# CHESAPEAKE BAY PROGRAM BLIND AUDIT

# **Fiscal Year 2021 Final Report**

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

# SUBMITTED BY: Jerome M. Frank, Senior FRA Program Coordinator

Chesapeake Biological Laboratory University of Maryland Center for Environmental Science P.O. Box 38 Solomons, MD 20688-0038

# January 2022

Technical Report Series No. TS-775-21 of the University of Maryland Center for Environmental Science Ref. No. [UMCES]CBL 2022-023

January 2022

# TABLE OF CONTENTS

Introduction	. 1
Materials and Methods	. 1
Results	
Discussion	
Conclusion	

# LIST OF TABLES

Table 1. Participants in the Fall 2020 and Spring 2021 Chesapeake Bay Blind Audit Program

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Fall 2020 and Spring 2021 Blind Audit, Including Distribution of Reported Concentrations from the Mean

 Table 3.
 Summary of Prepared and Reported Concentrations for Each Analyte in the Fall 2020

 and Spring 2021 Blind Audit, Including Comparison to Prepared Concentration

### APPENDICES

Appendix 1. Fall 2020 and Spring 2021 Reported Data, Prepared Concentrations and Percent Recoveries

# LIST OF FIGURES

Figure 1. Particulate carbon, particulate nitrogen, particulate phosphorus, chlorophyll *a*, and total dissolved nitrogen for fall 2020

Figure 2. Total dissolved phosphorus, dissolved organic carbon, and ammonium for fall 2020

Figure 3. Nitrite plus nitrate, orthophosphate, and total suspended solids for fall 2020

Figure 4. Particulate carbon, particulate nitrogen, particulate phosphorus, chlorophyll *a*, and total dissolved nitrogen for spring 2021

Figure 5. Total dissolved phosphorus, dissolved organic carbon, and ammonium for spring 2021

Figure 6. Nitrite plus nitrate, orthophosphate, and total suspended solids for spring 2021

# 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, its tributaries, or similar systems. The concentrations of these samples, which are unknown to the recipient analysts, are compared to their prepared concentrations, or in the case of particulate samples, the range of values reported.

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 and 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 National Pollutant Discharge Elimination System (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 quality assurance and quality control (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. 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 less (or at least consistent) 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 twenty-third 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 6 April 2021 and 20 June 2021. Participating laboratories and contact personnel are found in Table 1.

Parameters measured were: total dissolved organic nitrogen, total dissolved organic phosphorus, nitrate+nitrite, ammonium, orthophosphate 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-*a* 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 (ASTM Type 1). 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 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 orthophosphate). 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, 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 analytical batch. 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 vacuum filtered (</= 10 in Hg, or 5 psi) from the batch sample with care, taken to shake (or constantly stir) the batch before each filtration to ensure homogeneity. 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 *a* 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 homogenized with a magnetic stirrer. While stirring continued, an aliquot was transferred 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 utilized in those participants' coolers.

# RESULTS

Tables and figures summarizing results from the fall 2020 and spring 2021 audits are found at the end of the report. Data review was requested of participants when submitted data that was more than twenty percent outside of the mean of all data submitted for that parameter and there did not appear to be high degree of variability across results. Some parameters, such as chlorophyll, have an inherently higher degree of variability. Review of chlorophyll data is requested less often that other parameters.

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

# **Dissolved Fraction**

# Total Dissolved Nitrogen:

Results from both the fall 2020 and spring 2021 audits were about as in past audits, with only two laboratories reporting a concentration that was not close (> +/- 3 SD from mean) to other participants, one in each survey, at both concertation levels (2/50). For both surveys only one (1/50) reported value fell into "warning" category (> +/- 2 SD from mean), and the percent coefficient of variation (%CV) for all four groupings were below 10% (range: 4.6-9.8). Higher %CV were seen with the fall 2020 results (7.6 and 9.8). This was not a result of less participants reporting TDN (28 total values reported fall 2020, and 28 for spring 2021) in either survey, nor a single gross excursion from the mean by one laboratory as in past surveys, but simply driven by the higher variability of reported values in fall 2020.

### Total Dissolved Phosphorus:

The fall 2020 reported TDP values did not agree with each other well (%CV 16.8 and 22.8), and many did not recover the prepared values either (17 pass, 6 warnings 5 failures). Spring 2021 had good agreement among participants (%CV 6.5 and 6.9), and all but one value was within the acceptance range (26 pass, 1 warning, 1 failure) of recovery of the expected value. Agreement among participants for this parameter is usually good (<10%CV), so fall 2020 variance is surprising. Poor recovery across the entire cohort usually indicates error in either the preparation of the sample or calculation of the expected value, but the range of values reported does not fit that hypothesis. Worth of note, the fall 2020 expected values were slightly lower that those of recent surveys.

<u>Ammonium</u>: All reported concentrations for both audits were consistently close to other laboratories' reported concentrations for the spring 2021 survey, less so for the fall 2020. For both surveys only four (4/64) reported values that fell into "warning" category (> +/- 2 SD from mean), no values failed, but the percent coefficient of variation (%CV) for three of the four groupings were outside of the ten percent threshold (12.0, 16.7, and 27.6%). Eighteen reported values that differed from the expected value by more than 10% (<90, or >110% recovery), and nine exceeded the 20% threshold, though it should be noted these variances were dispersed across the cohort, while in the past one or two laboratories are often responsible for the bulk of the flagged values.

<u>Nitrate + Nitrite:</u> There was reasonably good agreement among all laboratories for both concentration levels, for both audits. Only two (2/65) reported values that fell into "warning" category (> +/- 2 SD from mean), and despite three values being flagged as "fail," the percent coefficients of variation (%CV) for all four groupings were below the ten percent threshold (range: 5.4-9.4). Six reported values differed from the expected value by more than 10% (<90, or >110% recovery), and two exceeded the 20% threshold (both in the fall 2020 survey).

<u>Orthophosphate:</u> Reasonably good agreement was found among all laboratories for both concentration levels, for both audits. Only four values overall warranted a flag; two (2/65) reported values fell into the "warning" category (> +/-2 SD from mean), and two values failed. The percent coefficients of variation (%CV) for both low concentration groups were above the ten percent threshold (F20 12.7%, S21 15.0 %) This was driven completely by a single submission in each grouping, one that was significantly high, and the other low. Dropping these values would lower the %CV of each group well below the 10% threshold. Eight reported values differed from the expected value by more than 10% (<90, or >110% recovery), while three exceeded the 20% threshold.

<u>Dissolved Organic Carbon</u>: Particularly good agreement was found among all laboratories for low and high concentrations for both audits. Five (5/42) reported values fell into the "warning" category (> +/-2 SD from mean), and no reported value failed. The percent coefficients of variation (%CV) for both low concentration and high groups, for all groupings were below the ten percent threshold (F20 7.4 & 3.7%, S21 6.1 & 4.6%). Eight reported values exceeded the expected value by more than ten percent, and one value exceeded the failure threshold (</ >20%).

# **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 4.

<u>Particulate Carbon:</u> Particularly good agreement was found among all laboratories for the fall 2020 and spring 2021, with coefficients of variation of 3.2 and 2.6%, and it should be noted that this was better than the previous three Blind Audit surveys (FY2018, 5.0-9.0%, FY2019 9.0-9.9%, FY2020 5.3-6.9). Only one (1/18) value received a warning flag (> +/-2 SD from mean), and none failed.

Particulate Nitrogen: Results for particulate nitrogen followed the same pattern as particulate carbon for the spring, with a coefficient of variation 4.8%, but fall 2020 was more variable at 18.2%. This was driven by a single reported value. FY21 simultaneously performed better and worse than much of the previous three Blind Audit surveys (FY2018, 7.3-9.7%, FY2019 12.3-15.9%, FY2020 2.1-2.8). As in FY 2020, only one (1/17) value received a warning flag (> +/-2 SD from mean), and none failed.

<u>Particulate Phosphorus:</u> Resonable agreement was found among all laboratories for the fall 2020 and spring 2021, with coefficients of variation of 7.1% and 14.6%, and it should be noted that this was similar to the previous three Blind Audit surveys (FY2018, 10.4-19.2%, FY2019 8.7-14.9%, FY20 6.7-9.6%). One anonymously low value drove the fall 2020 %CV above ten percent. None of the reported values from either survey received a warning flag (> +/-2 SD from

mean), but one did fail.

<u>Chlorophyll a:</u> Chlorophyll a results for the fall 2020 and spring 2021 audit displayed the degree of variability (%CV 17.6%, 22.7%, respectively) expected for a multi-laboratory comparison of low concentrations of an environmentally transitory compound, and consistent with past audits; %CV F17 23.1%, S18 23.3%, F18 25.3%, and S19 26.2%, F19 28.3%. No values were flagged with a warning or failing label (> +/-2 SD, or > +/-3 SD from mean, respectively).

<u>Total Suspended Solids</u>: The usual good agreement was found among all laboratories for the fall 2020 and spring 2021, with coefficients of variation of 4.4 and 4.9%, which is the least combined variability of the last four audits (FY18 7.7-9.7%, FY19 4.5-7.6%, FY20 5.5 and 6.6%). No reported values from either survey received a warning flag (> +/-2 SD from mean), and none failed. All but a few reported values (30/33) fell within 10% (<90, or >110% recovery) of the expected value.

# 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 (MDL) 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 0.05 mg N/L. Any total dissolved nitrogen measurement has a potential 0.05 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 25% associated with it; whereas, a 1.20 mg N/L concentration has an analytical variability of 4%.

<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 +/- two 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 (Environmental Resource Associates), 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 two standard deviations PASS and those greater than three standard deviations FAIL. Results between two and three standard deviations receive the WARN flag.

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 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 approximately the same number were in the "warning" category as in most of the previous studies, and that only <u>two</u> values in the entire study "failed."

Data sets with relatively small standard deviations yielded more potentially extraneous "warning" points. For example, in the fall 2015 blind audit of high level ammonium concentration, the prepared concentration was 0.361 mg N/L and the mean reported concentration was 0.365 mg N/L and reported concentrations ranged from 0.337-0.395 mg N/L. The coefficient of variation was 4%. Thirteen laboratories reported results for this high level sample that were within two standard deviations (S.D. 0.014 mg N/L) of the mean. Since the standard deviation was so small, two laboratories' reported results for this sample that were between two and three standard deviations of the mean, so were labeled WARN. Thus, by that measure of accuracy, most of the data "passed" and two were "warned." This ammonium 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 fall 2015 high level ammonium data were within 9% 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 10% of the prepared concentration were considered as PASS. Reported data that were 80-90% or 110 -120% of the prepared concentration were tabulated as WARN. Reported data that were <80% or >120% of the prepared concentration were tabulated 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 spring 2016 blind audit of 0.014 mg N/L prepared for ammonium has a PASS category (+/-10%) of only 0.013 - 0.015 mg N/L. For the spring 2016 blind audit, eight out of twelve participating laboratories reported results that fell in the WARN or FAIL category, 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 all participants to accurately measure low level ammonium from concentrates provided to them. It would be important to know if there is also 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 ammonium reported values in past audits; however, when comparing with other participants, the coefficient of variation remains remarkably small. For example, fall 2019 reported data based on comparisons with other participants, the low level ammonium mean was 0.042 mg N/L, S.D. 0.005, C.V. 10.8%.

There was less divergence between participants for the fall 2012 through fall 2014 low level ammonium samples than in audits of fall 2011 and spring 2012. For these most recent prepared ammonium samples, the proportion of the standard deviation to the mean was approximately the same as it had been for the last few years. Variation around the mean for low level ammonium reported concentrations resulted in coefficients of variation of 16% for fall 2015 concentration of 0.025 mg NH4-N/L; 19% for spring 2016 concentration of 0.014. For the spring 2014 audit, the

coefficient of variation for 0.022 mg NH4-N/L was 20% mg NH4-N/L. The coefficient of variation was 16% for 0.042 mg NH4-N/L (Fall 2006) and 39% for 0.036 mg NH4-N/L (Spring 2007). This indicates that inter-laboratory comparisons of any ammonium data prepared by most laboratories from concentrates below 0.042 mg N/L may be improving. In fact, since spring 2017 all but one observed coefficient of variation for low level ammonium was below 20%, and five of those six values were below 15%. This was not the case for fall 2020 as %CV for each survey was above 15%, 16.7 and 27.6%. The variance at the low level (27.6%) was the highest of all reported parameters.

It is worth noting that the coefficient of variation for the higher concentration ammonium samples of Spring 2019 was 24%, but would drop to 14% if one result were excluded. That result was the single value that failed due to its value being more than three standard deviations from the mean. Likewise it is also worth noting that the lower concentration set from the same audit had two values fail by the same criteria, but the coefficient of variation was 5.4%, with all results included.

Also, the number of participants that were placed in the WARN or FAIL category for the spring 2020 high and low level total dissolved phosphorus sample was suspiciously high; all submitted results. However the coefficients of variation was 6.8 and 4.9%, respectively, for these groups of data. It can be stated with confidence that there was most likely preparation error with this sample, rendering the expected concentration moot.

<u>Acceptance Limits of Provided Particulate Samples:</u> For each study, particulate carbon, nitrogen, phosphorus and chlorophyll *a* 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 and nitrogen for the fall 2020 and spring 2021 audits, with the exception of PN F20.

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 spring 1998 was approximately 0.45 mg C/L, and in fall 2018 was approximately 2.2 mg C/L. Particulate phosphorus in spring 2014 was 0.0091 mg P/L and in spring 1999 was 0.0529 mg P/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. Subtle entry or calculation errors may have gone undetected.

The fall 2007 and spring 2008 audits were the first 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. This improvement in reporting did not extend to the fall 2008 through fall 2010 audits. At last, for the spring 2011 audit, no participant noted any discrepancies when all were contacted to review their data. We had returned to that 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. Unfortunately, for the fall 2011 blind audit, results were reported and then later corrected. The next five audits (spring 2012 through spring 2014), no participant noted any discrepancies when all were contacted to review their data. This improvement in reporting did not extend to the next audits; fall through spring 2021. Results were reported late, or reported and then later corrected, or even retracted.

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 spring 2021 participants reported only two significant digits for some analytes, thus potentially giving substantial under or over estimates for the comparisons.

# CONCLUSION

Now that forty-seven rounds of the Blind Audit Program have been completed, some consistent patterns have been observed that warrant action or further investigation:

1. Results for particulate carbon and nitrogen were generally consistent between laboratories. Reported concentrations of particulate analytes have usually been similar between laboratories participating in the Blind Audit Program. This was true again this year. Observed %CV values from fall 2015 through spring 2021 (22 surveys) all below 20%. All but two below 15%.

2. In contrast to particulate carbon and nitrogen, particulate phosphorus concentrations have shown more variability between participating laboratories in some audit years. This year all participants reported particulate phosphorus concentrations were consistent with each other (7.1 and 14.6%). Note, spring 2020 demonstrated the best agreement during the period of fall 2015 through spring 2021 (22 surveys) with %CV of 6.7.

3. For all participating laboratories in both audits, there was remarkable consistency between participating laboratories in the measurement of total suspended solids from suspensions of infusorial earth.

4. Most of the chlorophyll *a* results for the fall 2020 and spring 2021 audits displayed agreement that was remarkable for multi-laboratory comparison of low concentrations of an environmentally transitory compound. Two laboratories were consistently different from those of the "consensus" concentrations for both audits. One of the two is usually produces results at the low end of the concentration range, while the other laboratory varies more in their performance relative to other participants. This warrants continued observation.

5. 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.

6. 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 total dissolved phosphorus, ammonium and orthophosphate. 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.

7. Care should continue to be taken when completing report forms. For the fall 2020 and spring 2021 blind audits, a few results were reported with insufficient significant digits, or were illegible and required clarification.

Typically, a comment would be made regarding some results being submitted late, but due to the COVID 19 impacts on all facilities involved with Blind Audit it is more appropriate to commend those who managed to submit results and answer any questions regarding those results in a timely manner.

Table 1. Participants in Fall 2020 and Spring 2021 Blind Audit Program.

Participant Institution	Point of Contact	Phone	Email
Old Dominion University, Water Quality Laboratory ( <b>ODU</b> )	Suzanne Doughton	757-451-3044	sdoughte@odu.edu
University of Maryland, Horn Point Laboratory ( <b>HPL</b> )	Erica Kiss	410-221-8317	ekiss@umces.edu
Virginia Institute of Marine Science, Analytical Service Center ( <b>VIMS</b> )	Carol Pollard	804-684-7213	pollard@vims.edu
Virginia Division of Consolidated Laboratory Services ( <b>DCLS</b> )	Jay Armstrong	804-648-4480 x328	jay.armstrong@dgs.virginia.gov
Maryland Department of Health (MDH)	Cynthia Stevenson	443-681-3851	cynthia.stevenson@maryland.gov
University of Maryland Chesapeake Biological Laboratory (CBL)	Jerry Frank	410-326-7252	frank@umces.edu
Delaware Department of Natural Resources ( <b>DNREC</b> )	Kathy Knowles	302-739-9276	kathy.knowles@state.de.us
Academy of Natural Science of Philadelphia ( <b>ACNAT</b> )	Paul Kiry	215-299-1076	prk42@drexel.edu
Pennsylvania DEP, Bureau of Laboratories ( <b>PADEP</b> )	Cristina Vega Ramirez Anthony Friedline	717-346-8230	cvegaramir@pa.gov anfriedlin@pa.gov
Massachusetts Water Resources Authority, Central Laboratory ( <b>MWRA</b> )	Jennifer Constantino	617-660-7808	jennifer.constantino@mwra.com
Hampton Roads Sanitation District, Central Environmental Laboratory ( <b>HRSD</b> )	Reggie Morgan Angelina Moore	757-460-4210 757-460-4261	rmorgan@hrsd.com amoore@hrsd.com
Occoquan Watershed Monitoring Lab (OWML)	Dongmei Alvi	703-361-5606	dongmei@vt.edu
University of Connecticut Center for Environmental Science & Engineering ( <b>UCONN)</b>	Chris Perkins	860-486-2668	christopher.perkins@uconn.edu
New Jersey Department of Health (NJDH)	Doug Haltmeier	609-530-2801	douglas.haltmeier@doh.nj.gov
Sprague River Water Quality Laboratory ( <b>SRWQL</b> )	Ben A. Harris	541-827-5231	ben.harris@klamathtribes.com
University of Maryland Appalachian Laboratory ( <b>AL</b> )	Katie Kline	301-689-7122	kkline@umces.edu
Anne Arundel County Community College Environmental Cntr (AACC)	Tammy Domanski	443-994-9236	tldomanski@aacc.edu
Interstate Environmental Commission (IEC)	Evelyn Powers	347-803-0422	epowers@iec-nynjct.org

 Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Fall

 2020 and the Spring 2021 Blind Audit, Including Distribution of Reported Concentrations from the Mean.

Parameter			N	umber of L	aboratorie	s
	Concer	tration in mg/L	Stan	dard Deviat	ions from N	lean
			<1	1-2	2-3	>3
	Mean	S.D.	PASS	PASS	WARN	FAIL
Fall 2020						
Total Dissolved Nitrogen	0.3462	0.026	9	4	0	0
Total Dissolved Phosphorus	0.0217	0.005	11	1	1	0
Total Dissolved Nitrogen	0.6919	0.068	13	1	0	1
Total Dissolved Phosphorus	0.0414	0.007	12	2	1	0
Ammonium	0.0225	0.006	11	2	1	0
Nitrite+nitrate	0.0702	0.007	12	1	1	0
Phosphate	0.0193	0.002	12	2	1	0
Ammonium	0.0435	0.007	13	1	2	0
Nitrite+nitrate	0.1422	0.012	14	2	0	1
Phosphate	0.0373	0.003	13	1	1	1
Dissolved Organic Carbon	2.15	0.159	8	1	1	0
Dissolved Organic Carbon	5.18	0.190	8	1	1	0
Total Suspended Solids	65.4	2.855	12	4	1	0
Chlorophyll	13.22	2.328	10	5	0	0
Particulate Carbon	1.5172	0.048	6	3	0	0
Particulate Nitrogen	0.2398	0.044	7	1	1	0
Particulate Phosphorus	0.0187	0.001	7	2	0	0
Spring 2021						
Total Dissolved Nitrogen	0.7286	0.034	10	2	1	0
Total Dissolved Phosphorus	0.0823	0.005	12	0	0	1
Total Dissolved Nitrogen	1.4406	0.074	8	6	0	1
Total Dissolved Phosphorus	0.1317	0.009	13	1	2	0
Ammonium	0.0418	0.005	10	5	1	0
Nitrite+nitrate	0.1408	0.008	14	0	1	1
Phosphate	0.0315	0.005	14	1	0	1
Ammonium	0.0843	0.005	11	7	0	0
Nitrite+nitrate	0.5620	0.031	15	2	0	1
Phosphate	0.0554	0.002	12	6	0	0
Dissolved Organic Carbon	3.17	0.195	8	1	2	0
Dissolved Organic Carbon	9.16	0.421	7	3	1	0
Total Suspended Solids	53.5	2.623	12	2	2	0
Chlorophyll	13.01	2.965	10	5	0	0
Particulate Carbon	2.0929	0.055	5	3	0	0
Particulate Nitrogen	0.3913	0.019	7	1	0	0
Particulate Phosphorus	0.0460	0.007	8	1	0	1

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

					Number of Labo	oratories
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
Fall 2020		Min -	· Max	PASS	WARN	FAIL
Total Dissolved Nitrogen	0.3530	0.3180	0.4260	12	0	1
Total Dissolved						
Phosphorus	0.0190	0.0172	0.0355	7	3	3
Total Dissolved Nitrogen	0.7050	0.6160	0.9120	12	2	1
Total Dissolved						
Phosphorus	0.0380	0.0340	0.0610	10	3	2
Ammonium	0.0210	0.0129	0.0397	4	5	5
Nitrite+nitrate	0.0701	0.0510	0.0818	12	1	1
Phosphate	0.0186	0.0155	0.0265	10	4	1
Ammonium	0.0420	0.0280	0.0599	9	4	3
Nitrite+nitrate	0.1401	0.1030	0.1590	14	2	1
Phosphate	0.0371	0.0320	0.0436	13	3	0
Dissolved Organic Carbon	1.997	1.92	2.50	7	2	1
Dissolved Organic Carbon	4.993	4.98	5.60	9	1	0
Total Suspended Solids	68.1	56.9	68.9	16	1	0
Spring 2021						
Total Dissolved Nitrogen	0.7190	0.6380	0.7800	12	1	1
Total Dissolved						
Phosphorus	0.0780	0.0774	0.0994	12	0	0
Total Dissolved Nitrogen	1.4380	1.3400	1.6100	14	1	0
Total Dissolved						
Phosphorus	0.1270	0.1130	0.1570	14	1	1
Ammonium	0.0420	0.0346	0.053	8	7	1
Nitrite+nitrate	0.1401	0.1150	0.1590	14	2	0
Phosphate	0.0297	0.0282	0.0479	13	1	2
Ammonium	0.0850	0.0759	0.094	16	2	0
Nitrite+nitrate	0.5605	0.5130	0.6600	17	1	0
Phosphate	0.0557	0.0530	0.0584	18	0	0
Dissolved Organic Carbon	2.996	2.91	3.57	7	4	0
Dissolved Organic Carbon	8.987	8.66	10.01	10	1	0
Total Suspended Solids	54.3	46.3	56.4	14	2	0

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

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.318	Ρ	0.3530	90.1	0.78	Р	0.7190	108.5
TDP (mg P/L)	0.0172	Р	0.0190	90.5	0.0782	Р	0.0780	100.3
TDN (mg N/L)	0.66	Р	0.7050	93.6	1.36	Р	1.4380	94.6
TDP (mg P/L)	0.036	Р	0.0380	94.7	0.126	Р	0.1270	99.2
NH4 (mg N/L)	0.0253	F	0.021	120.5	0.0476	W	0.042	113.3
NO23 (mg N/L)	0.0762	Р	0.0701	108.7	0.143	Р	0.1401	102.1
PO4 (mg P/L)	0.0188	Р	0.0186	101.1	0.0288	Р	0.0297	97.0
NH4 (mg N/L)	0.049	W	0.042	116.7	0.086	Р	0.085	101.2
NO23 (mg N/L)	0.141	Р	0.1401	100.6	0.553	Р	0.5605	98.7
PO4 (mg P/L)	0.0361	Р	0.0371	97.3	0.0545	Р	0.0557	97.8
DOC (mg C/L)	*	*	1.9970	*	*	*	2.9960	*
DOC (mg C/L)	*	*	4.9930	*	*	*	8.9870	*
TSS (mg/L)	67.7	Р	68.1	99.4	*	*	54.3	*
CHL (ug/L)	16.85	NA	NA	NA	18.9	NA	NA	NA
PC (mg C/L)	1.555	NA	NA	NA	1.99	NA	NA	NA
PN (mg N/L)	0.2215	NA	NA	NA	0.345	NA	NA	NA
PP (mg P/L)	0.0199	NA	NA	NA	0.0446	NA	NA	NA

### Academy of Natural Science of Philadelphia (ACNAT)

\*Sample not sent to participant: sample not requested, parameter or concentration range not routine, or no value submitted by participant "W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations (see Table 2)

#### Virginia Institute of Marine Science, Analytical Service Center (VIMS)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.345	Р	0.3530	97.7	0.7413	Р	0.7190	103.1
TDP (mg P/L)	0.018	Р	0.0190	94.7	0.0774	Р	0.0780	99.2
TDN (mg N/L)	0.6737	Р	0.7050	95.6	1.4554	Р	1.4380	101.2
TDP (mg P/L)	0.0355	Р	0.0380	93.4	0.124	Р	0.1270	97.6
NH4 (mg N/L)	0.0397	F	0.021	189.0	0.0346	W	0.042	82.4
NO23 (mg N/L)	0.0716	Р	0.0701	102.1	0.1411	Р	0.1401	100.7
PO4 (mg P/L)	0.0177	Р	0.0186	95.2	0.0287	Р	0.0297	96.6
NH4 (mg N/L)	0.0599	F	0.042	142.6	0.0759	W	0.085	89.3
NO23 (mg N/L)	0.151	Р	0.1401	107.8	0.5402	Р	0.5605	96.4
PO4 (mg P/L)	0.0372	Р	0.0371	100.3	0.0548	Р	0.0557	98.4
DOC (mg C/L)	*	*	1.9970	*	*	*	2.9960	*
DOC (mg C/L)	*	*	4.9930	*	*	*	8.9870	*
TSS (mg/L)	68.8	Р	68.1	101.0	52.2	Р	54.3	96.1
CHL (ug/L)	16.71	NA	NA	NA	14.09	NA	NA	NA
PC (mg C/L)	1.438	NA	NA	NA	2.095	NA	NA	NA
PN (mg N/L)	0.2225	NA	NA	NA	0.3905	NA	NA	NA
PP (mg P/L)	0.0197	NA	NA	NA	0.0518	NA	NA	NA

#### Hampton Roads Sanitation District, Central Environmetal Laboratory (HRSD)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentratio	n	Concentration	Recovered
TDN (mg N/L)	*	*	0.3530	*	*	*	0.7190	*
TDP (mg P/L)	*	*	0.0190	*	*	*	0.0780	*
TDN (mg N/L)	0.912	F	0.7050	129.4	1.52	Р	1.4380	105.7
TDP (mg P/L)	0.039	Р	0.0380	102.6	0.138	Р	0.1270	108.7
NH4 (mg N/L)	*	*	0.021	*	*	*	0.042	*
NO23 (mg N/L)	*	*	0.0701	*	*	*	0.1401	*
PO4 (mg P/L)	*	*	0.0186	*	*	*	0.0297	*
NH4 (mg N/L)	0.042	Р	0.042	100.0	0.083	Р	0.085	97.6
NO23 (mg N/L)	0.151	Р	0.1401	107.8	0.543	Р	0.5605	96.9
PO4 (mg P/L)	0.036	Р	0.0371	97.0	0.055	Р	0.0557	98.7
DOC (mg C/L)	2.3	W	1.9970	115.2	3.33	W	2.9960	111.1
DOC (mg C/L)	5.28	Р	4.9930	105.7	9.57	Р	8.9870	106.5
TSS (mg/L)	66.6	Р	68.1	97.8	53.7	Р	54.3	98.9
CHL (ug/L)	12.2	NA	NA	NA	10.5	NA	NA	NA
PC (mg C/L)	*	NA	NA	NA	*	NA	NA	NA
PN (mg N/L)	*	NA	NA	NA	*	NA	NA	NA
PP (mg P/L)	*	NA	NA	NA	*	NA	NA	NA

\*Sample not sent to participant: sample not requested, parameter or concentration range not routine, or no value submitted by participant "W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations (see Table 2)

#### University of Maryland, Horn Point Laboratory (HPL)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	*	*	0.3530	*	0.738	Р	0.7190	102.6
TDP (mg P/L)	*	*	0.0190	*	0.0815	Р	0.0780	104.5
TDN (mg N/L)	*	*	0.7050	*	1.5	Р	1.4380	104.3
TDP (mg P/L)	*	*	0.0380	*	0.137	Р	0.1270	107.9
NH4 (mg N/L)	*	*	0.021	*	0.0408	Р	0.042	97.1
NO23 (mg N/L)	*	*	0.0701	*	0.139	Р	0.1401	99.2
PO4 (mg P/L)	*	*	0.0186	*	0.0314	Р	0.0297	105.7
NH4 (mg N/L)	*	*	0.042	*	0.091	Р	0.085	107.1
NO23 (mg N/L)	*	*	0.1401	*	0.544	Р	0.5605	97.1
PO4 (mg P/L)	*	*	0.0371	*	0.0567	Р	0.0557	101.8
DOC (mg C/L)	*	*	1.9970	*	*	*	2.9960	*
DOC (mg C/L)	*	*	4.9930	*	*	*	8.9870	*
TSS (mg/L)	*	*	68.1	*	54.4	Р	54.3	100.2
CHL (ug/L)	*	NA	NA	NA	12.8	NA	NA	NA
PC (mg C/L)	*	NA	NA	NA	*	NA	NA	NA
PN (mg N/L)	*	NA	NA	NA	*	NA	NA	NA
PP (mg P/L)	*	NA	NA	NA	0.0567	NA	NA	NA

#### Delaware Department of Natural Resources (DNREC)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.351	Р	0.3530	99.4	0.723	Р	0.7190	100.6
TDP (mg P/L)	0.023	F	0.0190	121.1	0.0804	Р	0.0780	103.1
TDN (mg N/L)	0.716	Р	0.7050	101.6	1.43	Р	1.4380	99.4
TDP (mg P/L)	0.054	F	0.0380	142.1	0.134	Р	0.1270	105.5
NH4 (mg N/L)	0.028	F	0.021	133.3	0.0425	Р	0.042	101.2
NO23 (mg N/L)	0.067	Р	0.0701	95.6	0.115	W	0.1401	82.1
PO4 (mg P/L)	0.022	W	0.0186	118.3	0.0327	W	0.0297	110.1
NH4 (mg N/L)	0.05	W	0.042	119.0	0.0883	Р	0.085	103.9
NO23 (mg N/L)	0.138	Р	0.1401	98.5	0.522	Р	0.5605	93.1
PO4 (mg P/L)	0.042	W	0.0371	113.2	0.0579	Р	0.0557	103.9
DOC (mg C/L)	2	Р	1.9970	100.2	2.91	Р	2.9960	97.1
DOC (mg C/L)	5	Р	4.9930	100.1	8.94	Р	8.9870	99.5
TSS (mg/L)	65.4	Р	68.1	96.0	53.8	Р	54.3	99.1
CHL (ug/L)	17.45	NA	NA	NA	17.25	NA	NA	NA
PC (mg C/L)	*	NA	NA	NA	*	NA	NA	NA
PN (mg N/L)	*	NA	NA	NA	*	NA	NA	NA
PP (mg P/L)	0.0175	NA	NA	NA	0.0484	NA	NA	NA

\*Sample not sent to participant: sample not requested, parameter or concentration range not routine, or no value submitted by participant "W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations (see Table 2)

#### Division of Consolidated Laboratory Services (DCLS)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.344	Р	0.3530	97.5	0.735	Р	0.7190	102.2
TDP (mg P/L)	0.022	W	0.0190	115.8	0.081	Р	0.0780	103.8
TDN (mg N/L)	0.682	Р	0.7050	96.7	1.424	Р	1.4380	99.0
TDP (mg P/L)	0.038	Р	0.0380	100.0	0.13	Р	0.1270	102.4
NH4 (mg N/L)	0.02	Р	0.021	95.2	0.047	W	0.042	111.9
NO23 (mg N/L)	0.069	Р	0.0701	98.4	0.141	Р	0.1401	100.6
PO4 (mg P/L)	0.018	Р	0.0186	96.8	0.03	Р	0.0297	101.0
NH4 (mg N/L)	0.045	Р	0.042	107.1	0.088	Р	0.085	103.5
NO23 (mg N/L)	0.139	Р	0.1401	99.2	0.544	Р	0.5605	97.1
PO4 (mg P/L)	0.037	Р	0.0371	99.7	0.057	Р	0.0557	102.3
DOC (mg C/L)	2.09	Р	1.9970	104.7	3.02	Р	2.9960	100.8
DOC (mg C/L)	4.98	Р	4.9930	99.7	8.91	Р	8.9870	99.1
TSS (mg/L)	66	Р	68.1	96.9	55	Р	54.3	101.3
CHL (ug/L)	13.5	NA	NA	NA	12.8	NA	NA	NA
PC (mg C/L)	1.555	NA	NA	NA	2.115	NA	NA	NA
PN (mg N/L)	0.2285	NA	NA	NA	0.4065	NA	NA	NA
PP (mg P/L)	0.0204	NA	NA	NA	0.0468	NA	NA	NA

#### Unversity of Maryland, Chesapeake Biological Laboratory (CBL)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	•		•		•		•	
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.35	Р	0.3530	99.2	0.71	Р	0.7190	98.7
TDP (mg P/L)	0.0187	Р	0.0190	98.4	0.0812	Р	0.0780	104.1
TDN (mg N/L)	0.71	Р	0.7050	100.7	1.36	Р	1.4380	94.6
TDP (mg P/L)	0.0388	Ρ	0.0380	102.1	0.1312	Р	0.1270	103.3
NH4 (mg N/L)	0.025	W	0.021	119.0	0.0425	Р	0.042	101.2
NO23 (mg N/L)	0.076	Р	0.0701	108.4	0.159	W	0.1401	113.5
PO4 (mg P/L)	0.0183	Р	0.0186	98.4	0.0297	Р	0.0297	100.0
NH4 (mg N/L)	0.046	Р	0.042	109.5	0.0836	Р	0.085	98.4
NO23 (mg N/L)	0.149	Р	0.1401	106.4	0.561	Р	0.5605	100.1
PO4 (mg P/L)	0.0392	Р	0.0371	105.7	0.0549	Р	0.0557	98.6
DOC (mg C/L)	1.92	Р	1.9970	96.1	3.08	Р	2.9960	102.8
DOC (mg C/L)	5.05	Р	4.9930	101.1	8.66	Р	8.9870	96.4
TSS (mg/L)	64.2	Р	68.1	94.3	55	Р	54.3	101.3
CHL (ug/L)	11.57	NA	NA	NA	14.15	NA	NA	NA
PC (mg C/L)	1.515	NA	NA	NA	2.095	NA	NA	NA
PN (mg N/L)	0.2405	NA	NA	NA	0.4095	NA	NA	NA
PP (mg P/L)	0.02	NA	NA	NA	0.0498	NA	NA	NA

\*Sample not sent to participant: sample not requested, parameter or concentration range not routine, or no value submitted by participant "W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations (see Table 2)

### Virginia Polytechnic Institute, Occoquan Watershed Monitoring Laboratory (OWML)

	Fall 2020		Fall 2020	Fall 2020	S	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	F	Reported		Prepared	Percent
	Concentration		Concentration	Recovered		Concentration		Concentration	Recovered
TDN (mg N/L)	0.426	F	0.3530	120.7	0	0.638	W	0.7190	88.7
TDP (mg P/L)	0.019	Р	0.0190	100.0	0	0.082	Р	0.0780	105.1
TDN (mg N/L)	0.742	Р	0.7050	105.2	1	1.36	Р	1.4380	94.6
TDP (mg P/L)	0.061	F	0.0380	160.5	0	0.132	Р	0.1270	103.9
NH4 (mg N/L)	0.025	W	0.021	119.0	0	0.053	F	0.042	126.2
NO23 (mg N/L)	0.051	F	0.0701	72.8	0	0.137	Р	0.1401	97.8
PO4 (mg P/L)	0.019	Р	0.0186	102.2	0	0.03	Р	0.0297	101.0
NH4 (mg N/L)	0.046	Р	0.042	109.5	0	0.094	W	0.085	110.6
NO23 (mg N/L)	0.103	W	0.1401	73.5	0	0.583	Р	0.5605	104.0
PO4 (mg P/L)	0.036	Р	0.0371	97.0	0	0.055	Р	0.0557	98.7
DOC (mg C/L)	2.15	Р	1.9970	107.7	3	3.57	W	2.9960	119.2
DOC (mg C/L)	5.33	Р	4.9930	106.7	1	10.01	W	8.9870	111.4
TSS (mg/L)	66.2	Р	68.1	97.2	5	53.6	Ρ	54.3	98.7
CHL (ug/L)	10.45	NA	NA	NA	7	7.26	NA	NA	NA
PC (mg C/L)	1.574	NA	NA	NA	k	*	NA	NA	NA
PN (mg N/L)	0.3555	NA	NA	NA	*	*	NA	NA	NA
PP (mg P/L)	*	NA	NA	NA	k	*	NA	NA	NA

### Maryland Department of Health (MDH)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.348	Р	0.3530	98.6	0.705	Р	0.7190	98.1
TDP (mg P/L)	0.0225	W	0.0190	118.4	0.0791	Р	0.0780	101.4
TDN (mg N/L)	0.659	Р	0.7050	93.5	1.38	Р	1.4380	96.0
TDP (mg P/L)	0.0397	Р	0.0380	104.5	0.128	Р	0.1270	100.8
NH4 (mg N/L)	0.0129	F	0.021	61.4	0.0403	Р	0.042	96.0
NO23 (mg N/L)	0.0723	Р	0.0701	103.1	0.145	Р	0.1401	103.5
PO4 (mg P/L)	0.0186	Р	0.0186	100.0	0.0321	Р	0.0297	108.1
NH4 (mg N/L)	0.0312	F	0.042	74.3	0.0826	Р	0.085	97.2
NO23 (mg N/L)	0.145	Р	0.1401	103.5	0.575	Р	0.5605	102.6
PO4 (mg P/L)	0.0362	Р	0.0371	97.6	0.0584	Р	0.0557	104.8
DOC (mg C/L)	2.07	Р	1.9970	103.7	3.06	Р	2.9960	102.1
DOC (mg C/L)	5.02	Р	4.9930	100.5	9.09	Р	8.9870	101.1
TSS (mg/L)	68.9	Р	68.1	101.2	55	Р	54.3	101.3
CHL (ug/L)	12	NA	NA	NA	12.7	NA	NA	NA
PC (mg C/L)	1.43	NA	NA	NA	2.115	NA	NA	NA
PN (mg N/L)	0.2555	NA	NA	NA	0.4	NA	NA	NA
PP (mg P/L)	0.0193	NA	NA	NA	0.0415	NA	NA	NA

\*Sample not sent to participant: sample not requested, parameter or concentration range not routine, or no value submitted by participant "W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations (see Table 2)

#### Massachusetts Water Resource Authority, Central Laboratory (MWRA)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.334	Р	0.3530	94.6	0.757	Р	0.7190	105.3
TDP (mg P/L)	0.0355	F	0.0190	186.8	0.0994	F	0.0780	127.4
TDN (mg N/L)	0.616	W	0.7050	87.4	1.42	Р	1.4380	98.7
TDP (mg P/L)	0.045	W	0.0380	118.4	0.157	F	0.1270	123.6
NH4 (mg N/L)	0.0199	Р	0.021	94.8	0.0353	W	0.042	84.0
NO23 (mg N/L)	0.0697	Р	0.0701	99.4	0.143	Р	0.1401	102.1
PO4 (mg P/L)	0.0172	Р	0.0186	92.5	0.0286	Р	0.0297	96.3
NH4 (mg N/L)	0.0391	Р	0.042	93.1	0.0785	Р	0.085	92.4
NO23 (mg N/L)	0.139	Р	0.1401	99.2	0.565	Р	0.5605	100.8
PO4 (mg P/L)	0.0362	Р	0.0371	97.6	0.0555	Р	0.0557	99.6
DOC (mg C/L)	*	*	1.9970	*	*	*	2.9960	*
DOC (mg C/L)	*	*	4.9930	*	*	*	8.9870	*
TSS (mg/L)	62.2	Р	68.1	91.3	47.8	W	54.3	88.0
CHL (ug/L)	14.8	NA	NA	NA	11.56	NA	NA	NA
PC (mg C/L)	1.52	NA	NA	NA	2.135	NA	NA	NA
PN (mg N/L)	0.2245	NA	NA	NA	0.3975	NA	NA	NA
PP (mg P/L)	0.0163	NA	NA	NA	0.0437	NA	NA	NA

#### Old Dominion University, Water Quality Laboratory (ODU)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	•		•		•		•	
	Concentration		Concentration	Recovered	Concentratio		Concentration	Recovered
TDN (mg N/L)	0.353	Р	0.3530	100.0	0.72	Р	0.7190	100.1
TDP (mg P/L)	0.0172	Р	0.0190	90.5	0.0836	Р	0.0780	107.2
TDN (mg N/L)	0.701	Р	0.7050	99.4	1.44	Р	1.4380	100.1
TDP (mg P/L)	0.0381	Р	0.0380	100.3	0.134	Р	0.1270	105.5
NH4 (mg N/L)	0.0186	W	0.021	88.6	0.0374	W	0.042	89.0
NO23 (mg N/L)	0.0662	Р	0.0701	94.4	0.14	Р	0.1401	99.9
PO4 (mg P/L)	0.0191	Р	0.0186	102.7	0.0297	Р	0.0297	100.0
NH4 (mg N/L)	0.0453	Р	0.042	107.9	0.0832	Р	0.085	97.9
NO23 (mg N/L)	0.134	Р	0.1401	95.6	0.546	Р	0.5605	97.4
PO4 (mg P/L)	0.0353	Р	0.0371	95.1	0.0566	Р	0.0557	101.6
DOC (mg C/L)	2.05	Р	1.9970	102.7	2.99	Р	2.9960	99.8
DOC (mg C/L)	5.05	Р	4.9930	101.1	8.72	Р	8.9870	97.0
TSS (mg/L)	63.4	Р	68.1	93.1	54.1	Р	54.3	99.6
CHL (ug/L)	13.7	NA	NA	NA	14.95	NA	NA	NA
PC (mg C/L)	1.525	NA	NA	NA	2.025	NA	NA	NA
PN (mg N/L)	0.196	NA	NA	NA	0.3875	NA	NA	NA
PP (mg P/L)	0.0184	NA	NA	NA	0.0467	NA	NA	NA

\*Sample not sent to participant: sample not requested, parameter or concentration range not routine, or no value submitted by participant "W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations (see Table 2)

#### Pennsylvania Department of Environmental Protection, Bureau of Laboratories (PADEP)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	*	*	0.3530	*	*	*	0.7190	*
TDP (mg P/L)	*	*	0.0190	*	*	*	0.0780	*
TDN (mg N/L)	0.64	Р	0.7050	90.8	1.34	Р	1.4380	93.2
TDP (mg P/L)	0.041	Р	0.0380	107.9	0.134	Р	0.1270	105.5
NH4 (mg N/L)	*	*	0.021	*	*	*	0.042	*
NO23 (mg N/L)	*	*	0.0701	*	*	*	0.1401	*
PO4 (mg P/L)	*	*	0.0186	*	*	*	0.0297	*
NH4 (mg N/L)	0.028	F	0.042	66.7	0.077	Р	0.085	90.6
NO23 (mg N/L)	0.15	Р	0.1401	107.1	0.57	Р	0.5605	101.7
PO4 (mg P/L)	0.04	Р	0.0371	107.8	0.054	Р	0.0557	96.9
DOC (mg C/L)	2.16	Р	1.9970	108.2	3.23	Р	2.9960	107.8
DOC (mg C/L)	5.32	Р	4.9930	106.5	9.12	Р	8.9870	101.5
TSS (mg/L)	65.2	Р	68.1	95.7	54	Р	54.3	99.4
CHL (ug/L)	11.9	NA	NA	NA	8.71	NA	NA	NA
PC (mg C/L)	*	NA	NA	NA	*	NA	NA	NA
PN (mg N/L)	*	NA	NA	NA	*	NA	NA	NA
PP (mg P/L)	*	NA	NA	NA	*	NA	NA	NA

#### New Jersey Department of HeathIth (NJDH)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	*	*	0.3530	*	*	*	0.7190	*
TDP (mg P/L)	0.0216	W	0.0190	113.7	0.0833	Р	0.0780	106.8
TDN (mg N/L)	*	*	0.7050	*	*	*	1.4380	*
TDP (mg P/L)	0.0426	W	0.0380	112.1	0.134	Р	0.1270	105.5
NH4 (mg N/L)	0.0217	Р	0.021	103.3	0.042	Р	0.042	100.0
NO23 (mg N/L)	0.0818	W	0.0701	116.7	0.144	Р	0.1401	102.8
PO4 (mg P/L)	0.0155	W	0.0186	83.3	0.0282	Р	0.0297	94.9
NH4 (mg N/L)	0.0444	Р	0.042	105.7	0.0845	Р	0.085	99.4
NO23 (mg N/L)	0.159	W	0.1401	113.5	0.585	Р	0.5605	104.4
PO4 (mg P/L)	0.032	W	0.0371	86.3	0.0533	Р	0.0557	95.7
DOC (mg C/L)	2.26	W	1.9970	113.2	3.3	W	2.9960	110.1
DOC (mg C/L)	5.22	Р	4.9930	104.5	9.77	Р	8.9870	108.7
TSS (mg/L)	66.4	Р	68.1	97.5	54.1	Р	54.3	99.6
CHL (ug/L)	*	NA	NA	NA	*	NA	NA	NA
PC (mg C/L)	*	NA	NA	NA	*	NA	NA	NA
PN (mg N/L)	*	NA	NA	NA	*	NA	NA	NA
PP (mg P/L)	*	NA	NA	NA	*	NA	NA	NA

\*Sample not sent to participant: sample not requested, parameter or concentration range not routine, or no value submitted by participant "W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations (see Table 2)

#### Sprague River Water Quality Laboratory (SRWQL)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.327	Р	0.3530	92.6		*	0.7190	*
TDP (mg P/L)	0.028	F	0.0190	147.4		*	0.0780	*
TDN (mg N/L)	0.657	Р	0.7050	93.2		*	1.4380	*
TDP (mg P/L)	0.041	Р	0.0380	107.9		*	0.1270	*
NH4 (mg N/L)	0.025	W	0.021	119.0	0.038	Р	0.042	90.5
NO23 (mg N/L)	0.072	Р	0.0701	102.7	0.137	Р	0.1401	97.8
PO4 (mg P/L)	0.019	Р	0.0186	102.2	0.029	Р	0.0297	97.6
NH4 (mg N/L)	0.049	W	0.042	116.7	0.077	Р	0.085	90.6
NO23 (mg N/L)	0.143	Р	0.1401	102.1	0.513	Р	0.5605	91.5
PO4 (mg P/L)	0.037	Р	0.0371	99.7	0.053	Р	0.0557	95.2
DOC (mg C/L)	*	*	1.9970	*		*	2.9960	*
DOC (mg C/L)	*	*	4.9930	*		*	8.9870	*
TSS (mg/L)	68.9	Р	68.1	101.2	56.4	Р	54.3	103.9
CHL (ug/L)	13.3	NA	NA	NA	12.8	NA	NA	NA
PC (mg C/L)	*	NA	NA	NA		NA	NA	NA
PN (mg N/L)	*	NA	NA	NA		NA	NA	NA
PP (mg P/L)	*	NA	NA	NA		NA	NA	NA

#### University of Maryland Appalachian Laboratory (AL)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.328	Р	0.3530	92.9	0.769	Р	0.7190	107.0
TDP (mg P/L)	0.0189	Р	0.0190	99.5	0.0838	Р	0.0780	107.4
TDN (mg N/L)	0.674	Р	0.7050	95.6	1.61	W	1.4380	112.0
TDP (mg P/L)	0.0382	Р	0.0380	100.5	0.135	Р	0.1270	106.3
NH4 (mg N/L)	*	*	0.021	*	0.0388	Р	0.042	92.4
NO23 (mg N/L)	*	*	0.0701	*	0.14	Р	0.1401	99.9
PO4 (mg P/L)	0.0209	W	0.0186	112.4	0.0299	Р	0.0297	100.7
NH4 (mg N/L)	*	*	0.042	*	0.0837	Р	0.085	98.5
NO23 (mg N/L)	0.143	Р	0.1401	102.1	0.568	Р	0.5605	101.3
PO4 (mg P/L)	0.0436	W	0.0371	117.5	0.0557	Р	0.0557	100.0
DOC (mg C/L)	*	*	1.9970	*	3.37	W	2.9960	112.5
DOC (mg C/L)	*	*	4.9930	*	9.13	Р	8.9870	101.6
TSS (mg/L)	63.7	Р	68.1	93.5	46.3	W	54.3	85.3
CHL (ug/L)	*	NA	NA	NA	*	NA	NA	NA
PC (mg C/L)	*	NA	NA	NA	*	NA	NA	NA
PN (mg N/L)	*	NA	NA	NA	*	NA	NA	NA
PP (mg P/L)	*	NA	NA	NA	*	NA	NA	NA

\*Sample not sent to participant: sample not requested, parameter or concentration range not routine, or no value submitted by participant "W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations (see Table 2)

#### Anne Arundle County Community College Environmental Center (AACC)

	Fall 2020		Fall 2020	Fall 2020		Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent		Reported		Prepared	Percent
	Concentration		Concentration	Recovered Concentration		า	Concentration	Recovered	
TDN (mg N/L)	*	*	0.3530	*		*	*	0.7190	*
TDP (mg P/L)	*	*	0.0190	*		*	*	0.0780	*
TDN (mg N/L)	*	*	0.7050	*		*	*	1.4380	*
TDP (mg P/L)	*	*	0.0380	*		*	*	0.1270	*
NH4 (mg N/L)	0.0152	F	0.021	72.4		0.0373	W	0.042	88.8
NO23 (mg N/L)	0.07	Р	0.0701	99.9		0.142	Р	0.1401	101.4
PO4 (mg P/L)	0.0265	F	0.0186	142.5		0.0367	F	0.0297	123.6
NH4 (mg N/L)	0.0423	Р	0.042	100.7		0.0786	Р	0.085	92.5
NO23 (mg N/L)	0.139	Р	0.1401	99.2		0.574	Р	0.5605	102.4
PO4 (mg P/L)	*	*	0.0371	*		0.0565	Р	0.0557	101.4
DOC (mg C/L)	*	*	1.9970	*		*	*	2.9960	*
DOC (mg C/L)	*	*	4.9930	*		*	*	8.9870	*
TSS (mg/L)	56.9	W	68.1	83.6		*	*	54.3	*
CHL (ug/L)	11.84	NA	NA	NA		*	NA	NA	NA
PC (mg C/L)	*	NA	NA	NA		*	NA	NA	NA
PN (mg N/L)	*	NA	NA	NA		*	NA	NA	NA
PP (mg P/L)	*	NA	NA	NA		*	NA	NA	NA

#### Interstate Environmental Commission (IEC)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.32	Р	0.3530	90.7	0.725	Р	0.7190	100.8
TDP (mg P/L)	*	*	0.0190	*	*	*	0.0780	*
TDN (mg N/L)	0.625	W	0.7050	88.7	1.48	Р	1.4380	102.9
TDP (mg P/L)		*	0.0380	*	0.113	W	0.1270	89.0
NH4 (mg N/L)	0.0187	W	0.021	89.0	0.0494	W	0.042	117.6
NO23 (mg N/L)	0.0711	Р	0.0701	101.4	0.142	Р	0.1401	101.4
PO4 (mg P/L)	0.0187	Р	0.0186	100.5	0.0479	F	0.0297	161.3
NH4 (mg N/L)	0.0369	W	0.042	87.9	0.0926	Р	0.085	108.9
NO23 (mg N/L)	0.156	W	0.1401	111.3	0.66	W	0.5605	117.8
PO4 (mg P/L)	0.0371	Ρ	0.0371	100.0	0.0533	Р	0.0557	95.7
DOC (mg C/L)	*	*	1.9970	*	*	*	2.9960	*
DOC (mg C/L)	*	*	4.9930	*	*	*	8.9870	*
TSS (mg/L)	67.1	Р	68.1	98.5	56.1	Р	54.3	103.3
CHL (ug/L)	8.9	NA	NA	NA	16.18	NA	NA	NA
PC (mg C/L)	*	NA	NA	NA	*	NA	NA	NA
PN (mg N/L)	*	NA	NA	NA	*	NA	NA	NA
PP (mg P/L)	*	NA	NA	NA	*	NA	NA	NA

\*Sample not sent to participant: sample not requested, parameter or concentration range not routine, or no value submitted by participant "W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations (see Table 2)

#### University of Connecticut Center for Environmental Science and Engineering (UCONN)

	Fall 2020		Fall 2020	Fall 2020	Spring 2021		Spring 2021	Spring 2021
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.357	Р	0.3530	101.1	0.73	Р	0.7190	101.5
TDP (mg P/L)	0.021	W	0.0190	110.5	0.079	Р	0.0780	101.3
TDN (mg N/L)	0.712	Р	0.7050	101.0	1.529	Р	1.4380	106.3
TDP (mg P/L)	0.034	W	0.0380	89.5	0.12	Р	0.1270	94.5
NH4 (mg N/L)	0.021	Р	0.021	100.0	0.042	Р	0.042	100.0
NO23 (mg N/L)	0.069	Р	0.0701	98.4	0.144	Р	0.1401	102.8
PO4 (mg P/L)	0.021	W	0.0186	112.9	0.03	Р	0.0297	101.0
NH4 (mg N/L)	0.043	Р	0.042	102.4	0.09	Р	0.085	105.9
NO23 (mg N/L)	0.139	Р	0.1401	99.2	0.57	Р	0.5605	101.7
PO4 (mg P/L)	0.037	Р	0.0371	99.7	0.055	Р	0.0557	98.7
DOC (mg C/L)	2.5	F	1.9970	125.2	3	Р	2.9960	100.1
DOC (mg C/L)	5.6	W	4.9930	112.2	8.8	Р	8.9870	97.9
TSS (mg/L)	65.1	Р	68.1	95.6	54	Р	54.3	99.4
CHL (ug/L)	13.23	NA	NA	NA	11.35	NA	NA	NA
PC (mg C/L)	1.543	NA	NA	NA	2.173	NA	NA	NA
PN (mg N/L)	0.214	NA	NA	NA	0.394	NA	NA	NA
PP (mg P/L)	0.0175	NA	NA	NA	0.03	NA	NA	NA

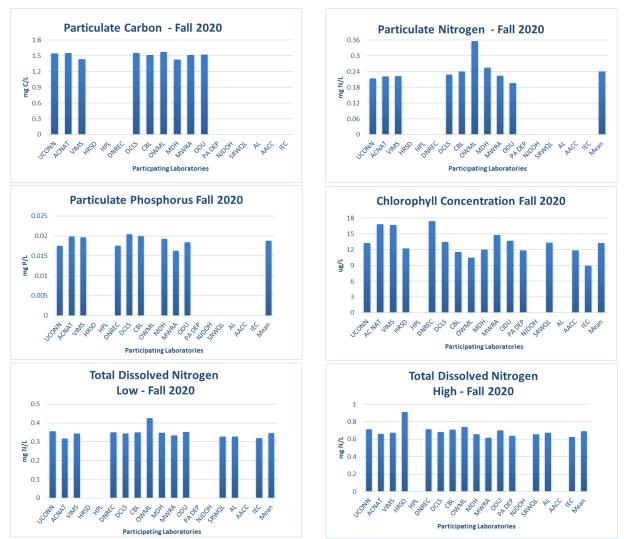
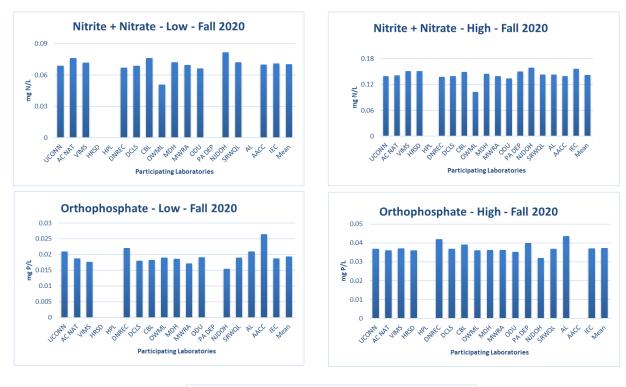


Figure 1. Particulate carbon, nitrogen and phosphorus; chlorophyll *a*, and total dissolved nitrogen. Fall 2020



Figure 2. Total dissolved phosphorus; dissolved organic carbon, amd ammonium. Fall 2020



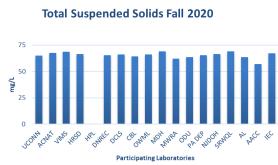


Figure 3. Nitrite plus nitrate, orthophosphate, and total suspended solids. Fall 2020

24

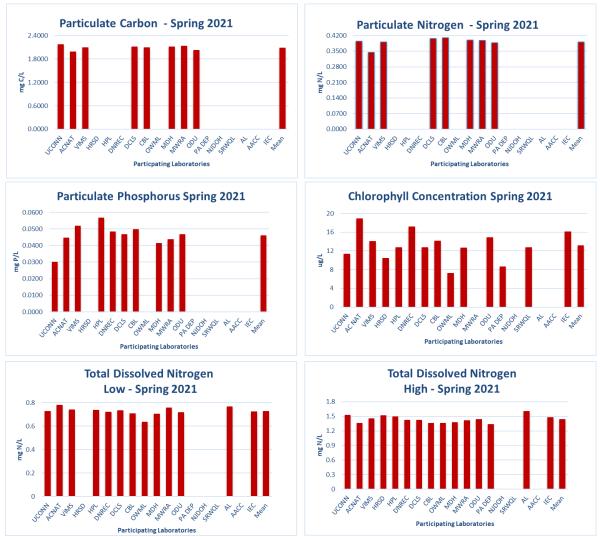


Figure 4. Particulate carbon, nitrogen and phosphorus; chlorophyll *a*, and total dissolved nitrogen. Spring 2021.

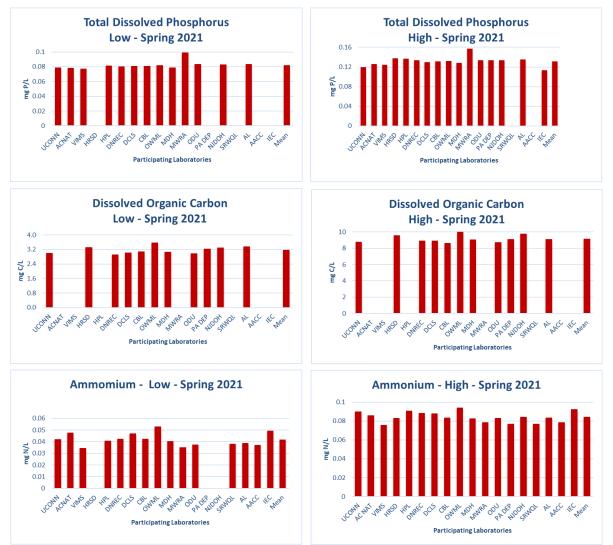


Figure 5. Total dissolved phosphorus; dissolved organic carbon, amd ammonium. Spring 2021.

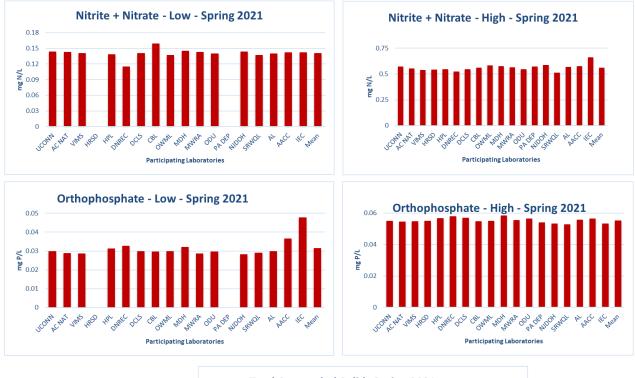




Figure 6. Nitrite plus nitrate, orthophosphate, and total suspended solids. Spring 2021.