Ref. No. [UMCES]CBL 08-048

FINAL REPORT

CHESAPEAKE BAY PROGRAM BLIND AUDIT

Fiscal Year 2008 Final Report

PREPARED FOR:

Maryland Department of Natural Resources
Resource Assessment Administration
Water and Habitat Quality Program
580 Taylor Avenue
Tawes State Office Building
Annapolis, MD 21401

SUBMITTED BY:

Carl F. Zimmermann, Senior FRA Program Coordinator
and
Carolyn Keefe, Senior Faculty Research Assistant

Chesapeake Biological Laboratory
University of Maryland Center for Environmental Science
P.O. Box 38
Solomons, MD 20688-0038

June 2008

Technical Report Series No. TS-554-08
of the University of Maryland Center for Environmental Science

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICES

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 NH4-N/L would be comparable to 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 tenth 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 15 August 2007 and 28 January 2008. Participating laboratories and contact personnel are found in Table 1.

Parameters measured were: total dissolved nitrogen (organic N), total dissolved phosphorus (organic P), nitrate+nitrite, ammonium, phosphate 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 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 (Potassium hydrogen phthalate), 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 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 2007 and winter 2008 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. 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: For the prepared high level concentrations, most participants reported approximately the same concentration. For the low level concentration, there was slightly more variability between participants and from the prepared concentration. One participant's result for the low concentration sample from both audits was lower than results for all other participants and, also, 16% and 26% less than the prepared concentrations. Another participant's result for the low concentration sample from both audits was higher than results for all other participants and, also, 17 and 33% more than the prepared concentrations.

Total Dissolved Phosphorus: With the exception of one participant's result for the low concentration from the winter 2008 audit, results for all the audits (both low and high concentrations) had approximately the same agreement with the prepared concentration and between the participants. The variation of the data reported by participants for the low level winter 2008 audit was somewhat larger, i.e., the proportion of the standard deviation to the mean of the reported low level data was a bit large, and so was the divergence from the prepared concentration.

Ammonium: With the exception of one participant, results for both concentrations of ammonium sample for the summer 2007 audit had close agreement between participants. There was little divergence between participants for the winter 2008 audits, although most reported concentrations for the low concentration were 10-14% below the prepared concentration. The variation between the reported and prepared concentration for the low level ammonium winter 2008 audit was a bit less than in the past 4 years.

Nitrate + Nitrite: For the prepared high level concentrations of nitrate + nitrite, most participants reported approximately the same concentration. For the low level nitrate + nitrite concentration, there was slightly more variability between participants and from the prepared concentration.

Orthophosphate: For the prepared high level concentrations of orthophosphate, most participants reported approximately the same concentration and with little variability from the prepared concentration. For the low level orthophosphate concentration audits, there was considerable variability between participants and from the prepared concentration. For the summer 2007 low level concentration, no participant reported a concentration within ± 10% of the prepared concentration. More of the reported values were greater than the prepared concentration of 0.0074 mg P/L. The mean of the reported concentrations was 0.0097 mg P/L, S.D. 0.0034, CV 34%.

Dissolved Organic Carbon: For both audits, there was generally approximately the same agreement with the prepared concentration and between participants. For both concentrations for the winter 2008 audit, two participants reported concentrations that were about 30% higher than the prepared concentration.

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 Figs. 1 and 5. Particulate Carbon: Particulate C results for both audits revealed close agreement between all participating laboratories (Table 2). Again, this is remarkably close agreement for multi-laboratory comparison of samples of a natural population!

Particulate Nitrogen: Particulate N results for both audits revealed close agreement between all participating laboratories (Table 2). One laboratory was biased about 7% lower than the mean for the summer 2007 audit, and about 10% higher than the mean for the winter 2008 audit.

Particulate Phosphorus: Particulate P results for both audits revealed very close agreement between all participating laboratories (Table 2). As in past years, this was remarkably close agreement for comparison of samples of a natural population by multiple laboratories.

Chlorophyll: Chlorophyll results for both audits displayed the usual close agreement that was remarkable for multi-laboratory comparison of such low concentrations of an environmentally transitory compound. One laboratory's data for both audits were considerably different from all other participants' data. Their summer 2007 reported concentration was about an order of magnitude lower than the other participants' data. Their winter 2008 reported concentration was about triple the other participants' data.

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 2007 sample, 14.0 mg/L was prepared, and there was a consistent slight negative bias reported by most participants. For the winter 2008 sample, 20.0 mg/L was prepared but, there was, again, a consistent negative bias reported by most participants. The negative bias reported for these two audits was less than in past years. There was less variability between results of both audits than reported by participants in most previous audits.

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 $\pm$ 2 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 2 standard deviations "pass", and those greater than 3 standard deviations "fail". Results between 2 and 3 standard deviations are in the "warning" category.

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 one value in the entire study fell in the "fail" category.

Data sets with relatively small standard deviations yielded more potentially extraneous "warning" points. For example, in the summer 2007 blind audit of high level nitrate+nitrite concentration, the mean reported concentration was 0.619 mg N/L and reported concentrations ranged from 0.556-.634 mg N/L. The coefficient of variation was ONLY 2.1%! Eleven laboratories reported results for this high level sample that were within two standard deviations (S.D. $\pm$ 0.0130 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 "fail," although all of the reported data were within $\pm$12% of the prepared concentration. Thus, by that measure of accuracy, most of the data "passed" and one was "warned." This nitrate+nitrite 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.

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 $\pm$10% of the prepared concentration were listed as "pass." Reported data that were 80-90% or 110 -120% of the prepared concentration were listed as "warn." Reported data that were <80% or >120% of the prepared concentration were listed 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, the summer 2007 blind audit of 0.0074 mg P/L prepared for orthophosphate has a "pass" category ($\pm$10%) of only 0.0067 - 0.0081 mg P/L. All nine participating laboratories reported results that fell in the "warn" and "fail" categories, indicating that their reported concentrations were greater than $\pm$10% of the prepared concentration in this low range. These results could be interpreted as an inability for all participants to accurately measure low level orthophosphate 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 low level orthophosphate summer 2006 reported data based on comparisons

with other participants (mean 0.0098, S.D. 0.0018, C.V. 18.5%).

As with all past blind audits, the standard deviations for the low level ammonium samples were less than those for the higher level ammonium samples. The proportions of the standard deviations to the means for the low level ammonium samples were not as large as they have been for the last few years; i.e., coefficients of variation were 14% for 0.029 mg NH4-N/L (Summer 2007) and 11% for 0.036 mg NH4-N/L (Winter 2008). The coefficient of variation was 16% for 0.042 mg NH4-N/L (Summer 2006) and 39% for 0.036 mg NH4-N/L (Winter 2007). The reduced variation in reported concentrations of low level ammonium for these blind audits probably indicates that inter-laboratory comparisons of any ammonium data prepared by laboratories from concentrates below 0.031 mg N/L, although somewhat unreliable, have improved over the past few years.

There were twelve instances where concentrations reported for dissolved constituents 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 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 concentration for particulate carbon, nitrogen and phosphorus for both the summer 2007 and winter 2008 audits.

Data for particulate nitrogen at one laboratory for both these audits fell in the "warn" category based on the VERY SMALL standard deviations of the reported data. For the blind audit in summer 2007 was about 7% less than the concentration reported by the other participants. However, in winter 2008, that laboratory's reported concentration was about 10% higher than the other participants' data.

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 summer 2007 was approximately 2.35 mg C/L.

The proportions of the standard deviations to the means for particulate phosphorus were low (6%) for the summer 2007 blind audit, and for the winter 2008 blind audit (10%). The proportion of the standard deviation to the mean had been high for particulate phosphorus in both 2002 blind audits. This contrasted to most previous years of blind audits in which the coefficient of variation for particulate phosphorus was the lowest of the particulate fractions. In both 2002 blind audits, one or two laboratories' reported concentrations were visibly different from the mean, thus increasing the coefficient of variation. The sample sizes were only five or seven, so it was not surprising that these differences were insufficient to generate a warning. These particulate phosphorus data comparisons are an obvious example of the danger 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. New participants had been added to the blind audit program in 2001 and 2002; however, no laboratory expressed uncertainty in its reported particulate phosphorus concentrations. No laboratory reported concentrations for particulate phosphorus that were consistently different from the range of the other reported concentrations for both 2002 blind audits. All participants' reported concentrations were quite similar for the winter 2003 through winter 2008 blind audits, leading us to conclude that inter-laboratory comparison of other particulate phosphorus data would be valid.

Reporting Data Accurately: Data originally reported by all participants for both these blind audits appeared, on casual inspection, to be reported accurately. In fact, no participant noted any discrepancies when all were contacted to review their data. For the FIRST TIME EVER 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 have improved their reporting practices! Other subtle entry or calculation errors may have gone undetected.

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, 2002, 2003, 2005, 2006, 2007 and winter 2008 participants reported only two significant digits for some analytes, thus potentially giving substantial under or over estimates for the comparisons.

CONCLUSION

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

1. Reported concentrations of analytes were usually similar between laboratories participating in the Blind Audit Program. With the exception of chlorophyll, 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 execute and report these measurements with accuracy and precision, reporting the appropriate number of significant digits.

2. 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, orthophosphate and total dissolved phosphorus. 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.

3. The variation in reported concentrations of low level ammonium for both these blind audits, and several previous audits, probably indicates that inter-laboratory comparisons of any ammonium data prepared from concentrates with resultant concentrations below 0.031 mg N/L would be unreliable. It would be important to know if there is also a difficulty in measuring natural low level samples.

4. For all participating laboratories, there was remarkable consistency in the measurement of total suspended solids from suspensions of infusorial earth; however, there was consistent, slight negative bias in the measurements, when compared to the prepared concentrations. This occurred in past years as well, but the negative bias for these audits was less than in the past.

5. 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 other particulate phosphorus data should be valid. The proportion of the standard deviation to the mean had been high for particulate phosphorus in both blind audits in 2001 and 2002. This contrasted to all three previous years, in which the coefficient of variation for particulate phosphorus was usually the lowest of the particulate fractions.

6. Care should continue to be taken when completing report forms. For the summer 2007 and winter 2008 blind audits, some results were AGAIN (!) reported with insufficient significant digits. For both these blind audit, no results were reported and then later corrected. Over the course of the years, a few laboratories had repeatedly made calculation 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 2007 and Winter 2008 Blind Audit Program.

Institution	Contact Person	Phone	Dissolved	Particulate	Chlorophyll a	DOC	TSS
Old Dominion University, Water Quality Lab, (ODU)	Suzanne Doughton	757-451-3044	X	X	X		X
University of MD, Horn Point Laboratory (HPL)	Lois Lane	410-221-8252	X	X	X	X	X
Virginia Institute of Marine Science (VIMS)	Carol Pollard	804-684-7213	X	X	X		X
Virginia Div, Consolidated Lab Services (DCLS)	Jay Armstrong	804-648-4480 x328	X	X	X	X	X
MD Dept Health and Mental Hygiene (DHMH)	Asoka Katumuluwa	410-767-5034	X	X	X	X	X
Univ. of MD Chesapeake Bio Lab (CBL)	Carl Zimmermann	410-326-7252	X	X	X	X	X
University of Delaware (UDEL)	Joe Scudlark	302-645-4300	X				
Delaware Dept. of Natural Resources (DELDNR)	Ben Pressly	302-739-9942	X	X	X	X	X
Morgan State University. Estuarine Research Center (ANSERC)	Richard Lacouture	410-586-9721			X		
Academy of Natural Science of Philadelphia (PAACAD)	Paul Kiry	215-299-1076	X	X	X	X	X
PA DEP, Bureau of Laboratories (PADEP)	James Yoder	717-346-7200	X				X
MWRA, Water Quality Laboratory (MWRA)	Jennifer Prasse	617-660-7808	X	X	X	X	X
Hampton Roads Sanitation District (HRSD)	Stacie Metzler	757-460-4217	X			X	X

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Summer 2007 and the Winter 2008 Blind Audit, Including Distribution of Reported Concentrations from the Mean.

Parameter	Concentration in mg/L		Number of Laboratories			
			Standard Deviations from Mean			
			<1	1-2	2-3	>3
	Mean	S.D.	PASS	PASS	WARN	FAIL
Summer 2007						
Total Dissolved Nitrogen	0.359	0.045	6	3		
Total Dissolved Nitrogen	0.829	0.079	8	2	1	
Total Dissolved Phosphorus	0.0231	0.0023	6	3		
Total Dissolved Phosphorus	0.0359	0.0026	5	6		
Ammonium	0.0242	0.0034	7		1	
Ammonium	0.110	0.0194	9		1	
Nitrate + Nitrite	0.0482	0.0032	7	1	1	
Nitrate + Nitrite	0.619	0.0130	8	2		1
Orthophosphate	0.0097	0.0034	6	3		
Orthophosphate	0.0513	0.0022	6	5		
Dissolved Organic Carbon	2.93	0.203	6	2	1	
Dissolved Organic Carbon						
Particulate Carbon	2.35	0.0645	6	3		
Particulate Nitrogen	0.430	0.0111	7	1	1	
Particulate Phosphorus	0.0365	0.0023	5	4		
Total Suspended Solids	13.1	0.81	8	1	1	
Winter 2008						
Total Dissolved Nitrogen	0.309	0.047	7	2		
Total Dissolved Nitrogen	0.808	0.110	8	3		
Total Dissolved Phosphorus	0.0128	0.0014	8		1	
Total Dissolved Phosphorus	0.0365	0.0025	7	4		
Ammonium	0.0308	0.0035	8	1	1	
Ammonium	0.162	0.0179	10	1	1	
Nitrate + Nitrite	0.0349	0.0048	5	5		
Nitrate + Nitrite	0.637	0.0419	9	2	1	
Orthophosphate	0.0093	0.0013	8	1	1	
Orthophosphate	0.0152	0.0012	10	1	1	
Dissolved Organic Carbon	2.36	0.241	7		1	
Dissolved Organic Carbon	3.23	0.441	5	3		
Particulate Carbon	1.45	0.031	6	3		
Particulate Nitrogen	0.180	0.0096	6	2	1	
Particulate Phosphorus	0.0152	0.0015	7	1	1	
Total Suspended Solids	18.2	0.96	8	3		

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

			Number of Laboratories		
Parameter	Prepared Concentration mg/L	Reported Concentration Range mg/L	Within 90% - 110% of Prepared Concentration	Within 80 -90%, or 110-120% of Prepared Concentration	<80%, or >120% of Prepared Concentration
			PASS	WARN	FAIL
Summer 2007					
Total Dissolved Nitrogen	0.355	0.298-0.435	5	3	1
Total Dissolved Nitrogen	0.824	0.732-.988	8	3	
Total Dissolved Phosphorus	0.0211	0.0195-0.0265	6	1	2
Total Dissolved Phosphorus	0.0336	0.0326-0.04	7	4	
Ammonium	0.029**	0.0171-0.0268	2	4	2
Ammonium	0.122	0.058-0.124	7	2	1
Nitrate + Nitrite	0.0490	0.0412-0.0517	5	1	
Nitrate + Nitrite	0.630	0.556-0.634	7	1	
Orthophosphate	0.0074**	0.005-0.015		3	6
Orthophosphate	0.0484	0.0489-0.0552	9	1	
Dissolved Organic Carbon	2.80	2.49-3.17	6	3	
Dissolved Organic Carbon					
Total Suspended Solids	14.0	11.8-15.0	8	2	
Winter 2008					
Total Dissolved Nitrogen	0.298	0.226-.395	6	1	2
Total Dissolved Nitrogen	0.753	0.662-1.02	7	2	2
Total Dissolved Phosphorus	0.0115**	0.0096-0.014	2	6	1
Total Dissolved Phosphorus	0.0346	0.032-0.04	7	4	
Ammonium	0.036**	0.026-0.039	1	7	2
Ammonium	0.168	0.11-0.181	11		1
Nitrate + Nitrite	0.0350	0.0274-0.042	5	4	1
Nitrate + Nitrite	0.630	0.593-0.742	10	2	
Orthophosphate	0.0089**	0.0075-0.012	6	3	1
Orthophosphate	0.0149	0.0136-0.018	11		1
Dissolved Organic Carbon	2.20	2.158-2.9	6	1	1
Dissolved Organic Carbon	3.00	2.778-4.02	6		2
Total Suspended Solids	20.0	16.9-20	7	4	

**For very low concentrations of prepared samples, it may be appropriate to broaden the acceptance boundaries.

Appendix 1. Summer 2007 and Winter 2008 Reported Data, Prepared Concentrations and Percent Recoveries. Warnings based on standard deviation of the mean of reported concentrations are listed.

Virginia Institute of Marine Science

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.2979	.355	83.8	.2261	.298	75.9
TDN (mg N/L)	.7891	.824	95.8	.7148	.753	94.9
TDP (mg P/L)	.0261	.0211	123.7	.0096 WARN	.0115**	83.5
TDP (mg P/L)	.0361	.0336	107.4	.0320	.0346	92.5
NH4 (mg N/L)	.0256	.029**	88.3	.0294	.036**	81.7
NH4 (mg N/L)	.1126	.122	92.3	.1577	.168	93.9
NO3 + NO2 (mg N/L)	.0458	.0490	93.5	.0274	.0350	78.3
NO3 + NO2 (mg N/L)	.6067	.630	96.3	.6393	.630	101.5
PO4 (mg P/L)	.0098	.0074**	132.4	.0105	.0089**	118.0
PO4 (mg P/L)	.0529	.0484	109.3	.0153	.0149	102.7
Particulate C (mg C/L)	2.379			1.505		
Particulate N (mg N/L)	.4195			.1780		
Particulate P (mg P/L)	.0347			.0166		
Chlorophyll (µg/L)				9.445		
Total Suspended Solids (mg/L)	13.25	14.0	94.6	17.45	20.0	87.2

**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.
"WARN" based on standard deviation of all participants' reported concentrations

Appendix I. *Continued*

Delaware DNR

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.435	.355	122.5	.349	.298	117.1
TDN (mg N/L)	.988 WARN	.824	119.9	.809	.753	107.4
TDP (mg P/L)	.0265	.0211	125.6	.013	.0115**	113.0
TDP (mg P/L)	.0388	.0336	115.5	.036	.0346	104.0
NH4 (mg N/L)		.029**		.039 WARN	.036**	108.3
NH4 (mg N/L)		.122		.181	.168	107.7
NO3 + NO2 (mg N/L)	.050	.0490	102.0	.042	.0350	120.0
NO3 + NO2 (mg N/L)	.556 FAIL	.630	88.3	.623	.630	98.9
PO4 (mg P/L)	.015	.0074**	202.7	.012 WARN	.0089**	134.8
PO4 (mg P/L)	.055	.0484	113.6	.018 WARN	.0149	120.8
Particulate C (mg C/L)	2.43			1.47		
Particulate N (mg N/L)	.441			.180		
Particulate P (mg P/L)	.0337			.0121 WARN		
Chlorophyll (µg/L)	13.85			11.0		
DOC (mg C/L)	3.14	2.80	112.1	2.21	2.20	100.5
DOC (mg C/L)				2.98	3.00	99.3
Total Suspended Solids (mg/L)	13.0	14.0	92.9	19.0	20.0	95.0

**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.
"WARN" based on standard deviation of all participants' reported concentrations.

Appendix I. *Continued.*

University of Delaware

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
NH4 (mg N/L)				.030	.036**	83.3
NH4 (mg N/L)				.167	.168	99.4
NO3 + NO2 (mg N/L)				.032	.0350	91.4
NO3 + NO2 (mg N/L)				.621	.630	98.6
PO4 (mg P/L)				.0095	.0089**	106.7
PO4 (mg P/L)				.016	.0149	107.4

Academy of Natural Sciences of Philadelphia

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.314	.355	88.5	.271	.298	90.9
TDN (mg N/L)	.732	.824	88.8	.662	.753	87.9
TDP (mg P/L)	.0195	.0211	92.4	.0124	.0115**	107.8
TDP (mg P/L)	.0326	.0336	97.0	.0336	.0346	97.1
NH4 (mg N/L)	.0251	.029**	86.6	.0310	.036**	86.1
NH4 (mg N/L)	.119	.122	97.5	.162	.168	96.4
NO3 + NO2 (mg N/L)	.0412 WARN	.0490	84.1	.0290	.0350	82.9
NO3 + NO2 (mg N/L)	.5962	.630	94.6	.593	.630	94.1
PO4 (mg P/L)	.00841	.0074**	113.6	.0075	.0089**	84.3
PO4 (mg P/L)	.0493	.0484	101.9	.0136	.0149	91.3
Particulate C (mg C/L)	2.23			1.47		
Particulate N (mg N/L)	.407 WARN			.1995 WARN		
Particulate P (mg P/L)	.0370			.01535		
Chlorophyll (µg/L)	8.94			6.08		
Total Suspended Solids (mg/L)	12.4	14.0	88.6	16.9	20.0	84.5

**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.
"WARN" based on standard deviation of all participants' reported concentrations

Appendix I. *Continued.*

Morgan State University Estuarine Research Center

Parameter	Summer 2007 Reported		% Recovered	Winter 2008 Reported		% Recovered
Chlorophyll (µg/L)				6.9		

Old Dominion University

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.364	.355	102.5	.313	.298	105.0
TDN (mg N/L)	.793	.824	96.2	.757	.753	100.5
TDP (mg P/L)	.0212	.0211	100.5	.0130	.0115**	113.0
TDP (mg P/L)	.0330	.0336	98.2	.0364	.0346	105.2
NH4 (mg N/L)	.0210	.029**	72.4	.0322	.036**	89.4
NH4 (mg N/L)	.1157	.122	94.8	.1709	.168	101.7
NO3 + NO2 (mg N/L)	.0478	.0490	97.6	.0365	.0350	104.3
NO3 + NO2 (mg N/L)	.630	.630	100.0	.6988	.630	110.9
PO4 (mg P/L)	.0090	.0074**	121.6	.0095	.0089**	106.7
PO4 (mg P/L)	.0524	.0484	108.3	.0149	.0149	100.0
Particulate C (mg C/L)	2.41			1.4145		
Particulate N (mg N/L)	.434			.1682		
Particulate P (mg P/L)	.0379			.01585		
Chlorophyll (µg/L)	11.32			10.04		
DOC (mg C/L)	2.88	2.80	102.9	2.158	2.20	98.1
DOC (mg C/L)				2.778	3.00	92.6
Total Suspended Solids (mg/L)	13.38	14.0	95.6	18.32	20.0	91.6

Appendix I. *Continued.*

Virginia Division of Consolidated Laboratory Services

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.341	.355	96.1	.310	.298	104.0
TDN (mg N/L)	.800	.824	97.1	.755	.753	100.3
TDP (mg P/L)	.022	.0211	104.3	.014	.0115**	121.7
TDP (mg P/L)	.036	.0336	107.1	.035	.0346	101.2
NH4 (mg N/L)	.025	.029**	86.2	.029	.036**	80.6
NH4 (mg N/L)	.118	.122	96.7	.157	.168	93.5
NO3 + NO2 (mg N/L)	.050	.0490	102.0	.033	.0350	94.3
NO3 + NO2 (mg N/L)	.628	.630	99.7	.610	.630	96.8
PO4 (mg P/L)	.011	.0074**	148.6	.010	.0089**	112.4
PO4 (mg P/L)	.050	.0484	103.3	.015	.0149	100.7
Particulate C (mg C/L)	2.358			1.435		
Particulate N (mg N/L)	.432			.1795		
Particulate P (mg P/L)	.0392			.0148		
Chlorophyll (µg/L)	11.32			7.07		
DOC (mg C/L)	2.49 WARN	2.80	88.9		2.20	
DOC (mg C/L)					3.00	
Total Suspended Solids (mg/L)		14.0		19.0	20.0	95.0

**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.
"WARN" based on standard deviation of all participants' reported concentrations

Appendix I. *Continued.*

Hampton Roads Sanitation District

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.83	.824	100.7	1.02	.753	135.5
TDP (mg P/L)	.04	.0336	119.0	.04	.0346	115.6
NH4 (mg N/L)	.10	.122	82.0	.11 WARN	.168	65.5
NO3 + NO2 (mg N/L)	.63	.630	100.0	.63	.630	100.0
PO4 (mg P/L)	.049	.0484	101.2	.016	.0149	107.4
DOC (mg C/L)	3.17	2.80	113.2	2.90 WARN	2.20	131.8
DOC (mg C/L)				3.80	3.00	126.7
Total Suspended Solids (mg/L)	13.0	14.0	92.9	19.0	20.0	95.0

**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.
"WARN" based on standard deviation of all participants' reported concentrations

PADEP Water Quality Laboratory

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.85	.824	103.2	.75	.753	99.6
TDP (mg P/L)	.033	.0336	98.2	.035	.0346	101.2
NH4 (mg N/L)	.11	.122	90.2	.16	.168	95.2
NO3 + NO2 (mg N/L)	.63	.630	100.0	.62	.630	98.4
PO4 (mg P/L)	.049	.0484	101.2	.014	.0149	94.0
DOC (mg C/L)	2.87	2.80	102.5	2.26	2.20	102.7
DOC (mg C/L)				2.97	3.00	99.0
Total Suspended Solids (mg/L)	15.0 WARN	14.0	107.1	20.0	20.0	100.0

**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.
"WARN" based on standard deviation of all participants' reported concentrations

Appendix I. *Continued.*

UMCES Horn Point Laboratory

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.416	.355	117.2	.395	.298	132.6
TDN (mg N/L)	.921	.824	111.8	.847	.753	112.5
TDP (mg P/L)	.0229	.0211	108.5	.0138	.0115**	120.0
TDP (mg P/L)	.037	.0336	110.1	.0397	.0346	114.7
NH4 (mg N/L)	.0267	.029**	92.1	.0323	.036**	89.7
NH4 (mg N/L)	.122	.122	100.0	.1755	.168	104.5
NO3 + NO2 (mg N/L)	.0493	.0490	100.6	.0343	.0350	98.0
NO3 + NO2 (mg N/L)	.6075	.630	96.4	.6071	.630	96.4
PO4 (mg P/L)	.0050	.0074**	67.6	.0084	.0089**	94.4
PO4 (mg P/L)	.0515	.0484	106.4	.0147	.0149	98.7
Particulate C (mg C/L)	2.33			1.471		
Particulate N (mg N/L)	.432			.1835		
Particulate P (mg P/L)	.0397			.01725		
Chlorophyll (μg/L)	1.13			26.50		
DOC (mg C/L)	2.82	2.80	100.7	2.201	2.20	100.0
DOC (mg C/L)				2.976	3.00	99.2
Total Suspended Solids (mg/L)	13.0	14.0	92.9	18.0	20.0	90.0

Appendix I. *Continued.*

UMCES Chesapeake Biological Laboratory

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.361	.355	101.7	.306	.298	102.7
TDN (mg N/L)	.807	.824	97.9	.772	.753	102.5
TDP (mg P/L)	.0223	.0211	105.7	.0137	.0115**	119.1
TDP (mg P/L)	.0346	.0336	103.0	.0382	.0346	110.4
NH4 (mg N/L)	.026	.029**	89.7	.026	.036**	72.2
NH4 (mg N/L)	.117	.122	95.9	.168	.168	100.0
NO3 + NO2 (mg N/L)	.0509	.0490	103.9	.040	.0350	114.3
NO3 + NO2 (mg N/L)	.634	.630	100.6	.742 WARN	.630	117.8
PO4 (mg P/L)	.0063	.0074**	85.1	.0085	.0089**	95.5
PO4 (mg P/L)	.0489	.0484	101.0	.0141	.0149	94.6
Particulate C (mg C/L)	2.28			1.43		
Particulate N (mg N/L)	.435			.184		
Particulate P (mg P/L)	.0339			.0157		
Chlorophyll (μg/L)	11.12			9.71		
DOC (mg C/L)	3.02	2.80	107.9	2.39	2.20	108.6
DOC (mg C/L)				3.23	3.00	107.7
Total Suspended Solids (mg/L)	13.2	14.0	94.3	18.3	20.0	91.5

**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.
"WARN" based on standard deviation of all participants' reported concentrations

Appendix I. *Continued.*

MD DHMH Division of Environmental Chemistry Nutrients Laboratory

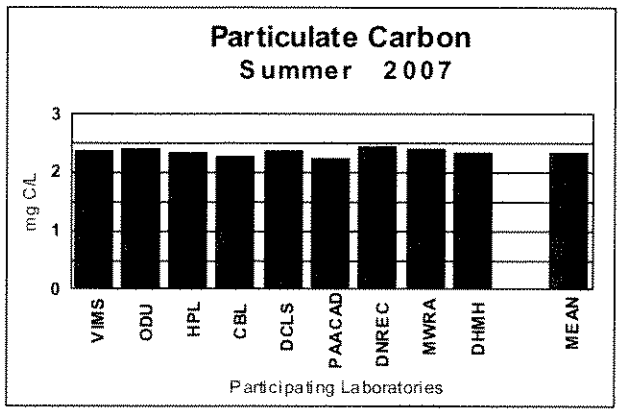
Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.329	.355	92.7	.289	.298	97.1
TDN (mg N/L)	.753	.824	91.4	.996	.753	132.3
TDP (mg P/L)	.0223	.0211	105.7	.0136	.0115**	118.3
TDP (mg P/L)	.0347	.0336	103.3	.0382	.0346	110.4
NH4 (mg N/L)	.0171 WARN	.029**	59.1	.0276	.036**	76.7
NH4 (mg N/L)	.0577 WARN	.122	47.3	.160	.168	95.2
NO3 + NO2 (mg N/L)	.0517	.0490	105.5	.0402	.0350	114.9
NO3 + NO2 (mg N/L)	.619	.630	98.3	.636	.630	101.0
PO4 (mg P/L)	.0145	.0074**	195.9	.00911	.0089**	102.4
PO4 (mg P/L)	.0525	.0484	108.5	.0155	.0149	104.0
Particulate C (mg C/L)	2.34			1.416		
Particulate N (mg N/L)	.443			.178		
Particulate P (mg P/L)	.0354			.0142		
Chlorophyll (µg/L)	10.76			7.95		
DOC (mg C/L)	2.93	2.80	104.6	2.28	2.20	103.6
DOC (mg C/L)				3.12	3.00	104.0
Total Suspended Solids (mg/L)	12.9	14.0	92.1	16.95	20.0	84.8

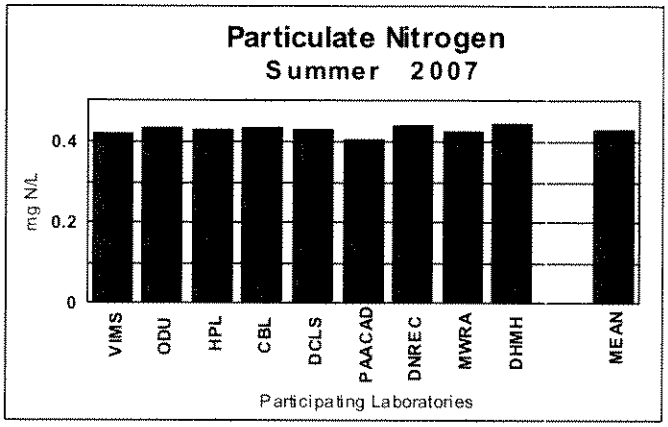
**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.
"WARN" based on standard deviation of all participants' reported concentrations

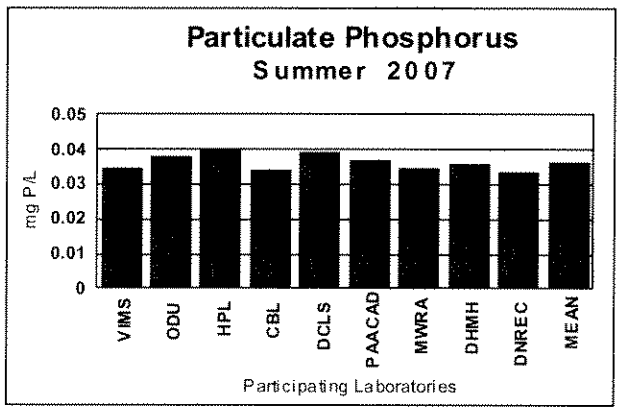
Appendix I. *Continued.*

MWRA Water Quality Laboratory

Parameter	Summer 2007 Reported	Summer 2007 Prepared	% Recovered	Winter 2008 Reported	Winter 2008 Prepared	% Recovered
TDN (mg N/L)	.376	.355	105.9	.318	.298	106.7
TDN (mg N/L)	.878	.824	106.6	.809	.753	107.4
TDP (mg P/L)	.0250	.0211	118.5	.0117	.0115**	101.7
TDP (mg P/L)	.0393	.0336	117.0	.0371	.0346	107.2
NH4 (mg N/L)	.0268	.029**	92.4	.0316	.036**	87.8
NH4 (mg N/L)	.124	.122	101.6	.172	.168	102.4
NO3 + NO2 (mg N/L)	.0470	.0490	95.9	.0350	.0350	100.0
NO3 + NO2 (mg N/L)	.620	.630	98.4	.625	.630	99.2
PO4 (mg P/L)	.00856	.0074**	115.7	.00809	.0089**	90.9
PO4 (mg P/L)	.0552	.0484	114.0	.0154	.0149	103.4
Particulate C (mg C/L)	2.395			1.43		
Particulate N (mg N/L)	.4255			.1665		
Particulate P (mg P/L)	.0348			.0149		
Chlorophyll (µg/L)	12.45			10.3		
DOC (mg C/L)	3.02	2.80	107.9	2.46	2.20	111.8
DOC (mg C/L)				4.02	3.00	134.0
Total Suspended Solids (mg/L)	11.8	14.0	84.3	17.8	20.0	89.0







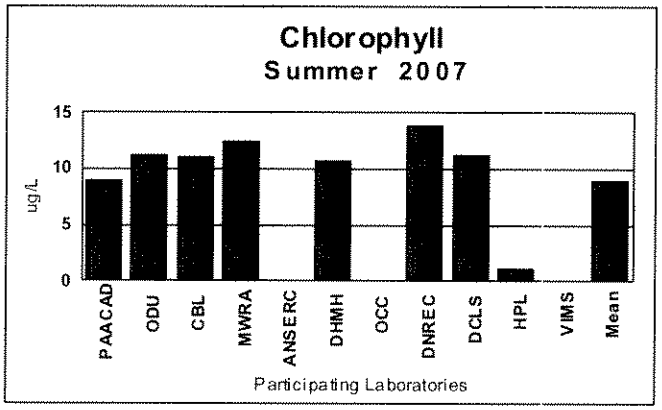
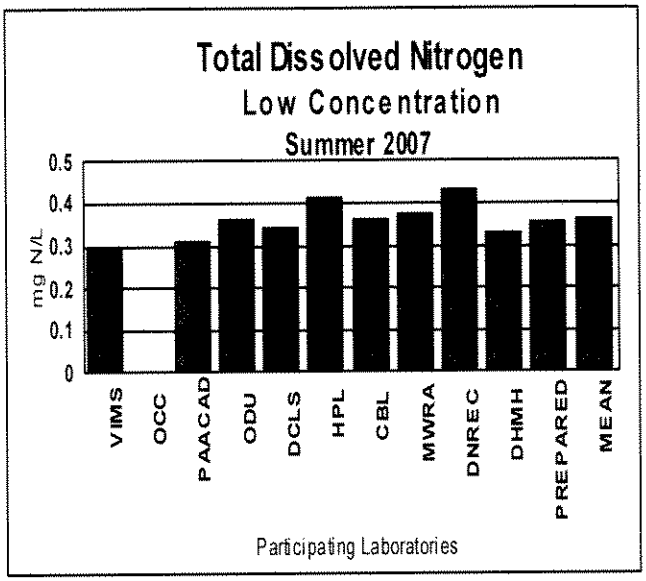
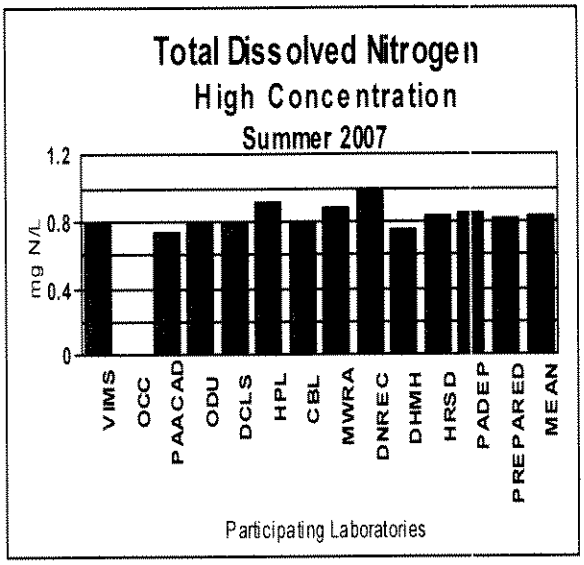
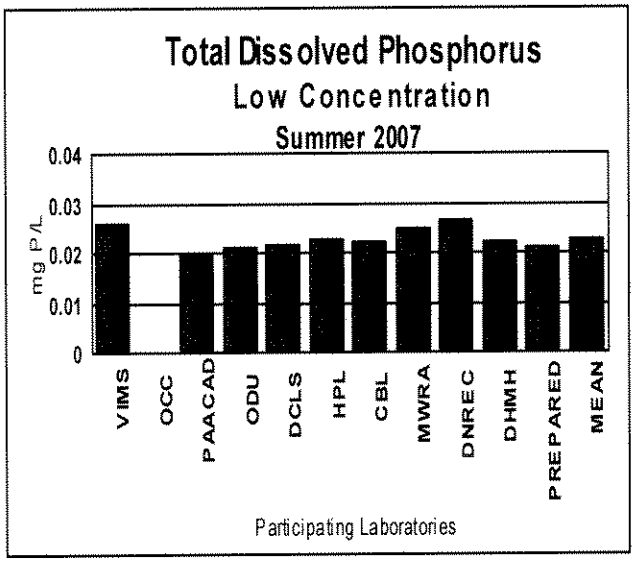


Figure 1. Particulate carbon, nitrogen and phosphorus; chlorophyll, Summer 2007.







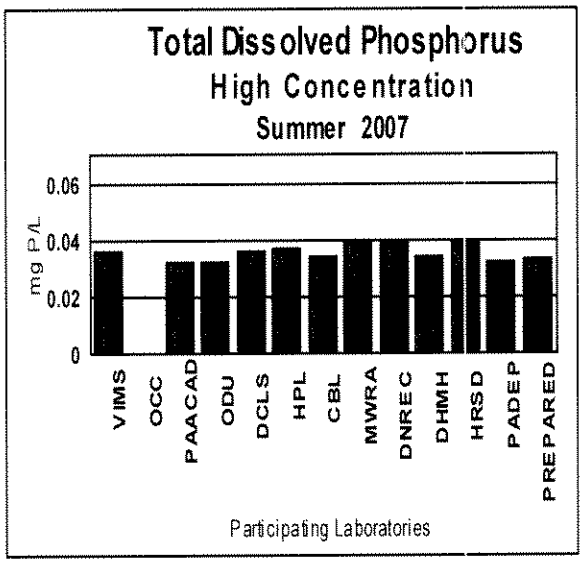


Figure 2. Total dissolved nitrogen and phosphorus, Summer 2007.

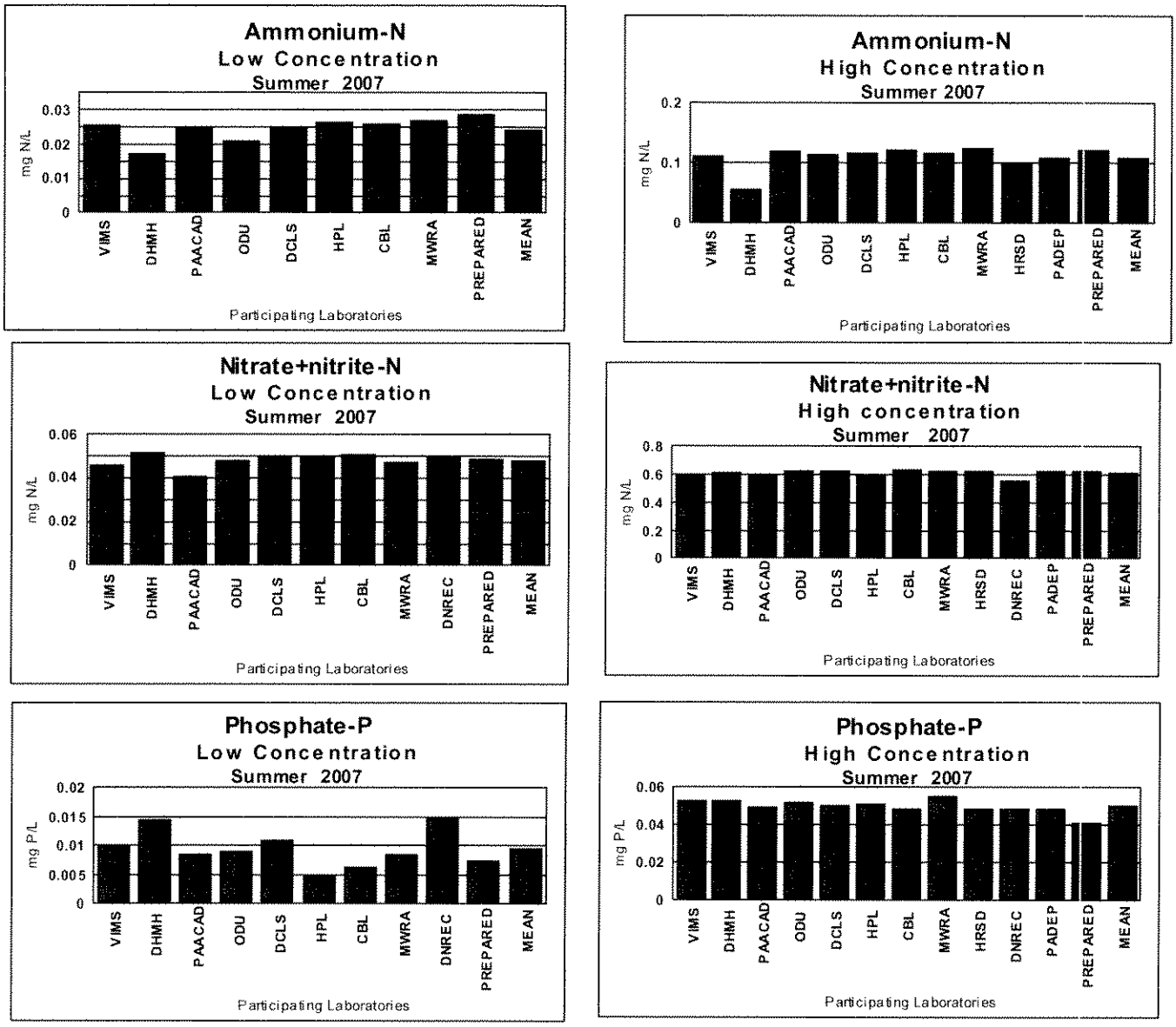


Figure 3. Dissolved inorganic nitrogen and phosphorus, Summer 2007.

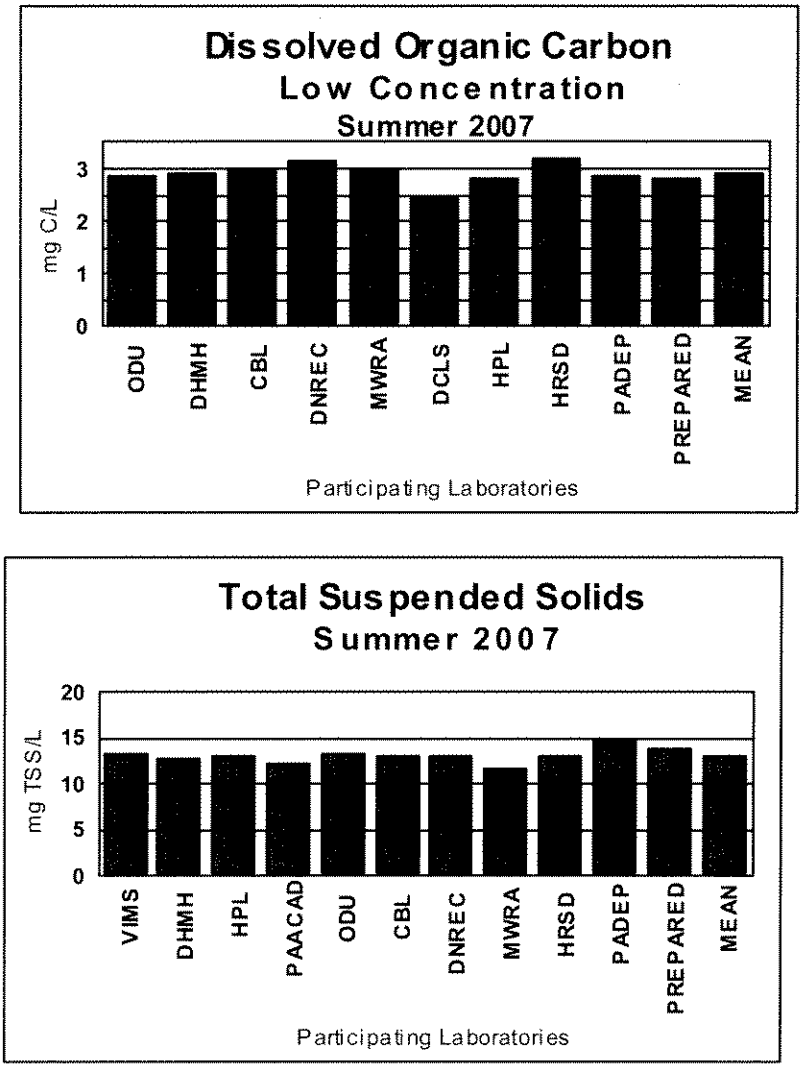
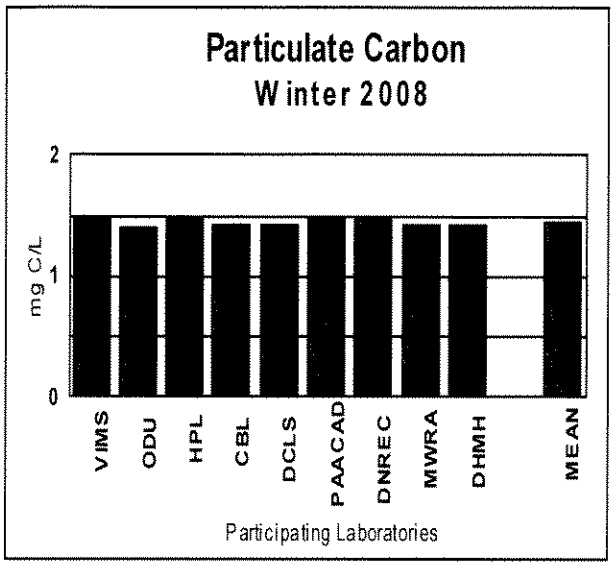
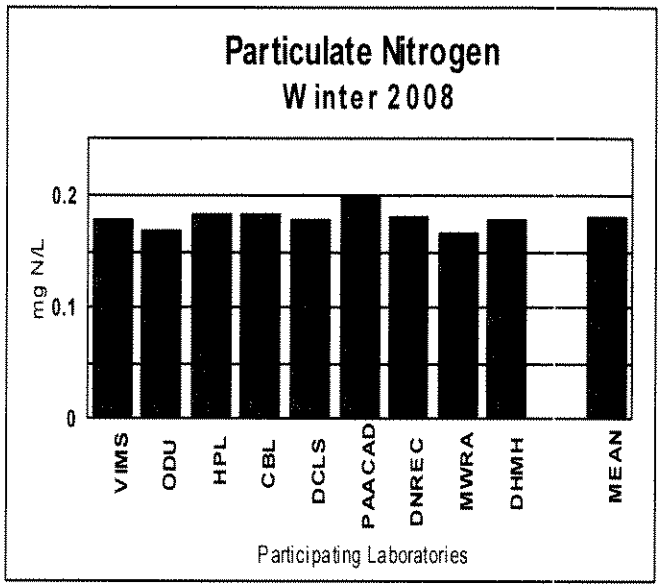
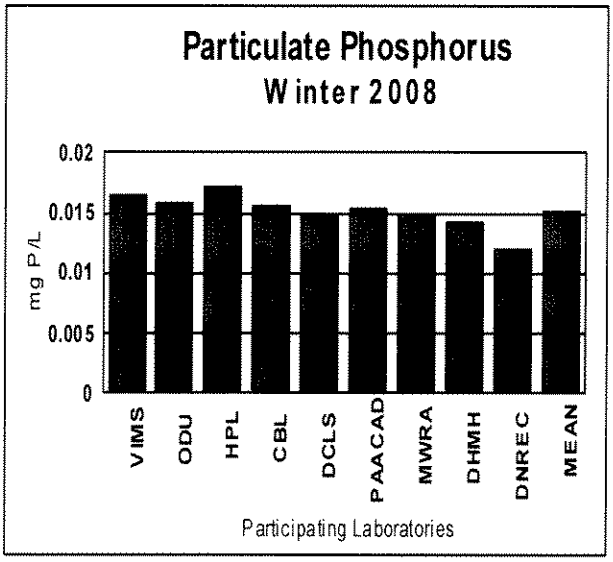


Figure 4. Dissolved organic carbon and total suspended solids, Summer 2007.







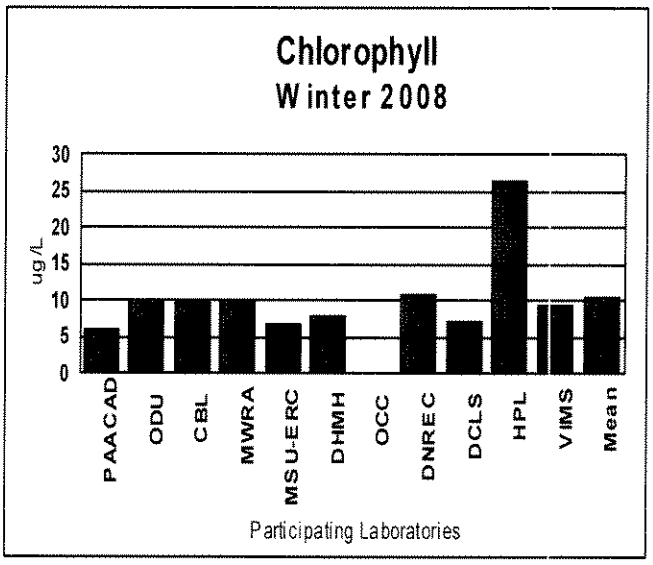
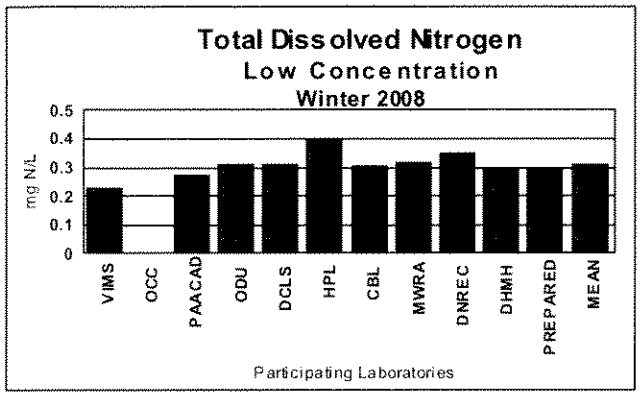
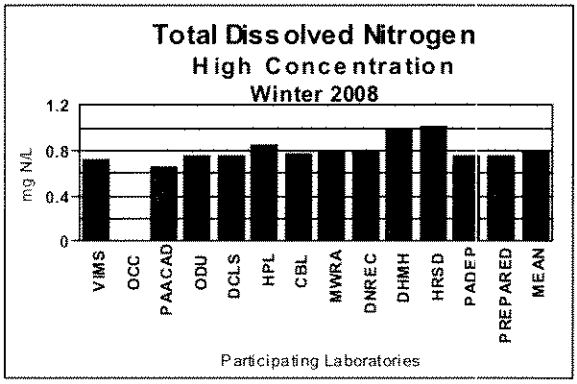
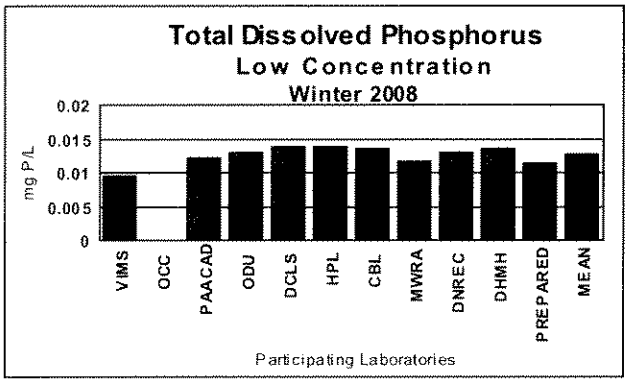


Figure 5. Particulate carbon, nitrogen and phosphorus; chlorophyll, Winter 2008.







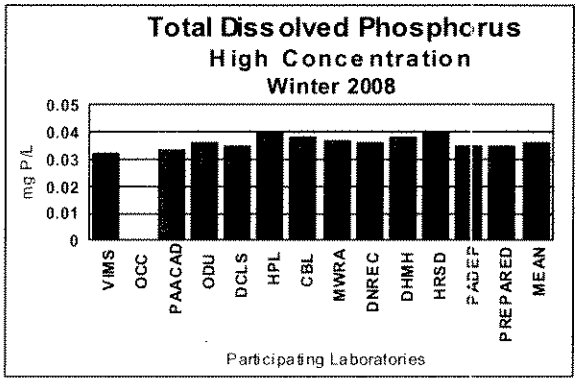


Figure 6. Total dissolved nitrogen and phosphorus, Winter 2008.

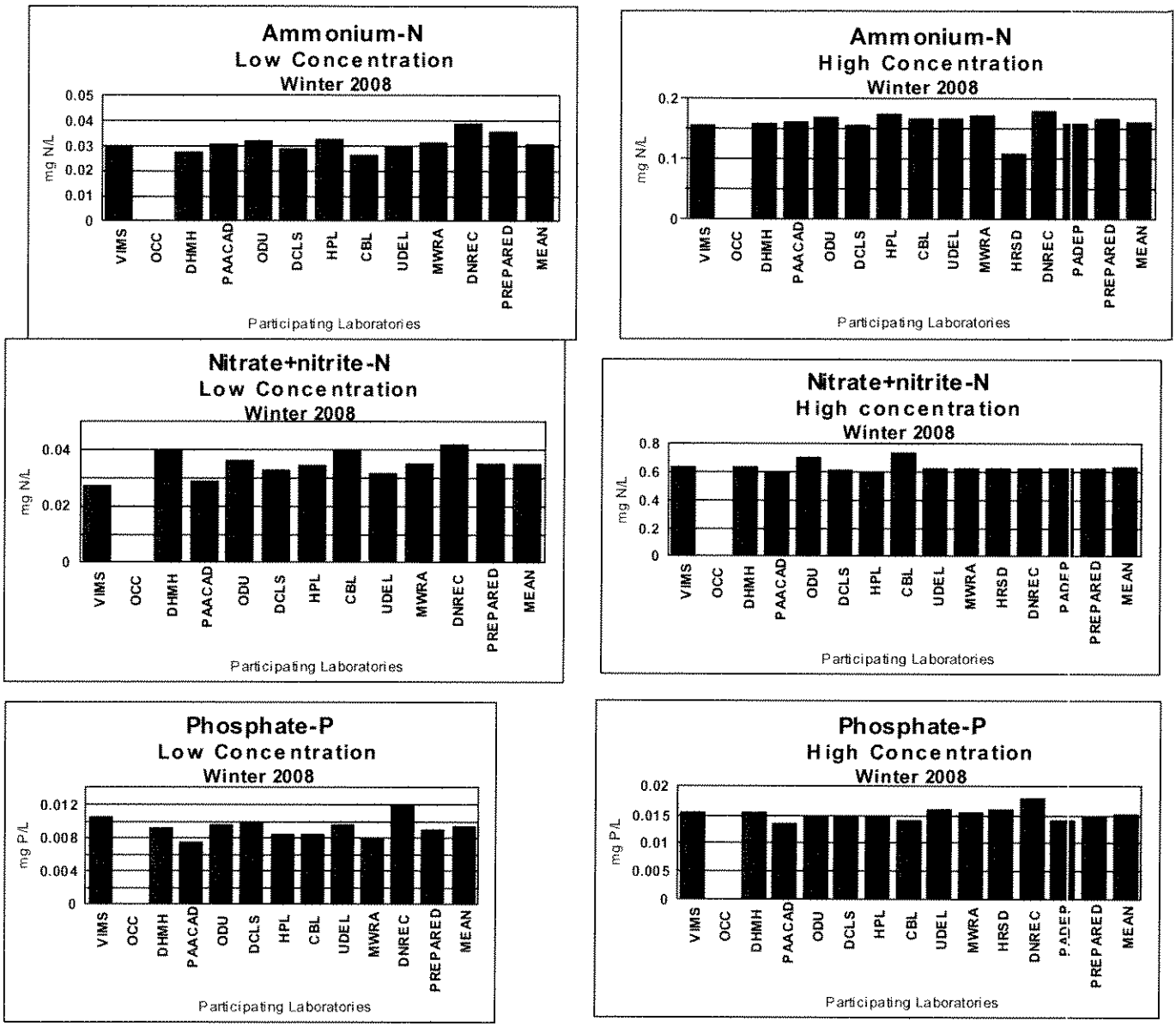
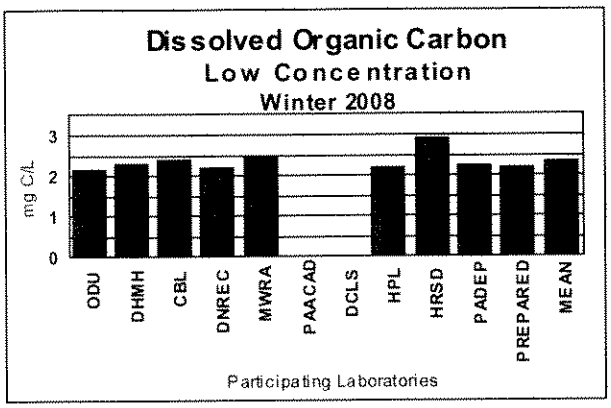
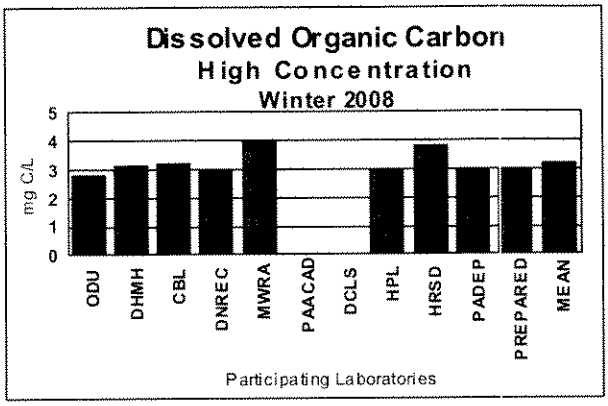


Figure 7. Dissolved inorganic nitrogen and phosphsorus, Winter 2008.





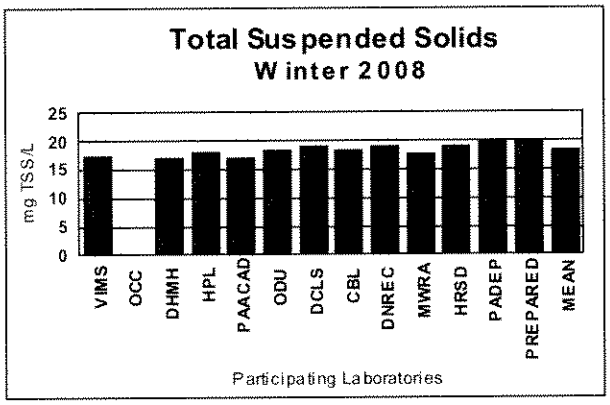


Figure 8. Dissolved organic carbon and total suspended solids, Summer 2007.