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UNH Monitoring Activities that Support the National Coastal Assessment in 2007

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A Final Report to

The New Hampshire Estuaries Project

Submitted by

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July 11, 2008

Executive Summary

The National Coastal Assessment is an Environmental Protection Agency program to monitor the health of the nation's estuaries using nationally standardized methods and a probabilistic sampling design. Dedicated EPA funding for the National Coastal Assessment ceased after 2006. Therefore, the NH Department of Environmental Services and the New Hampshire Estuaries Project contributed funds to continue a portion of the National Coastal Assessment in 2007. Water quality measurements were successfully made during 2007 at 25 randomly located stations throughout the Great Bay Estuary and Hampton-Seabrook Harbor. These data will be combined with samples collected in 2006 for probabilistic assessments of estuarine water quality during the 2006-2007 period in the NHEP Water Quality Indicators Report in 2009.

Introduction

The purpose of this project is for the New Hampshire Estuaries Project of the University of New Hampshire (UNH) to implement estuarine monitoring activities that support the National Coastal Assessment. The National Coastal Assessment is an Environmental Protection Agency (EPA) program to monitor the health of the nation's estuaries using nationally standardized methods and a probabilistic sampling design. The Department of Environmental Services (DES) and UNH participated in the National Coastal Assessment during the original 7-year effort (2000-2006). Dedicated EPA funding for the National Coastal Assessment ceased after 2006. The program produced valuable data to determine the quality of all of New Hampshire's estuarine waters and to provide data for regional and national assessments. Therefore, DES and UNH contributed funds to continue a portion of the National Coastal Assessment in 2007.

Funding provided by DES and NHEP in provided for the collection of all field data and samples during the 2007 season as well as data management and quality assurance tasks. UNH researchers at Jackson Estuarine Laboratory were selected for the work because UNH has seven years of experience with the National Coastal Assessment methods and study design. Following nationally standardized methods is critical to the success of the project. UNH purchased all the equipment needed for the project during the period when the program was supported by EPA grant funding. Cooperation between National Coastal Assessment field crews and other UNH monitoring programs also provide opportunities for efficiency and cost savings.

The total project costs were budgeted to be $28,001. The New Hampshire Estuaries Project at UNH contributed $20,001 for the project. DES provided $8,000 through grant funding to the State from the Environmental Protection Agency and the National Oceanic and Atmospheric Administration.

Project Goals and Objectives

The following are the work tasks for this project from the cooperative project agreement.

COLLECT SAMPLES AND FIELD DATA FOR THE YEAR 2 OF THE 2006-2007 STUDY DESIGN

UNH will collect water samples and measure physicochemical parameters at 25 sampling locations. Following National Coastal Assessment (NCA) protocols, water samples will be collected from multiple depths at stations where the water is greater than 2 meters. Field duplicate water samples will be collected at three stations for quality assurance. Field measurements and water samples will be collected using National Coastal Assessment protocols with the exception of photosynthetically active radiation (PAR) which will be measured using GBNERR SWMP protocols (attached). The stations for this task are provided in the attached table.

CONDUCT LABORATORY ANALYSIS OF WATER SAMPLES

UNH will analyze each water sample, including field duplicate samples, for the parameters listed below. Samples will be analyzed by the Water Quality Analysis Laboratory or Jackson Estuarine Laboratory following the protocols in the NCA Quality Assurance Project Plan.

Water Quality Analysis Laboratory
Dissolved nitrite+nitrate (NO23)
Dissolved ammonia (NH4)
Total dissolved nitrogen (TDN)
Particulate nitrogen (PN)
Particulate carbon (PC)
Dissolved orthophosphate (PO4)
Total dissolved phosphorus (TDP)
Particulate phosphorus (PP)
Dissolved silica (SiO2)
Colored dissolved organic matter (CDOM)

Jackson Estuarine Laboratory
Chlorophyll a (Chla)
Total suspended solids (TSS)
Fecal coliform bacteria (FC)
Escherichia coli (EC)
Enterococci (Ent)

PREPARE FIELD SAMPLING SUMMARY

UNH will prepare a memo describing the field sampling activities completed by UNH during the 2007 field season through December 2007. In this memo, UNH will specify which work tasks from the 2007 workplan were successfully completed, highlight any work tasks that were not completed, and explain any difficulties encountered. The deliverable for this task will be due by January 31, 2008.

CONDUCT QUALITY ASSURANCE REVIEW OF FIELD AND LABORATORY DATA

UNH will be responsible for checking the field and laboratory data from 2007 for errors or omissions. UNH will proof the field data sheets and data entry into the Form Flow software. UNH will also review the quality assurance samples for bacteria, nutrient, and particulate results and summarize the information in a Quality Assurance Report. The deliverable for this task will be due by March 31, 2008.

PREPARE DATABASES FOR SAMPLING RESULTS

UNH Marine Program will compile all field and laboratory data generated by UNH into a database. The database will be provided to the NHEP. The deliverable for this task will be due by March 31, 2008.

SUPPORT THE NHEP MONITORING PROGRAM

UNH JEL staff will meet as needed with the NHEP Coastal Scientist. The UNH JEL staff will provide technical and advisory support for the NHEP Coastal Scientist by participating in the NHEP Technical Advisory Committee and by providing access to data sets and other information as requested.

Methods

The field and analytical methods for this project followed the Quality Assurance Project Plan for the National Coastal Assessment. A brief description of the project follows:

STUDY DESIGN: PARAMETERS -- THE WATER COLUMN IS TESTED FOR: TEMPERATURE, SALINITY, PH, DISSOLVED OXYGEN, SECCHI DEPTH, LIGHT ATTENUATION, NUTRIENTS (NO2+NO3, NH4, PO4, SI), CHLOROPHYLL-A, AND BACTERIA INDICATOR SPECIES (FECAL COLIFORMS, E.COLI, ENTEROCOCCUS). SAMPLING FREQUENCY -- ALL THE STATIONS IN A PROBABILISTIC DESIGN ARE TESTED ONCE FOR EACH PARAMETER. THE PROBABLISTIC DESIGNS CONSIST OF 50 STATIONS THAT ARE SAMPLED OVER A TWO

YEAR PERIOD (25 STATIONS PER YEAR). STATIONS – 50 RANDOMLY ASSIGNED
STATIONS THROUGHOUT THE ESTUARIES.

QUALITY ASSURANCE DOCUMENT: THIS PROJECT IS BEING COMPLETED FOLLOWING
THE QA PROTOCOLS FROM THE NATIONAL COASTAL ASSESSMENT PROBABILITY
BASED MONITORING PROGRAM. DOCUMENT AVAILABLE AT:
HTTP://WWW.EPA.GOV/EMAP/NCA/HTML/DOCS/QAPROJPLAN.HTML

Results and Discussion

Field collection and analytical measurements were completed without significant deviations from the
Quality Assurance Project Plan.   Field sampling activities are summarized in Appendix A. Laboratory
quality assurance tests are provided in Appendix B. Data quality objective tests by DES are provided in
Appendix C.

All valid results were imported to the DES Environmental Monitoring Database.

Conclusions

Conclusions will be drawn from these data in the NHEP Water Quality Indicators report in 2009.

Appendix A

2007 NH NCA Field Sampling Effort

Final Summary Report: March, 2008

Dr. Stephen H. Jones, Mr. Colin Edwards & Mr. Nathan Horton

2007 marked the 8[h] year of the NH NCA program, and the 2nd year in a 2-year sampling cycle. The targeted area of assessment continued to be the estuarine waters of New Hampshire and a small part of Maine. Boundaries include the upper ends of waterbodies at head of tide, and at the mouth of Portsmouth Harbor and Hampton Harbor by articulation with the Atlantic Ocean. The basic strata for New Hampshire are the Great Bay Estuary, Rye Harbor and Hampton Harbor.

The monitoring program employs a probabilistic design using ecological response indicators, along with diagnostic indicators. No pre-existing monitoring stations from other monitoring programs have been incorporated into the probabilistic design, since none fit the requirements of randomness. A grid overlay of equal size hexagons was used for spatial distribution of random sampling stations. Three stations for each hexagon were randomly selected and designated as A, B, or C. Field technicians always first attempt to sample at station A. If samples cannot be collected based on physical conditions or other reasons, technicians have had to move to station B, and so on. The present system consists of 50 sampling locations, 25 of which are sampled each year.

In 2007, New Hampshire continued to implement the base NCA program, which included collecting the base program parameters in accordance with the probabilistic sampling design.   NH NCA continued to target 25 sample sites per year over a 2-year period for water sampling.

Water

The 2007 NH NCA continued the NCA base program for the base program water parameters. An additional sampling design involved monthly water collection at 8 sites, 4 as part of the NCA program and 4 that are part of the GBNERR-SWM program, to provide a more temporally intensive assessment of seasonal differences in bacteria.

Water Quality-*nutrient indicators*

The baseline water sampling for nutrient indicators took place from August 7-September 11, 2007. Successful sampling occurred at all 25 of the targeted sites. The monthly sampling for nutrient indicators occurred from July 3 to August 21, 2007.

Water-*bacterial indicators*

NH NCA 2007 also continued water sampling for bacterial indicators of fecal contamination. The bacterial water quality monitoring design included the measurement of 3 bacterial indicators at each NCA site at the same time of the base program water

collection. In addition, NH NCA collected monthly water samples for bacterial indicators at the 8 sites.

The baseline water sampling for bacterial indicators took place from August 7-September 11, 2007. Successful sampling occurred at all 25 of the targeted sites. The monthly sampling for bacterial indicators at the NCA sites occurred from July 3 to August 21, 2007. Extra summertime samples were collected at the NCA sites during July and August. All targeted samples were successfully collected at all 4 sites. Water samples were collected at the 4 GBNERR stations monthly from April 25 to December 18, 2007 at high and low tide, to coincide with water sampling for nutrient analysis by the GBNERR SWMP program. All targeted samples were collected. All bacterial analyses were conducted at JEL.

Appendix B

2007
New Hampshire
National Coastal Assessment
QA Report

March, 2008

Submitted by

Dr. Stephen H. Jones
University of New Hampshire
Center for Marine Biology
Department of Natural Resources
Jackson Estuarine laboratory
Durham, NH 03824

The New Hampshire NCA program used two University of New Hampshire laboratories in 2007 for analysis of samples. These were the UNH Jackson Estuarine Laboratory Microbiology Lab (JELmicro) and the UNH Water Quality Analysis Laboratory (WQAL). JELmicro conducted all bacterial, chlorophyll *a* and total suspended solids analyses. All other nutrient analyses were conducted by WQAL. The minimum detection limits (MDL) and analytical methods used are listed in Table 1.

Table 1. MDL and analytical methods used for analyzing nutrients, chlorophyll a, total suspended solids and bacteria.

Parameter	MDL	Units	Method
Enterococci	1	cfu/100 ml	Method 1106.1
Fecal coliforms	1	cfu/100 ml	Rippey, et al. (1987)
E. coli	1	cfu/100 ml	Method 1103.1
TSS	1	mg/L	JEL SOP 1.05
Chlorophyll *a*	0.2	µg/L	SM17 10200 H
Ammonium	6.3	µg N/L	US EPA Method 350.1
Nitrate + nitrite	4.23	µg N/L	US EPA Method 353.3
Nitrite	4.23	µg N/L	US EPA Method 354.1
Total dissolved N (TDN)	0.1	mg N/L	Merriam et al. 1996
Phosphate	4.2	µg P/L	US EPA Method 365.2
Total dissolved P (TDP)	16.8	µg P/L	US EPA Method 365.2
Particulate P (PP)	20	µg P/L	Aspila et al. 1976; US EPA Method 365.2
Particulate N (PN)	0.01	mg N/L	US EPA EMAP QAPP method
Particulate C (PC)	0.01	mg C/L	US EPA EMAP QAPP method
Silica	0.04	mg SiO2/L	US EPA Method 370.1

NUTRIENT SAMPLE ANALYSES

The UNH WQAL conducted 10 different analyses on NH-NCA water samples in 2007. The complete QA data report is included as Appendix A. A summary of the results for replicate, spike, QC sample and "standards run as unknowns" analyses is presented below (Table 2). All analyses were targeted to have measured concentrations fall within 15% differences for replicates (RPD), recovery of known amounts (spikes), certified concentrations (QC samples) and prepared concentrations (standards). Differences of >15% were considered failures except when the absolute difference in values was ≤ MDL or values for averages were <10x the MDL.

Table 2. QA analysis results for replicate samples, spikes, standards and QC samples run every 10-12 samples: NH-NCA 2007. Numbers in parentheses are analyses where the results were outside of acceptable range but with absolute value differences ≤MDL or with averages < 10x the MDL. (ND = not done)

Analysis	Replicates		Spikes		Standards		QC samples	
	analyses	accepted	analyses	accepted	analyses	accepted	analyses	accepted
NH_4	4	4	4	4 (1)	19	19 (5)	7	7
NO_3+NO_2	5	5(2)	ND	ND	17	17 (2)	8	8
TDN	9	9	ND	ND	29	29 (3)	4	4
PO_4	8	7 (2)	8	8 (1)	18	18 (2)	8	8
TDP	11	11 (1)	7	7 (1)	16	16 (3)	8	8
PP	3	3	ND	ND	9	9 (1)	4	4
PN	2	1 (1)	ND	ND	ND	ND	2	2 (1)
PC	2	2	ND	ND	ND	ND	2	2
SiO_2	8	8	8	8	19	19 (7)	11	11

There were no instances of non-accepted QA analysis.

CHLOROPHYLL *a* AND TSS SAMPLE ANALYSES

The JEL microbiology lab conducted all chlorophyll *a* and TSS analyses. No standards of reference material chlorophyll *a* samples were run in 2007.

Table 3. Relative percent difference (RPD) in measured chlorophyll *a* and total suspended solids (TSS) values for duplicate QA samples: NH-NCA 2007.

	Chlorophyll *a* duplicate QA samples	RPD	TSS duplicate QA samples	RPD
July	0	N/A	0	N/A
August	1	13.3%	1	58.8%
September	2	5.71% & 22.22%	2	15.38% & 0.0%

None of the RPD values for chlorophyll *a* analyses fell outside of the precision goal of 30%.   Most of the RPD values for the TSS analyses were within the precision goal of 30%; the one exception was 59% and represented duplicate concentrations that were relatively high (15 and 27.5 mg/l).

BACTERIAL SAMPLES

The JEL microbiology lab also conducted all bacterial analyses, including fecal coliform, *Escherichia coli*, and enterococci in water. QA analyses included positive and negative controls, blanks, and duplicate analyses of water samples. The results are summarized in Table 4.

Table 4. QA analysis results for positive and negative controls and blanks run with each sample batch: NH-NCA 2007.

Month	Batches- +/- controls	# unacceptable	Batches- blanks	# unacceptable
April	0	0	0	0
May	0	0	0	0
June	1	0	1	0
July	2	0	2	0
August	3	0	3	0
September	2	0	2	0
October	1	0	1	0
November	1	0	1	0
December	0	0	0	0

The results for the filtration blanks were all acceptable in that no colonies were detected on any blank filters. The results for the positive and negative controls were also all acceptable.

The results for duplicate sample analyses for fecal coliforms, *E. coli* and enterococci are presented below in Table 5.

Table 5. Precision criterion values for bacterial indicator concentrations in the first 15 duplicate samples each month: NH-NCA 2007.

Month	Fecal Coliforms n =	Prec. Crit.	*E.coli* n =	Prec. Crit.	Enterococci n =	Prec. Crit.
April	8	0.5513	8	0.5461	7	0.7916
May	8	0.4082	8	0.4110	4	0.9106
June	8	0.6718	8	0.6753	8	0.9196
July	13	0.6856	13	0.6949	13	0.6000
August	15	0.5290	15	0.5505	15	0.6633
September	14	0.4170	14	0.4462	10	0.5741
October	10	0.4319	10	1.016	8	1.007
November	10	0.5942	10	0.6434	9	0.2711
December	4	0.7392	4	0.8204	3	0.7924

The precision criterion values for duplicate sample analyses were acceptable overall. There was some variability through the year, where slightly higher values would result from using a preponderance of data with relatively low (<5 cfu/100 ml) bacterial concentrations. The targeted number of monthly samples was 15, but this number of samples was only attained in August; all available sample analyses were used in the other months.

REFERENCES

Aspila, I., H. Agemian and A.S.Y. Chau. 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst, 101:187-197.

Merriam, J.L, W.H. McDowell, W.S. Currie, 1996. A high-temperature catalytic oxidation technique for determining total dissolved nitrogen. *Soil Science Society of America Journal*, 60(4) 1050-1055

Rippey, S.R., W.N. Adams and W.D. Watkins. 1987. Enumeration of fecal coliforms and *E. coli* in marine and estuarine waters: an alternative to the APHA-MPN approach. J. Wat. Pollut. Cont. Fed. 59: 795-798.

QC report for 2007 NH-NCA samples
Analyzed for nutrients by the Water Quality Analysis Lab at UNH

Prepared by Jeff Merriam
Lab Manager
Water Quality Analysis Lab
UNH
215 James Hall

NO$_3$+NO$_2$ Analyzed by discrete colorimetric analysis (Cd-Cu reduction) using a SmartChem discrete analyzer, based on USEPA 353.3. Samples were analyzed in 1 batch. Method Detection Limit (MDL) was calculated to be 4.23 ug N/L. Spikes were not performed due to instrument limitations with this method.

Table 1. Replicate Data. Samples were replicated every 10-12 samples. Replicates must fall within 15% relative percent difference (RPD = abs(dup1-dup2)/average of dup1 and dup 2). A difference greater than 15% is failure (unless the absolute difference between the value and the average of the two is < 5 ug N/L), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

Sample Replicate Data

Run ID	SampleID	NO3+NO2	Avg Conc ug N/L	Abs. Dif. ug N/L	RPD %
071206 NO3 and NO2 01.xls	44949	169	172	3	1.7%
071206 NO3 and NO2 01.xls	44949_Dup	175			
071206 NO3 and NO2 01.xls	73695	19	18	1	4.8%
071206 NO3 and NO2 01.xls	73695_Dup	17			
071206 NO3 and NO2 01.xls	73704	13	13	0	0.3%
071206 NO3 and NO2 01.xls	73704_Dup	13			
071206 NO3 and NO2 01.xls	73713	5	3	2	47.1%
071206 NO3 and NO2 01.xls	73713_Dup	2			
071206 NO3 and NO2 01.xls	73722	5	3	2	52.2%
071206 NO3 and NO2 01.xls	73722_Dup	2			

Table 2. Quality Control Samples (QCS).   QCS (from Ultra Scientific) are analyzed periodically (approximately every 10 samples) in each sample analysis batch to assure accuracy. A difference greater than 15% is failure (unless the absolute difference between the values is < 5 ug N/L, or the value is less than 5x the MDL) and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

QCS Data

Run ID	SampleID	NO3+NO2 Calc Conc ug N/L	Cert. Conc ug N/L	%Accuracy
071206 NO3 and NO2 01.xls	QC	21	21	100.7%
071206 NO3 and NO2 01.xls	QC	21	21	104.3%
071206 NO3 and NO2 01.xls	QC	21	21	104.8%
071206 NO3 and NO2 01.xls	QC	22	21	107.6%
071206 NO3 and NO2 01.xls	QC	22	21	105.6%
071206 NO3 and NO2 01.xls	QC	18	21	87.3%
071206 NO3 and NO2 01.xls	QC	20	21	99.1%
071206 NO3 and NO2 01.xls	QC	20	21	99.5%

Table 3. Standards run as Unknowns. Standards run as unknowns are analyzed periodically (approximately every 10 samples) in each sample analysis batch to assure precision. A difference greater than 15% is failure (unless the absolute difference between the values is < 5 ug N/L or the value is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

Standards as Unknowns

Run ID	Sample	Calc Conc ug N/L	Prep Conc ug N/L	Abs Diff ug N/L	%difference
071206 NO3 and NO2 01.xls	std1	5	6	1	13.3%
071206 NO3 and NO2 01.xls	std1	7	6	1	22.5%
071206 NO3 and NO2 01.xls	std2	10	10	0	0.7%
071206 NO3 and NO2 01.xls	std2	11	10	1	5.6%
071206 NO3 and NO2 01.xls	std2	11	10	1	6.9%
071206 NO3 and NO2 01.xls	std2	10	10	0	2.9%
071206 NO3 and NO2 01.xls	std3	19	20	0	2.4%
071206 NO3 and NO2 01.xls	std3	16	20	4	18.8%
071206 NO3 and NO2 01.xls	std4	50	50	0	0.9%
071206 NO3 and NO2 01.xls	std4	51	50	1	1.9%
071206 NO3 and NO2 01.xls	std4	52	50	2	3.7%
071206 NO3 and NO2 01.xls	std5	103	102	1	1.1%
071206 NO3 and NO2 01.xls	std5	108	102	6	6.2%
071206 NO3 and NO2 01.xls	std6	209	203	6	2.9%
071206 NO3 and NO2 01.xls	std6	202	203	2	0.8%
071206 NO3 and NO2 01.xls	std6	204	203	1	0.6%
071206 NO3 and NO2 01.xls	std6	207	203	4	1.8%

NH$_4$ Analyzed by discrete colorimetric analysis using a SmartChem discrete analyzer, based on USEPA 350.1. Samples were analyzed in 2 batches. Method Detection Limit (MDL) was calculated to be 5 ug N/L. Spikes were performed every 10 to 12 samples.

Table 1. Replicate and Spike data. Samples replicated every 10-12 samples. Replicates must fall within 15% relative percent difference (RPD = abs(dup1-dup2)/average of dup1 and dup 2). A difference greater than 15% is failure (unless the absolute difference between the value and the average of the two is < 5 ug N/L or the average of the values is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Spikes must show 85% to 115% recovery. A recovery <85% or >115% over the entire batch is generally considered failure (unless the sample is less than 10X the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Some of our NH$_4$ spikes were out of tolerance, despite tight precision of the replicates and accurate measurement of the Quality Control Samples. Because nothing else looked bad on these runs, the data were used. I suspect our instrument performed spikes are not as precise as we hoped they are. Further explanations when necessary are provided.

Sample Replicate Data

Replicate

Run ID	Sample	Calc Conc ug N/L	ug N/L		Abs. Dif. ug N/L	RPD %	re o
071114 NH4 03.xls	73697	5	6	Average	0	1.6%	1
071114 NH4 03.xls	73697_Dup	6	71	Amount added			
071114 NH4 03.xls	73697_Spike	88	77	What spike should be			
071114 NH4 03.xls	73707	16	16	Average	0	2.2%	1
071114 NH4 03.xls	73707_Dup	15	71	Amount added			
071114 NH4 03.xls	73707_Spike	95	87	What spike should be			
071114 NH4 03.xls	73803	48	48	Average	0	0.9%	9
071114 NH4 03.xls	73803_Dup	49	71	Amount added			
071114 NH4 03.xls	73803_Spike	120	120	What spike should be			
071114 NH4 04.xls	std2	9	10	Average	1	6.1%	1
071114 NH4 04.xls	std2_Dup	8	71	Amount added			
071114 NH4 04.xls	std2_Spike	88	75	What spike should be			

Table 2. Quality Control Samples (QCS). QCS (from Ultra Scientific) are analyzed periodically (approximately every 10samples) in each sample analysis batch to assure accuracy. A difference greater than 15% is failure (unless the absolute difference between the values is < 5 ug N/L or the value is less than 5x the MDL) and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

QCS Data

NH4

Run ID	Sample	Calc Conc ug N/L	Cert. Conc ug N/L	%Accuracy
071114 NH4 03.xls	QC	53	61	86.5%
071114 NH4 03.xls	QC	56	61	91.8%
071114 NH4 03.xls	QC	56	61	92.2%
071114 NH4 03.xls	QC	56	61	91.4%
071114 NH4 04.xls	QC	55	61	90.2%
071114 NH4 04.xls	QC	55	61	89.8%
071114 NH4 04.xls	QC	59	61	96.1%

Table 3. Standards run as Unknowns. Standards run as unknowns are analyzed periodically (approximately every 10 samples) in each sample analysis batch to assure precision. A difference greater than 15% is considered failure (unless the absolute difference between the values is < 5 ug N/L or the value is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

Stds as Unknowns

Run ID	Sample	Prep Conc	Calc Conc	Abs Diff	%difference
071114 NH4 03.xls	std1	4	6	1	24.1%
071114 NH4 03.xls	std1	7	6	1	25.8%
071114 NH4 03.xls	std2	12	10	2	24.5%
071114 NH4 03.xls	std2	11	10	1	9.6%
071114 NH4 03.xls	std3	15	19	4	22.0%
071114 NH4 03.xls	std4	51	49	2	3.2%
071114 NH4 03.xls	std4	51	49	2	3.9%
071114 NH4 03.xls	std5	103	99	3	3.4%
071114 NH4 03.xls	std6	202	198	5	2.3%
071114 NH4 03.xls	std6	201	198	3	1.7%
071114 NH4 03.xls	std6	199	198	1	0.7%
071114 NH4 04.xls	std1	6	6	0	1.5%
071114 NH4 04.xls	std2	9	10	1	6.1%
071114 NH4 04.xls	std2	8	10	1	15.1%
071114 NH4 04.xls	std3	17	19	2	9.6%
071114 NH4 04.xls	std4	50	49	1	1.5%
071114 NH4 04.xls	std5	104	99	5	5.3%
071114 NH4 04.xls	std6	208	198	10	5.1%
071114 NH4 04.xls	std6	210	198	13	6.4%

TDN. Analyzed by High Temperature Catalytic Oxidation with chemiluminescent detection using a Shimadzu Carbon analyzer and N detector. Method based on Merriam, J.L, W.H. McDowell, W.S. Currie, 1996. A high-temperature catalytic oxidation technique for determining total dissolved nitrogen. *Soil Science Society of America Journal*, 60(4) 1050-1055. Samples were analyzed in 2 batches. Method Detection Limit (MDL) was calculated to be 0.07 mg N/L.

Table 1. Replicate and Spike data. Samples were replicated every 10-12 samples. Replicates must fall within 15% relative percent difference (RPD = abs(dup1-dup2)/average of dup1 and dup 2). A difference greater than 15% is failure (unless the absolute difference between the value and the average of the two is < 0.07 mg N/L or the average of the values is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Spikes must show 85% to 115% recovery. A recovery <85% or >115% over the entire batch is generally considered failure (unless the sample is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Further explanations when necessary are provided.

Sample Replicate Data

Run ID	Sample	TDN mg N/L	Avg TDN mg N/L	Replicate Abs. Dif. mg N/L	RPD %
NPOC and TDN 071204 TOCVb.xls	73690	2.43	2.40	0.03	1.30%
NPOC and TDN 071204 TOCVb.xls	73690r	2.37			
NPOC and TDN 071204 TOCVb.xls	73695	1.75	1.80	0.04	2.40%
NPOC and TDN 071204 TOCVb.xls	73695r	1.84			
NPOC and TDN 071204 TOCVb.xls	73703	1.49	1.72	0.24	13.66%
NPOC and TDN 071204 TOCVb.xls	73703r	1.96			
NPOC and TDN 071204 TOCVb.xls	73806	5.88	5.81	0.07	1.24%
NPOC and TDN 071204 TOCVb.xls	73806r	5.73			
NPOC and TDN 071204 TOCVb.xls	Lamprey River	0.24	0.25	0.01	4.18%
NPOC and TDN 071204 TOCVb.xls	Lamprey River	0.26			
NPOC and TDN 071206pm TOCVb.xls	73717	0.21	0.21	0.00	1.75%
NPOC and TDN 071206pm TOCVb.xls	73717r	0.21			
NPOC and TDN 071206pm TOCVb.xls	73744	0.49	0.50	0.01	2.24%
NPOC and TDN 071206pm TOCVb.xls	73744r	0.51			
NPOC and TDN 071206pm TOCVb.xls	73758	0.26	0.25	0.01	2.11%
NPOC and TDN 071206pm TOCVb.xls	73758r	0.25			
NPOC and TDN 071206pm TOCVb.xls	Lamprey River	0.24	0.26	0.02	5.94%
NPOC and TDN 071206pm TOCVb.xls	Lamprey River	0.27			

Table 2. Quality Control Samples (QCS).   QCS (from Ultra Scientific) are analyzed periodically (approximately every 20 samples) in each sample analysis batch to assure accuracy.   A difference greater than 15% is failure (unless the absolute difference

between the values is < 0.07 mg N/L or the value is less than 5x the MDL) and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. The QCS we used for most of the runs was old and showed generally lower than expected values. This was corrected as soon as possible. Explanations when necessary are provided.

QCS Data

Run ID	Sample	Calc Conc mg N/L	Cert. Conc mg N/L	%Accuracy
NPOC and TDN 071204 TOCVb.xls	QC N	2.07	2.33	89.0%
NPOC and TDN 071204 TOCVb.xls	QC N	2.26	2.33	97.1%
NPOC and TDN 071206pm TOCVb.xls	QC N	2.13	2.33	91.4%
NPOC and TDN 071206pm TOCVb.xls	QC N	2.27	2.33	97.5%

Table 3. Standards run as Unknowns. Standards run as unknowns are analyzed periodically (approximately every 10 samples) in each sample analysis batch to assure precision. A difference greater than 15% is considered failure (unless the absolute difference between the values is < 0.07 mg N/L or the value is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

Stds as Unknowns

Run ID	Sample	Calc Conc mg N/L	Prep Conc mg N/L	Abs Diff	%difference
NPOC and TDN 071204 TOCVb.xls	std1	0.41	0.40	0.01	3.4%
NPOC and TDN 071204 TOCVb.xls	std1	0.40	0.40	0.00	0.5%
NPOC and TDN 071204 TOCVb.xls	std2	1.14	1.17	0.03	2.4%
NPOC and TDN 071204 TOCVb.xls	std2	1.10	1.17	0.07	6.4%
NPOC and TDN 071204 TOCVb.xls	std2	1.15	1.17	0.02	1.8%
NPOC and TDN 071204 TOCVb.xls	std3	1.95	1.96	0.01	0.3%
NPOC and TDN 071204 TOCVb.xls	std3	1.82	1.96	0.14	7.2%
NPOC and TDN 071204 TOCVb.xls	std3	1.94	1.96	0.02	1.0%
NPOC and TDN 071204 TOCVb.xls	std4	3.97	3.96	0.01	0.2%
NPOC and TDN 071204 TOCVb.xls	std4	3.81	3.96	0.15	3.8%
NPOC and TDN 071204 TOCVb.xls	std4	4.04	3.96	0.08	1.9%
NPOC and TDN 071206pm TOCVb.xls	std1	0.12	0.10	0.02	21.8%
NPOC and TDN 071206pm TOCVb.xls	std1	0.14	0.10	0.04	45.5%
NPOC and TDN 071206pm TOCVb.xls	std2	0.21	0.20	0.01	7.3%
NPOC and TDN 071206pm TOCVb.xls	std2	0.22	0.20	0.02	9.4%
NPOC and TDN 071206pm TOCVb.xls	std2	0.21	0.20	0.01	7.1%
NPOC and TDN 071206pm TOCVb.xls	std2	0.25	0.20	0.05	25.4%
NPOC and TDN 071206pm TOCVb.xls	std3	0.56	0.55	0.01	2.3%
NPOC and TDN 071206pm TOCVb.xls	std3	0.54	0.55	0.01	1.1%
NPOC and TDN 071206pm TOCVb.xls	std3	0.56	0.55	0.01	2.0%
NPOC and TDN 071206pm TOCVb.xls	std4	1.00	1.05	0.05	4.3%
NPOC and TDN 071206pm TOCVb.xls	std4	1.02	1.05	0.03	2.5%
NPOC and TDN 071206pm TOCVb.xls	std4	1.05	1.05	0.00	0.2%
NPOC and TDN 071206pm TOCVb.xls	std5	1.98	2.04	0.06	3.1%

NPOC and TDN 071206pm TOCVb.xls	std5	1.99	2.04	0.05	2.2%
NPOC and TDN 071206pm TOCVb.xls	std5	1.98	2.04	0.06	3.0%
NPOC and TDN 071206pm TOCVb.xls	std5	2.06	2.04	0.02	1.0%
NPOC and TDN 071206pm TOCVb.xls	std6	4.96	4.93	0.03	0.6%
NPOC and TDN 071206pm TOCVb.xls	std6	4.81	4.93	0.12	2.4%

PO$_4$. Analyzed by discrete colorimetric analysis using a SmartChem discrete analyzer, based on USEPA 365.2. Samples were analyzed in 1 batch. Method Detection Limit (MDL) was calculated to be 5 ug P/L. Spikes were performed every 10 to 12 samples.

Table 1. Replicate and Spike data. Samples were replicated every 10-12 samples. Replicates must fall within 15% relative percent difference (RPD = abs(dup1-dup2)/average of dup1 and dup 2). A difference greater than 15% is failure (unless the absolute difference between the value and the average of the two is < 5 ug P/L or the average of the replicates is less than 10x MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Spikes must show 85% to 115% recovery. A recovery <85% or >115% over the entire batch is generally considered failure (unless the sample is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Further explanations when necessary are provided.

Sample Replicate Data

| | | Calc Conc | Replicate | | Abs. Dif. | RPD | % recovery | |
Run ID	Sample	ug P/L	ug P/L		ug P/L	%	of spike	
071207 PO4 01.xls	73693	22	21	Average	0	1.4%	96.1%	
071207 PO4 01.xls	73693_Dup	21	26	Amount Added				
071207 PO4 01.xls	73693_Spike	46	48	What spike should be				
071207 PO4 01.xls	73703	12	18	Average	6	34.8%	110.5%	
071207 PO4 01.xls	73703_Dup	24	26	Amount added				
071207 PO4 01.xls	73703_Spike	49	44	What spike should be				
071207 PO4 01.xls	73713	27	28	Average	1	3.5%	97.1%	
071207 PO4 01.xls	73713_Dup	29	26	Amount added				
071207 PO4 01.xls	73713_Spike	53	54	What spike should be				
071207 PO4 01.xls	73723	28	25	Average	3	12.3%	96.7%	
071207 PO4 01.xls	73723_Dup	22	26	Amount added				
071207 PO4 01.xls	73723_Spike	50	51	What spike should be				
071207 PO4 01.xls	73733	3	4	Average	0	8.1%	87.8%	
071207 PO4 01.xls	73733_Dup	4	26	Amount added				
071207 PO4 01.xls	73733_Spike	26	30	What spike should be				
071207 PO4 01.xls	73743	20	19	Average	1	4.1%	81.4%	< than 10x
071207 PO4 01.xls	73743_Dup	19	26	Amount added				
071207 PO4 01.xls	73743_Spike	37	46	What spike should be				
071207 PO4 01.xls	73755	2	1	Average	1	84.3%	98.6%	
071207 PO4 01.xls	73755_Dup	0	26	Amount added				
071207 PO4 01.xls	73755_Spike	27	27	What spike should be				
071207 PO4 01.xls	74087	1	1	Average	0	25.5%	102.2%	
071207 PO4 01.xls	74087_Dup	1	26	Amount added				
071207 PO4 01.xls	74087_Spike	28	27	What spike should be				

Table 2. Quality Control Samples (QCS). QCS (from Ultra Scientific) are analyzed periodically (approximately every 20 samples) in each sample analysis batch to assure

accuracy. A difference greater than 15% is failure (unless the absolute difference between the values is < 5 ug P/L or the value is less than 5x the MDL) and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

QCS Data

Run ID	Sample	PO4 Calc Conc ug P/L	Cert. Conc ug P/L	%Accuracy
071207 PO4 01.xls	QC	62	61	102.7%
071207 PO4 01.xls	QC	63	61	104.0%
071207 PO4 01.xls	QC	63	61	104.0%
071207 PO4 01.xls	QC	65	61	107.0%
071207 PO4 01.xls	QC	62	61	102.1%
071207 PO4 01.xls	QC	62	61	101.7%
071207 PO4 01.xls	QC	65	61	106.6%
071207 PO4 01.xls	QC	64	61	105.0%

Table 3. Standards run as Unknowns. Standards run as unknowns are analyzed periodically (approximately every 10 samples) in each sample analysis batch to assure precision. A difference greater than 15% is considered failure (unless the absolute difference between the values is < 5 ug P/L or the average of the two values is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

Standards as Unknowns

Run ID	Sample	Prep Conc	Calc Conc	Abs Diff	%difference
071207 PO4 01.xls	std1	6	6	0	4.7%
071207 PO4 01.xls	std1	6	4	2	28.6%
071207 PO4 01.xls	std1	6	4	1	25.2%
071207 PO4 01.xls	std2	10	9	0	2.2%
071207 PO4 01.xls	std2	10	8	1	12.6%
071207 PO4 01.xls	std2	10	10	1	10.3%
071207 PO4 01.xls	std3	20	18	1	7.1%
071207 PO4 01.xls	std3	20	19	1	4.1%
071207 PO4 01.xls	std4	49	46	3	5.3%
071207 PO4 01.xls	std4	49	48	1	2.1%
071207 PO4 01.xls	std4	49	50	1	1.2%
071207 PO4 01.xls	std5	99	99	0	0.1%
071207 PO4 01.xls	std5	99	100	1	1.2%
071207 PO4 01.xls	std5	99	103	4	3.6%
071207 PO4 01.xls	std6	201	200	1	0.4%
071207 PO4 01.xls	std6	201	204	3	1.5%
071207 PO4 01.xls	std6	201	206	5	2.3%

071207 PO4 01.xls	std6	201	204	3	1.6%

TDP. A filtered sample is digested using persulfate oxidation. The digest is analyzed by discrete colorimetric analysis using a SmartChem discrete analyzer, based on USEPA 365.2. Samples were analyzed in 1 batch. Method Detection Limit (MDL) was calculated to be 10 ug P/L. Spikes were performed every 10 to 12 samples.

Table 1. Replicate and Spike data. Samples were replicated every 10-12 samples. Replicates must fall within 15% relative percent difference (RPD = abs(dup1-dup2)/average of dup1 and dup 2). A difference greater than 15% is failure (unless the absolute difference between the value and the average of the two is < 10 ug P/L or the average of the values is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Spikes must show 85% to 115% recovery. A recovery <85% or >115% over the entire batch is generally considered failure (unless the sample is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Further explanations when necessary are provided.

Sample Replicate Data

Run ID	Sample	Calc Conc ug P/L	ug P/L		Replicate Abs. Dif. ug P/L	RPD %
071203 TDP 01.xls	72841	21	22	Average	0	0.7%
071203 TDP 01.xls	72841_Dup	22	39	Amount Added		
071203 TDP 01.xls	72841_Spike	55	61	What Spike Should be		
071203 TDP 01.xls	72851	23	22	Average	1	4.9%
071203 TDP 01.xls	72851_Dup	20	39	Amount Added		
071203 TDP 01.xls	72851_Spike	61	61	What Spike Should be		
071203 TDP 01.xls	73689	39	38	Average	1	2.4%
071203 TDP 01.xls	73689_Dup	37	39	Amount Added		
071203 TDP 01.xls	73689_Spike	67	77	What Spike Should be		
071203 TDP 01.xls	73697	30	28	Average	1	4.6%
071203 TDP 01.xls	73697r	30	28	Average	2	8.2%
071203 TDP 01.xls	73697r_Dup	25	28	Amount Added		
071203 TDP 01.xls	73697r_Spike	56	39	What Spike Should be		
071203 TDP 01.xls	73707	32	33	Average	1	3.6%
071203 TDP 01.xls	73707_Dup	34	39	Amount Added		
071203 TDP 01.xls	73707_Spike	69	73	What Spike Should be		
071203 TDP 01.xls	73712	70	64	Average	6	8.7%
071203 TDP 01.xls	73712r	58				
071203 TDP 01.xls	73716	20	22	Average	1	6.3%
071203 TDP 01.xls	73716_Dup	23	39	Amount Added		
071203 TDP 01.xls	73716_Spike	61	61	What Spike Should be		
071203 TDP 01.xls	73978	16	17	Average	1	4.5%
071203 TDP 01.xls	73978_Dup	17	39	Amount Added		

071203 TDP 01.xls	73978_Spike	59	56	What Spike Should be		
071203 TDP 01.xls	73978r	25	19	Average	6	28.3%
071203 TDP 01.xls	73993	18	19	Average	1	4.8%
071203 TDP 01.xls	73993r	20				

Table 2. Quality Control Samples (QCS). QCS (from Ultra Scientific) are analyzed periodically (approximately every 10 samples) in each sample analysis batch to assure accuracy. NP Check 500 is a solution made at the WQAL of EDTA and Sodium Pyrophospate to check the digestion efficiency of the analysis. A difference greater than 15% from the certified or prepared value is failure (unless the absolute difference between the values is < 10 ug P/L or the value is less than 5x the MDL) and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

QCS Data

Run ID	Sample	Calc Conc ug P/L	Cert. Conc/Prep Conc ug P/L	%Accuracy
071203 TDP 01.xls	QC	3299	3380	97.6%
071203 TDP 01.xls	QC	3280	3380	97.0%
071203 TDP 01.xls	QC	3306	3380	97.8%
071203 TDP 01.xls	QC	3347	3380	99.0%
071203 TDP 01.xls	QC	3335	3380	98.7%
071203 TDP 01.xls	QC	3274	3380	96.9%
071203 TDP 01.xls	NP check 500	551	544	101.2%
071203 TDP 01.xls	NP check 500	551	551	99.9%

Table 3. Standards run as Unknowns. Standards run as unknowns are analyzed periodically (approximately every 10 samples) in each sample analysis batch to assure precision. A difference from the prepared concentration of more than 10% requires further investigation of that run. A difference greater than 15% is considered failure (unless the absolute difference between the values is < 10 ug P/L), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

Standards as Unknowns

Run ID	Sample	Prep Conc	Calc Conc	Abs Diff	%difference	Expl
071203 TDP 01.xls	std1	10	14	3	31.8%	
071203 TDP 01.xls	std1	10	14	4	37.6%	
071203 TDP 01.xls	std1	10	3	8	73.4%	
071203 TDP 01.xls	std2	30	76	46	154.0%	Was
071203 TDP 01.xls	std2	30	75	45	150.9%	Was
071203 TDP 01.xls	std2	30	80	50	166.0%	Was
071203 TDP 01.xls	std3	50	50	0	0.0%	
071203 TDP 01.xls	std3	50	53	3	6.0%	
071203 TDP 01.xls	std3	50	51	1	2.4%	
071203 TDP 01.xls	std4	100	98	2	2.4%	
071203 TDP 01.xls	std4	100	97	3	3.0%	

071203 TDP 01.xls	std4	100	102	1	1.5%
071203 TDP 01.xls	std5	216	226	10	4.8%
071203 TDP 01.xls	std5	216	227	11	5.0%
071203 TDP 01.xls	std5	216	229	13	6.2%
071203 TDP 01.xls	std6	514	519	5	1.1%
071203 TDP 01.xls	std6	514	523	9	1.8%
071203 TDP 01.xls	std6	514	535	21	4.1%
071203 TDP 01.xls	std6	514	533	19	3.7%

PP. Particulate P was measured based on Aspila, I., H. Agemian and A.S.Y. Chau. 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst, 101:187-197. Briefly, a known volume of sample is filtered through a glass fiber filter. The filter is then dried, and combusted at 550 C for 1.5 hours. Phosphorous is extracted from the filter using 1N HCl. The extract is analyzed by discrete colorimetric analysis using a SmartChem discrete analyzer, based on USEPA 365.2. Samples were analyzed in 1 batch. Method Detection Limit (MDL) was estimated to be to be 20 ug P/L (5 times the PO_4 MDL) in the extract.

Table 1. Replicate data. Extracts were replicated every 10-12 samples. Replicates must fall within 15% relative percent difference (RPD = abs(dup1-dup2)/average of dup1 and dup 2). A difference greater than 15% is failure (unless the absolute difference between the value and the average of the two is < 20 ug P/L, or the average of the value is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Further explanations when necessary are provided.

Sample Replicate Data

Run ID	Sample	Calc Conc ug P/L	Average ug P/L	Replicate Abs. Dif. ug P/L	RPD %
080221 TPP 04.xlsx	73699	86	85	1.008963	1.18%
080221 TPP 04.xlsx	73699_Dup	84			
080221 TPP 04.xlsx	73709	51	52	1.36507	2.60%
080221 TPP 04.xlsx	73709_Dup	54			
080221 TPP 04.xlsx	73719	54	56	1.36507	2.45%
080221 TPP 04.xlsx	73719_Dup	57			

Table 2. Quality Control Samples (QCS).   QCS (from Ultra Scientific) are analyzed periodically (approximately every 10 samples) in each sample analysis batch to assure accuracy. A difference greater than 15% from the certified or prepared value is failure (unless the absolute difference between the values is < 20 ug P/L or the value is less than 5x the MDL) and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

QCS Data

Run ID	Sample	PO4 Calc Conc ug P/L	Cert. Conc ug P/L	%Accuracy
080221 TPP 04.xlsx	QCP	34	29	114.18%
080221 TPP 04.xlsx	QCP	33	29	110.96%
080221 TPP 04.xlsx	QCP	33	29	112.17%
080221 TPP 04.xlsx	QCP	33	29	111.76%

Table 3. Standards run as Unknowns. Standards run as unknowns are analyzed periodically (approximately every 10 samples) in each sample analysis batch to assure precision. A difference from the prepared concentration of more than 10% requires further investigation of that run. A difference greater than 15% is considered failure (unless the sample is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

Standards as Unknowns

Run ID	Sample	Prep Conc	Calc Conc	Abs Diff	%difference
080221 TPP 04.xlsx	std 1	10	8	2	16.6%
080221 TPP 04.xlsx	std 2	30	31	1	4.8%
080221 TPP 04.xlsx	std 2	30	31	1	3.2%
080221 TPP 04.xlsx	std 3	50	48	1	2.3%
080221 TPP 04.xlsx	std 4	100	97	3	2.9%
080221 TPP 04.xlsx	std 4	100	97	2	2.1%
080221 TPP 04.xlsx	std 5	199	200	0	0.2%
080221 TPP 04.xlsx	std 5	199	201	2	1.1%
080221 TPP 04.xlsx	std 5	199	199	0	0.2%

PC and PN A known volume of sample is filtered through a glass fiber filter. The filter is then dried. Particulate C and N was measured on a Perkin Elmer 2400 using thermal conductivity. Samples were analyzed in 1 batch. A blank and standard were analyzed approximately every 12 samples and were used to modify the calibration if necessary. Replicates of filters were impossible, as there was only one filter. However, Quality Control Samples were run approximately every 12 samples, and used to assess precision and accuracy. The manufacturer claims an accuracy of 0.4% and precision of 0.3%.

Table 1. Replicate and Quality Control data. Quality Control Samples were analyzed every 12 samples (approximately) to assure accuracy and precision.

Run ID	Sample	Measured %C	Measured %N	Avg Meas %C	Avg Meas. %N	Precision C %CV	Precision N %CV	UNH Historic %C
1/22/2008	NIST 1575	49.45%	1.25%	49.43%	1.08%	0.05%	22.66%	49.40%
1/22/2008	NIST 1575	49.41%	0.91%					
1/22/2008	NIST 2709	1.25%	0.24%	1.20%	0.16%	6.20%	70.89%	1.07%
1/22/2008	NIST 2709	1.14%	0.08%					

SiO$_2$ Analyzed by discrete colorimetric analysis using a SmartChem discrete analyzer, based on USEPA 370.1. Samples were analyzed in 1 batch. Method Detection Limit (MDL) was calculated to be 0.04 mg SiO$_2$/L. Spikes were performed every 10 to 12 samples.

Table 1. Replicate and Spike data. Samples replicated every 10-12 samples. Replicates must fall within 15% relative percent difference (RPD = abs(dup1-dup2)/average of dup1 and dup 2). A difference greater than 15% is failure (unless the absolute difference between the value and the average of the two is < 0.04 mg SiO$_2$/L or the average of the values is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Spikes must show 80% to 120% recovery. A recovery <80% or >120% over the entire batch is generally considered failure (unless the sample is less than 10X the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Further explanations when necessary are provided. Further explanations when necessary are provided.

	SampleID	SIO2 Calc Conc mg SiO2/L	mg SiO2/L		+ / - Abs. Diff.	+ / - %diff.	%rec of s
071219 SiO2 01.xls	72919	1.15	1.16	Average	0.01	0.90%	110
071219 SiO2 01.xls	72919_Dup	1.17	5.73	Amount Added			
071219 SiO2 01.xls	72919_Spike	7.63	6.89	What Spike Should Be			
071219 SiO2 01.xls	72933	0.42	0.42	Average	0.00	0.05%	110
071219 SiO2 01.xls	72933_Dup	0.42	5.73	Amount Added			
071219 SiO2 01.xls	72933_Spike	6.77	6.15	What Spike Should Be			
071219 SiO2 01.xls	73527	0.60	0.61	Average	0.00	0.56%	107
071219 SiO2 01.xls	73527_Dup	0.61	5.73	Amount Added			
071219 SiO2 01.xls	73527_Spike	6.83	6.34	What Spike Should Be			
071219 SiO2 01.xls	73699	0.76	0.76	Average	0.00	0.34%	105
071219 SiO2 01.xls	73699_Dup	0.76	5.73	Amount Added			
071219 SiO2 01.xls	73699_Spike	6.83	6.49	What Spike Should Be			

071219 SiO2 01.xls	73709	0.35	0.36	Average	0.01	3.63%	102
071219 SiO2 01.xls	73709_Dup	0.37	5.73	Amount Added			
071219 SiO2 01.xls	73709_Spike	6.23	6.09	What Spike Should Be			
071219 SiO2 01.xls	73722	0.47	0.48	Average	0.01	2.86%	102
071219 SiO2 01.xls	73722_Dup	0.49	5.73	Amount Added			
071219 SiO2 01.xls	73722_Spike	6.39	6.21	What Spike Should Be			
071219 SiO2 01.xls	74182	2.09	2.10	Average	0.01	0.64%	104
071219 SiO2 01.xls	74182_Dup	2.11	5.73	Amount Added			
071219 SiO2 01.xls	74182_Spike	8.17	7.83	What Spike Should Be			
071219 SiO2 01.xls	74199	2.53	2.50	Average	0.02	0.98%	101
071219 SiO2 01.xls	74199_Dup	2.48	5.73	Amount Added			
071219 SiO2 01.xls	74199_Spike	8.33	8.23	What Spike Should Be			

Table 2. Quality Control Samples (QCS).   QCS (from Ultra Scientific) are analyzed periodically (approximately every 10samples) in each sample analysis batch to assure accuracy.   A difference greater than 15% is failure (unless the absolute difference between the values is < 0.04 mg SiO_2/L or the value is less than 5x the MDL) and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

QCS Data

		Calc Conc mg SiO2/L	Cert. Conc mg SiO2/L	%Accuracy
071219 SiO2 01.xls	SIQC	1.88	1.68	111.73%
071219 SiO2 01.xls	SIQC	1.86	1.68	110.92%
071219 SiO2 01.xls	SIQC	1.86	1.68	110.87%
071219 SiO2 01.xls	SIQC	1.87	1.68	111.06%
071219 SiO2 01.xls	SIQC	1.82	1.68	108.63%
071219 SiO2 01.xls	SIQC	1.90	1.68	113.33%
071219 SiO2 01.xls	SIQC	1.87	1.68	111.31%
071219 SiO2 01.xls	SIQC	1.88	1.68	111.64%
071219 SiO2 01.xls	SIQC	1.88	1.68	111.90%
071219 SiO2 01.xls	SIQC	1.83	1.68	108.63%
071219 SiO2 01.xls	SIQC	1.82	1.68	108.34%

Table 3. Standards run as Unknowns. Standards run as unknowns are analyzed periodically (approximately every 10 samples) in each sample analysis batch to assure precision. A difference greater than 15% is considered failure (unless the absolute difference between the values is < 0.04 mg SiO_2/L or the value is less than 10x the MDL), and results in re-analysis of the entire sample queue, unless there is a very reasonable and supported explanation for the inconsistency. Explanations when necessary are provided.

Standards as Unknowns

Run ID	Sample	Prep Conc	Calc Conc	Abs Diff	%difference
071219 SiO2 01.xls	std 1	0.02	0.02	0.01	23.97%
071219 SiO2 01.xls	std 1	0.02	0.01	0.01	64.40%
071219 SiO2 01.xls	std 1	0.02	0.02	0.01	23.11%
071219 SiO2 01.xls	std 2	0.05	0.03	0.01	29.07%
071219 SiO2 01.xls	std 2	0.05	0.03	0.01	27.78%
071219 SiO2 01.xls	std 2	0.05	0.04	0.01	17.30%
071219 SiO2 01.xls	std 3	0.10	0.08	0.02	17.14%
071219 SiO2 01.xls	std 3	0.10	0.09	0.01	8.81%
071219 SiO2 01.xls	std 3	0.10	0.09	0.01	9.71%
071219 SiO2 01.xls	std 4	0.54	0.55	0.00	0.72%
071219 SiO2 01.xls	std 4	0.54	0.55	0.00	0.69%
071219 SiO2 01.xls	std 4	0.54	0.56	0.02	2.98%
071219 SiO2 01.xls	std 5	1.03	1.03	0.00	0.17%
071219 SiO2 01.xls	std 5	1.03	1.04	0.02	1.65%
071219 SiO2 01.xls	std 5	1.03	1.05	0.03	2.53%
071219 SiO2 01.xls	std 6	1.97	1.94	0.03	1.54%
071219 SiO2 01.xls	std 6	1.97	1.98	0.01	0.28%
071219 SiO2 01.xls	std 6	1.97	1.96	0.02	0.83%
071219 SiO2 01.xls	std 6	1.97	1.93	0.05	2.40%

Appendix C

MEMORANDUM

To: Jennifer Hunter, NHEP Director

From: Phil Trowbridge, NHEP/NHDES Coastal Scientist

Date: May 19, 2008

Re: Quality Assurance Memo, NCA 2007 New Hampshire field and laboratory data

The New Hampshire Department of Environmental Services (NHDES), the U.S. Environmental Protection Agency (EPA) and the University of New Hampshire (UNH) partnered in 2007 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 New Hampshire Estuaries Project, 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 2007 are listed in the following table by media. The actual station visits are compared to the expected visits from the 2007 workplan. There are no major data gaps for the NCA design stations.

<div align="center">Station Visits For 2007 Sampling Season</div>

Medium	Date Range	Planned	Actual	Comments
Sediment	NA	0	0	No sediment samples collected in 2007
Water	8/7/07- 9/11/07	25	25	38 water samples collected including depth duplicates and QC samples
Fish Trawls	NA	0	0	No fish trawls in 2007
Fish Tissue	NA	0	0	No fish samples collected in 2007
Monthly Water	NA	0	0	Monthly trend sample were collected by the GBNERR/UNH Program
Summer bacteria	7/3/07- 8/21/07	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.
Check station locations from field sheets for consistency with study design
- Station visits were within 0.13 minutes of design sites, 0.05 minutes on average, which is acceptable (<0.5 minutes is acceptable).
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

- The following table shows the results from YSI6600 sonde (surface and bottom combined). The values are within the expected range for each parameter. The values from 2007 are similar to the values from 2006.

Parameter	Units	2006			2007		
		N	Ave	Max	N	Ave	Max
DISSOLVED OXYEN	MG/L	117	8.7	14.6	49	8.2	9.8
PH	---	115	7.8	8.2	49	7.9	8.1
SALINITY	PPT	117	20.3	31.9	49	29.6	33.5
TEMPERATURE WATER	DEG C	117	18.5	26.7	49	19.4	25.1

The difference between readings from the YSI6600 datasonde and an independently calibrated YSI-85 meter were mostly within data quality objectives (<1 deg C, <1 ppt, <0.5 mg/L DO). For the paired measurements, only 1 of 40 and 7 of 40 pairs for temperature and salinity, respectively, failed the criteria. The maximum difference between the two meters for temperature was 1.4 deg C. The maximum difference between the two meters for salinity was 1.8 ppt. Differences of this magnitude are unlikely to be important for the purposes of classifying the salinity regime of the estuary for the station visit.

C. CTD File Check

Check that file names for CTD casts match station IDs

- Ecowatch files are available for 40 of the 40 water station visits. The Ecowatch file names were edited to match station names.

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 7 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 -0.28 to -0.95 m^{-1}, which is within the expected range for NH's estuaries. The r-squared for the regressions was between 0.949-0.999.

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 coastl07.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 orthophosphate. Six of 25 samples for silica were missing. 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 52 replicates, 27 of 27 spikes, 54 of 54 QC samples, and 127 of 127 standards run as unknowns.
- For chlorophyll-a samples, lab duplicate samples were all within acceptable limits. One of the three field replicate QC samples for TSS was above the acceptable limits. For this sample (NH07-0024A), one result was 15 and the other was 27.5 mg/L (RPD=59%). However, the two other replicate QC samples were within acceptable limits. No quality control tests with standard reference materials were performed for these parameters.
- 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 2007 water chemistry data and compared to statistics for the 2006 dataset. The analysis identified one anomaly. The maximum value for chlorophyll-a in 2007 (60.9 ug/L) was much higher than the maximum value from 2006 (10.4 ug/L). The high value was observed at NH07-0025A on 8/13/07. This station is in the Squamscott River where high chlorophyll-a values have been observed in the past. No exceptions were reported on the field sheet for this station visit. The second highest chlorophyll-a value from 2007 was 10 ug/L, which matches the data from 2006. Therefore, the chlorophyll-a value from NH07-0025A was considered valid and retained in the database.

Parameter	Fraction	2006			2007		
		N	Ave	Max	N	Ave	Max
CARBON, ORGANIC	DISSOLVED	NA	NA	NA	36	2.438	6.790
CARBON, SUSPENDED	TOTAL	68	0.995	2.740	32	0.402	3.113
CDOM-AG440		NA	NA	NA	28	0.622	2.130
CDOM-SLOPE		NA	NA	NA	28	0.016	0.017
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN		79	2.948	10.400	34	4.768	60.900
DISSOLVED OXYEN		117	8.697	14.600	49	8.153	9.800
ENTEROCOCCUS		63	47.806	752.000	32	54.391	555.000
ESCHERICHIA COLI		74	78.389	564.000	39	33.705	280.000
LIGHT ATTENUATION COEFFICIENT		18	-1.315	-0.302	7	-0.612	-0.280
NITROGEN, AMMONIA AS N	DISSOLVED	60	0.057	0.234	22	0.024	0.169
NITROGEN, DISSOLVED	TOTAL	72	0.306	1.050	34	0.180	0.390
NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	DISSOLVED	65	0.077	0.296	30	0.017	0.039
NITROGEN, NITRITE (NO2) AS N	DISSOLVED	15	0.006	0.009	1	0.009	0.009
NITROGEN, SUSPENDED	TOTAL	68	0.115	0.428	29	0.077	0.529
PH		115	7.823	8.200	49	7.853	8.100
PHEOPHYTIN-A	SUSPENDED	80	2.699	10.100	36	2.542	17.600
PHOSPHORUS AS P	DISSOLVED	71	0.027	0.057	36	0.040	0.066
PHOSPHORUS AS P	SUSPENDED	70	0.027	0.083	28	0.010	0.063
PHOSPHORUS, ORTHOPHOSPHATE AS P	DISSOLVED	63	0.016	0.038	34	0.026	0.045
SALINITY		117	20.279	31.900	49	29.557	33.500

SECCHI DISK TRANSPARENCY		40	1.018	4.200	9	1.611	4.200
SILICA AS SIO2	DISSOLVED	70	1.002	4.550	27	0.407	1.280
SOLIDS, SUSPENDED	TOTAL	78	16.256	47.000	36	14.023	52.000
TEMPERATURE WATER		117	18.541	26.700	49	19.371	25.100
TOTAL FECAL COLIFORM		76	83.375	590.000	39	34.410	280.000

Evaluate field replicate samples for systematic errors
Four pairs of field duplicate samples were analyzed by the laboratory, resulting in 52 parameter comparisons. Only one of the 52 parameter comparisons failed the acceptance criteria established by DES (30% RPD or less than a trivially small difference). The pair that failed the test was TSS at station NH07-0024A, which was discussed previously. Because there was only one failure, there is no evidence of systematic sampling errors. The TSS data for station NH07-0024A were marked as not valid in the database. These data will not be used for 305(b) assessments or NHEP reporting.

E. Summary
NHDES has completed a quality assurance review of the 2007 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.