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CHESAPEAKE BAY PROGRAM BLIND AUDIT

FISCAL YEAR 2003 FINAL REPORT

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7 July 2003

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICES

7 July 2003

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 sixth 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 19 February 2003. 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 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. 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.

7 July 2003

RESULTS

Tables and figures summarizing results from the winter 2003 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. We contacted participants whose reported concentration(s) appeared "out 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 and Appendix 1).

DISSOLVED FRACTION

Total Dissolved Nitrogen: The prepared low level concentration was 0.353 mg N/L and 0.299-0.380 mg N/L was reported by participants. The prepared high level concentration was 0.988 mg N/L and 0.909-0.958 mg N/L was reported by participants; that is, all were within ± 10% of the prepared concentration.

Total Dissolved Phosphorus: The prepared low level concentration was 0.0211 mg P/L and 0.0150-0.0254 mg P/L was reported by participants. The prepared high level concentration was 0.0383 mg P/L and 0.0325-0.0490 mg P/L was reported by participants.

Ammonium: The prepared low level concentration was 0.0273 mg N/L and 0.0223-0.037 mg N/L was reported by participants. The prepared high level concentration was 0.134 mg N/L and 0.125-0.160 mg N/L was reported by participants.

Nitrate + Nitrite: The prepared low level concentration was 0.084 mg N/L and 0.0738-0.088 mg N/L was reported by participants. The prepared high level concentration was 0.392 mg N/L and 0.360-0.415 mg N/L was reported by participants; that is, all were within ± 10% of the prepared concentration.

Orthophosphate: The prepared low level concentration was 0.0119 mg P/L and 0.0079-0.014 mg P/L was reported by participants. The prepared high level concentration was 0.0536 mg P/L and 0.049-0.0561 mg P/L was reported by participants; that is, all were within ± 10% of the prepared concentration.

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 for 10-13 other samples from this batch. The coefficients of variation of particulate nitrogen and carbon concentrations in 13 samples from the common container were 1.8% and 2.0%, respectively. For particulate phosphorus, the coefficient of variation (N=10) was 11.9%. Particulate results are graphically presented in Figure 1.

7 July 2003

Particulate Nitrogen: Particulate N results revealed fairly close agreement between participating laboratories (Table 2). For the winter sample, the mean was 0.243 mg N/L ± 0.0223 S.D. The percent coefficient of variation among the laboratories participating in the audit was 9% (N=8). This was somewhat more variable than the 1.8% variability found for 13 samples from this batch that were analyzed by CBL, but still remarkably close agreement for comparison of samples of a natural population by multiple laboratories.

Particulate Carbon: Particulate C results revealed generally close agreement between participating laboratories (Table 2). The mean was 1.697 mg C/L ± 0.0886 S.D. The percent coefficient of variation among the laboratories participating in the audit was 5.2% (N=8), somewhat more variable than the 2.0% variability found for 13 samples from this batch that were analyzed by CBL. Again, this is remarkably close agreement for multi-laboratory comparison of samples of a natural population!

Particulate Phosphorus: Particulate P results also revealed close agreement between participating laboratories (Table 2). The mean was 0.0139 mg P/L ± 0.0008 S.D. The percent coefficient of variation among the laboratories participating in the audit was 5.7% (N=6) which was less than the 11.9% variability found for 10 samples from this batch analyzed by CBL. This, too, is remarkably close agreement for multi-laboratory comparison of samples of a natural population.

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 $\pm$ 2 standard deviations and is developed from regression equations from Water Pollution Performance Evaluation Studies. A recently purchased set of these standards gave a true total P value of 3.00 mg P/L with a 95% CI of 2.47-3.42 mg P/L. The lower end of the 95% CI recovery allows 82% recovery of the true concentration. This type of statistical analysis was not performed on the Blind Audit Program samples prepared for this study prior to their distribution to the participants.

7 July 2003

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 no data points fell in the Afail@ category, and about the same number were in the Awarning@ category as in previous studies.

The data sets with relatively small standard deviations yielded more Awarning@ 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, so it was labeled as a Awarning, although all of the reported data were within $\pm$ 10% of the prepared concentration. Thus, by that measure of accuracy, all the data "passed." 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.

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 2003 blind audit of 0.0273 mg N/L prepared for ammonium has a “pass” category (± 10%) of only 0.0246-0.0300 mg P/L. Six out of fifteen participating laboratories reported results that fell in the “warn” and “fail” categories, indicating that the between-laboratory precision was greater than ± 10% 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.

There were four 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 were Delaware DNR’s low level total dissolved nitrogen sample, Horn Point Laboratory’s low level total dissolved phosphorus sample, Chesapeake Biological Laboratory’s high level ammonium sample, and USDA’s low level ammonium sample. No laboratory reported concentrations for an individual analyte that were widely different from the range of the other reported concentrations for both concentration ranges of 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 Atrue@ 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 for particulate phosphorus was quite low (5.7%) for the winter 2003 blind audit. 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 blind audit.

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, 2002 and winter 2003 participants reported only two significant digits, thus potentially giving substantial under or over estimates for the comparisons.

CONCLUSION

Now that eleven 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 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. 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 proportion of the standard deviation to the mean was small for particulate phosphorus for the winter 2003 blind audit. 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, plus winter 2003, 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. For the winter 2003 blind audit, 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 Winter 2003 Blind Audit Program

Institution	Contact Person	Phone	Dissolved	Particulate	Chlorophyll a
Old Dominion University, Water Quality Lab (**ODU**)	Suzanne Doughton	757-451-3043	X	X	X
U Maryland, Horn Pt. Lab (**HPL**)	Lois Lane	410-221-8252	X	X	
Virginia Institute of Marine Science (**VIMS**)	Carol Pollard	804-684-7213	X	X	X
Va. Div. Consolidated Lab Services (**DCLS**)	Jay Armstrong	804-786-7748	X	X	X
Va. Tech. Occoquan Lab (**OCC**)	Mary Lou Daniel	703-361-5606	X		X
Md. Dept. Health & Mental Hygiene (**DHMH**)	Asoka Katumuluwa	410-767-5034	X		X
U Maryland, Chesapeake Biol. Lab. (**CBL**)	Carl Zimmermann	410-326-7252	X	X	X
USDA, ARS, Animal Manure & Byproducts Lab (**USDA**)	Jack Meisinger	301-504-5276	X		
U Delaware (**UDEL**)	Joe Scudlark	302-645-4300	X		
Delaware DNR (**DELDNR**)	Ben Pressly	302-739-4771	X		X
U Maryland, Appalachian Lab (**AEL**)	Katie Kline	301-689-7122	X	X	
Academy of Natural Sciences, 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
USGS, National Water Quality Lab (**USGS**)	Mary Cast	303-236-3463	X	X	X
U Maryland, CBL, Siefert Lab (**Siefert**)	Ron Siefert	410-326-7386	X		

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Winter 2003 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**
Total Dissolved Nitrogen	0.350	0.0243	8		1	
Total Dissolved Nitrogen	0.9376	0.0150	6	3		
Total Dissolved Phosphorus	0.0227	0.0031	8		1	
Total Dissolved Phosphorus	0.0412	0.0044	7	2		
Ammonium	0.028	0.0042	10	3	1	
Ammonium	0.140	0.0097	9	4	1	
Nitrate + Nitrite	0.081	0.0039	9	4		
Nitrate + Nitrite	0.393	0.0146	10	2	1	
Orthophosphate	0.011	0.0016	9	3		
Orthophosphate	0.052	0.0024	8	4		
Particulate Carbon	1.697	0.0886	5	3		
Particulate Nitrogen	0.243	0.0223	7		1	
Particulate Phosphorus	0.01395	0.0008	5	1		

Table 3. Summary of Prepared and Reported Concentrations for Each Analyte, Including Comparison to 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**
Total Dissolved Nitrogen	0.353	0.299-0.380	8	1	
Total Dissolved Nitrogen	0.988	0.909-0.958	9		
Total Dissolved Phosphorus	0.0211	0.0150-0.0254	5	3	1
Total Dissolved Phosphorus	0.0383	0.0325-0.049	5	3	1
Ammonium	0.0273	0.0223-0.037	9	3	3
Ammonium	0.134	0.125-0.160	11	3	
Nitrate + Nitrite	0.084	0.0738-0.088	12	1	
Nitrate + Nitrite	0.392	0.360-0.415	13		
Orthophosphate	0.0119	0.0079-0.014	8	4	1
Orthophosphate	0.0536	0.049-0.0561	13		

Appendix 1. Winter 2003 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	Reported	Prepared	% Recovered
NH4 (mg N/L)	0.0274	0.0273	100
NH4 (mg N/L)	0.1258	0.134	94
NO3 + NO2 (mg N/L)	0.0790	0.084	94
NO3 + NO2 (mg N/L)	0.3944	0.392	101
PO4 (mg P/L)	0.0105	0.0119	88
PO4 (mg P/L)	0.0521	0.0536	97
Particulate C (mg C/L)	1.598		
Particulate N (mg N/L)	0.237		
Chlorophyll (µg/L)	11.31		

Occoquan Watershed Monitoring Laboratory

Parameter	Reported	Prepared	% Recovered
TDN (mg N/L)	0.380	0.353	108
TDN (mg N/L)	0.957	0.988	97
TDP (mg P/L)	0.023	0.0211	109
TDP (mg P/L)	0.040	0.0383	104
NH4 (mg N/L)	0.034	0.0273	125
NH4 (mg N/L)	0.135	0.134	101
NO3 + NO2 (mg N/L)	0.082	0.084	98
NO3 + NO2 (mg N/L)	0.395	0.392	101
PO4 (mg P/L)	0.014	0.0119	118
PO4 (mg P/L)	0.049	0.0536	91
Chlorophyll (µg/L)	12.6		

Delaware DNR

Parameter	Reported	Prepared	% Recovered
TDN (mg N/L)	0.299 WARN	0.353	85
TDN (mg N/L)	0.933	0.988	94
TDP (mg P/L)	0.022	0.0211	104
TDP (mg P/L)	0.049	0.0383	128
NH4 (mg N/L)	0.034	0.0273	125
NH4 (mg N/L)	0.142	0.134	106
NO3 + NO2 (mg N/L)	0.088	0.084	105
NO3 + NO2 (mg N/L)	0.404	0.392	103
PO4 (mg P/L)	0.013	0.0119	109
PO4 (mg P/L)	0.052	0.0536	97
Chlorophyll (µg/L)	17.9		

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

University of Delaware

Parameter	Reported	Prepared	% Recovered
NH4 (mg N/L)	0.025	0.0273	92
NH4 (mg N/L)	0.150	0.134	112
NO3 + NO2 (mg N/L)	0.080	0.084	95
NO3 + NO2 (mg N/L)	0.386	0.392	98
PO4 (mg P/L)	0.010	0.0119	84
PO4 (mg P/L)	0.055	0.0536	103
Particulate C (mg C/L)	1.715		
Particulate N (mg N/L)	0.255		
Chlorophyll (µg/L)	17.17		

UMCES Appalachian Laboratory

Parameter	Reported	Prepared	% Recovered
TDN (mg N/L)	0.3496	0.353	99
TDN (mg N/L)	0.9331	0.988	94
TDP (mg P/L)	0.0233	0.0211	110
TDP (mg P/L)	0.0411	0.0383	107
NH4 (mg N/L)	0.0260	0.0273	95
NH4 (mg N/L)	0.1417	0.134	106
NO3 + NO2 (mg N/L)	0.0738	0.084	88
NO3 + NO2 (mg N/L)	0.4019	0.392	103
PO4 (mg P/L)	0.0116	0.0119	97
PO4 (mg P/L)	0.0561	0.0536	105
Particulate C (mg C/L)	1.7461		
Particulate N (mg N/L)	0.1960 WARN		
Particulate P (mg P/L)	0.0125		

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

Academy of Natural Sciences of Philadelphia

Parameter	Reported	Prepared	% Recovered
TDN (mg N/L)	0.334	0.353	95
TDN (mg N/L)	0.909	0.988	92
TDP (mg P/L)	0.0224	0.0211	106
TDP (mg P/L)	0.0399	0.0383	104
NH4 (mg N/L)	0.0301	0.0273	110
NH4 (mg N/L)	0.137	0.134	102
NO3 + NO2 (mg N/L)	0.0800	0.084	95
NO3 + NO2 (mg N/L)	0.396	0.392	101
PO4 (mg P/L)	0.0121	0.0119	102
PO4 (mg P/L)	0.0522	0.0536	97
Particulate C (mg C/L)	1.715		
Particulate N (mg N/L)	0.227		
Particulate P (mg P/L)	0.0145		
Chlorophyll (µg/L)	11.15		

Academy of Natural Sciences Estuarine Research Center

Parameter	Reported	Prepared	% Recovered
Chlorophyll (µg/L)	8.01		

Old Dominion University

Parameter	Reported	Prepared	% Recovered
TDN (mg N/L)	0.366	0.353	104
TDN (mg N/L)	0.958	0.988	97
TDP (mg P/L)	0.0247	0.0211	117
TDP (mg P/L)	0.0436	0.0383	114
NH4 (mg N/L)	0.0262	0.0273	96
NH4 (mg N/L)	0.1325	0.134	99
NO3 + NO2 (mg N/L)	0.0804	0.084	96
NO3 + NO2 (mg N/L)	0.3871	0.392	99
PO4 (mg P/L)	0.0112	0.0119	94
PO4 (mg P/L)	0.0537	0.0536	100
Particulate C (mg C/L)	1.8327		
Particulate N (mg N/L)	0.2626		
Particulate P (mg P/L)	0.0144		
Chlorophyll (µg/L)	9.84		

Virginia Division of Consolidated Laboratory Services

Parameter	Reported	Prepared	% Recovered
TDN (mg N/L)	0.372	0.353	105
TDN (mg N/L)	0.939	0.988	95
TDP (mg P/L)	0.023	0.0211	109
TDP (mg P/L)	0.040	0.0383	104
NH4 (mg N/L)	0.031	0.0273	114
NH4 (mg N/L)	0.152	0.134	113
NO3 + NO2 (mg N/L)	0.087	0.084	104
NO3 + NO2 (mg N/L)	0.407	0.392	104
PO4 (mg P/L)	0.012	0.0119	101
PO4 (mg P/L)	0.056	0.0536	104
Particulate P (mg P/L)	0.0136		
Chlorophyll (µg/L)	17.66		

UMCES Horn Point Laboratory

Parameter	Reported	Prepared	% Recovered
TDN (mg N/L)	0.341	0.353	97
TDN (mg N/L)	0.930	0.988	94
TDP (mg P/L)	0.0150 WARN	0.0211	71
TDP (mg P/L)	0.0325	0.0383	85
NH4 (mg N/L)	0.0262	0.0273	96
NH4 (mg N/L)	0.136	0.134	101
NO3 + NO2 (mg N/L)	0.0813	0.084	97
NO3 + NO2 (mg N/L)	0.360 WARN	0.392	92
PO4 (mg P/L)	0.00790	0.0119	66
PO4 (mg P/L)	0.0521	0.0536	97
Particulate C (mg C/L)	1.735		
Particulate N (mg N/L)	0.2545		

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

UMCES Chesapeake Biological Laboratory

Parameter	Reported	Prepared	% Recovered
TDN (mg N/L)	0.362	0.353	103
TDN (mg N/L)	0.946	0.988	96
TDP (mg P/L)	0.0254	0.0211	120
TDP (mg P/L)	0.0438	0.0383	114
NH4 (mg N/L)	0.029	0.0273	106
NH4 (mg N/L)	0.160 WARN	0.134	119
NO3 + NO2 (mg N/L)	0.0865	0.084	103
NO3 + NO2 (mg N/L)	0.415	0.392	106
PO4 (mg P/L)	0.0115	0.0119	97
PO4 (mg P/L)	0.0513	0.0536	96
Particulate C (mg C/L)	1.55		
Particulate N (mg N/L)	0.257		
Particulate P (mg P/L)	0.0140		
Chlorophyll (µg/L)	19.08		

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

UMCES Chesapeake Biological Laboratory, Siefert Group

Parameter	Reported	Prepared	% Recovered
NH4 (mg N/L)	0.024	0.0273	88
NH4 (mg N/L)	0.138	0.134	103

USDA, ARS, Animal Manure and By-Products Laboratory

Parameter	Reported	Prepared	% Recovered
NH4 (mg N/L)	0.037 WARN	0.0273	136
NH4 (mg N/L)	0.146	0.134	109
NO3 + NO2 (mg N/L)	0.083	0.084	99
NO3 + NO2 (mg N/L)	0.400	0.392	102

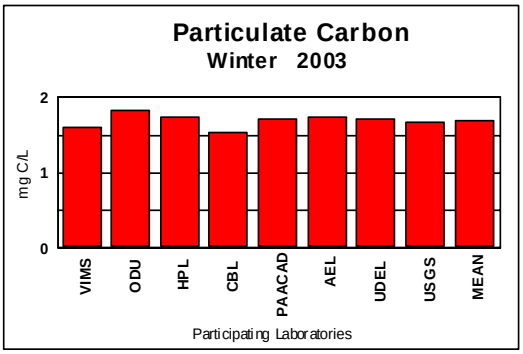
"WARN" based on standard deviation of all participants' reported concentrations

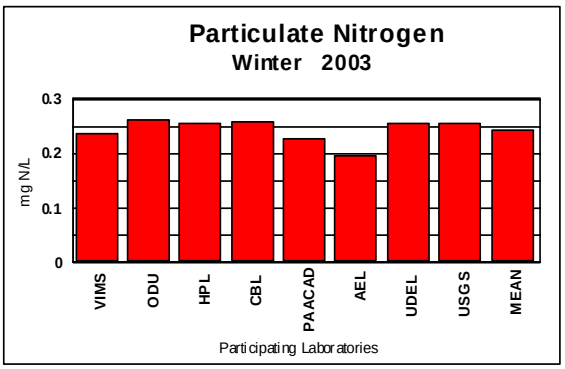
MD DHMH Division of Environmental Chemistry Nutrients Laboratory

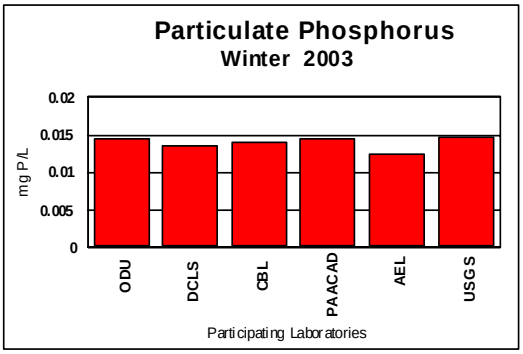
Parameter	Reported	Prepared	% Recovered
NH4 (mg N/L)	0.0267	0.0273	98
NH4 (mg N/L)	0.138	0.134	103
NO3 + NO2 (mg N/L)	0.0801	0.084	95
NO3 + NO2 (mg N/L)	0.397	0.392	101
PO4 (mg P/L)	0.0101	0.0119	85
PO4 (mg P/L)	0.0498	0.0536	93
Chlorophyll (µg/L)	16.4		

USGS, National Water Quality Laboratory

Parameter	Reported	Prepared	% Recovered
TDN (mg N/L)	0.346	0.353	98
TDN (mg N/L)	0.933	0.988	94
TDP (mg P/L)	0.0251	0.0211	119
TDP (mg P/L)	0.0411	0.0383	107
NH4 (mg N/L)	0.0223	0.0273	82
NH4 (mg N/L)	0.125	0.134	93
NO3 + NO2 (mg N/L)	0.0781	0.084	93
NO3 + NO2 (mg N/L)	0.372	0.392	95
PO4 (mg P/L)	0.0120	0.0119	101
PO4 (mg P/L)	0.0498	0.0536	93
Particulate C (mg C/L)	1.674		
Particulate N (mg N/L)	0.254		
Particulate P (mg P/L)	0.0147		
Chlorophyll (μg/L)	13.05		







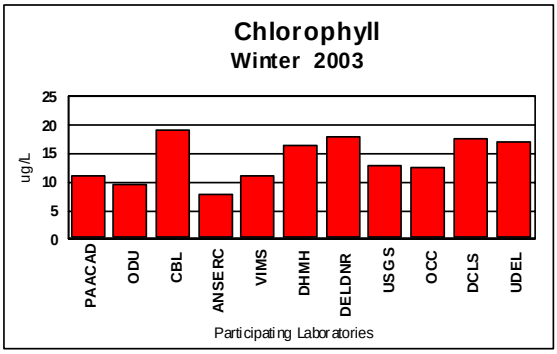
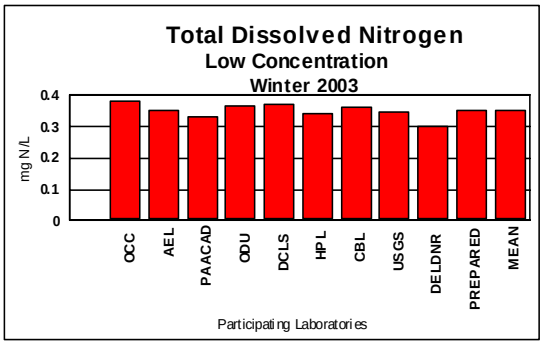
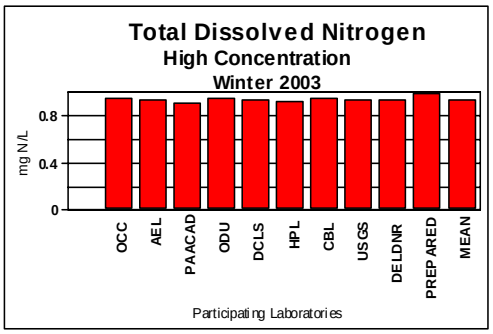
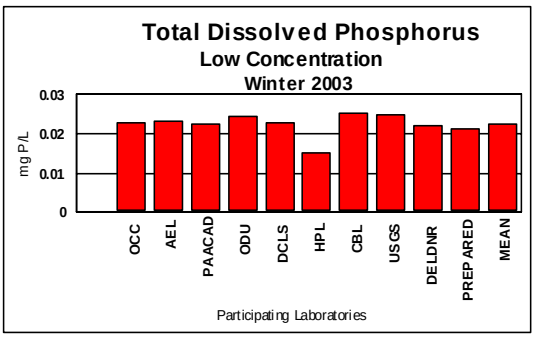


Figure 1. Particulate carbon, nitrogen and phosphorus; chlorophyll, Winter 2003.







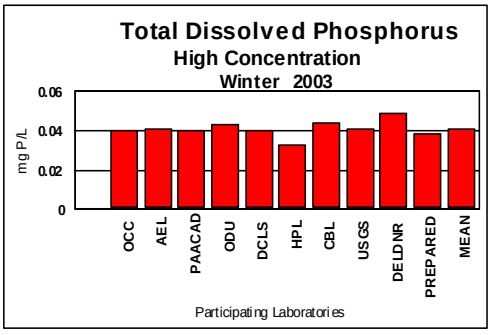


Figure 2. Total dissolved nitrogen and phosphorus, Winter 2003.

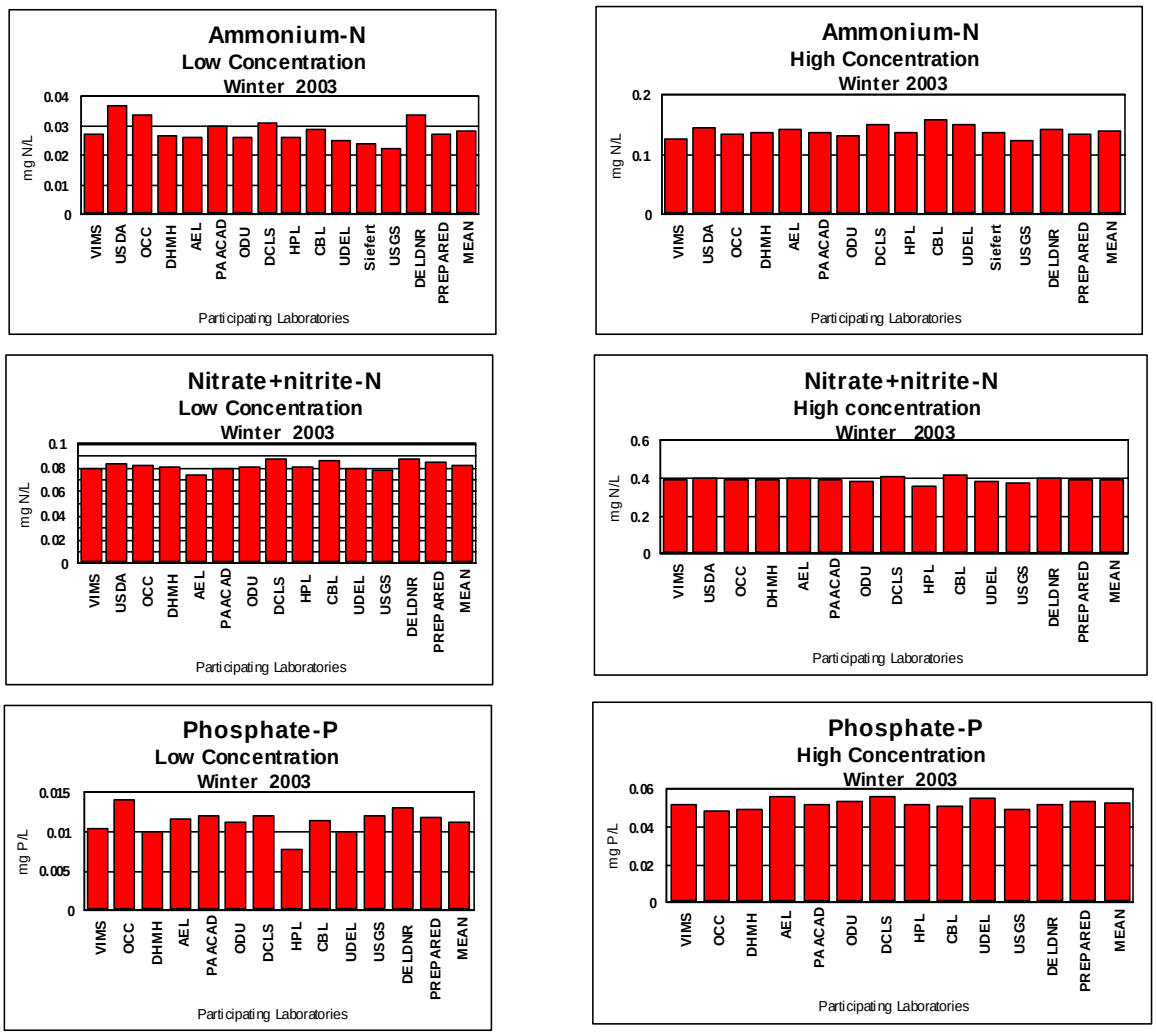


Figure 3. Dissolved inorganic nitrogen and phosphorus, Winter 2003.