

# **FINAL REPORT**

## **CHESAPEAKE BAY PROGRAM BLIND AUDIT**

**Fiscal Year 2013 Final Report**

**PREPARED FOR:**

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Water and Habitat Quality Program  
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## INTRODUCTION

The purpose of this Blind Audit Program is to provide samples of specific nutrient analytes at concentrations commonly found in estuarine systems for analysis by laboratories that analyze water samples collected from the Chesapeake Bay and its tributaries. The concentrations of these samples, which are unknown to the recipient analysts, are compared to their prepared concentrations.

In the early years of the Chesapeake Bay Program, U.S. EPA provided blind audit samples on an irregular basis to laboratories analyzing Chesapeake Bay water samples. However, these audit samples were designed for waste water/drinking water applications rather than for estuarine water applications. Consequently, the concentrations were much higher than normally occur in the Bay and did not provide a reasonable estimate of accuracy for low level nutrient concentrations. For example, a blind audit concentration of 1.0 mg NH<sub>4</sub>-N/L would be comparable to National Pollutant Discharge Elimination System (NPDES) water samples, but would be at least an order of magnitude greater than concentrations normally occurring in most parts of Chesapeake Bay.

The only continuous program providing an estimate of laboratory performance has been the Chesapeake Bay Coordinated Split Sample Program (CSSP). Data generated from this program provide the only long term QA/QC data base to compare nutrient measurements provided by laboratories analyzing water samples collected from Chesapeake Bay and its tributaries. Samples for CSSP are natural water samples collected from Chesapeake Bay or a tributary. Briefly, a common unfiltered water sample is distributed to the various field/laboratory personnel who, in turn, subsample into dissolved and particulate fractions. These are analyzed and the results compared to those of other participating laboratories. Resulting data analysis can show how field filtration techniques and/or laboratory practices affect data variability. CSSP samples are each subject to cumulative errors of analytical determinations from variation in both field and laboratory procedures. Also, these data sets cannot definitively determine the accuracy of laboratory analyses.

The current Blind Audit Program has been designed to complement the CSSP. Blind Audit particulate samples distributed to participants have few cumulative errors associated with field filtering and subsampling procedures. Prepared concentrates of dissolved substances, whose concentrations are unknown to the analysts, are provided so that laboratory accuracy can be assessed.

This is the fifteenth year of the Blind Audit Program and it is the continued intent of this program to provide unknown, low level dissolved and particulate nutrient samples to laboratories analyzing Chesapeake Bay Program nutrients, as well as to other laboratories interested in participating in the Blind Audit Program.

## MATERIALS AND METHODS

Blind Audit samples were sent to participating laboratories on 28 August 2012 and 11 March 2013. Participating laboratories and contact personnel are found in Table 1.

Parameters measured were: total dissolved organic nitrogen, total dissolved organic phosphorus, nitrate+nitrite, ammonium, orthophosphate and dissolved organic carbon. High and low concentration samples were provided for each analyte. Particulate carbon, nitrogen and phosphorus, chlorophyll and total suspended solids, were also provided for those laboratories that routinely analyze these parameters. Chlorophyll *a* samples were natural population

samples collected from the mouth of the Patuxent River.

Dissolved Blind Audit concentrates were prepared by careful dilution of high quality standards using 18.3 megohm deionized water. The concentrates were sealed in 20 mL ampoules for shipment to participants. One ampoule contained a concentrate of an organic nitrogen compound and an organic phosphorus compound to be diluted for the analysis of low level total dissolved nitrogen and total dissolved phosphorus. A second ampoule contained a concentrate of an organic nitrogen compound and an organic phosphorus compound to be diluted for the analysis of higher level total dissolved nitrogen and total dissolved phosphorus. A third ampoule contained a concentrate to be diluted for the analysis of low level inorganic nutrients (ammonium, nitrate and phosphate). A fourth ampoule contained a concentrate to be diluted for the analysis of higher level inorganic nutrients. The fifth and sixth ampoules contained a low and high concentration of dissolved organic carbon, respectively. At each participating laboratory, an aliquot from each ampoule was diluted and analyzed according to accompanying instructions for preparation and dilution. These Blind Audit samples were then inserted randomly in a typical estuarine sample set. Final concentrations were reported for each diluted concentrate according to the dilution instructions provided.

Particulate analytes are measured by analyzing suspended material concentrated on filter pads. There are no commercially available suspensions of pure carbon, nitrogen or phosphorus compounds, so a natural sample was subsampled onto filter pads for analysis by participating laboratories. A batch water sample was collected from the CBL pier, and subsampled for particulate samples of carbon, nitrogen and phosphorus. Particulate C/N samples were filtered from the batch sample with care taken to shake the batch before each filtration to ensure homogeneity. Vacuum filtration was used to process the filters. Samples were dried completely (overnight at 47°C) before shipment. Two samples on 25 mm GF/F pads were sent to each laboratory for analysis.

The same general procedure was followed for particulate phosphorus samples in which they were concentrated by vacuum filtration on 47 mm GF/F pads.

Filter pads were sent to each laboratory for the analysis of particulate C, N, and P. The volume of sample filtered was noted in the instructions so that each laboratory could report concentrations in mg/L. Samples for chlorophyll *a* analysis were filtered from natural population samples onto 47 mm GF/F filter pads. Replicate pads were provided to participating laboratories.

Total suspended solids blind audits were prepared as follows: A suspension of a known mass of infusorial earth in deionized water was stirred with a magnetic stirrer. While stirring continued, an aliquot was subsampled by pipette into a screw cap vial for each participating laboratory. Detailed instructions explaining how to prepare this concentrate for total suspended solids analysis were also provided.

Samples were sent in coolers via next day carrier to the participating laboratories. A cold temperature was required for chlorophyll samples, so frozen cold packs were packed in those participants' coolers.

## RESULTS

Tables and figures summarizing results from the summer 2012 and winter 2013 audit are found at the end of the report. Shortly after the completion of the study, a brief data report, including the concentrations of the prepared samples, was sent to each participant for them to check their data. The prepared values for the winter 2013 samples were inadvertently not sent to participants. These data reviews served as a final check of data before preparing this final report.

Concentrations were assessed statistically by calculating the mean and standard deviation of each sample set, then calculating how many standard deviations separated each laboratory's reported concentration from that mean (Table 2). The percent recovery of each laboratory's reported concentration relative to the prepared concentration was also calculated for the dissolved analytes (Table 3 and Appendix 1).

### DISSOLVED FRACTION

Total Dissolved Nitrogen: Results from the summer 2012 and winter 2013 were excellent. Low and high reported concentrations had mean values that closely reflected the prepared concentrations. For example, the reported low concentrations of total dissolved N for summer 2012 were extremely close to the prepared concentration (prepared low: 0.212 mg N/L with mean reported concentration of 0.210 mg N/L).

Total Dissolved Phosphorus: All results for both summer 2012 and winter 2013 samples were consistently close to other laboratories' reported concentrations. Coefficients of variation were 6-16 %; however, there appeared to be an error in preparation of the concentrates for the laboratories to dilute. There was a consistent positive bias of about 140% for all reported concentrations relative to the calculated concentration of the prepared sample.

Ammonium: Analysis of low level samples for winter 2013 provided a mean concentration of 0.018 mg N/L compared to the prepared concentration of 0.021 mg N/L. Variation around that mean resulted in a coefficient of variation of 25.5%. Low level summer 2012 results were better, probably since the provided concentration was greater. The resulting coefficient of variation was 10.2%, while the over-all mean concentration was 0.039 mg N/L compared to the prepared concentration of 0.042 mg N/L. Results for both summer and winter high level concentrations were in close agreement with prepared concentrations and coefficients of variation of less than 10% were obtained.

Nitrate + Nitrite: Particularly good agreement was found among the laboratories for low and high concentrations for both audits, except the low level sample of winter 2013. Except for that winter 2013 sample, mean concentrations closely approximated prepared concentrations and low standard deviations provided percent coefficients of variation of less than 10%.

Orthophosphate: Low level concentrations for summer 2012 and winter 2013 were extremely variable, with coefficients of variation of 29% and 22%. Results of the high level concentrations were much closer, with coefficients of variation of 5% and 10%. However, there appeared to be an error in preparation of both the high and low level orthophosphate summer 2012 concentrates for the laboratories to dilute. There was a consistent positive bias in all reported summer 2012 orthophosphate concentrations—a mean of 167% for the low level sample and 123% for the high level sample.

Dissolved Organic Carbon: Particularly good agreement was found among the laboratories for low and high concentrations for both audits. Coefficients of variation were 4-5% for both concentration ranges for both audits. For these two rounds, all laboratories reported results that were very close to the prepared concentrations.

## **PARTICULATE FRACTION**

Again, it should be noted that particulate carbon, nitrogen and phosphorus samples were filtered from a common estuarine water sample and, consequently, are not true blind audit samples produced from pure constituents. Particulate results are graphically presented in Figures 1 and 4.

Particulate Carbon: Among laboratory agreement was very close for the summer 2012 audit with a coefficient of variation of 4%. The winter results were not as close. A coefficient of variation of 15% was determined, due largely to one laboratory's low reported concentration (Table 2).

Particulate Nitrogen: Results for particulate nitrogen followed the same pattern as particulate C. The coefficient of variation for the summer was 10% but the coefficient of variation for the winter 2013 was 15%, due largely to one laboratory's low reported concentration.

Particulate Phosphorus: Particulate phosphorus concentrations showed remarkably close agreement between all but one of the participating laboratories (coefficient of variation of 66%) for the summer audit. That laboratory reported a result approximately four times greater than the other laboratories. The winter results were less variable with a coefficient of variation of 5%.

Chlorophyll: Most of the chlorophyll *a* results for the summer 2012 and winter 2013 audits displayed the usual close agreement that was remarkable for multi-laboratory comparison of low concentrations of an environmentally transitory compound. A few results were considerably different from the "consensus" concentrations. The coefficients of variation were 31% for the summer 2012 samples and 46% for the winter 2013 samples.

Total Suspended Solids: The concentrate of infusorial earth suspended in deionized water was suspended further in deionized water by each laboratory, then concentrated on a filter pad and weighed. For the summer 2012 sample, 25.0 mg/L was prepared. One laboratory reported a concentration that was nearly half that reported by the other laboratories, but the coefficient of variation was only 12%. For the winter 2013 sample, 30.0 mg/L was prepared but, again, a (different) laboratory reported low results. The winter 2013 coefficient of variation was 7%.

## **DISCUSSION**

Several important issues should be considered when assessing whether individual Blind Audit results are within acceptable limits.

Variation Associated With An Analytical Method: As we have noted in previous Blind Audit Reports, analytical variability is associated with any quantitative determination. The method detection limit (three times the standard deviation of seven low level replicate natural samples) is often used to express that level of variation. Total dissolved nitrogen data provide a good example. The detection limit at CBL has been determined to be 0.02 mg N/L. Any total dissolved nitrogen measurement has a potential 0.02 mg N/L variability associated with it. This variability, when expressed as a percent of the TRUE concentration, can be extremely large for

low level concentrations and fairly low for higher concentrations. For example, a 0.20 mg N/L concentration has an analytical variability of 10% associated with it; whereas, a 1.20 mg N/L concentration has an analytical variability of 2%.

Acceptance Limits of Provided Dissolved Samples: Companies that prepare large quantities of performance evaluation samples assign acceptable confidence limits around the TRUE value. In one case (SPEX, CertiPrep), the mean recovery and standard deviation are later reported along with the true concentration and the 95% confidence interval (CI). The 95% CI is the mean recovery +/- two standard deviations and is developed from regression equations from Water Pollution Performance Evaluation Studies. A recently purchased set of these standards gave a true total P value of 3.00 mg P/L with a 95% CI of 2.47-3.42 mg P/L. The lower end of the 95% CI recovery allows 82% recovery of the true concentration. This type of statistical analysis was not performed on the Blind Audit Program samples prepared for this study prior to their distribution to the participants.

Parameters assessed in the Blind Audit do not have predetermined acceptance limits, so we are following the statistical procedure of ERA, an approved source of wastewater and drinking water proficiency samples, and the State of Wisconsin Proficiency Testing program. They average the results for each parameter and at each concentration, then calculate the standard deviation from the mean. Results that are within two standard deviations PASS and those greater than three standard deviations FAIL. Results between two and three standard deviations receive the WARN flag.

Most of the data comparisons based on standard deviations showed similar characteristics (Table 2); that is, the reported concentrations were similar, and one or two concentrations fell slightly beyond one standard deviation from the mean of all data for that portion of the study. Apparently, it is a statistical "reality" in small sample sets with little variability between individual values, that at least one value will lie just beyond one standard deviation from the mean. Thus, for most of the data sets compared by means and standard deviations, all the reported concentrations "passed." It should also be noted that approximately the same number were in the "warning" category as in most of the previous studies, and that only four values in the entire study "failed."

Data sets with relatively small standard deviations yielded more potentially extraneous "warning" points. For example, in the summer 2012 blind audit of high level ammonium concentration, the prepared concentration was 0.254 mg N/L and the mean reported concentration was 0.256 mg N/L (!) and reported concentrations ranged from 0.240-0.277 mg N/L. The coefficient of variation was ONLY 3.9%! Twelve laboratories reported results for this high level sample that were within two standard deviations (S.D. 0.010 mg N/L) of the mean. Since the standard deviation was so small, one laboratory's reported result for this sample was between two and three standard deviations of the mean, so was labeled WARN. Thus, by that measure of accuracy, most of the data "passed" and one was "warned." This ammonium data comparison points toward a form of circular reasoning in these statistical assessments. The data being evaluated are also the data that were used to calculate the mean and standard deviation to which the data are being compared. All of the reported data were within 9% of the prepared concentration!

Data were also assessed by comparing reported concentrations to those that had been prepared (Table 3). Groupings of data in PASS, WARN, and FAIL categories were arbitrarily set. Reported data that were within 10% of the prepared concentration were considered as PASS. Reported data that were 80-90% or 110 -120% of the prepared concentration were tabulated as WARN. Reported data that were <80% or >120% of the prepared concentration were tabulated as FAIL.

When comparing reported concentrations to those prepared, the lower concentration ranges had more data that fell in WARN and FAIL categories than the higher level concentrations, i.e., there was less accuracy at the lower concentration ranges (Table 3). The acceptance criteria for low concentration samples are quite narrow. For example, for winter 2013 blind audit of 0.021 mg N/L prepared for ammonium has a PASS category (+/-10%) of only 0.019 - 0.023 mg N/L. For the winter 2013 blind audit, six out of twelve participating laboratories reported results that fell in the FAIL category, indicating that their reported concentrations were greater than +/-20% of the prepared concentration in this low range. These results could be interpreted as an inability for all participants to accurately measure low level ammonium from concentrates provided to them. It would be important to know if there is also a difficulty in measuring natural low level samples. An alternative interpretation would be that it may be appropriate to broaden the acceptance boundaries for very low concentrations of prepared samples. There was also a broad range in percentage recovery of low level ammonium reported values in past audits; however, when comparing with other participants, the coefficient of variation remains remarkably small. For example, winter 2013 reported data based on comparisons with other participants was mean 0.018 mg N/L, S.D. 0.005, C.V. 25%.

There was less divergence between participants for the summer 2012 and winter 2013 low level ammonium samples than in audits of summer 2011 and winter 2012. The proportions of the standard deviations to the means for the low level ammonium samples were smaller than they have been for the last few years. For the summer 2012 audit, the coefficient of variation for 0.042 mg NH<sub>4</sub>-N/L was 10%!! The coefficient of variation was 16% for 0.042 mg NH<sub>4</sub>-N/L (Summer 2006) and 39% for 0.036 mg NH<sub>4</sub>-N/L (Winter 2007). This indicates that inter-laboratory comparisons of any ammonium data prepared by laboratories from concentrates below 0.042 mg N/L could probably be somewhat improving!

Unlike the results of past years, there appeared to be NO (!) consistent negative bias for total suspended solids for both audits for all the laboratories' data.

There were ten instances where concentrations reported for dissolved constituents or total suspended solids fell in the WaRN or FAIL category based on the standard deviation of all participants' reported concentrations and also in the WARN or FAIL category based on percent recovery. These are listed for the individual laboratories in Appendix 1.

Acceptance Limits of Provided Particulate Samples: For each study, particulate carbon, nitrogen, phosphorus and chlorophyll a samples were filtered from a common estuarine water sample and, consequently, are not true blind audit samples made from pure constituents. There is no "true" or prepared concentration with which to compare. The standard deviation was less than 10% of the mean reported concentrations for particulate carbon and nitrogen for the summer 2012 audit. The standard deviation was about 15% of the mean reported concentration for particulate carbon and nitrogen for the winter 2013 audit, due largely to one laboratory's low reported concentrations. For particulate phosphorus, one laboratory's reported concentration was about four times that of the mean of the other participants' data for the summer 2012 audit. For the winter 2013 audit, there was much closer agreement between reported concentrations of particulate phosphorus, with a coefficient of variation of less than 5%.

Over the years, the concentration of particulate constituents provided to the participants has varied randomly over approximately a five-fold range. For example, particulate carbon in winter 1998 was approximately 0.45 mg C/L, and in winter 2013 was approximately 2.35 mg C/L.

Reporting Data Accurately: Most data originally reported by all participants for both these blind



audits appeared, on casual inspection, to be reported accurately. Subtle entry or calculation errors may have gone undetected.

The summer 2007 and winter 2008 audits were the first pair of audits in which no participant noted any discrepancies when all were contacted to review their data. No results were miscalculated (and later corrected), or had “slipped a decimal” or exhibited some other obvious entry error that could have been easily avoided. After years of reporting “difficulties,” participants had improved their reporting practices! Sadly, this improvement in reporting did not extend to the summer 2008 through summer 2010 audits. At last, for the winter 2011 audit, no participant noted any discrepancies when all were contacted to review their data. We had returned to that great condition where no results were miscalculated (and later corrected), or had “slipped a decimal” or exhibited some other obvious entry error that could have been easily avoided. Sadly, for the summer 2011 blind audit, results were AGAIN (!) reported and then later corrected. Results that had been entered on the wrong parts of the results form were noted as FAIL, but the corrected data were used for statistical comparisons. Happily, for the winter 2012, summer 2012 and winter 2013 audits, no participant noted any discrepancies when all were contacted to review their data.

The number of significant figures reported in analytical results can significantly affect data comparability in a blind audit study. If a laboratory reports only two significant figures (for whatever reasons) and an audit sample has a prepared concentration expressed in three significant figures, then substantial under or over estimates of the comparative concentration can be reported. For example, if a 0.032 mg P/L sample has been prepared and a laboratory only reports two significant figures, i.e., 0.03 mg P/L, then the results expressed are 86% of the prepared value. During the 2000 study, all participants reported three significant digits for most parameters. It is noteworthy that the 2000 study's coefficients of variation were, generally, smaller than in the previous two years, probably a result of comparisons of data containing the appropriate number of significant digits. Unfortunately, some 2001 through winter 2012 participants reported only two significant digits for some analytes, thus potentially giving substantial under or over estimates for the comparisons.

## **CONCLUSION**

Now that thirty one rounds of the Blind Audit Program have been completed, some consistent patterns have been observed that warrant action or further investigation:

1. Results for particulate carbon and nitrogen were generally consistent between laboratories. Reported concentrations of particulate analytes have usually been similar between laboratories participating in the Blind Audit Program. For the summer 2012 audit, total suspended solids, chlorophyll *a* and particulate phosphorus reported concentrations from a few laboratories displayed some wide divergence from the range of the other reported concentrations. For the winter 2013 audit, one laboratory reported concentrations of particulate carbon and nitrogen that were widely different from the range of the other reported concentrations. For particulate carbon and nitrogen, that laboratory's reported concentrations were about 60% of the mean of the other participants' data for the winter 2013 audit. The proportion of the standard deviation to the mean was in its usual range for all participants for the summer 2012 blind audit. Still, this indicates that most participating laboratories usually execute and report these measurements with accuracy and precision, reporting the appropriate number of significant digits.
2. The proportion of the standard deviation to the mean was small for particulate phosphorus for the winter 2003 through winter 2008 blind audits, so inter-laboratory comparison of particulate phosphorus data should have been valid. The proportion of the standard deviation to the mean

was higher for particulate phosphorus in the blind audits of summer 2008 through winter 2010 and, again, in winter and summer 2012. This contrasted to all the previous years, in which the coefficient of variation for particulate phosphorus was usually the lowest of the particulate fractions. For the four audits of summer 2010 through summer 2011 and winter 2013, the proportion of the standard deviation to the mean was small for particulate phosphorus. Therefore, inter-laboratory comparison of particulate phosphorus data usually should be valid.

3. For all but one (different) participating laboratory in each audit, there was remarkable consistency between participating laboratories in the measurement of total suspended solids from suspensions of infusorial earth. There no longer appears to be a consistent negative bias in all the laboratories' data.

4. Reported concentrations of dissolved analytes were usually similar between laboratories participating in the Blind Audit Program. No laboratory reported concentrations for individual analytes that were widely different from the range of the other reported concentrations for both blind audits. This indicates that most participating laboratories usually execute and report these measurements with accuracy and precision, reporting the appropriate number of significant digits.

5. When comparing reported concentrations to those prepared, the lower concentration ranges had more data that fell beyond +/- 10% of the prepared sample than the higher level concentration ranges, i.e., there was less accuracy at the lower concentration ranges. This was particularly apparent for ammonium and orthophosphate. The categories for PASS, WARN, and FAIL for low concentration samples are quite narrow. Therefore, for very low concentrations of prepared samples, it may be appropriate to broaden the acceptance boundaries.

6. There was less variation in reported concentrations of low level ammonium for both these blind audits, in comparison to several previous audits. This probably indicates that inter-laboratory comparisons of any ammonium data prepared from concentrates with resultant concentrations below 0.042 mg N/L could be improving.

7. Care should continue to be taken when completing report forms. For the summer 2012 and winter 2013 blind audits, some results were AGAIN (!) reported with insufficient significant digits. No results were reported and subsequently corrected!! Over the course of the years, a few laboratories repeatedly have made calculation or entry errors that were later corrected. It is hoped that corrections of these lapses have served as reminders of the importance to continuously check many aspects of data management to ensure overall data quality.

Table 1. Participants in the Summer 2012 and Winter 2013 Blind Audit Program.

Participant Institution	Point of Contact	Phone	Dissolved	Particulate	Chlorophyll a	DOC	TSS
Old Dominion University, Water Quality Laboratory (ODU)	Suzanne Doughton	757-451-3044	X	X	X	X	X
University of Maryland, Horn Point Laboratory (HPL)	Jennifer O'Keefe Suttles	410-221-8276	X	X	X	X	X
Virginia Institute of Marine Science, Analytical Service Center (VIMS)	Carol Pollard	804-684-7213	X	PP ONLY	X	NO	X
Virginia Division of Consolidated Laboratory Services (DCLS)	Jay Armstrong	804-648-4480 x328	X	X	X	X	X
Maryland Department of Health and Mental Hygiene (DHMH)	Shala Ameli	410-767-6190	X	X	X	X	X
University of Maryland Chesapeake Biological Laboratory (CBL)	Carl Zimmermann & Kathy Wood	410-326-7252	X	X	X	X	X
Delaware Department of Natural Resources (DNREC)	Ben Pressly	302-739-9942	X	X	X	X	X
Academy of Natural Science of Philadelphia (ACNAT)	Paul Kiry	215-299-1076	NH4 ONLY	PCPN ONLY	X	NO	X
Pennsylvania DEP, Bureau of Laboratories (PADEP)	Frank Lozupone & Mike Azar	717-346-8227	HIGH SAMPLES	NO	NO	X	X
Massachusetts Water Resources Authority, Central Laboratory (MWRA)	Jennifer Constantino	617-660-7808	X	X	X	NO	X
Hampton Roads Sanitation District, Central Environmental Laboratory (HRSD)	Stacie Metzler	757-460-4217	HIGH SAMPLES	NO	X	X	X
Occoquan Watershed Monitoring Lab (OCC)	Dongmei Wang	703-361-5606 x118	X		X	X	X
University of Connecticut Center for Environmental Science & Engineering (UCONN)	Chris Perkins	860-486-2668	X	PCPN	X	X	X
New Jersey Department of Health (NJDH)	Doug Haltmeier	609-530-2801	TDP	PCPN		NO	X

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Summer 2012 and the Winter 2013 Blind Audit, Including Distribution of Reported Concentrations from the Mean.

Parameter	Concentration in mg/L		Number of Laboratories			
			Standard Deviations from Mean			
	Mean	S.D.	<1 PASS	1-2 PASS	2-3 WARN	>3 FAIL
<b>Summer 2012</b>						
Total Dissolved Nitrogen	0.210	0.0264	9	1	1	
Total Dissolved Nitrogen	0.879	0.0965	12			1
Total Dissolved Phosphorus	0.0165	0.0026	9	3		
Total Dissolved Phosphorus	0.0649	0.0035	9	5		
Ammonium	0.039	0.004	8	3		
Ammonium	0.256	0.010	11	2	1	
Nitrate + Nitrite	0.0709	0.0069	9	1	1	
Nitrate + Nitrite	0.832	0.0374	10	3	1	
Orthophosphate	0.0050	0.0015	7	4		
Orthophosphate	0.0554	0.0030	10	4		
Dissolved Organic Carbon	2.02	0.08	7	3		
Dissolved Organic Carbon	4.96	0.21	8	2		
Particulate Carbon	1.85	0.077	6	4		
Particulate Nitrogen	0.329	0.0314	8	1	1	
Particulate Phosphorus	0.0295	0.0194	9		1	
Total Suspended Solids	24.5	3.0	13			1
<b>Winter 2013</b>						
Total Dissolved Nitrogen	0.367	0.0144	6	4		
Total Dissolved Nitrogen	0.722	0.0429	11			1
Total Dissolved Phosphorus	0.0265	0.0036	8	2	1	
Total Dissolved Phosphorus	0.0534	0.0058	10	2	1	
Ammonium	0.018	0.005	8	5		
Ammonium	0.215	0.019	13	1		1
Nitrate + Nitrite	0.0131	0.0040	10	1	1	
Nitrate + Nitrite	0.692	0.0300	10	3	1	
Orthophosphate	0.0079	0.0017	8	3		
Orthophosphate	0.0367	0.0038	10	3		
Dissolved Organic Carbon	3.22	0.17	7	3		
Dissolved Organic Carbon	7.06	0.27	6	4		
Particulate Carbon	2.35	0.361	9		1	
Particulate Nitrogen	0.322	0.0477	8	1	1	
Particulate Phosphorus	0.0255	0.0012	5	3		
Total Suspended Solids	29.9	2.2	12	1		1

Table 3. Summary of Prepared and Reported Concentrations for Each Analyte and Percent Recovery of the Prepared Concentration by Participating Laboratories

Parameter	Prepared Concentration mg/L	Reported Concentration Range mg/L	Number of Laboratories		
			Within 90% - 110% of Prepared Concentration	Within 80 -90%, or 110-120% of Prepared Concentration	<80%, or >120% of Prepared Concentration
			PASS	WARN	FAIL
<b>Summer 2012</b>					
Total Dissolved Nitrogen	0.212	0.150-0.255	8	2	1
Total Dissolved Nitrogen	0.917	0.560-0.943	12		1
Total Dissolved Phosphorus	0.011**	0.0132-0.0215		1	11
Total Dissolved Phosphorus	0.048**	0.0580-0.0700			14
Ammonium	0.042	0.033-0.047	7	2	2
Ammonium	0.254	0.240-0.277	14		
Nitrate + Nitrite	0.07	0.0600-0.0907	9	1	1
Nitrate + Nitrite	0.84	0.746-0.896	13	1	
Orthophosphate	0.003**	0.0023-0.0070	1	1	9
Orthophosphate	0.045**	0.0496-0.0600	1	3	10
Dissolved Organic Carbon	1.995	1.88-2.12	10		
Dissolved Organic Carbon	4.987	4.56-5.17	10		
Total Suspended Solids	25.0	14.1-26.5	13		1
<b>Winter 2013</b>					
Total Dissolved Nitrogen	0.353	0.347-0.395	9	1	
Total Dissolved Nitrogen	0.705	0.681-0.859	11		1
Total Dissolved Phosphorus	0.0190**	0.0220-0.0354		2	9
Total Dissolved Phosphorus	0.0380**	0.0450-0.0700		1	12
Ammonium	0.021*	0.012-0.026	3	3	6
Ammonium	0.212	0.193-0.280	13		1
Nitrate + Nitrite	0.0140	0.0020-0.0202	7	2	2
Nitrate + Nitrite	0.700	0.644-0.761	13		
Orthophosphate	0.0070*	0.0050-0.0113	7		4
Orthophosphate	0.0370	0.0300-0.0440	10	3	
Dissolved Organic Carbon	2.992	3.03-3.55	7	3	
Dissolved Organic Carbon	6.982	6.78-7.49	10		
Total Suspended Solids	30.0	23.0-32.2	13		1

\*The prepared sample concentration was quite low, so the acceptance boundaries are narrow.

\*\*Most of the values reported were greater than the calculated concentration based on dilution of the provided concentrate. It appears that there was a mistake in preparation of this concentrate for dilution by the participants.

## Appendix 1. Summer 2012 and Winter 2013 Reported Concentrations, Prepared Concentrations and Percent Recoveries.

**University of Connecticut Center for Environmental Science and Engineering (UCONN)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.218		0.212	102.8	0.358		0.353	101.4
TDN (mg N/L)	0.918		0.917	100.1	0.681		0.705	96.6
TDP (mg P/L)	0.017	F**	0.011	154.5	0.022	W	0.019	115.8
TDP (mg P/L)	0.058	F**	0.048	120.8	0.045	W	0.038	118.4
NH4 (mg N/L)	0.047	W	0.042	111.9	0.014	F	0.021	66.7
NH4 (mg N/L)	0.254		0.254	100.0	0.204		0.212	96.2
NO2+NO3 (mg N/L)	0.07		0.07	100.0	0.012	W	0.014	85.7
NO2+NO3 (mg N/L)	0.852		0.84	101.4	0.672		0.7	96.0
PO4 (mg P/L)	0.007	F**	0.003	233.3	0.005	F	0.007	71.4
PO4 (mg P/L)	0.054	W**	0.045	120.0	0.031	W	0.037	83.8
PC (mg C/L)	1.915		NA	NA	2.543		NA	NA
PN (mg N/L)	0.301		NA	NA	0.305		NA	NA
PP (mg P/L)	0.0875	W	NA	NA	*		NA	NA
CHLA (ug/L)	5.2		NA	NA	50.6		NA	NA
DOC (mg C/L)	*		1.995	*	*		2.992	*
DOC (mg C/L)	*		4.987	*	*		6.982	*
TSS (mg/L)	24.9		25	99.6	30.4		30	101.3

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

**Academy of Natural Science of Philadelphia (ACNAT)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.255	W	0.212	120.3	*		0.353	*
TDN (mg N/L)	0.894		0.917	97.5	*		0.705	*
TDP (mg P/L)	0.0143	F**	0.011	130.0	*		0.019	*
TDP (mg P/L)	0.0602	F**	0.048	125.4	*		0.038	*
NH4 (mg N/L)	*		0.042	*	0.0176	W	0.021	83.8
NH4 (mg N/L)	0.252		0.254	99.2	0.217		0.212	102.4
NO2+NO3 (mg N/L)	*		0.07	*	*		0.014	*
NO2+NO3 (mg N/L)	0.789		0.84	93.9	*		0.7	*
PO4 (mg P/L)	*		0.003	*	*		0.007	*
PO4 (mg P/L)	0.0555	F**	0.045	123.3	*		0.037	*
PC (mg C/L)	1.82		NA	NA	1.28	W	NA	NA
PN (mg N/L)	0.361		NA	NA	0.209	W	NA	NA
PP (mg P/L)	0.022		NA	NA	*		NA	NA
CHLA (ug/L)	9.24		NA	NA	16.35		NA	NA
DOC (mg C/L)	*		1.995	*	*		2.992	*
DOC (mg C/L)	*		4.987	*	*		6.982	*
TSS (mg/L)	25.8		25	103.2	31.4		30	104.7

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Appendix 1 cont'. Summer 2012 and Winter 2013 Reported Concentrations, Prepared Concentrations and Percent Recoveries.

**Virginia Institute of Marine Science, Analytical Service Center (VIMS)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.1934		0.212	91.2	0.3871		0.353	109.7
TDN (mg N/L)	0.8308		0.917	90.6	0.7253		0.705	102.9
TDP (mg P/L)	0.0142	F**	0.011	129.1	0.025	F	0.019	131.6
TDP (mg P/L)	0.0632	F**	0.048	131.7	0.0517	F	0.038	136.1
NH4 (mg N/L)	0.0329	F	0.042	78.3	0.0126	F	0.021	60.0
NH4 (mg N/L)	0.247		0.254	97.2	0.193		0.212	91.0
NO2+NO3 (mg N/L)	0.0691		0.07	98.7	0.0138		0.014	98.6
NO2+NO3 (mg N/L)	0.7465	W	0.84	88.9	0.7073		0.7	101.0
PO4 (mg P/L)	0.0023	**	0.003	76.7	0.0069		0.007	98.6
PO4 (mg P/L)	0.0496	**	0.045	110.2	0.036		0.037	97.3
PC (mg C/L)	*		*	NA	*		NA	NA
PN (mg N/L)	*		*	NA	*		NA	NA
PP (mg P/L)	0.0239		NA	NA	0.0268		NA	NA
CHLA (ug/L)	14.39		NA	NA	24.91		NA	NA
DOC (mg C/L)	*		1.995	*	*		2.992	*
DOC (mg C/L)	*		4.987	*	*		6.982	*
TSS (mg/L)	25.1		25	100.4	30.3		30	101.0

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

**Hampton Roads Sanitation District, Central Environmental Laboratory (HRSD)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	*		0.212		*		0.353	*
TDN (mg N/L)	0.56	F	0.917	61.1	0.7		0.705	99.3
TDP (mg P/L)	*	**	0.011	*	*		0.019	*
TDP (mg P/L)	0.07	F**	0.048	145.8	0.07	F	0.038	184.2
NH4 (mg N/L)	*		0.042	*	*		0.021	*
NH4 (mg N/L)	0.25		0.254	98.4	0.22		0.212	103.8
NO2+NO3 (mg N/L)	*		0.07	*	*		0.014	*
NO2+NO3 (mg N/L)	0.83		0.84	98.8	0.66		0.7	94.3
PO4 (mg P/L)	*	**	0.003	*	*		0.007	*
PO4 (mg P/L)	0.057	F**	0.045	126.7	0.04		0.037	108.1
PC (mg C/L)	*		NA	NA	*		NA	NA
PN (mg N/L)	*		NA	NA	*		NA	NA
PP (mg P/L)	*		NA	NA	*		NA	NA
CHLA (ug/L)	8.9		NA	NA	11.7		NA	NA
DOC (mg C/L)	2.11		1.995	105.8	3.35	W	2.992	112.0
DOC (mg C/L)	5.12		4.987	102.7	7.48		6.982	107.1
TSS (mg/L)	25.6		25	102.4	30.8		30	102.7

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Appendix 1 cont'. Summer 2012 and Winter 2013 Reported Concentrations, Prepared Concentrations and Percent Recoveries.

**University of Maryland, Horn Point Laboratory (HPL)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.185	W	0.212	87.3	0.367		0.353	104.0
TDN (mg N/L)	0.943		0.917	102.8	0.731		0.705	103.7
TDP (mg P/L)	0.014	F**	0.011	127.3	0.0256	F	0.019	134.7
TDP (mg P/L)	0.0636	F**	0.048	132.5	0.0532	F	0.038	140.0
NH4 (mg N/L)	0.0381		0.042	90.7	0.017	W	0.021	81.0
NH4 (mg N/L)	0.246		0.254	96.9	0.204		0.212	96.2
NO2+NO3 (mg N/L)	0.0693		0.07	99.0	0.0138		0.014	98.6
NO2+NO3 (mg N/L)	0.817		0.84	97.3	0.689		0.7	98.4
PO4 (mg P/L)	0.0029	**	0.003	96.7	0.0071		0.007	101.4
PO4 (mg P/L)	0.05	W**	0.045	111.1	0.0391		0.037	105.7
PC (mg C/L)	1.908		NA	NA	2.41		NA	NA
PN (mg N/L)	0.3295		NA	NA	0.3295		NA	NA
PP (mg P/L)	0.0232		NA	NA	0.0266		NA	NA
CHLA (ug/L)	15.25		NA	NA	17.48		NA	NA
DOC (mg C/L)	1.877		1.995	94.1	3.03		2.992	101.3
DOC (mg C/L)	4.798		4.987	96.2	6.83		6.982	97.8
TSS (mg/L)	25.6		25	102.4	30.9		30	103.0

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

**Delaware Department of Natural Resources (DNREC)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.232		0.212	109.4	0.395	W	0.353	111.9
TDN (mg N/L)	0.925		0.917	100.9	0.859	F	0.705	121.8
TDP (mg P/L)	0.015	F**	0.011	136.4	0.0354	F	0.019	186.3
TDP (mg P/L)	0.0683	F**	0.048	142.3	0.0511	F	0.038	134.5
NH4 (mg N/L)	0.0429		0.042	102.1	0.0122	F	0.021	58.1
NH4 (mg N/L)	0.2768		0.254	109.0	0.2032		0.212	95.8
NO2+NO3 (mg N/L)	0.0724		0.07	103.4	0.0152		0.014	108.6
NO2+NO3 (mg N/L)	0.8226		0.84	97.9	0.7013		0.7	100.2
PO4 (mg P/L)	0.0062	F**	0.003	206.7	0.0113	F	0.007	161.4
PO4 (mg P/L)	0.0582	F**	0.045	129.3	0.0395		0.037	106.8
PC (mg C/L)	1.72		NA	NA	2.397		NA	NA
PN (mg N/L)	0.315		NA	NA	0.337		NA	NA
PP (mg P/L)	0.0228		NA	NA	*		NA	NA
CHLA (ug/L)	15.14		NA	NA	21.5		NA	NA
DOC (mg C/L)	1.96		1.995	98.2	3.55	W	2.992	118.6
DOC (mg C/L)	4.56		4.987	91.4	7.42		6.982	106.3
TSS (mg/L)	26.5		25	106.0	31.67		30	105.6

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations



Appendix 1 cont'. Summer 2012 and Winter 2013 Reported Concentrations, Prepared Concentrations and Percent Recoveries.

**Division of Consolidated Laboratory Services (DCLS)**

Parameter	Summer 2012 Reported Concentration	Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration	Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.227	0.212	107.1	0.376	0.353	106.5
TDN (mg N/L)	0.896	0.917	97.7	0.712	0.705	101.0
TDP (mg P/L)	0.014 F**	0.011	127.3	0.029 F	0.019	152.6
TDP (mg P/L)	0.064 F**	0.048	133.3	0.05 F	0.038	131.6
NH4 (mg N/L)	0.0382	0.042	91.0	0.015 F	0.021	71.4
NH4 (mg N/L)	0.253	0.254	99.6	0.214	0.212	100.9
NO2+NO3 (mg N/L)	0.0694	0.07	99.1	0.013	0.014	92.9
NO2+NO3 (mg N/L)	0.8615	0.84	102.6	0.693	0.7	99.0
PO4 (mg P/L)	0.0035 W**	0.003	116.7	0.0073	0.007	104.3
PO4 (mg P/L)	0.0524 W**	0.045	116.4	0.037	0.037	100.0
PC (mg C/L)	1.85	NA	NA	2.45	NA	NA
PN (mg N/L)	0.319	NA	NA	0.34	NA	NA
PP (mg P/L)	0.0274	NA	NA	0.0243	NA	NA
CHLA (ug/L)	13.6	NA	NA	17.85	NA	NA
DOC (mg C/L)	2.06	1.995	103.3	3.25	2.992	108.6
DOC (mg C/L)	5.1	4.987	102.3	6.95	6.982	99.5
TSS (mg/L)	24	25	96.0	28.5	30	95.0

\* No sample sent to participant - sample not requested, pa

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

**University of Maryland, Chesapeake Biological Laboratory (CBL)**

Parameter	Summer 2012 Reported Concentration	Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration	Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.222	0.212	104.7	0.362	0.353	102.5
TDN (mg N/L)	0.904	0.917	98.6	0.718	0.705	101.8
TDP (mg P/L)	0.0132 W**	0.011	120.0	0.0223 W	0.019	117.4
TDP (mg P/L)	0.0645 F**	0.048	134.4	0.0467 F	0.038	122.9
NH4 (mg N/L)	0.0426	0.042	101.4	0.022	0.021	104.8
NH4 (mg N/L)	0.2752	0.254	108.3	0.211	0.212	99.5
NO2+NO3 (mg N/L)	0.0706	0.07	100.9	0.0134	0.014	95.7
NO2+NO3 (mg N/L)	0.896	0.84	106.7	0.686	0.7	98.0
PO4 (mg P/L)	0.0048 F**	0.003	160.0	0.007	0.007	100.0
PO4 (mg P/L)	0.0546 F**	0.045	121.3	0.0336	0.037	90.8
PC (mg C/L)	1.82	NA	NA	2.52	NA	NA
PN (mg N/L)	0.312	NA	NA	0.331	NA	NA
PP (mg P/L)	0.0238	NA	NA	0.0246	NA	NA
CHLA (ug/L)	16.28	NA	NA	21.9	NA	NA
DOC (mg C/L)	2.12	1.995	106.3	3.09	2.992	103.3
DOC (mg C/L)	5.1	4.987	102.3	6.89	6.982	98.7
TSS (mg/L)	24.9	25	99.6	28.3	30	94.3

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Appendix 1 cont'. Summer 2012 and Winter 2013 Reported Concentrations, Prepared Concentrations and Percent Recoveries.

**Virginia Polytechnic Institute, Occoquan Watershed Monitoring Laboratory (OCC)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.15	F	0.212	70.8	0.367		0.353	104.0
TDN (mg N/L)	0.88		0.917	96.0	0.712		0.705	101.0
TDP (mg P/L)	0.02	F**	0.011	181.8	0.023	F	0.019	121.1
TDP (mg P/L)	0.06	F**	0.048	125.0	0.052	F	0.038	136.8
NH4 (mg N/L)	0.04		0.042	95.2	0.025	W	0.021	119.0
NH4 (mg N/L)	0.26		0.254	102.4	0.216		0.212	101.9
NO2+NO3 (mg N/L)	0.06	W	0.07	85.7	0.002	F	0.014	14.3
NO2+NO3 (mg N/L)	0.82		0.84	97.6	0.761		0.7	108.7
PO4 (mg P/L)	0.005	F**	0.003	166.7	0.009	F	0.007	128.6
PO4 (mg P/L)	0.06	F**	0.045	133.3	0.04		0.037	108.1
PC (mg C/L)	1.76		NA	NA	2.47		NA	NA
PN (mg N/L)	0.41		NA	NA	0.414		NA	NA
PP (mg P/L)	*		NA	NA	*		NA	NA
CHLA (ug/L)	6.6		NA	NA	9.75		NA	NA
DOC (mg C/L)	2.1		1.995	105.3	3.156		2.992	105.5
DOC (mg C/L)	5.1		4.987	102.3	6.816		6.982	97.6
TSS (mg/L)	25.6		25	102.4	29		30	96.7

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

**Maryland Department of Health and Mental Hygiene (DHMH)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.204		0.212	96.2	0.352		0.353	99.7
TDN (mg N/L)	0.918		0.917	100.1	0.706		0.705	100.1
TDP (mg P/L)	0.0189	F**	0.011	171.8	0.0271	F	0.019	142.6
TDP (mg P/L)	0.0659	F**	0.048	137.3	0.056	F	0.038	147.4
NH4 (mg N/L)	0.0332	F	0.042	79.0	0.0227		0.021	108.1
NH4 (mg N/L)	0.257		0.254	101.2	0.216		0.212	101.9
NO2+NO3 (mg N/L)	0.0695		0.07	99.3	0.0157	W	0.014	112.1
NO2+NO3 (mg N/L)	0.838		0.84	99.8	0.711		0.7	101.6
PO4 (mg P/L)	0.00552	F**	0.003	184.0	0.0108	F	0.007	154.3
PO4 (mg P/L)	0.0561	F**	0.045	124.7	0.0335		0.037	90.5
PC (mg C/L)	1.823		NA	NA	2.476		NA	NA
PN (mg N/L)	0.311		NA	NA	0.3265		NA	NA
PP (mg P/L)	0.0248		NA	NA	0.0249		NA	NA
CHLA (ug/L)	12.34		NA	NA	21.085		NA	NA
DOC (mg C/L)	1.94		1.995	97.2	3.43	W	2.992	114.6
DOC (mg C/L)	4.62		4.987	92.6	7.49		6.982	107.3
TSS (mg/L)	25.8		25	103.2	31.6		30	105.3

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Appendix 1 cont'. Summer 2012 and Winter 2013 Reported Concentrations, Prepared Concentrations and Percent Recoveries.

**Massachusetts Water Resource Authority, Central Laboratory (MWRA)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.22		0.212	103.8	0.359		0.353	101.70
TDN (mg N/L)	0.931		0.917	101.5	0.708		0.705	100.43
TDP (mg P/L)	0.0179	F**	0.011	162.7	0.0282	F	0.019	148.42
TDP (mg P/L)	0.0692	F**	0.048	144.2	0.0566	F	0.038	148.95
NH4 (mg N/L)	0.0421		0.042	100.2	0.0161	F	0.021	76.67
NH4 (mg N/L)	0.261		0.254	102.8	0.212		0.212	100.00
NO2+NO3 (mg N/L)	0.0697		0.07	99.6	0.013		0.014	92.86
NO2+NO3 (mg N/L)	0.798		0.84	95.0	0.644		0.7	92.00
PO4 (mg P/L)	0.00528	F**	0.003	176.0	0.00767		0.007	109.57
PO4 (mg P/L)	0.0588	F**	0.045	130.7	0.0374		0.037	101.08
PC (mg C/L)	1.945		NA	NA	2.545		NA	NA
PN (mg N/L)	0.306		NA	NA	0.3235		NA	NA
PP (mg P/L)	0.02		NA	NA	0.0237		NA	NA
CHLA (ug/L)	16.85		NA	NA	22		NA	NA
DOC (mg C/L)	*		1.995	*	*		2.992	*
DOC (mg C/L)	*		4.987	*	*		6.982	*
TSS (mg/L)	14.1	F	25	56.4	30.2		30	100.67

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

**Old Dominion University, Water Quality Laboratory (ODU)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	0.203		0.212	95.8	0.347		0.353	98.3
TDN (mg N/L)	0.938		0.917	102.3	0.707		0.705	100.3
TDP (mg P/L)	0.0182	F**	0.011	165.5	0.0256	F	0.019	134.7
TDP (mg P/L)	0.0677	F**	0.048	141.0	0.0524	F	0.038	137.9
NH4 (mg N/L)	0.0396		0.042	94.3	0.0198		0.021	94.3
NH4 (mg N/L)	0.257		0.254	101.2	0.2024		0.212	95.5
NO2+NO3 (mg N/L)	0.0688		0.07	98.3	0.0128		0.014	91.4
NO2+NO3 (mg N/L)	0.8372		0.84	99.7	0.658		0.7	94.0
PO4 (mg P/L)	0.0069	F**	0.003	230.0	0.0069		0.007	98.6
PO4 (mg P/L)	0.0564	F**	0.045	125.3	0.0365		0.037	98.6
PC (mg C/L)	1.972		NA	NA	2.44		NA	NA
PN (mg N/L)	0.322		NA	NA	0.3		NA	NA
PP (mg P/L)	0.0198		NA	NA	0.0259		NA	NA
CHLA (ug/L)	16.02		NA	NA	22		NA	NA
DOC (mg C/L)	2.006		1.995	100.6	3.121		2.992	104.3
DOC (mg C/L)	4.929		4.987	98.8	7		6.982	100.3
TSS (mg/L)	26.15		25	104.6	32.19		30	107.3

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Appendix 1 cont'. Summer 2012 and Winter 2013 Reported Concentrations, Prepared Concentrations and Percent Recoveries.

**Pennsylvania Department of Environmental Protection, Bureau of Laboratories (PADEP)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	*		0.212	*	*		0.353	*
TDN (mg N/L)	0.86		0.917	93.8	0.71		0.705	100.7
TDP (mg P/L)	**		0.011	*	*		0.019	*
TDP (mg P/L)	0.068	F**	0.048	141.7	0.054	F	0.038	142.1
NH4 (mg N/L)	*		0.042	*	*		0.021	*
NH4 (mg N/L)	0.24		0.254	94.5	0.28	F	0.212	132.1
NO2+NO3 (mg N/L)	*		0.07	*	*		0.014	*
NO2+NO3 (mg N/L)	0.85		0.84	101.2	0.72		0.7	102.9
PO4 (mg P/L)	**		0.003	*	*		0.007	*
PO4 (mg P/L)	0.058	F**	0.045	128.9	0.044	W	0.037	118.9
PC (mg C/L)	*		NA	NA	*		NA	NA
PN (mg N/L)	*		NA	NA	*		NA	NA
PP (mg P/L)	*		NA	NA	*		NA	NA
CHLA (ug/L)	*		NA	NA	*		NA	NA
DOC (mg C/L)	2.04		1.995	102.3	3.13		2.992	104.6
DOC (mg C/L)	5.09		4.987	102.1	6.78		6.982	97.1
TSS (mg/L)	23		25	92.0	23	F	30	76.7

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

**New Jersey Department of Health (NJDH)**

Parameter	Summer 2012 Reported Concentration		Summer 2012 Prepared Concentration	Summer 2012 Percent Recovered	Winter 2013 Reported Concentration		Winter 2013 Prepared Concentration	Winter 2013 Percent Recovered
TDN (mg N/L)	*		0.212	*	*		0.353	*
TDN (mg N/L)	*		0.917	*	*		0.705	*
TDP (mg P/L)	0.0215	F**	0.011	195.5	0.0283	F	0.019	148.9
TDP (mg P/L)	0.0661	F**	0.048	137.7	0.0554	F	0.038	145.8
NH4 (mg N/L)	0.037	W	0.042	88.1	0.0264	F	0.021	125.7
NH4 (mg N/L)	0.248		0.254	97.6	0.211		0.212	99.5
NO2+NO3 (mg N/L)	0.0907	F	0.07	129.6	0.0202	F	0.014	144.3
NO2+NO3 (mg N/L)	0.887		0.84	105.6	0.664		0.7	94.9
PO4 (mg P/L)	0.00516	F**	0.003	172	0.0075		0.007	107.1
PO4 (mg P/L)	0.0549	F**	0.045	122	0.03	W	0.037	81.1
PC (mg C/L)	*		NA	NA	*		NA	NA
PN (mg N/L)	*		NA	NA	*		NA	NA
PP (mg P/L)	*		NA	NA	*		NA	NA
CHLA (ug/L)	*		NA	NA	*		NA	NA
DOC (mg C/L)	1.99		1.995	99.7	3.05		2.992	101.9
DOC (mg C/L)	5.17		4.987	103.7	6.96		6.982	99.7
TSS (mg/L)	25.7		25	102.8	30.7		30	102.3

\* No sample sent to participant - sample not requested, parameter or concentration range not routine

\*\* Prepared sample concentration suspect

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

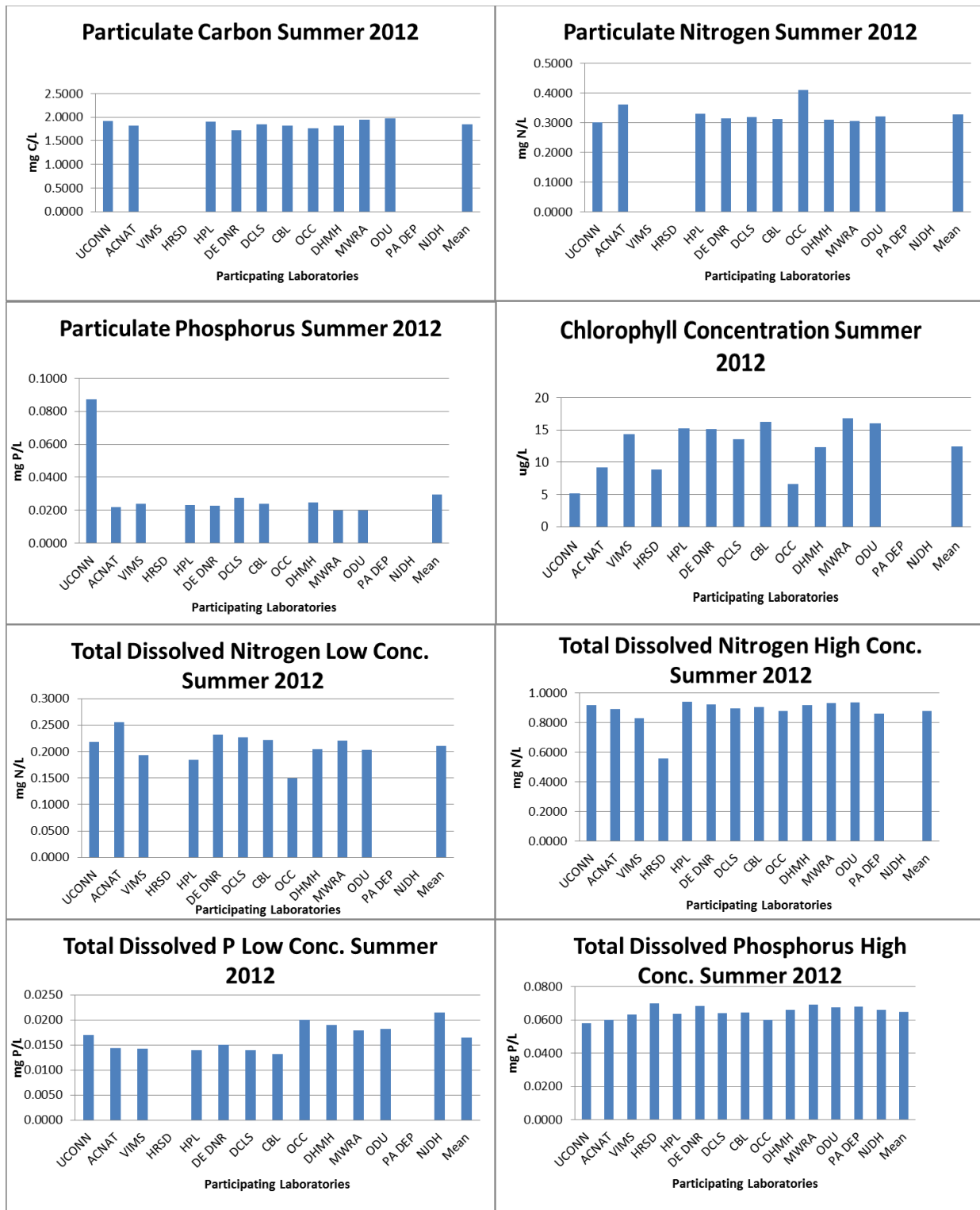


Figure 1. Particulate carbon, nitrogen and phosphorus; Chlorophyll a, and total dissolved nitrogen and phosphorus. Summer 2012

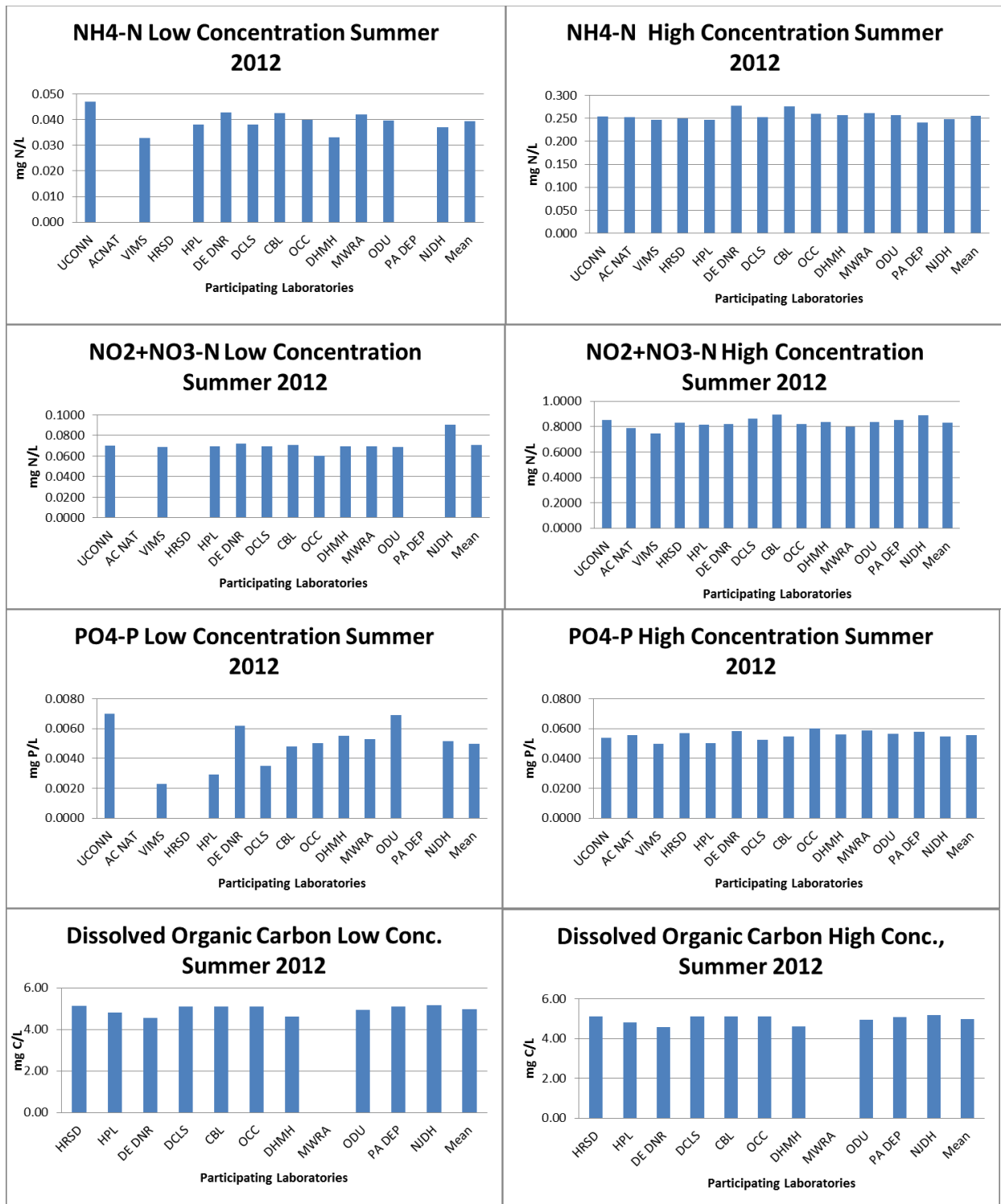


Figure 2. Dissolved inorganic nitrogen and phosphorus; dissolved organic carbon, Summer 2012

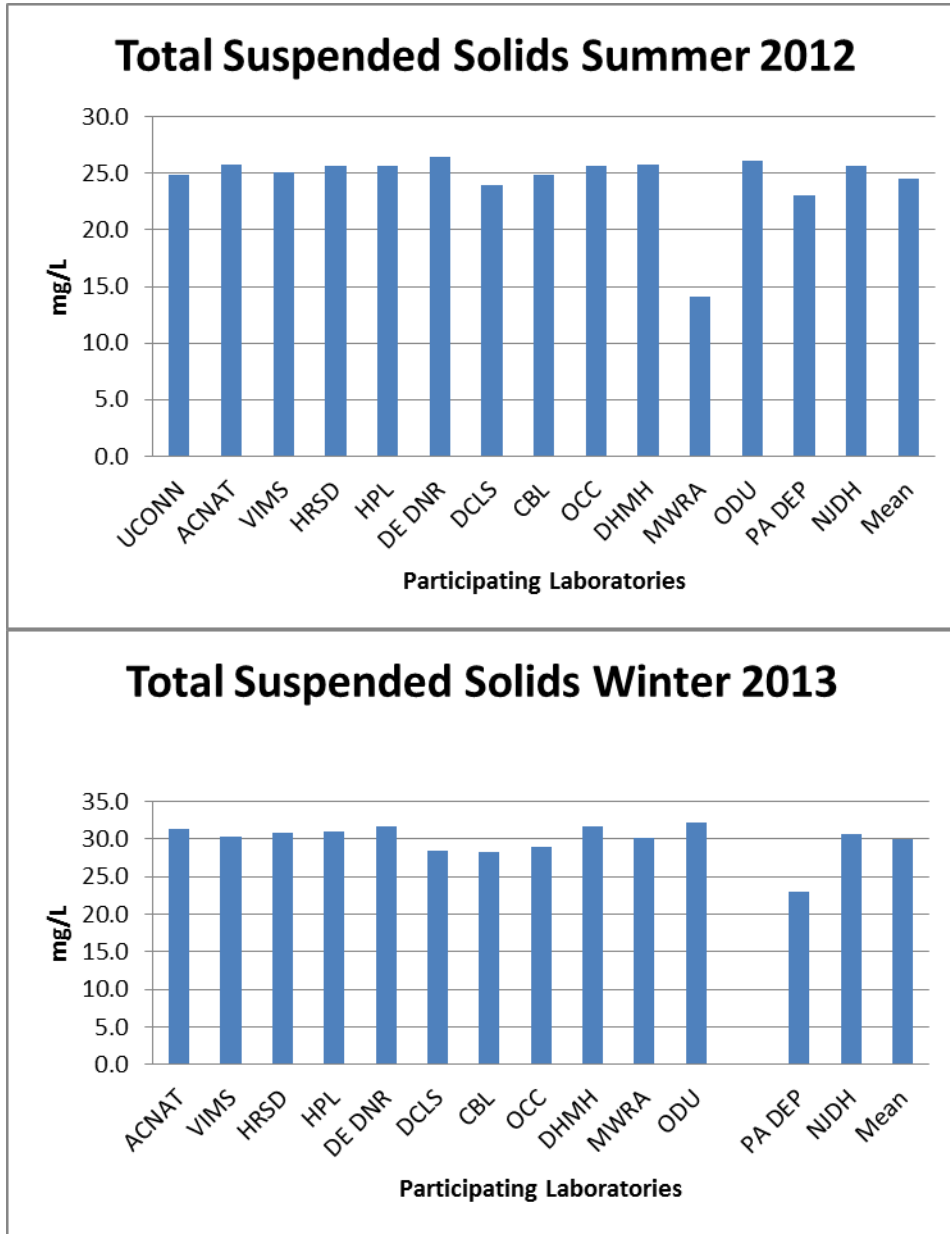


Figure 3. Total suspended solids, summer 2012 & winter 2013

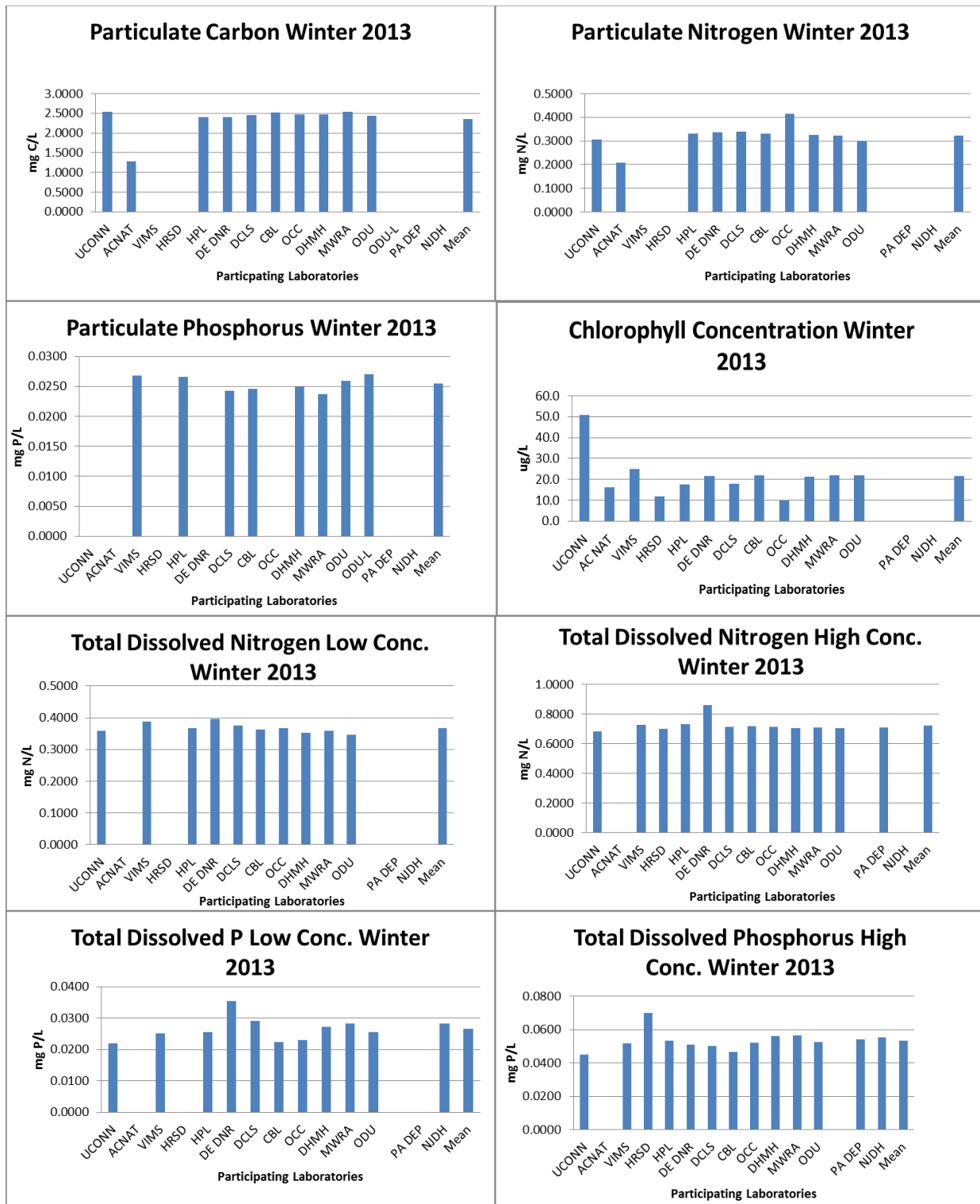


Figure 4. Particulate carbon, nitrogen and phosphorus; Chlorophyll a, and total dissolved nitrogen and phosphorus. Winter 2013



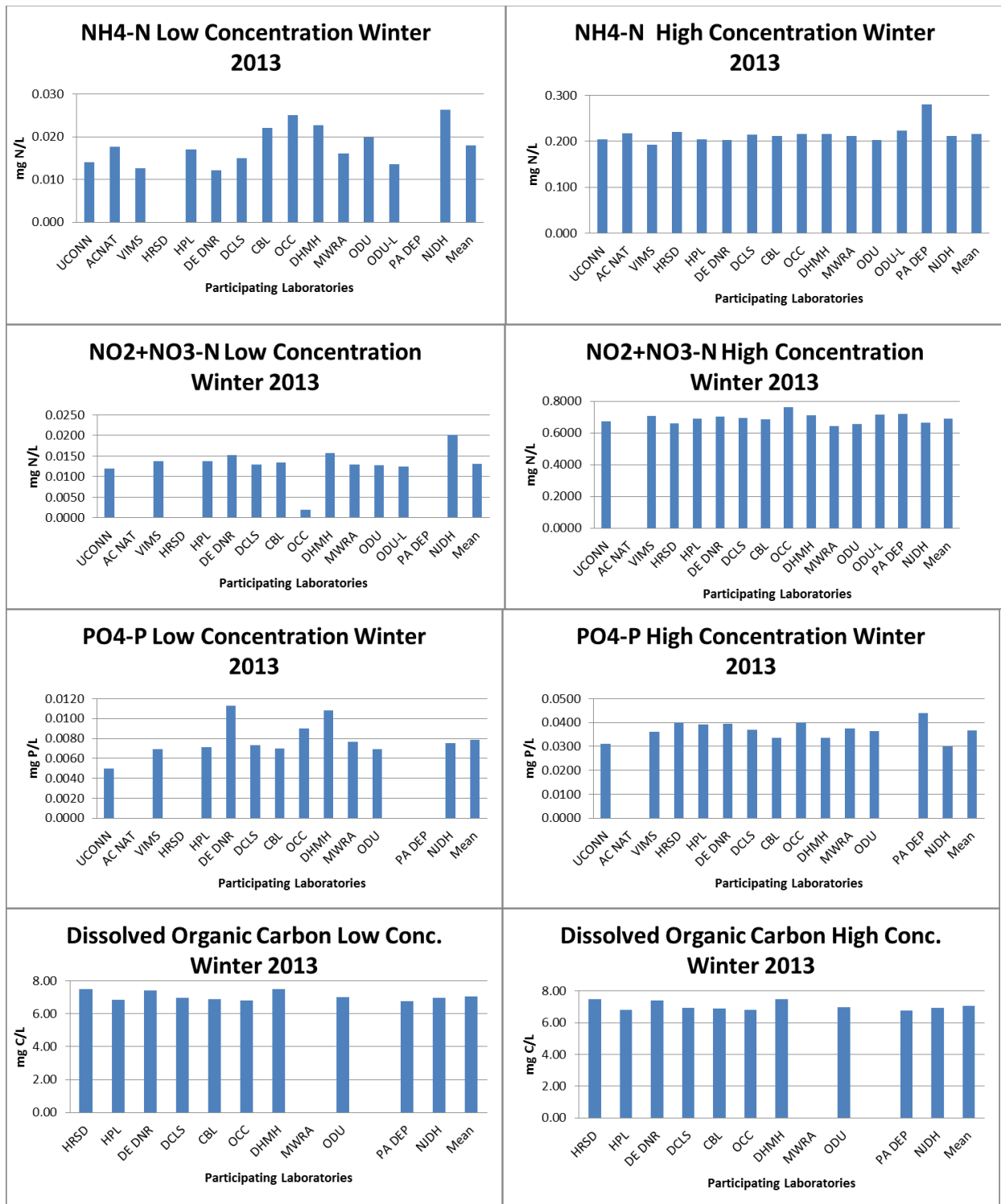


Figure 5. Dissolved inorganic nitrogen and phosphorus; dissolved organic carbon, Winter 2013