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CHESAPEAKE BAY PROGRAM BLIND AUDIT

FISCAL YEAR 2005 FINAL REPORT

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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 25 August 2004 and 07 February 2005. Participating laboratories and contact personnel are found in Table 1.

Parameters measured were: total dissolved nitrogen (organic N), total dissolved phosphorus (organic P), nitrate+nitrite, ammonium, phosphate and dissolved organic

carbon. High and low concentration samples were provided for each analyte. Particulate carbon, nitrogen and phosphorus, chlorophyll and total suspended solids, were also provided for those laboratories that routinely analyze these parameters. Chlorophyll samples were natural population samples collected from the mouth of the Patuxent River.

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

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

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

Filter pads were sent to each laboratory for the analysis of particulate C, N, and P. The volume of sample filtered was noted in the instructions so that each laboratory could report concentrations in mg/L. Samples for chlorophyll analysis were filtered from natural 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 2004 and winter 2005 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 were closer to the prepared concentrations in summer 2004 than in winter 2005, but the agreement between laboratories was approximately the same for both audits.

Total Dissolved Phosphorus: Results for all the audits had approximately the same agreement with the prepared concentration and between the participants.

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 also large.

Nitrate + Nitrite: For the prepared high level concentrations of nitrate + nitrite, most participants reported approximately the same concentration. In fact, for the winter audit, all were within $\pm$ 10% of the prepared concentration. For the low level nitrate + nitrite concentration, there was more variability between participants and from the prepared concentration. The prepared concentration for the low level summer audit was below the detection limit of one participant (PADEP), so that concentration was not included in the calculation of mean and standard deviation.

Orthophosphate: For the prepared high level concentrations of orthophosphate, most participants reported approximately the same concentration. For the low level orthophosphate concentration, there was more 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), so that concentration was not included in the calculation of mean and standard deviation.

Dissolved Organic Carbon: Results for all the audits had approximately the same agreement with the prepared concentration and between the participants. Only one reported concentration was beyond $\pm$ 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 summer 2004 revealed fairly close agreement between all but one of the participating laboratories (Table 2). For the winter 2004 samples, there was closer agreement. 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 summer 2004 revealed close agreement between all participating laboratories (Table 2). Particulate C results for winter 2005 also revealed generally close agreement between all two of the participating laboratories. Again, this is remarkably close agreement for multi-laboratory comparison of samples of a natural population!

Particulate Phosphorus: Particulate P results for summer 2004 revealed fairly close agreement between all but one of the participating laboratories (Table 2). For the winter 2004 samples, there was closer agreement. As in past years, this was still 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 2004 sample, 18.6 mg/L was prepared, and very little variation from that concentration was reported by all participants. For the winter 2005 sample, 18.0 mg/L was prepared but, there was a consistent negative bias reported by all.

DISCUSSION

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

Variation Associated With An Analytical Method: As we have noted in previous Blind Audit Reports, analytical variability is associated with any quantitative determination. The method detection limit (three times the standard deviation of seven low level replicate natural samples) is often used to express that level of variation. Total dissolved nitrogen data provide a good example. The detection limit at CBL has been determined to be 0.02 mg N/L. Any total dissolved nitrogen measurement has a potential 0.02 mg N/L variability associated with it. This variability, when expressed as a percent of the "true" concentration, can be extremely large for low level concentrations and fairly low for higher concentrations. For example, a 0.20 mg N/L concentration has an analytical variability of 10% associated with it; whereas, a 1.20 mg N/L concentration has an analytical variability of 2%.

Acceptance Limits of Provided Dissolved Samples: Companies that prepare large quantities of performance evaluation samples assign acceptable confidence limits

around the “true” value. In one case (SPEX, CertiPrep), the mean recovery and standard deviation are later reported along with the true concentration and the 95% confidence interval (CI). The 95% CI is the mean recovery ± 2 standard deviations and is developed from regression equations from Water Pollution Performance Evaluation Studies. A recently purchased set of these standards gave a true total P value of 3.00 mg P/L with a 95% CI of 2.47-3.42 mg P/L. The lower end of the 95% CI recovery allows 82% recovery of the true concentration. This type of statistical analysis was not performed on the Blind Audit Program samples prepared for this study prior to their distribution to the participants.

Parameters assessed in the Blind Audit do not have predetermined acceptance limits, so we are following the statistical procedure of ERA, an approved source of wastewater and drinking water proficiency samples, and the State of Wisconsin Proficiency Testing program. They average the results for each parameter and at each concentration, then calculate the standard deviation from the mean. Results that are within 2 standard deviations “pass”, and those greater than 3 standard deviations “fail”. Results between 2 and 3 standard deviations are in the “warning” category.

Most of the data comparisons based on standard deviations showed similar characteristics (Table 2); that is, the reported concentrations were similar, and one or two concentrations fell slightly beyond one standard deviation from the mean of all data for that portion of the study. Apparently, it is a statistical “reality” in small sample sets with little variability between individual 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 more were in the “warning” category than in most of the previous studies.

The data sets with relatively small standard deviations yielded more “warning” 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 “warning, although <u>all but one</u> of the reported data were within ± 10% of the prepared concentration. Thus, by that measure of accuracy, all but one of the data “passed.” This total dissolved nitrogen data comparison points toward a form of circular reasoning in these statistical assessments. The data being evaluated are also the data that were used to calculate the mean and standard deviation to which the data are being compared.

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

When comparing reported concentrations to those prepared, the lower concentration ranges had more data that fell in the "warn" and "fail" categories than the higher level concentrations,
i.e., there was less accuracy at the lower concentration ranges (Table 3). The acceptance criteria for low concentration samples are quite narrow. For example, the Winter 2005 blind audit of 0.029 mg N/L prepared for ammonium has a "pass" category (± 10%) of only 0.0261-0.0319 mg N/L. Seven out of twelve participating laboratories reported results that fell in the "warn" and "fail" 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 ammonium from concentrates provided to them. It would be important to know if there is also a difficulty in measuring natural low level samples. An alternative interpretation would be that it may be appropriate to broaden the acceptance boundaries for very low concentrations of prepared samples.

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 26% and 24%. 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 2004, 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.

There were fifteen instances where concentrations reported for dissolved constituents fell in the "warn" category based on the standard deviation of all participants' reported concentrations and also in the "warn" or "fail" category based on percent recovery. These instances include Delaware DNR's low level nitrate + nitrite and high level ammonium winter 2005 samples. Also, in this category was University of Delaware's low level total dissolved nitrogen sample for the winter 2005 audit. The Academy of Natural Sciences of Philadelphia's high level dissolved organic carbon summer 2003 sample was in this group. Virginia Division of Consolidated Laboratory Services high level dissolved organic carbon winter 2005 sample was also in this group. Chesapeake Biological Laboratory's low level ammonium sample in summer 2004 was in this group. MWRA Water Quality Laboratory's low level total dissolved phosphorus summer 2004 sample was in this group. All of VIMS' low level total dissolved nitrogen and low level nitrate + nitrite samples in the summer 2004 and winter 2005 audits were in this group, as were their high level nitrate + nitrite and both orthophosphate samples from the summer 2004 audit and their high level total dissolved nitrogen sample from the winter 2005 audit. Also in this category were Pennsylvania DEP low level nitrate + summer 2004 samples and low level orthophosphate winter 2005 samples since they were reported as below the detection limits of the prepared concentrations.

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 but one instance, the standard deviation was less than 15% 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 proportions of the standard deviations to the means for particulate phosphorus were low (15.7%) for the summer 2004 blind audit, and even lower for the winter 2005 blind audit (2.9%). 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 2005 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 "slipped 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 fifteen 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 an individual analyte that were widely 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 ± 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 "pass, warn and fail" for low concentration samples are quite narrow. Therefore, for very low concentrations of prepared samples, it may be appropriate to broaden the acceptance boundaries.

3. The 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 0.031 mg N/L would be unreliable. It would be important to know if there is also a difficulty in measuring natural low level samples.

4. 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 2005 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 2004 and winter 2005 blind audits, some results were AGAIN (!) miscalculated (and later corrected), or reported 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. Therefore, these lapses could be construed as common reporting practices that would have deleterious effects on the overall data quality of those laboratories.

Table 1. Participants in the Summer 2004 and Winter 2005 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
U Maryland, Horn Pt. Lab (**HPL**)	Lois Lane	410-221-8252	X	X		X	
Virginia Institute of Marine Science (**VIMS**)	Carol Pollard	804-684-9749	X	X	X		X
Va. Div. Consolidated Lab Services (**DCLS**)	Jay Armstrong	804-648-4480 ext 328	X	X	X	X	X
Va. Tech. Occoquan Lab (**OCC**)	Mary Lou Daniel	703-361-5606	X		X	X	X
Md. Dept. Health & Mental Hygiene (**DHMH**)	Asoka Katumuluwa	410-767-5034	X	X	X	X	X
U Maryland, Chesapeake Biol. Lab. (**CBL**)	Carl Zimmermann	410-326-7252	X	X	X	X	X
U Delaware (**UDEL**)	Joe Scudlark	302-645-4300	X	X			X
Delaware DNR (**DELDNR**)	Ben Pressly	302-739-4771	X		X	X	X
U Maryland, Appalachian Lab (**AEL**)	Katie Kline **SUMMER ONLY**	301-689-7122	X	X		X	X
Morgan State Univ. Estuarine Res. Center (**ANSERC**)	Richard Lacouture	410-586-9700			X		
Academy of Natural Sciences 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	X
PADEP, Bureau of Laboratories (**PADEP**)	Richard Sheibley	717-705-2425	X				X
MWRA, Water Quality Laboratory (**MWRA**)	Jennifer Prasse	617-660-7808	X	X	X	X	X

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Summer 2004 and the Winter 2005 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 2004						
Total Dissolved Nitrogen	0.407	0.0389	11	1	1	
Total Dissolved Nitrogen	0.937	0.0613	4	7	2	
Total Dissolved Phosphorus	0.0306	0.0030	7	4	1	
Total Dissolved Phosphorus	0.0502	0.0052	10	3		
Ammonium	0.0265	0.0069	11	3		
Ammonium	0.146	0.0139	11	2	1	
Nitrate + Nitrite	0.0243	0.0086	10	2	1 & (1)	
Nitrate + Nitrite	0.661	0.0347	10	3	1	
Orthophosphate	0.0110	0.0031	11	2	1	
Orthophosphate	0.0404	0.0037	11	2	1	
Dissolved Organic Carbon	1.52	0.0546	5	3		
Dissolved Organic Carbon	6.98	0.2221	5	3		
Particulate Carbon	1.54	0.0613	7	4		
Particulate Nitrogen	0.278	0.0228	9	1	1	
Particulate Phosphorus	0.0222	0.0035	7	1	1	
Total Suspended Solids	17.5	1.072	9	3		
Winter 2005						
Total Dissolved Nitrogen	0.378	0.0477	8		2	
Total Dissolved Nitrogen	0.849	0.0463	7	2		1
Total Dissolved Phosphorus	0.0218	0.0024	7	3		
Total Dissolved Phosphorus	0.0372	0.0046	6	4		
Ammonium	0.031	0.0099	9	3		
Ammonium	0.128	0.0054	8	3	1	
Nitrate + Nitrite	0.050	0.0021	9	1	1	1
Nitrate + Nitrite	0.632	0.0245	7	5		
Orthophosphate	0.008	0.0017	8	3 & (1)		
Orthophosphate	0.045	0.0022	7	5		
Dissolved Organic Carbon	2.04	0.0830	4	3		
Dissolved Organic Carbon	6.08	0.3161	5	1	1	
Particulate Carbon	1.80	0.0841	7		2	
Particulate Nitrogen	0.265	0.0240	7	2		
Particulate Phosphorus	0.0215	0.0006	5	2		
Total Suspended Solids	18.3	1.37	9	2		

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% to 110% of Prepared Concentration	Within 80-90%, or 110-120% of Prepared Concentration	Less than 80%, or Greater than 120% of Prepared Concentration
			PASS	**WARN**	**FAIL**
Summer 2004					
Total Dissolved Nitrogen	0.41	0.326-0.445	11	1	1
Total Dissolved Nitrogen	0.91	0.827-1.04	12	1	
Total Dissolved Phosphorus	0.0278	0.027-0.0368	8	1	3
Total Dissolved Phosphorus	0.0451	0.0433-0.0603	7	4	2
Ammonium	0.0311**	0.0149-0.0403	2	4	8
Ammonium	0.143	0.112-0.169	10	3	1
Nitrate + Nitrite	0.0196	0.017-0.05	7	4	3
Nitrate + Nitrite	0.672	0.5716-0.713	13	1	
Orthophosphate	0.0104**	0.0038-0.017	7	2	5
Orthophosphate	0.0402	0.0318-0.0459	11	2	1
Dissolved Organic Carbon	1.50	1.436-1.60	8		
Dissolved Organic Carbon	7.00	6.60-7.21	8		
Total Suspended Solids	18.6	15.4-19.0	10	2	
Winter 2005					
Total Dissolved Nitrogen	0.355	0.2369-0.492	7	1	3
Total Dissolved Nitrogen	0.8236	0.706-0.941	8	2	1
Total Dissolved Phosphorus	0.0211	0.0190-0.0254	7	2	2
Total Dissolved Phosphorus	0.0336	0.0317-0.0450	6	1	4
Ammonium	0.029**	0.0171-0.05	5	4	3
Ammonium	0.122	0.119-0.14	11	1	
Nitrate + Nitrite	0.049	0.0409-0.055	10	2	
Nitrate + Nitrite	0.63	0.595-0.671	12		
Orthophosphate	0.0074**	0.006-0.011	6	2	4
Orthophosphate	0.0484	0.0415-0.049	8	4	
Dissolved Organic Carbon	2.00	1.94-2.17	7		
Dissolved Organic Carbon	6.00	5.68-6.72	6	1	
Total Suspended Solids	20.0	16.0-21.0	7	4	

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

Appendix 1. Summer 2004 and Winter 2005 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 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.3264 WARN	.41	79.6	.2369 WARN	.355	66.7
TDN (mg N/L)	.8274 WARN	.91	90.9	.7062 WARN	.8236	85.7
TDP (mg P/L)	.0294	.0278	105.7	.0196	.0211	92.9
TDP (mg P/L)	.0433	.0451	96	.0317	.0336	94.3
NH4 (mg N/L)	.0149	.0311	47.9**	.0297	.029	102.4
NH4 (mg N/L)	.1331	.143	93.1	.1213	.122	99.4
NO3 + NO2 (mg N/L)	.0328 WARN	.0196	167.3	.0409 WARN	.049	83.5
NO3 + NO2 (mg N/L)	.5716 WARN	.672	85.1	.5977	.63	94.9
PO4 (mg P/L)	.0038 WARN	.0104	36.5**	.0078	.0074	105.4
PO4 (mg P/L)	.0318 WARN	.0402	79.1	.0415	.0484	85.7
Particulate C (mg C/L)	1.546			1.9865 WARN		
Particulate N (mg N/L)	.2745			.271		
Particulate P (mg P/L)	.0217			.0227		
Chlorophyll (μg/L)	9.09			10.03		
Total Suspended Solids (mg/L)	17.7	18.6	95.2	17.2	20.0	86.0

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

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

Occoquan Watershed Monitoring Laboratory

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.445	.41	108.5	.337	.355	94.9
TDN (mg N/L)	.968	.91	106.4	.848	.8236	103.0
TDP (mg P/L)	.034	.0278	122.3	.025	.0211	118.5
TDP (mg P/L)	.050	.0451	110.9	.045	.0336	133.9
NH4 (mg N/L)	.025	.0311	80.4**	.048	.029	165.5**
NH4 (mg N/L)	.153	.143	107.	.129	.122	105.7
NO3 + NO2 (mg N/L)	.022	.0196	112.2	.049	.049	98.0
NO3 + NO2 (mg N/L)	.665	.672	99.0	.671	.63	106.5
PO4 (mg P/L)	.017	.0104	163.5**	.011	.0074	148.6**
PO4 (mg P/L)	.044	.0402	109.4	.049	.0484	101.2
Particulate C (mg C/L)	1.58					
Particulate N (mg N/L)	0.30					
Chlorophyll (μg/L)	8.8			13.1		
DOC (mg C/L)	1.5	1.5	100.	1.94	2.0	97
DOC (mg C/L)	6.6	7.0	94.3	5.68	6.0	94.7
Total Suspended Solids (mg/L)	16	18.6	86.	17.0	20.0	85.0

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

Delaware DNR

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.383	.41	93.4	.222	.355	62.5
TDN (mg N/L)	1.04	.91	114.3	.586	.8236	71.1
TDP (mg P/L)	.0273	.0278	98.2	.00752	.0211	35.6
TDP (mg P/L)	.045	.0451	99.8	.0116	.0336	34.5
NH4 (mg N/L)	.0403	.0311	129.6**	.03	.029	103.4
NH4 (mg N/L)	.158	.143	110.5	.14 WARN	.122	114.8
NO3 + NO2 (mg N/L)	.0231	.0196	117.9	.055 WARN	.049	112.2
NO3 + NO2 (mg N/L)	.651	.672	96.9	.669	.63	106.2
PO4 (mg P/L)	.0151	.0104	145.2**	.01	.0074	135**
PO4 (mg P/L)	.0459	.0402	114.2	.047	.0484	97.1
Chlorophyll (μg/L)	11.2			21.4		
DOC (mg C/L)	1.48	1.5	98.7	2.09	2.0	104.5
DOC (mg C/L)	6.92	7.0	98.9	5.93	6.0	98.8
Total Suspended Solids (mg/L)	19.0	18.6	102.2	19.0	20.0	95.0

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

University of Delaware

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)				0.492 WARN	.355	138.6
TDN (mg N/L)				0.941	.8236	114.3
TDP (mg P/L)				0.0203	.0211	96.2
TDP (mg P/L)				0.0395	.0336	117.6
NH4 (mg N/L)	.021	.0311	67.5**	0.0171	.029	59.0**
NH4 (mg N/L)	.148	.143	103.5	0.126	.122	103.3
NO3 + NO2 (mg N/L)	.022	.0196	112.2	0.0496	.049	101.2
NO3 + NO2 (mg N/L)	.693	.672	103.1	0.595	.63	94.4
PO4 (mg P/L)	.01	.0104	96.2	0.007	.0074	94.6
PO4 (mg P/L)	.043	.0402	107.0	0.044	.0484	90.9
Particulate C (mg C/L)				1.875		
Particulate N (mg N/L)				0.233		
Chlorophyll (μg/L)				16.7		
Total Suspended Solids (mg/L)				17.8	20.0	89.0

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

UMCES Appalachian Laboratory

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered
TDN (mg N/L)	.436	.41	106.3
TDN (mg N/L)	.9802	.91	107.7
TDP (mg P/L)	.0294	.0278	105.8
TDP (mg P/L)	.0466	.0451	103.3
NH4 (mg N/L)	.0217	.0311	69.8**
NH4 (mg N/L)	.1401	.143	98
NO3 + NO2 (mg N/L)	.0201	.0196	102.6
NO3 + NO2 (mg N/L)	.6236	.672	92.8
PO4 (mg P/L)	.0122	.0104	117.3**
PO4 (mg P/L)	.0396	.0402	98.5
Particulate C (mg C/L)	1.654		
Particulate N (mg N/L)	.304		
Particulate P (mg P/L)	.017		
DOC (mg C/L)	1.44	1.5	96.0
DOC (mg C/L)	7.21	7.0	103
Total Suspended Solids (mg/L)	15.4	18.6	82.8

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

Academy of Natural Sciences of Philadelphia

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.414	.41	101	.36	.355	101.4
TDN (mg N/L)	.936	.91	102.9	.821	.8236	99.7
TDP (mg P/L)	.028	.0278	100.7	.0205	.0211	97.2
TDP (mg P/L)	.0465	.0451	103.1	.0365	.0336	108.6
NH4 (mg N/L)	.0304	.0311	97.7	.0258	.029	89.0**
NH4 (mg N/L)	.1435	.143	100.3	.121	.122	99.2
NO3 + NO2 (mg N/L)	.0215	.0196	109.7	.0495	.049	101.0
NO3 + NO2 (mg N/L)	.665	.672	99.0	.603	.63	95.7
PO4 (mg P/L)	.0111	.0104	106.7	.0065	.0074	87.8**
PO4 (mg P/L)	.0404	.0402	100.5	.0427	.0484	88.2
Particulate C (mg C/L)	1.62			1.865		
Particulate N (mg N/L)	.222 WARN			.224		
Particulate P (mg P/L)	.0300 WARN			.0221		
Chlorophyll (μg/L)	10.6			18.0		
Total Suspended Solids (mg/L)	17.7	18.6	95.2	19.6	20.0	98.0

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

Morgan State University Estuarine Research Center

Parameter	Summer 2004 Reported	Prepared	% Recovered	Winter 2005 Reported	Prepared	% Recovered
Chlorophyll (μg/L)	7.5			13.4		

Old Dominion University

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.418	.41	102.0	.334	.355	94.1
TDN (mg N/L)	.924	.91	101.5	.781	.8236	94.8
TDP (mg P/L)	.0292	.0278	105.0	.0199	.0211	94.3
TDP (mg P/L)	.0491	.0451	108.9	.0323	.0336	96.1
NH4 (mg N/L)	.026	.0311	83.6**	.0257	.029	88.6**
NH4 (mg N/L)	.1566	.143	109.5	.1287	.122	105.5
NO3 + NO2 (mg N/L)	.0207	.0196	105.6	.0489	.049	99.8
NO3 + NO2 (mg N/L)	.6813	.672	101.4	.624	.63	99.0
PO4 (mg P/L)	.0096	.0104	92.3	.0097	.0074	131.1**
PO4 (mg P/L)	.0419	.0402	104.2	.0476	.0484	98.3
Particulate C (mg C/L)	1.476			1.618 WARN		
Particulate N (mg N/L)	.255			.2727		
Particulate P (mg P/L)	.0209			.0204		
Chlorophyll (μg/L)	10.6			12.7		
Total Suspended Solids (mg/L)	16.9	18.6	90.9	21.0	20.0	105.0

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

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

Virginia Division of Consolidated Laboratory Services

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.4362	.41	106.4	.384	.355	108.2
TDN (mg N/L)	.9996	.91	109.8	.89	.8236	108.1
TDP (mg P/L)	.0318	.0278	114.4	.024	.0211	113.7
TDP (mg P/L)	.0528	.0451	117.1	.041	.0336	122.0
NH4 (mg N/L)	.024	.0311	77.2**	.025	.029	86.2**
NH4 (mg N/L)	.162	.143	113.3	.128	.122	104.9
NO3 + NO2 (mg N/L)	.017	.0196	86.7	.048	.049	98.0
NO3 + NO2 (mg N/L)	.699	.672	104.0	.644	.63	102.2
PO4 (mg P/L)	.0106	.0104	101.9	.008	.0074	108.1
PO4 (mg P/L)	.0391	.0402	97.3	.045	.0484	93.0
Particulate C (mg C/L)	1.549			1.814		
Particulate N (mg N/L)	.288			.269		
Particulate P (mg P/L)	.0216			.0219		
Chlorophyll (μg/L)	7.32			15.2		
DOC (mg C/L)	1.5	1.5	100	2.04	2.0	102
DOC (mg C/L)	6.75	7.0	96.4	6.72 WARN	6.0	112
Total Suspended Solids (mg/L)	17.0	18.6	91.4	19.0	20.0	95.0

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

UMCES Horn Point Laboratory

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.445	.41	108.5	.373	.355	105.1
TDN (mg N/L)	.974	.91	107	.835	.8236	101.4
TDP (mg P/L)	.0342	.0278	123	.0204	.0211	96.7
TDP (mg P/L)	.0533	.0451	118.2	.0337	.0336	100.3
NH4 (mg N/L)	.0244	.0311	78.5**	.0303	.029	104.5
NH4 (mg N/L)	.1435	.143	100.3	.1304	.122	106.9
NO3 + NO2 (mg N/L)	.0207	.0196	105.6	.048	.049	98.0
NO3 + NO2 (mg N/L)	.667	.672	99.3	.626	.63	99.4
PO4 (mg P/L)	.0105	.0104	101	.006	.0074	81.1**
PO4 (mg P/L)	.041	.0402	102	.0434	.0484	89.7
Particulate C (mg C/L)	1.479			1.815		
Particulate N (mg N/L)	.2868			.284		
Chlorophyll (ug/L)	10.3			18.4		

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

UMCES Chesapeake Biological Laboratory

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.42	.41	102.4	.359	.355	101.1
TDN (mg N/L)	.909	.91	99.9	.813	.8236	98.7
TDP (mg P/L)	.0306	.0278	110	.0216	.0211	102.4
TDP (mg P/L)	.0494	.0451	109.5	.0342	.0336	101.8
NH4 (mg N/L)	.021 WARN	.0311	67.5**	.028	.029	96.6
NH4 (mg N/L)	.112	.143	78.3	.119	.122	97.5
NO3 + NO2 (mg N/L)	.0212	.0196	108.2	.0499	.049	101.8
NO3 + NO2 (mg N/L)	.713	.672	106.1	.617	.63	97.9
PO4 (mg P/L)	.0109	.0104	104.8	.0074	.0074	100
PO4 (mg P/L)	.0419	.0402	104.2	.0452	.0484	93.4
Particulate C (mg C/L)	1.52			1.80		
Particulate N (mg N/L)	.29			.2845		
Particulate P (mg P/L)	.0206			.0218		
Chlorophyll (μg/L)	12.6			20.2		
DOC (mg C/L)	1.6	1.5	106.7	2.17	2.0	108.5
DOC (mg C/L)	7.12	7.0	101.7	6.05	6.0	100.8
Total Suspended Solids (mg/L)	17.4	18.6	93.5	18.6	20.0	93.0

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

MD DHMH Division of Environmental Chemistry Nutrients Laboratory

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.406	.41	99			
TDN (mg N/L)	.923	.91	101.4			
TDP (mg P/L)						
TDP (mg P/L)	.059	.0451	130.8			
NH4 (mg N/L)	.029	.0311	93.2	.0256	.029	88.3**
NH4 (mg N/L)	.169	.143	118.2	.126	.122	103.3
NO3 + NO2 (mg N/L)	.031	.0196	158.2	.0472	.049	96.3
NO3 + NO2 (mg N/L)	.656	.672	97.6	.629	.63	99.8
PO4 (mg P/L)	.008	.0104	76.9**	.0072	.0074	97.3
PO4 (mg P/L)	.034	.0402	84.6	.0432	.0484	89.3
Particulate C (mg C/L)	1.45			1.764		
Particulate N (mg N/L)	.275			.265		
Particulate P (mg P/L)	.0235			.0213		
Chlorophyll (μg/L)	10.2			14.2		
DOC (mg C/L)	1.53	1.5	102	1.95	2.0	97.5
DOC (mg C/L)	7.16	7.0	102.3	6.08	6.0	101.3
Total Suspended Solids (mg/L)	18.2	18.6	97.8	18.4	20.0	92.0

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

USGS, National Water Quality Laboratory

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered
TDN (mg N/L)	.419	.41	102.2
TDN (mg N/L)	.962	.91	105.7
TDP (mg P/L)	.030	.0278	107.9
TDP (mg P/L)	.052	.0451	115.3
NH4 (mg N/L)	.026	.0311	83.6**
NH4 (mg N/L)	.144	.143	100.7
NO3 + NO2 (mg N/L)	.019	.0196	96.9
NO3 + NO2 (mg N/L)	.668	.672	99.4
PO4 (mg P/L)	.012	.0104	115.4**
PO4 (mg P/L)	.042	.0402	104.5
Particulate C (mg C/L)	1.531		
Particulate N (mg N/L)	.281		
Particulate P (mg P/L)	.0211		
Chlorophyll (μg/L)	6.2		
DOC (mg C/L)	1.517	1.50	101.1
DOC (mg C/L)	6.942	7.0	99.2
Total Suspended Solids (mg/L)	19	18.6	102.2

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

MWRA WATER QUALITY LABORATORY

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.414	.41	101	.360	.355	101.4
TDN (mg N/L)	.903	.91	99.2	.858	.8236	104.2
TDP (mg P/L)	.0368 WARN	.0278	132.4	.0254	.0211	120.4
TDP (mg P/L)	.0603	.0451	133.7	.041	.0336	122.0
NH4 (mg N/L)	.027	.0311	86.8**	.0309	.029	106.6
NH4 (mg N/L)	.147	.143	102.8	.129	.122	105.7
NO3 + NO2 (mg N/L)	.0196	.0196	100	.0505	.049	103.1
NO3 + NO2 (mg N/L)	.665	.672	99.0	.649	.63	103
PO4 (mg P/L)	.0106	.0104	101.9	.0067	.0074	90.5
PO4 (mg P/L)	.0419	.0402	104.2	.0466	.0484	96.3
Particulate C (mg C/L)	1.53			1.87		
Particulate N (mg N/L)	.277			.2875		
Particulate P (mg P/L)	.0235			.0212		
Chlorophyll (μg/L)	12.7			17.5		
DOC (mg C/L)	1.59	1.50	106	2.1	2.0	105
DOC (mg C/L)	7.17	7.0	102.4	6.0	6.0	100
Total Suspended Solids (mg/L)	17.5	18.6	94.1	17.8	20	89.0

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

PADEP WATER QUALITY LABORATORY

Parameter	Summer 2004 Reported	Summer 2004 Prepared	% Recovered	Winter 2005 Reported	Winter 2005 Prepared	% Recovered
TDN (mg N/L)	.33	.41	80.5	.40	.355	112.7
TDN (mg N/L)	.83 WARN	.91	91.2	.85	.8236	103.2
TDP (mg P/L)	.027	.0278	97.1	.019	.0211	90.0
TDP (mg P/L)	.045	.0451	99.8	.032	.0336	95.2
NH4 (mg N/L)	.04	.0311	128.6**	.05	.029	172.4**
NH4 (mg N/L)	.14	.143	97.9	.13	.122	106.6
NO3 + NO2 (mg N/L)	< .05 WARN	.0196	(255.1)***	.05	.049	102.0
NO3 + NO2 (mg N/L)	.64	.672	95.2	.62	.63	98.4
PO4 (mg P/L)	.013	.0104	125.**	< .01	.0074	(135.1)***
PO4 (mg P/L)	.039	.0402	97.	.042	.0484	86.8
Total Suspended Solids (mg/L)	18.0	18.6	96.8	16.0	20	80.0

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

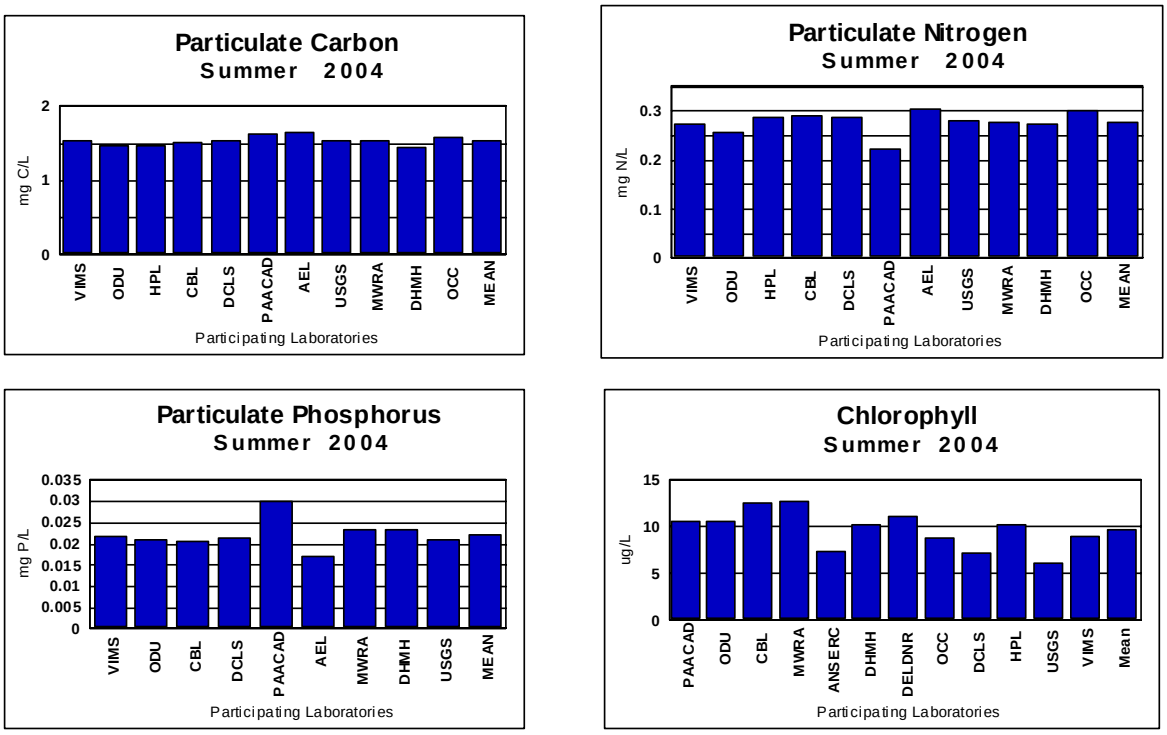


Figure 1. Particulate carbon, nitrogen and phosphorus; chlorophyll, Summer 2004.

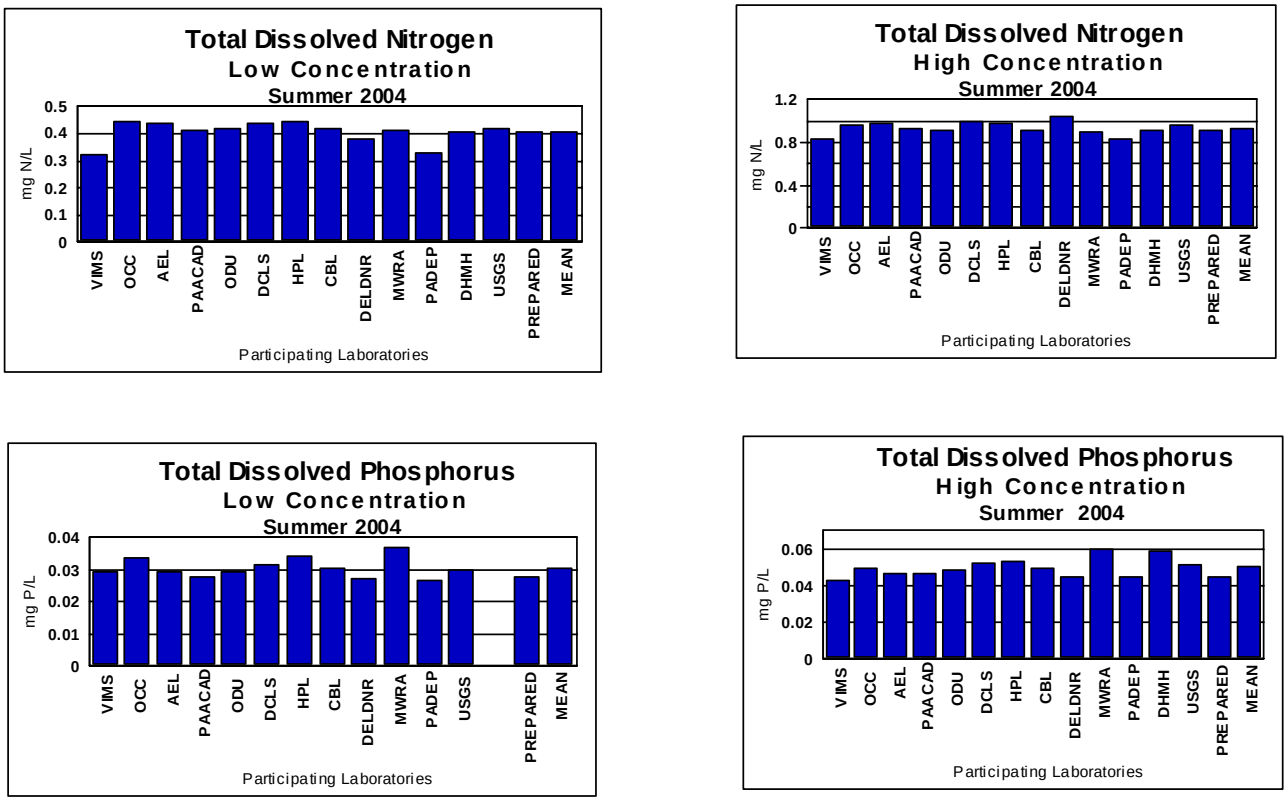


Figure 2. Total dissolved nitrogen and phosphorus, Summer 2004.

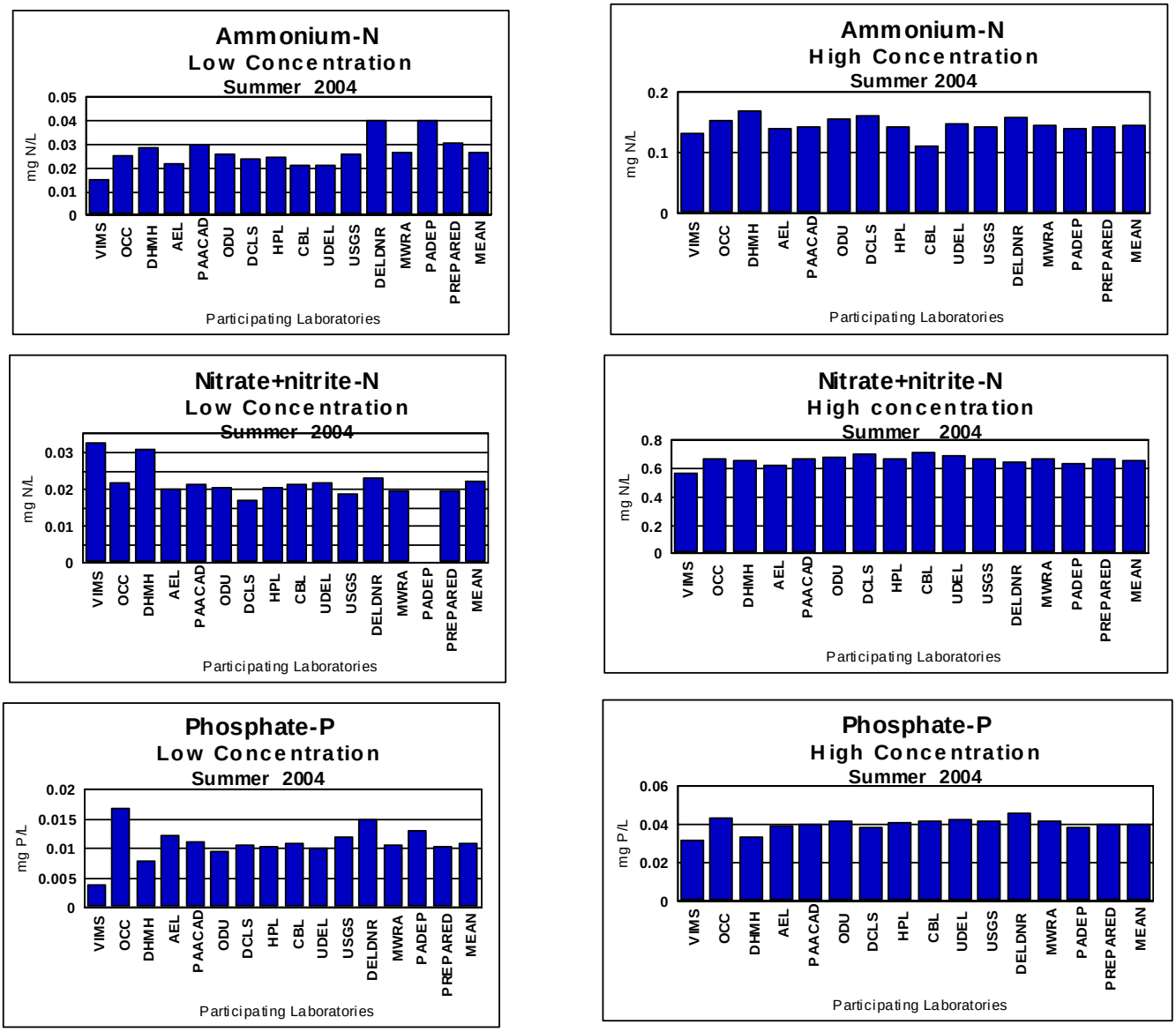
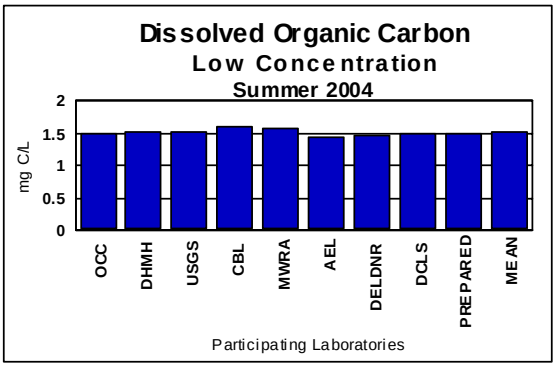
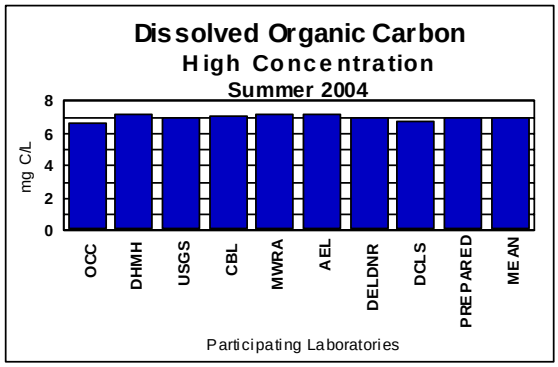


Figure 3. Dissolved inorganic nitrogen and phosphorus, Summer 2004.





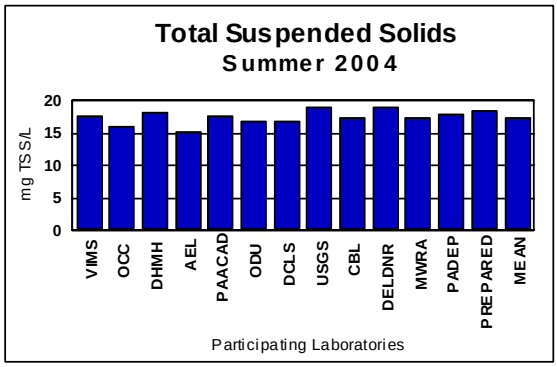
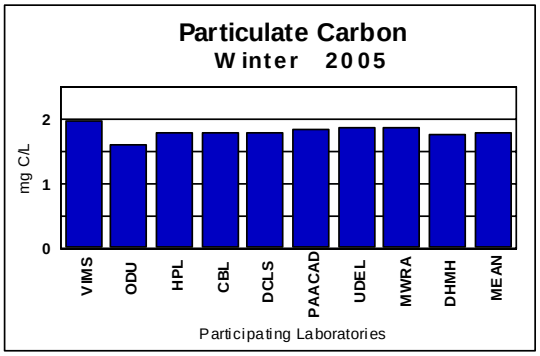
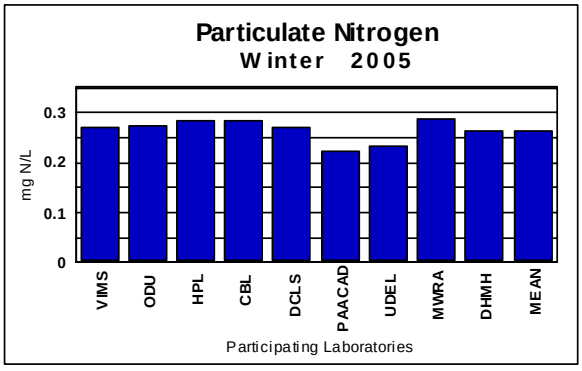
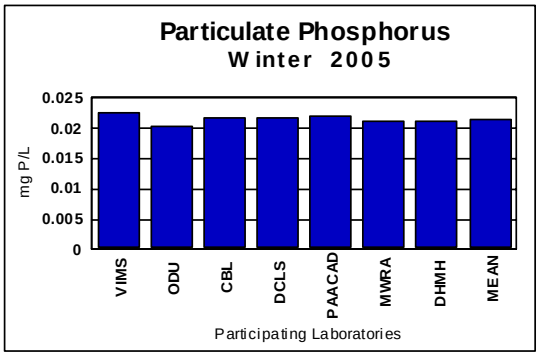


Figure 4. Dissolved organic carbon and total suspended solids, Summer 2004.







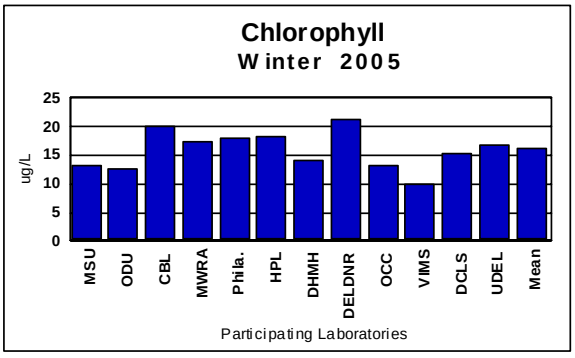


Figure 5. Particulate carbon, nitrogen and phosphorus; chlorophyll, Winter 2005.

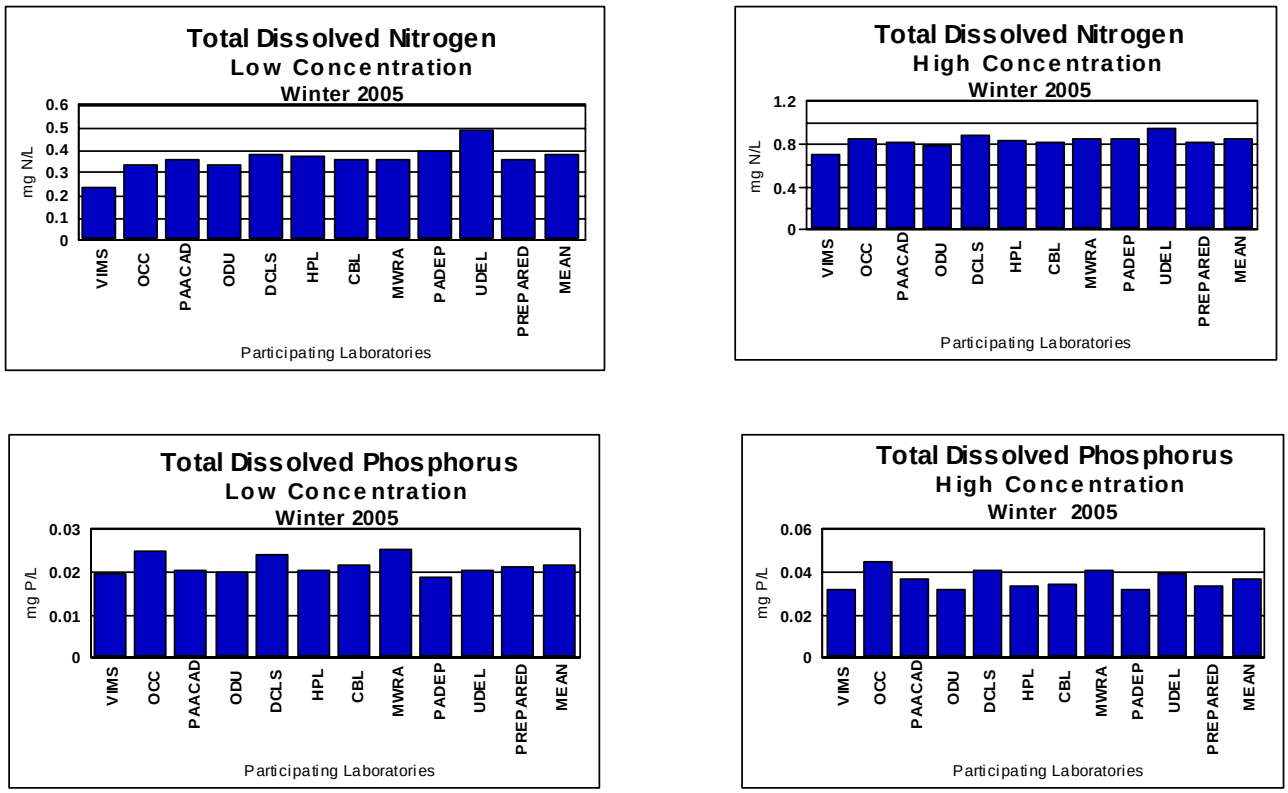


Figure 6. Total dissolved nitrogen and phosphorus, Winter 2005.

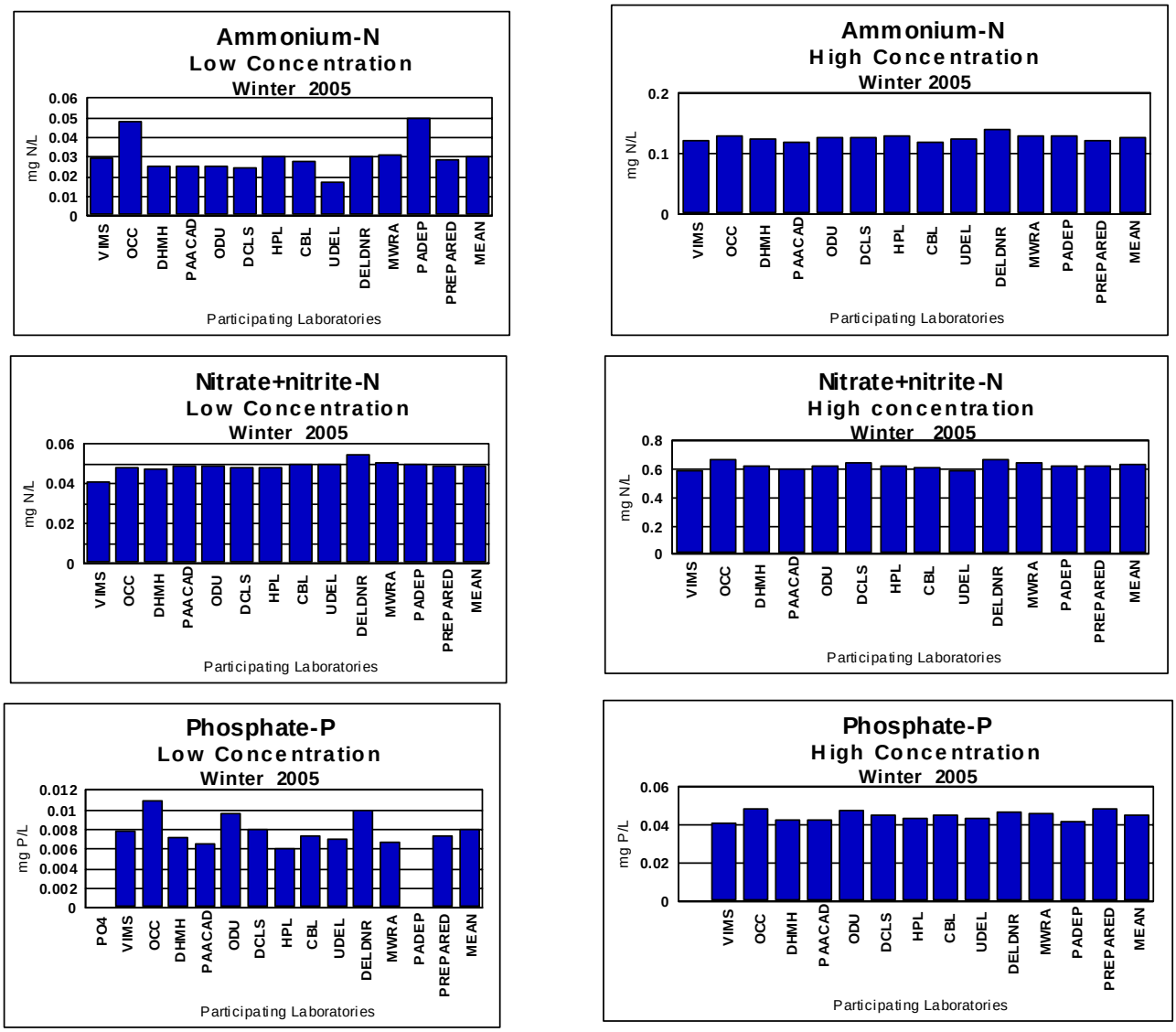
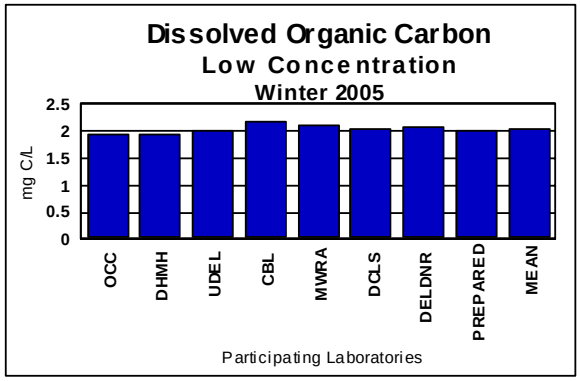
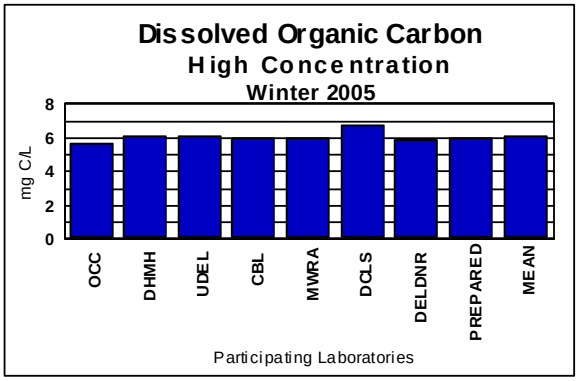


Figure 7. Dissolved inorganic nitrogen and phosphorus, Winter 2005.





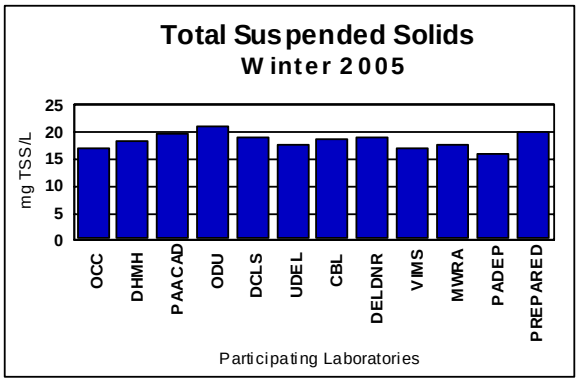


Figure 8. Dissolved organic carbon and total suspended solids, Winter 2005.