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FINAL REPORT

CHESAPEAKE BAY PROGRAM BLIND AUDIT

Fiscal Year 2006 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 eighth 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 22 August 2005 and 6 February 2006. 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 -47EC) 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 populations samples onto 47 mm GF/F filter pads. Replicate pads were provided to participating laboratories.

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 2005 and winter 2006 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: Results for all the audits had approximately the same agreement with the prepared concentration and between the participants.

Total Dissolved Phosphorus: Results for all the audits 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 ammonium audits was quite large, i.e., the proportions of the standard deviations to the means for the low level ammonium samples were quite large.

Ammonium: Results for the high concentration ammonium audits 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 ammonium audits was quite large, i.e., the proportions of the standard deviations to the means for the low level ammonium samples were quite large. The variation between the reported and prepared concentrations was generally less than in the past 2 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 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. For the low level orthophosphate concentration, there was considerable variability between participants and from the prepared concentration. The prepared concentration for the low level winter audit was below the detection limit of one participant (PADEP).

Dissolved Organic Carbon: Results for both audits had approximately the same agreement with the prepared concentration and between the participants. For the low level dissolved organic carbon concentration, there was more variability between participants and from the prepared concentration. For the high level concentration winter 2006 audit, all reported concentrations were within 10% of 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 Figures 1 and 5.

Particulate Nitrogen: Particulate N results for both audits revealed fairly close agreement between all but one of the participating laboratories (Table 2). As in past years, this was still remarkably close agreement for comparison of samples of a natural population by multiple laboratories.

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

Particulate Phosphorus: Particulate P results for summer 2005 revealed very close agreement between all of the participating laboratories (Table 2). For the winter 2006 samples, there was still close agreement, although the concentration of the natural sample was half that of the summer 2005 sample. As in past years, this was remarkably close agreement for comparison of samples of a natural population by multiple laboratories.

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 2005 sample, 86 mg/L was prepared, and there was a consistent slight negative bias reported by all of the participants. For the winter 2005 sample, 10.0 mg/L was prepared but, there was, again, a consistent negative bias reported by most participants.

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 Atrue@ 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 Atrue@ 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 $\forall$ 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 Apass@, and those greater than 3 standard deviations Afail@. Results between 2 and 3 standard deviations are in the Awarning@ 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 Areality@ in small sample sets with little variability between individual points, that at least one point 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 Apassed.@ It should also be noted that approximately the same number were in the Awarning@ category as in most of the previous studies, and that two data points fell in the Afail@ category in each audit.

Data sets with relatively small standard deviations yielded more Awarning@ points. For example, in the summer 2004 blind audit of high level total dissolved nitrogen concentration, the mean reported concentration was 0.937 mg N/L and reported concentrations ranged from 0.827-1.04 mg N/L (Coefficient of Variation, 6.5%). Ten laboratories reported results for this high level sample that were within two standard deviations (S.D. ∀ 0.0613 mg N/L) of the mean. Since the standard deviation was so small, two laboratories= reported results for this sample were between two and three standard deviations of the mean, so were labeled as a Awarning,@ although all but one of the reported data were within ∀10% of the prepared concentration. Thus, by that measure of accuracy, all but one of the data Apassed.@ 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.

For the summer 2005 and winter 2006 blind audits there were no instances in which reported concentrations were within ∀10% of the prepared concentration but received a Awarning@ for being more than two standard deviations from the mean of other participants.

Data were also assessed by comparing reported concentrations to those that had been prepared (Table 3). Groupings of data in Apass, warn and fail@ categories were arbitrarily set. Reported data that were within ∀10% of the prepared concentration were listed as Apass.@ Reported data that were 80-90% or 110 -120% of the prepared concentration were listed as Awarn.@ Reported data that were <80% or >120% of the prepared concentration were listed as Afail.@

When comparing reported concentrations to those prepared, the lower concentration ranges had more data that fell in Awarn@ and Afail@ 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 2005 blind audit of 0.0056 mg P/L prepared for orthophosphate has a Apass@ category (∀10%) of only 0.0050 - 0.0062 mg P/L. Nine out of thirteen participating laboratories reported results that fell in the Awarn@ and Afail@ categories, indicating that their reported concentrations were greater than ∀10% of the prepared concentration in this low range. These results could be interpreted as an inability for most 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 2005 reported data based on comparisons with other participants (mean 0.0070, S.D. 0.0031).

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. However, the proportions of the standard deviations to the means for the low level ammonium samples were, again, quite large;

i.e., coefficients of variation were 23% and 24% for 0.036 mg NH4-N/L. The same concentration sample was provided for both the summer 2005 and winter 2006 low level ammonium audits. The coefficient of variation for the .026 mg N/L ammonium sample for winter 2002 was 20%. The coefficient of variation for the .0273 mg N/L ammonium sample for winter 2003 was 15%. As we reported in past years, the large 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 would still be unreliable. These data indicate that comparison of multi-laboratory natural sample data below 0.036 mg NH4-N/L might be unreliable.

There were nineteen instances where concentrations reported for dissolved constituents fell in the Awarn@ or Afail@ category based on the standard deviation of all participants= reported concentrations and also in the Awarn@ or Afail@ 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 Atrue@ or prepared concentration with which to compare. In all but one instance, the standard deviation was less than 15% of the mean reported concentration for particulate carbon and nitrogen. Data for particulate carbon and nitrogen at one laboratory for both blind audits in this study were not in close agreement with the other participants= data. In summer 2004, their results were in agreement with other participants. They had no particulate carbon and nitrogen data for winter 2005.

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 2002 was approximately 2.34 mg C/L.

The proportions of the standard deviations to the means for particulate phosphorus were low (7.2%) for the summer 2005 blind audit, and for the winter 2006 blind audit (13.0%). 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 2006 blind audits, leading us to conclude that inter-laboratory comparison of other particulate phosphorus data would be valid.

Reporting Data Accurately: A surprisingly large percentage of results were miscalculated (and later corrected), or had Aslipped a decimal@ or exhibited some other obvious entry error that could have been easily avoided. 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 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 and winter 2005 participants reported only two significant digits, thus potentially giving substantial under or over estimates for the comparisons.

CONCLUSION

Now that seventeen 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. Only one 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. The categories for Apass, 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 large variation in reported concentrations of low level ammonium for both blind audits and several previous audits, probably indicates that inter-laboratory comparisons of any ammonium data prepared from concentrates below 0.036 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. There was remarkable consistency in the measurement of total suspended solids from the suspensions of infusorial earth; however, there was a consistent negative bias in the measurements, when compared to the prepared concentrations. Further checks will be made of the preparation steps for subsampling the suspensions that are sent to participants.

5. The proportion of the standard deviation to the mean was small for particulate phosphorus for the winter 2003 through winter 2006 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 2005 and winter 2006 blind audits, some results were AGAIN (!) miscalculated (and later corrected), or

reported with insufficient significant digits, or contained some other error that could have been easily avoided. Over the course of the years, a few laboratories have repeatedly made calculation errors that were later corrected. It is hoped that the corrections of these lapses will 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 2005 and Winter 2006 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	
Virginia Institute of Marine Science (**VIMS**)	Carol Pollard	804-684-9749	X	X	X		X
Virginia Div, Consolidated Lab Services (**DCLS**)	Jay Armstrong	804-648-4480 x328	X	X	X	X	X
Virginia Tech. Occoquan Lab (**OCC**)	Mary Lou Daniel	703-361-5606	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	X			X
Delaware Dept. of Natural Resources (**DELDNR**)	Ben Pressly	302-739-4771	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
USGS National Water Quality Lab (**USGS**)	Mary Cast (summer only)	303-236-3463	X	X	X	X	
PA DEP, Bureau of Laboratories (**PADEP**)	Richard Shelbley	717-795-2425	X				X
MWRA, Water Quality Laboratory (**MWRA**)	Jennifer Prasse	617-860-7808	X	X	X	X	X
Hampton Roads Sanitation District (**HRSD**)	Stacey Hetzler	757-460-4217	X			X	X

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Summer 2005 and the Winter 2006 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 2005						
Total Dissolved Nitrogen	0.301	0.0448	9		2	
Total Dissolved Nitrogen	0.657	0.0430	9	1	1	
Total Dissolved Phosphorus	0.0209	0.0055	6	5		
Total Dissolved Phosphorus	0.0506	0.0077	8	2	1	
Ammonium	0.0341	0.0079	11			1
Ammonium	0.1082	0.0176	9	2	1	
Nitrate + Nitrite	0.0495	0.0057	10	2	1	
Nitrate + Nitrite	0.848	0.0321	12			1
Orthophosphate	0.0070	0.0031	10	3		
Orthophosphate	0.0394	0.0025	9	4		
Dissolved Organic Carbon	1.857	0.3016	8		1	
Dissolved Organic Carbon	5.427	0.3247	7	2		
Particulate Carbon	1.44	0.199	11		1	
Particulate Nitrogen	0.257	0.0362	9	3		
Particulate Phosphorus	0.0219	0.0016	7	1		
Total Suspended Solids	78.65	5.336	9	3		
Winter 2006						
Total Dissolved Nitrogen	0.280	0.0595	9	1	1	
Total Dissolved Nitrogen	0.832	0.0600	10		1	1
Total Dissolved Phosphorus	0.0184	0.0035	7	4		
Total Dissolved Phosphorus	0.0490	0.0041	8	3	1	
Ammonium	0.036	0.0136	11		1	
Ammonium	0.324	0.0218	8	4	1	
Nitrate + Nitrite	0.034	0.0033	8	4		
Nitrate + Nitrite	0.816	0.0168	8	5		
Orthophosphate	0.0100	0.0013	10	1	1	
Orthophosphate	0.0180	0.0019	10	2	1	
Dissolved Organic Carbon	1.80	0.134	5	4	1	
Dissolved Organic Carbon	3.99	0.187	5	5		
Particulate Carbon	1.33	0.506	9		1	
Particulate Nitrogen	0.176	0.0139	8	1	1	
Particulate Phosphorus	0.0134	0.0017	6	2		
Total Suspended Solids	8.53	0.966	8	2		1

Table 3. Summary of Prepared and Reported Concentrations for Each Analyte, Including Percent Recovery of the Prepared Concentration

			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 2005					
Total Dissolved Nitrogen	0.298	0.2-0.392	9	1	2
Total Dissolved Nitrogen	0.653	0.55-.7061	11	1	
Total Dissolved Phosphorus	0.018**	0.011-0.029	3	3	5
Total Dissolved Phosphorus	0.0461	0.032-0.0611	4	4	3
Ammonium	0.036**	0.0275-0.058	6	4	2
Ammonium	0.100	0.08-0.153	9	1	2
Nitrate + Nitrite	0.049	0.038-0.063	9	2	2
Nitrate + Nitrite	0.868	0.7471-0.871	12	1	
Orthophosphate	0.0056**	0.0029-0.013	4	2	7
Orthophosphate	0.0424	0.035-0.043	9	4	
Dissolved Organic Carbon	1.70	1.65-2.6	6	2	1
Dissolved Organic Carbon	5.40	4.91-6.1	8	1	
Total Suspended Solids	86	68.4-83.8	9	2	1
Winter 2006					
Total Dissolved Nitrogen	0.27	0.198-0.404	6	2	3
Total Dissolved Nitrogen	0.81	0.6-0.96	10	1	1
Total Dissolved Phosphorus	0.0154**	0.0125-0.0234	4	4	3
Total Dissolved Phosphorus	0.0461	0.04-0.0564	8	3	1
Ammonium	0.036**	0.0259-0.075	2	6	4
Ammonium	0.315	0.29-0.369	12	1	
Nitrate + Nitrite	0.035	0.0409-0.055	9	2	1
Nitrate + Nitrite	0.812	0.7922-0.848	13		
Orthophosphate	0.0089**	0.0082-0.013	8	3	1
Orthophosphate	0.0186	0.0165-0.022	8	5	
Dissolved Organic Carbon	1.70	1.60-2.3	7	2	1
Dissolved Organic Carbon	4.00	3.7-4.21	9		
Total Suspended Solids	10.0	3.95-10	6	2	3

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

Appendix 1. Summer 2005 and Winter 2006 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 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.286	.298	96.0	.2949	.27	109.2
TDN (mg N/L)	.7061	.653	108.1	.7959	.81	98.3
TDP (mg P/L)	.0152	.018	84.4**	.0146	.0154	94.8**
TDP (mg P/L)	.047	.0461	102.0	.0423	.0461	91.8
NH4 (mg N/L)	.032	.036	88.9**	.0259	.036	71.9**
NH4 (mg N/L)	.1078	.100	107.8	.3217	.315	102.1
NO3 + NO2 (mg N/L)	.038	.049	77.6	.0304	.035	86.9
NO3 + NO2 (mg N/L)	.7471 FAIL	.868	86.1	.7922	.812	97.6
PO4 (mg P/L)	.0029	.0056	51.8**	.0087	.0089	97.8**
PO4 (mg P/L)	.0351	.0424	82.8	.0165	.0186	88.7
Particulate C (mg C/L)	1.312			1.20		
Particulate N (mg N/L)	.2550			.175		
Particulate P (mg P/L)	.0204			.0136		
Chlorophyll (□g/L)	10.92			10.1		
Total Suspended Solids (mg/L)	83.8	86	97.4	3.95 FAIL	10.0	39.5

AWARN@ and AFAIL@ based on standard deviation of all participants= reported concentrations
**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.

Appendix I. *Continued.*

Occoquan Watershed Monitoring Laboratory

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.392 WARN	.298	131.5	.259	.27	95.9
TDN (mg N/L)	.695	.653	106.4	.788	.81	97.3
TDP (mg P/L)		.018		.018	.0154	116.9**
TDP (mg P/L)		.0461		.05	.0461	108.5
NH4 (mg N/L)	.058 FAIL	.036	161.1**	.047	.036	130.6**
NH4 (mg N/L)	.153 WARN	.100	153.0	.343	.315	108.9
NO3 + NO2 (mg N/L)	.063 WARN	.049	128.6	.036	.035	102.9
NO3 + NO2 (mg N/L)	.865	.868	99.7	.812	.812	100
PO4 (mg P/L)	.013	.0056	232.1**	.010	.0089	112.4**
PO4 (mg P/L)	.043	.0424	101.4	.022 WARN	.0186	118.3
Particulate C (mg C/L)	2.04 WARN			2.85 WARN		
Particulate N (mg N/L)	.18			.208 WARN		
Chlorophyll (□g/L)	15.6			12.3		
DOC (mg C/L)	1.65	1.7	97.1	1.74	1.7	102.4
DOC (mg C/L)	4.91	5.4	90.9		4.0	
Total Suspended Solids (mg/L)	83	86	96.5	8.6	10.0	86.0

AWARN@ and AFAIL@ based on standard deviation of all participants= reported concentrations
**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.

Appendix I. *Continued.*

Delaware DNR

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.342	.298	114.8	.198	.27	73.3
TDN (mg N/L)	.688	.653	105.4	.775	.81	95.7
TDP (mg P/L)	.011	.018	61.1**	.023	.0154	149.4**
TDP (mg P/L)	.032 WARN	.0461	69.4	.042	.0461	91.1
NH4 (mg N/L)		.036		.075 WARN	.036	208.3**
NH4 (mg N/L)		.100		.336	.315	106.7
NO3 + NO2 (mg N/L)	.051	.049	104.1	.039	.035	111.4
NO3 + NO2 (mg N/L)	.834	.868	96.1	.822	.812	101.2
PO4 (mg P/L)	.013	.0056	232.1**	.013 WARN	.0089	146.1**
PO4 (mg P/L)	.042	.0424	99.1	.021	.0186	112.9
Particulate C (mg C/L)	1.53			1.13		
Particulate N (mg N/L)	.295			.169		
Particulate P (mg P/L)	.0224			.0130		
Chlorophyll (□g/L)	25.0			10.3		
DOC (mg C/L)	2.6 FAIL	1.7	152.9	2.3 WARN	1.7	135.3
DOC (mg C/L)	6.1	5.4	113.0	4.2	4.0	105.0
Total Suspended Solids (mg/L)	70.	86	81.4	9.0	10.0	90.0

AWARN@ and AFAIL@ based on standard deviation of all participants= reported concentrations
**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.

Appendix I. *Continued.*

University of Delaware

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
NH4 (mg N/L)	.0356	.036	98.9**	.0361	.036	100.3**
NH4 (mg N/L)	.1055	.100	105.5	.318	.315	101.0
NO3 + NO2 (mg N/L)	.0503	.049	102.7	.0352	.035	100.6
NO3 + NO2 (mg N/L)	.8597	.868	99.0	.819	.812	100.9
PO4 (mg P/L)	.0044	.0056	78.6**	.0091	.0089	102.2**
PO4 (mg P/L)	.0403	.0424	95.0	.017	.0186	91.4
Particulate C (mg C/L)	1.43					
Particulate N (mg N/L)	.217					

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

Appendix I. *Continued.*

Academy of Natural Sciences of Philadelphia

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.279	.298	93.6	.232	.27	85.9
TDN (mg N/L)	.633	.653	96.9	.878	.81	108.4
TDP (mg P/L)	.0179	.018	99.4**	.0125	.0154	81.2**
TDP (mg P/L)	.0470	.0461	102.0	.0470	.0461	102.0
NH4 (mg N/L)	.0326	.036	90.6**	.0290	.036	80.6**
NH4 (mg N/L)	.104	.100	104.0	.299	.315	94.9
NO3 + NO2 (mg N/L)	.0475	.049	96.9	.0275	.035	78.6
NO3 + NO2 (mg N/L)	.848	.868	97.7	.798	.812	98.3
PO4 (mg P/L)	.0055	.0056	98.2**	.0095	.0089	106.7**
PO4 (mg P/L)	.0365	.0424	86.1	.0185	.0186	99.5
Particulate C (mg C/L)	1.44			1.25		
Particulate N (mg N/L)	.234			.15		
Particulate P (mg P/L)	.0251			.0166		
Chlorophyll (□g/L)	17.0			16.0		
DOC (mg C/L)	1.70	1.7	100	1.86	1.7	109.4
DOC (mg C/L)	5.36	5.4	99.3	4.01	4.0	100.2
Total Suspended Solids (mg/L)	81.1	86	94.3	7.3	10.0	73.0

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

Appendix I. *Continued.*

Morgan State University Estuarine Research Center

Parameter	Summer 2005 Reported	Prepared	% Recovered	Winter 2006 Reported	Prepared	% Recovered
Chlorophyll (□g/L)	21.9			12.8		

Appendix I. *Continued.*

Old Dominion University

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.300	.298	100.7	.404 WARN	.27	149.6
TDN (mg N/L)	.665	.653	101.8	.96 WARN	.81	118.5
TDP (mg P/L)	.0188	.018	104.4**	.0234	.0154	151.9**
TDP (mg P/L)	.0499	.0461	108.2	.0564	.0461	122.3
NH4 (mg N/L)	.0299	.036	83.1**	.0276	.036	76.7**
NH4 (mg N/L)	.1042	.100	104.2	.3132	.315	99.4
NO3 + NO2 (mg N/L)	.0476	.049	97.1	.0324	.035	92.6
NO3 + NO2 (mg N/L)	.8471	.868	97.6	.7965	.812	98.1
PO4 (mg P/L)	.0058	.0056	103.6**	.0093	.0089	104.5**
PO4 (mg P/L)	.0408	.0424	96.2	.0185	.0186	99.5
Particulate C (mg C/L)	1.31			1.15		
Particulate N (mg N/L)	.2254			.169		
Particulate P (mg P/L)	.0209			.0127		
Chlorophyll (□g/L)	16.1			15.7		
Total Suspended Solids (mg/L)	81.92	86	95.3	9.28	10.0	92.8

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

Appendix I. *Continued.*

Virginia Division of Consolidated Laboratory Services

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.314	.298	105.4	.27	.27	100
TDN (mg N/L)	.632	.653	96.8	.83	.81	102.5
TDP (mg P/L)	.027	.018	150.0**	.018	.0154	116.9**
TDP (mg P/L)	.053	.0461	115.0	.046	.0461	99.8
NH4 (mg N/L)	.029	.036	80.6**	.030	.036	83.3**
NH4 (mg N/L)	.098	.100	98.0	.369	.315 WARN	117.1
NO3 + NO2 (mg N/L)	.047	.049	95.9	.033	.035	94.3
NO3 + NO2 (mg N/L)	.859	.868	99.0	.82	.812	101.0
PO4 (mg P/L)	.007	.0056	125.0**	.010	.0089	112.4**
PO4 (mg P/L)	.04	.0424	94.3	.019	.0186	102.2
Particulate C (mg C/L)	1.339			1.20		
Particulate N (mg N/L)	.273			.180		
Particulate P (mg P/L)	.0212			.0133		
Chlorophyll (□g/L)	15.					
DOC (mg C/L)	1.65	1.7	97.1	1.956	1.7	115.1
DOC (mg C/L)	5.154	5.4	95.4	3.67	4.0	91.8
Total Suspended Solids (mg/L)	82.0	86	95.3	9.0	10.0	90.0

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

Appendix I. *Continued.*

Hampton Roads Sanitation District

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)		.653		.6 FAIL	.81	74.1
TDP (mg P/L)		.0461		.04 WARN	.0461	86.8
NH4 (mg N/L)		.100		.29	.315	92.1
NO3 + NO2 (mg N/L)		.868		.84	.812	103.4
PO4 (mg P/L)		.0424		.02	.0186	107.5
DOC (mg C/L)		1.7		1.6	1.7	94.1
DOC (mg C/L)		5.4		3.74	4.0	93.5
Total Suspended Solids (mg/L)		86		7.0	10.0	70.0

AWARN@ and AFAIL@ based on standard deviation of all participants= reported concentrations

Appendix I. *Continued.*

UMCES Horn Point Laboratory

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.297	.298	99.7	.330	.27	122.2
TDN (mg N/L)	.651	.653	99.7	.859	.81	106.0
TDP (mg P/L)	.0191	.018	106.1**	.0160	.0154	103.9**
TDP (mg P/L)	.0532	.0461	115.4	.0505	.0461	109.5
NH4 (mg N/L)	.0328	.036	91.1**	.0316	.036	87.8**
NH4 (mg N/L)	.128	.100	128.0	.346	.315	109.8
NO3 + NO2 (mg N/L)	.0487	.049	99.4	.0371	.035	106.0
NO3 + NO2 (mg N/L)	.862	.868	99.3	.814	.812	100.2
PO4 (mg P/L)	.0057	.0056	101.8**	.0087	.0089	97.8**
PO4 (mg P/L)	.0406	.0424	95.8	.017	.0186	91.4
Particulate C (mg C/L)	1.36			1.15		
Particulate N (mg N/L)	.275			.176		
Chlorophyll (□g/L)	17.2					
DOC (mg C/L)		1.7		1.70	1.7	100
DOC (mg C/L)		5.4		3.89	4.0	97.2
Total Suspended Solids (mg/L)	80.4	86	93.5		10.0	

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

Appendix I. *Continued.*

UMCES Chesapeake Biological Laboratory

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.313	.298	105.0	.287	.27	106.3
TDN (mg N/L)	.646	.653	98.9	.825	.81	101.9
TDP (mg P/L)	.0201	.018	111.7**	.0162	.0154	105.2**
TDP (mg P/L)	.0495	.0461	107.4	.0484	.0461	105.0
NH4 (mg N/L)	.036	.036	100**	.032	.036	88.9**
NH4 (mg N/L)	.107	.100	107.0	.323	.315	102.5
NO3 + NO2 (mg N/L)	.0507	.049	103.5	.0352	.035	100.6
NO3 + NO2 (mg N/L)	.866	.868	99.8	.826	.812	101.7
PO4 (mg P/L)	.0053	.0056	94.6**	.0082	.0089	92.1**
PO4 (mg P/L)	.0407	.0424	96.0	.0166	.0186	89.2
Particulate C (mg C/L)	1.43			1.18		
Particulate N (mg N/L)	.305			.185		
Particulate P (mg P/L)	.0226			.0127		
Chlorophyll (□g/L)	15.2			15.9		
DOC (mg C/L)	1.74	1.7	102.4	1.79	1.7	105.3
DOC (mg C/L)	5.49	5.4	101.7	4.08	4.0	102.0
Total Suspended Solids (mg/L)	83.6	86	97.2	8.8	10.0	88.0

**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 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.272	.298	91.3	.251	.27	93.0
TDN (mg N/L)	.639	.653	97.9	.783	.81	96.7
TDP (mg P/L)	.0278	.018	154.4**	.0173	.0154	112.3**
TDP (mg P/L)	.0611	.0461	132.5	.0478	.0461	103.7
NH4 (mg N/L)	.0323	.036	89.7**	.0297	.036	82.5**
NH4 (mg N/L)	.102	.100	102.0	.311	.315	98.7
NO3 + NO2 (mg N/L)	.0542	.049	110.6	.0381	.035	108.9
NO3 + NO2 (mg N/L)	.868	.868	100	.848	.812	104.4
PO4 (mg P/L)	.0063	.0056	112.5**	.00887	.0089	99.7**
PO4 (mg P/L)	.0407	.0424	96.0	.0163	.0186	87.6
Particulate C (mg C/L)	1.339			1.13		
Particulate N (mg N/L)	.277			.171		
Particulate P (mg P/L)	.0203			.0106		
Chlorophyll (□g/L)	14.7			13.1		
DOC (mg C/L)	1.7	1.7	100	1.60	1.7	94.1
DOC (mg C/L)	5.44	5.4	100.7	4.06	4.0	101.5
Total Suspended Solids (mg/L)	68.4	86	79.5	9.35	10.0	93.5

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

Appendix I. *Continued.*

USGS, National Water Quality Laboratory

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.308	.298	103.4	.298	.27	110.4
TDN (mg N/L)	.695	.653	106.4	.824	.81	101.7
TDP (mg P/L)	.0203	.018	112.8**	.0164	.0154	106.5**
TDP (mg P/L)	.0529	.0461	114.8	.0512	.0461	111.1
NH4 (mg N/L)	.034	.036	94.4**	.029	.036	80.6**
NH4 (mg N/L)	.104	.100	104.0	.298	.315	94.6
NO3 + NO2 (mg N/L)	.047	.049	95.9	.034	.035	97.1
NO3 + NO2 (mg N/L)	.847	.868	97.6	.809	.812	99.6
PO4 (mg P/L)	.007	.0056	125.0**	.010	.0089	112.4**
PO4 (mg P/L)	.039	.0424	92.0	.018	.0186	96.8
Particulate C (mg C/L)	1.373			1.18		
Particulate N (mg N/L)	.281			.179		
Chlorophyll (□g/L)	12.3			13.6		
DOC (mg C/L)	1.777	1.7	104.5	1.7	1.7	100
DOC (mg C/L)	5.333	5.4	98.8	3.7	4.0	92.5
Total Suspended Solids (mg/L)	73	86	84.9	10.0	10.0	100

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

Appendix I. *Continued.*

MWRA WATER QUALITY LABORATORY

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.304	.298	102.0	.285	.27	105.6
TDN (mg N/L)	.686	.653	105.1	.788	.81	97.3
TDP (mg P/L)	.0232	.018	128.9**	.021	.0154	136.4**
TDP (mg P/L)	.0600	.0461	130.2	.0526	.0461	114.1
NH4 (mg N/L)	.0275	.036	76.4**	.0338	.036	93.9**
NH4 (mg N/L)	.105	.100	105.0	.314	.315	99.7
NO3 + NO2 (mg N/L)	.0485	.049	99.0	.0353	.035	100.9
NO3 + NO2 (mg N/L)	.871	.868	100.3	.809	.812	99.6
PO4 (mg P/L)	.00496	.0056	88.6**	.0096	.0089	107.9**
PO4 (mg P/L)	.0379	.0424	89.4	.019	.0186	102.2
Particulate C (mg C/L)	1.40			1.20		
Particulate N (mg N/L)	.266			.177		
Particulate P (mg P/L)	.022			.0148		
Chlorophyll (□g/L)	18.4			14.4		
DOC (mg C/L)	1.99	1.7	117.1	1.96	1.7	115.3
DOC (mg C/L)	5.60	5.4	103.7	4.21	4.0	105.2
Total Suspended Solids (mg/L)	78.6	86	91.4	9.0	10.0	90.0

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

Appendix I. *Continued.*

PADEP WATER QUALITY LABORATORY

Parameter	Summer 2005 Reported	Summer 2005 Prepared	% Recovered	Winter 2006 Reported	Winter 2006 Prepared	% Recovered
TDN (mg N/L)	.2	.298	67.1 WARN		.27	
TDN (mg N/L)	.55	.653	84.2 WARN		.81	
TDP (mg P/L)	.029	.018	161.1**		.0154	
TDP (mg P/L)	.051	.0461	110.6		.0461	
NH4 (mg N/L)	.03	.036	83.3**		.036	
NH4 (mg N/L)	.08	.100	80.0		.315	
NO3 + NO2 (mg N/L)	.04	.049	81.6		.035	
NO3 + NO2 (mg N/L)	.85	.868	97.9		.812	
PO4 (mg P/L)	.01***	.0056	178.6**		.0089	
PO4 (mg P/L)	.035	.0424	82.5		.0186	
DOC (mg C/L)	1.91	1.7	112.4		1.7	
DOC (mg C/L)	5.46	5.4	101.1		4.0	
Total Suspended Solids (mg/L)	78.	86	90.7		10.0	

**The prepared sample concentration was quite low, so the acceptance boundaries are narrow.
***The prepared sample concentration was below the detection limit.
AWARN@ based on standard deviation of all other participants= reported concentrations

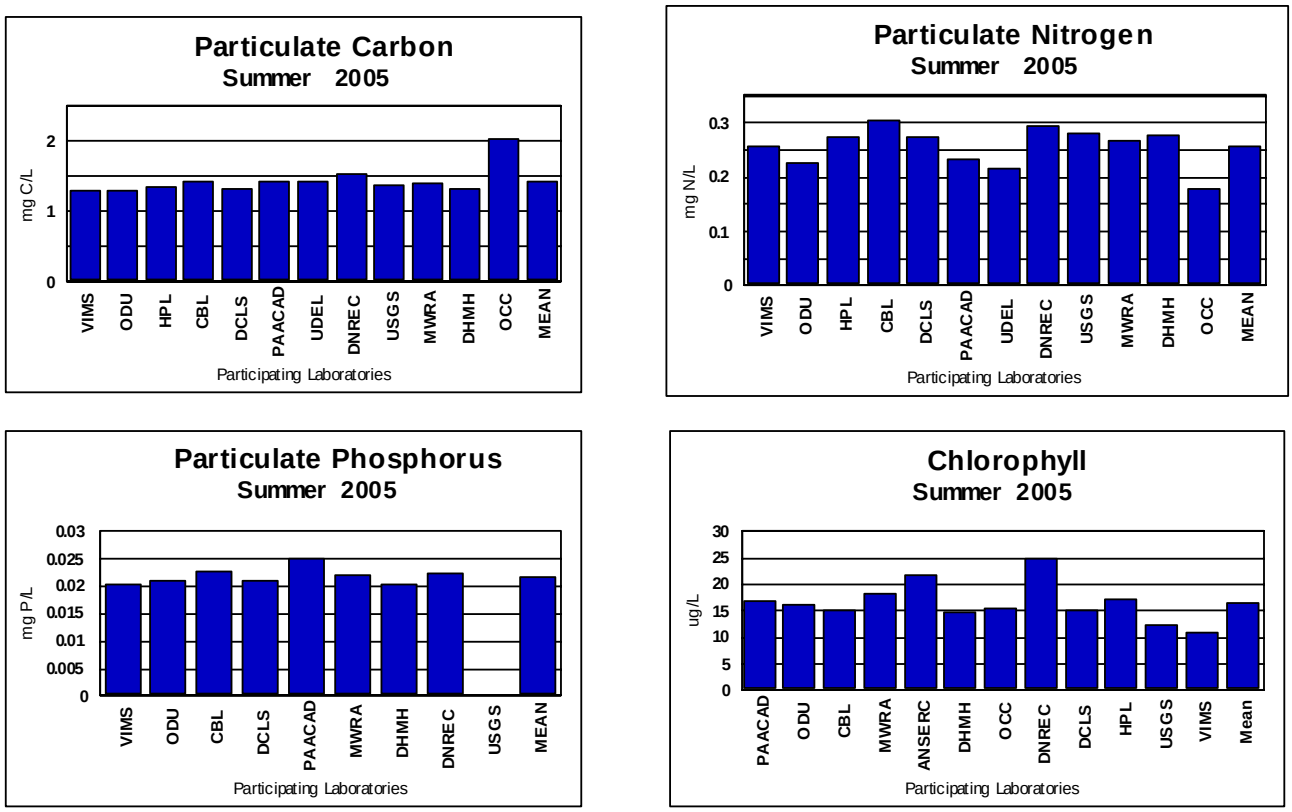
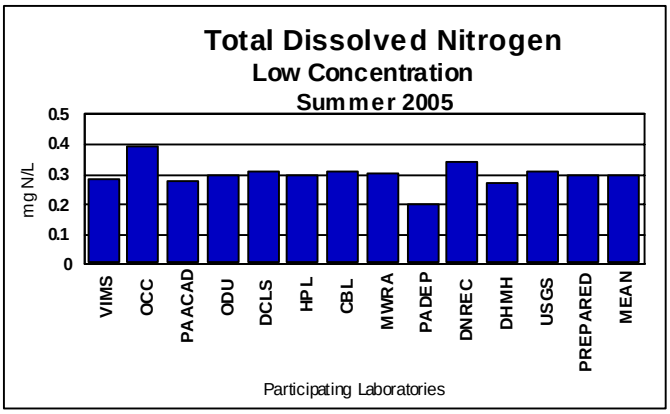
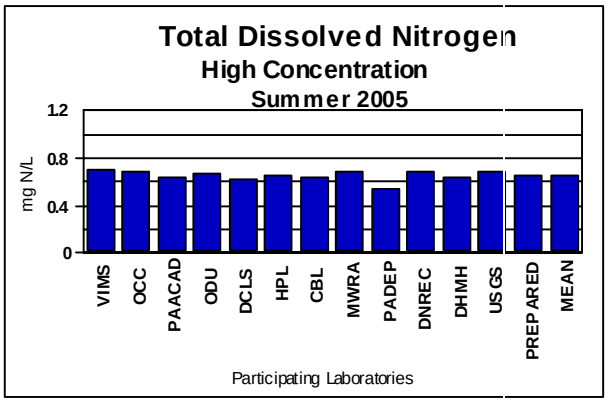
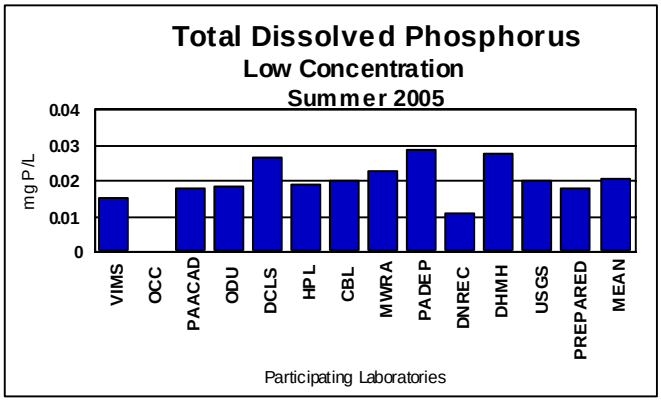


Figure 1. Particulate carbon, nitrogen and phosphorus; chlorophyll, Summer 2005.







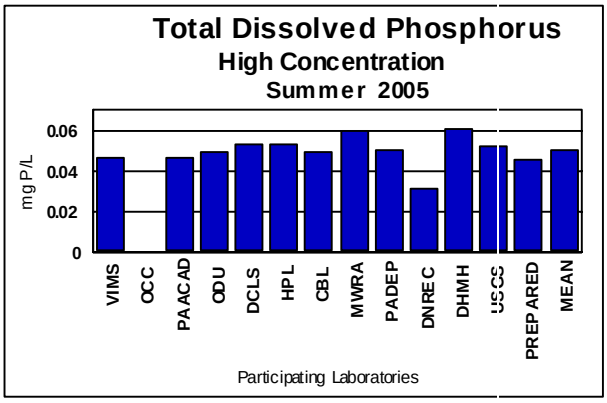
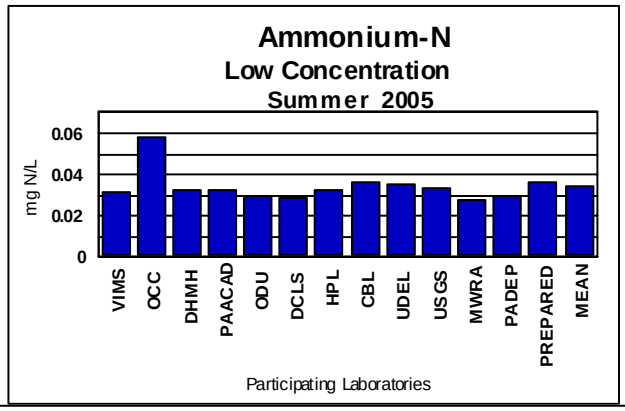
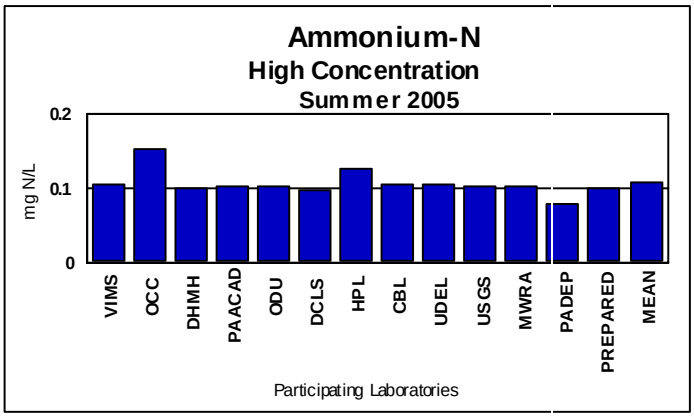
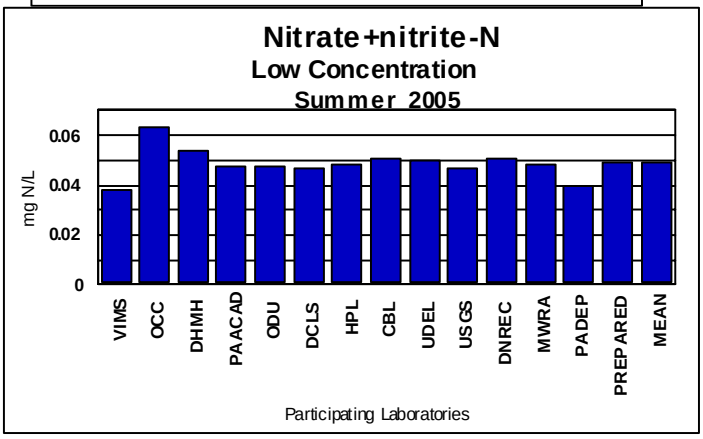
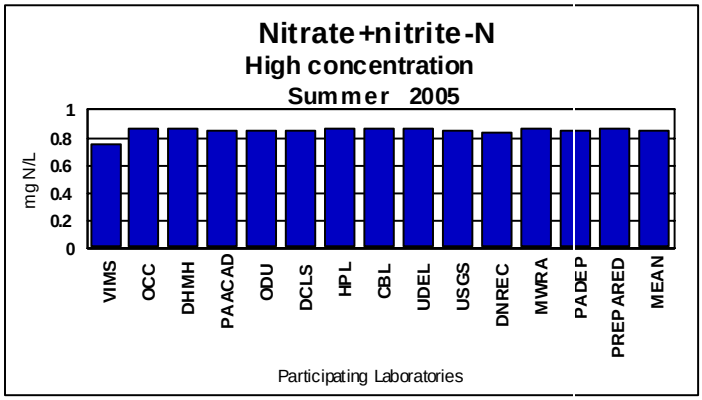


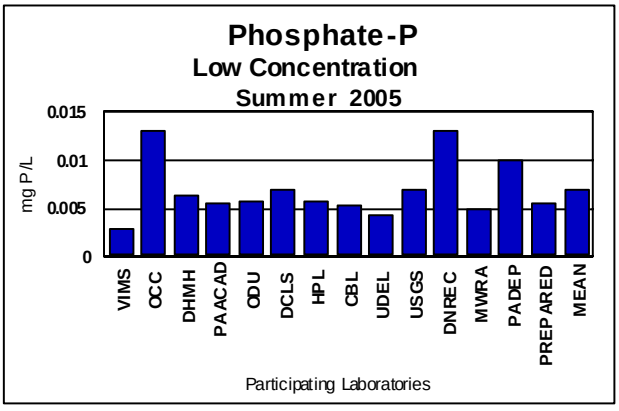
Figure 2. Total dissolved nitrogen and phosphorus, Summer 2005.











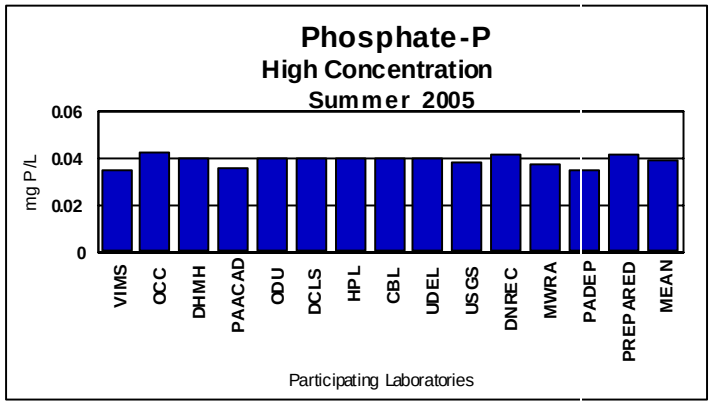
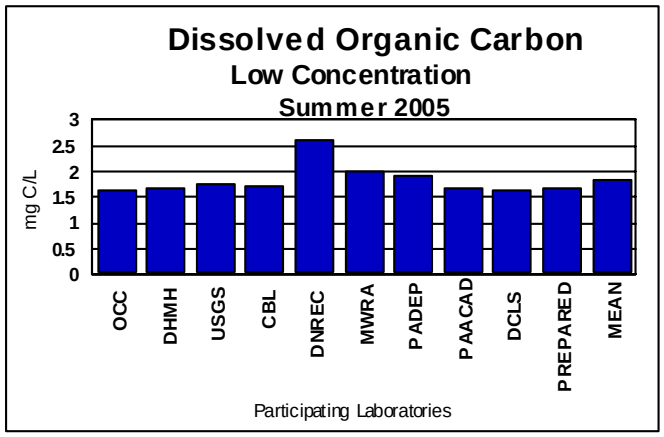
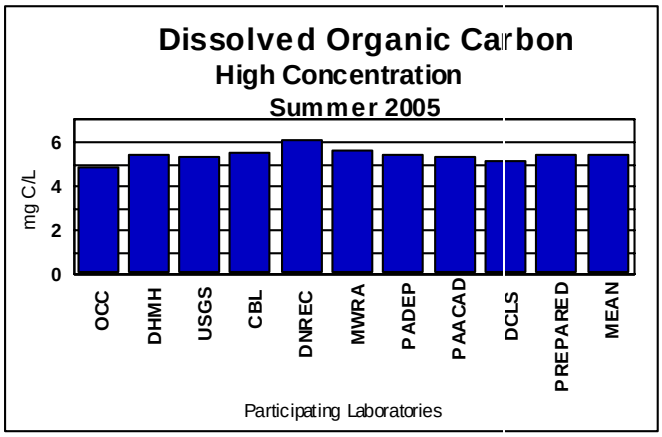


Figure 3. Dissolved inorganic nitrogen and phosphorus, Summer 2005.





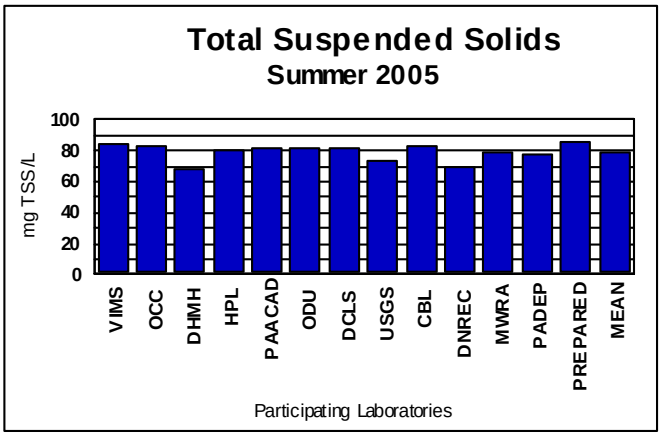
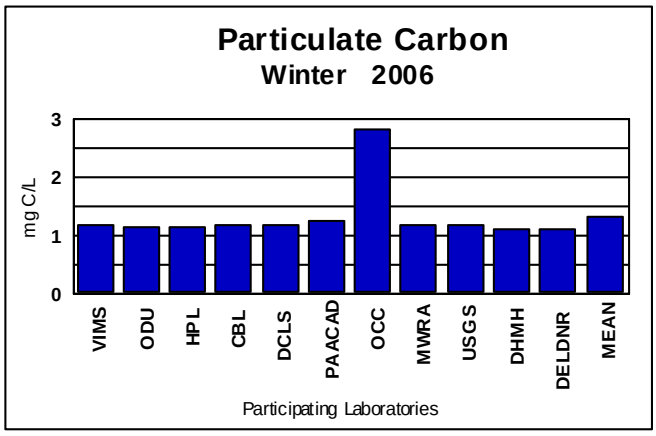
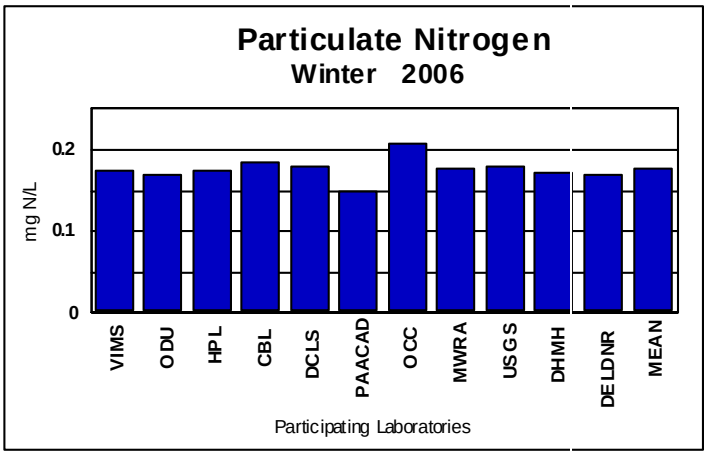
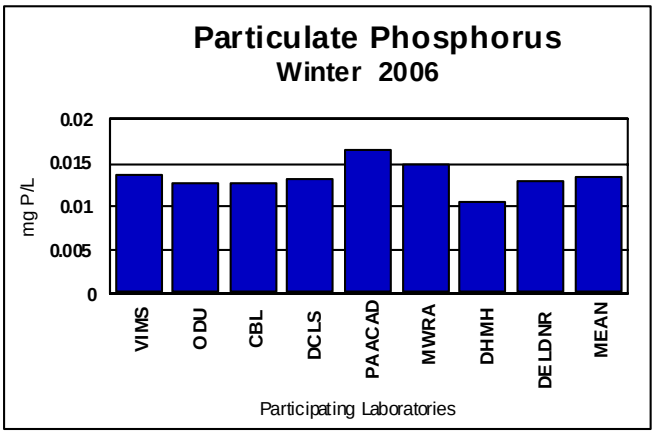


Figure 4. Dissolved organic carbon and total suspended solids, Summer 2005.







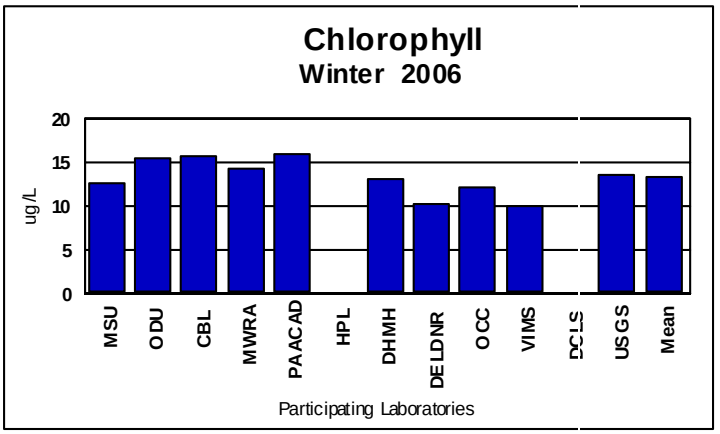
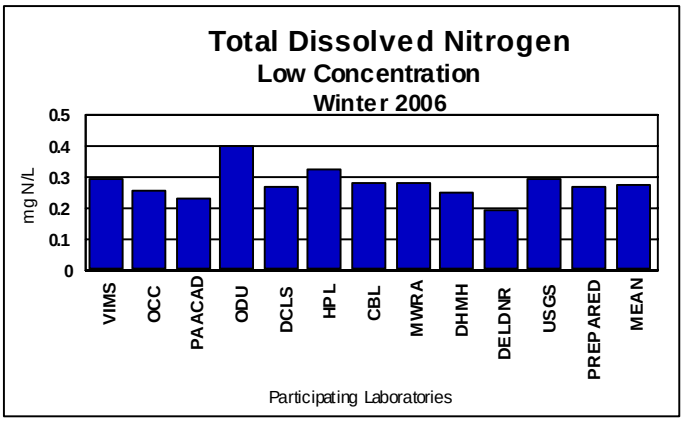
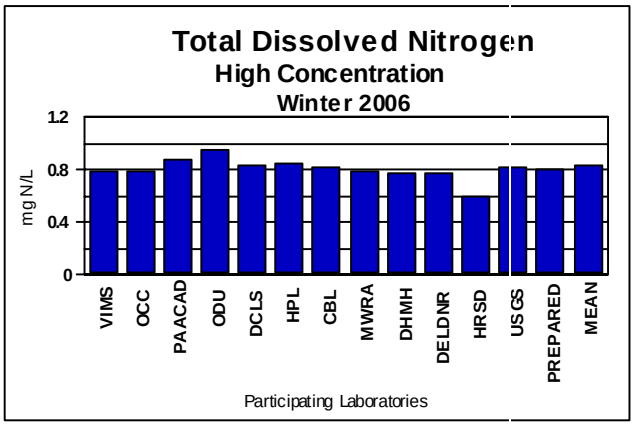
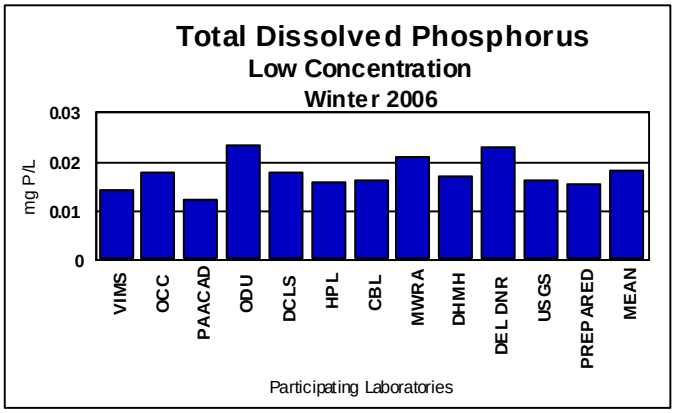


Figure 5. Particulate carbon, nitrogen and phosphorus; chlorophyll, Winter 2006.







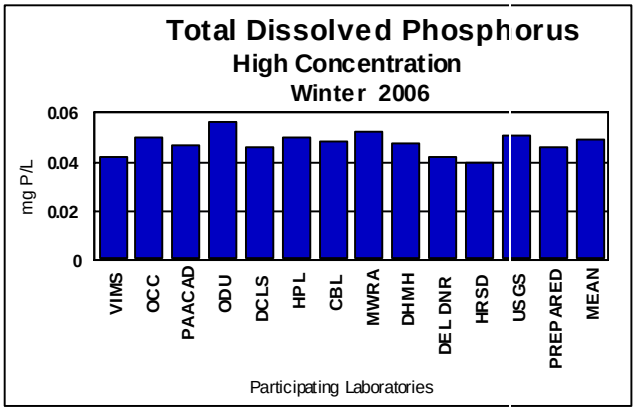
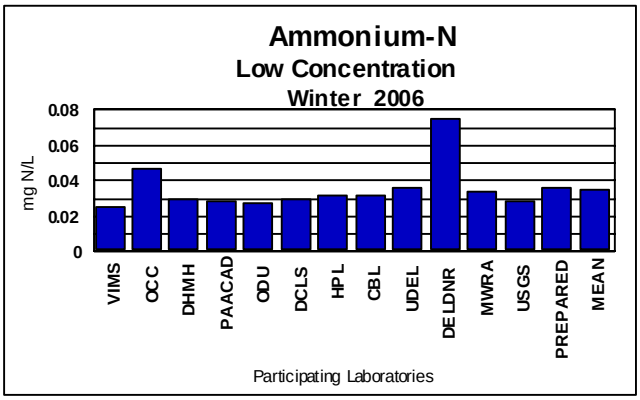
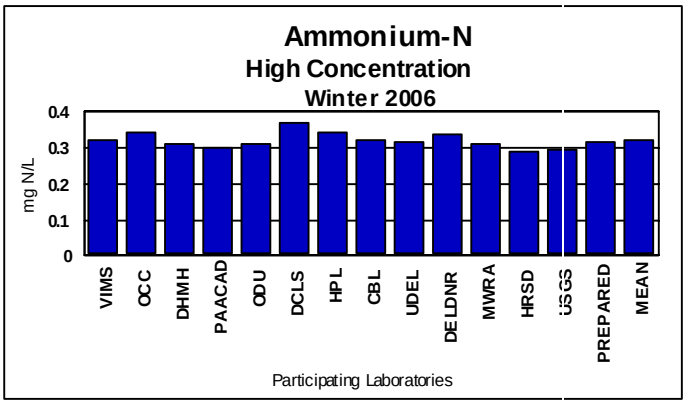
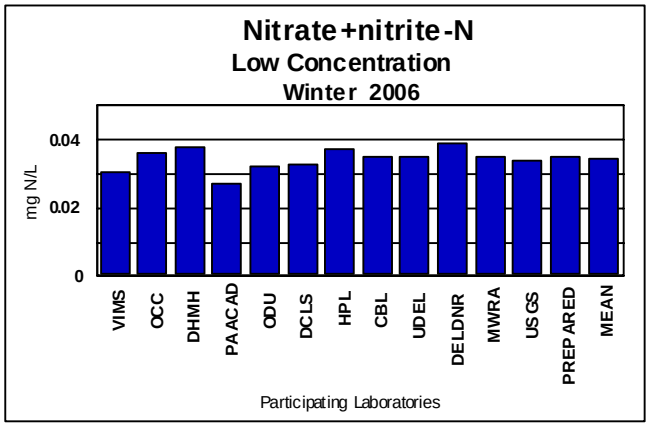
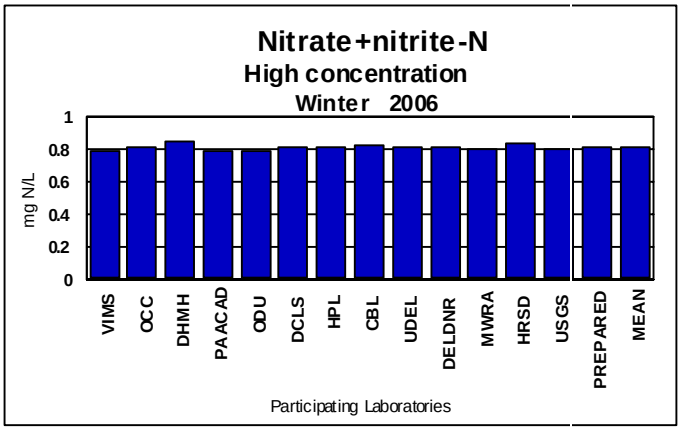


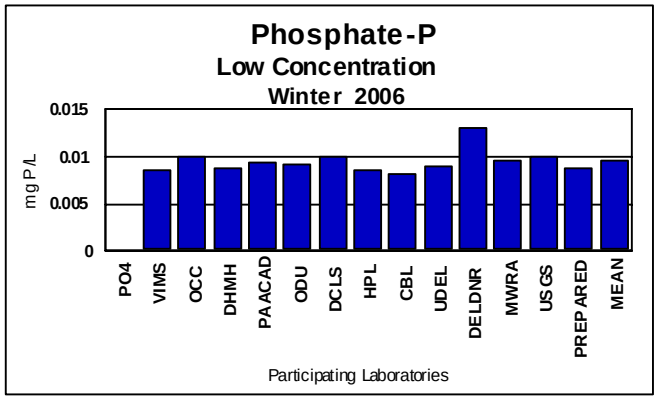
Figure 6. Total dissolved nitrogen and phosphorus, Winter 2006











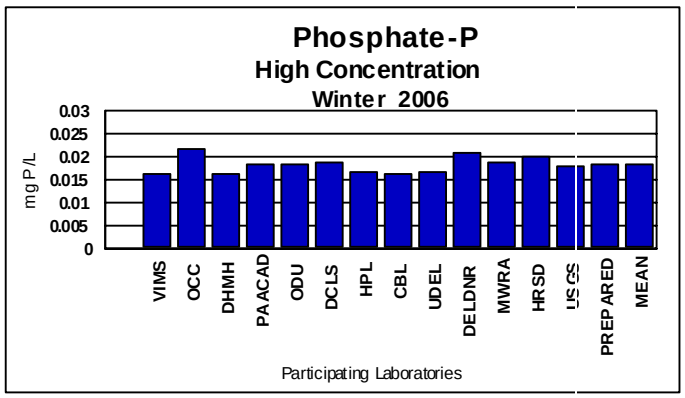
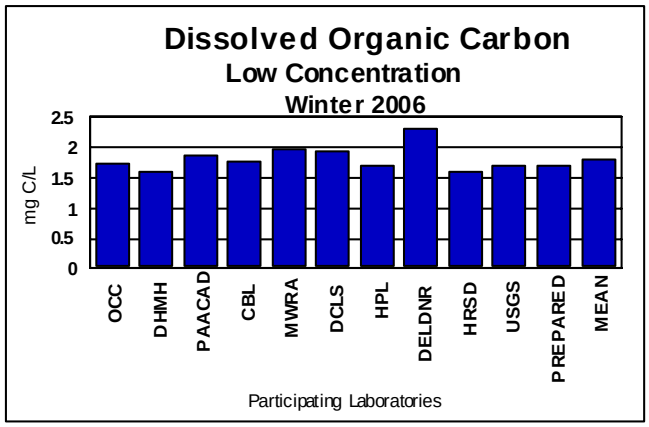
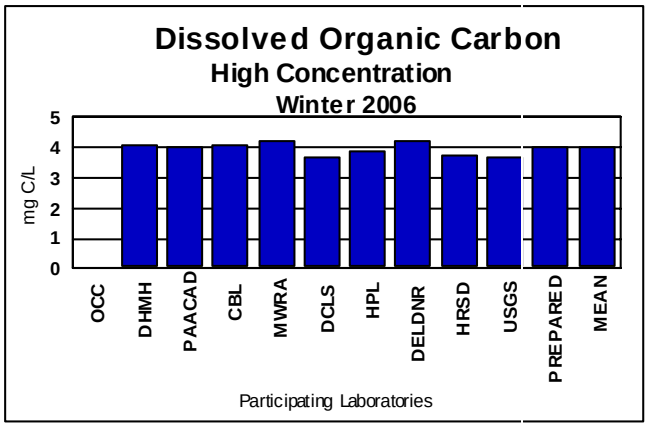


Figure 7. Dissolved inorganic nitrogen and phosphorus, Winter 2006.





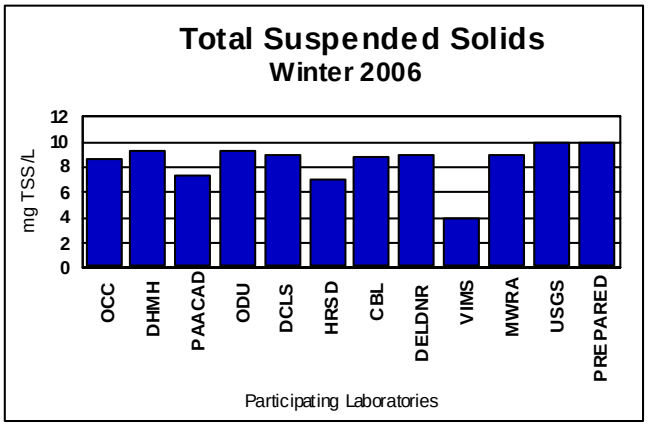


Figure 8. Dissolved organic carbon and total suspended solids, Winter 2006.