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FINAL REPORT

CHESAPEAKE BAY PROGRAM BLIND AUDIT

Fiscal Year 2012 Final Report

PREPARED FOR:

Maryland Department of Natural Resources Resource Assessment Administration Water and Habitat Quality Program Annapolis, MD 21401

SUBMITTED BY:

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INTRODUCTION

The purpose of this Blind Audit Program is to provide samples of specific nutrient analytes at concentrations commonly found in estuarine systems for analysis by laboratories that analyze water samples collected from the Chesapeake Bay and its tributaries. The concentrations of these samples, which are unknown to the recipient analysts, are compared to their prepared concentrations.

In the early years of the Chesapeake Bay Program, U.S. EPA provided blind audit samples on an irregular basis to laboratories analyzing Chesapeake Bay water samples. However, these audit samples were designed for waste water/drinking water applications rather than for estuarine water applications. Consequently, the concentrations were much higher than normally occur in the Bay and did not provide a reasonable estimate of accuracy for low level nutrient concentrations. For example, a blind audit concentration of 1.0 mg NH4-N/L would be comparable to NPDES water samples, but would be at least an order of magnitude greater than concentrations normally occurring in most parts of Chesapeake Bay.

The only continuous program providing an estimate of laboratory performance has been the Chesapeake Bay Coordinated Split Sample Program (CSSP). Data generated from this program provide the only long term QA/QC data base to compare nutrient measurements provided by laboratories analyzing water samples collected from Chesapeake Bay and its tributaries. Samples for CSSP are natural water samples collected from Chesapeake Bay or a tributary. Briefly, a common unfiltered water sample is distributed to the various field/laboratory personnel who, in turn, subsample into dissolved and particulate fractions. These are analyzed and the results compared to those of other participating laboratories. Resulting data analysis can show how field filtration techniques and/or laboratory practices affect data variability. CSSP samples are each subject to cumulative errors of analytical determinations from variation in both field and laboratory procedures. Also, these data sets cannot definitively determine the accuracy of laboratory analyses.

The current Blind Audit Program has been designed to complement the CSSP. Blind Audit particulate samples distributed to participants have few cumulative errors associated with field filtering and subsampling procedures. Prepared concentrates of dissolved substances, whose concentrations are unknown to the analysts, are provided so that laboratory accuracy can be assessed.

This is the fourteenth year of the Blind Audit Program and it is the continued intent of this program to provide unknown, low level dissolved and particulate nutrient samples to laboratories analyzing Chesapeake Bay Program nutrients, as well as to other laboratories interested in participating in the Blind Audit Program.

MATERIALS AND METHODS

Blind Audit samples were sent to participating laboratories on 22 August 2011 and 20 February 2012. 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 of higher level total dissolved nitrogen and 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 population samples onto 47 mm GF/F filter pads. Replicate pads were provided to participating laboratories.

Total suspended solids blind audits were prepared as follows: 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 2011 and winter 2012 audit are found at the end of the report. Shortly after the completion of the study, a brief data report, including the concentrations of the prepared samples, was sent to each participant for them to check their data. These data reviews served as a final check of data before preparing this final report.

Concentrations were assessed statistically by calculating the mean and standard deviation of each sample set, then calculating how many standard deviations separated each laboratory's reported concentration from that mean (Table 2). The percent recovery of each laboratory's reported concentration relative to the prepared concentration was also calculated for the dissolved analytes (Table 3 and Appendix 1).

DISSOLVED FRACTION

<u>Total Dissolved Nitrogen:</u> Results from the summer 2011 and winter 2012 were excellent. Low and high reported concentrations had mean values that closely reflected the prepared concentrations. For example, both low and high concentrations of total dissolved N for winter 2012 were extremely close to the prepared concentrations (prepared low: 0.24 mg N/L with a mean concentrations of 0.2404 mg N/L; prepared high 0.568 mg N/L with a mean concentration of 0.5625 mg N/L. Coefficients of variation were 10.3% and 8.9%, respectively).

<u>Total Dissolved Phosphorus:</u> Results for both summer 2011 and winter 2012 samples were consistently good. Low and high mean concentrations for the summer results closely approximated the prepared values and while the coefficient of variation for the winter 2012 low level sample was 17%, the coefficient of variation for the winter 2012 high concentration was 6.4%

<u>Ammonium</u>: Analysis of low level samples for summer 2011 provided a mean concentration of 0.035 mg N/L compared to the prepared concentration of 0.038 mg N/L. Variation around that mean resulted in a coefficient of variation of 15.7%. Low level winter 2012 results were not as good, particularly since one laboratory reported a result nearly an order of magnitude greater than the expected concentration. The resulting coefficient of variation was 76.3%, while the overall mean concentration was 0.0349 mg N/L compared to the prepared concentration of 0.034 mg N/L. Results for both summer and winter high level concentrations were in close agreement with prepared concentrations and coefficients of variation of less than 10% were obtained.

<u>Nitrate + Nitrite:</u> Particularly good agreement was found among the laboratories for low and high concentrations for both summer 2011 and winter 2012 audits. Mean concentrations closely approximated prepared concentrations and low standard deviations provided percent coefficients of variation of less than 10%.

<u>Orthophosphate:</u> Low level concentrations for summer 2011 and winter 2012 were extremely variable. For example, the mean concentration for summer 2011 was twice as high as the prepared concentration with only 1-2 labs reporting results that approached the prepared concentration. Results of the high level concentrations were extremely good. The mean concentrations were almost identical to the prepared values and the percent coefficients of variation were less than 10% in both summer and winter audits.

<u>Dissolved Organic Carbon</u>: Concentration ranges for both audits ranged from 1.5 to 4.6 mg C/L. Percent coefficients of variation for the low concentration were 10.5% and 11.8% and high concentration percent coefficients of variation of 3.8% and 5.8% for summer and winter, respectively. For these two rounds, most laboratories reported results that were very close to the prepared concentrations.

PARTICULATE FRACTION

Again, it should be noted that particulate carbon, nitrogen and phosphorus samples were filtered from a common estuarine water sample and, consequently, are not true blind audit samples

produced from pure constituents. Particulate results are graphically presented in Figures 1 and 5.

<u>Particulate Carbon:</u> Among laboratory agreement was very close for the summer 2011 audit with a coefficient of variation of 8%. The winter results were not as close. A coefficient of variation of 23% was determined, due largely to one laboratory's low reported concentration (Table 2).

<u>Particulate Nitrogen:</u> Results for particulate nitrogen followed the same pattern as particulate C. The coefficient of variation for the summer was 5.8% but the coefficient of variation for the winter 2012 was 27%, largely due to one laboratory's low reported concentration.

<u>Particulate Phosphorus:</u> Particulate phosphorus concentrations showed remarkably close agreement between all participating laboratories (coefficient of variation of 10%) for the summer audit. The winter results were more variable and a coefficient of variation of 23% was determined. One laboratory reported a result approximately 40-50% greater than the other laboratories.

<u>Chlorophyll:</u> Most of the chlorophyll *a* results for the summer 2011 audit displayed the usual close agreement that was remarkable for multi-laboratory comparison of low concentrations of an environmentally transitory compound, with the exception of one laboratory that reported a concentration an order of magnitude less. Winter 2012 results showed close agreement among participating laboratories (mean value: 11.6 ug/L; standard deviation: 2.16, with a resulting coefficient of variation of 18.6%.

<u>Total Suspended Solids:</u> 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 2011 sample, 17.0 mg/L was prepared, and there was a consistent slight negative bias reported by all participants. One laboratory reported a concentration that was nearly half than that reported by the other laboratories. For the winter 2012 sample, 12.0 mg/L was prepared but, there was, again, a consistent negative bias reported by all participants. The same laboratory that reported low results for the summer audit reported low results for the winter audit, with approximately the same margin of difference.

DISCUSSION

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

<u>Variation Associated With An Analytical Method:</u> 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. <u>Any</u> 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%.

<u>Acceptance Limits of Provided Dissolved Samples:</u> 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% Cl of 2.47-3.42 mg P/L. The lower end of the 95% Cl 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 values, that at least one value will lie just beyond one standard deviations, all the reported concentrations "passed." It should also be noted that approximately the same number were in the "warning" category as in most of the previous studies, and that only four values in the entire study fell in the "fail" category.

Data sets with relatively small standard deviations yielded more potentially extraneous "warning" points. For example, in the winter 2012 blind audit of high level nitrate + nitrite concentration, the mean reported (and prepared!) concentration was 0.868 mg N/L and reported concentrations ranged from 0.82-0.9319 mg N/L. The coefficient of variation was ONLY 3.4%! Twelve laboratories reported results for this high level sample that were within two standard deviations (S.D. \pm 0.0292 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 was labeled "warn." Thus, by that measure of accuracy, most of the data "passed" and one was "warned." This nitrate + nitrite 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. <u>All</u> of the reported data were within $\pm7\%$ of the prepared concentration!

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 $\pm 10\%$ 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 "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, for summer 2011 blind audit of 0.0022 mg P/L prepared for orthophosphate has a "pass" category (\pm 10%) of only 0.0020 - 0.0024 mg P/L. For the summer 2011 blind audit, nine out of ten participating laboratories reported results that fell in the "fail" category, indicating that their reported concentrations were greater than \pm 20% of the prepared concentration in this low range. These results could be interpreted as an inability for all participants to accurately measure low level orthophosphate from concentrates provided to

them. It would be important to know if there is also a difficulty in measuring natural low level samples. An alternative interpretation would be that it may be appropriate to broaden the acceptance boundaries for very low concentrations of prepared samples. There was also a broad range in percentage recovery of low level orthophosphate reported values in past audits; however, when comparing with other participants, the coefficient of variation remains remarkably small. For example, summer 2011 reported data based on comparisons with other participants was mean 0.0043, S.D. 0.0014, C.V. 33%.

There was considerable divergence between participants for the winter 2012 low level ammonium sample. One participant's reported winter 2012 low level concentration was about four times higher than the other reported values and the prepared concentration. For all past blind audits, the standard deviations for the low level ammonium samples were less than those for the higher level ammonium samples; however, that was not the case for the winter 2012 low level ammonium blind audit. The proportions of the standard deviations to the means for the low level ammonium samples were larger than they have been for the last few years. For the winter 2012 audit, the coefficient of variation for 0.034 mg NH4-N/L was 76%. The coefficient of variation was 16% for 0.042 mg NH4-N/L (Summer 2006) and 39% for 0.036 mg NH4-N/L (Winter 2007). This indicates that inter-laboratory comparisons of any ammonium data prepared by laboratories from concentrates below 0.042 mg N/L are probably somewhat unreliable.

There were fifteen instances where concentrations reported for dissolved constituents or total suspended solids fell in the "warn" or "fail" category based on the standard deviation of all participants' reported concentrations and also in the "warn" or "fail" category based on percent recovery. These are listed for the individual laboratories in Appendix 1.

<u>Acceptance Limits of Provided Particulate Samples</u>: 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. The standard deviation was less than 10% of the mean reported concentrations for particulate carbon, nitrogen and phosphorus for the summer 2011 audit. The standard deviation was 23 to 27% of the mean reported concentration for particulate carbon, nitrogen and phosphorus for particulate carbon and nitrogen, one laboratory's reported concentrations were about 25% of the mean of the other participants' data for the winter 2012 audit. For particulate phosphorus, another laboratory's reported concentration was about double that of the mean of the other participants' data for the winter 2012 audit.

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 2007 was approximately 2.35 mg C/L.

<u>Reporting Data Accurately:</u> Most data originally reported by all participants for both these blind audits appeared, on casual inspection, to be reported accurately. A few of the results for both these blind audits were miscalculated (and later corrected), or had "slipped a decimal" or exhibited some other obvious entry error that could have been easily avoided. As in past years, contacting the participants resolved these reporting discrepancies, but has not always improved their subsequent reporting practices. Other subtle entry or calculation errors may have gone undetected.

The summer 2007 and winter 2008 audits were the only pair of audits in which no participant noted any discrepancies when all were contacted to review their data. No results were miscalculated (and later corrected), or had "slipped a decimal" or exhibited some other obvious entry error that could have been easily avoided. After years of reporting "difficulties," participants had improved their reporting practices! Sadly, this improvement in reporting did not extend to the summer 2008 through summer 2010 audits. At last, for the winter 2011 audit, no participant noted any discrepancies when all were contacted to review their data. We had returned to that great condition where no results were miscalculated (and later corrected), or had "slipped a decimal" or exhibited some other obvious entry error that could have been easily avoided. Sadly, for the summer 2011 blind audit, results were AGAIN (!) reported and then later corrected. Results that had been entered on the wrong parts of the results form were noted as "FAIL," but the corrected data were used for statistical comparisons. Happily, for the winter 2012 audit, no participant noted any discrepancies when all were contacted to review their data.

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 through winter 2012 participants reported only two significant digits for some analytes, thus potentially giving substantial under or over estimates for the comparisons.

CONCLUSION

Now that twenty nine 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 particulate analytes have usually been similar between laboratories participating in the Blind Audit Program. For the summer 2011 audit, with the exception of chlorophyll *a*, no laboratory reported concentrations for individual analytes that were widely different from the range of the other reported concentrations. For the winter 2012 audit, one (usually different) laboratory reported concentrations of particulate carbon, nitrogen, phosphorus or total suspended solids; that were widely different from the range of the other reported concentrating laboratories usually execute and report these measurements with accuracy and precision, reporting the appropriate number of significant digits.

2. Reported concentrations of dissolved analytes were usually similar between laboratories participating in the Blind Audit Program. No laboratory reported concentrations for individual analytes that were widely different from the range of the other reported concentrations for <u>both</u> blind audits. This indicates that most participating laboratories usually execute and report these measurements with accuracy and precision, reporting the appropriate number of significant digits.

3. When comparing reported concentrations to those prepared, the lower concentration ranges had more data that fell beyond $\pm 10\%$ 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, orthophosphate and total dissolved phosphorus. 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.

4. The variation in reported concentrations of low level ammonium for both these blind audits, and several previous audits, probably indicates that inter-laboratory comparisons of any

ammonium data prepared from concentrates with resultant concentrations below 0.042 mg N/L would be unreliable. It would be important to know if there is also difficulty in measuring natural low level samples.

5. For all but one of the participating laboratories, there was remarkable consistency between participating laboratories in the measurement of total suspended solids from suspensions of infusorial earth; however, there was consistent, slight negative bias in the measurements, when compared to the prepared concentrations. This slight negative bias occurred in all past years as well.

6. The proportion of the standard deviation to the mean was small for particulate phosphorus for the winter 2003 through winter 2008 blind audits, so inter-laboratory comparison of particulate phosphorus data should have been valid. The proportion of the standard deviation to the mean was higher for particulate phosphorus in the blind audits of summer 2008 through winter 2010 and, again, in winter 2012. This contrasted to all the previous years, in which the coefficient of variation for particulate phosphorus was usually the lowest of the particulate fractions. For the three audits of summer 2010 through summer 2011, the proportion of the standard deviation to the mean was small for particulate phosphorus. Therefore, inter-laboratory comparison of particulate phosphorus data usually should be valid.

7. The proportions of the standard deviation to the means for particulate carbon and nitrogen were higher for the winter 2012 blind audit than for most previous audits. For particulate carbon and nitrogen, one laboratory's reported concentrations were about 25% of the mean of the other participants' data for the winter 2012 audit. The proportion of the standard deviation to the mean was in its usual range for all participants for the summer 2011 blind audit.

8. Care should continue to be taken when completing report forms. For the summer 2011 and winter 2012 blind audits, some results were AGAIN (!) reported with insufficient significant digits. For the summer 2011 blind audit, results were AGAIN (!) reported and then later corrected. For the winter 2012 blind audit, no results were reported and subsequently corrected. Results that had been entered on the wrong parts of the results form were noted as "FAIL," but the corrected data were used for statistical comparisons. Over the course of the years, a few laboratories repeatedly have made calculation or entry errors that were later corrected. It is hoped that corrections of these lapses serve as reminders of the importance to continuously check many aspects of data management to ensure overall data quality.

| Institution | Contact Person | Phone | Dissolved | Particulate | Chlorophyll a | DOC | TSS |
|-------------------------------|------------------|--------------|-----------|-------------|---------------|-----|-----|
| Old Dominion University, | · | | | | | | |
| Water Quality Lab, (ODU) | Suzanne Doughton | 757-451-3043 | Х | Х | Х | Х | Х |
| University of MD, Horn | | | | | | | |
| Point Laboratory (HPL) | Jennifer O'Keefe | 410-221-8276 | Х | Х | Х | Х | Х |
| Virginia Institute of Marine | | | | | | | |
| Science (VIMS) | Carol Pollard | 804-684-7213 | Х | Part P only | Х | | Х |
| Virginia Div, Consolidated | | 804-648-4480 | | | | | |
| Lab Services (DCLS) | Jay Armstrong | x328 | Х | Х | Х | Х | Х |
| MD Dept Health and | | | | | | | |
| Mental Hygiene (DHMH) | Shala Ameli | 410-767-6190 | Х | Х | Х | Х | Х |
| Univ. of MD Chesapeake | | | | | | | |
| Bio Lab (CBL) | Carl Zimmermann | 410-326-7252 | Х | Х | Х | Х | Х |
| Delaware Dept. of Natural | | | | | | | |
| Resources (DNREC) | Ben Pressly | 302-739-9942 | Х | Х | Х | Х | Х |
| Academy of Natural | | | | | | | |
| Science of Philadelphia | Paul Kiry | 215-299-1076 | Х | Х | Х | | Х |
| (PAACAD) | - | | | | | | |
| PA DEP, Bureau of | | | | | | | |
| Laboratories (PADEP) | James Yoder | 717-346-8232 | Х | | | Х | Х |
| MWRA, Water Quality | | | | | | | |
| Laboratory (MWRA) | Jennifer Prasse | 617-660-7808 | Х | Х | Х | | Х |
| Hampton Roads Sanitation | | | | | | | |
| District (HRSD) | Stacie Metzler | 757-460-4217 | Х | | | Х | Х |
| Occoquan Watershed | | 703-361-5606 | | | | | |
| Monitoring Lab (OCC) | Dongmei Wang | x118 | Х | | Х | Х | Х |
| U of Connecticut Center | <u> </u> | | | | | | |
| for Environmental Sci. & | Chris Perkins | 860-486-2668 | Х | Х | Х | Х | Х |
| Engineering (UCONN) | | | | | | | |

Table 1. Participants in the Summer 2011 and Winter 2012 Blind Audit Program.

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Summer 2011 and the Winter 2012 Blind Audit, Including Distribution of Reported Concentrations from the Mean.

| Parameter | Concentration in mg/L | | N | Number of Laboratories | | | |
|----------------------------|-----------------------|--------|------|------------------------|--------------|------|--|
| | | | Stan | dard Deviat | tions from M | ean | |
| | | | <1 | 1-2 | 2-3 | >3 | |
| | Mean | S.D. | PASS | PASS | WARN | FAIL | |
| Summer 2011 | | | | | | | |
| Total Dissolved Nitrogen | 0.283 | 0.0374 | 9 | 1 | 1 | | |
| Total Dissolved Nitrogen | 0.976 | 0.0554 | 9 | 3 | 1 | | |
| Total Dissolved Phosphorus | 0.0110 | 0.0014 | 7 | 4 | | | |
| Total Dissolved Phosphorus | 0.0394 | 0.0021 | 9 | 4 | | | |
| Ammonium | 0.0351 | 0.0055 | 9 | 1 | 1 | | |
| Ammonium | 0.210 | 0.0097 | 9 | 4 | | | |
| Nitrate + Nitrite | 0.0593 | 0.0026 | 9 | 1 | 1 | | |
| Nitrate + Nitrite | 0.942 | 0.0489 | 11 | | 2 | | |
| Orthophosphate | 0.0043 | 0.0014 | 7 | 3 | | | |
| Orthophosphate | 0.0518 | 0.0028 | 8 | 5 | | | |
| Dissolved Organic Carbon | 1.77 | 0.187 | 7 | 2 | 1 | | |
| Dissolved Organic Carbon | 4.78 | 0.181 | 6 | 3 | | 1 | |
| Particulate Carbon | 2.02 | 0.17 | 6 | 3 | | | |
| Particulate Nitrogen | 0.330 | 0.0157 | 6 | 3 | | | |
| Particulate Phosphorus | 0.0316 | 0.0032 | 7 | 3 | | | |
| Total Suspended Solids | 16.0 | 0.86 | 10 | 1 | 1 | 1 | |
| Winter 2012 | | | | | | | |
| Total Dissolved Nitrogen | 0.240 | 0.0247 | 8 | 2 | 1 | | |
| Total Dissolved Nitrogen | 0.562 | 0.0506 | 10 | 2 | 1 | | |
| Total Dissolved Phosphorus | 0.0124 | 0.0021 | 8 | 3 | | | |
| Total Dissolved Phosphorus | 0.0373 | 0.0024 | 8 | 5 | | | |
| Ammonium | 0.0349 | 0.0267 | 10 | | 1 | | |
| Ammonium | 0.151 | 0.0141 | 11 | 1 | 1 | | |
| Nitrate + Nitrite | 0.0347 | 0.0028 | 9 | 1 | 1 | | |
| Nitrate + Nitrite | 0.868 | 0.0292 | 9 | 3 | 1 | | |
| Orthophosphate | 0.0047 | 0.0017 | 8 | 3 | | | |
| Orthophosphate | 0.0473 | 0.0021 | 10 | 2 | 1 | | |
| Dissolved Organic Carbon | 1.56 | 0.169 | 8 | 3 | | | |
| Dissolved Organic Carbon | 4.61 | 0.281 | 8 | 3 | | | |
| Particulate Carbon | 1.46 | 0.34 | 10 | | | 1 | |
| Particulate Nitrogen | 0.194 | 0.0518 | 9 | 1 | 1 | | |
| Particulate Phosphorus | 0.0197 | 0.0045 | 9 | | 1 | | |
| Total Suspended Solids | 10.7 | 1.83 | 12 | | | 1 | |

Table 3. Summary of Prepared and Reported Concentrations for Each Analyte and Percent Recovery of the Prepared Concentration by Participating Laboratories

| | | | | Number of Labo | ratories |
|----------------------------|-----------------------------------|--|--|--|---|
| Parameter | Prepared Concentration mg/L | Reported Concentration Range mg/L | Within 90% - 110% of Prepared Concentration | Within 80 -90%, or 110-120% of Prepared Concentration | <80%, or >120% of Prepared Concentration |
| | | | PASS | WARN | FAIL |
| Summer 2011 | | | | | |
| Total Dissolved Nitrogen | 0.27 | 0.25-0.3609 | 8 | 1 | 2 |
| Total Dissolved Nitrogen | 0.994 | 0.86-1.06 | 11 | 2 | |
| Total Dissolved Phosphorus | 0.0096 | 0.0088-0.0125 | 5 | 2 | 4 |
| Total Dissolved Phosphorus | 0.0384 | 0.0362-0.0434 | 11 | 1 | 1 |
| Ammonium | 0.038** | 0.03-0.044 | 5 | 4 | 2 |
| Ammonium | 0.21 | 0.191-0.2193 | 12 | 1 | |
| Nitrate + Nitrite | 0.056 | 0.0547-0.0648 | 9 | 2 | |
| Nitrate + Nitrite | 0.98 | 0.84-1.062 | 12 | 1 | |
| Orthophosphate | 0.0022** | 0.0026-0.005 | | 1 | 9 |
| Orthophosphate | 0.0481 | 0.047-0.0553 | 9 | 4 | |
| Dissolved Organic Carbon | 1.60 | 1.575-2.16 | 6 | 2 | 2 |
| Dissolved Organic Carbon | 4.60 | 4.584-6.55 | 9 | | 1 |
| Total Suspended Solids | 17.0 | 11-16.5 | 10 | 2 | 1 |
| Winter 2012 | | | | | |
| Total Dissolved Nitrogen | 0.24 | 0.213-0.3038 | 8 | 2 | 1 |
| Total Dissolved Nitrogen | 0.568 | 0.50-0.70 | 10 | 2 | 1 |
| Total Dissolved Phosphorus | 0.0115 | 0.0098-0.0145 | 4 | 4 | 3 |
| Total Dissolved Phosphorus | 0.0365 | 0.0340.0405 | 11 | 1 | |
| Ammonium | 0.034** | 0.02-0.032 | 3 | 4 | 4 |
| Ammonium | 0.147 | 0.1355-0.19 | 12 | | 1 |
| Nitrate + Nitrite | 0.035 | 0.029-0.04 | 9 | 2 | |
| Nitrate + Nitrite | 0.868 | 0.82-0.9319 | 13 | | |
| Orthophosphate | 0.0037** | 0.0033-0.008 | 2 | 3 | 6 |
| Orthophosphate | 0.0474 | 0.0423-0.05 | 12 | 1 | |
| Dissolved Organic Carbon | 1.50 | 1.325-1.88 | 8 | 1 | 2 |
| Dissolved Organic Carbon | 4.60 | 4.21-5.03 | 10 | 1 | |
| Total Suspended Solids | 12.0 | 5.0-12.0 | 9 | 3 | 1 |

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

Appendix 1. Summer 2011 and Winter 2012

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 2011 | Summer 2011 | Summer 2011 | Winter 2012 | Winter 2012 | Winter 2012 |
|-------------------------|----------------|----------------|-------------|----------------|----------------|----------------|
| | Prepared | Reported | % Recovered | Prepared | Reported | % |
| | 0.07 | 0 0000** | 400 7 | 0.04 | 0.0550 | Recovered |
| TDN (mg N/L) | 0.27 | 0.3609** | 133.7 | 0.24 | 0.2558 | 106.6 |
| TDN (mg N/L) | 0.994 | 0.995 | 100.1 | 0.568 | 0.5993 | 105.5 |
| TDP (mg P/L) | 0.0096 | 0.0114 | 118.7 | 0.0115 | 0.0138 | 120.0 |
| TDP (mg P/L) | 0.0384 | 0.0434 | 113.0 | 0.0365 | 0.035 | 95.9 |
| NH4 (mg N/L) | 0.038 | 0.0331 | 87.1 | 0.034 | 0.0234 | 68.8 |
| NH4 (mg N/L) | 0.21 | 0.2193 | 104.4 | 0.147 | 0.1415 | 96.2 |
| NO3+NO2 (mg N/L) | 0.056 | 0.0581 | 103.7 | 0.035 | 0.0347 | 99.1 |
| NO3+NO2 (mg N/L) | 0.98 | 0.937 | 95.6 | 0.868 | 0.904 | 104.1 |
| PO4 (mg P/L) | 0.0022 | 0.0041 | 186.4 | 0.0037 | 0.0019 | 51.3 |
| PO4 (mg P/L) | 0.0481 | 0.0536 | 111.4 | 0.0474 | 0.0448 | 94.5 |
| Part. C (mg C/L) | | | | | 1.669 | |
| Part. N (mg N/L) | | | | | 0.2105 | |
| Part. P (mg P/L) | | 0.0373 | | | 0.0318** | |
| DOC (mg C/L) | 1.60 | | | 1.50 | | |
| DOC (mg C/L) | 4.60 | | | 4.60 | | |
| Chlorophyll (µg/L) | | 10.04 | | | 9.03 | |
| Total Susp. S (mg/L) | 17.0 | 16.5 | 97.0 | 12.0 | 11.2 | 93.3 |

**WARN based on Standard Deviation of all participants' reported concentration.

Old Dominion University WQL

| Parameter | Summer | Summer | Summer 2011 | Winter | Winter | Winter |
|-------------------------|------------------|------------------|--------------|------------------|------------------|-----------------|
| | 2011 Prepared | 2011 Reported | % Recovered | 2012 Prepared | 2012 Reported | 2012 % |
| | Fiepaieu | Reported | 70 Recovered | Fiepaleu | Reported | 70 Recovered |
| TDN (mg N/L) | 0.27 | 0.264 | 97.8 | 0.24 | 0.242 | 100.8 |
| TDN (mg N/L) | 0.994 | 0.992 | 99.8 | 0.568 | 0.543 | 95.6 |
| TDP (mg P/L) | 0.0096 | 0.0114 | 118.7 | 0.0115 | 0.0113 | 98.3 |
| TDP (mg P/L) | 0.0384 | 0.0413 | 107.6 | 0.0365 | 0.0354 | 97.0 |
| NH4 (mg N/L) | 0.038 | 0.0369 | 97.1 | 0.034 | 0.0237 | 69.7 |
| NH4 (mg N/L) | 0.21 | 0.2123 | 101.1 | 0.147 | 0.1478 | 100.5 |
| NO3+NO2 (mg | 0.056 | 0.0596 | 106.4 | 0.035 | 0.0342 | 97.7 |
| N/L) | 0.00 | 0.0504 | 00.0 | 0.000 | 0.0004 | <u> </u> |
| NO3+NO2 (mg N/L) | 0.98 | 0.9501 | 96.9 | 0.868 | 0.8621 | 99.3 |
| PO4 (mg P/L) | 0.0022 | 0.0026 | 118.2 | 0.0037 | 0.0049 | 132.4 |
| PO4 (mg P/L) | 0.0481 | 0.0536 | 111.4 | 0.0474 | 0.0473 | 99.8 |
| Part. C (mg C/L) | | 2.266 | | | 1.47 | |
| Part. N (mg N/L) | | 0.349 | | | 0.1895 | |
| Part. P (mg P/L) | | 0.0277 | | | 0.0188 | |
| DOC (mg C/L) | 1.60 | 1.575 | 98.4 | 1.50 | 1.325 | 88.3 |
| DOC (mg C/L) | 4.60 | 4.584 | 99.6 | 4.60 | 4.396 | 95.6 |
| Chlorophyll (µg/L) | | 15.49 | | | 11.37 | |
| Total Susp. S (mg/L) | 17.0 | 15.71 | 92.4 | 12.0 | 11.54 | 96.2 |
| | | | | | | |

| Parameter | Summer | Summer | Summer 2011 | Winter | Winter | Winter |
|-------------------------|------------------|------------------|---------------|------------------|------------------|-----------|
| | 2011 Prepared | 2011 Reported | % Recovered | 2012 Prepared | 2012 Reported | 2012 % |
| | ricparea | Reported | 70 1100000100 | ricparca | Reported | Recovered |
| TDN (mg N/L) | 0.27 | 0.25 | 92.6 | 0.24 | 0.214 | 89.2 |
| TDN (mg N/L) | 0.994 | 0.88 | 88.5 | 0.568 | 0.51 | 89.8 |
| TDP (mg P/L) | 0.0096 | 0.01** | 104.2 | 0.0115 | 0.01 | 87.0 |
| TDP (mg P/L) | 0.0384 | 0.04** | 104.2 | 0.0365 | 0.04 | 109.6 |
| NH4 (mg N/L) | 0.038 | 0.04 | 105.3 | 0.034 | 0.03 | 88.2 |
| NH4 (mg N/L) | 0.21 | 0.22 | 104.7 | 0.147 | 0.16 | 108.8 |
| NO3+NO2 (mg N/L) | 0.056 | 0.05 | 89.3 | 0.035 | 0.04 | 114.3 |
| NO3+NO2 (mg N/L) | 0.98 | 0.92 | 93.9 | 0.868 | 0.87 | 100.2 |
| PO4 (mg P/L) | 0.0022 | | | 0.0037 | 0.008 | 216.2 |
| PO4 (mg P/L) | 0.0481 | 0.049 | 101.9 | 0.0474 | 0.05 | 105.5 |
| Part. C (mg C/L) | | | | | 1.55 | |
| Part. N (mg N/L) | | | | | 0.276 | |
| Part. P (mg P/L) | | | | | | |
| DOC (mg C/L) | 1.60 | 1.60 | 100.0 | 1.50 | 1.5 | 100.0 |
| DOC (mg C/L) | 4.60 | 4.60 | 100.0 | 4.60 | 4.5 | 97.8 |
| Chlorophyll (µg/L) | | 11.5 | | | | |
| Total Susp. S (mg/L) | 17.0 | 15.5 | 91.2 | 12.0 | 10.6 | 88.3 |

Virginia Tech Occoquan Watershed Monitoring Laboratory

(mg/L) **FAIL due to concentrations reported in improper positions on reporting form

Virginia Division of Consolidated Laboratory Services

| Parameter | Summer 2011 | Summer 2011 | Summer 2011 | Winter 2012 | Winter 2012 | Winter 2012 |
|-------------------------|----------------|----------------|-------------|----------------|----------------|----------------|
| | Prepared | Reported | % Recovered | Prepared | Reported | % Recovered |
| TDN (mg N/L) | 0.27 | 0.27 | 100.0 | 0.24 | 0.233 | 97.1 |
| TDN (mg N/L) | 0.994 | 0.953 | 95.9 | 0.568 | 0.5502 | 96.9 |
| TDP (mg P/L) | 0.0096 | 0.0104 | 108.3 | 0.0115 | 0.011 | 95.6 |
| TDP (mg P/L) | 0.0384 | 0.0365 | 95.1 | 0.0365 | 0.034 | 93.1 |
| NH4 (mg N/L) | 0.038 | 0.033 | 86.8 | 0.034 | 0.0264 | 77.6 |
| NH4 (mg N/L) | 0.21 | 0.181 | 86.2 | 0.147 | 0.1355 | 92.2 |
| NO3+NO2 (mg N/L) | 0.056 | 0.058 | 103.6 | 0.035 | 0.0337 | 96.3 |
| NO3+NO2 (mg N/L) | 0.98 | 0.94 | 95.9 | 0.868 | 0.8565 | 98.7 |
| PO4 (mg P/L) | 0.0022 | 0.0038 | 172.7 | 0.0037 | 0.0037 | 100.0 |
| PO4 (mg P/L) | 0.0481 | 0.05 | 103.9 | 0.0474 | 0.0454 | 98.8 |
| Part. C (mg C/L) | | 2.185 | | | 1.55 | |
| Part. N (mg N/L) | | 0.346 | | | 0.206 | |
| Part. P (mg P/L) | | 0.0304 | | | 0.0176 | |
| DOC (mg C/L) | 1.60 | 1.63 | 101.9 | 1.50 | 1.469 | 97.9 |
| DOC (mg C/L) | 4.60 | 4.62 | 100.4 | 4.60 | 4.526 | 98.4 |
| Chlorophyll (µg/L) | | 15.2 | | | 12.3 | |
| Total Susp. S (mg/L) | 17.0 | 16.0 | 94.1 | 12.0 | 12.0 | 100.0 |

| nampton Road. | ounnation | District | | | | |
|-------------------------|----------------|----------------|-------------|----------------|----------------|----------------|
| Parameter | Summer 2011 | Summer 2011 | Summer 2011 | Winter 2012 | Winter 2012 | Winter 2012 |
| | Prepared | Reported | % Recovered | Prepared | Reported | % |
| TDN (mg N/L) | 0.27 | | | 0.24 | | Recovered |
| TDN (mg N/L) | 0.994 | 0.86** | 86.5 | 0.568 | 0.5 | 88.0 |
| TDP (mg P/L) | 0.0096 | | | 0.0115 | | |
| TDP (mg P/L) | 0.0384 | 0.04 | 104.2 | 0.0365 | 0.04 | 109.6 |
| NH4 (mg N/L) | 0.038 | | | 0.034 | | |
| NH4 (mg N/L) | 0.21 | 0.22 | 104.8 | 0.147 | 0.16 | 108.8 |
| NO3+NO2 (mg N/L) | 0.056 | | | 0.035 | | |
| NO3+NO2 (mg N/L) | 0.98 | 0.95 | 96.9 | 0.868 | 0.84 | 96.8 |
| PO4 (mg P/L) | 0.0022 | | | 0.0037 | | |
| PO4 (mg P/L) | 0.0481 | | | 0.0474 | 0.048 | 101.3 |
| Part. C (mg C/L) | | | | | | |
| Part. N (mg N/L) | | | | | | |
| Part. P (mg P/L) | | | | | | |
| DOC (mg C/L) | 1.60 | 1.88 | 117.5 | 1.50 | 1.55 | 103.3 |
| DOC (mg C/L) | 4.60 | 4.84 | 105.2 | 4.60 | 4.81 | 104.6 |
| Chlorophyll (µg/L) | | | | | 8.9 | |
| Total Susp. S (mg/L) | 17.0 | 16.3 | 95.9 | 12.0 | 11.2 | 93.3 |

**WARN based on Standard Deviation of all participants' reported concentrations.

Delaware DNREC-Division of Water, Environmental Laboratory Section

| Delaware Diviki | | | | ory occure | | |
|-------------------------|----------------|----------------|-------------|----------------|----------------|----------------|
| Parameter | Summer 2011 | Summer 2011 | Summer 2011 | Winter 2012 | Winter 2012 | Winter 2012 |
| | Prepared | Reported | % Recovered | Prepared | Reported | % |
| | | | | | | Recovered |
| TDN (mg N/L) | 0.27 | 0.305 | 113.0 | 0.24 | 0.3038** | 140.8 |
| TDN (mg N/L) | 0.994 | 1.00 | 100.6 | 0.568 | 0.601 | 105.8 |
| TDP (mg P/L) | 0.0096 | 0.0132 | 137.5 | 0.0115 | 0.0138 | 120.0 |
| TDP (mg P/L) | 0.0384 | 0.0367 | 95.6 | 0.0365 | 0.0351 | 96.2 |
| NH4 (mg N/L) | 0.038 | 0.044 | 115.8 | 0.034 | 0.1147** | 337.5 |
| NH4 (mg N/L) | 0.21 | 0.202 | 96.2 | 0.147 | 0.1591 | 108.2 |
| NO3+NO2 (mg N/L) | 0.056 | 0.0612 | 109.3 | 0.035 | 0.0362 | 103.4 |
| NO3+NO2 (mg N/L) | 0.98 | 0.961 | 98.1 | 0.868 | 0.8373 | 96.5 |
| PO4 (mg P/L) | 0.0022 | 0.0065 | 295.4 | 0.0037 | 0.0059 | 159.5 |
| PO4 (mg P/L) | 0.0481 | 0.0541 | 112.5 | 0.0474 | 0.0493 | 104.0 |
| Part. C (mg C/L) | | 2.2 | | | 1.614 | |
| Part. N (mg N/L) | | 0.341 | | | 0.207 | |
| Part. P (mg P/L) | | 0.0311 | | | 0.02 | |
| DOC (mg C/L) | 1.60 | 2.09 | 130.6 | 1.50 | 1.88 | 125.3 |
| DOC (mg C/L) | 4.60 | 5.05 | 109.8 | 4.60 | 5.157 | 112.1 |
| Chlorophyll (µg/L) | | 16.1 | | | 12.35 | |
| Total Susp. S (mg/L) | 17.0 | 16.0 | 94.1 | 12.0 | 11.97 | 99.7 |

(mg/L) **WARN based on Standard Deviation of all participants' reported concentrations

| Parameter | Summer | Summer | Summer 2011 | Winter | Winter | Winter |
|-----------------------------|------------------|------------------|-------------|------------------|------------------|-----------|
| | 2011 Broporod | 2011 Beported | % Recovered | 2012 Droporod | 2012 Benerted | 2012 % |
| | Prepared | Reported | % Recovered | Prepared | Reported | Recovered |
| TDN (mg N/L) | 0.27 | 0.343 | 127.0 | 0.24 | 0.241 | 100.4 |
| TDN (mg N/L) | 0.994 | 1.06 | 106.6 | 0.568 | 0.552 | 97.2 |
| TDP (mg P/L) | 0.0096 | 0.012 | 125.0 | 0.0115 | 0.0107 | 93.0 |
| TDP (mg P/L) | 0.0384 | 0.038 | 99.0 | 0.0365 | 0.0349 | 96.0 |
| NH4 (mg N/L) | 0.038 | 0.0374 | 98.4 | 0.034 | 0.0292 | 85.9 |
| NH4 (mg N/L) | 0.21 | 0.22 | 104.8 | 0.147 | 0.148 | 100.7 |
| NO3+NO2 (mg | 0.056 | 0.0567 | 101.2 | 0.035 | 0.037 | 105.7 |
| N/L) NO3+NO2 (mg N/L) | 0.98 | 0.926 | 94.5 | 0.868 | 0.867 | 99.5 |
| PO4 (mg P/L) | 0.0022 | 0.0029 | 131.8 | 0.0037 | 0.00409 | 110.5 |
| PO4 (mg P/L) | 0.0481 | 0.0499 | 103.7 | 0.0474 | 0.0483 | 101.8 |
| Part. C (mg C/L) | | 1.77 | | | 0.447*** | |
| Part. N (mg N/L) | | 0.309 | | | 0.0556** | |
| Part. P (mg P/L) | | 0.0328 | | | 0.0156 | |
| DOC (mg C/L) | 1.60 | 2.16** | 135.0 | 1.50 | 1.46 | 97.3 |
| DOC (mg C/L) | 4.60 | 6.55*** | 142.4 | 4.60 | 4.21 | 91.5 |
| Chlorophyll (µg/L) | | 1.57 | | | 9.14 | |
| Total Susp. S (mg/L) | 17.0 | 14.7 | 86.5 | 12.0 | 10.05 | 83.7 |

Academy of Natural Sciences of Philadelphia

(mg/L) **WARN and ***FAIL based on Standard Deviation of all participants' reported concentrations

Pennsylvania DEP Laboratory

| Parameter | Summer | Summer | Summer 2011 | Winter | Winter | Winter |
|-----------------------------|----------|----------|-------------|----------|----------|-----------|
| 1 arameter | 2011 | 2011 | | 2012 | 2012 | 2012 |
| | Prepared | Reported | % Recovered | Prepared | Reported | % |
| TDN (mg N/L) | 0.27 | | | 0.24 | | Recovered |
| TDN (mg N/L) | 0.994 | 1.04 | 104.6 | 0.568 | 0.70** | 123.2 |
| TDP (mg P/L) | 0.0096 | | | 0.0115 | | |
| TDP (mg P/L) | 0.0384 | 0.041 | 106.8 | 0.0365 | 0.04 | 109.6 |
| NH4 (mg N/L) | 0.038 | | | 0.034 | | |
| NH4 (mg N/L) | 0.21 | 0.20 | 95.2 | 0.147 | 0.19** | 129.3 |
| NO3+NO2 (mg | 0.056 | | | 0.035 | | |
| N/L) NO3+NO2 (mg N/L) | 0.98 | 0.97 | 99.0 | 0.868 | 0.87 | 100.2 |
| PO4 (mg P/L) | 0.0022 | | | 0.0037 | | |
| PO4 (mg P/L) | 0.0481 | 0.047 | 97.7 | 0.0474 | 0.049 | 103.4 |
| Part. C (mg C/L) | | | | | | |
| Part. N (mg N/L) | | | | | | |
| Part. P (mg P/L) | | | | | | |
| DOC (mg C/L) | 1.60 | 1.63 | 101.9 | 1.50 | 1.54 | 102.7 |
| DOC (mg C/L) | 4.60 | 4.85 | 105.4 | 4.60 | 4.47 | 97.2 |
| Chlorophyll (µg/L) | | | | | | |
| Total Susp. S (mg/L) | 17.0 | 11.0*** | 64.7 | 12.0 | 5.0*** | 41.7 |

WARN and *FAIL based on Standard Deviation of all participants' reported concentrations

| Parameter | Summer | Summer | Summer 2011 | Winter | Winter | Winter |
|-------------------------|----------|----------|-------------|----------|----------|----------------|
| | 2011 | 2011 | | 2012 | 2012 | 2012 |
| | Prepared | Reported | % Recovered | Prepared | Reported | % Recovered |
| TDN (mg N/L) | 0.27 | 0.259 | 95.9 | 0.24 | 0.222 | 92.5 |
| TDN (mg N/L) | 0.994 | 0.97 | 97.6 | 0.568 | 0.545 | 96.0 |
| TDP (mg P/L) | 0.0096 | 0.0095 | 99.0 | 0.0115 | 0.0113 | 98.3 |
| TDP (mg P/L) | 0.0384 | 0.04 | 104.2 | 0.0365 | 0.0395 | 108.2 |
| NH4 (mg N/L) | 0.038 | 0.036 | 94.7 | 0.034 | 0.0294 | 86.5 |
| NH4 (mg N/L) | 0.21 | 0.21 | 100.0 | 0.147 | 0.148 | 100.7 |
| NO3+NO2 (mg N/L) | 0.056 | 0.0586 | 104.6 | 0.035 | 0.0344 | 98.3 |
| NO3+NO2 (mg N/L) | 0.98 | 0.934 | 95.3 | 0.868 | 0.889 | 102.4 |
| PO4 (mg P/L) | 0.0022 | 0.0033 | 150.0 | 0.0037 | 0.0033 | 89.2 |
| PO4 (mg P/L) | 0.0481 | 0.0549 | 114.1 | 0.0474 | 0.0423** | 89.2 |
| Part. C (mg C/L) | | 1.9 | | | 1.556 | |
| Part. N (mg N/L) | | 0.322 | | | 0.207 | |
| Part. P (mg P/L) | | 0.0365 | | | 0.0187 | |
| DOC (mg C/L) | 1.60 | | | 1.50 | 1.46 | 97.3 |
| DOC (mg C/L) | 4.60 | | | 4.60 | 4.49 | 97.6 |
| Chlorophyll (µg/L) | | 13.5 | | | 15.02 | |
| Total Susp. S (mg/L) | 17.0 | 15.2 | 89.4 | 12.0 | 10.2 | 85.0 |

UMCES Horn Point Laboratory

(mg/L) **WARN based on Standard Deviation of all participants' reported concentrations.

UMCES Chesapeake Biological Laboratory

| Parameter | Summer | Summer | Summer 2011 | Winter | Winter | Winter |
|-------------------------|------------------|------------------|---------------|------------------|------------------|-----------|
| | 2011 Prepared | 2010 Reported | % Recovered | 2012 Prepared | 2012 Reported | 2012 % |
| | riepareu | Reported | 70 INECOVERED | riepareu | Reported | Recovered |
| TDN (mg N/L) | 0.27 | 0.26 | 96.3 | 0.24 | 0.213 | 88.7 |
| TDN (mg N/L) | 0.994 | 0.97 | 97.6 | 0.568 | 0.527 | 92.8 |
| TDP (mg P/L) | 0.0096 | 0.0088 | 91.7 | 0.0115 | 0.0098 | 85.2 |
| TDP (mg P/L) | 0.0384 | 0.037 | 96.3 | 0.0365 | 0.0367 | 100.5 |
| NH4 (mg N/L) | 0.038 | 0.04 | 105.3 | 0.034 | 0.028 | 82.3 |
| NH4 (mg N/L) | 0.21 | 0.218 | 103.8 | 0.147 | 0.141 | 95.9 |
| NO3+NO2 (mg | 0.056 | 0.0648** | 115.7 | 0.035 | 0.029** | 82.8 |
| N/L) | 0.00 | 4 000** | 400.4 | 0.000 | 0 004 0** | 4074 |
| NO3+NO2 (mg N/L) | 0.98 | 1.062** | 108.4 | 0.868 | 0.9319** | 107.4 |
| PO4 (mg P/L) | 0.0022 | 0.0041 | 186.4 | 0.0037 | 0.0044 | 118.9 |
| PO4 (mg P/L) | 0.0481 | 0.053 | 110.2 | 0.0474 | 0.0482 | 101.7 |
| Part. C (mg C/L) | | 1.95 | | | 1.5 | |
| Part. N (mg N/L) | | 0.334 | | | 0.196 | |
| Part. P (mg P/L) | | 0.0307 | | | 0.0185 | |
| DOC (mg C/L) | 1.60 | 1.86 | 116.2 | 1.50 | 1.86 | 124.0 |
| DOC (mg C/L) | 4.60 | 4.92 | 106.9 | 4.60 | 5.03 | 109.3 |
| Chlorophyll (µg/L) | | 16.2 | | | 12.97 | |
| Total Susp. S (mg/L) | 17.0 | 15.4 | 90.6 | 12.0 | 11.3 | 94.2 |

(mg/L) **WARN based on Standard Deviation of all participants' reported concentrations

MD DHMH Division of Environmental Chemistry Nutrients Laboratory

| Parameter Summer Summer Summer 2011 Winter Winter Winter | | | | | | |
|--|----------|----------|-------------|----------|----------|----------------|
| Falamelei | 2011 | 2011 | Summer 2011 | 2012 | 2012 | Winter 2012 |
| | Prepared | Reported | % Recovered | Prepared | Reported | % |
| | | | | | | Recovered |
| TDN (mg N/L) | 0.27 | 0.252 | 93.3 | 0.24 | 0.242 | 100.8 |
| TDN (mg N/L) | 0.994 | 0.996 | 100.2 | 0.568 | 0.554 | 97.5 |
| TDP (mg P/L) | 0.0096 | 0.0119 | 124.0 | 0.0115 | 0.0145 | 126.1 |
| TDP (mg P/L) | 0.0384 | 0.0392 | 102.1 | 0.0365 | 0.036 | 98.6 |
| NH4 (mg N/L) | 0.038 | 0.024** | 63.1 | 0.034 | 0.02 | 58.8 |
| NH4 (mg N/L) | 0.21 | 0.202 | 96.2 | 0.147 | 0.139 | 94.5 |
| NO3+NO2 (mg N/L) | 0.056 | 0.0606 | 108.2 | 0.035 | 0.036 | 102.8 |
| NO3+NO2 (mg N/L) | 0.98 | 0.952 | 97.1 | 0.868 | 0.862 | 99.3 |
| PO4 (mg P/L) | 0.0022 | 0.00351 | 159.5 | 0.0037 | 0.007 | 189.2 |
| PO4 (mg P/L) | 0.0481 | 0.0504 | 104.8 | 0.0474 | 0.048 | 101.3 |
| Part. C (mg C/L) | | 1.941 | | | 1.542 | |
| Part. N (mg N/L) | | 0.343 | | | 0.205 | |
| Part. P (mg P/L) | | 0.0287 | | | 0.0205 | |
| DOC (mg C/L) | 1.60 | 1.76 | 110.0 | 1.50 | 1.50 | 100.0 |
| DOC (mg C/L) | 4.60 | 4.85 | 105.4 | 4.60 | 4.51 | 98.0 |
| Chlorophyll (µg/L) | | 13.46 | | | | |
| Total Susp. S (mg/L) | 17.0 | 16 | 94.2 | 12.0 | 11.7 | 97.5 |

(mg/L) **WARN based on Standard Deviation of all participants' reported concentrations.

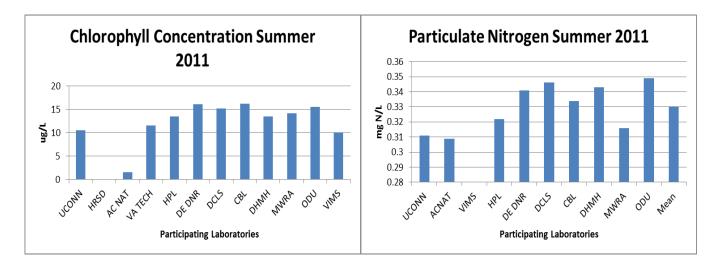
MWRA Water Quality Laboratory

| Parameter | Summer | Summer | Summer 2011 | Winter | Winter | Winter |
|-------------------------|------------------|------------------|--------------|------------------|------------------|-----------|
| | 2011 Prepared | 2011 Reported | % Recovered | 2012 Prepared | 2012 Reported | 2012 % |
| | riepaieu | Reported | 70 Necovereu | riepareu | Reported | Recovered |
| TDN (mg N/L) | 0.27 | 0.286 | 105.9 | 0.24 | 0.242 | 100.8 |
| TDN (mg N/L) | 0.994 | 0.986 | 99.2 | 0.568 | 0.566 | 99.6 |
| TDP (mg P/L) | 0.0096 | 0.0125 | 130.2 | 0.0115 | 0.0144 | 125.2 |
| TDP (mg P/L) | 0.0384 | 0.0414 | 107.8 | 0.0365 | 0.0405 | 111.0 |
| NH4 (mg N/L) | 0.038 | 0.0322 | 84.7 | 0.034 | 0.0272 | 80.0 |
| NH4 (mg N/L) | 0.21 | 0.208 | 99.0 | 0.147 | 0.151 | 102.7 |
| NO3+NO2 (mg | 0.056 | 0.0547 | 97.7 | 0.035 | 0.0325 | 92.9 |
| N/L) | | | <u></u> | | | |
| NO3+NO2 (mg N/L) | 0.98 | 0.84** | 85.7 | 0.868 | 0.88 | 101.4 |
| PO4 (mg P/L) | 0.0022 | 0.0067 | 304.5 | 0.0037 | 0.00388 | 104.9 |
| PO4 (mg P/L) | 0.0481 | 0.0553 | 115.0 | 0.0474 | .0481 | 101.5 |
| Part. C (mg C/L) | | 2.02 | | | 1.55 | |
| Part. N (mg N/L) | | 0.316 | | | 0.1995 | |
| Part. P (mg P/L) | | 0.0321 | | | 0.0187 | |
| DOC (mg C/L) | 1.60 | | | 1.50 | | |
| DOC (mg C/L) | 4.60 | | | 4.60 | | |
| Chlorophyll (µg/L) | | 14.1 | | | 13.3 | |
| Total Susp. S (mg/L) | 17.0 | 18.2** | 95.3 | 12.0 | 11.5 | 95.8 |

(mg/L) **WARN based on Standard Deviation of all participants' reported concentrations

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|-------------------------|----------------|----------------|---------------------|----------------|----------------|----------------|
| Parameter | Summer 2011 | Summer 2011 | Summer 2011 | Winter 2012 | Winter 2012 | Winter 2012 |
| | Prepared | Reported | % Recovered | Prepared | Reported | % |
| | | | | | | Recovered |
| TDN (mg N/L) | 0.27 | 0.27 | 100.0 | 0.24 | 0.236 | 98.3 |
| TDN (mg N/L) | 0.994 | 1.009 | 101.5 | 0.568 | 0.565 | 99.5 |
| TDP (mg P/L) | 0.0096 | 0.01 | 104.2 | 0.0115 | 0.016 | 139.1 |
| TDP (mg P/L) | 0.0384 | 0.037 | 96.3 | 0.0365 | 0.038 | 104.1 |
| NH4 (mg N/L) | 0.038 | 0.03 | 78.9 | 0.034 | 0.032 | 94.1 |
| NH4 (mg N/L) | 0.21 | 0.201 | 95.7 | 0.147 | 0.145 | 98.6 |
| NO3+NO2 (mg N/L) | 0.056 | 0.06 | 107.1 | 0.035 | 0.034 | 97.1 |
| NO3+NO2 (mg N/L) | 0.98 | 0.935 | 95.4 | 0.868 | 0.82 | 94.5 |
| PO4 (mg P/L) | 0.0022 | 0.005 | 227.3 | 0.0037 | 0.005 | 135.1 |
| PO4 (mg P/L) | 0.0481 | 0.047 | 97.7 | 0.0474 | 0.046 | 97.0 |
| Part. C (mg C/L) | | 1.912 | | | 1.562 | |
| Part. N (mg N/L) | | 0.311 | | | 0.187 | |
| Part. P (mg P/L) | | 0.029 | | | 0.0165 | |
| DOC (mg C/L) | 1.60 | | | 1.50 | 1.61 | 107.3 |
| DOC (mg C/L) | 4.60 | | | 4.60 | 4.66 | 101.3 |
| Chlorophyll (µg/L) | | 10.5 | | | | |
| Total Susp. S (mg/L) | 17.0 | 16.0 | 94.1 | 12.0 | 11.4 | 95.0 |
| | | | | | | |



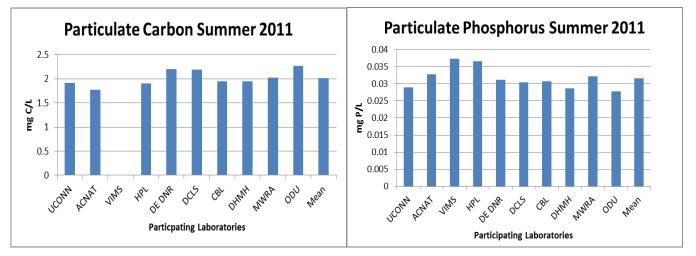
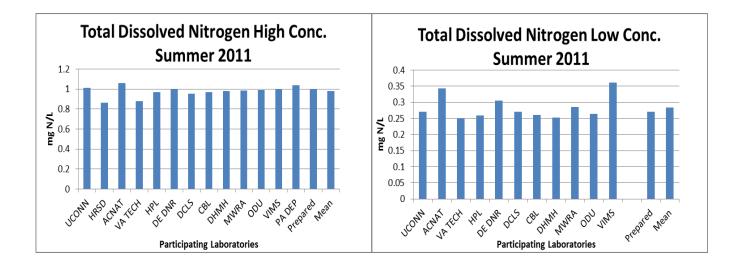


Figure 1. Particulate carbon, nitrogen, phosphorus and chlorophyll, Summer 2011.



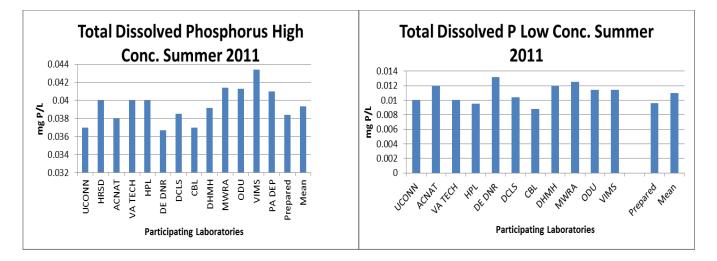


Figure 2. Total dissolved nitrogen and phosphorus, Summer 2011.

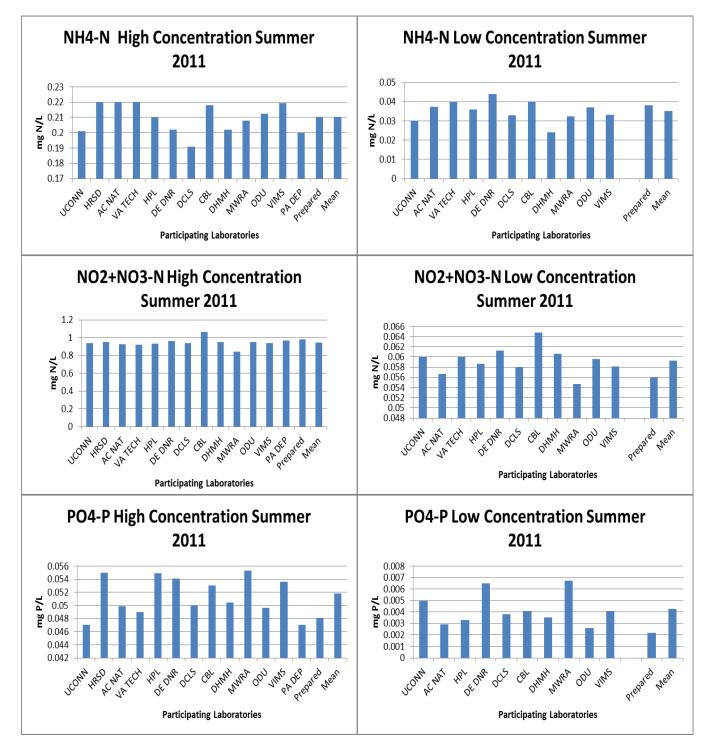


Figure 3. Dissolved inorganic nutrients, Summer 2011.

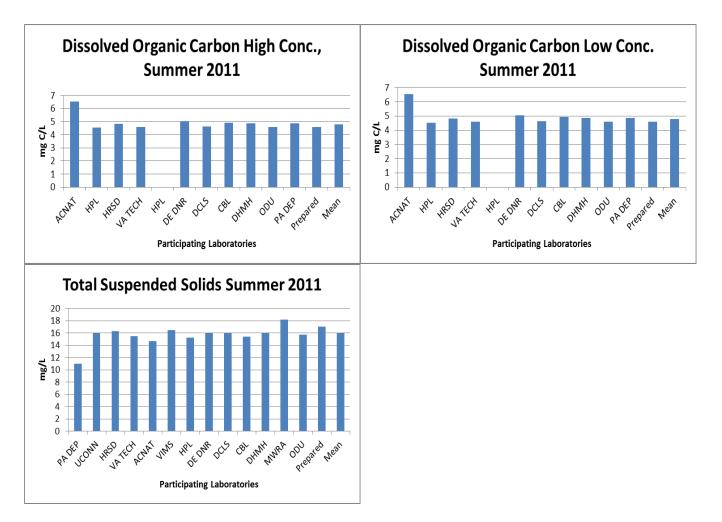


Figure 4. Dissolved organic carbon and total suspended solids, Summer 2011.

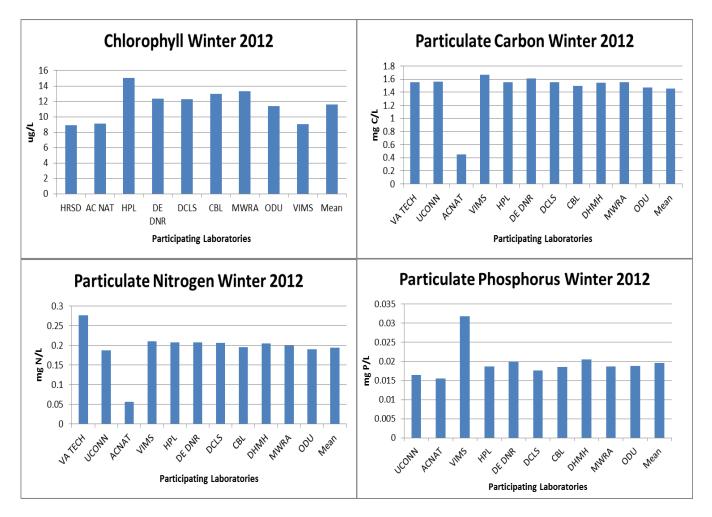


Figure 5. Particulate carbon, nitrogen, phosphorus and chlorophyll, Winter 2012.

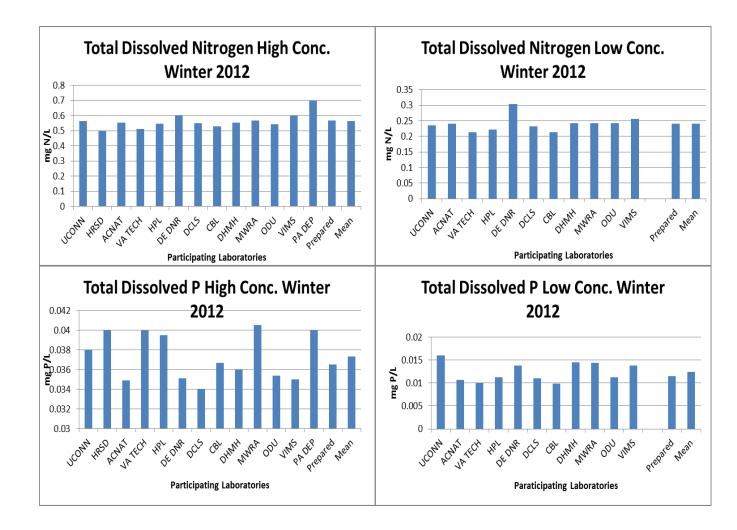


Figure 6. Total dissolved nitrogen and phosphorus, Winter 2012.

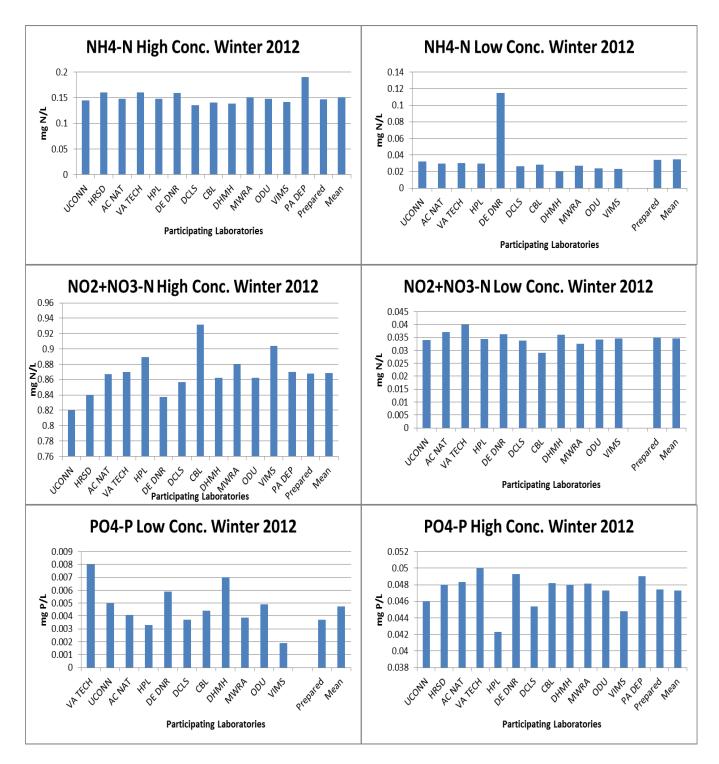


Figure 7. Dissolved inorganic nutrients, Winter 2012.

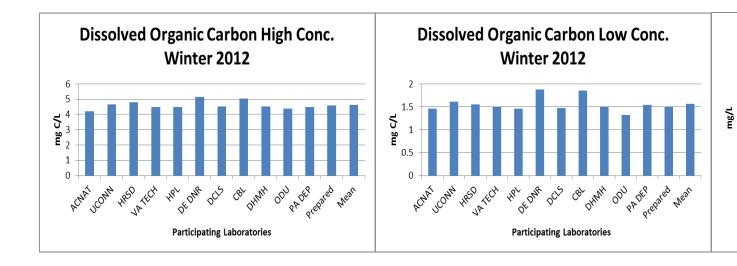


Figure 8. Dissolved organic carbon and total suspended solids, Winter 2012.