Ref. No. (UMCES) CBL 04-077

CHESAPEAKE BAY PROGRAM BLIND AUDIT

FISCAL YEAR 2004 FINAL REPORT

SUBMITTED BY:

Carl Zimmermann
Carolyn Keefe
Nutrient Analytical Services Laboratory
Chesapeake Biological Laboratory
P.O. Box 38
Solomons, MD 20688-0038

24 June 2004

Submitted to: Maryland Dept. of Natural Resources
Resource Assessment Administration
Water and Habitat Quality Program
Annapolis, Maryland

Technical Report Series Number TS-442-04-CBL of the
University of Maryland Center for Environmental Science

TABLE OF CONTENTS

Introduction……3
Materials and Methods……3
Results……5
Discussion……6
Conclusion……10

LIST OF TABLES

Table 1. Participants in the Summer 2003 and Winter 2004 Chesapeake Bay Blind Audit Program

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Summer 2003 and Winter 2004 Blind Audit, Including Distribution of Reported Concentrations from the Mean

Table 3. Summary of Prepared and Reported Concentrations for Each Analyte in the Summer 2003 and Winter 2004 Blind Audit, Including Comparison to Prepared Concentration

LIST OF FIGURES

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

Figure 2. Total dissolved nitrogen and phosphorus, Summer 2003

Figure 3. Dissolved inorganic nitrogen and phosphorus, Summer 2003

Figure 4. Dissolved organic carbon and total suspended solids, Summer 2003

Figure 5. Particulate carbon, nitrogen and phosphorus; chlorophyll, Winter 2004

Figure 6. Total dissolved nitrogen and phosphorus, Winter 2004

Figure 7. Dissolved inorganic nitrogen and phosphorus, Winter 2004

Figure 8. Dissolved organic carbon and total suspended solids, Winter 2004

APPENDICES

Appendix 1. Summer 2003 and Winter 2004 Reported Data, Prepared Concentrations and Percent Recoveries

Appendix 2. Instructions for Summer 2003 and Winter 2004 Blind Audit Sample Preparation

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 seventh 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. This year, for the first time, dissolved organic carbon and total suspended solids samples were included in the Blind Audit Program.

MATERIALS AND METHODS

Blind Audit samples were sent to participating laboratories on 04 August 2003 and 09 February 2004. 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 2003 and winter 2004 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 some 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 in summer 2003 was 0.300 mg N/L and 0.282-0.515 mg N/L was reported by participants. The prepared low level concentration in winter 2004 was 0.277 mg N/L and 0.234-0.300 mg N/L was reported by participants. The prepared high level concentration in summer 2003 was 0.959 mg N/L and 0.88-1.04 mg N/L was reported by participants; that is, all were within $\pm$ 10% of the prepared concentration. The prepared high level concentration in winter 2004 was 1.108 mg N/L and 0.913-1.18 mg N/L was reported by participants. One participating laboratory analyzed the samples by the Kjeldahl technique. Their reported concentrations were similar to those of the other participants.

Total Dissolved Phosphorus: The prepared low level concentration in summer 2003 was 0.0168 mg P/L and 0.0131-0.032 mg P/L was reported by participants. The prepared low level concentration in winter 2004 was 0.021 mg P/L and 0.0136-0.026 mg P/L was reported by participants. The prepared high level concentration in summer 2003 was 0.0432 mg P/L and 0.040-0.050 mg P/L was reported by participants. The prepared high level concentration in winter 2004 was 0.0557 mg P/L and 0.0508-0.0641 mg P/L was reported by participants. One participating laboratory digested the samples by the Kjeldahl technique, then analyzed the resultant solution for phosphorus. Their reported concentrations were similar to those of the other participants.

Ammonium: The prepared low level concentration in summer 2003 was 0.0280 mg N/L and 0.0054-0.041 mg N/L was reported by participants. The prepared low level concentration in winter 2004 was 0.0310 mg N/L and 0.0134-0.037 mg N/L was reported by participants. The prepared high level concentration in summer 2003 was 0.280 mg N/L and 0.2258-0.305 mg N/L was reported by participants. The prepared high level concentration in winter 2004 was 0.310 mg N/L and 0.2454-0.397 mg N/L was reported by participants.

Nitrate + Nitrite: The prepared low level concentration in summer 2003 was 0.0152 mg N/L and 0.0071-0.034 mg N/L was reported by participants. The prepared low level concentration in winter 2004 was 0.031 mg N/L and 0.0228-0.040 mg N/L was reported by participants. The prepared high level concentration in summer 2003 was 0.735 mg N/L and 0.6629-0.765 mg N/L was reported by participants; that is, all were within ± 10% of the prepared concentration. The prepared high level concentration in winter 2004 was 0.861 mg N/L and 0.7815-0.909 mg N/L was reported by participants; that is, all were AGAIN (!) within ± 10% of the prepared concentration.

Orthophosphate: The prepared low level concentration in summer 2003 was 0.0093 mg P/L and 0.0050-0.014 mg P/L was reported by participants. The prepared low level concentration in winter 2004 was 0.0089 mg P/L and 0.0069-0.0153 mg P/L was reported by participants. The prepared high level concentration in summer 2003 was 0.0279 mg P/L and 0.0250-0.0298 mg P/L was reported by participants; that is, all were within ± 10% of the prepared concentration. The prepared high level concentration in winter 2004 was 0.0335 mg P/L and 0.0260-0.0488 mg P/L was reported by participants.

Dissolved Organic Carbon: The prepared low level concentration in summer 2003 was 3.00 mg C/L and 2.95-3.65 mg C/L was reported by participants. The prepared low level concentration in winter 2004 was 2.50 mg C/L and 2.48-3.086 mg C/L was reported by participants. The prepared high level concentration in summer 2003 was 5.00 mg C/L and 4.56-6.20 mg C/L was reported by participants. The prepared high level concentration in winter 2004 was 4.60 mg C/L and 4.365-5.757 mg C/L was reported by participants.

PARTICULATE FRACTION

Again, it should be noted that particulate carbon, nitrogen and phosphorus samples were filtered from a common estuarine water sample and, consequently, are not true blind audit samples produced from pure constituents. To assess the variability found in a natural sample, a test of repeated analyses at one laboratory (CBL) was completed for 8-16 other samples from each batch. The coefficients of variation of particulate nitrogen and carbon concentrations in samples from the common container, in winter 2004, were 3.5% and 2.3% (N=16), respectively. For particulate phosphorus, the coefficients of variation were 10.9% (N=8) in summer 2003 and 4.0% (N=10) in winter 2004. Particulate results are graphically presented in Figures 1 and 5.

Particulate Nitrogen: Particulate N results for summer 2003 revealed fairly close agreement between all but one of the participating laboratories (Table 2), with a reported mean of 0.424 mg N/L ± 0.147 S.D. For the winter 2004 samples, there was closer agreement, with a mean of 0.259 mg N/L ± 0.0378 S.D. The percent coefficient of variation among the laboratories participating in the winter 2004 audit was 14.6% (N=10). This was somewhat more variable than the 3.5% variability found for 16 other 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 for summer 2003 revealed close agreement between all participating laboratories. The mean was 1.93 mg C/L ± 0.0471 S.D. Particulate C results for winter 2004 also revealed generally close agreement between participating laboratories (Table

2). The mean for winter 2004 was 1.83 mg C/L ± 0.152 S.D. The percent coefficient of variation among the laboratories participating in the audit was 8.3% (N=10), somewhat more variable than the 2.3% variability found for 16 other 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 in summer 2003 also revealed close agreement between participating laboratories (Table 2). The mean was 0.0390 mg P/L ± 0.0017 S.D. The percent coefficient of variation among the laboratories participating in the audit was 4.1% (N=7) which was less than the 10.9% variability found for 8 other samples from this batch analyzed by CBL (mean 0.0402 mg P/L). There was also close inter-laboratory agreement in particulate P results for winter 2004, although the concentration was less than half of that in the summer. The mean concentration reported by the laboratories was 0.0201 mg P/L ± 0.0012 S.D., which is quite similar to the mean (0.0189 mg P/L) found for 10 other samples from this batch analyzed by CBL. The coefficient of variation for the participants was 5.8 %, while CBL's coefficient of variation was 4.0%. This, too, is remarkably close agreement for multi-laboratory comparison of samples of a natural population.

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 2003 sample, 42.2 mg/L was prepared and 34.3-41.2 mg/L was reported by participants. For the winter 2004 sample, 17.8 mg/L was prepared and 10.8-16.2 mg/L was reported by participants. In both instances, there was a consistent negative bias by all. The mean concentration for the winter 2004 sample reported by the laboratories was 14.1 mg/L ± 1.74 S.D., which is quite similar to the mean (13.8 mg/L) found for 5 other samples from this batch analyzed by CBL. The coefficient of variation for the participants was 12.3 %, while CBL's coefficient of variation was 4.5%.

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 2003 blind audit of high level nitrate concentration, the mean reported concentration was 0.723 mg N/L and reported concentrations ranged from 0.663-0.765 mg N/L.(Coefficient of Variation, 3.0%). Twelve laboratories reported results for this high level nitrate sample that were within two standard deviations (S.D. ± 0.0252 mg N/L) of the mean. Since the standard deviation was so small, one laboratory's reported result for this sample was between two and three standard deviations of the mean, so it was labeled as a "warning, although <u>all</u> of the reported data were within ± 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 2004 blind audit of 0.0310 mg N/L prepared for ammonium has a "pass" category (± 10%) of only 0.0279-0.0341 mg P/L. Twelve out of fifteen 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 24% and 29%. 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%. 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 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 total dissolved nitrogen summer 2003 sample, low level nitrate + nitrite summer 2003 sample, and both high and low level orthophosphate winter 2004 samples. Also, in this category was University of Delaware's low level orthophosphate summer 2003 sample. The Academy of Natural Sciences of Philadelphia's high level dissolved organic carbon summer 2003 sample was in this group. Seifert's laboratory's high level ammonium winter 2004 sample was in this group. All of VIMS' ammonium samples in the summer 2003 and winter 2004 audits were in this group, as were their high level total dissolved nitrogen and low level total dissolved phosphorus winter 2004 samples. Also in this category were Pennsylvania DEP, high level total dissolved nitrogen and low level nitrate + nitrite winter 2004 samples.

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 quite low (4.1%) for the summer 2003 blind audit, and also for the winter 2004 blind audit (5.8%). 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, summer 2003 and winter 2004 blind audits, leading us to conclude that inter-laboratory comparison of other particulate phosphorus data would be valid.

June 18, 2004June 18, 2004Reporting 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 2004 participants reported only two significant digits, thus potentially giving substantial under or over estimates for the comparisons.

CONCLUSION

Now that thirteen 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, summer 2003 and winter 2004 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 2003 and winter 2004 blind audits, some results were 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 2003 and Winter 2004 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
USDA, ARS, Animal Manure & Byproducts Lab (**USDA**)	Jack Meisinger	301-504-6524	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	301-689-7122	X	X		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	X	X
USGS, National Water Quality Lab (**USGS**)	Mary Cast	303-236-3463	X	X	X	X	X
U Maryland, CBL, Siefert Lab (**Siefert**)	Ron Siefert	410-326-7386	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

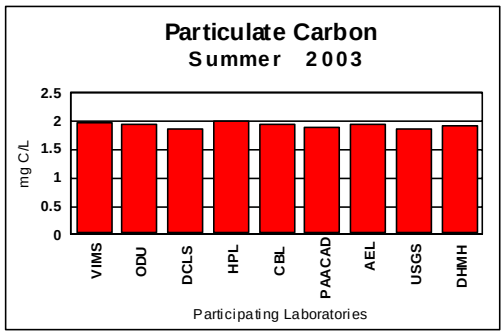
Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Winter 2003 Blind Audit, Including Distribution of Reported Concentrations from the Mean

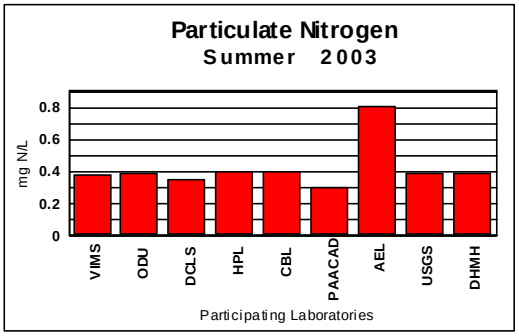
Parameter	Concentration in mg/L		**Number of Laboratories**			
			Standard Deviations from Mean			
			<1	1-2	2-3	>3
	Mean	S.D.	**PASS**	**PASS**	**WARN**	**FAIL**
Summer 2003						
Total Dissolved Nitrogen	0.325	0.0687	9		1	
Total Dissolved Nitrogen	0.954	0.0456	7	3		
Total Dissolved Phosphorus	0.0177	0.0080	8	1		
Total Dissolved Phosphorus	0.0455	0.0031	6	4		
Ammonium	0.027	0.0078	11	2	1	
Ammonium	0.278	0.0195	11	2	1	
Nitrate + Nitrite	0.0160	0.0082	9	2	1	
Nitrate + Nitrite	0.723	0.0252	10	2	1	
Orthophosphate	0.0100	0.0022	10	1	1	
Orthophosphate	0.0270	0.0013	9	2	1	
Dissolved Organic Carbon	3.20	0.254	6	1		
Dissolved Organic Carbon	5.13	0.480	6	1	1	
Particulate Carbon	1.933	0.0471	6	3		
Particulate Nitrogen	0.424	0.1469	8		1	
Particulate Phosphorus	0.0390	0.0017	5	2		
Total Suspended Solids	39.0	2.00	7	1	1	
Winter 2004						
Total Dissolved Nitrogen	0.272	0.0228	7	4		
Total Dissolved Nitrogen	1.054	0.0806	9		2	
Total Dissolved Phosphorus	0.0219	0.0035	8	2	1	
Total Dissolved Phosphorus	0.0595	0.0042	7	3	1	
Ammonium	0.0280	0.0068	10	4	1	
Ammonium	0.315	0.0341	12	1	2	
Nitrate + Nitrite	0.0310	0.0043	11	3	1	
Nitrate + Nitrite	0.834	0.0339	10	4	1	
Orthophosphate	0.0100	0.0022	11	2	1	
Orthophosphate	0.0330	0.0060	12	1	1	
Dissolved Organic Carbon	2.77	0.205	5	3		
Dissolved Organic Carbon	4.94	0.511	4	4		
Particulate Carbon	1.83	0.152	9		1	
Particulate Nitrogen	0.259	0.0378	8	1	1	
Particulate Phosphorus	0.0201	0.0012	6	1		
Total Suspended Solids	14.08	1.74	9	3		

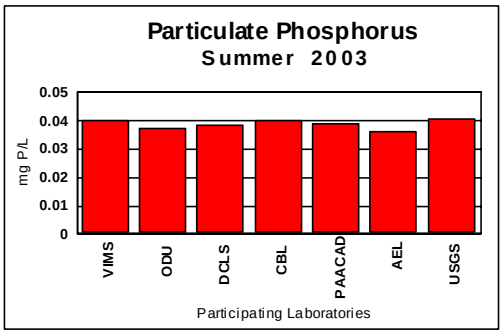
Table 3. Summary of Prepared and Reported Concentrations for Each Analyte, Including Percent Recovery of the Prepared Concentration

			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 2003					
Total Dissolved Nitrogen	0.300	0.282-0.515	8	1	1
Total Dissolved Nitrogen	0.959	0.88-1.04	10		
Total Dissolved Phosphorus	0.0168	0.0131-0.032	3	3**	3**
Total Dissolved Phosphorus	0.0432	0.040-0.050	8	2	
Ammonium	0.028	0.0054-0.041	9	2**	3**
Ammonium	0.280	0.226-0.305	13	1	
Nitrate + Nitrite	0.0152	0.0071-0.034	6	2**	4**
Nitrate + Nitrite	0.735	0.663-0.765	13		
Orthophosphate	0.0093	0.005-0.014	5	3**	4**
Orthophosphate	0.0279	0.0250-0.0298	12		
Dissolved Organic Carbon	3.0	2.95-3.65	5	1	1
Dissolved Organic Carbon	5.0	4.56-6.2	7		1
Total Suspended Solids	42.2	34.3-41.2	8	1	
Winter 2004					
Total Dissolved Nitrogen	0.277	0.234-0.300	9	2	
Total Dissolved Nitrogen	1.108	0.913-1.18	9	2	
Total Dissolved Phosphorus	0.021	0.0136-0.026	4	5**	2**
Total Dissolved Phosphorus	0.0557	0.0508-0.0641	6	5	
Ammonium	0.0310	0.0134-0.037	3	8**	4**
Ammonium	0.310	0.2454-0.397	12	1	2
Nitrate + Nitrite	0.0310	0.0228-0.040	10	2**	3**
Nitrate + Nitrite	0.861	0.7815-0.909	15		
Orthophosphate	0.0089	0.0069-0.0153	6	1**	6**
Orthophosphate	0.0335	0.026-0.0488	7	5	2
Dissolved Organic Carbon	2.5	2.48-3.09	3	4	1
Dissolved Organic Carbon	4.6	4.365-5.76	6		2
Total Suspended Solids	17.8	10.8-16.2	1	6	5

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







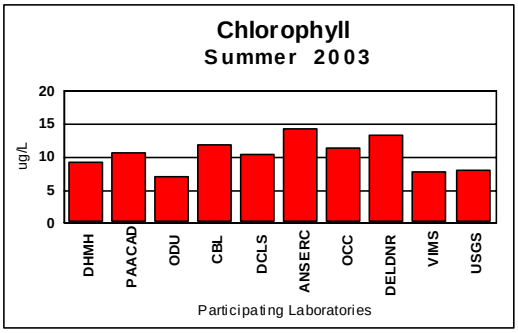
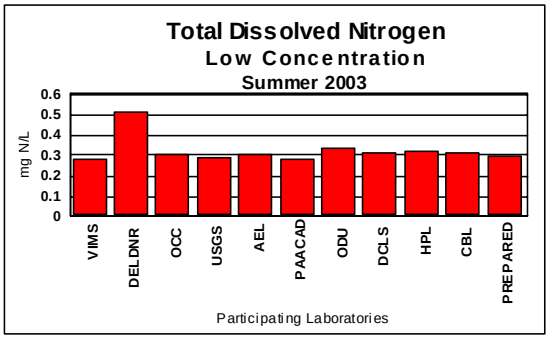
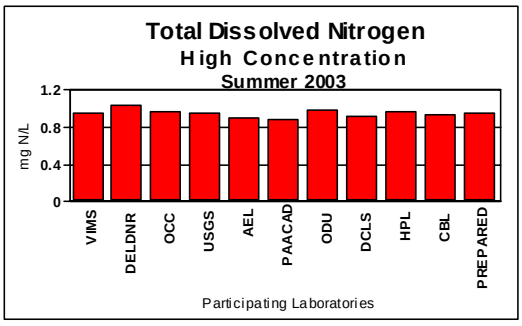
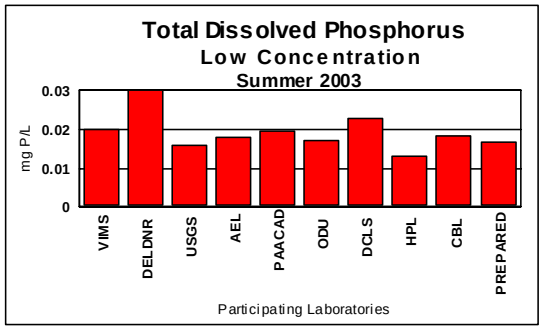


Figure 1. Particulate carbon, nitrogen and phosphorus; chlorophyll, Summer 2003.







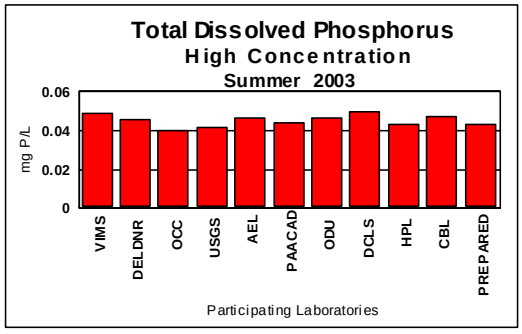
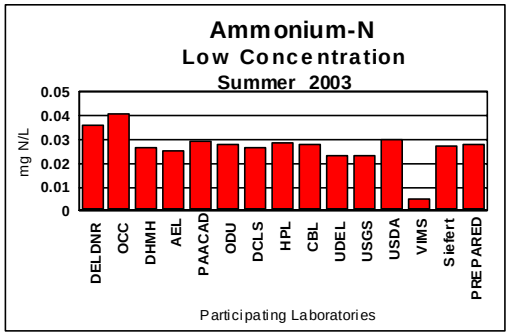
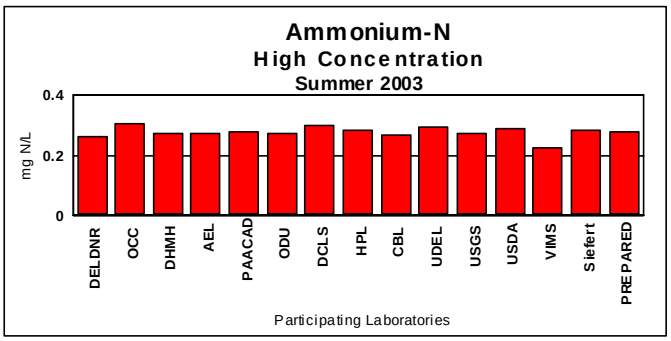
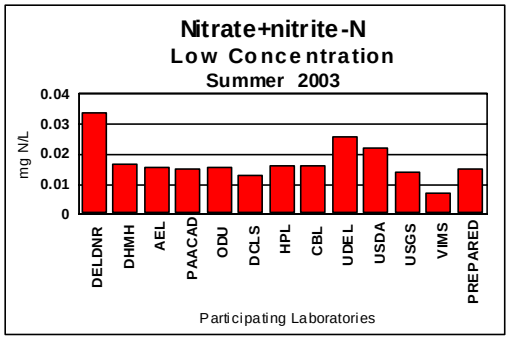
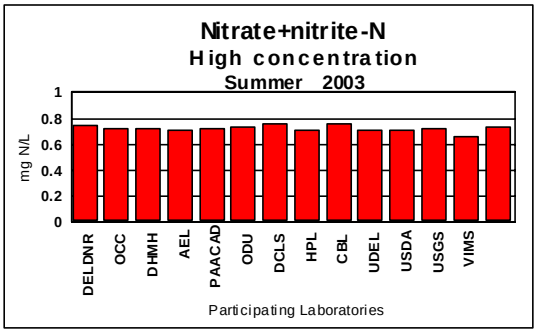


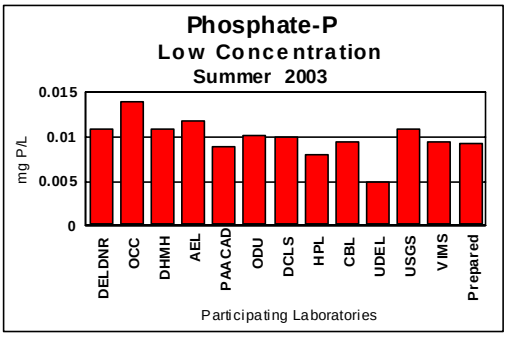
Figure 2. Total dissolved nitrogen and phosphorus, Summer 2003.











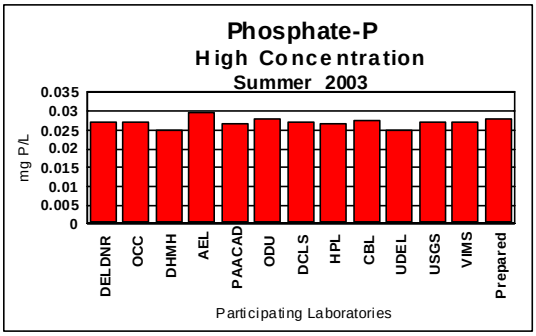
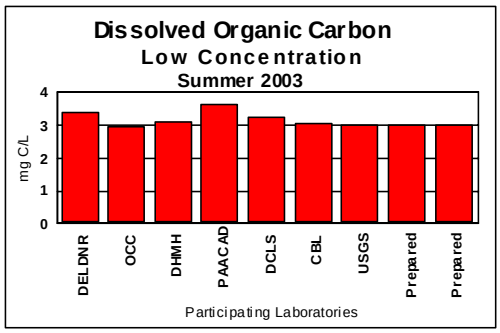
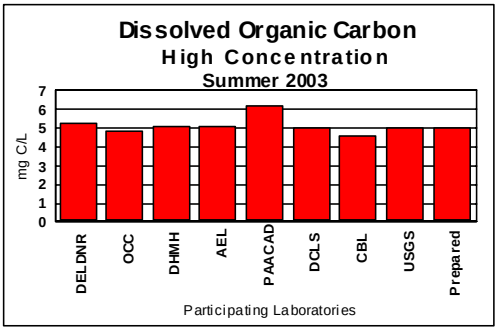


Figure 3. Dissolved inorganic nitrogen and phosphorus, Summer 2003.





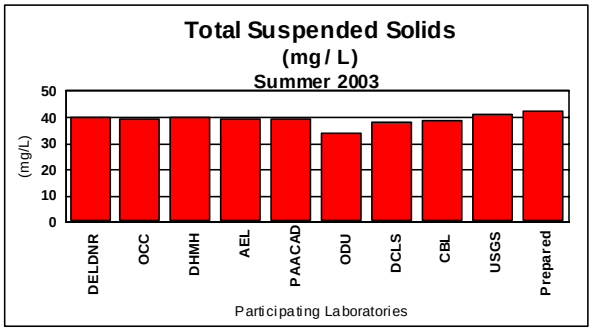
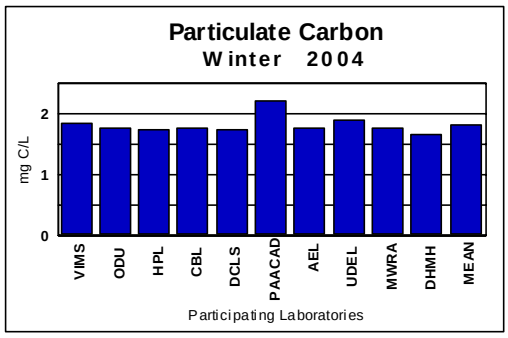
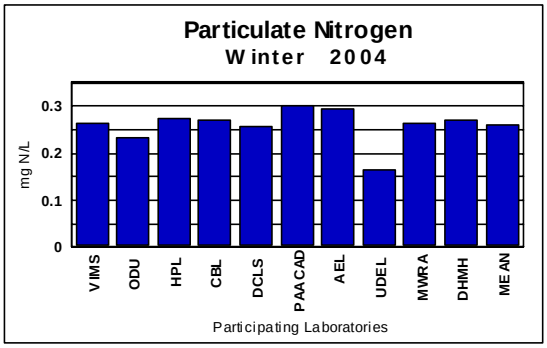
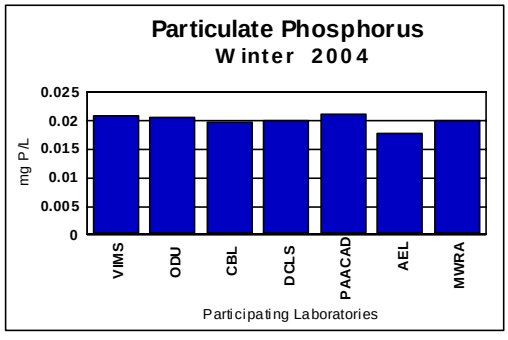


Figure 4. Dissolved organic carbon and total suspended solids, Summer 2003







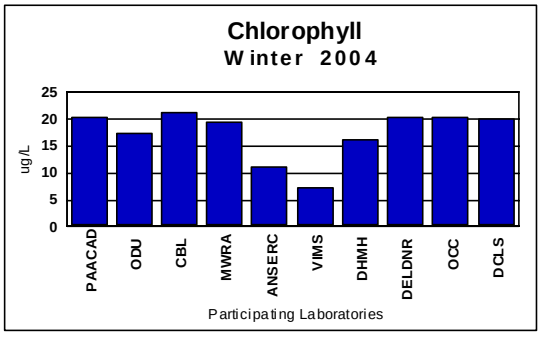
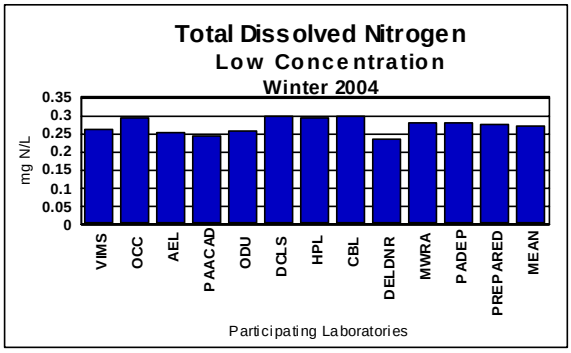
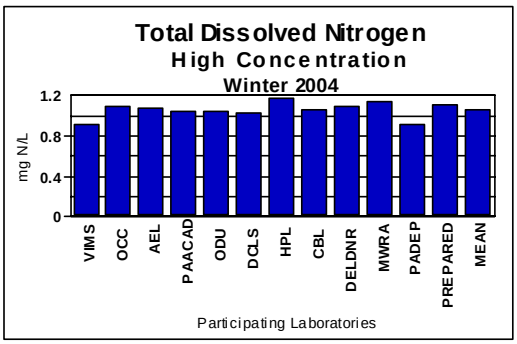
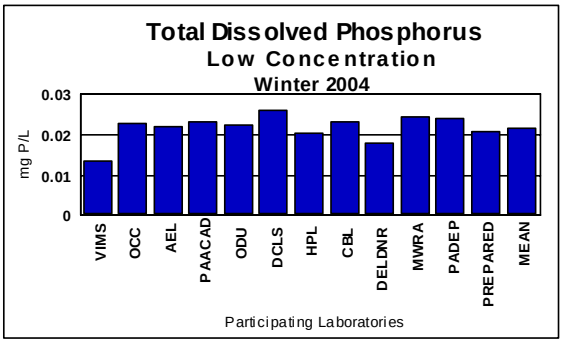


Figure 5. Particulate carbon, nitrogen and phosphorus; chlorophyll, Winter 2004.







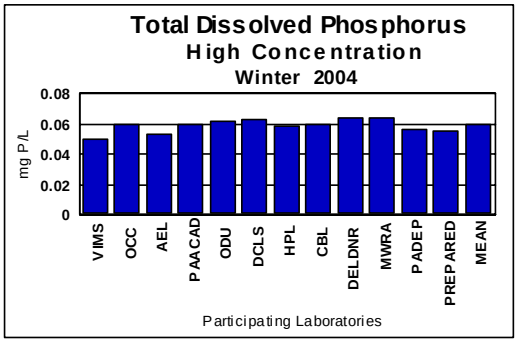


Figure 6. Total dissolved nitrogen and phosphorus, Winter 2004.

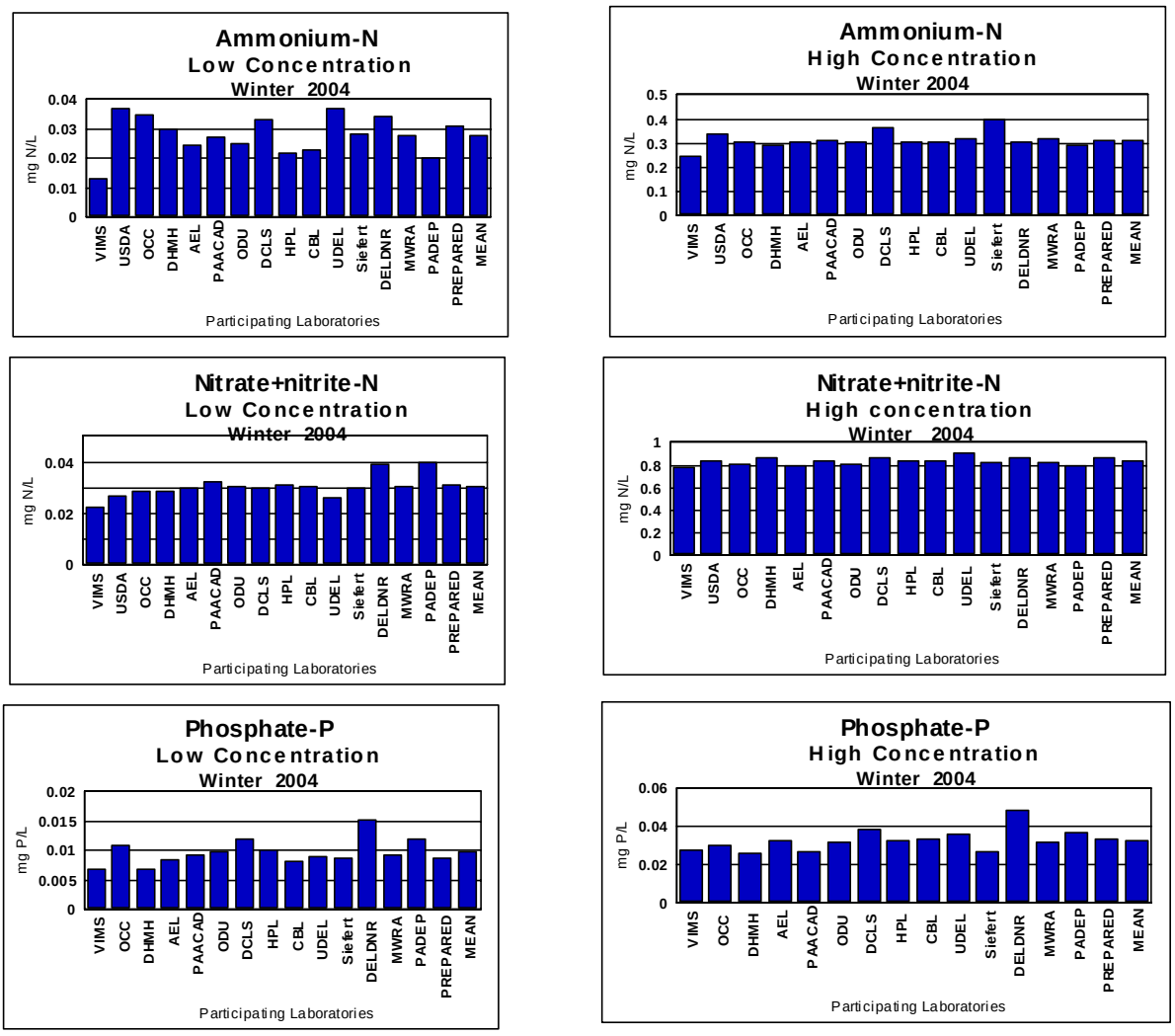


Figure 7. Dissolved inorganic nitrogen and phosphorus, Winter 2004.

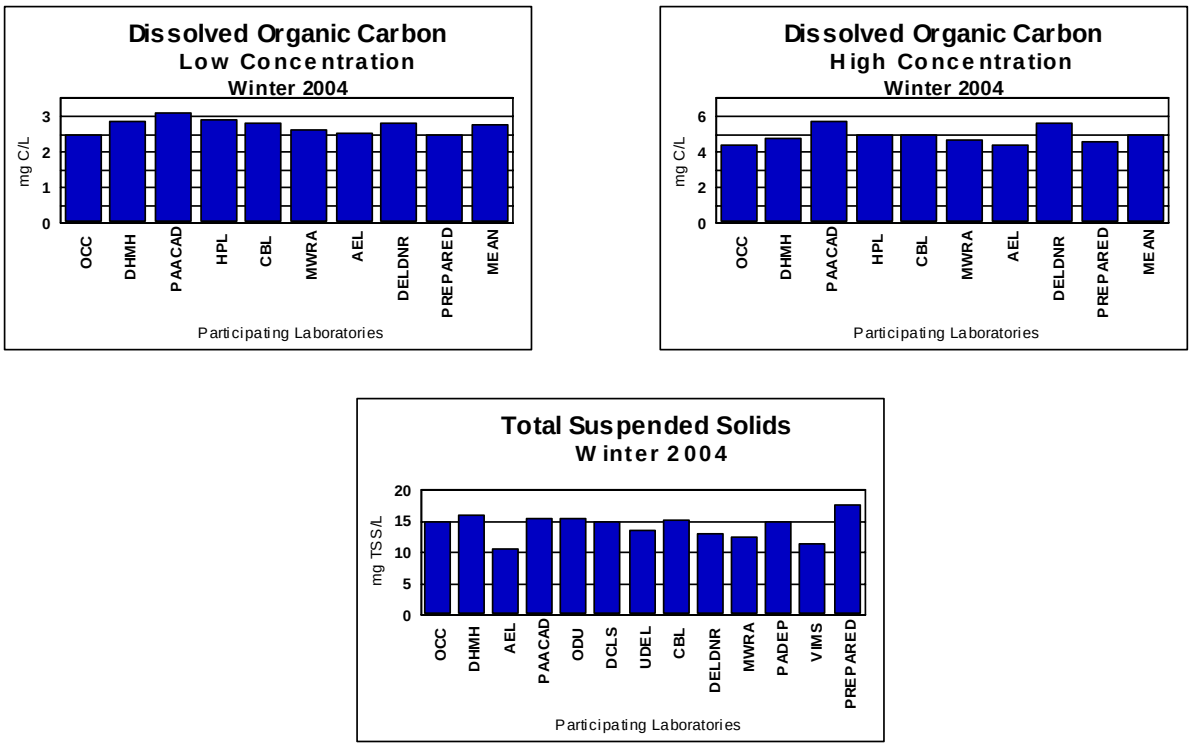


Figure 8. Dissolved organic carbon and total suspended solids, Winter 2004.

Appendix 1. Summer 2003 and Winter 2004 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 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.2829	0.300	94	0.261	0.277	94
TDN (mg N/L)	0.951	0.959	99	0.913 WARN	1.108	82
TDP (mg P/L)	0.02	0.0168	119**	0.0136 WARN	0.021	65**
TDP (mg P/L)	0.0488	0.0432	113	0.0508 WARN	0.0557	91
NH4 (mg N/L)	0.0054 WARN	0.028	19**	0.0134 WARN	0.031	43**
NH4 (mg N/L)	0.2258 WARN	0.28	81	0.2454 WARN	0.31	79
NO3 + NO2 (mg N/L)	0.0071	0.0152	47**	0.0228	0.031	74**
NO3 + NO2 (mg N/L)	0.6629 WARN	0.735	90	0.7815	0.861	91
PO4 (mg P/L)	0.0094	0.0093	101	0.0069	0.0089	78**
PO4 (mg P/L)	0.0269	0.0279	96	0.0275	0.0335	82
Particulate C (mg C/L)	1.979			1.863		
Particulate N (mg N/L)	0.378			0.265		
Particulate P (mg P/L)	0.040			0.021		
Chlorophyll (μg/L)	7.94			7.4		
Total Suspended Solids (mg/L)				11.6	17.8	65

"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 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.302	0.300	101	0.293	0.277	106
TDN (mg N/L)	0.973	0.959	101	1.09	1.108	98
TDP (mg P/L)	NA	0.0168		0.023	0.021	110**
TDP (mg P/L)	0.04	0.0432	93	0.06	0.0557	108
NH4 (mg N/L)	0.041	0.028	146**	0.035	0.031	113**
NH4 (mg N/L)	0.305	0.28	109	0.307	0.31	99
NO3 + NO2 (mg N/L)	NA	0.0152		0.029	0.031	94
NO3 + NO2 (mg N/L)	0.719	0.735	98	0.81	0.861	94
PO4 (mg P/L)	0.014	0.0093	151**	0.011	0.0089	124**
PO4 (mg P/L)	0.027	0.0279	97	0.03	0.0335	90
Chlorophyll (μg/L)	11.4			20.5		
DOC (mg C/L)	2.95	3.0	98	2.48	2.5	99
DOC (mg C/L)	4.86	5.0	97	4.4	4.6	96
Total Suspended Solids (mg/L)	39.6	42.2	94	15	17.8	84

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

Delaware DNR

Parameter	Summer 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.515 WARN	0.300	172	0.234	0.277	84
TDN (mg N/L)	1.04	0.959	108	1.09	1.108	98
TDP (mg P/L)	0.032	0.0168	190**	0.018	0.021	86**
TDP (mg P/L)	0.046	0.0432	106	0.064	0.0557	115
NH4 (mg N/L)	0.036	0.028	129**	0.0344	0.031	111**
NH4 (mg N/L)	0.263	0.28	94	0.307	0.31	99
NO3 + NO2 (mg N/L)	0.034 WARN	0.0152	224**	0.0389	0.031	125**
NO3 + NO2 (mg N/L)	0.745	0.735	101	0.869	0.861	101
PO4 (mg P/L)	0.013	0.0093	140**	0.0153 WARN	0.0089	172**
PO4 (mg P/L)	0.028	0.0279	100	0.0488 WARN	0.0335	146
Chlorophyll (μg/L)	13.3			20.6		
DOC (mg C/L)	3.4	3.0	113	2.8	2.5	112
DOC (mg C/L)	5.3	5.0	106	5.62	4.6	122
Total Suspended Solids (mg/L)	40	42.2	95	13	17.8	73

"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 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
NH4 (mg N/L)	0.023	0.028	82**	0.037	0.031	119**
NH4 (mg N/L)	0.295	0.28	105	0.322	0.31	104
NO3 + NO2 (mg N/L)	0.026	0.0152	171**	0.026	0.031	84**
NO3 + NO2 (mg N/L)	0.712	0.735	97	0.909 WARN	0.861	106
PO4 (mg P/L)	0.005 WARN	0.0093	54**	0.009	0.0089	101
PO4 (mg P/L)	0.025	0.0279	90	0.036	0.0335	107
Particulate C (mg C/L)				1.92		
Particulate N (mg N/L)				0.166 WARN		
Total Suspended Solids (mg/L)				13.6	17.8	76

“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 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.305	0.300	102	0.2529	0.277	91
TDN (mg N/L)	0.904	0.959	94	1.074	1.108	97
TDP (mg P/L)	0.0179	0.0168	107	0.0221	0.021	105
TDP (mg P/L)	0.0463	0.0432	107	0.0539	0.0557	97
NH4 (mg N/L)	0.0255	0.028	91	0.0248	0.031	80**
NH4 (mg N/L)	0.2735	0.28	98	0.3089	0.31	100
NO3 + NO2 (mg N/L)	0.0157	0.0152	103	0.0298	0.031	96
NO3 + NO2 (mg N/L)	0.715	0.735	97	0.7916	0.861	92
PO4 (mg P/L)	0.0119	0.0093	128**	0.0086	0.0089	97
PO4 (mg P/L)	0.0298 WARN	0.0279	107	0.0332	0.0335	99
Particulate C (mg C/L)	1.941			1.78		
Particulate N (mg N/L)	0.808 WARN			0.295		
Particulate P (mg P/L)	0.037			0.0178		
DOC (mg C/L)	NA	3.0		2.53	2.5	101
DOC (mg C/L)	5.07	5.0	101	4.365	4.6	95
Total Suspended Solids (mg/L)	39.4	42.2	93	10.8	17.8	61

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

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

Academy of Natural Sciences of Philadelphia

Parameter	Summer 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.282	0.300	94	0.245	0.277	88
TDN (mg N/L)	0.88	0.959	92	1.04	1.108	94
TDP (mg P/L)	0.0195	0.0168	116**	0.0235	0.021	112**
TDP (mg P/L)	0.0441	0.0432	102	0.0605	0.0557	109
NH4 (mg N/L)	0.0296	0.028	106	0.0273	0.031	88**
NH4 (mg N/L)	0.278	0.28	99	0.312	0.31	101
NO3 + NO2 (mg N/L)	0.0153	0.0152	101	0.0323	0.031	104
NO3 + NO2 (mg N/L)	0.724	0.735	99	0.84	0.861	98
PO4 (mg P/L)	0.00897	0.0093	96	0.00936	0.0089	105
PO4 (mg P/L)	0.0265	0.0279	95	0.0271	0.0335	81
Particulate C (mg C/L)	1.899			2.22 WARN		
Particulate N (mg N/L)	0.304			0.300		
Particulate P (mg P/L)	0.039			0.0212		
Chlorophyll (μg/L)	10.8			20.3		
DOC (mg C/L)	3.65	3.0	122	3.086	2.5	123
DOC (mg C/L)	6.2 WARN	5.0	124	5.757	4.6	125
Total Suspended Solids (mg/L)	39.5	42.2	94	15.5	17.8	87

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

Academy of Natural Sciences Estuarine Research Center

Parameter	Summer 2003 Reported	Prepared	% Recovered	Winter 2004 Reported	Prepared	% Recovered
Chlorophyll (μg/L)	14.4			11.2		

Old Dominion University

Parameter	Summer 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.334	0.300	111	0.258	0.277	93
TDN (mg N/L)	0.995	0.959	104	1.05	1.108	95
TDP (mg P/L)	0.0173	0.0168	103	0.0223	0.021	106
TDP (mg P/L)	0.0468	0.0432	108	0.0621	0.0557	111
NH4 (mg N/L)	0.0281	0.028	100	0.025	0.031	81**
NH4 (mg N/L)	0.2735	0.28	98	0.3078	0.31	99
NO3 + NO2 (mg N/L)	0.0155	0.0152	102	0.0307	0.031	99
NO3 + NO2 (mg N/L)	0.7291	0.735	99	0.813	0.861	94
PO4 (mg P/L)	0.0102	0.0093	110**	0.0098	0.0089	110**
PO4 (mg P/L)	0.0278	0.0279	100	0.0322	0.0335	96
Particulate C (mg C/L)	1.964			1.77		
Particulate N (mg N/L)	0.394			0.233		
Particulate P (mg P/L)	0.0151			0.0206		
Chlorophyll (μg/L)	7.15			17.3		
Total Suspended Solids (mg/L)	34.3 WARN	42.2	81	15.52	17.8	87

"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 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.314	0.300	105	0.297	0.277	107
TDN (mg N/L)	0.929	0.959	97	1.032	1.108	93
TDP (mg P/L)	0.023	0.0168	137**	0.026	0.021	124**
TDP (mg P/L)	0.05	0.0432	116	0.063	0.0557	113
NH4 (mg N/L)	0.027	0.028	96	0.033	0.031	106
NH4 (mg N/L)	0.300	0.28	107	0.364	0.31	117
NO3 + NO2 (mg N/L)	0.013	0.0152	86**	0.030	0.031	97
NO3 + NO2 (mg N/L)	0.765	0.735	104	0.869	0.861	101
PO4 (mg P/L)	0.01	0.0093	108	0.012	0.0089	135**
PO4 (mg P/L)	0.027	0.0279	97	0.039	0.0335	116
Particulate C (mg C/L)	1.86			1.76		
Particulate N (mg N/L)	0.355			0.255		
Particulate P (mg P/L)	0.0385			0.0202		
Chlorophyll (μg/L)	10.6			20		
DOC (mg C/L)	3.24	3.0	108			
DOC (mg C/L)	4.99	5.0	100			
Total Suspended Solids (mg/L)	38	42.2	90	15.0	17.8	84

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

UMCES Horn Point Laboratory

Parameter	Summer 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.316	0.300	105	0.292	0.277	105
TDN (mg N/L)	0.977	0.959	102	1.18	1.108	106
TDP (mg P/L)	0.0131	0.0168	78**	0.0204	0.021	97
TDP (mg P/L)	0.0436	0.0432	101	0.0593	0.0557	106
NH4 (mg N/L)	0.0286	0.028	102	0.022	0.031	71**
NH4 (mg N/L)	0.284	0.28	101	0.304	0.31	98
NO3 + NO2 (mg N/L)	0.0162	0.0152	107	0.0314	0.031	101
NO3 + NO2 (mg N/L)	0.71	0.735	97	0.836	0.861	97
PO4 (mg P/L)	0.0081	0.0093	87**	0.0101	0.0089	113**
PO4 (mg P/L)	0.0266	0.0279	95	0.0326	0.0335	97
Particulate C (mg C/L)	1.995			1.758		
Particulate N (mg N/L)	0.402			0.274		
DOC (mg C/L)				2.91	2.5	116
DOC (mg C/L)				4.92	4.6	107

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

UMCES Chesapeake Biological Laboratory

Parameter	Summer 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.309	0.300	103	0.300	0.277	108
TDN (mg N/L)	0.941	0.959	98	1.067	1.108	96
TDP (mg P/L)	0.0186	0.0168	111**	0.0233	0.021	111**
TDP (mg P/L)	0.0473	0.0432	109	0.0601	0.0557	108
NH4 (mg N/L)	0.028	0.028	100	0.023	0.031	74**
NH4 (mg N/L)	0.269	0.28	96	0.305	0.31	98
NO3 + NO2 (mg N/L)	0.016	0.0152	105	0.0303	0.031	98
NO3 + NO2 (mg N/L)	0.759	0.735	103	0.841	0.861	98
PO4 (mg P/L)	0.0094	0.0093	101	0.0082	0.0089	92
PO4 (mg P/L)	0.0277	0.0279	99	0.0338	0.0335	101
Particulate C (mg C/L)	1.96			1.78		
Particulate N (mg N/L)	0.397			0.271		
Particulate P (mg P/L)	0.0404			0.0198		
Chlorophyll (μg/L)	11.9			21.3		
DOC (mg C/L)	3.04	3.0	101	2.81	2.5	112
DOC (mg C/L)	4.56	5.0	91	4.93	4.6	107
Total Suspended Solids (mg/L)	38.6	42.2	91	15.2	17.8	85

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

UMCES Chesapeake Biological Laboratory, Siefert Group

Parameter	Summer 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
NH4 (mg N/L)	0.0271	0.028	97	0.0285	0.031	92
NH4 (mg N/L)	0.288	0.28	103	0.397 WARN	0.31	128
NO3 + NO2 (mg N/L) (by IC)				0.030	0.031	97
NO3 + NO2 (mg N/L) (by IC)				0.825	0.861	96
PO4 (mg P/L) (by IC)				0.0088	0.0089	99
PO4 (mg P/L) (by IC)				0.027	0.0335	81

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

USDA, ARS, Animal Manure and By-Products Laboratory

Parameter	Summer 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
NH4 (mg N/L)	0.030	0.028	107	0.037	0.031	119**
NH4 (mg N/L)	0.292	0.28	104	0.338	0.31	109
NO3 + NO2 (mg N/L)	0.022	0.0152	145**	0.027	0.031	87**
NO3 + NO2 (mg N/L)	0.715	0.735	97	0.838	0.861	97

MD DHMH Division of Environmental Chemistry Nutrients Laboratory

Parameter	Summer 2003 Reported	Summer 2003 Prepared	% Recovered	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
NH4 (mg N/L)	0.027	0.028	96	0.030	0.031	97
NH4 (mg N/L)	0.275	0.28	98	0.290	0.31	94
NO3 + NO2 (mg N/L)	0 .017	0.0152	112**	0.029	0.031	94
NO3 + NO2 (mg N/L)	0.72	0.735	98	0.866	0.861	101
PO4 (mg P/L)	0.0110	0.0093	118**	0.007	0.0089	79**
PO4 (mg P/L)	0.0250	0.0279	90	0.026	0.0335	78
Particulate C (mg C/L)	1.925			1.68		
Particulate N (mg N/L)	0.395			0.27		
Chlorophyll (μg/L)	9.3			16.2		
DOC (mg C/L)	3.1	3.0	103	2.88	2.5	115
DOC (mg C/L)	5.1	5.0	102	4.8	4.6	104
Total Suspended Solids (mg/L)	40.2	42.2	95	16.2	17.8	91

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

USGS, National Water Quality Laboratory

Parameter	Summer 2003 Reported	Summer 2003 Prepared	% Recovered
TDN (mg N/L)	0.289	0.300	96
TDN (mg N/L)	0.953	0.959	99
TDP (mg P/L)	0.016	0.0168	95
TDP (mg P/L)	0.042	0.0432	97
NH4 (mg N/L)	0.023	0.028	82**
NH4 (mg N/L)	0.272	0.28	97
NO3 + NO2 (mg N/L)	0.014	0.0152	92
NO3 + NO2 (mg N/L)	0.721	0.735	98
PO4 (mg P/L)	0.011	0.0093	118**
PO4 (mg P/L)	0.027	0.0279	97
Particulate C (mg C/L)	1.861		
Particulate N (mg N/L)	0.387		
Particulate P (mg P/L)	0.039		
Chlorophyll (μg/L)	8.1		
DOC (mg C/L)	2.989	3.0	100
DOC (mg C/L)	4.999	5.0	100
Total Suspended Solids (mg/L)	41.2	42.2	98

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

MWRA WATER QUALITY LABORATORY

Parameter	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.279	0.277	101
TDN (mg N/L)	1.14	1.108	103
TDP (mg P/L)	0.0244	0.021	116**
TDP (mg P/L)	0.0641	0.0557	115
NH4 (mg N/L)	0.0277	0.031	89**
NH4 (mg N/L)	0.321	0.31	104
NO3 + NO2 (mg N/L)	0.0305	0.031	98
NO3 + NO2 (mg N/L)	0.825	0.861	96
PO4 (mg P/L)	0.00943	0.0089	106
PO4 (mg P/L)	0.0322	0.0335	96
Particulate C (mg C/L)	1.77		
Particulate N (mg N/L)	0.264		
Particulate P (mg P/L)	0.0202		
Chlorophyll (μg/L)	19.6		
DOC	2.63	2.5	105
DOC	4.7	4.6	102
Total Suspended Solids (mg/L)	12.5	17.8	70

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

PADEP WATER QUALITY LABORATORY

Parameter	Winter 2004 Reported	Winter 2004 Prepared	% Recovered
TDN (mg N/L)	0.28	0.277	101
TDN (mg N/L)	0.92 WARN	1.108	83
TDP (mg P/L)	0.024	0.021	114**
TDP (mg P/L)	0.057	0.0557	102
NH4 (mg N/L)	0.02	0.031	65**
NH4 (mg N/L)	0.29	0.31	94
NO3 + NO2 (mg N/L)	0.04 WARN	0.031	129**
NO3 + NO2 (mg N/L)	0.8	0.861	93
PO4 (mg P/L)	0.012	0.0089	135**
PO4 (mg P/L)	0.037	0.0335	110
Total Suspended Solids (mg/L)	15	17.8	84

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

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