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2004 Great Bay Organic Nitrogen (PON & DON) and Light Extinction (PAR) Monitoring Program

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A Final Report to

The New Hampshire Estuaries Project

Submitted by

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Introduction

Nitrogen is most often considered to be the limiting nutrient for plant growth in marine waters. As a result, knowledge of nitrogen loading and ambient water-column concentrations are considered to be critical to understanding the response of aquatic ecosystems to nutrient over-enrichment—a process known as eutrophication when it results in the excess production of organic matter.

Plant production in many estuarine systems may also be limited by light availability as a result of high levels of turbidity in the water resulting from sediments, dissolved organic matter, and phytoplankton in the water column. Light limitation resulting from human-induced increases in turbidity is known to be particularly deliterious to seagrass production/distribution in some ecosystems and also play an important role in determining how phytoplankton respond to nutrient enrichment.

EPA is developing water qulaity criteria for estuaries that require knowledge of both total nitrogen and light availability (measured as photsynthetically active radiation, PAR). Through the National Estuarine Research Reserve (NERR) System-Wide Monitoring Program (SWMP), inorganic nutrient concentrations, chlorophyll-a concetration, and a number of hydrographic and water quality parameters are sampled on a monthly basis at 7 sites in the Great Bay system. In addition, these same parameters, as well as bacteria concentrations, are measured at a number of sites in Great Bay and Hampton Harbor through the National Coastal Assessment (NCA) funded through the EPA.

This project takes advantage of these existing monitoring activities to collect and analyze for particulate organic nitrogen (PON), dissolved organic nitrogen (DON) and photosynthetically active radiation (PAR) at a up to 10 existing sample sites in the New Hampshire seacoast region. When combined with existing dissolved inorganic nitrogen measurements, PON and DON allow the entire Total Nitrogen (TN) pool to be quantified. PAR measurements provide, for the first time, an estimate of the light availability in the system.

Project Goals and Objectives

UNH completed this project under contract to the NH Estuaries Project (Project ID #04-M-2; CE-991711-06 and CE-991711-08). The project goals and objectives per the contract were to:

> (1) conduct PON and DON monitoring for the April – December sampling season at the Lamprey River (LR), Squamscott River (SQ), Chapman's Landing (CL), Oyster River (OR), Great Bay (GB) and Coastal Marine Lab (CML); Cocheco River (NCA 0058); Salmon Falls River (NCA 0062); Bellamy River (NCA 0052) and Hampton Harbor (NCA 0007) sites; and

(2) conduct PAR monitoring for the April – December sampling season at as many of the sites above as possible.

The goal was to provide 125 measurements for PON and DON and 66 measurements of PAR during the sampling period. The final work product was agreed to be an Excel data file containing hydrographic, PON, DON and PAR data for all of these sites.

Methods

The methods for this project followed the procedures specified in the approved QA Project Plan (Pennock and Trowbridge, 2003).

Results and Discussion

In this first year of sampling, we discovered that logistical limitations associated with the various types of sampling (e.g. boat vs. automobile vs. pier) and the constraints of the individual programs (e.g. NCA time limitations that limited PAR measurements) required modification of the original sampling plan. Overall, as shown in the table below, we were able to obtain 86 discrete estimates for the attenuation coefficient (PAR), 102 measurements for particulate carbon and nitrogen (PC/PN), 140 measurements of total dissolved nitrogen (TDN) and 138 measurements of dissolved organic nitrogen (DON). We performed replicate analyses on all parameters except for PAR (statistics were generated from duplicate estimates at 1 location). Laboratory analyses fell within the accepted guidelines detailed in the approved QA Project Plan (Pennock and Trowbridge, 2003).

Statistical analysis on replicate data showed the following error estimates for field replicates:

Parameter	Location	Stations	Analyses	Mean	SD	% SE
PAR	All Data	136	86	-1.713		
PAR	Adams Point QA	3	9	-1.02	0.12	15.5%
POC	All Data	107	203	0.8750		24.9%
PON	All Data	107	203	0.1053		4.6%
TDN	All Data	136	257	0.4018		13.7%
DON	All Data	136	256	0.1751		8.7%

This analysis suggests that our estimates of light attenuation should be expected to be good to +/- ~15.5% (note that the SE is elevated as a result of extreme variance during one of the QA samplings). For POC, a parameter that is not called for in the monitoring program but which is obtained for no additional cost as part of the PON analysis, field replicates were good to +/- 24.9%, while PON measurements showed a much lower percent error of 4.6%. TDN measurements, which require a significant amount of analytical processing, showed a percent error of 13.7% for field replicates. DON, which is a calculated parameter that combines the errors associated with field collection, TDN analysis

and the error associated with the analysis of NH_4, NO_3 and NO_2 displayed an error of, 8.7% for field replicates.

Differences between POC, PON and TDN replicate samples were compared to data quality objectives of 30% RPD and 0.5, 0.1 and 0.5 mg/L, respectively. Replicate samples that failed both tests should be rejected. For POC, PON and TDN, only six, four and two pairs of replicate samples failed both tests. Replicate samples for DON were not tested because this parameter is calculated as the difference between TDN and DIN. Therefore, the majority of the data met the data quality objectives of the study. The data quality objectives for the study are different from those listed in the QAPP but were mutually agreed upon by UNH and the NHEP Coastal Scientist.

In 2004 we were able to collect PAR measurements 86 PAR measurements (goal = 66). We also performed significantly more than the estimated 125 analyses for PON (actual = 203) and DON (actual = 256) as a result of our desire to obtain strong estimates of the field variability associated with each measurement.

The CD included with this report contains data files in an Excel format that is consistent with NERR SWMP CDMO requirements. Included are the following required parameters for this project: Record #; Funding Source for Sampling Effort; Sample Date; Site/Station Name; Tidal Stage; Bottom Depth; Temperature; Salinity; Oxygen Concentration; Oxygen Percent Saturation; pH; Total Dissolved Nitrogen (TDN); Dissolved Organic Nitrogen (DON); Particulate Organic Carbon (POC); Particulate Organic Nitrogen (PON); and Attenuation Coefficient (K_d). Nutrient values that fall below prescribed MDL's have been changed to '-9999' in the data file.

Data contained in this file are scheduled to be submitted to NERR CDMO on May 15th, 2005. It is subject to review and potential revision by the NERR CDMO.

Conclusions and Recommendations

The PON, DON and PAR monthly monitoring program provides important data on nitrogen concentration and light availability in the Great Bay estuary. When combined with the NERRS SWMP program, these data provide comprehensive coverage of the Great Bay estuary and allow total nitrogen concentrations to be calculated for use in nutrient criteria measurements.

Sampling procedures were not as consistent as desired as a result of logistical limitations in meshing these additional samples into the existing NCA and GB SWMP sampling programs. These issues were generally resolved as the year moved along; however, additional efforts and support will be required to insure that the data collected through these different programs are ultimately as seamless as possible.

References

Pennock and Trowbridge (2003) UNH Nutrient and Light Extinction Monitoring Program Quality Assurance Project Plan, Version 4, Final. University of New Hampshire and NH Estuaries Project, August 8, 2003.

2004 Organic Nitrogen (PON & DON) and Light Extinction (PAR) Monitoring Program Meta-Data (Appendix 1)

Research Methods

Monthly monitoring is conducted during ice-free seasons (generally April through December) as part of the GB NERR System-Wide Monitoring Program and National Coastal Assessment at the following locations:

Funding Source	Station Name	Station ID	Tide Stage	Lat Deg	Lat Minute	Long Deg	Long Minute
NERR	Adams Point	AP	L&H	43	5.495	70	51.821
NERR	Great Bay	GB	L	43	4.367	70	52.311
NERR	Lamprey River	LR	L&H	43	4.697	70	56.092
NERR	Oyster River	OR	L&H				
NERR	Squamscott Railroad Bridge	SQ	L	43	3.182	70	54.754
NERR	Squamscott Chapman's Landing	CL	L&H	43	2.500	70	55.569
NERR	Coastal Marine Lab	CML	L&H				
NCA	Cocheco River	CR	Variable	43	11.717	70	51.452
NCA	Salmon Falls	SF	Variable	43	11.857	70	49.251
NCA	Bellamy River	BR	Variable	43	8.055	70	50.865
NCA	Hampton Harbor	HH	Variable	42	53.766	70	49.502

Samples are generally collected by small boat except for the Coastal Marine Lab site, which is accessed by vehicle. During certain periods of particularly stormy weather or when the channel markers are not present (generally in April), a subset of the normal stations may be sampled by vehicle; these cases are noted in the meta-data.

At each station, a hand-held YSI multi-probe is used to measure temperature, salinity, dissolved oxygen, dissolved oxygen percent saturation and pH (for NCA stations), in the surface water (~0.5m). Nutrient samples are collected in acid-washed and DI-water rinsed 1-liter HDPE bottles at ~0.5m depth, placed on ice in a cooler and processed upon return to the laboratory. Photosynthetically Active Radiation (PAR) profiles are made at as many stations as possible using a LiCor Quantum Irradiance Meter.

All nutrient processing and analysis methods and PAR profiling methods are detailed in the 2003 UNH Nutrient and Light Extinction Monitoring Program Quality Assurance Project Plan (Pennock & Trowbridge, 2003).

Deviations in Sampling Procedures for 2004

<u>January</u>

- Icing Conditions; no samples collected.

February
- Icing Conditions; no samples collected.

March
- Icing Conditions; no samples collected.

April
- NERR samples collected by vehicle due to the lack of channel markers, no access to SQ site.
- Limited PAR measurements taken as a result of vehicle-based sampling.

May
- PAR measurements not possible during NCA surveys due to logistical limitations.
- Limited station access due to vehicle-based sampling (No SQ sample).

June
- PAR measurements not possible during NCA surveys due to logistical limitations.

July
- PAR measurements not possible during NCA surveys due to logistical limitations.

August
- PAR measurements not possible during NCA surveys due to logistical limitations.

September
- PAR measurements not possible during NCA surveys due to logistical limitations.
- No PAR at CL due to instrument malfunction.

October
- PAR measurements not possible during NCA surveys due to logistical limitations.

November
- PAR measurements not possible during NCA surveys due to logistical limitations.
- Not enough depth to record PAR at OR (Low Tide)
- Several missing NCA Nutrient samples due to error in sample cataloguing.

December
- PAR measurements not possible during NCA surveys due to logistical limitations.
- Limited PAR measurement due to vehicle-based sampling.
- Par values for CML deleted.