
welinwq	10/15/2018 9:00	10/16/2018 9:45
welinwq	11/28/2018 10:15	11/29/2018 11:00
welinwq	12/17/2018 10:30	12/18/2018 11:15

Grab Sampling (once monthly):

Site Date and Time of Grabs

welinnut 1/31/2018 10:40
welinnut 1/31/2018 10:41
welinnut 2/28/2018 11:40
welinnut 2/28/2018 11:41
welinnut 3/21/2018 9:16
welinnut 3/21/2018 9:17
welinnut 4/24/2018 10:50
welinnut 4/24/2018 10:51
welinnut 5/16/2018 10:50
welinnut 5/16/2018 10:51
welinnut 6/19/2018 11:40
welinnut 6/19/2018 11:41
welinnut 7/17/2018 10:35
welinnut 7/17/2018 10:36
welinnut 8/21/2018 10:01
welinnut 8/21/2018 10:02
welinnut 9/24/2018 11:01
welinnut 9/24/2018 11:02
welinnut 10/16/2018 10:30
welinnut 10/16/2018 10:31
welinnut 11/29/2018 12:20

welinnut 11/29/2018 12:21
welinnut 12/18/2018 14:00
welinnut 12/18/2018 14:01

Site Date and Time of Grabs

**No grabs from Jan, Feb, March, and Dec due to ice conditions*

welhtnut 01/31/2018 09:00
welhtnut 01/31/2018 09:01
welhtnut 02/28/2018 10:01
welhtnut 02/28/2018 10:02
welhtnut 04/24/2018 10:30
welhtnut 04/24/2018 10:31
welhtnut 05/16/2018 10:30
welhtnut 05/16/2018 10:31
welhtnut 06/19/2018 11:30
welhtnut 06/19/2018 11:31
welhtnut 07/17/2018 10:00
welhtnut 07/17/2018 10:01
welhtnut 08/21/2018 09:50
welhtnut 08/21/2018 09:51
welhtnut 09/24/2018 10:45
welhtnut 09/24/2018 10:46
welhtnut 10/16/2018 11:30
welhtnut 10/16/2018 11:31
welhtnut 11/29/2018 12:10
welhtnut 11/29/2018 12:11
welhtnut 12/18/2018 08:00
welhtnut 12/18/2018 08:01

Site Date and Time of Grabs

**No grabs from Jan, Feb, and March due to ice conditions*

wellmnut 01/31/2018 08:45
wellmnut 01/31/2018 08:46
wellmnut 02/28/2018 11:03
wellmnut 02/28/2018 11:04
wellmnut 04/24/2018 08:45
wellmnut 04/24/2018 08:46
wellmnut 05/16/2018 08:45
wellmnut 05/16/2018 08:46
wellmnut 06/19/2018 10:20
wellmnut 06/19/2018 10:21
wellmnut 07/17/2018 08:30
wellmnut 07/17/2018 08:31
wellmnut 08/21/2018 08:45
wellmnut 08/21/2018 08:46
wellmnut 09/24/2018 08:50
wellmnut 09/24/2018 08:51
wellmnut 10/16/2018 09:52
wellmnut 10/16/2018 09:53
wellmnut 11/29/2018 10:00
wellmnut 11/29/2018 10:01
wellmnut 12/18/2018 08:02

welmnut 12/18/2018 08:03

<u>Site</u>	<u>Date and time of Grabs</u>
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**No grabs from Jan-Mar due to ice conditions*

welmnut	01/31/2018 08:30
welmnut	01/31/2018 08:31
welmnut	02/28/2018 10:05
welmnut	02/28/2018 10:06
welmnut	04/24/2018 09:30
welmnut	04/24/2018 09:31
welmnut	05/16/2018 09:30
welmnut	05/16/2018 09:31
welmnut	06/19/2018 10:05
welmnut	06/19/2018 10:06
welmnut	07/17/2018 09:00
welmnut	07/17/2018 09:01
welmnut	08/21/2018 08:30
welmnut	08/21/2018 08:31
welmnut	09/24/2018 09:50
welmnut	09/24/2018 09:51
welmnut	10/16/2018 09:40
welmnut	10/16/2018 09:41
welmnut	11/29/2018 10:45
welmnut	11/29/2018 10:46
welmnut	12/18/2018 08:04
welmnut	12/18/2018 08:05

7) Associated researchers and projects–

Please visit our website: www.wellsreserve.org/research.htm for further information on the Wells NERR research program

The Research Program at the Wells NERR conducts and supports research, monitoring, workshops, and research/resource management planning of relevance at local, regional and national levels. The overall aim of our work is to produce science-based information needed to sustain or restore Gulf of Maine coastal habitats and resources, especially those found in salt marsh estuaries and watersheds. During 2003-2004 many different studies involving scores of scientists, students, staff and volunteers focused on several related themes: 1) the quality of water resources in salt marsh estuaries and watersheds 2) land conservation strategies to protect coastal watersheds 3) factors controlling salt marsh accretion, erosion and plant community vigor 4) the value of salt marsh as habitat for fish, shellfish and birds, 5) restoration of salt marsh habitat degraded through human actions, and 6) understanding the ecology and functions of salt marsh habitat.

NERRS SWMP Program

As part of the SWMP long-term monitoring program, WEL NERR also monitors meteorological and nutrient/chlorophyll data which may be correlated with this water quality dataset. These data are available from the Research Coordinator or online at www.nerrsdata.org.

Estuarine Water Resource Quality

Water quality is monitored continuously at several stations with automated instruments as part of the NERRS system-wide monitoring program, as well as bimonthly at 15-20 stations through our WET volunteer

monitoring program. Our water quality work has contributed to the designation of several Priority Watersheds in coastal Southern Maine by the Maine Department of Environmental Protection.

Seacoast Watershed Information Manager (Project S.W.I.M.)

The Seacoast Watershed Information Manager (Project S.W.I.M.) will be an online resource to help local planners and the public evaluate, conserve, and restore coastal watershed resources along the Maine and New Hampshire seacoast by developing a website that describes the region and its resources, provides access to GIS data and other relevant information, and includes a decision-support tool that examines the impact of growth and development on water resources. It will include:

- A Narrative that informs local resource planners and the public by describing development impacts, water resources, and land use.
- Socioeconomic Analysis focused on water resource use as it relates to human activities.
- Land Use Change Assessments focusing on shoreland and permeability.
- A Data Clearinghouse providing users access to key data needed for local and regional-scale resource management.
- A GIS-based Decision Support Tool to help communities manage and protect water resources by considering how water supply, water quality and land use change are affected by land use planning decisions.

The Project focuses on the coastal watersheds from the Cocheco and Salmon Falls River in New Hampshire to the Kennebec River in Maine. These 15 watersheds include 38 municipalities and cover 1,800 square miles. The Wells National Estuarine Research Reserve is the lead partner with support from NOAA's Coastal Services Center Landscape Characterization and Restoration Program and the Great Bay National Estuarine Research Reserve.

Salt Marsh Habitats and Communities

Factors that control the dynamics and vigor of salt marsh plant communities and marsh peat formation consequently determine the ability of a salt marsh to persist in the face of sea level rise. Through a combination of experimental manipulations and long term monitoring, a number of multi-year studies are currently producing data to answer questions concerning the sustainability of salt marsh habitats in this region. These studies are looking at nutrient-plant relations, plant community responses to physical and hydrologic disturbance, and the relative contribution of short-term natural events (e.g. storms) and human activities (dredging, tidal restriction) on patterns of sediment accretion and erosion. The Reserve's marshes and beaches are already among the best studied sites in the U.S. with regard to long term accretion and erosion (over thousands of years).

8) Distribution –

NOAA retains the right to analyze, synthesize and publish summaries of the NERRS System-wide Monitoring Program data. The NERRS retains the right to be fully credited for having collected and process the data. Following academic courtesy standards, the NERR site where the data were collected should be contacted and fully acknowledged in any subsequent publications in which any part of the data are used. The data set enclosed within this package/transmission is only as good as the quality assurance and quality control procedures outlined by the enclosed metadata reporting statement. The user bears all responsibility for its subsequent use/misuse in any further analyses or comparisons. The Federal government does not assume liability to the Recipient or third persons, nor will the Federal government reimburse or indemnify the Recipient for its liability due to any losses resulting in any way from the use of this data.

Requested citation format:

NOAA National Estuarine Research Reserve System (NERRS). System-wide Monitoring Program. Data accessed from the NOAA NERRS Centralized Data Management Office website: www.nerrsddata.org; accessed 12 October 2016.

NERR nutrient data and metadata can be obtained from the Research Coordinator at the individual NERR site (please see Principal investigators and contact persons), from the Data Manager at the Centralized Data Management Office (please see personnel directory under the general information link on the CDMO home page) and online at the CDMO home page www.nerrsddata.org. Data are available in comma separated version format.

II. Physical Structure Descriptors

9) Entry verification –

Excel data files containing measured values (except for Chl-a which is analyzed at Wells NERR) are received from the Virginia Institute of Marine Science (VIMS) and are used to generate only one calculated value which is DIN. Both directly measured and calculated values were entered into this document by Jeremy Miller from files and notes kept by Jeremy Miller and from files delivered by VIMS. The SWMP technicians at Wells NERR were responsible for a visual QA/QC to make sure no entry errors are present. The original Excel files received from VIMS are archived on the Wells NERR server and a Maxtor One Touch external hard drive. Edited files containing additional calculated parameters are archived on the Maxtor One Touch external hard drive.

Nutrient data are entered into a Microsoft Excel worksheet and processed using the NutrientQAQC Excel macro. The NutrientQAQC macro sets up the data worksheet, metadata worksheets, and MDL worksheet; adds chosen parameters and facilitates data entry; allows the user to set the number of significant figures to be reported for each parameter and rounds using banker's rounding rules; allows the user to input MDL values and then automatically flags/codes measured values below MDL and inserts the MDL; calculates parameters chosen by the user and automatically flags/codes for component values below MDL, negative calculated values, and missing data; allows the user to apply QAQC flags and codes to the data; produces summary statistics; graphs selected parameters for review; and exports the resulting data file to the CDMO for tertiary QAQC and assimilation into the CDMO's authoritative online database.

10) Parameter titles and variable names by category –

Required NOAA/NERRS System-wide Monitoring Program nutrient parameters are denoted by an asterisks “*”.

Data Category	Parameter	Variable Name	Units of Measure
Phosphorus and Nitrogen:	*Orthophosphate	PO4F	mg/L as P
	*Ammonium, Filtered	NH4F	mg/L as N
	*Nitrite + Nitrate, Filtered	NO23F	mg/L as N
	Dissolved Inorganic Nitrogen	DIN	mg/L as N
Plant Pigments:	*Chlorophyll a	CHLA_N	µg/L
Other Lab Parameters:	Silicate, Filtered	SiO4F	mg/L as SI

Notes:

1. Time is coded based on a 2400 clock and is referenced to Standard Time.
2. Reserves have the option of measuring either NO₂ and NO₃ or they may substitute NO₃ for individual analyses if they can show that NO₂ is a minor component relative to NO₃. WELLS NERR has shown NO₂ to be a minor component.

11) Measured or calculated laboratory parameters –

- a) **Parameters measured directly**
 - Nitrogen species: NH₄F, NO₃F
 - Phosphorus species: PO₄F
 - Other: CHLA_N, SiO₄F
- b) **Calculated parameters**
 - DIN NO₃F+NH₄F

12) Limits of detection –

Method Detection Limits (MDL), the lowest concentration of a parameter that an analytical procedure can reliably detect, have been established by VIMS and at the Lachat Instrument website (<http://www.lachatinstruments.com/applications/AppsSearch.asp>).

Table 1 (below) gives the Method Detection Limits (MDL) for measured water quality parameters: the following MDL's were provided by the laboratory at the time the data indicated were provided.

Table 1. MDLs for reported parameters

Parameter	Start Date	End Date	MDL	Revisited
CHLA_N	01/01/18	12/31/18	0.11	n/a*
PO ₄ F	01/01/18	12/31/18	0.0016	Jan 2018
NH ₄ F	01/01/18	12/31/18	0.0062	Jan 2018
NO ₃ F	01/01/18	12/31/18	0.0055	Jan 2018
SiO ₄ F	01/01/18	12/31/18	0.0620	Jan 2018

NOTE regarding Chlorophyll *a* limits of measurement:

The following article describes the method used:

"Method 445.0 *In Vitro* Determination of Chlorophyll *a* and Pheophytin *a* in Marine and Freshwater Algae by Fluorescence"

Elizabeth J. Arar and Gary B. Collins

Revision 1.2, September 1997

National Exposure Research Laboratory, Office of Research and Development, USEPA, Cincinnati, OH 45268

The above article states in section 1.2:

"Instrument detection limits of 0.05 µg chl *a*/L and 0.06 µg pheo *a*/L in a solution of 90% acetone were determined by this laboratory. Method detection limits (MDL) using mixed assemblages of algae provide little information because the fluorescence of other pigments interferes in the fluorescence of chlorophyll *a* and pheophytin *a*. A single lab estimated detection limit for chlorophyll *a* was determined to be 0.11 µg/L in 10 mL of final extraction solution. The upper limit of the linear dynamic range for the instrumentation used in this method evaluation was 250 µg chl *a*/L."

*The reserve has not been doing an internal MDL verification for chlorophyll *a* per SWMP protocols, but will begin annual verification moving forward. The MDL in use is reasonable per the documentation above.

13) Laboratory methods –

Section 13, part I: Analysis conducted at Virginia Institute of Marine Science (VIMS). Once filtered, nutrient samples are frozen at -80°C then shipped overnight to VIMS where they are held at -20°C until analyzed.

Parameter: Orthophosphate (PO₄F)

Method References: Virginia Institute of Marine Science Analytical Service Center.

SKALAR Method: O-Phosphate / Total Phosphate Catnr. 503-365.1, issue 042993/MH/93-Demo1.

Murphy, J. and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chim. Acta* 27:31-36. EPA 600/R-97/072 Method 365.5 Determination of Orthophosphate in Estuarine and Coastal Waters by Automated Colorimetric Analysis. IN: *Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition*. National Exposure Research Laboratory, Office of Research and Development. U.S. EPA, Cincinnati, Ohio 45268.

Method Descriptor: Instrumentation: SKALAR San-Plus continuous flow autoanalyzer. Ammonium molybdate and antimony potassium tartrate react in a sulfuric acid environment to form an antimony-phospho-molybdo complex, which is reduced to a blue colored complex by ascorbic acid. Reaction is heat catalyzed at 40°C and measured colorimetrically at 880 nm. The range is 1-50 ppb. Preservation Method: 100 ml of a sample is filtered through 0.45 µm Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47 mm GF/C filter may be used to filter the sample prior to filtering through the 0.45 µm Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and placed in the freezer until shipment time arrives the following day.

Parameter: Nitrate + Nitrite (NO₃F)

Method References: Virginia Institute of Marine Science Analytical Service Center.

SKALAR Method: Nitrate + Nitrite/ Total Dissolved Nitrogen Catnr. 461-353.2 issue

120293/MH/93128060. U.S. EPA. 1974 *Methods for Chemical Analysis of Water and Wastes*, pp. 207-212. Wood, E.D., F.A.G. Armstrong and F.A. Richards. 1967. Determination of nitrate in seawater by cadmium-copper reduction to nitrite. *J. Mar. Biol. Assoc. U.K.* 47: 23. Grasshoff, K., M. Ehrhardt and K. Kremling. 1983. *Methods of Seawater Analysis*. Verlag Chemie, Federal Republic of Germany. 419 pp. EPA 600/R-97/072 Method 353.4 Determination of Nitrate and Nitrite in Estuarine and Coastal Waters by Gas Segmented Flow Colorimetric Analysis. IN: *Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition*. National Exposure Research Laboratory, Office of Research and Development U.S. EPA, Cincinnati, Ohio 45268.

Method Descriptor: Instrumentation: SKALAR San-Plus continuous flow autoanalyzer. Nitrate is reduced to nitrite by a copper/cadmium reductor column. The nitrite ion then reacts with sulfanilimide to form a diazo compound. This compound then couples with n-1-naphthylenediamine dihydrochloride to form a reddish/purple azo dye and is read colorimetrically at 540 nm. Nitrate concentration is obtained by subtracting the corresponding nitrite value from the NO₃- + NO₂- concentration. The color development chemistry is the same as that used in Nitrite. Range is 0.01-1.2 mg/L.

Preservation Method: 100 ml of a sample is filtered through 0.45 µm Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47 mm GF/C filter may be used to filter the sample prior to filtering through the 0.45 µm Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and placed in the freezer until shipment time arrives the following day.

Parameter: Ammonia (NH₄F)

Method References: Virginia Institute of Marine Science Analytical Service Center. U.S. EPA. 1974.

Methods for Chemical Analysis of Water and Wastes, pp. 168-174. *Standard Methods for the Examination of Water and Wastewater*, 14th edition. p 410. Method 418A and 418B (1975). *Annual Book of ASTM Standards*, Part 31. "Water", Standard 1426-74, Method A, p 237 (1976). EPA 600/R-97/072 Method 349.0.

Determination of Ammonia in Estuarine and Coastal Waters by Gas Segmented Continuous Flow Colorimetric Analysis. IN: Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices - 2nd Edition. National Exposure Research Laboratory, Office of Research and Development U.S. EPA, Cincinnati, Ohio 45268.

Method Descriptor: Instrument is SKALAR San-Plus continuous flow autoanalyzer. Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside. Reaction is heat catalyzed at 37°C and is measured colorimetrically at 660 nm. The range is 0.01-2.0 mg/L.

Preservation Method: 100 ml of a sample is filtered through 0.45 µm Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47 mm GF/C filter may be used to filter the sample prior to filtering through the 0.45 µm Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and placed in the freezer until shipment time arrives the following day.

Parameter: Silicate (SiO₄F)

Method References:

Virginia Institute of Marine Science Analytical Service Center. Technicon Industrial Systems Method: Silica. 1973. Technicon Auto-analyzer II Industrial Method No. 186-72W, Silicates in Water and Seawater.
U.S. EPA. 1982. Methods for Chemical Analysis of Water and Wastewater, 18th edition. Method 4500-Si F. Automated Method for Molybdate-Reactive Silica. pp. 4-122 through 4-123.
Grasshoff, K., M. Ehrhardt and K. Kremling. 1983. Methods of Seawater Analysis. Verlag Chemie, Federal Republic of Germany. pp. 175-180.

Method Descriptor:

Instrumentation: SKALAR San-Plus continuous flow autoanalyzer.
The determination of soluble silica is based on the reduction

Preservation Method:

100 ml of a sample is filtered through 0.45 µm Millipore filters using a vacuum-pump and a filtering flask apparatus. If samples are extremely dirty a 47 mm GF/C filter may be used to filter the sample prior to filtering through the 0.45 µm Millipore filter. The liquid volume of the filtered sample is collected into a Nalgene bottle and placed in the refrigerator until shipment time arrives the following day. Samples may be kept up to 28 days.

Section 13, part II: Analysis conducted at Wells NERR.
Analyses conducted by Wells NERR.

Parameter: Chlorophyll a (CHLA_N)

Method References:

Wells National Estuarine Research Reserve Coastal Ecology Center Laboratory
Strickland, J.D.H., and Parson, T.R. 1972. A Practical Handbook of Seawater Analysis. Fish. Res. Bd. Canada 167:310.
TD-10-AU-005-CE Field Fluorometer Operating Manual. Version 1.4. April 1999. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.
EPA - Method 445.0. In Vitro Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluorescence.
Using the Turner Designs Model 10 Analog, The 10AU Digital, Or the TD-700 Fluorometer with EPA Method 445.0. January 19, 1999. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.
A Procedure For Measuring Extracted Chlorophyll a Free From The Errors Associated With Chlorophyll b and Pheopigments. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086. This method was developed by Dr. Nicholas A. Welschmeyer of Moss Landing Marine Laboratories, Moss Landing, CA. A paper by Dr. Welschmeyer, Fluorometric Analysis of Chlorophyll a in the presence of Chlorophyll b and Pheopigments, which details his research, appears in Limnology and Oceanography (June 1994).

Method Description:

Instrumentation: Turner Designs 10-AU-005-CE Field fluorometer.

The Chl-a processing methodology here at the Wells NERR Research Laboratory follows the non-acidification method, “A Procedure For Measuring Extracted Chlorophyll a Free From The Errors Associated With Chlorophyll b and Pheopigments”, adapted from the EPA Method 445.0: “In Vitro Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluorescence.” The method used requires filtering a known quantity of water through a glass fiber filter (47 mm GF/F). The sample is steeped in 90% acetone at least 2 hours and not exceeding 24 hours at 4°C, in the dark. The samples are centrifuged and read on the fluorometer. If the samples cannot be read within that time period, they are stored in the research freezer at -20°C.

Preservation Method:

This methodology includes filtering 500 ml of a sample through 47 mm Whatman® GF/F filters using a vacuum pump and filter flask apparatus. The Whatman type GF/F filter is either folded immediately after sample filtering, enclosed in a waxed paper envelope, placed in a petri dish, wrapped with aluminum foil, placed in a sealed freezer bag, and placed in the freezer until analysis. The final concentration of Chl-a = $(F \times v)/V$; where F = the direct fluorescence reading, v = volume of the extract, and V = volume of sample filtered.

14) Field and Laboratory QAQC programs –

a) Precision

- i) **Field variability** – True field replicates are taken at each site during grab sampling. Both replicate grabs are taken one immediately after the other.
- ii) **Laboratory variability** – none
- iii) **Inter-organizational splits** – same samples were not split or analyzed by two different labs

b) Accuracy

- i) **Sample spikes** – none
- ii) **Standard reference material analysis** – See lab SOP above
- iii) **Cross calibration exercises** – The Wells NERR did not participate in any cross lab comparisons.

15) QAQC flag definitions –

QAQC flags provide documentation of the data and are applied to individual data points by insertion into the parameter's associated flag column (header preceded by an F_). QAQC flags are applied to the nutrient data during secondary QAQC to indicate data that are out of sensor range low (-4), rejected due to QAQC checks (-3), missing (-2), optional and were not collected (-1), suspect (1), and that have been corrected (5). All remaining data are flagged as having passed initial QAQC checks (0) when the data are uploaded and assimilated into the CDMO ODIS as provisional plus data. The historical data flag (4) is used to indicate data that were submitted to the CDMO prior to the initiation of secondary QAQC flags and codes (and the use of the automated primary QAQC system for WQ and MET data). This flag is only present in historical data that are exported from the CDMO ODIS.

- 4 Outside Low Sensor Range
- 3 Data Rejected due to QAQC
- 2 Missing Data

- 1 Optional SWMP Supported Parameter
- 0 Data Passed Initial QAQC Checks
- 1 Suspect Data
- 4 Historical Data: Pre-Auto QAQC
- 5 Corrected Data

16) QAQC code definitions –

QAQC codes are used in conjunction with QAQC flags to provide further documentation of the data and are also applied by insertion into the associated flag column. There are three (3) different code categories, general, sensor, and comment. General errors document general problems with the sample or sample collection, sensor errors document common sensor or parameter specific problems, and comment codes are used to further document conditions or a problem with the data. Only one general or sensor error and one comment code can be applied to a particular data point. However, a record flag column (F_Record) in the nutrient data allows multiple comment codes to be applied to the entire data record.

General errors

GCM	Calculated value could not be determined due to missing data
GCR	Calculated value could not be determined due to rejected data
GDM	Data missing or sample never collected
GQD	Data rejected due to QA/QC checks
GQS	Data suspect due to QA/QC checks
GSM	See metadata

Sensor errors

SBL	Value below minimum limit of method detection
SCB	Calculated value could not be determined due to a below MDL component
SCC	Calculation with this component resulted in a negative value
SNV	Calculated value is negative
SRD	Replicate values differ substantially
SUL	Value above upper limit of method detection

Parameter Comments

CAB	Algal bloom
CDR	Sample diluted and rerun
CHB	Sample held beyond specified holding time
CIP	Ice present in sample vicinity
CIF	Flotsam present in sample vicinity
CLE	Sample collected later/earlier than scheduled
CRE	Significant rain event
CSM	See metadata
CUS	Lab analysis from unpreserved sample

Record comments

CAB	Algal bloom
CHB	Sample held beyond specified holding time
CIP	Ice present in sample vicinity
CIF	Flotsam present in sample vicinity
CLE	Sample collected later/earlier than scheduled
CRE	Significant rain event
CSM	See metadata
CUS	Lab analysis from unpreserved sample

Cloud cover

CCL	clear (0-10%)
CSP	scattered to partly cloudy (10-50%)
CPB	partly to broken (50-90%)
COC	overcast (>90%)
CFY	foggy
CHY	hazy
CCC	cloud (no percentage)

Precipitation

PNP	none
PDR	drizzle
PLR	light rain
PHR	heavy rain
PSQ	squally
PFQ	frozen precipitation (sleet/snow/freezing rain)
PSR	mixed rain and snow

Tide stage

TSE	ebb tide
TSF	flood tide
TSH	high tide
TSL	low tide

Wave height

WH0	0 to <0.1 meters
WH1	0.1 to 0.3 meters
WH2	0.3 to 0.6 meters
WH3	0.6 to > 1.0 meters
WH4	1.0 to 1.3 meters
WH5	1.3 or greater meters

Wind direction

N	from the north
NNE	from the north northeast
NE	from the northeast
ENE	from the east northeast
E	from the east
ESE	from the east southeast
SE	from the southeast
SSE	from the south southeast
S	from the south
SSW	from the south southwest
SW	from the southwest
WSW	from the west southwest
W	from the west
WNW	from the west northwest
NW	from the northwest
NNW	from the north northwest

Wind speed

WS0	0 to 1 knot
WS1	> 1 to 10 knots
WS2	> 10 to 20 knots
WS3	> 20 to 30 knots
WS4	> 30 to 40 knots
WS5	> 40 knots

17) Other remarks/notes –

Data may be missing due to problems with sample collection or processing. Laboratories in the NERRS System submit data that are censored at a lower detection rate limit, called the Method Detection Limit or MDL. MDLs for specific parameters are listed in the Laboratory Methods and Detection Limits Section (Section II, Part 12) of this document. Concentrations that are less than this limit are censored with the use of a QAQC flag and code, and the reported value is the method detection limit itself rather than a measured value. For example, if the measured concentration of NO₂3F was 0.0005 mg/l as N (MDL=0.0008), the reported value would be 0.0008 and would be flagged as out of sensor range low (-4) and coded SBL. In addition, if any of the components used to calculate a variable are below the MDL, the calculated variable is removed and flagged/coded -4 SCB. If a calculated value is negative, it is rejected and all measured components are marked suspect. If additional information on MDL's or missing, suspect, or rejected data is needed, contact the Research Coordinator at the Reserve submitting the data.

Note: The way below MDL values are handled in the NERRS SWMP dataset was changed in November of 2011. Previously, below MDL data from 2007-2010 were also flagged/coded, but either reported as the measured value or a blank cell. Any 2007-2011 nutrient/pigment data downloaded from the CDMO prior to November of 2011 will reflect this difference.

MARCH 2018 Data: No data was collected in March due to Construction at our sampling location which made the dock inaccessible. All others missed due to ice.

JULY 2018 SM Grab Samples: Data are missing because samples were left out of the cooler and not processed due to getting warm.

Sample/Parameter Hold Times: All parameters and sample types (diel and grabs) are run simultaneously at the Virginia Institute of Marine Science's Analytical Laboratory. Chla samples are run in house at the Wells NERR Coastal Ecology Laboratory.

Once processed, both nutrient and chlorophyll samples are held at -20°C. NERRS SOP allows nutrient samples to be held for up to 28 days (CHLA for 30), plus allows for up to 5 days for collecting, processing, and shipping samples. Samples held beyond that time period are flagged suspect and coded CHB.

<u>Date of analysis</u>		
<u>Sample Collection (both diel and grabs)</u>	<u>PO4F, NH4F, NO23F, and SiO4F</u>	<u>Chla</u>
January 29-30	2/14/18	4/3/18*
February 26-27	3/21/18	4/16/18*
March 20-21	No samples collected	N/A
April 23-24	5/15/18	6/29/18*
May 15-16	6/12/18	7/18/18*
June 18-19	7/11/18	8/15/18*
July 16-17	8/3/18	9/21/18*
August 20-21	9/10/18	9/21/18
September 23-24	10/4/18	10/16/18
October 15-16	10/29/18	12/13/18*
November 28-29	1/4/19*	12/13/18
December 17-18	3/13/19*	2/17/19*

*Samples marked with an asterisk were held longer than allowed by NERR SWMP protocols.

References

Holden, W.F. 1997. Fresh water suspended sediments and nutrient influx into the Little River and Webhannet River estuaries, Wells, ME. Dissertation, Boston University, Boston, MA. 279 pp.

Mariano, C.G. and FitzGerald, D.M. 1989. Sediment transport patterns and hydraulics at Wells inlet, Maine. Boston University, Boston, MA. 143 pp.

Ward, L.G. 1993. Precipitation, streamflow, and water characteristics of the Webhannet River Estuary, Wells, Maine. Jackson Estuarine Research Lab, University of New Hampshire department of Earth Sciences, Durham, NH. 101 pp.

Wells National Estuarine Research Reserve. 1996. Reserve Management Plan. Reserve Management Authority, Wells, Me. 241 pp.