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FINAL REPORT

CHESAPEAKE BAY PROGRAM BLIND AUDIT

Fiscal Year 2019 Final Report

PREPARED FOR:

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

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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, its tributaries, or similar systems. The concentrations of these samples, which are unknown to the recipient analysts, are compared to their prepared concentrations, or on 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/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 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 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 twenty-first 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 17 December 2018 and 14 May 2019. 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. The concentrates were sealed in 20 mL ampoules for shipment to participants. One ampoule contained a concentrate of an organic nitrogen compound and an organic phosphorus compound to be diluted for the analysis of low level total dissolved nitrogen and total dissolved phosphorus. A second ampoule contained a concentrate of an organic nitrogen compound and an organic phosphorus compound to be diluted for the analysis of higher level total dissolved nitrogen and total dissolved phosphorus. A 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 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 vacuum filtered (</= 10 in Hg, or 5 psi) from the batch sample with care taken to shake 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 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 utilized in those participants' coolers.

RESULTS

Tables and figures summarizing results from the fall 2018 and spring 2019 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

<u>Total Dissolved Nitrogen:</u> Results from both the fall 2018 and spring 2019 audits were about as in past audits, with one laboratory reporting a concentration that was not close to other participants for the fall 2018 low concentration sample. This laboratory produced a result that was again at the extreme for the higher concentration samples but the value was in closer agreement with the other participants. This laboratory produced high results for the spring 2019 survey as well, but one lab reported a higher result at each concentration level.

<u>Total Dissolved Phosphorus:</u> Most reported concentrations for both fall 2018 and spring 2019 samples were consistently close to other laboratories' reported concentrations. The low concentration values reported for fall 2018 had a higher degree of variability than the other three sets of data for this parameter.

<u>Ammonium</u>: All reported concentrations for both audits were consistently close to other laboratories' reported concentrations. At least one lab stood out each audit with a reported result that differed noticeably from the cohort. For the fall 2018 high concentration sample three laboratories reported such values.

<u>Nitrate + Nitrite:</u> Particularly good agreement was found among most laboratories for both concentration levels, for both audits. The expected and mean concentrations for each of the four sets were as follows: fall 2018 low concentration 0.1467/0.1401 mg N/L, fall 2018 high concentration 0.4869/0.4902 mg N/L, spring 2019 low 0.0714/0.0701 mg N/L, and spring 2019 high 0.5718/0.5743 mg N/L.

<u>Orthophosphate:</u> Good agreement was found among most laboratories for both low level and high level concentrations for both fall 2018 and spring 2019 audits, but with one or two (spring 2018, high) participants producing results not in good agreement with the group as a whole. It should be noted that the coefficient of variation for both concentration levels for spring 2019 were anomalously high (39% and 44%) but that these drop to 6.6% and 4.8% if the results of one laboratory are excluded.

<u>Dissolved Organic Carbon:</u> Particularly good agreement was found among all laboratories for low and high concentrations for both audits.

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> Among laboratory agreement was close for the fall 2018 and spring 2019, with coefficients of variation of 9.9% and 9.0%, but were still slightly higher than the previous Blind Audit (FY2018, 5-9%).

<u>Particulate Nitrogen:</u> Results for particulate nitrogen followed the same pattern as particulate carbon for both audits with coefficients of variation 12.3 – 15.9%. Again, as with carbon, these results varied more than those of the previous audit, 7-10%.

<u>Particulate Phosphorus:</u> Particulate phosphorus concentrations showed some variability between the participating laboratories with one laboratory reporting a substantially different concentration from the other participants for the fall 2018 audit and a different laboratory doing the same for the spring 2019 audit.

<u>Chlorophyll a:</u> Most chlorophyll a results for the fall 2018 and spring 2019 audits displayed the degree of variability expected for a multi-laboratory comparison of low concentrations of an environmentally transitory compound. The coefficients of variation were 25.3% for the fall/fall 2016 samples and 26.2% for the spring/spring 2018 samples. It should be noted that this drops to 15.1% for the fall 2018 set when the results of two laboratories' are excluded, and 11.4% for spring 2019 when four laboratories' results are excluded. The results excluded in this comparison were two or more standard deviations from the mean of all results.

<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 fall 2018 sample, 57.5 mg/L was prepared and for the spring 2019 sample, 83.4 mg/L was prepared, obtaining coefficients of variation only 4.5-7.6% for each audit.

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 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 three 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, spring 2016 reported data based on comparisons with other participants, the low level ammonium mean was 0.0189 mg N/L, S.D. 0.0035, C.V. 19%.

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.

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 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 fall 2018 high level total dissolved phosphorus sample was suspiciously high; fifteen of the sixteen submitting results. However the coefficient of variation was 6.4% for this group of data. It can be stated with confidence that there was most likely preparation error with this sample, rendering the expected concentration moot.

Overall there were twenty-five 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. These are listed for the individual laboratories in Appendix 1.

<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 2018 and spring 2019 audits.

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 spring 2013 was approximately 2.35 mg C/L. Particulate phosphorus in spring 2014 was 0.0091 mg P/L and in spring 1999 was 0.0529 mg P/L.

Reporting Data Accurately: 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 2019. Results were reported late, or reported and then later corrected

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 2019 participants reported only two significant digits for some analytes, thus potentially giving substantial under or over estimates for the comparisons.

CONCLUSION

Now that forty-three 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.

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, with fall 2018 showing better agreement across the cohort of participants.

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 2018 and spring 2019 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 2018 and spring 2019 blind audits, a few results were reported with insufficient significant digits. For the fall 2018 and spring 2019 blind audits, some results were reported late, or reported and subsequently corrected. It is hoped that corrections of these lapses have served as reminders of the importance to continuously check many aspects of sample preparation and data management to ensure overall data quality

Table 1. Participants in Fall 2018 and Spring 2019 Blind Audit Program.

Participant Institution	Point of Contact	Phone	Email
Old Dominion University, Water Quality Laboratory (ODU)	Suzanne Doughton	757-451-3044	sdoughte@odu.edu
University of Maryland, Horn Point Laboratory (HPL)	Erica Kiss	410-221-8317	ekiss@umces.edu
Virginia Institute of Marine Science, Analytical Service Center (VIMS)	Carol Pollard	804-684-7213	pollard@vims.edu
Virginia Division of Consolidated Laboratory Services (DCLS)	Jay Armstrong	804-648-4480 x328	jay.armstrong@dgs.virginia.gov
Maryland Department of Health (MDH)	Shala Ameli	410-767-6190	shahla.ameli@maryland.gov
University of Maryland Chesapeake Biological Laboratory (CBL)	Jerry Frank	410-326-7252	frank@umces.edu
Delaware Department of Natural Resources (DNREC)	Cathy Sim Kathy Knowles	302-739-9276	catherine.sim@state.de.us kathy.knowles@state.de.us
Academy of Natural Science of Philadelphia (ACNAT)	Paul Kiry	215-299-1076	kiry@ansp.org
Pennsylvania DEP, Bureau of Laboratories (PADEP)	Jennifer Fesler Anthony Friedline	717-346-8232	jenfesler@pa.gov anfriedlin@pa.gov
Massachusetts Water Resources Authority, Central Laboratory (MWRA)	Jennifer Constantino	617-660-7808	jennifer.constantino@mwra.com
Hampton Roads Sanitation District, Central Environmental Laboratory (HRSD)	Reggie Morgan Angelina Moore	757-460-4210 757-460-4261	rmorgan@hrsd.com amoore@hrsd.com
Occoquan Watershed Monitoring Lab (OWML)	Dongmei Wang	703-361-5606	dongmw4@vt.edu
University of Connecticut Center for Environmental Science & Engineering (UCONN)	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 (SRWQL)	Jeff Wyant	541-783-2149	jeff.wyant@klamathtribes.com
Microbac Laboratories Inc. (MICRO)	Vassiliki Shinas Mike Arbaugh	410-633-1800	Vassiliki.Shinas@microbac.com Mike.Arbaugh@microbac.com
University of Maryland Appalachian Laboratory (AL)	Katie Kline	301-689-7122	kkline@al.umces.edu
Department of Energy and the Environment (DOEE)	AI Robertson	410-305-2643	Robertson.AI@epa.gov
Anne Arundel County Community College Environmental Cntr (AACC)	Tammy Domanski	443-994-9236	tldomanski@aacc.edu

Table 2. Summary of Mean Concentration and Standard Deviation for Each Group of Analytes in the Fall2019 and the Spring 2019 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	tions from N	lean
			<1	1-2	2-3	>3
	Mean	S.D.	PASS	PASS	WARN	FAIL
Fall 2019						
Total Dissolved Nitrogen	0.3413	0.0490	11	1	1	0
Total Dissolved Phosphorus	0.0262	0.0035	9	5	0	0
Total Dissolved Nitrogen	0.8397	0.0482	11	3	1	0
Total Dissolved Phosphorus	0.0695	0.0046	13	1	2	0
Ammonium	0.0621	0.0070	13	1	1	0
Nitrite+nitrate	0.1467	0.0149	12	1	1	0
Phosphate	0.0124	0.0021	11	3	1	0
Ammonium	0.2460	0.0385	15	2	1	0
Nitrite+nitrate	0.4869	0.0284	12	3	2	0
Phosphate	0.0375	0.0067	15	1	2	0
Dissolved Organic Carbon	4.14	0.23	10	1	1	0
Dissolved Organic Carbon	8.13	0.41	9	3	0	0
Total Suspended Solids	75.3	5.9	15	0	2	0
Chlorophyll	23.23	6.09	12	2	1	0
Particulate Carbon	2.0234	0.2102	9	0	1	0
Particulate Nitrogen	0.3545	0.0459	8	2	1	0
Particulate Phosphorus	0.0490	0.0045	9	1	1	0
Spring 2019						
Total Dissolved Nitrogen	0.2216	0.0346	11	1	1	0
Total Dissolved Phosphorus	0.0179	0.0015	8	6	0	0
Total Dissolved Nitrogen	0.6944	0.0646	12	1	2	0
Total Dissolved Phosphorus	0.0495	0.0038	10	6	0	0
Ammonium	0.0344	0.0086	14	0	0	1
Nitrite+nitrate	0.0714	0.0108	13	1	1	0
Phosphate	0.0171	0.0078	14	0	0	1
Ammonium	0.2573	0.0144	16	0	2	0
Nitrite+nitrate	0.5718	0.0213	13	3	1	0
Phosphate	0.0616	0.0247	17	0	0	1
Dissolved Organic Carbon	3.13	0.21	7	4	0	0
Dissolved Organic Carbon	8.04	0.38	6	5	0	0
Total Suspended Solids	55.1	2.6	16	0	0	1
Chlorophyll	14.48	3.92	11	3	1	0
Particulate Carbon	1.9396	0.1821	10	0	1	0
Particulate Nitrogen	0.2797	0.0468	8	2	1	0

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 2019			PASS	WARN	FAIL
Total Dissolved Nitrogen	0.3380	0.2570-0.4710	11	0	2
Total Dissolved Phosphorus	0.0210	0.0216-0.0321	2	6	6
Total Dissolved Nitrogen	0.8460	0.7690-0.9610	14	1	0
Total Dissolved Phosphorus	0.0590	0.0631-0.0806	1	12	3
Ammonium	0.0590	0.0500-0.0830	11	2	2
Nitrite+nitrate	0.1401	0.1340-0.1840	11	0	3
Phosphate	0.0119	0.0101-0.0180	7	6	2
Ammonium	0.2120	0.2130-0.3520	11	4	3
Nitrite+nitrate	0.4902	0.4460-0.5500	15	2	0
Phosphate	0.037	0.0285-0.0570	13	2	3
Dissolved Organic Carbon	3.999	3.75-4.70	11	1	0
Dissolved Organic Carbon	7.999	7.33-8.81	11	1	0
Total Suspended Solids	83.4	61.0-81.0	11	4	2
Spring 2019					
Total Dissolved Nitrogen	0.2120	0.1910-0.3150	12	0	2
Total Dissolved Phosphorus	0.0170	0.0158-0.0200	10	4	0
Total Dissolved Nitrogen	0.6790	0.6200-0.8480	13	1	1
Total Dissolved Phosphorus	0.0460	0.0440-0.0570	11	4	1
Ammonium	0.0340	0.0260-0.0605	6	6	3
Nitrite+nitrate	0.0701	0.0420-0.0912	9	4	2
Phosphate	0.0149	0.0136-0.0450	13	1	1
Ammonium	0.2540	0.2270-0.3020	16	2	0
Nitrite+nitrate	0.5743	0.5420-0.6300	17	0	0
Phosphate	0.0557	0.0500-0.1600	16	1	1
Dissolved Organic Carbon	2.997	2.80-3.49	9	2	0
Dissolved Organic Carbon	7.993	7.55-8.73	11	0	0
Total Suspended Solids	57.5	46.0-57.4	12	5	0

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

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.3070	Р	0.3380	90.8	0.2010	Р	0.2120	94.8
TDP (mg P/L)	0.0260	Р	0.0210	123.8	0.0190	Р	0.0170	111.8
TDN (mg N/L)	0.8190	Р	0.8460	96.8	0.6680	Р	0.6790	98.4
TDP (mg P/L)	0.0670	Р	0.0590	113.6	0.0500	Р	0.0460	108.7
NH4 (mg N/L)	0.0600	Р	0.0590	101.7	0.0260	Р	0.0340	76.5
NO23 (mg N/L)	0.1450	Р	0.1401	103.5	0.0660	Р	0.0701	94.2
PO4 (mg P/L)	0.0130	Р	0.0119	109.2	0.0150	Р	0.0149	100.7
NH4 (mg N/L)	0.2320	Р	0.2120	109.4	0.2570	Р	0.2540	101.2
NO23 (mg N/L)	0.4850	Р	0.4902	98.9	0.5520	Р	0.5743	96.1
PO4 (mg P/L)	0.0350	Р	0.037	94.3	0.0570	Р	0.0557	102.3
DOC (mg C/L)	4.16	Р	3.999	104.1	2.80	Р	2.997	93.4
DOC (mg C/L)	8.81	Р	7.999	110.1	7.60	Р	7.993	95.1
TSS (mg/L)	79.3	Р	83.4	95.1	55.6	Р	57.5	96.7
CHL (ug/L)	29.20	Р	NA	NA	16.10	Р	NA	NA
PC (mg C/L)	2.131	Р	NA	NA	2.10	Р	NA	NA
PN (mg N/L)	0.344	Р	NA	NA	0.27	Р	NA	NA
PP (mg P/L)	0.048	Р	NA	NA	0.034	Р	NA	NA
* No sample sen	t to participant -	sample i	not requested, para	meter or conce	ntration range not ro	outine		

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

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Academy of Natural Science of Philadelphia (ACNAT)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported	ł	Prepared	Percent
	Concentration		Concentration	Recovered	Concentration	<u>ו</u>	Concentration	Recovered
TDN (mg N/L)	0.3350	Р	0.3380	99.1	0.2020) P	0.2120	95.3
TDP (mg P/L)	0.0239	Р	0.0210	113.8	0.0186	βP	0.0170	109.4
TDN (mg N/L)	0.8610	Р	0.8460	101.8	0.6420) P	0.6790	94.6
TDP (mg P/L)	0.0663	Р	0.0590	112.4	0.0454	1 P	0.0460	98.7
NH4 (mg N/L)	0.0588	Р	0.0590	99.7	0.033	7 P	0.0340	99.1
NO23 (mg N/L)	0.1410	Р	0.1401	100.6	0.0709	P	0.0701	101.1
PO4 (mg P/L)	0.0102	Р	0.0119	85.7	0.016 [,]	I P	0.0149	108.1
NH4 (mg N/L)	0.2260	Р	0.2120	106.6	0.2600) P	0.2540	102.4
NO23 (mg N/L)	0.4900	Р	0.4902	100.0	0.5660) P	0.5743	98.6
PO4 (mg P/L)	0.0339	Р	0.037	91.4	0.055	I P	0.0557	98.9
DOC (mg C/L)	*	*	3.999	*		* *	2.997	*
DOC (mg C/L)	*	*	7.999	*		* *	7.993	*
TSS (mg/L)	*	*	83.4	*	55.4	1 P	57.5	96.3
CHL (ug/L)	27.80	Р	NA	NA	17.10) P	NA	NA
PC (mg C/L)	1.51	W	NA	NA	1.46	6 W	NA	NA
PN (mg N/L)	0.267	Р	NA	NA	0.20) P	NA	NA
PP (mg P/L)	0.0453	Р	NA	NA	0.0399) P	NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported Concentration		Prepared Concentration	Percent Recovered	Reported Concentration		Prepared Concentration	Percent Recovered
TDN (mg N/L)	0.3654	Р	0.3380	108.1	0.2172	Р	0.2120	102.5
TDP (mg P/L)	0.0248	P	0.0210	118.1	0.0158	P	0.0170	92.9
TDN (mg N/L)	0.8934	P	0.8460	105.6	0.6729	P	0.6790	99.1
TDP (mg P/L)	0.0686	Р	0.0590	116.3	0.0465	Р	0.0460	101.1
NH4 (mg N/L)	0.0621	Р	0.0590	105.3	0.0274	Р	0.0340	80.6
NO23 (mg N/L)	0.1534	Р	0.1401	109.5	0.0653	Р	0.0701	93.2
PO4 (mg P/L)	0.0111	Р	0.0119	93.3	0.0136	Р	0.0149	91.3
NH4 (mg N/L)	0.2315	Р	0.2120	109.2	0.2558	Р	0.2540	100.7
NO23 (mg N/L)	0.5485	W	0.4902	111.9	0.5460	Р	0.5743	95.1
PO4 (mg P/L)	0.0352	Р	0.037	94.9	0.0566	Р	0.0557	101.6
DOC (mg C/L)	*	*	3.999	*	*	*	2.997	*
DOC (mg C/L)	*	*	7.999	*	*	*	7.993	*
TSS (mg/L)	79.2	Р	83.4	95.0	56.3	Р	57.5	97.9
CHL (ug/L)	29.15	Р	NA	NA	20.71	Р	NA	NA
PC (mg C/L)	2.2330	Р	NA	NA	*	*	NA	NA
PN (mg N/L)	0.3280	Р	NA	NA	*	*	NA	NA
PP (mg P/L)	0.0519	Р	NA	NA	0.0282	Р	NA	NA
* No sample sen	t to participant -	sample i	not requested, para	meter or concer	tration range not ro	utine		

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

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Hampton Roads Sanitation District, Central Environmetal Laboratory (HRSD)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	*	*	0.3380	*	*	*	0.2120	*
TDP (mg P/L)	*	*	0.0210	*	*	*	0.0170	*
TDN (mg N/L)	0.8690	Р	0.8460	102.7	0.8480	W	0.6790	124.9
TDP (mg P/L)	0.0690	Р	0.0590	116.9	0.0440	Р	0.0460	95.7
NH4 (mg N/L)	*	*	0.0590	*	*	*	0.0340	*
NO23 (mg N/L)	*	*	0.1401	*	*	*	0.0701	*
PO4 (mg P/L)	*	*	0.0119	*	*	*	0.0149	*
NH4 (mg N/L)	0.2260	Р	0.2120	106.6	0.2500	Р	0.2540	98.4
NO23 (mg N/L)	0.4490	Р	0.4902	91.6	0.5420	Р	0.5743	94.4
PO4 (mg P/L)	0.0360	Р	0.0371	97.0	0.0520	Р	0.0557	93.4
DOC (mg C/L)	4.11	Р	3.999	102.8	3.05	Р	2.997	101.8
DOC (mg C/L)	7.94	Р	7.999	99.3	7.55	Р	7.993	94.5
TSS (mg/L)	73.7	Р	83.4	88.4	57.4	Р	57.5	99.8
CHL (ug/L)	20.50	Р	NA	NA	5.95	W	NA	NA
PC (mg C/L)	*	*	NA	NA	*	*	NA	NA
PN (mg N/L)	*	*	NA	NA	*	*	NA	NA
PP (mg P/L)	*	*	NA	NA	*	*	NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine

University of Maryland, Horn Point Laboratory (HPL)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.3350	Р	0.3380	99.1	0.2170	Р	0.2120	102.4
TDP (mg P/L)	0.0261	Р	0.0210	124.3	0.0183	Р	0.0170	107.6
TDN (mg N/L)	0.8390	Р	0.8460	99.2	0.6820	Р	0.6790	100.4
TDP (mg P/L)	0.0716	Р	0.0590	121.4	0.0522	Р	0.0460	113.5
NH4 (mg N/L)	0.0613	Р	0.0590	103.9	0.0310	Р	0.0340	91.2
NO23 (mg N/L)	0.1390	Р	0.1401	99.2	0.0701	Р	0.0701	100.0
PO4 (mg P/L)	0.0110	Р	0.0119	92.4	0.0143	Р	0.0149	96.0
NH4 (mg N/L)	0.2330	Р	0.2120	109.9	0.2670	Р	0.2540	105.1
NO23 (mg N/L)	0.4900	Р	0.4902	100.0	0.5720	Р	0.5743	99.6
PO4 (mg P/L)	0.0357	Р	0.037	96.2	0.0569	Р	0.0557	102.2
DOC (mg C/L)	*	*	3.999	*	*	*	2.997	*
DOC (mg C/L)	*	*	7.999	*	*	*	7.993	*
TSS (mg/L)	79.7	Р	83.4	95.6	55.8	Р	57.5	97.0
CHL (ug/L)	24.40	Р	NA	NA	13.80	Р	NA	NA
PC (mg C/L)	*	*	NA	NA	2.0400	Р	NA	NA
PN (mg N/L)	0.3510	Р	NA	NA	0.2890	Р	NA	NA
PP (mg P/L)	0.0594	W	NA	NA	0.0331	Р	NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Delaware Department of Natural Resources (DNREC)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	 Concentration		Concentration	Recovered
TDN (mg N/L)	0.3320	Р	0.3380	98.2	0.2080	Р	0.2120	98.1
TDP (mg P/L)	0.0310	Р	0.0210	147.6	0.0173	Р	0.0170	101.8
TDN (mg N/L)	0.8180	Р	0.8460	96.7	0.6600	Р	0.6790	97.2
TDP (mg P/L)	0.0710	Р	0.0590	120.3	0.0504	Р	0.0460	109.6
NH4 (mg N/L)	0.0670	Р	0.0590	113.6	0.0384	Р	0.0340	112.9
NO23 (mg N/L)	0.1730	Р	0.1401	123.5	0.0820	Р	0.0701	117.0
PO4 (mg P/L)	0.0140	Р	0.0119	117.6	0.0161	Р	0.0149	108.1
NH4 (mg N/L)	0.3520	W	0.2120	166.0	0.2570	Р	0.2540	101.2
NO23 (mg N/L)	0.5500	W	0.4902	112.2	0.5830	Р	0.5743	101.5
PO4 (mg P/L)	0.0380	Р	0.037	102.4	0.0590	Р	0.0557	105.9
DOC (mg C/L)	4.00	Р	3.999	100.0	3.20	Р	2.997	106.8
DOC (mg C/L)	7.90	Р	7.999	98.8	8.17	Р	7.993	102.2
TSS (mg/L)	79.6	Р	83.4	95.4	56.5	Р	57.5	98.3
CHL (ug/L)	30.55	Р	NA	NA	18.10	Р	NA	NA
PC (mg C/L)	1.8400	Р	NA	NA	1.8800	Р	NA	NA
PN (mg N/L)	0.3360	Р	NA	NA	0.2840	Р	NA	NA
PP (mg P/L)	0.0460	Р	NA	NA	0.0285	Р	NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine

Division of Consolidated Laboratory Services (DCLS)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.3660	Р	0.3380	108.3	0.2200	Р	0.2120	103.8
TDP (mg P/L)	0.0270	Р	0.0210	128.6	0.0160	Р	0.0170	94.1
TDN (mg N/L)	0.8530	Р	0.8460	100.8	0.6840	Р	0.6790	100.7
TDP (mg P/L)	0.0670	Р	0.0590	113.6	0.0480	Р	0.0460	104.3
NH4 (mg N/L)	0.0640	Р	0.0590	108.5	0.0290	Р	0.0340	85.3
NO23 (mg N/L)	0.1390	Р	0.1401	99.2	0.0710	Р	0.0701	101.3
PO4 (mg P/L)	0.0120	Р	0.0119	100.8	0.0140	Р	0.0149	94.0
NH4 (mg N/L)	0.2370	Р	0.2120	111.8	0.2560	Р	0.2540	100.8
NO23 (mg N/L)	0.4860	Р	0.4902	99.1	0.5780	Р	0.5743	100.6
PO4 (mg P/L)	0.0370	Р	0.037	99.7	0.0500	Р	0.0557	89.8
DOC (mg C/L)	4.06	Р	3.999	101.5	3.11	Р	2.997	103.8
DOC (mg C/L)	7.91	Р	7.999	98.9	7.96	Р	7.993	99.6
TSS (mg/L)	78.0	Р	83.4	93.5	57.0	Р	57.5	99.1
CHL (ug/L)	18.20	Р	NA	NA	15.20	Р	NA	NA
PC (mg C/L)	2.1100	Р	NA	NA	1.9800	Р	NA	NA
PN (mg N/L)	0.3390	Р	NA	NA	0.2840	Р	NA	NA
PP (mg P/L)	0.0486	Р	NA	NA	0.0272	Р	NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Unversity of Maryland, Chesapeake Biological Laboratory (CBL)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019	1	Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reporte	b	Prepared	Percent
	Concentration		Concentration	Recovered	Concentratio	า	Concentration	Recovered
TDN (mg N/L)	0.3360	Р	0.3380	99.4	0.209) P	0.2120	98.6
TDP (mg P/L)	0.0234	Р	0.0210	111.4	0.015	3 P	0.0170	92.9
TDN (mg N/L)	0.8540	Р	0.8460	100.9	0.681) P	0.6790	100.3
TDP (mg P/L)	0.0685	Р	0.0590	116.1	0.048	3 P	0.0460	106.1
NH4 (mg N/L)	0.0590	Р	0.0590	100.0	0.036) P	0.0340	105.9
NO23 (mg N/L)	0.1530	Р	0.1401	109.2	0.091	2 P	0.0701	130.1
PO4 (mg P/L)	0.0111	Р	0.0119	93.3	0.015	2 P	0.0149	102.0
NH4 (mg N/L)	0.2440	Р	0.2120	115.1	0.265) P	0.2540	104.3
NO23 (mg N/L)	0.4820	Р	0.4902	98.3	0.583	5 P	0.5743	101.6
PO4 (mg P/L)	0.0385	Р	0.037	103.8	0.058	1 P	0.0557	104.3
DOC (mg C/L)	4.27	Р	3.999	106.8	3.1	3 P	2.997	104.4
DOC (mg C/L)	8.17	Р	7.999	102.1	8.2	5 P	7.993	103.2
TSS (mg/L)	80.5	Р	83.4	96.5	55.) P	57.5	95.7
CHL (ug/L)	19.40	Р	NA	NA	15.3	3 P	NA	NA
PC (mg C/L)	2.0600	Р	NA	NA	2.070) P	NA	NA
PN (mg N/L)	0.3465	Р	NA	NA	0.283	5 P	NA	NA
PP (mg P/L)	0.0500	Р	NA	NA	0.027	5 P	NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.4710	W	0.3380	139.3	0.2760	Р	0.2120	130.2
TDP (mg P/L)	0.0300	Р	0.0210	142.9	0.0160	Р	0.0170	94.1
TDN (mg N/L)	0.9610	W	0.8460	113.6	0.8340	W	0.6790	122.8
TDP (mg P/L)	0.0800	W	0.0590	135.6	0.0500	Р	0.0460	108.7
NH4 (mg N/L)	0.0830	W	0.0590	140.7	0.0410	Р	0.0340	120.6
NO23 (mg N/L)	0.1840	W	0.1401	131.3	0.0800	Р	0.0701	114.1
PO4 (mg P/L)	0.0150	Р	0.0119	126.1	0.0160	Р	0.0149	107.4
NH4 (mg N/L)	0.3230	Р	0.2120	152.4	0.2660	Р	0.2540	104.7
NO23 (mg N/L)	0.4580	Р	0.4902	93.4	0.6300	W	0.5743	109.7
PO4 (mg P/L)	0.0570	W	0.037	153.6	0.0540	Р	0.0557	96.9
DOC (mg C/L)	3.75	Р	3.999	93.8	2.90	Р	2.997	96.7
DOC (mg C/L)	7.33	Р	7.999	91.6	7.61	Р	7.993	95.2
TSS (mg/L)	77.8	Р	83.4	93.3	54.9	Р	57.5	95.5
CHL (ug/L)	25.00	Р	NA	NA	9.74	Р	NA	NA
PC (mg C/L)	2.0100	Р	NA	NA	1.8830	Р	NA	NA
PN (mg N/L)	0.4490	W	NA	NA	0.3842	Р	NA	NA
PP (mg P/L)	*	Р	NA	NA	*	*	NA	NA

Virginia Polytechnic Institute, Occoquan Watershed Monitoring Laboratory (OWML)

* No sample sent to participant - sample not requested, parameter or concentration range not routine "W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Maryland Department of Health (MDH)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.3300	Р	0.3380	97.6	0.2030	Р	0.2120	95.8
TDP (mg P/L)	0.0216	Р	0.0210	102.9	0.0185	Р	0.0170	108.8
TDN (mg N/L)	0.8390	Р	0.8460	99.2	0.6450	Р	0.6790	95.0
TDP (mg P/L)	0.0631	Р	0.0590	106.9	0.0440	Р	0.0460	95.7
NH4 (mg N/L)	0.0609	Р	0.0590	103.2	0.0270	Р	0.0340	79.4
NO23 (mg N/L)	0.1450	Р	0.1401	103.5	0.0780	Р	0.0701	111.3
PO4 (mg P/L)	0.0132	Р	0.0119	110.9	0.0158	Р	0.0149	106.0
NH4 (mg N/L)	0.2280	Р	0.2120	107.5	0.2530	Р	0.2540	99.6
NO23 (mg N/L)	0.5030	Р	0.4902	102.6	0.5870	Р	0.5743	102.2
PO4 (mg P/L)	0.0360	Р	0.037	97.0	0.0569	Р	0.0557	102.2
DOC (mg C/L)	3.97	Р	3.999	99.3	3.20	Р	2.997	106.8
DOC (mg C/L)	7.80	Р	7.999	97.5	8.00	Р	7.993	100.1
TSS (mg/L)	79.0	Р	83.4	94.7	54.8	Р	57.5	95.3
CHL (ug/L)	26.20	Р	NA	NA	17.50	Р	NA	NA
PC (mg C/L)	2.1300	Р	NA	NA	1.8400	Р	NA	NA
PN (mg N/L)	0.3660	Р	NA	NA	0.2140	Р	NA	NA
PP (mg P/L)	0.0440	Р	NA	NA	0.0263	Р	NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine

					Carlage 2010		Caring 2010		
	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019	
	Reported		Prepared	Percent	Reported	1	Prepared	Percent	
	Concentration		Concentration	Recovered	Concentration	1	Concentration	Recovered	
TDN (mg N/L)	0.3680	Р	0.3380	108.9	0.2110) P	0.2120	99.5	
TDP (mg P/L)	0.0321	Р	0.0210	152.9	0.0184	I P	0.0170	108.2	
TDN (mg N/L)	0.8460	Р	0.8460	100.0	0.7250) P	0.6790	106.8	
TDP (mg P/L)	0.0806	W	0.0590	136.6	0.0521	Р	0.0460	113.3	
NH4 (mg N/L)	0.0578	Р	0.0590	98.0	0.0360) P	0.0340	105.9	
NO23 (mg N/L)	0.1400	Р	0.1401	99.9	0.0678	B P	0.0701	96.7	
PO4 (mg P/L)	0.0132	Р	0.0119	110.9	0.0158	B P	0.0149	106.0	
NH4 (mg N/L)	0.2390	Р	0.2120	112.7	0.2550) P	0.2540	100.4	
NO23 (mg N/L)	0.4840	Р	0.4902	98.7	0.5570) P	0.5743	97.0	
PO4 (mg P/L)	0.0386	Р	0.037	104.0	0.0564	P	0.0557	101.3	
DOC (mg C/L)	*	*	3.999	*	لا	*	2.997	*	
DOC (mg C/L)	*	*	7.999	*	k.	* *	7.993	*	
TSS (mg/L)	70.0	Р	83.4	83.9	53.7	' P	57.5	93.4	
CHL (ug/L)	11.4	Р	NA	NA	8.96	6 P	NA	NA	
PC (mg C/L)	2.1800	Р	NA	NA	2.0700) P	NA	NA	
PN (mg N/L)	0.3660	Р	NA	NA	0.2810) P	NA	NA	
PP (mg P/L)	0.0448	Р	NA	NA	0.0236	6 P	NA	NA	
* No sample sen	* No sample sent to participant - sample not requested, parameter or concentration range not routine								

Massachusetts Water Resource Authority, Central Laboratory (MWRA)

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Old Dominion University, Water Quality Laboratory (ODU)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019)	Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reporte		Prepared	Percent
	Concentration		Concentration	Recovered	Concentratio	n	Concentration	Recovered
TDN (mg N/L)	0.3060	Р	0.3380	90.5	0.210	0 P	0.2120	99.1
TDP (mg P/L)	0.0246	Р	0.0210	117.1	0.017	3 P	0.0170	101.8
TDN (mg N/L)	0.7690	Р	0.8460	90.9	0.692	0 P	0.6790	101.9
TDP (mg P/L)	0.0670	Р	0.0590	113.6	0.050	0 P	0.0460	108.7
NH4 (mg N/L)	0.0587	Р	0.0590	99.5	0.028	1 P	0.0340	82.6
NO23 (mg N/L)	0.1360	Р	0.1401	97.1	0.070	3 P	0.0701	100.3
PO4 (mg P/L)	0.0111	Р	0.0119	93.3	0.014	5 P	0.0149	97.3
NH4 (mg N/L)	0.2210	Р	0.2120	104.2	0.254	0 P	0.2540	100.0
NO23 (mg N/L)	0.4770	Р	0.4902	97.3	0.574	0 P	0.5743	99.9
PO4 (mg P/L)	0.0355	Р	0.037	95.7	0.056	8 P	0.0557	102.0
DOC (mg C/L)	3.97	Р	3.999	99.3	2.9	4 P	2.997	98.1
DOC (mg C/L)	8.21	Р	7.999	102.6	7.9	2 P	7.993	99.1
TSS (mg/L)	73.1	Р	83.4	87.6	56.	4 P	57.5	98.1
CHL (ug/L)	25.30	Р	NA	NA	17.2	0 P	NA	NA
PC (mg C/L)	2.0300	Р	NA	NA	1.960	0 P	NA	NA
PN (mg N/L)	0.4070	Р	NA	NA	0.273	0 P	NA	NA
PP (mg P/L)	0.0480	Р	NA	NA	0.026	9 P	NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported	ł	Prepared	Percent
	Concentration		Concentration	Recovered	Concentration	า	Concentration	Recovered
TDN (mg N/L)	*	*	0.3380	*		* *	0.2120	*
TDP (mg P/L)	*	*	0.0210	*		* *	0.0170	*
TDN (mg N/L)	0.8000	Р	0.8460	94.6	0.6200) P	0.6790	91.3
TDP (mg P/L)	0.0680	Р	0.0590	115.3	0.0570) P	0.0460	123.9
NH4 (mg N/L)	*	*	0.0590	*		* *	0.0340	*
NO23 (mg N/L)	*	*	0.1401	*		* *	0.0701	*
PO4 (mg P/L)	*	*	0.0119	*		* *	0.0149	*
NH4 (mg N/L)	0.2200	Р	0.2120	103.8	0.2450) P	0.2540	96.5
NO23 (mg N/L)	0.4900	Р	0.4902	100.0	0.5800) P	0.5743	101.0
PO4 (mg P/L)	0.0380	Р	0.037	102.4	0.0540) P	0.0557	96.9
DOC (mg C/L)	4.18	Р	3.999	104.5	3.16	6 P	2.997	105.4
DOC (mg C/L)	7.96	Р	7.999	99.5	8.08	3 P	7.993	101.1
TSS (mg/L)	63.0	W	83.4	75.5	46.0) F	57.5	80.0
CHL (ug/L)	22.70	Р	NA	NA	11.60) P	NA	NA
PC (mg C/L)	*	*	NA	NA		* *	NA	NA
PN (mg N/L)	*	*	NA	NA		* *	NA	NA
PP (mg P/L)	*	*	NA	NA		* *	NA	NA

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

* No sample sent to participant - sample not requested, parameter or concentration range not routine

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

New Jersey Department of HeathIth (NJDH)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	*	*	0.3380	*	*	*	0.2120	*
TDP (mg P/L)	0.0306	Р	0.0210	145.7	0.0193	Р	0.0170	113.5
TDN (mg N/L)	*	*	0.8460	*	*	*	0.6790	*
TDP (mg P/L)	0.0692	Р	0.0590	117.3	0.0458	Р	0.0460	99.6
NH4 (mg N/L)	0.0604	Р	0.0590	102.4	0.0293	Р	0.0340	86.2
NO23 (mg N/L)	0.1340	Р	0.1401	95.6	0.0789	Р	0.0701	112.6
PO4 (mg P/L)	0.0101	Р	0.0119	84.9	0.0138	Р	0.0149	92.6
NH4 (mg N/L)	0.2300	Р	0.2120	108.5	0.2470	Р	0.2540	97.2
NO23 (mg N/L)	0.4770	Р	0.4902	97.3	0.5900	Р	0.5743	102.7
PO4 (mg P/L)	0.0285	Р	0.037	76.8	0.0509	Р	0.0557	91.4
DOC (mg C/L)	4.70	W	3.999	117.5	3.49	Р	2.997	116.4
DOC (mg C/L)	8.72	Р	7.999	109.0	8.55	Р	7.993	107.0
TSS (mg/L)	81.0	Р	83.4	97.1	55.6	Р	57.5	96.7
CHL (ug/L)	*	*	NA	NA	*	*	NA	NA
PC (mg C/L)	*	*	NA	NA	*	*	NA	NA
PN (mg N/L)	*	*	NA	NA	*	*	NA	NA
PP (mg P/L)	*	*	NA	NA	*	*	NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	0.3280	Р	0.3380	97.0	0.3150	W	0.2120	148.6
TDP (mg P/L)	0.0233	Р	0.0210	111.0	0.0200	Р	0.0170	117.6
TDN (mg N/L)	0.7800	Р	0.8460	92.2	0.6960	Р	0.6790	102.5
TDP (mg P/L)	0.0674	Р	0.0590	114.2	0.0540	Р	0.0460	117.4
NH4 (mg N/L)	0.0611	Р	0.0590	103.6	0.0370	Р	0.0340	108.8
NO23 (mg N/L)	0.1350	Р	0.1401	96.4	0.0680	Р	0.0701	97.0
PO4 (mg P/L)	0.0105	Р	0.0119	88.2	0.0140	Р	0.0149	94.0
NH4 (mg N/L)	0.2210	Р	0.2120	104.2	0.2570	Р	0.2540	101.2
NO23 (mg N/L)	0.4640	Р	0.4902	94.7	0.5680	Р	0.5743	98.9
PO4 (mg P/L)	0.0349	Р	0.037	94.1	0.0600	Р	0.0557	107.7
DOC (mg C/L)	*	*	3.999	*	*	*	2.997	*
DOC (mg C/L)	*	*	7.999	*	*	*	7.993	*
TSS (mg/L)	75.8	Р	83.4	90.9	56.7	Р	57.5	98.6
CHL (ug/L)	27.65	Р	NA	NA	15.70	Р	NA	NA
PC (mg C/L)	*	*	NA	NA	*	*	NA	NA
PN (mg N/L)	*	*	NA	NA	*	*	NA	NA
PP (mg P/L)	*	*	NA	NA	*	*	NA	NA

Sprague River Water Quality Laboratory (SRWQL)

* No sample sent to participant - sample not requested, parameter or concentration range not routine

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Microbac (MICRO)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	*	*	0.3380	*	*	*	0.2120	*
TDP (mg P/L)	*	*	0.0210	*	*	*	0.0170	*
TDN (mg N/L)	*	*	0.8460	*	*	*	0.6790	*
TDP (mg P/L)	*	*	0.0590	*	*	*	0.0460	*
NH4 (mg N/L)	*	*	0.0590	*	*	*	0.0340	*
NO23 (mg N/L)	*	*	0.1401	*	*	*	0.0701	*
PO4 (mg P/L)	*	*	0.0119	*	*	*	0.0149	*
NH4 (mg N/L)	0.3000	Р	0.2120	141.5	*	*	0.2540	*
NO23 (mg N/L)	0.4460	Р	0.4902	91.0	*	*	0.5743	*
PO4 (mg P/L)	0.0300	Р	0.037	80.9	*	*	0.0557	*
DOC (mg C/L)	4.29	Р	3.999	107.3	*	*	2.997	*
DOC (mg C/L)	8.27	Р	7.999	103.4	*	*	7.993	*
TSS (mg/L)	61.0	W	83.4	73.1	*	*	57.5	*
CHL (ug/L)	11.00	W	NA	NA	*	*	NA	*
PC (mg C/L)	*	*	NA	NA	*	*	NA	*
PN (mg N/L)	*	*	NA	NA	*	*	NA	*
PP (mg P/L)	*	*	NA	NA	*	*	NA	*

* No sample sent to participant - sample not requested, parameter or concentration range not routine

Appendix 1 Cont'. Fall 2018 and Spring 2019 Reported Concentrations, Prepared Concentrations and Recoveries

	Fall 2018		Fall 2018	Fall 2018	Spring 2019)	Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reporte	d	Prepared	Percent
	Concentration		Concentration	Recovered	Concentratio	n	Concentration	Recovered
TDN (mg N/L)	0.2570	Р	0.3380	76.0	0.191	0 P	0.2120	90.1
TDP (mg P/L)	0.0220	Р	0.0210	104.8	0.020	0 P	0.0170	117.6
TDN (mg N/L)	0.7940	Р	0.8460	93.9	0.666	0 P	0.6790	98.1
TDP (mg P/L)	0.0680	Р	0.0590	115.3	0.053	9 P	0.0460	117.2
NH4 (mg N/L)	0.0670	Р	0.0590	113.6	0.035	1 P	0.0340	103.2
NO23 (mg N/L)	0.1370	Р	0.1401	97.8	0.069	5 P	0.0701	99.1
PO4 (mg P/L)	0.0130	Р	0.0119	109.2	0.016	7 P	0.0149	112.1
NH4 (mg N/L)	0.2520	Р	0.2120	118.9	0.258	0 P	0.2540	101.6
NO23 (mg N/L)	0.4980	Р	0.4902	101.6	0.567	0 P	0.5743	98.7
PO4 (mg P/L)	0.0500	Р	0.037	134.8	0.056	8 P	0.0557	102.0
DOC (mg C/L)	4.20	Р	3.999	105.0	3.4	2 P	2.997	114.1
DOC (mg C/L)	8.49	Р	7.999	106.1	8.7	3 P	7.993	109.2
TSS (mg/L)	76.5	Р	83.4	91.7	53.	8 P	57.5	93.6
CHL (ug/L)	*	*	NA	NA		* P	NA	NA
PC (mg C/L)	*	*	NA	NA	2.050	0 P	NA	NA
PN (mg N/L)	*	*	NA	NA	0.306	0 P	NA	NA
PP (mg P/L)	0.0530	Р	NA	NA	0.027	0 P	NA	NA
* No sample sent to participant - sample not requested, parameter or concentration range not routine								

University of Maryland Appalachian Laboratory (AL)

"W" Warn and "F" Fail based on standard deviation of all participants' reported concentrations

Department of Energy and Environment (DOEE)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	*	*	0.3380	*	*	*	0.2120	*
TDP (mg P/L)	*	*	0.0210	*	*	*	0.0170	*
TDN (mg N/L)	*	*	0.8460	*	*	*	0.6790	*
TDP (mg P/L)	*	*	0.0590	*	*	*	0.0460	*
NH4 (mg N/L)	0.0500	Р	0.0590	84.7	*	*	0.0340	*
NO23 (mg N/L)	*	*	0.1401	*	*	*	0.0701	*
PO4 (mg P/L)	0.0180	W	0.0119	151.3	*	*	0.0149	*
NH4 (mg N/L)	0.2130	Р	0.2120	100.5	0.2270	W	0.2540	89.4
NO23 (mg N/L)	*	*	0.4902	*	*	*	0.5743	*
PO4 (mg P/L)	0.0380	Р	0.037	102.4	0.0580	Р	0.0557	104.1
DOC (mg C/L)	*	*	3.999	*	*	*	2.997	*
DOC (mg C/L)	*	*	7.999	*	*	*	7.993	*
TSS (mg/L)	73.0	Р	83.4	87.5	56.0	Р	57.5	97.4
CHL (ug/L)	*	*	NA	NA	*	*	NA	NA
PC (mg C/L)	*	*	NA	NA	*	*	NA	NA
PN (mg N/L)	*	*	NA	NA	*	*	NA	NA
PP (mg P/L)	*	*	NA	NA	*	*	NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine

Anne Arundle County Community College Environmental Center (AACC)

	Fall 2018		Fall 2018	Fall 2018	Spring 2019		Spring 2019	Spring 2019
	Reported		Prepared	Percent	Reported		Prepared	Percent
	Concentration		Concentration	Recovered	Concentration		Concentration	Recovered
TDN (mg N/L)	*	*	0.3380	*	*	*	0.2120	*
TDP (mg P/L)	*	*	0.0210	*	*	*	0.0170	*
TDN (mg N/L)	*	*	0.8460	*	*	*	0.6790	*
TDP (mg P/L)	*	*	0.0590	*	*	*	0.0460	*
NH4 (mg N/L)	*	*	0.0590	*	0.0605	F	0.0340	177.9
NO23 (mg N/L)	*	*	0.1401	*	0.0420	W	0.0701	59.9
PO4 (mg P/L)	*	*	0.0119	*	0.0450	F	0.0149	302.0
NH4 (mg N/L)	*	*	0.2120	*	0.3020	F	0.2540	118.9
NO23 (mg N/L)	*	*	0.4902	*	0.5450	Р	0.5743	94.9
PO4 (mg P/L)	*	*	0.037	*	0.1600	F	0.0557	287.3
DOC (mg C/L)	*	*	3.999	*	*	*	2.997	*
DOC (mg C/L)	*	*	7.999	*	*	*	7.993	*
TSS (mg/L)	*	*	83.4	*	*	*	57.5	*
CHL (ug/L)	*	*	NA	NA	14.10	Р	NA	NA
PC (mg C/L)	*	*	NA	NA	*		NA	NA
PN (mg N/L)	*	*	NA	NA	*		NA	NA
PP (mg P/L)	*	*	NA	NA	*		NA	NA

* No sample sent to participant - sample not requested, parameter or concentration range not routine



Figure 1. Particulate carbon, nitrogen and phosphorus; chlorophyll *a*, and total dissolved nitrogen. Fall 2018

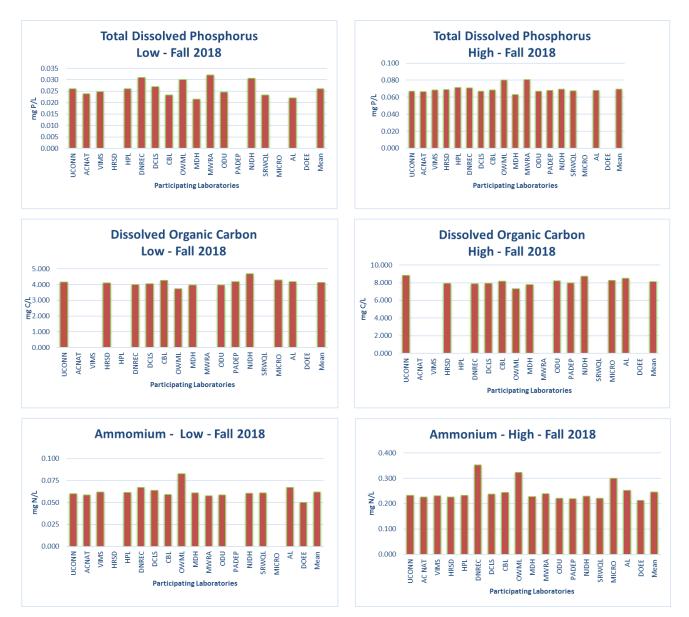
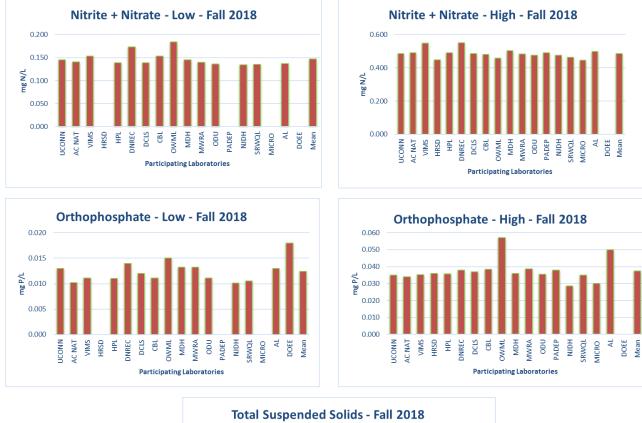


Figure 2. Total dissolved phosphorus; dissolved organic carbon, amd ammonium. Fall 2018



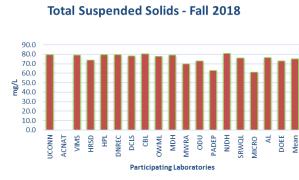
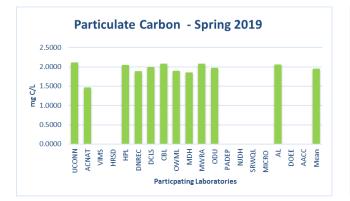
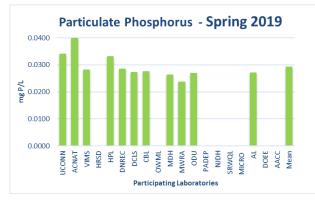
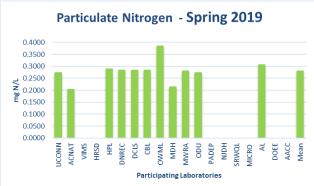
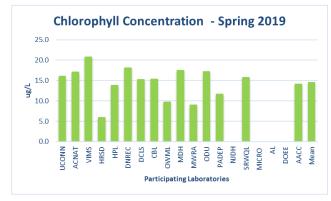


Figure 3. Nitrite plus nitrate, orthophosphate, and total suspended solids. Fall 2018









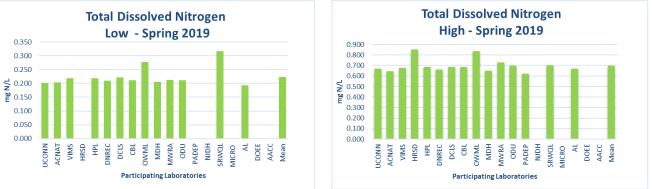
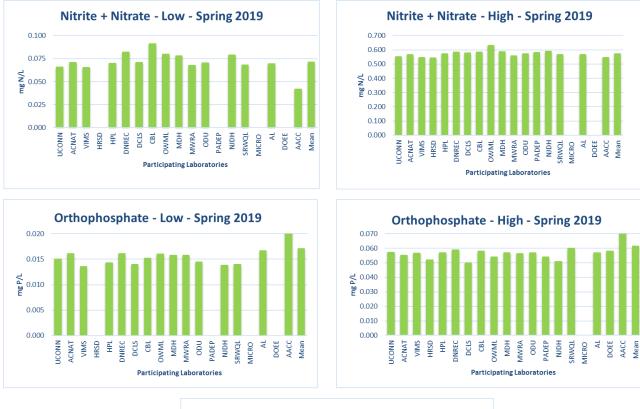


Figure 4. Particulate carbon, nitrogen and phosphorus; chlorophyll *a*, and total dissolved nitrogen. Spring 2019.



Figure 5. Total dissolved phosphorus; dissolved organic carbon, amd ammonium. Spring 2019.



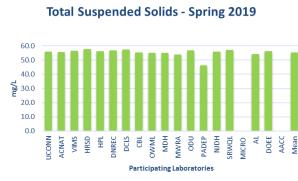


Figure 6. Nitrite plus nitrate, orthophosphate, and total suspended solids. Spring 2019.