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CHESAPEAKE BAY PROGRAM BLIND AUDIT

2002 FINAL REPORT

SUBMITTED BY:

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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 fifth 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 20 February 2002 and 19 August 2002. Participating laboratories and contact personnel are found in Table 1.
Parameters measured were: total dissolved nitrogen, total dissolved phosphorus, nitrate+nitrite, ammonium and phosphate. High and low concentration samples were provided for each analyte. Particulate carbon, nitrogen and phosphorus samples, as well as chlorophyll, 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. 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 off the CBL pier in February and August, 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 47ÇC) 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. Chlorophyll results were reported as μg/L.

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 2002 are found at the end of the report. Shortly after the completion of each study, a brief data report, including the concentrations of the prepared samples, was sent to each participant. We contacted participants whose reported concentration(s) appeared Aout of line.@ In several instances, they checked and corrected their concentration calculations, and, then, submitted corrected data.

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).

DISSOLVED FRACTION

Total Dissolved Nitrogen: The prepared low level winter concentration was 0.154 mg N/L and 0.141-0.198 mg N/L was reported by participants. The prepared high level winter concentration was 0.440 mg N/L and 0.395-0.491 mg N/L was reported by participants. The prepared low level summer concentration was 0.300 mg N/L and 0.271-0.429 mg N/L was reported by participants. The prepared high level summer concentration was 0.945 mg N/L and 0.883-1.02 mg N/L was reported by participants; that is, all were within c10% of the prepared high level summer concentration (Figures 2 and 5).

Total Dissolved Phosphorus: The prepared low level winter concentration was 0.0108 mg P/L and 0.0100-0.0156 mg P/L was reported by participants. The prepared high level winter concentration was 0.0240 mg P/L and 0.0238-0.0320 mg P/L was reported by participants. The prepared low level summer concentration was 0.0170 mg P/L and 0.0155-0.0205 mg P/L was reported by participants. The prepared high level summer concentration was 0.0430 mg P/L and 0.0404-0.0550 mg P/L was reported by participants (Figures 2 and 5).

Ammonium: The prepared low level winter concentration was 0.026 mg N/L and 0.015-0.0333 mg N/L was reported by participants. The prepared high level winter concentration was 0.192 mg N/L and 0.1811-0.218 mg N/L was reported by participants (Figure 3). Both prepared inorganic nutrient concentrates for the summer blind audit inadvertently contained no ammonium.

Nitrate + Nitrite: The prepared low level winter concentration was 0.0233 mg N/L and 0.0168-0.0250 mg N/L was reported by participants. The prepared high level winter concentration was 0.735 mg N/L and 0.714-0.794 mg N/L was reported by participants; that is, all were within c10% of the prepared concentration. The prepared low level summer concentration was 0.0175 mg N/L and 0.0004-0.0500 mg N/L was reported by participants. The prepared high level summer concentration was 0.875 mg N/L and 0.822-0.956 mg N/L was reported by participants; that is, all were, again, within c10% of the prepared concentration (Figures 3 and 6).

Orthophosphate: The prepared low level winter concentration was 0.0120 mg P/L and 0.0110-0.035 mg P/L was reported by participants. The prepared high level winter concentration was 0.0496 mg P/L and 0.042-0.077 mg P/L was reported by participants. Both prepared inorganic nutrient concentrates for the summer blind audit inadvertently contained an unintended, relatively moderate or large amount of orthophosphate. When diluted by participants, they reported a mean concentration of 0.0461 mg P/L c 0.0015 S.D., coefficient of variation only 3.18% for one sample. When diluted by participants, they reported a mean concentration of 0.432 mg P/L c 0.0136 S.D., coefficient of variation only 3.15% for the other sample. All participants were able to recognize the relatively moderate to high concentrations presented and analyze them with remarkably great inter-laboratory precision (Figures 3 and 6).

PARTICULATE FRACTION

Again, it should be noted that these samples were filtered from a common estuarine water sample and, consequently, are not true blind audit samples produced from pure constituents. To assess the variability found in a natural sample, a test of repeated analyses at one laboratory (CBL) was completed in January 1998. The coefficients of variation of particulate nitrogen and carbon concentrations in 12 samples from a common container were 5.1% and 12.1%, respectively. For particulate phosphorus, the coefficient of variation (N=8) was 3.1%.

Particulate Nitrogen: Particulate N results revealed close agreement between participating laboratories in both audits (Table 2). For the winter sample, the mean was 0.0834 mg N/L c 0.0133 S.D. For the summer sample the mean was 0.394 mg N/L c 0.025 S.D. The percent coefficient of variation among the laboratories participating in the audit was 16% (N=8) for the winter, and 6.3% (N=6) for the summer (Figures 1 and 4). These were somewhat more variable than the 5.1% variability found for 12 samples analyzed by one laboratory in January 1998.

Particulate Carbon: Particulate C results revealed close agreement between participating laboratories in both audits (Table 2). For the winter sample, the mean was 0.5405 mg C/L c 0.0409 S.D. For the summer sample the mean was 2.34 mg C/L c 0.076 S.D. The percent coefficient of variation among the laboratories participating in the audit was 7.6% (N=8) for the winter, and 3.2% (N=6) for the summer (Figures 1 and 4). These were less than the 12.1% variability found for 12 samples analyzed by one laboratory in January 1998.

Particulate Phosphorus: Particulate P results revealed close agreement between participating laboratories in both audits (Table 2). For the winter sample, the mean was 0.0099 mg P/L c 0.0038 S.D. For the summer sample, the mean was 0.0339 mg P/L c 0.0098 S.D. The percent coefficient of variation among the laboratories participating in the audit was 38% (N=7) for the winter, and 29% (N=5) for the summer (Figures 1 and 4). These were quite large in comparison to the 3.1% variability found for 8 samples analyzed by one laboratory in January 1998.

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 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 " 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.

Data were also assessed by comparing reported concentrations to those that were prepared (Table 3). Groupings of data in Apass, warn and fail@ categories were arbitrarily set. Reported data that were within ç10% 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.@

Most of the data comparisons based on standard deviations showed similar characteristics (Tables 2 and 3); 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 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 passed. It should also be noted that no data points fell in the fail category, and about the same number were in the warning category as in previous years.

The data sets with relatively small standard deviations yielded more warning points. For example, in the Winter 2002 blind audit of high level nitrate concentration, the mean reported concentration was 0.743 mg N/L and reported concentrations ranged from 0.714-0.794 mg N/L (Coefficient of Variation, 3.0%). Nine laboratories reported results for this high level nitrate sample that were within one standard deviation (0.0224 mg N/L) of the mean. Since the standard deviation was so small, one laboratory=s reported results for this sample were between one and two standard deviations of the mean; and one laboratory=s results were between two and three standard deviations of the mean, so it was labeled as a warning. This nitrate data comparison points toward a form of circular reasoning in these statistical assessments. The data being evaluated are also the data that were used to calculate the mean and standard deviation to which the data are being compared. All of the reported data were within ç10% of the prepared concentration. Thus, by that measure of accuracy, all the data Apassed.@

When comparing reported concentrations to those prepared, the lower concentration ranges had more data that fell in the 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 Winter 2002 blind audit of 0.012

mg P/L prepared for orthophosphate has a Apass@ category (c10%) of only 0.0108-0.0132 mg P/L. Nine out of eleven participating laboratories reported results that fell in the Awarn@ and Afail@ categories, because the between-laboratory precision was greater than c10% of the prepared concentration at this concentration level. Therefore, for very low concentrations of prepared samples, it may be appropriate to broaden the acceptance boundaries.

No laboratory reported concentrations for an individual analyte that were consistently different from the range of the other reported concentrations for both sets of blind audit samples tested for that analyte.

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. In all instances, the standard deviation was less than 20% of the mean reported concentration for particulate carbon and nitrogen. 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 proportion of the standard deviation to the mean was 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. We had attributed this good replication to low sampling error due to the large volume filtered for particulate phosphorus. 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. The concentration of particulate phosphorus in the winter blind audit was among the lowest ever provided, apparently reducing participants= accuracy and precision. The summer particulate phosphorus blind audit concentration was among the highest ever provided, so it would be expected that the reported data would have little variability. A visual inspection of the summer particulate phosphorus data indicates that one reported concentration was clearly different from the others, but there were so few participants that it did not generate a Awarning.@ 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 have been added to the blind audit program in 2001 and 2002; however, no laboratory has 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.

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 and also 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 expected 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 and 2002 participants reported only two significant digits, thus potentially giving substantial under or over estimates for the comparisons.

CONCLUSIONS

Now that ten 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. No laboratory reported concentrations for an individual analyte that were consistently different from the range of the other reported concentrations for both concentration ranges tested for that analyte. 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 ç10% of the prepared sample than the higher level concentration ranges, i.e., there was less accuracy at the lower concentration ranges. 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 proportion of the standard deviation to the mean was high for particulate phosphorus in the four blind audits conducted in 2001 and 2002. This contrasted to all three previous years of blind audits in which the coefficient of variation for particulate phosphorus was usually the lowest of the particulate fractions.

4. Care should continue to be taken when completing report forms. During 2002 some results were miscalculated (and later corrected), or reported insufficient significant digits, or contained some other error that could have been easily avoided. These lapses could be construed as common reporting practices that would have deleterious effects on the overall data quality of that laboratory.

Table 1. Participants in the 2002 Chesapeake Bay Blind Audit Program

Institution	Contact Person	Phone	Dissolved	Particulate	Chl. *a*
Old Dominion University, Water Quality Lab (ODU)	Suzanne Doughten	757-451-3043	X	X	X
U. Maryland, HPL (HPL)	Lois Lane	410-221-8252	X	X	
Virginia Institute of Marine Science (VIMS)	Carol Pollard	804-642-7213	X	X	X
Va. Div. Consol. Lab Services (DCLS)	Jay Armstrong	804-559-3247	X	X	X
Va. Tech. Occaquan Lab (OCC)	Mary Lou Daniel	703-361-5606	X		X
Md. Dept. Heath & Mental Hygiene (DHMH)	Deborah Miller-Tuck	410-767-6180	X		X
U. Maryland, CBL (CBL)	Carl Zimmermann	410-326-7252	X	X	X
USDA, ARS, Animal Manure and By-products Lab (USDA)	Jack Meisinger	301-504-5276	X		
Univ. Delaware (UDEL)	Joe Scudlark	302-645-4300	X	X	
Delaware DNR (Del. DNR)	Ben Pressly	302-739-4771	X		X
U. Maryland , AL (AEL)	Katie Kline	301-689-7122	X	X	
Academy of Natural Science, Estuarine Research Center (ANSERC)	Richard Lacoutre	410-586-9700			X
Academy of Natural Sciences of Philadeophia (PAACAD)	Paul Kiry	215-299-1076	X	X	X

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in Each of the Blind Audits, Including Distribution of Reported Concentrations from the Mean.

Parameter			**Number of Laboratories**			
			Standard Deviations from Mean			
			<1	1-2	2-3	>3
	Mean	S.D.	**PASS**	**PASS**	**WARN**	**FAIL**
Winter 2002						
Total Dissolved Nitrogen	0.162	0.0186	6	3		
Total Dissolved Nitrogen	0.440	0.0312	7	2		
Total Dissolved Phosphorus	0.0127	0.0019	5	4		
Total Dissolved Phosphorus	0.0267	0.0031	7	2		
Ammonium	0.026	0.0051	8	3	1	
Ammonium	0.201	0.0114	7	5		
Nitrate+Nitrite	0.022	0.0025	8	2	1	
Nitrate+Nitrite	0.743	0.0224	9	1	1	
Orthophosphate	0.017	0.0063	10		1	
Orthophosphate	0.051	0.0090	10		1	
Particulate Carbon	0.5405	0.0409	6	2		
Particulate Nitrogen	0.0834	0.0133	6	1	1	
Particulate Phosphorus	0.0099	0.0038	4	3		
Summer 2002						
Total Dissolved Nitrogen	0.315	0.0484	8		1	
Total Dissolved Nitrogen	0.943	0.0502	7	4		
Total Dissolved Phosphorus	0.0177	0.0020	4	3		
Total Dissolved Phosphorus	0.0471	0.0049	5	2		
Nitrate+Nitrite	0.0190	0.0115	9	1	1	
Nitrate+Nitrite	0.877	0.0397	7	4		
Orthophosphate	.0460	0.0016	5	5		
Orthophosphate	0.432	0.0134	7	3		
Particulate Carbon	2.34	0.076	5	1		
Particulate Nitrogen	0.394	0.0249	4	2		
Particulate Phosphorus	0.0339	0.0098	4	1		

Table 3. Summary of Prepared and Reported Concentrations for Each Analyte in Each of the Blind Audits, Including Comparison to Prepared Concentration

Parameter			**Number of Laboratories**		
	Prepared Concentration	Reported Concentration Range	Within 90% to 110% of Prepared Concentration	Within 80-90%, or 110-120% of Prepared Concentration	Less than 80%, or Greater than 120% of Prepared Concentration
	mg/L	mg/L	**PASS**	WARN	FAIL
Winter 2002					
Total Dissolved Nitrogen	0.154	0.141-0.198	6	2	1
Total Dissolved Nitrogen	0.440	0.395-0.491	8	1	
Total Dissolved Phosphorus	0.0108	0.0100-0.0156	3	2 **	4 **
Total Dissolved Phosphorus	0.0240	0.0238-0.0320	5	2	2
Ammonium	0.026	0.015-0.0333	6	2 **	4 **
Ammonium	0.192	0.1811-0.218	9	3	
Nitrate+Nitrite	0.0233	0.0168-0.025	9	1	1
Nitrate+Nitrite	0.735	0.714-0.794	11		
Orthophosphate	0.0120	0.011-0.0168	2	1 **	8 **
Orthophosphate	0.0496	0.042-0.077	9	1	1
Summer 2002					
Total Dissolved Nitrogen	0.300	0.271-0.429	7	1	1
Total Dissolved Nitrogen	0.945	0.883-1.02	9		
Total Dissolved Phosphorus	0.0170	0.0155-0.0205	5	1	1
Total Dissolved Phosphorus	0.0430	0.0404-0.055	4	2	1
Nitrate+Nitrite	0.0175	0.0004-0.050	8	1	2
Nitrate+Nitrite	0.875	0.822-0.956	11		

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

Appendix. 2002 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

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
TDN (mg N/L)	0.150	0.154	97			
TDN (mg N/L)	0.433	0.440	98			
TDP (mg P/L)	0.0135	0.0108	125**			
TDP (mg P/L)	0.0275	0.0240	115			
NH4 (mg N/L)	0.0200	0.026	77**			
NH4 (mg N/L)	0.1875	0.192	98			
NO3+NO2 (mg N/L)	0.0230	0.0233	99			
NO3+NO2 (mg N/L)	0.760	0.735	103			
PO4 (mg P/L)	0.0150	0.0120	125**			
PO4 (mg P/L)	0.0475	0.0496	96			
Particulate C (mg C/L)	0.520					
Particulate N (mg N/L)	0.0740					
Particulate P (mg P/L)	0.0056					
Chlorophyll cg /L	3.35					

** Low concentration prepared sample with narrow acceptance boundaries

Occoquan Watershed Monitoring Laboratory

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
TDN (mg N/L)	0.170	0.154	110	0.299	0.300	100
TDN (mg N/L)	0.424	0.440	96	0.942	0.945	100
TDP (mg P/L)	0.013	0.0108	120**			
TDP (mg P/L)	0.024	0.0240	100			
NH4 (mg N/L)	0.026	0.026	100			
NH4 (mg N/L)	0.187	0.192	97			
NO3+NO2 (mg N/L)	0.024	0.0233	103	0.05 WARN	0.0175	286
NO3+NO2 (mg N/L)	0.754	0.735	103	0.888	0.875	101
PO4 (mg P/L)	0.016	0.0120	133**	0.047		
PO4 (mg P/L)	0.042	0.0496	85	0.426		
Chlorophyll cg /L				13.9		

** Low concentration prepared sample with narrow acceptance boundaries
AWARN@ based on standard deviation of mean of all participants= reported concentrations.

Delaware DNR

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
TDN (mg N/L)				0.429 WARN	0.300	143
TDN (mg N/L)				1.02	0.945	108
NO3+NO2 (mg N/L)				0.021	0.0175	120
NO3+NO2 (mg N/L)				0.833	0.875	95
PO4 (mg P/L)				0.044		
PO4 (mg P/L)				0.443		
Chlorophyll cg /L	5.0			18		

AWARN@ based on standard deviation of mean of all participants= reported concentrations.

APPENDIX (Cont.)

University of Delaware

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
TDN (mg N/L)	0.183	0.154	119	0.342	0.300	114
TDN (mg N/L)	0.471	0.440	107	1.01	0.945	107
TDP (mg P/L)	0.011	0.0108	102	0.02	0.0170	118
TDP (mg P/L)	0.026	0.0240	108	0.055	0.0430	128
NH4 (mg N/L)	0.026	0.026	100			
NH4 (mg N/L)	0.218	0.192	114			
NO3+NO2 (mg N/L)	0.025	0.0233	107	0.016	0.0175	91
NO3+NO2 (mg N/L)	0.752	0.735	102	0.928	0.875	106
PO4 (mg P/L)	0.015	0.0120	125**	0.046		
PO4 (mg P/L)	0.049	0.0496	99	0.435		
Particulate C (mg C/L)	0.536					
Particulate N (mg N/L)	0.085					
Particulate P (mg P/L)	0.0084					

** Low concentration prepared sample with narrow acceptance boundaries

Appalachian Laboratory

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
TDN (mg N/L)	0.152	0.154	99	0.2772	0.300	92
TDN (mg N/L)	0.4378	0.440	100	0.8954	0.945	95
TDP (mg P/L)	0.0156	0.0108	144**	0.0186	0.0170	109
TDP (mg P/L)	0.0315	0.0240	131	0.0465	0.0430	108
NH4 (mg N/L)	0.0248	0.026	95			
NH4 (mg N/L)	0.1995	0.192	104			
	0.0168					

NO3+NO2 (mg N/L)	WARN	0.0233	72	0.0004	0.0175	2
NO3+NO2 (mg N/L)	0.7464	0.735	102	0.9006	0.875	103
PO4 (mg P/L)	0.0168	0.0120	140**	0.0469		
PO4 (mg P/L)	0.0507	0.0496	102	0.4284		
Particulate C (mg C/L)	0.5628			2.334		
Particulate N (mg N/L)	0.1123 WARN			0.432		
Particulate P (mg P/L)	0.0109			0.0172		

** Low concentration prepared sample with narrow acceptance boundaries.
AWARN@ based on standard deviation of mean of all participants= reported concentrations.

APPENDIX (Cont.)

Academy of Natural Sciences of Philadelphia

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
TDN (mg N/L)	0.141	0.154	92	0.291	0.300	97
TDN (mg N/L)	0.400	0.440	91	0.883	0.945	93
TDP (mg P/L)	0.0125	0.0108	116**	0.0161	0.0170	95
TDP (mg P/L)	0.0240	0.0240	100	0.0404	0.0430	94
NH4 (mg N/L)	0.0330	0.026	127**			
NH4 (mg N/L)	0.212	0.192	110			
NO3+NO2 (mg N/L)	0.0223	0.0233	96	0.0185	0.0175	106
NO3+NO2 (mg N/L)	0.725	0.735	99	0.85	0.875	97
PO4 (mg P/L)	0.0130	0.0120	108	0.0441		
PO4 (mg P/L)	0.0481	0.0496	97	0.415		
Particulate C (mg C/L)	0.602			2.405		
Particulate N (mg N/L)	0.0768			0.356		
Particulate P (mg P/L)	0.0163			0.0428		
Chlorophyll cg /L	5.25			18.8		

** Low concentration prepared sample with narrow acceptance boundaries

Old Dominion University

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
TDN (mg N/L)	0.198	0.154	129	0.329	0.300	110

TDN (mg N/L)	0.491	0.440	112	0.972	0.945	103
TDP (mg P/L)	0.0106	0.0108	98	0.0155	0.0170	91
TDP (mg P/L)	0.0238	0.0240	99	0.0454	0.0430	106
NH4 (mg N/L)	0.0240	0.026	92			
NH4 (mg N/L)	0.1811	0.192	94			
NO3+NO2 (mg N/L)	0.0225	0.0233	97	0.0179	0.0175	102
NO3+NO2 (mg N/L)	0.7396	0.735	101	0.869	0.875	99
PO4 (mg P/L)	0.0151	0.0120	126**	0.0479		
PO4 (mg P/L)	0.0495	0.0496	100	0.450		
Particulate C (mg C/L)	0.467			2.42		
Particulate N (mg N/L)	0.0697			0.400		
Particulate P (mg P/L)	0.0103			0.0381		
Chlorophyll çg /L	5.47			11.6		

** Low concentration prepared sample with narrow acceptance boundaries

APPENDIX (Cont.)

Virginia Division of Consolidated Laboratory Services

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
TDN (mg N/L)	0.145	0.154	94	0.294	0.300	98
TDN (mg N/L)	0.449	0.440	102	0.892	0.945	94
TDP (mg P/L)	0.015	0.0108	139**	0.016	0.0170	94
TDP (mg P/L)	0.032	0.0240	133	0.043	0.0430	100
NH4 (mg N/L)	0.025	0.026	96			
NH4 (mg N/L)	0.215	0.192	112			
NO3+NO2 (mg N/L)	0.019	0.0233	82	0.018	0.0175	103
NO3+NO2 (mg N/L)	0.714	0.735	97	0.956	0.875	109
PO4 (mg P/L)	0.015	0.0120	125**	0.046		
PO4 (mg P/L)	0.051	0.0496	103	0.445		
Particulate C (mg C/L)	0.525			2.368		
Particulate N (mg N/L)	0.0830			0.400		
Particulate P (mg P/L)	0.0057			0.0355		
Chlorophyll çg /L				16.45		

** Low concentration prepared sample with narrow acceptance boundaries

UMCES Horn Point Laboratory

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
TDN (mg N/L)	0.160	0.154	104	0.271	0.300	90
TDN (mg N/L)	0.395	0.440	90	0.949	0.945	100
TDP (mg P/L)	0.0100	0.0108	93	0.0172	0.0170	101
TDP (mg P/L)	0.0249	0.0240	104	0.0508	0.0430	118
NH4 (mg N/L)	0.0333	0.026	128**			
NH4 (mg N/L)	0.203	0.192	106			
NO3+NO2 (mg N/L)	0.0234	0.0233	100	0.0174	0.0175	99
NO3+NO2 (mg N/L)	0.725	0.735	99	0.861	0.875	98
PO4 (mg P/L)	0.0110	0.0120	92	0.0440		
PO4 (mg P/L)	0.0487	0.0496	98	0.409		
Particulate C (mg C/L)	0.534			2.317		
Particulate N (mg N/L)	0.0767			0.393		

** Low concentration prepared sample with narrow acceptance boundaries

Academy of Natural Sciences Estuarine Research Center

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
Chlorophyll çg /L	3.0			14.4		

APPENDIX (Cont.)

UMCES Chesapeake Biological Laboratory

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
TDN (mg N/L)	0.162	0.154	105	0.301	0.300	100
TDN (mg N/L)	0.455	0.440	103	0.924	0.945	98
TDP (mg P/L)	0.0131	0.0108	121**	0.0205	0.0170	121
TDP (mg P/L)	0.027	0.0240	113	0.0486	0.0430	113
NH4 (mg N/L)	0.015 WARN	0.026	58**			
NH4 (mg N/L)	0.203	0.192	106			

NO3+NO2 (mg N/L)	0.0243	0.0233	104	0.0174	0.0175	99
NO3+NO2 (mg N/L)	0.794 WARN	0.735	108	0.822	0.875	94
PO4 (mg P/L)	0.0161	0.0120	134**	0.0482		
PO4 (mg P/L)	0.0504	0.0496	102	0.426		
Particulate C (mg C/L)	0.577			2.21		
Particulate N (mg N/L)	0.0900			0.382		
Particulate P (mg P/L)	0.0120			0.0358		
Chlorophyll cg /L	6.07			17.0		

** Low concentration prepared sample with narrow acceptance boundaries
AWARN@ based on standard deviation of mean of all participants= reported concentrations.

USDA, ARS, Animal Manure and By-products Laboratory

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
NH4 (mg N/L)	0.023	0.026	88**			
NH4 (mg N/L)	0.201	0.192	105			
NO3+NO2 (mg N/L)	0.021	0.0233	90	0.018	0.0175	103
NO3+NO2 (mg N/L)	0.727	0.735	99	0.877	0.875	100
PO4 (mg P/L)	0.035 WARN	0.0120	292**			
PO4 (mg P/L)	0.077 WARN	0.0496	155			

** Low concentration prepared sample with narrow acceptance boundaries
AWARN@ based on standard deviation of mean of all participants= reported concentrations.

MD DHMH Division of Environmental Chemistry Nutrients Laboratory

	Winter Reported	Winter Prepared	% Recovered	Summer Reported	Summer Prepared	% Recovered
NH4 (mg N/L)	0.0302	0.026	116**			
NH4 (mg N/L)	0.208	0.192	108			
NO3+NO2 (mg N/L)	0.0235	0.0233	101	0.0166	0.0175	95
NO3+NO2 (mg N/L)	0.731	0.735	99	0.863	0.875	99
PO4 (mg P/L)	0.0143	0.0120	119**	0.0454		
PO4 (mg P/L)	0.0458	0.0496	92	0.442		
Chlorophyll cg /L	4.4			14.7		

** Low concentration prepared sample with narrow acceptance boundaries

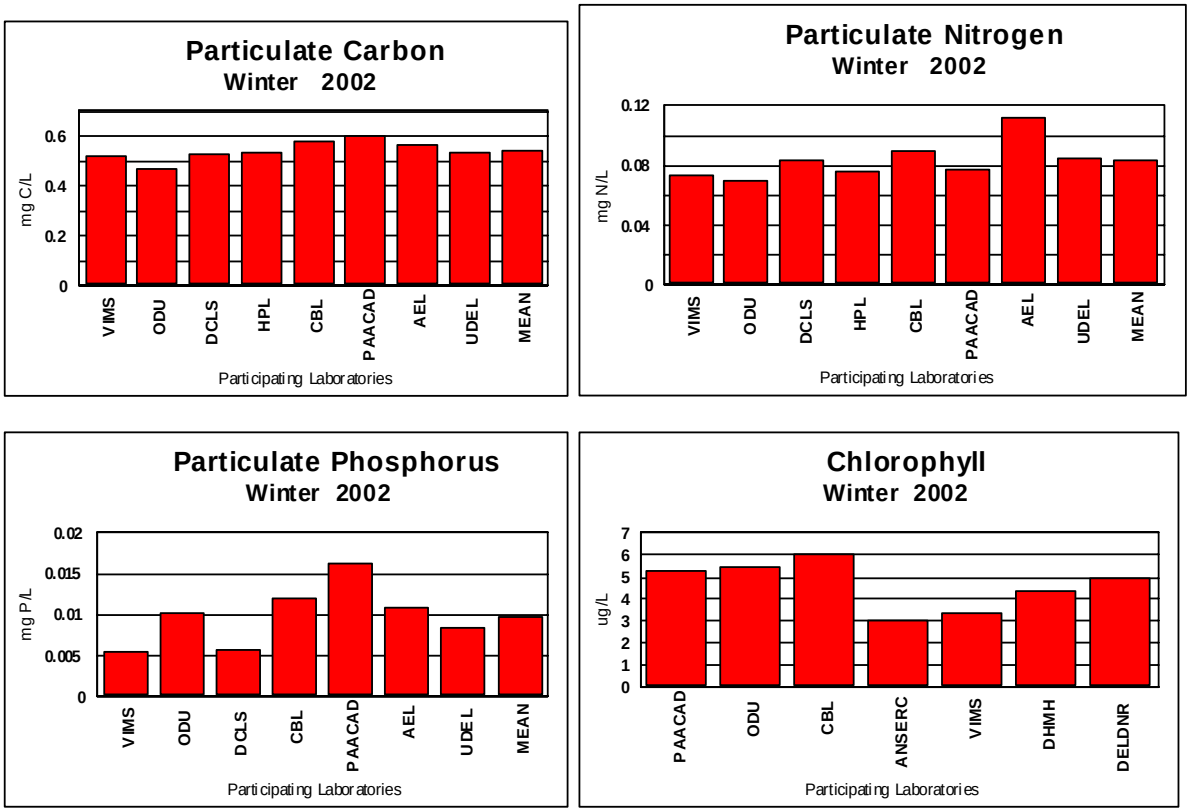
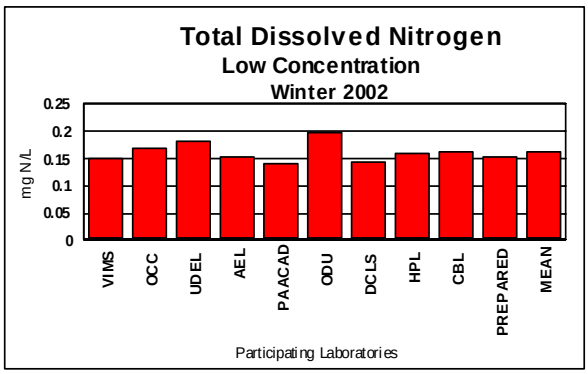
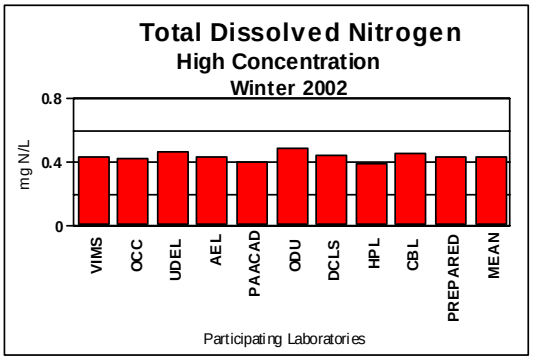
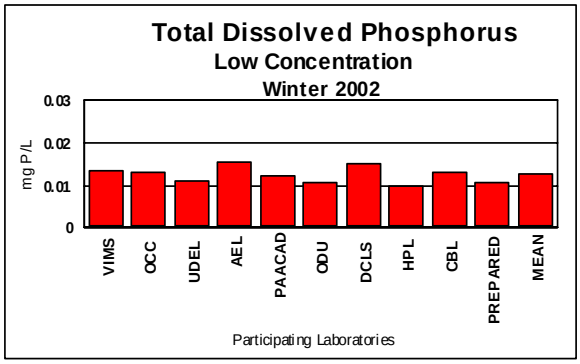


Figure 1. Particulate carbon, nitrogen and phosphorus; chlorophyll, Winter 2002.







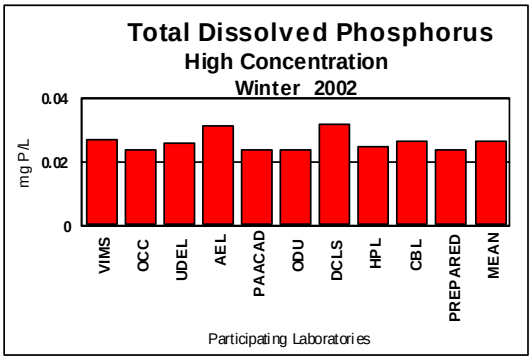


Figure 2. Total dissolved nitrogen and phosphorus, Winter 2002.

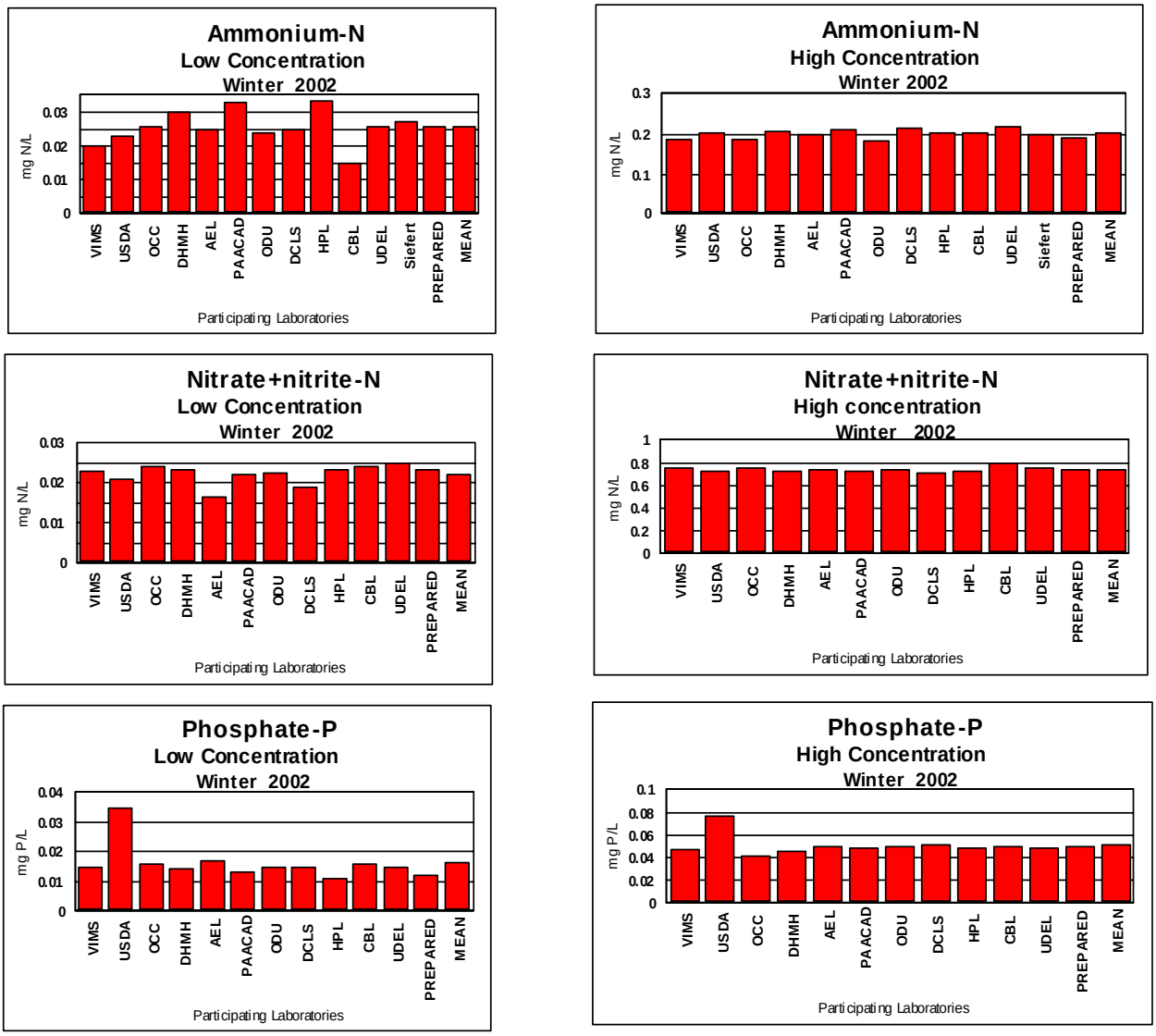


Figure 3. Dissolved inorganic nitrogen and phosphorus, Winter 2002.

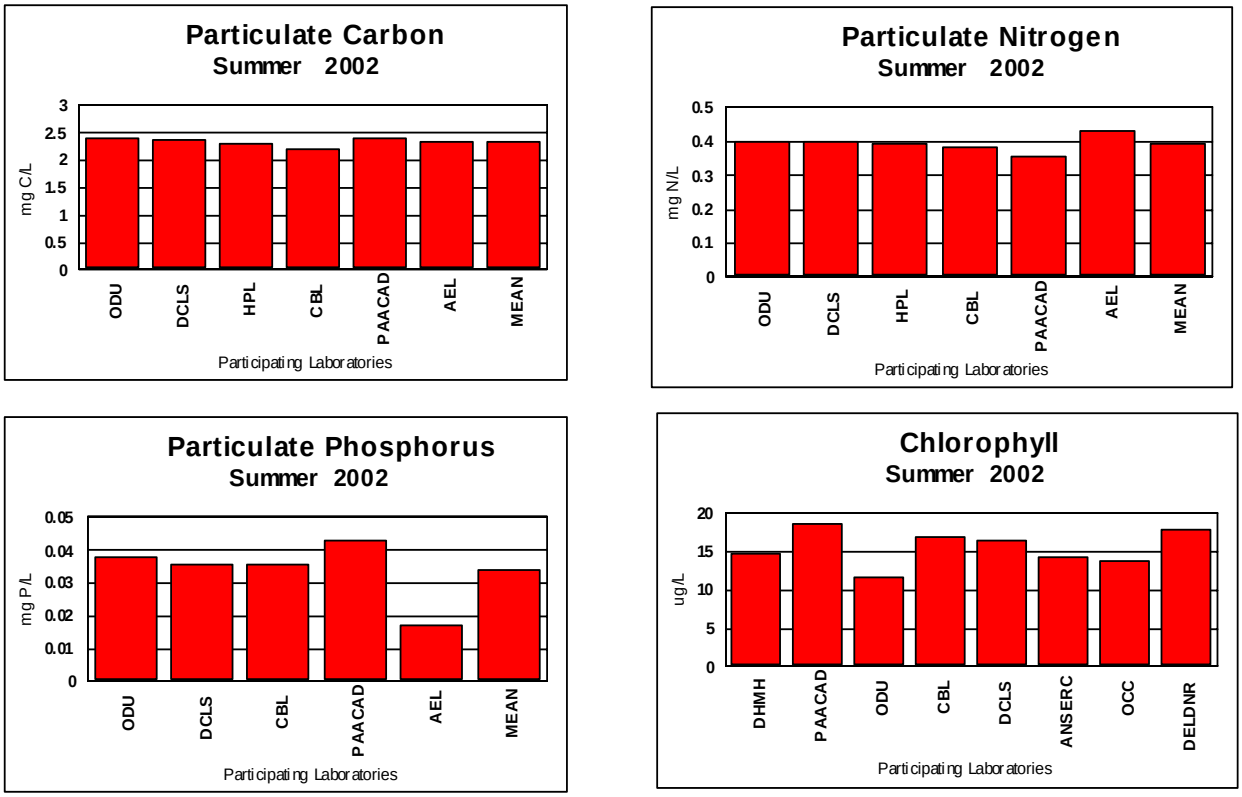
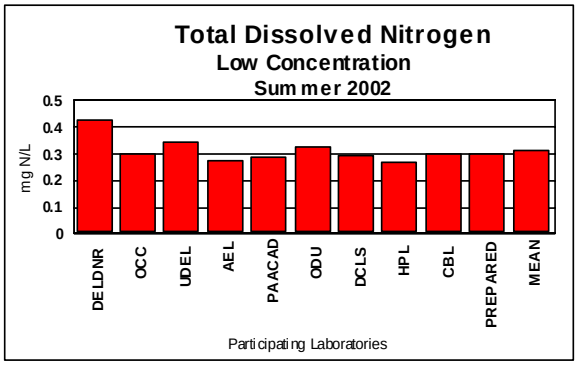
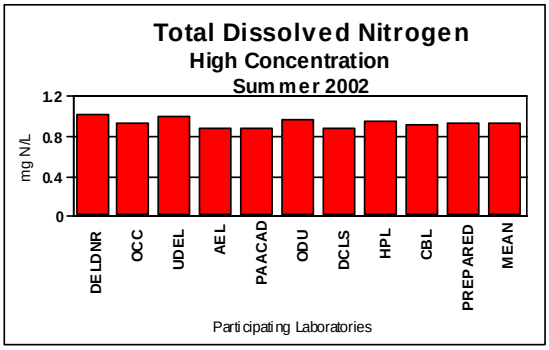
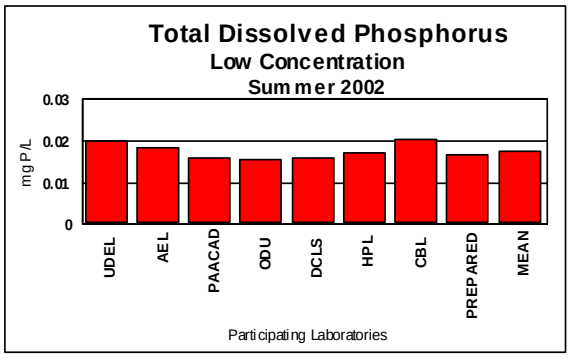


Figure 4. Particulate carbon, nitrogen and phosphorus; chlorophyll, Summer 2002.







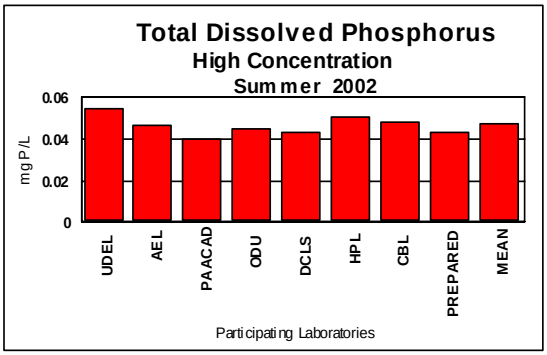


Figure 5. Total dissolved nitrogen and phosphorus, Summer 2002.

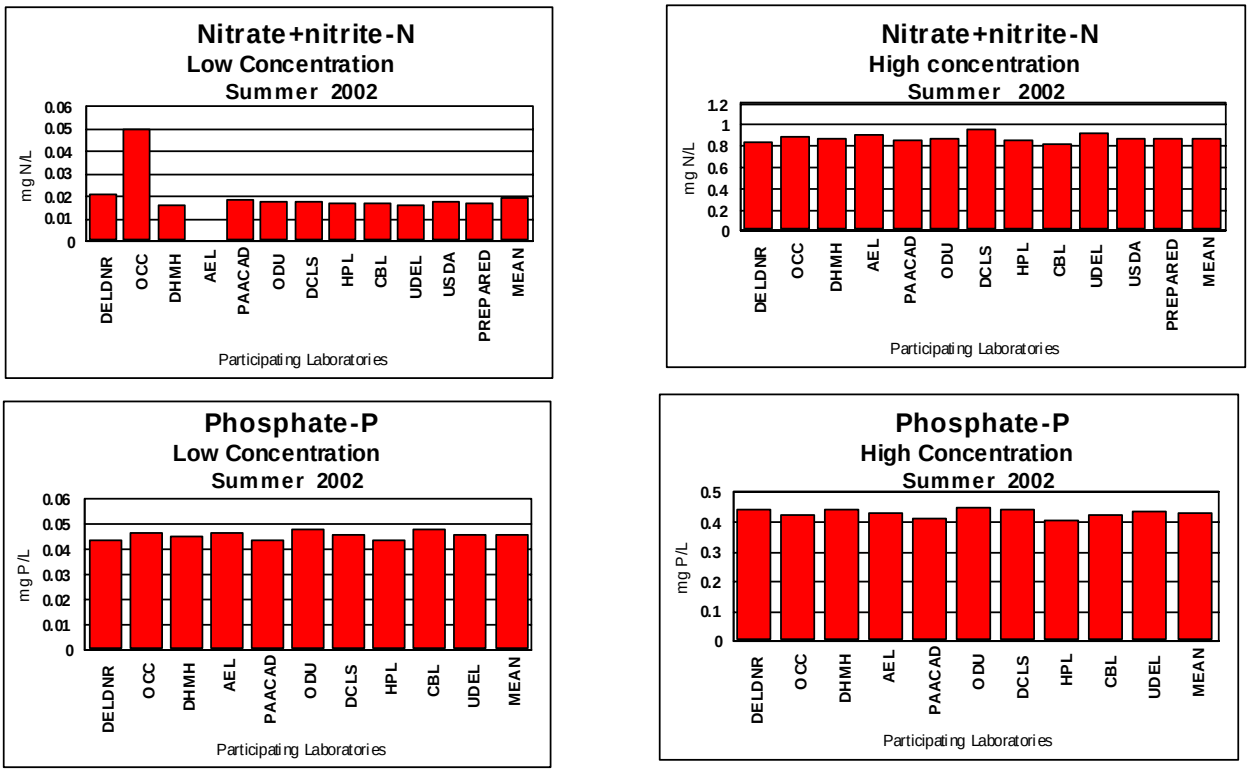


Figure 6. Dissolved inorganic nitrogen and phosphorus, Summer 2002.