

FINAL REPORT

CHESAPEAKE BAY PROGRAM BLIND AUDIT

Fiscal Year 2009 Final Report

PREPARED FOR:

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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 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 eleventh 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 13 August 2008 and 2 February 2009. 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 2008 and winter 2009 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 high concentration sample from the summer 2008 audit was higher than results for all other participants and, also, 51% more than the prepared concentration.

Total Dissolved Phosphorus: 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. Three participants' results for the low concentration sample from both audits were higher than results for most other participants and, also, 29-53% and 23-47% greater than the prepared concentrations. With those exceptions, results for all the audits (both low and high concentrations) had approximately the same agreement with the prepared concentration and between the participants.

Ammonium: With the exception of one participant, results for both concentrations of ammonium sample for the summer 2008 audit had close agreement between participants. There was little divergence between participants for the winter 2009 audits. The variation between the reported and prepared concentration for the low level ammonium winter 2009 audit was a bit less than in the past 5 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. One participant's reported concentration for summer 2008 low level concentration was double that which was prepared. The same participant's reported concentration for winter 2009 low level concentration was 29% of that which was prepared.

Orthophosphate: There were no data for the summer 2008 audit because of a preparation error. For the prepared high level concentration of orthophosphate for the winter audit, most participants reported approximately the same concentration with little variability from the prepared concentration. For the low level orthophosphate concentration winter 2009 audit, there was considerable variance between three of the participants from the prepared concentration.

Dissolved Organic Carbon: For both audits, there was, generally, approximate agreement with the prepared concentration and between participants.

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 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 less agreement between participating laboratories than in past years (Table 2). One laboratory's reported concentration was about double the mean of the other participants' data for the winter 2009 audit.

Particulate Phosphorus: Particulate P results for both audits revealed fairly close agreement between most participating laboratories, though not as close as in past years (Table 2). One laboratory's reported concentration was about half the mean of the other participants' data for the summer 2008 audit.

Chlorophyll: Chlorophyll results for the summer 2008 audit displayed the usual close agreement that was remarkable for multi-laboratory comparison of low concentrations of an environmentally transitory compound. The winter 2009 reported concentrations were lower and much more variable.

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 2008 sample, 9.5 mg/L was prepared, and there was a consistent slight negative bias reported by most participants. For the winter 2009 sample, 11.0 mg/L was prepared but, there was, again, a consistent negative bias reported by all participants. The negative bias reported for these two audits was less than in past years.

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 winter 2009 blind audit of low level total dissolved nitrogen concentration, the mean reported concentration was 0.312 mg N/L and reported concentrations ranged from 0.284-.353 mg N/L. The coefficient of variation was ONLY 6.3%! Nine laboratories reported results for this high level sample that were within two standard deviations (S.D. \pm 0.0196 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 18% of the prepared concentration. Thus, by that measure of accuracy, most of the data "passed" and one was "warned." This total dissolved nitrogen 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 winter 2009 blind audit of 0.0067 mg P/L prepared for orthophosphate has a "pass" category (\pm 10%) of only 0.0060 -

0.0074 mg P/L. Five out of 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 percentage recovery of low level orthophosphate reported values in past audits; however, when comparing with other participants, the coefficient of variation remains remarkably small. For example, summer 2006 reported data based on comparisons with other participants was 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 32% for 0.050 mg NH₄-N/L (Summer 2008) and 10% for 0.0429 mg NH₄-N/L (Winter 2009). 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 thirteen 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 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 22% of the mean reported concentration for particulate carbon, nitrogen and phosphorus for both the summer 2008 and winter 2009 audits.

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 high (22%) for the summer 2008 blind audit, and for the winter 2009 blind audit (19%). 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 these blind audits, one or two laboratories’ reported concentrations were visibly different from the mean, thus increasing the coefficient of variation. Although the sample size was only eight, it was not surprising that these differences were sufficient 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. 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: Most data originally reported by all participants for both these blind audits appeared, on casual inspection, to be reported accurately. A few of the results for both these blind audits were miscalculated (and later corrected), or had “slipped a decimal” or exhibited some other obvious entry error that could have been easily avoided. As in past years, contacting the participants usually resolved these reporting discrepancies, but has not always improved their subsequent reporting practices. Other subtle entry or calculation errors may have gone undetected.

The summer 2007 and winter 2008 audits were the only pair of audits in which 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 had improved their reporting practices! Sadly, this improvement in reporting did not extend to the summer 2008 and winter 2009 audits.

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, 2008 and winter 2009 participants reported only two significant digits for some analytes, thus potentially giving substantial under or over estimates for the comparisons.

CONCLUSION

Now that twenty three 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 particulate analytes were usually similar between laboratories participating in the Blind Audit Program. With the exception of chlorophyll for the winter 2009 audit, no laboratory reported concentrations for individual analytes that were widely different from the range of the other reported concentrations. This indicates that most participating laboratories execute and report these measurements with accuracy and precision, reporting the appropriate number of significant digits.
2. Reported concentrations of dissolved analytes were usually similar between laboratories participating in the Blind Audit Program. Except for the low level total dissolved phosphorus audit, 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.
3. When comparing reported concentrations to those prepared, the lower concentration ranges had more data that fell beyond $\pm 10\%$ 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.

4. 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.
5. 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.
6. 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 be valid. The proportion of the standard deviation to the mean was higher for particulate phosphorus in both blind audits in summer 2008 and winter 2009. This contrasted to all three previous years, in which the coefficient of variation for particulate phosphorus was usually the lowest of the particulate fractions.
7. The proportion of the standard deviation to the mean for particulate nitrogen was higher in both these blind audits (summer 2008 and winter 2009) than for most previous audits.
8. Care should continue to be taken when completing report forms. For the summer 2008 and winter 2009 blind audits, some results were AGAIN (!) reported with insufficient significant digits. For both these blind audit, results were AGAIN (!) reported and then later corrected. Over the course of the years, a few laboratories have repeatedly made calculation errors that were later corrected. It is hoped that corrections of these lapses serve as reminders of the importance to continuously check many aspects of data management to ensure overall data quality.

Table 1. Participants in the Summer 2008 and Winter 2009 Blind Audit Program.

Institution	Contact Person	Phone	Dissolved	Particulate	Chlorophyll a	DOC	TSS
Old Dominion University, Water Quality Lab, (ODU)	Suzanne Doughton	757-451-3043	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	410-586-9700			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
Occoquan Watershed Monitoring Lab (OCC)	Dongmei Wang	703-361-5606 x118	X	X	X	X	X

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Summer 2009 and the Winter 2009 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	1-2	2-3	>3
			PASS	PASS	WARN	FAIL
Summer 2008						
Total Dissolved Nitrogen	0.280	0.033	7	1	1	
Total Dissolved Nitrogen	0.5285	0.079	9	1	1	
Total Dissolved Phosphorus	0.0193	0.0025	7	1	1	
Total Dissolved Phosphorus	0.0465	0.0063	8	2	1	
Ammonium	0.050	0.0161	9	1		
Ammonium	0.132	0.0185	9	2	1	
Nitrate + Nitrite	0.0383	0.0115	9	1		
Nitrate + Nitrite	1.08	0.0588	9	2	1	
Orthophosphate						
Orthophosphate						
Dissolved Organic Carbon	2.22	0.137	8	3		
Dissolved Organic Carbon	3.52	0.158	9	1	1	
Particulate Carbon	1.06	0.0825	6	1	1	
Particulate Nitrogen	0.220	0.0072	5	3		
Particulate Phosphorus	0.0324	0.0071	6	1	1	
Total Suspended Solids	8.14	1.385	8	2	1	
Winter 2009						
Total Dissolved Nitrogen	0.312	0.0196	8	1	1	
Total Dissolved Nitrogen	0.991	0.0427	8	4		
Total Dissolved Phosphorus	0.0190	0.0036	7	3		
Total Dissolved Phosphorus	0.0453	0.0038	7	5		
Ammonium	0.039	0.0135	7	3		
Ammonium	0.147	0.0194	10	2	1	
Nitrate + Nitrite	0.0982	0.0229	10		1	
Nitrate + Nitrite	0.897	0.0617	11	1	1	
Orthophosphate	0.0067	0.0026	6	3		
Orthophosphate	0.0271	0.0021	9	4		
Dissolved Organic Carbon	2.29	0.127	7	4		
Dissolved Organic Carbon	5.66	0.221	7	3	1	
Particulate Carbon	1.06	0.077	7	3		
Particulate Nitrogen	0.158	0.0213	7	1	1	1
Particulate Phosphorus	0.0132	0.0024	6	1	1	
Total Suspended Solids	10.24	0.418	7	3	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
Summer 2008					
Total Dissolved Nitrogen	0.270	0.236-0.359	7	1	1
Total Dissolved Nitrogen	0.497	0.435-.75	10	1	
Total Dissolved Phosphorus	0.0163	0.0163-0.025	2	5	2
Total Dissolved Phosphorus	0.0422	0.039-0.06	7	3	1
Ammonium	0.046**	0.04-0.0957	8	1	1
Ammonium	0.122	0.109-0.175	9	2	1
Nitrate + Nitrite	0.0350	0.0322-0.07	8	1	1
Nitrate + Nitrite	1.12	1.00-1.21	11	1	
Orthophosphate					
Orthophosphate					
Dissolved Organic Carbon	2.20	1.99-2.49	10	1	
Dissolved Organic Carbon	3.60	3.12-3.74	10	1	
Total Suspended Solids	9.5	L 5-9.7	6	3	2
Winter 2009					
Total Dissolved Nitrogen	0.298	0.284-.353	9	1	
Total Dissolved Nitrogen	0.994	0.91-1.06	12		
Total Dissolved Phosphorus	0.0163**	0.0126-0.0249	4	1	5
Total Dissolved Phosphorus	0.0422	0.0392-0.0511	8	3	1
Ammonium	0.046**	0.0361-0.05	8	1	1
Ammonium	0.147	0.11-0.19	10		3
Nitrate + Nitrite	0.105	0.03-0.111	10		1
Nitrate + Nitrite	0.910	0.721-0.9615	12		1
Orthophosphate	0.0067**	0.0049-0.00887	4	1	4
Orthophosphate	0.0260	0.023-0.03	8	5	
Dissolved Organic Carbon	2.20	2.14-2.50	9	2	
Dissolved Organic Carbon	5.60	5.1-6.03	11		
Total Suspended Solids	11.0	9.4-10.71	11	1	

**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 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)		.270		.2987	.298	100.2
TDN (mg N/L)		.497		.9811	.994	98.7
TDP (mg P/L)		.0163		.0208	.0163**	127.6
TDP (mg P/L)		.0422		.0419	.0422	99.3
NH ₄ (mg N/L)		.046**		.0426	.046**	92.6
NH ₄ (mg N/L)		.122		.1513	.147	102.9
NO ₃ + NO ₂ (mg N/L)		.0350		.1051	.105	100.1
NO ₃ + NO ₂ (mg N/L)		1.12		.7210 WARN	.910	79.2
PO ₄ (mg P/L)				.0049	.0067**	73.1
PO ₄ (mg P/L)				.0296	.0260	113.8
Particulate C (mg C/L)				1.0899		
Particulate N (mg N/L)				.1306		
Chlorophyll (µg/L)				3.77		
Total Suspended Solids (mg/L)		9.5		10.6	11.0	96.4

**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 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)	.289	.270	107.0	.326	.298	109.4
TDN (mg N/L)	.508	.497	102.2	1.06	.994	106.6
TDP (mg P/L)	.0189	.0163	116.0	.0249	.0163**	152.8
TDP (mg P/L)	.0447	.0422	105.9	.0494	.0422	117.1
NH4 (mg N/L)	.0957 WARN	.046**	208.0		.046**	
NH4 (mg N/L)	.175 WARN	.122	143.4	.177	.147	120.4
NO3 + NO2 (mg N/L)	.0414	.0350	118.3	.111	.105	105.7
NO3 + NO2 (mg N/L)	1.08	1.12	96.4	.872	.910	95.8
PO4 (mg P/L)					.0067**	
PO4 (mg P/L)				.0278	.0260	106.9
Particulate C (mg C/L)	1.08			1.17		
Particulate N (mg N/L)	.212			.1575 (<.182)		
Particulate P (mg P/L)	.0271			.0105		
Chlorophyll (μ g/L)	14.0			8.41		
DOC (mg C/L)	2.31	2.20	105.0	2.41	2.20	109.5
DOC (mg C/L)	3.62	3.60	100.6	5.65	5.60	100.9
Total Suspended Solids (mg/L)	8.65	9.5	91.1	10.7	11.0	97.3

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

"WARN" based on standard deviation of all participants' reported concentrations

University of Delaware

Parameter	Summer 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
NH4 (mg N/L)	.0475	.046**	103.3	.0387	.046**	84.1
NH4 (mg N/L)	.1224	.122	100.3	.1464	.147	99.6
NO3 + NO2 (mg N/L)	.0322	.0350	92.0	.1026	.105	97.7
NO3 + NO2 (mg N/L)	1.000	1.12	89.3	.8756	.910	96.2
PO4 (mg P/L)				.0074	.0067**	110.4
PO4 (mg P/L)				.0260	.0260	100.0

Appendix I. *Continued.***Academy of Natural Sciences of Philadelphia**

Parameter	Summer 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)	.268	.270	99.3	.306	.298	102.7
TDN (mg N/L)	.480	.497	96.6	.969	.994	97.5
TDP (mg P/L)	.0181	.0163	111.0	.0126	.0163**	77.3
TDP (mg P/L)	.0412	.0422	97.6	.0392	.0422	92.9
NH ₄ (mg N/L)	.0454	.046**	98.7	.0416	.046**	90.4
NH ₄ (mg N/L)	.126	.122	103.3	.138	.147	93.9
NO ₃ + NO ₂ (mg N/L)	.0362	.0350	103.4	.106	.105	101.0
NO ₃ + NO ₂ (mg N/L)	1.09	1.12	97.3	.913	.910	100.3
PO ₄ (mg P/L)				.0071	.0067**	106.0
PO ₄ (mg P/L)				.0267	.0260	102.7
Particulate C (mg C/L)	1.06			1.08		
Particulate N (mg N/L)	.217			.148		
Particulate P (mg P/L)	.0356			.0182 WARN		
Chlorophyll (µg/L)	14.0			5.04		
DOC (mg C/L)	2.03	2.20	92.3	2.19	2.20	99.5
DOC (mg C/L)	3.40	3.60	94.4	5.29	5.60	94.5
Total Suspended Solids (mg/L)	9.0	9.5	94.7	10.6	11.0	96.4

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

“WARN” based on standard deviation of all participants’ reported concentrations

Morgan State University Estuarine Research Center

Parameter	Summer 2008 Reported		% Recovered	Winter 2009 Reported		% Recovered
Chlorophyll (µg/L)	8.64			2.67		

Appendix I. *Continued.***Old Dominion University**

Parameter	Summer 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)	.272	.270	100.7	.302	.298	101.3
TDN (mg N/L)	.512	.497	103.0	1.012	.994	101.8
TDP (mg P/L)	.0181	.0163	111.0	.0178	.0163**	109.2
TDP (mg P/L)	.0442	.0422	104.7	.0456	.0422	108.1
NH ₄ (mg N/L)	.0444	.046**	96.5	.0436	.046**	94.8
NH ₄ (mg N/L)	.1238	.122	101.5	.1413	.147	96.1
NO ₃ + NO ₂ (mg N/L)	.0343	.0350	98.0	.1018	.105	97.0
NO ₃ + NO ₂ (mg N/L)	1.0956	1.12	97.8	.8914	.910	98.0
PO ₄ (mg P/L)				.0073	.0067**	109.0
PO ₄ (mg P/L)				.0250	.0260	96.2
Particulate C (mg C/L)	1.24 WARN			1.014		
Particulate N (mg N/L)	.2258			.170		
Particulate P (mg P/L)	.0345			.0132		
Chlorophyll (µg/L)	13.78			7.68		
DOC (mg C/L)	2.195	2.20	99.8	2.157	2.20	98.0
DOC (mg C/L)	3.52	3.60	97.8	5.511	5.60	98.4
Total Suspended Solids (mg/L)	8.23	9.5	86.6	10.71	11.0	97.4

Occoquan Watershed Monitoring Laboratory

Parameter	Summer 2008	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
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	Reported					
TDN (mg N/L)	.359 WARN	.270	133.0	.32	.298	107.4
TDN (mg N/L)	.538	.497	108.2	.96	.994	96.6
TDP (mg P/L)	.025 WARN	.0163	153.4	.02	.0163**	122.7
TDP (mg P/L)	.055	.0422	130.3	.05	.0422	118.5
NH4 (mg N/L)	.04	.046**	87.0	.05	.046**	108.7
NH4 (mg N/L)	.13	.122	106.6	.14	.147	95.2
NO3 + NO2 (mg N/L)	.07 WARN	.0350	200.0	.03 WARN	.105	28.6
NO3 + NO2 (mg N/L)	1.17	1.12	104.5	.94	.910	103.3
PO4 (mg P/L)				L 0.01	.0067**	
PO4 (mg P/L)				.03	.0260	115.4
Particulate C (mg C/L)				.995		
Particulate N (mg N/L)				.303 FAIL		
Chlorophyll (μ g/L)	12.85			18.05		
DOC (mg C/L)	1.99	2.20	90.5	2.3	2.20	104.5
DOC (mg C/L)	3.12 WARN	3.60	86.7	5.1 WARN	5.60	91.1
Total Suspended Solids (mg/L)	8.9	9.5	93.7	10.0	11.0	90.9

"WARN" and "FAIL" based on standard deviation of all participants' reported concentrations

Appendix I. *Continued.***Virginia Division of Consolidated Laboratory Services**

Parameter	Summer 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)	.274	.270	101.5	.324	.298	108.7
TDN (mg N/L)	.518	.497	104.2	.947	.994	95.3
TDP (mg P/L)	.019	.0163	116.6	.017	.0163**	104.3
TDP (mg P/L)	.044	.0422	104.3	.045	.0422	106.6
NH ₄ (mg N/L)	.046	.046**	100.0	.044	.046**	95.7
NH ₄ (mg N/L)	.109	.122	89.3	.153	.147	104.1
NO ₃ + NO ₂ (mg N/L)	.036	.0350	102.9	.108	.105	102.9
NO ₃ + NO ₂ (mg N/L)	1.03	1.12	92.0	.930	.910	102.2
PO ₄ (mg P/L)				.009	.0067**	134.3
PO ₄ (mg P/L)				.028	.0260	107.7
Particulate C (mg C/L)	1.03			1.01		
Particulate N (mg N/L)	.227			.142		
Particulate P (mg P/L)	.0347			.0111		
Chlorophyll (µg/L)	11.1			4.91		
DOC (mg C/L)	2.20	2.20	100.0	2.21	2.20	100.5
DOC (mg C/L)	3.54	3.60	98.3	5.69	5.60	101.6
Total Suspended Solids (mg/L)	9	9.5	94.7	10	11.0	90.9

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

Hampton Roads Sanitation District

Parameter	Summer 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)	.75 WARN	.497	150.9	1.04	.994	104.6
TDP (mg P/L)	.06 WARN	.0422	142.2	.04	.0422	94.8
NH4 (mg N/L)	.16	.122	131.1	.11	.147	74.8
NO3 + NO2 (mg N/L)	1.21 WARN	1.12	108.0	.94	.910	103.3
PO4 (mg P/L)				.023	.0260	88.5
DOC (mg C/L)	2.18	2.20	99.1	2.29	2.20	104.1
DOC (mg C/L)	3.55	3.60	98.6	5.97	5.60	106.6
Total Suspended Solids (mg/L)	6.2	9.5	65.3	9.4 WARN	11.0	85.5

**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 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)	.54	.497	108.7	.91	.994	91.5
TDP (mg P/L)	.046	.0422	109.0	.044	.0422	104.3
NH4 (mg N/L)	.14	.122	114.8	.19	.147	129.3
NO3 + NO2 (mg N/L)	1.09	1.12	97.3	.95	.910	104.4
PO4 (mg P/L)				.026	.0260	100.0
DOC (mg C/L)	2.33	2.20	105.9	2.35	2.20	106.8
DOC (mg C/L)	3.63	3.60	100.8	5.63	5.60	100.5
Total Suspended Solids (mg/L)	L 5 WARN	9.5	52.6	10	11.0	90.9

**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 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)	.273	.270	101.1	.353 WARN	.298	118.5
TDN (mg N/L)	.521	.497	104.8	1.017	.994	102.3
TDP (mg P/L)	.0179	.0163	109.8	.0175	.0163**	107.4
TDP (mg P/L)	.0487	.0422	115.4	.0456	.0422	108.1
NH4 (mg N/L)	.043	.046**	93.5	.0361	.046**	78.5
NH4 (mg N/L)	.126	.122	103.3	.137	.147	93.2
NO3 + NO2 (mg N/L)	.033	.0350	94.3	.103	.105	98.1
NO3 + NO2 (mg N/L)	1.049	1.12	93.7	.916	.910	100.7
PO4 (mg P/L)				.0069	.0067**	103.0
PO4 (mg P/L)				.0299	.0260	115.0
Particulate C (mg C/L)	.993			1.19		
Particulate N (mg N/L)	.219			.204 WARN		
Particulate P (mg P/L)	.0422			.0148		
Chlorophyll (μ g/L)	14.32			7.82		
DOC (mg C/L)	2.23	2.20	101.4	2.14	2.20	97.3
DOC (mg C/L)	3.56	3.60	98.9	5.46	5.60	97.5
Total Suspended Solids (mg/L)	8.99	9.5	94.6	10.2	11.0	92.7

"WARN" based on standard deviation of all participants' reported concentrations

Appendix I. *Continued.***UMCES Chesapeake Biological Laboratory**

Parameter	Summer 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)	.272	.270	100.7	.297	.298	99.7
TDN (mg N/L)	.504	.497	101.4	.977	.994	98.3
TDP (mg P/L)	.0163	.0163	100.0	.0168	.0163**	103.1
TDP (mg P/L)	.0404	.0422	95.7	.0444	.0422	105.2
NH ₄ (mg N/L)	.046	.046**	100.0	.049	.046**	106.5
NH ₄ (mg N/L)	.116	.122	95.1	.148	.147	100.7
NO ₃ + NO ₂ (mg N/L)	.0343	.0350	98.0	.109	.105	103.8
NO ₃ + NO ₂ (mg N/L)	1.038	1.12	92.7	.9615	.910	105.7
PO ₄ (mg P/L)				.0072	.0067**	107.5
PO ₄ (mg P/L)				.0264	.0260	101.5
Particulate C (mg C/L)	1.07			.959		
Particulate N (mg N/L)	.231			.153		
Particulate P (mg P/L)	.0347			.0133		
Chlorophyll (µg/L)	13.8			6.22		
DOC (mg C/L)	2.49	2.20	113.2	2.50	2.20	113.6
DOC (mg C/L)	3.74	3.60	103.9	6.03	5.60	107.7
Total Suspended Solids (mg/L)	7.9	9.5	83.2	9.9	11.0	90.0

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

Appendix I. *Continued.***MD DHMH Division of Environmental Chemistry Nutrients Laboratory**

Parameter	Summer 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)	.236	.270	87.4	.284	.298	95.3
TDN (mg N/L)	.435	.497	87.5	.987	.994	99.3
TDP (mg P/L)	.021	.0163	128.8	.0239	.0163**	146.6
TDP (mg P/L)	.039	.0422	92.4	.0511	.0422	121.1
NH ₄ (mg N/L)	.047	.046**	102.2	.0424	.046**	92.2
NH ₄ (mg N/L)	.125	.122	102.5	.142	.147	96.6
NO ₃ + NO ₂ (mg N/L)	.033	.0350	94.3	.101	.105	96.2
NO ₃ + NO ₂ (mg N/L)	1.056	1.12	94.3	.873	.910	95.9
PO ₄ (mg P/L)				.0086	.0067**	128.4
PO ₄ (mg P/L)				.0253	.0260	97.3
Particulate C (mg C/L)	.963			1.041		
Particulate N (mg N/L)	.211			.171		
Particulate P (mg P/L)	.018 WARN			.0125		
Chlorophyll (µg/L)	13.7					
DOC (mg C/L)	2.26	2.20	102.7	2.43	2.20	110.5
DOC (mg C/L)	3.54	3.60	98.3	5.73	5.60	102.3
Total Suspended Solids (mg/L)	9.7	9.5	102.1	10.7	11.0	97.3

**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 2008 Reported	Summer 2008 Prepared	% Recovered	Winter 2009 Reported	Winter 2009 Prepared	% Recovered
TDN (mg N/L)	.279	.270	103.3	.306	.298	102.7
TDN (mg N/L)	.507	.497	102.0	1.03	.994	103.6
TDP (mg P/L)	.0192	.0163	117.8	.0189	.0163**	116.0
TDP (mg P/L)	.0483	.0422	114.5	.0476	.0422	112.8
NH4 (mg N/L)	.0472	.046**	102.6	.0406	.046**	88.3
NH4 (mg N/L)	.131	.122	107.4	.140	.147	95.2
NO3 + NO2 (mg N/L)	.0325	.0350	92.9	.103	.105	98.1
NO3 + NO2 (mg N/L)	1.06	1.12	94.6	.873	.910	95.9
PO4 (mg P/L)				.00887	.0067**	132.4
PO4 (mg P/L)				.0290	.0260	111.5
Particulate C (mg C/L)	1.06			1.01		
Particulate N (mg N/L)	.2185			.149		
Particulate P (mg P/L)	.0323			.0117		
Chlorophyll (μ g/L)	13.5			7.42		
DOC (mg C/L)	2.17	2.20	98.6	2.21	2.20	100.5
DOC (mg C/L)	3.49	3.60	96.9	5.62	5.60	100.4
Total Suspended Solids (mg/L)	7.97	9.5	83.9	10.1	11.0	91.8

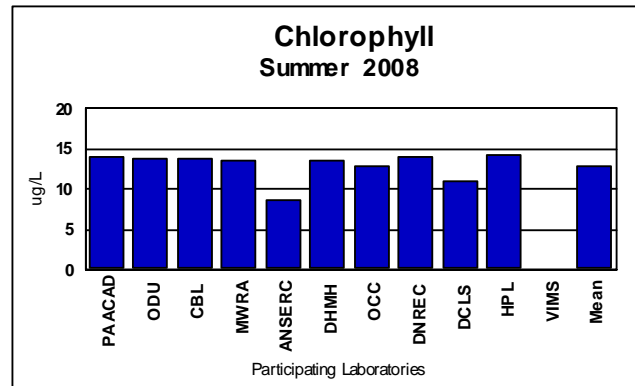
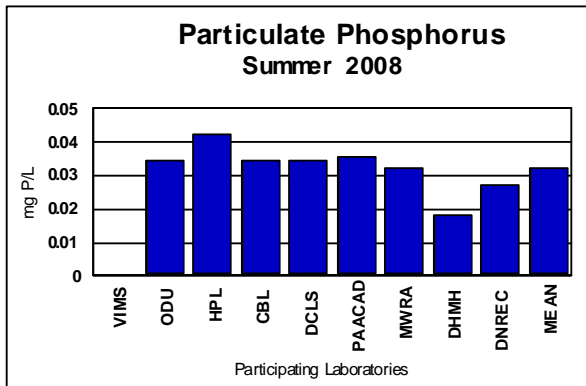
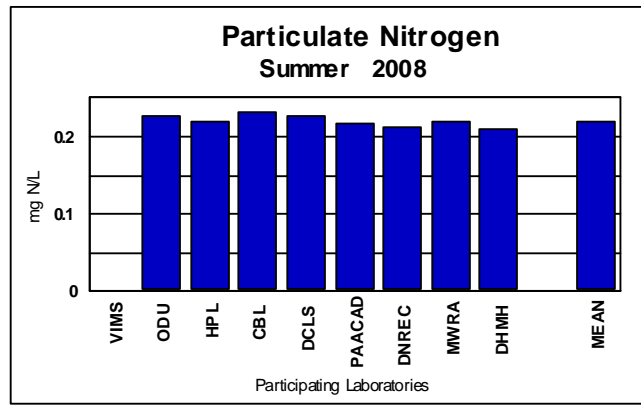
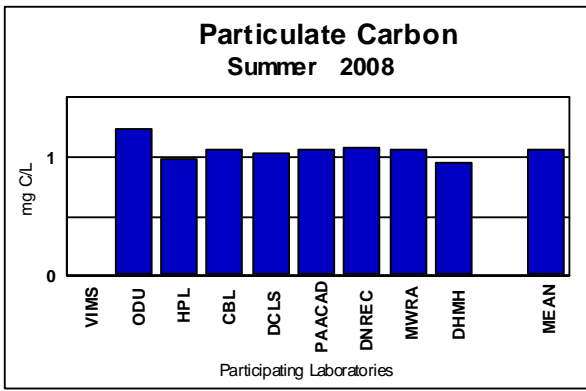


Figure 1. Particulate carbon, nitrogen and phosphorus; chlorophyll, Summer 2008.

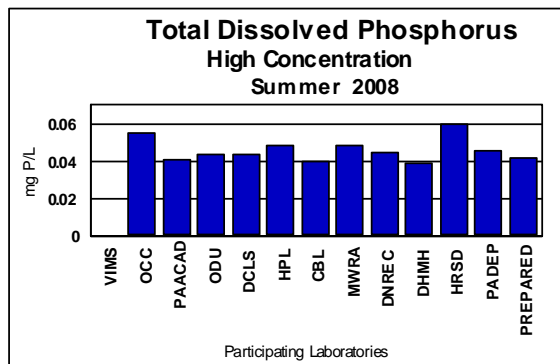
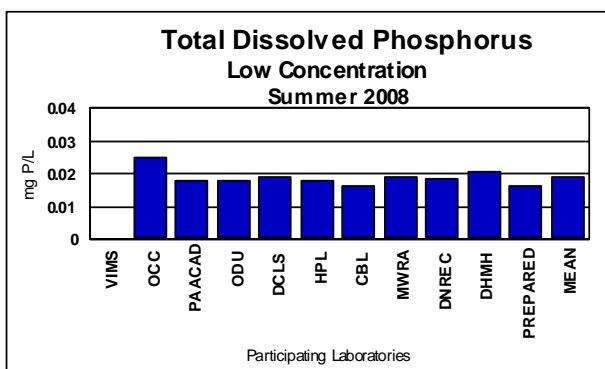
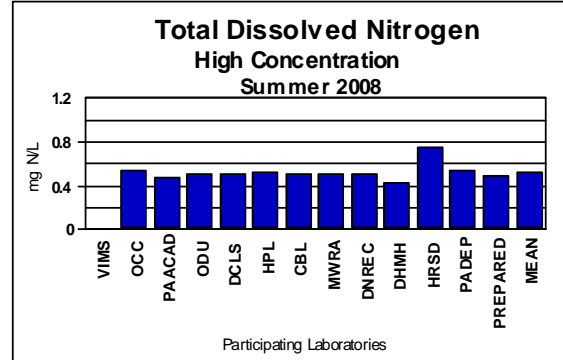
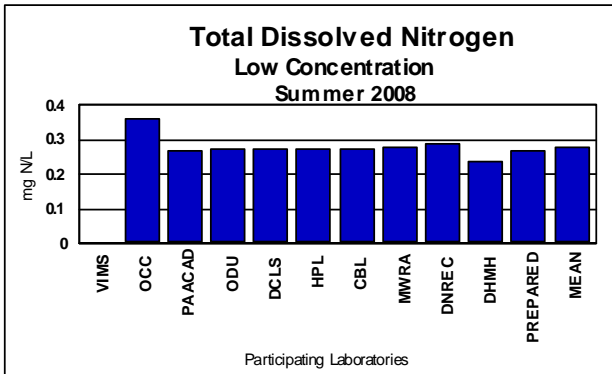


Figure 2. Total dissolved nitrogen and phosphorus, Summer 2008.

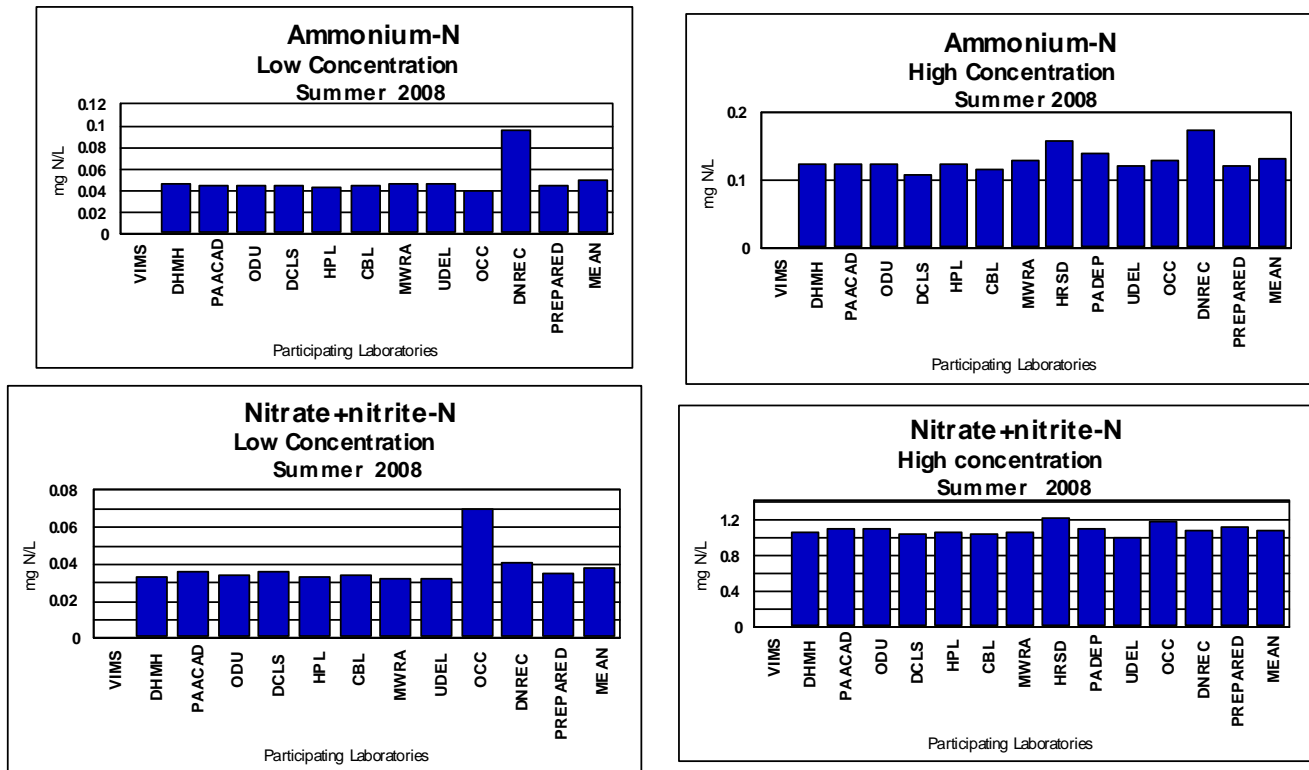


Figure 3. Dissolved inorganic nitrogen, Summer 2008.

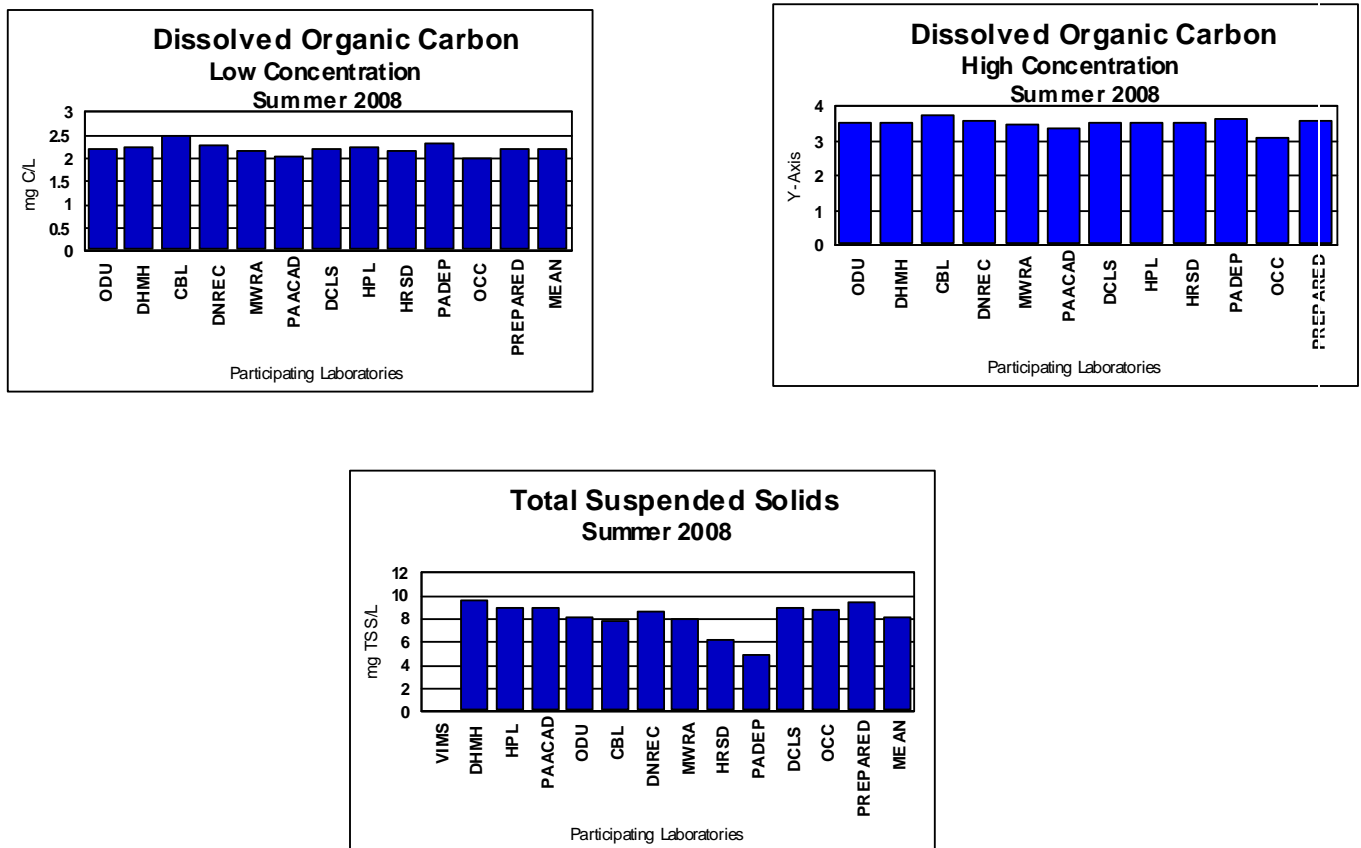


Figure 4. Dissolved organic carbon and total suspended solids, Summer 2008.

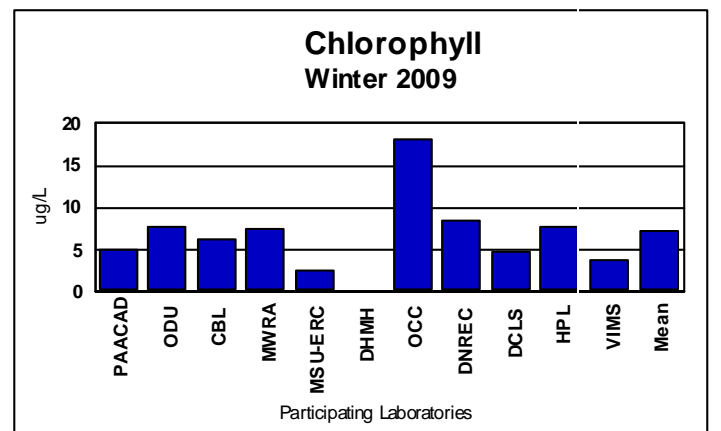
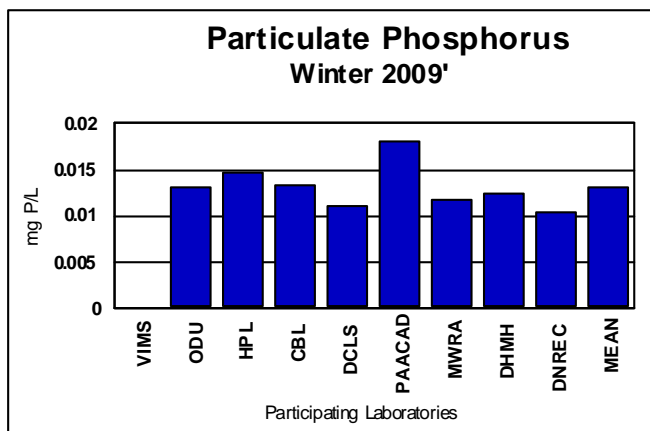
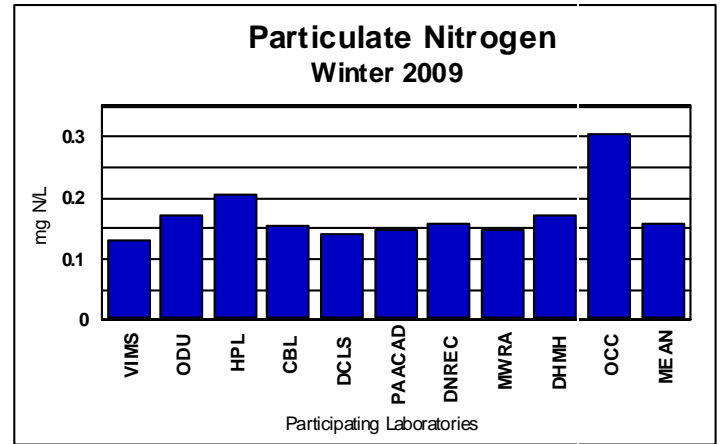
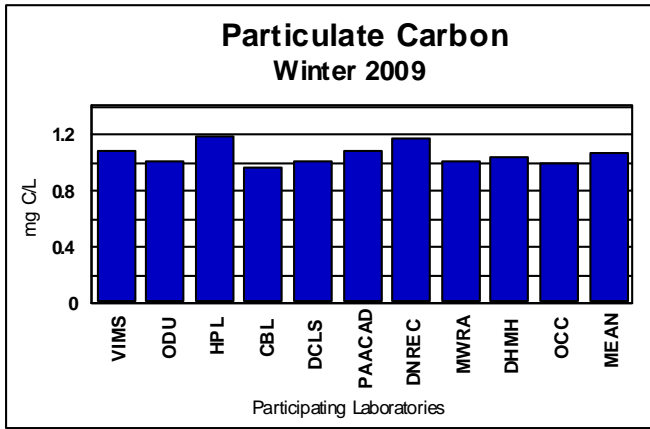


Figure 5. Particulate carbon, nitrogen and phosphorus; chlorophyll, Winter 2009.

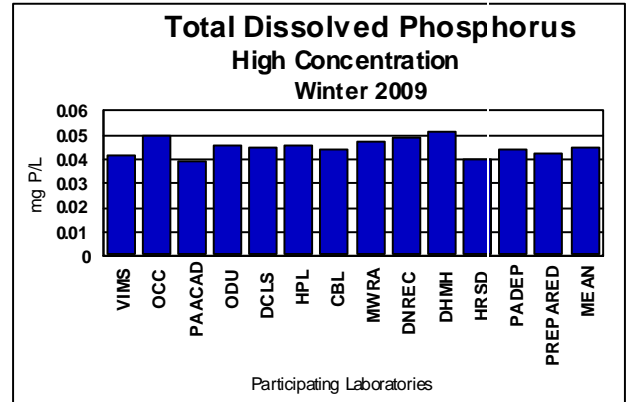
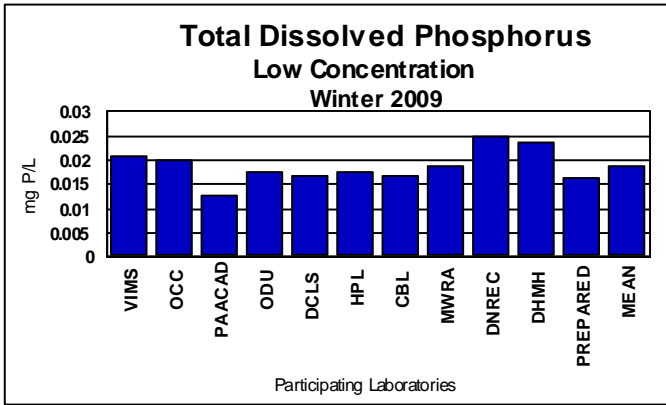
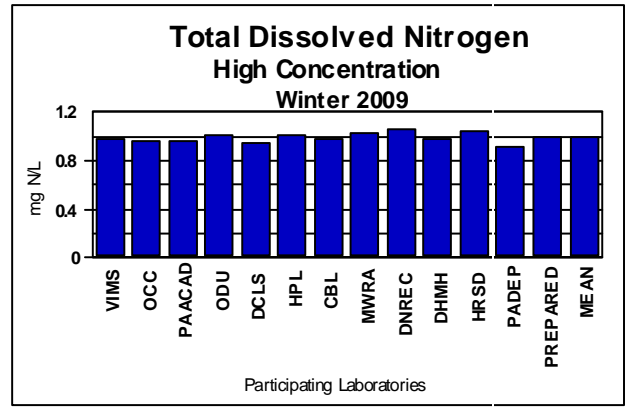
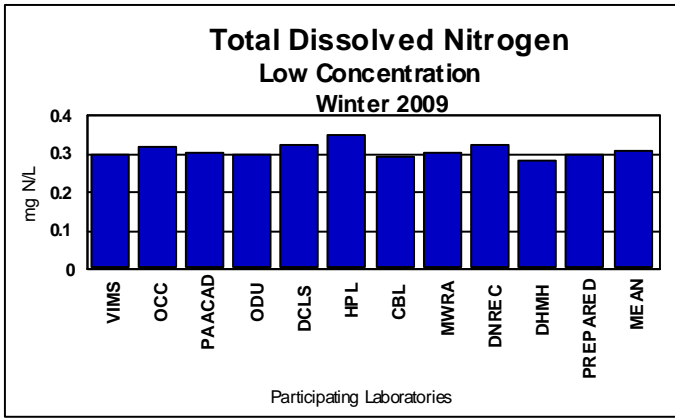


Figure 6. Total dissolved nitrogen and phosphorus, Winter 2009.

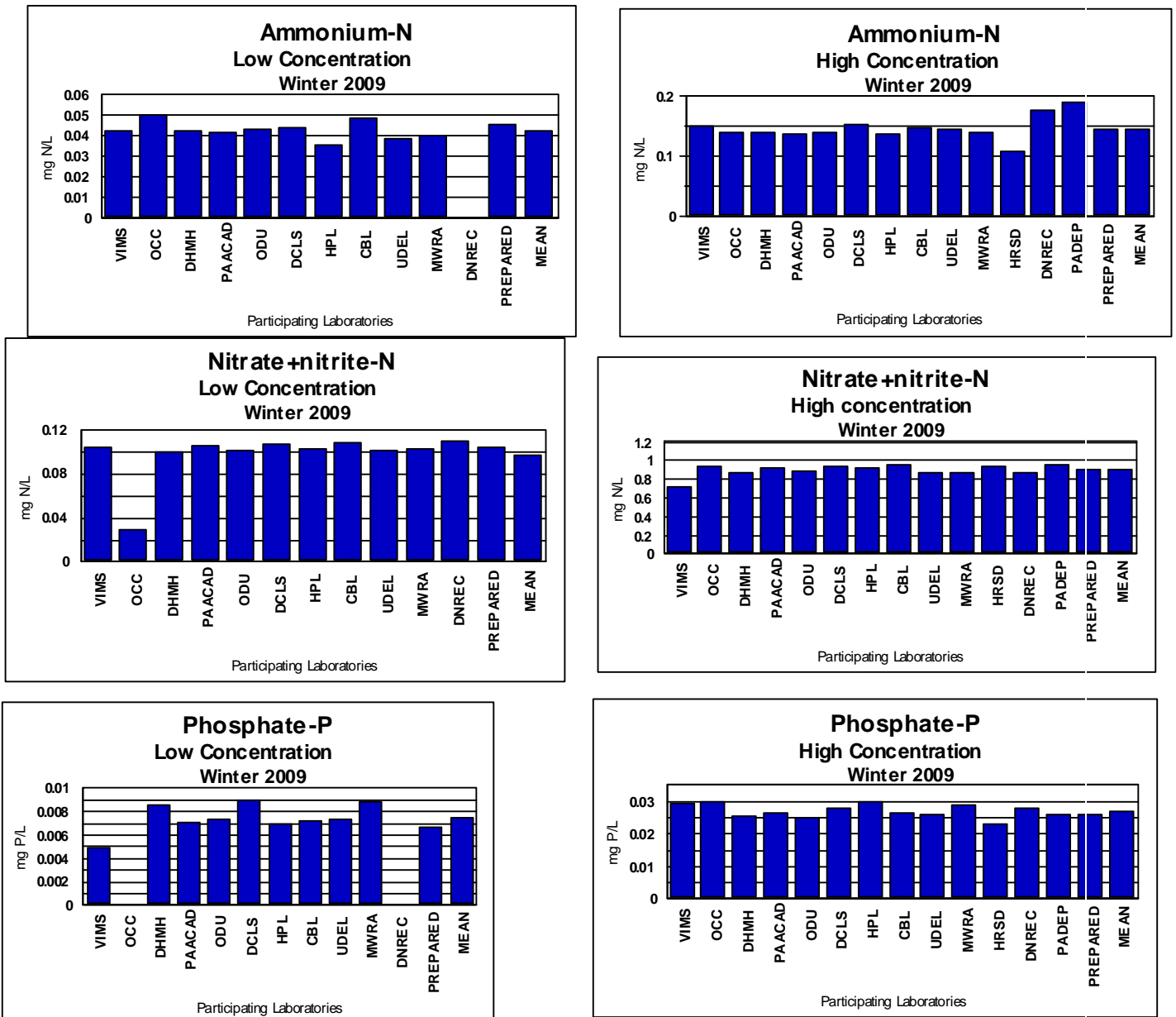


Figure 7. Dissolved inorganic nitrogen and phosphorus, Winter 2009.

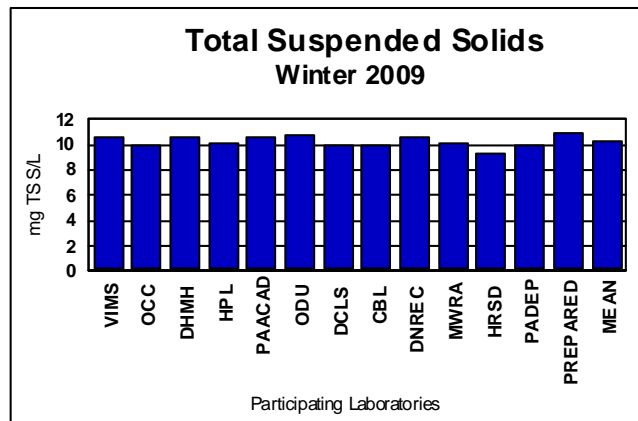
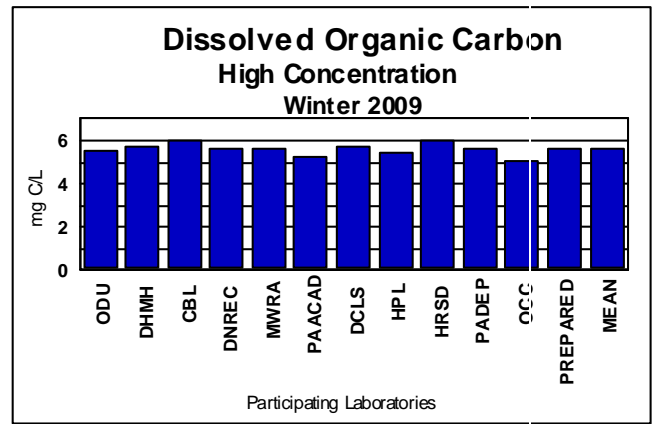
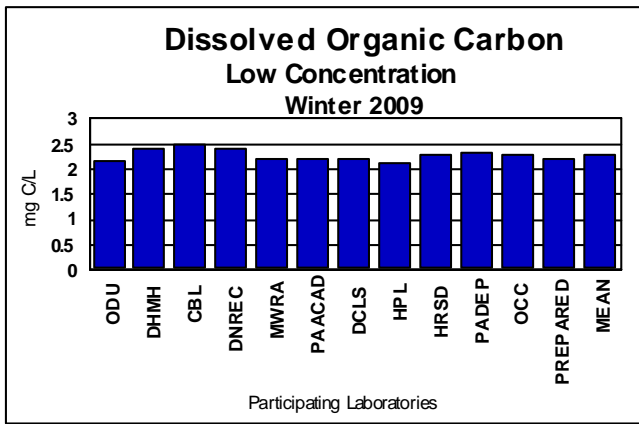


Figure 8. Dissolved organic carbon and total suspended solids, Winter 2009.