



# **Quality Assurance Project Plan**

For the
Maryland Department of Natural Resources
Chesapeake Bay
Water Quality Monitoring ProgramChemical and Physical Properties Component
for the period July 1, 2022 - June 30, 2023

May 29, 2022 DRAFT

Maryland State Archives MSA Series S1468 MSA Schedule # 2813 Revision 28

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# **Quality Assurance Project Plan for the**

Maryland Department of Natural Resources Chesapeake Bay Water Quality Monitoring Program -Chemical and Physical Properties Component for the period July 1, 2022 - June 30, 2023

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#### **PREFACE**

This document is intended to describe in detail the activities conducted under the Chemical and Physical Properties Component of the Maryland Department of Natural Resources Chesapeake Bay Water Quality Monitoring Program. This is a coordinated program consisting of several components conducted in a similar manner for identical purposes in both the tributaries and Mainstem of Maryland's Chesapeake Bay. This program is funded through the Maryland Department of Natural Resources and the U.S. Environmental Protection Agency.

This Quality Assurance Project Plan is available on-line by using publication type 'Quality Assurance Project Plan' to search the Monitoring News and Reports page of the Maryland Department of Natural Resources (DNR) Eyes on the Bay website: http://eyesonthebay.dnr.maryland.gov

## **Version History**

QAPP Version	Date Approved	Changes Made
25	Pending	Grammatical changes only
26	Pending	Hard copies of Chesapeake Bay Laboratory NASL methods were replaced with online links to those methods.
27	Pending	Updated minimum detection limit for ammonium, nitrite and particulate phosphorus. Addition of CBL error codes 14a and 14b. Missing samples in March, April and May 2020 due to COVID-19
28	Pending	Appendix 7 Split Sample Custody Log updated. Appendix 9 lab codes updated.

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# **Quality Assurance Project Plan** for the

## Maryland Department of Natural Resources Chesapeake Bay

## Water Quality Monitoring Program— Chemical and Physical Properties Component for the period July 1, 2022 - June 30, 2023

May 29, 2022

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#### ACRONYMS AND ABBREVIATIONS

AA - Autoanalyzer

AP - Above pycnocline

ARS - Analysis Request Sheet

B - Bottom sample

BP - Below pycnocline OR barometric pressure

C - Carbon

CBP - EPA's Chesapeake Bay Program

CBPO - EPA's Chesapeake Bay Program Office

CBL - University of Maryland's Chesapeake Biological Laboratory

CIMS - Chesapeake Information Management System

cm - centimeter

CSSP - Coordinated Split Sample Program

DAWG - Data Analysis Workgroup

DI - De-ionized

DIWG - Data Integrity Workgroup (a Chesapeake Bay Program workgroup, formerly AMQAW -

Analytical Methods and Quality Assurance Workgroup)

DL - Detection Limit

DNR - Maryland Department of Natural Resources

DO - Dissolved oxygen

DOC - Dissolved organic carbon

EPA - U.S. Environmental Protection Agency

g - Gram

H<sub>2</sub>O - Dihydrogen oxide (water)

H<sub>2</sub>S - Hydrogen sulfide

HCl - Hydrochloric acid

ITAT - Integrated Trends Analysis Team

L – Liter

LDO - Luminescent Dissolved Oxygen

m - Meter

MASC - Chesapeake Bay Program Monitoring and Analysis Subcommittee

MDE - Maryland Department of the Environment

MDE - Maryland Department of Health

MDL – Minimum Detection Limit

MgCO<sub>3</sub> - Magnesium carbonate

mg - Milligram

ml - Milliliter

N - Nitrogen

NASL - Chesapeake Biological Laboratory, Nutrient Analytical Services Laboratory

NIST - National Institute of Standards and Technology

nm - Nanometer

no. - Number

NO<sub>2</sub> - Nitrite

NO<sub>23</sub> - Nitrate + nitrite

NO<sub>3</sub> - Nitrate

NTU - Nephelometric Turbidity Units

OD - Optical density

P - Phosphorus

PAR - Photosynthetic Active Radiation

PC - Particulate carbon

PIP - Particulate Inorganic Phosphorus

PN - Particulate nitrogen

PO<sub>4</sub> - Phosphate

PP - Particulate phosphorus

ppt - Parts per thousand

QAO -Quality Assurance Officer (unless otherwise noted, this refers to the DNR QAO)

QAPP - Quality Assurance Project Plan

ROX - YSI 6150 Reliable Oxygen Sensor

R/V - Research vessel

S - Surface sample

SAS - Statistic Analysis System

STAR - Scientific, Technical Assessment & Reporting

SIF - Silica

Si – Dissolved Silicate

SOP - Standard Operating Procedure

TMAW - Tidal Monitoring and Analysis Workgroup

TDN - Total dissolved nitrogen

TDP - Total dissolved phosphorus

TPP - Total Particulate Phosphorus

TSS - Total suspended solids

TVS - Total Volatile Solids

USDI - U.S. Department of the Interior

USGS - U.S. Geological Survey

μg - Microgram

VSS - Volatile Suspended Solids

YSI - Yellow Springs Instruments

°C - degrees Celsius

#### INTRODUCTION

## 1.1. Background

At the completion of the U.S. Environmental Protection Agency's (EPA's) \$27 million study of Chesapeake Bay, the Agency published a document entitled *Chesapeake Bay: A Framework for Action* (EPA 1983). This report strongly recommended a long-term water quality monitoring program to serve the Bay's management community by accurately describing the current state of the Bay Mainstem and tidal tributaries (baseline or 'status') and detecting long-term changes (trends) resulting from human activities. Management strategies at that time were hindered by the lack of precise information about the Bay and its response to increasing or decreasing pollution.

Managers, scientists, and statisticians recognized that to establish baseline conditions and then begin to identify trends would require a multi-year effort on the order of a decade or more. Long-term data were needed to overcome the natural year-to-year variability that can obscure changes due to human activities. As the EPA study drew to a close, scientists and managers convened in workshops to formulate plans on several topics, including water quality monitoring. The monitoring workshop recommendations for chemical and physical measurements were published in the appendices of *Chesapeake Bay: A Framework for Action*. The appendices described the chemical/physical monitoring plan in terms of station locations, parameters to be measured, and sampling frequency.

This Quality Assurance Project Plan (QAPP) describes Maryland's implementation of the coordinated Maryland, Virginia, and EPA Chesapeake Bay monitoring program as outlined in *Chesapeake Bay: A Framework for Action* (EPA 1983) and *Chesapeake Bay Program, Methods and Quality Assurance for Chesapeake Bay Water Quality Monitoring Programs* (CBP 2017). This part of Maryland's Chesapeake Bay Water Quality Monitoring Program is known as the "Chemical and Physical Properties Component" and covers monitoring in the Maryland portion of the Mainstem as well as the tidal tributaries. Other components of the water quality program measure biological and process-oriented indicators of water quality; those components are not described in this document.

## 1.2. Objectives

The Maryland Department of Natural Resources (DNR) uses the data generated by means of the procedures in this QAPP to meet the five water quality monitoring objectives of the Chesapeake Bay Water Quality Monitoring Program:

- 1. Characterize the present state of the Bay Mainstem and its tributaries, including spatial and seasonal variation, using key water quality indicators.
- 2. Determine long-term trends or changes in key water quality indicators in relation to pollution control programs.

- 3. Integrate the information collected in all components of the monitoring program to gain a more comprehensive understanding of water quality processes and the relationship between water quality and living resources.
- 4. Track the progress of management strategies to reduce nutrient pollution.
- 5. Provide data for the Chesapeake Bay watershed and ecological models.

## 1.3. Sampling Design and Data Quality Objectives

#### 1.3.1. Parameters

The scope of work for this component of the coordinated Chesapeake Bay Water Quality Monitoring Program includes the measurement of chemical and physical parameters in the water column. Parameters such as nutrients, total suspended solids, chlorophyll a, dissolved oxygen and water clarity were selected to (1) provide information on eutrophication trends; (2) calibrate Bay water quality models; and (3) correlate living resources data to water quality data. Other parameters such as salinity and temperature are necessary to provide a more rigorous interpretation of these key water quality indicators. The same parameters are collected in the Mainstem, large tributaries (Potomac and Patuxent Rivers), and minor tributaries except for dissolved organic carbon and silica.

5-Day biochemical oxygen demand, total alkalinity and turbidity samples will be collected at lower Potomac River stations: MAT0016, MAT0078, PIS0033, RET2.1, RET2.2, RET2.4, TF2.1, TF2.2, TF2.3, TF2.4 and XFB1986.

Dissolved organic carbon sample collection during Mainstem cruises was discontinued from 1996-2016. Beginning in May 2017, DOC sampling resumed at stations CB1.1, CB1.2, CB3.3C, CB4.3 and CB5.2. Mainstem DOC samples will be collected from March through September only.

Silica (SIF) samples will be collected monthly, from the surface and above pycnocline layers, January through June 2023 at the plankton sampling stations (CB1.1, CB2.2, CB3.3C, CB4.3C, CB5.2, TF2.3, RET2.2, TF1.5, LE1.1, ET5.1 and WT5.1). Silica samples will not be collected at any Mainstem or tributary stations July through December 2023.

Nutrient samples will be collected during the second Mainstem cruises in June and August 2022. Nutrient samples will not be collected during the second Mainstem cruise in July 2022.

In 2019, Maryland Senate Bill 546, Nutrient Management – Monitoring and Enforcement, reinstated monitoring at nine stations on the Eastern Shore (TRQ0146, TRQ0088, CCM0069, XDJ9007, XCI4078, BXK0031, POK0087, XAK7810, MNK0146). The start of the sampling period for these sites was in January and February 2020.

(A complete list of parameters measured, and detection limits is provided in Section 2, Table 3.)

The information gained from analyzing the entire suite of parameters allows managers to determine whether water quality goals established for living resources have been met and aids managers in establishing programs to control point and non-point sources of pollutants to the Bay.

### 1.3.2. Spatial Aspects

A total of 22 Mainstem stations and 69 tributary stations are included in Maryland's Chemical and Physical Properties Component of the Chesapeake Bay Water Quality Monitoring Program (Figure 1 and Table 1). Station locations were selected to provide data that would satisfy the five objectives of the program stated above for the major tributaries and the Mainstem. The following describes the four sets of criteria used to determine the general location for stations:

<u>Primary Selection Criteria</u>. During the initial phases of the Bay Program, EPA developed a segmentation/characterization scheme of the Chesapeake Bay and its tributaries published in the appendices of *Chesapeake Bay: A Profile of Environmental Change* (EPA 1983). This scheme provided guidance for station selection by delimiting different regions (based on circulation, salinity, and geomorphology) such as tidal fresh, oligohaline, and mesohaline. Several primary goals were considered in selecting station locations. Selecting a suite of stations such that each segment would be characterized was the foremost goal. Another important criterion was the location of boundaries between segments (e.g., mouths of major tributaries and the upper boundary of the deep trough region). Boundary areas are important because of their influence on a particular region of the Bay or their relevance to problem areas. In large systems, i.e., the Potomac and Patuxent Rivers and the Mainstem, multiple stations were located in some of the major salinity zones due to the large size of these systems and their importance to management concerns. Existing water quality monitoring stations in the Potomac River and Patuxent River were incorporated into the Baywide network because of the wealth of historical data at these stations.

<u>Secondary Selection Criteria</u>. Locations of documented water quality problems in certain areas served as secondary considerations in locating stations. For example, additional stations were included in the lateral dimension of the deep trough region of the Mainstem to characterize the deep water anoxic/hypoxic conditions. Another example was the siting of stations in some of the smaller tributary segments in areas that were profoundly impacted by point sources. Stations sited in these affected areas provide excellent opportunities to assess the effectiveness of control strategies targeted at reducing these major impacts.

<u>Tertiary Selection Criteria</u>. Another consideration in siting stations was their proximity to important living resource habitats and living resource monitoring sites. This criterion was accommodated only if the primary and secondary criteria above were also satisfied. These stations provide valuable data to correlate with living resources monitoring and thereby help to resolve the link between water quality and fluctuations in living resources.

<u>Final Selection Criteria</u>. The fourth and final consideration in locating stations was the historical record of water quality sampling. If a station already had a record of previous water quality data *and* it satisfied the three sets of criteria stated above, the station was adopted for this program to permit comparisons with historical databases. In selecting stations for the Patuxent and Potomac Rivers, this criterion was elevated to a primary criterion. Additional historical stations in the Patuxent and Potomac were adopted into the Chesapeake Bay Program sampling program even if they did not fulfill all three sets of criteria above, because of the very long-term data sets associated with these stations.

Establishing Mid-Channel and Near-shore Stations. In both the Mainstem and tributaries, stations were selected in mid-channel locations to provide a characterization of the entire water column in that region and to capture the lowered oxygen levels in the deeper layers. The water column at mid-channel also provides a more stable environment than shallow locations, which are subject to ephemeral influences such as wind-driven resuspension of bottom sediments and periodic advection of deep-channel water masses; thus, mid-channel stations provide data with less short-term variability. Minimizing short-term variability is desirable in order to detect long-term trends. As mentioned above, in the Mainstem's deep trough region, lateral stations were established to track a particular concern. Two near-shore stations were located beside each of the four mid-channel stations. These near-shore stations were located at the 30-foot depth contour or at the boundary of adjacent embayments. Stations also were located at the boundary between the Mainstem and the two largest tributaries in Maryland—the Susquehanna and Potomac Rivers—to assess the water quality interactions occurring across these critical regions.

Updating the Segmentation Scheme. During 1997, a workgroup was established to re-evaluate the segmentation scheme using the data generated by the program from 1985-1996. DNR uses the current segmentation scheme established by the EPA Chesapeake Bay Program (CBP) to classify stations and analyze data (see Table 1). Under the new segmentation scheme, three segments (CHOTF, NANOH and HNGMH) do not include long-term stations. The Chesapeake Bay Program, Analytical Segmentation Scheme, Revisions, Decisions and Rationales, 1983-2003, 2005 Addendum, and the Chesapeake Bay Program Monitoring and Analysis Subcommittee Tidal Monitoring and Analysis Workgroup, October 2004 document: Chesapeake Bay Program, Analytical Segmentation Scheme, Revisions, Decisions and Rationales 1983-2003 provide detailed descriptions of the CBP's segmentation and its development. Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll a for the Chesapeake Bay and Its Tidal Tributaries, 2008 Technical Support for Criteria Assessment Protocols Addendum summarizes previous segmentation work and documents recommended refinements of the segmentation scheme to address dissolved oxygen and water clarity assessment issues. More recently, the Technical Addendum Ambient Water Quality Criteria for Dissolved Oxygen, Water Clarity and Chlorophyll a for the Chesapeake Bay and It's Tidal Tributaries, 2017 Technical Addendum, provides previously undocumented features of the present procedures as well as refinements and clarifications to the previously published Chesapeake Bay water quality criteria assessment procedures (U.S. EPA 2004a, 2007a, 2007b, 2008, 2010).

Note that a total of eight addendum documents have been published by EPA since April 2003. Four addenda were published documenting detailed refinements to the criteria attainment and assessment procedures (U.S. EPA 2004a, 2007a, 2008, 2010) previously published in the original April 2003 Chesapeake Bay water quality criteria document (U.S. EPA 2003a). One addendum published Chesapeake Bay numerical chlorophyll a criterion (U.S. EPA 2007b). Three addenda addressed detailed issues involving further delineation of tidal water designated uses (U.S. EPA 2004b, 2005, 2010) building from the original October 2003 tidal water designated uses document (U.S. EPA 2003b). Finally, one addendum documented the 92-segment Chesapeake Bay segmentation scheme (U.S. EPA 2008) after refinements to the Chesapeake Bay Program analytical segmentation schemes were documented (U.S. EPA 2005) building from the original U.S. EPA 2004 document (U.S. EPA 2004b). The 2017 addendum is the eighth addendum document developed through the Partnership and published by EPA.

### 1.3.3. Temporal Aspects

Water column samples are collected at least once a month at most stations, for a total of twelve samplings per year. In the Chesapeake Mainstem, sampling will be conducted twice monthly in June, July and August of 2022, and once monthly during the remaining months, for a total of fifteen samplings in the period of July 1, 2022 - June 30, 2023. Sampling during the second bi-weekly July 2022 survey will be comprised of water-column profiles only. Eastern and western transect Mainstem station samples will not be collected from November through February, resulting in only eleven samplings a year. On the Potomac and Patuxent and smaller tributaries, twelve samplings will be conducted per year. See Appendix 13, Log of Significant Changes, for details. Sampling frequency for each station is shown in Table 1. This frequency of sampling permits assessments to be made on a seasonal basis, which is a time scale consistent with many of the natural intra-annual changes in water quality indicators.

Because of the relatively small sample sizes resulting from only two to four sampling events per season, it is more difficult to detect seasonal trends in data from stations sampled only once per month. Nevertheless, with a long-term program, sufficient data can be collected to determine seasonal patterns in most water quality parameters at each site with high statistical confidence.

At its inception in 1984, the Chesapeake Bay monitoring program included 20 cruises each year in the Mainstem, Patuxent, Potomac, and smaller tributaries. In 1994, *An Assessment of the Power and Robustness of the Chesapeake Bay Program Water Quality Monitoring Program: Phase II - Refinement Evaluations* (Alden et al. 1994) concluded that although the 12-cruise scenario was less statistically powerful than the 20-cruise scenario, the 12-cruise scenario was adequate for the Chesapeake Bay Mainstem monitoring to capture long-term annual trends; the Chesapeake Bay Program decided on a 14-cruise scenario for the monitoring program. Based on these recommendations, in January 1996, Maryland dropped its Chesapeake Bay Mainstem January and February cruises and reduced its cruises in March, June, September, and October to once per month. Experience has since shown that this reduced sampling frequency can miss some extremely important climatic and biological events (e.g., the 100-year flood of January 1996). Therefore, CBP restored funding in Maryland for its January and February monitoring cruises beginning in January 1999, for a total of 16 cruises. When funding was available, a second June Mainstem cruise was also added to the sample schedule to better characterize the onset of summer hypoxia/anoxia conditions in deep water.

In November 2009, EPA funding reductions resulted in a resumption of a fifteen-cruise scenario. The Mainstem was sampled monthly and there are second cruises in June, July and August. Vertical profiles were executed but nutrient samples were not always collected on the second cruises.

Beginning in January 2010, due to further funding reductions, the number of times samples were collected at all stations in embayments, large tributaries, smaller tributaries, C&D Canal and Tangier Sound were reduced from previous levels to twelve times per year.

Due to funding cutbacks, sample collection ended at nine tributary stations in December 2013, Chicamacomico River: CCM0069; Manokin River: BXK0031, MNK0146; Nanticoke River: XDJ9007; Pocomoke River: POK0087, XAK7810; Transquaking River: TRQ0088, TRQ0146; and Wicomico River: XCI4078. Funding was reinstated in 2019 and monitoring recommenced in 2020.

This level of sampling frequency is judged to be the optimal allocation of effort given the limited level of resources. It provides for wide spatial coverage of almost every major tributary in Maryland as well as for information on the major systems that are the focus of major management strategies.

Figure 1. Map of Maryland Department of Natural Resources Chesapeake Bay Mainstem and Bay Tributary Water Quality Monitoring Stations.

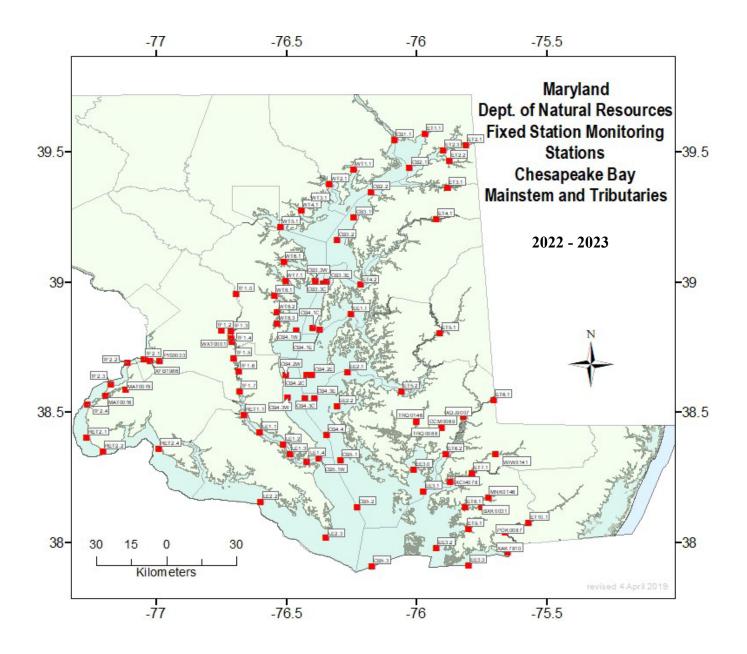


Table 1. Mainstem and Tributary sample locations and descriptions

						-			
Count	Station	Longitude	Latitude	Area	Ches.Bay Program Segment	Location/Depth	Sampling Coordination	Historical Station names	Annual Sample Freq. x No. Of Depths
1	CB1.1	-76.084808	39.54794	Mainstem	CBTF1	Mouth of Susquehanna River (700 yards from abandoned Light House on Hdg 040, 400 yards NNW of N 18 online with N 20); 5.7 m	PAR, VSS, plankton Mar - Nov whole water column composite live & fixed, DOC Mar-Nov	OEP XKH3147	15x2  14 sampling trips + 1 readings only
2	CB2.1	-76.025993	39.44149	Mainstem	CBTF1	SW of Turkey Point (1 nm from Turkey Pt Light on Hdg 240, 800 yards SE of RG A); 6.1m	PAR	CBI 927SS; OEP XJH6680	15x2  14 sampling trips + 1 readings only
3	CB2.2	-76.175789	39.34873	Mainstem	СВ2ОН	W of Still Pond (500 yards W of G 49, 1.75 nm S of Taylor Island Pt off Still Pond); 11.5m	PAR, VSS, plankton Mar- Nov whole water column composite live & fixed: Mar- Nov-whole water column composite picoplankton, DOC Mar-Sep	CBI 92OU, 921W, 922Y; OEP XJG0999	15x4  14 sampling trips + 1 readings only
4	CB3.1	-76.240501	39.2495	Mainstem	СВ2ОН	SE of Gunpowder Neck (2.1nm from south tip of Poole's Island Hdg 146, halfway between buoys 31 and 33); 11.2 m.	PAR	<b>CBI</b> 913R, 914S	15x4  14 sampling trips + 1 readings only
5	CB3.2	-76.306313	39.16369	Mainstem	СВЗМН	NW of Swan Pt (400 yards NW of Tolchester Channel 13,1.9 nm from Swam Point on Hdg 328); 11.5 m	PAR	CBI 909; OEP XHG4953, XHG9915	15x4 14 sampling trips + 1 readings only
6	CB3.3C	-76.359673	38.99596	Mainstem	СВЗМН	N of Bay Bridge (1.6 nm, from Sandy Pt Light on Hdg 145, 0.4 nm NNE of bridge at edge of cable cross). 20.7 m.	PAR, VSS, DNR plankton Jan-Dec- Above pycnocline composite-live & fixed. Jul- Sep-above pycnocline composite picoplankton, DOC Mar-Sep	CBI 858C, 859B; OEP XFH1373, XGF9784; EPA D2	15x4 14 sampling trips + 1 readings only
7	CB3.3E	-76.345169	39.00412	Mainstem	СВЗМН	NE of Bay Bridge (1.9nm from Sandy Pt Light on Hdg 260, 1 nm NNE of Bridge in East Channel); 8.2 m	PAR	CBI 859A; OEP XFH0293; EPA D3	11x2 Mar-Oct 10 sampling trips +1 readings only
8	CB3.3W	-76.3881	39.00462	Mainstem	СВЗМН	NW of Bay Bridge (0.7 nm from Sandy Pt Light on Hdg 210, 0.7 nm SE Sandy Pt Water Tank); 9.1m.	PAR	CBI 859D; OEP XHF0366; EPA D1	11x2 Mar-Oct 10 sampling trips +1 readings only

Count	Station	Longitude	Latitude	Area	Ches. Bay Program Segment	Location/Depth	Sampling Coordination	Historical Station names	Annual Sample Freq. x No. Of Depths
9	CB4.1C	-76.399452	38.82593	Mainstem	СМ4МН	SW of Kent Pt (0.5nm from Bloody Pt Light just West of line from Bloody Pt to G 83); 31.0 m	PAR	CBI 845G, 848E; OEP XFF9178; EPA '83DO	15x4 14 sampling trips + 1 readings only
10	CB4.1E	-76.371437	38.81809	Mainstem	СВ4МН	S of Kent Pt (1.4 nm SE Bloody Pt Light, 300 yards SW buoy 1 for Eastern Bay); 23.7 m	PAR	CBI 851N; EPA '83DO; OEP XFF9178	11x4 Mar- Oct 10 sampling trips +1 readings only
11	CB4.1W	-76.462715	38.81498	Mainstem	СВ4МН	SE of Horseshoe Pt (3.5nm from Bloody Pt. Light on Hdg 260, 1.6 nm E of Franklin Manor); 9.1 m	PAR	CBI 848G, H, I; OEP XFF1844, XFF8922	11x2 Mar-Oct 10 sampling trips +1 readings only
12	CB4.2C	-76.421265	38.64618	Mainstem	СВ4МН	SW of Tilghman Island (2nm from Sharps Island Light on Hdg 290, 300 yards NE of CR buoy) 26.2 m.	PAR	EPA '83DO; OEP XEF8648	15x4 14 sampling trips + 1 readings only
13	CB4.2E	-76.401314	38.64499	Mainstem	СВ4МН	SW of Tilghman Island (1.3nm from Sharps Island Light on Hdg 305, 0.9 nm E of CR buoy); 9.1 m	PAR	<b>OEP</b> XEF8859	11x2 Mar-Oct 10 sampling trips +1 readings only
14	CB4.2W	-76.502167	38.64354	Mainstem	СВ4МН	NW of Plum Pt (6nm from Sharps Island Light on Hdg 280, 1.0 nm E of Camp Roosevelt); 9.1 m	PAR	OEP XEF8699; EPA '83DO	11x2 Mar-Oct 10 sampling trips +1 readings only
15	CB4.3C	-76.42794	38.55505	Mainstem	СВ4МН	E of Dares Beach (0.5 nm W of R 78, 5.7 nm from Sharps Island Light, Hdg 220); 25.6 m.	PAR, VSS, plankton Jan- Dec-Above pycnocline composite-live & fixed. Jul- Sep-above pycnocline composite picoplankton, DOC Mar-Sep	OEP XEF3343	15x4  14 sampling trips + 1 readings only
16	CB4.3E	-76.391212	38.55624	Mainstem	СВ4МН	Mouth of Choptank River (1.7 nm. East of R78, 5 nm. from Sharps Island Light on Hdg 195); 21.6 m	PAR	OEP XEF3465	11x4 Mar-Oct 10 sampling trips +1 readings only
17	CB4.3W	-76.494019	38.55728	Mainstem	СВ4МН	E of Dares Beach (1nm. East of Dares Beach, 3nm. West of R78); 9.7 m	PAR	<b>CBI</b> 834H, J; <b>OEP</b> XEF3405	11x2 Mar-Oct 10 sampling trips +1 readings only

Count	Station	Longitude	Latitude	Area	Ches. Bay Program Segment	Location/Depth	Sampling Coordination	Historical Station names	Annual Sample Freq. x No. Of Depths
18	CB4.4	-76.34565	38.41457	Mainstem	CB4MH	NE of Cove Pt (2.4 nm from Cove Pt on Hdg 055); 28.6 m	PAR, Quarterly Split Sample Location	OEP XDF4693	15x4 14 sampling trips + 1 readings only
19	CB5.1	-76.292145	38.3187	Mainstem	CB5MH	E of Cedar Pt (1 nm. ENE of mid-channel buoy HI, 4nm. from Cedar Pt. on Hdg 070); 33.2 m	PAR	CBI 818N, 818P, 819N, 819O; OEP XCG9223	15x4 14 sampling trips + 1 readings only
20	CB5.2	-76.227867	38.13705	Mainstem	СВ5МН	Mid Bay E of Pt No Point (3 nm. From Point No Point Light on Hdg 080); 29.0 m	PAR, VSS, plankton Jan- Dec-Above pycnocline composite-live & fixed. Jul- Sep-above pycnocline composite picoplankton, DOC Mar-Sep	Benthos #58 (Versar); OEP XBG8262	15x4  14 sampling trips + 1 readings only
21	CB5.3	-76.171371	37.91011	Mainstem	СВ5МН	NE of Smith Point (2nm. from Smith Point Light toward on Hdg 020, intersect MD/VA line and transect from Smith Pt to Holland bar Light); 25.3 m	PAR	USGS 37524807, 6094200; OEP XAG4699	15x4  14 sampling trips + 1 readings only
22	TF1.0	-76.694107	38.95557	Patuxent	PAXTF	At bridge on US Rt. 50 (upstream side of bridge; USGS Gage No 59440); 3 m'''		OEP PXT0603; USGS 01594440; EPA E	12x1
23	TF1.2	-76.75087	38.8143	Patuxent	WBRT.F	Midstream of Western Branch at Water Street crossing in Upper Marlboro, MD; 3 m		OEP WXT0045	12x1
24	WXT0001	-76.713432	38.78539	Patuxent	WBRT.F	Western Brach from pier at Mt Calvert House in Upper Marlboro, 0.1 miles above mouth; 1.0 m			12x1
25	TF1.3	-76.712273	38.81092	Patuxent	PAXTF	Mid-channel from MD Rt. 4 bridge near Wayson's Corner; 3.7 m		<b>OEP</b> PXT0494; <b>EPA</b> E5, 5	12x1
26	TF1.4	-76.709267	38.77302	Patuxent	PAXTF	West Shore from main pier at Jackson Landing; just below confluence with Western Branch; 3.0 m		<b>OEP</b> PXT0456; <b>EPA</b> E6A	12x1
27	TF1.5	-76.701462	38.71012	Patuxent	PAXTF	Mid-channel at Nottingham, 11.1m	PAR, VSS, plankton Mar- Nov whole water column composite live and fixed, DOC Mar-Sep	<b>OEP</b> PXT0402; <b>EPA</b> E8	12x4
28	TF1.6	-76.683815	38.65845	Patuxent	PAXOH	Mid-channel off the wharf at Lower Marlboro, 6 m.	PAR	OEP XED9490; EPA E9; J.H. 5945	12x3

Count	Station	Longitude	Latitude	Area	Ches. Bay Program Segment	Location/Depth	Sampling Coordination	Historical Station names	Annual Sample Freq. x No. Of Depth
29	TF1.7	-76.681007	38.58211	Patuxent	PAXOH	Mid-channel on a transect heading of approx. 115 degrees from Jack's Creek; 3.1 m	PAR, VSS	<b>OEP</b> XED4892; <b>J.H.</b> 5946	12x2
30	RET1.1	-76.664291	38.4909	Patuxent	PAXMH	Mid channel, 0.5 km ENE of Long Point, 11.1 m	PAR	OEP XDE9401; EPA E14, 4, CB 1	12x4
31	LE1.1	-76.601761	38.42535	Patuxent	РАХМН	Mid-channel SSW of Jack Bay sand-spit. NE of Sandgates; 12.5	PAR, VSS, Jan-Dec above the pycnocline live and fixed composite plankton sample; July- September a fixed picoplankton sample from the above pycnocline composite, DOC Mar-Sep	<b>OEP</b> XDE5339; <b>EPA</b> E15	12x4
32	LE1.2	-76.511322	38.37887	Patuxent	PAXMH	Mid-channel,1.6 km SW of Petersons Pt.; 17.8 m	PAR	OEP XDE2792	12x4
33	LE1.3	-76.484901	38.3398	Patuxent	PAXMH	Mid-channel 1200 m due N of Pt. Patience, ESE of Half Pone Pt; 23.1 m	PAR, Mar-Nov Live plankton collected from the surface	OEP XDF0407	12x4
34	LE1.4	-76.421509	38.312	Patuxent	PAXMH	Mid-channel on a transect between Drum Pt. and Fishing Pt; 16.5m	PAR	OEP XCF8747	12x4
35	CB5.1W	-76.37574	38.32522	Mainstem	СВ5МН	Mid-channel on a transect between Cedar Pt and Cove Pt; 8.9m	PAR	OEP XCF9575	12x4
36	PIS0033	-76.986732	38.69842	Potomac	PISTF	Piscataway Creek at Maryland Rt. 210 crossing; 1 m	Sampled in coordination with mainstem		12x1
37	XFB1986	-77.02317	38.69787	Potomac	PISTF	Piscataway Creek off Ft. Washington Marina between DM4 and DM6, SW of dredged channel; 2m	Sampled in coordination with mainstem, plankton Mar- Nov live surface		12x1
38	MAT0078	-77.118645	38.58852	Potomac	MATTF	Mattawoman Creek at MD. Rt. 225 crossing; 1 m	Sampled in coordination with mainstem		12x1
39	MAT0016	-77.193451	38.56508	Potomac	MATTF	Mattawoman Creek at green day beacon 5 off Sweden Pt; 2 m	Sampled in coordination with mainstem, plankton Mar- Nov live surface	OEP XEA3687	12x1
40	TF2.1	-77.048759	38.70664	Potomac	POTTF	At FI buoy 77 off mouth of Piscataway Creek; 19 m	Sampled in coordination with mainstem, plankton Jul- Sep-live surface	OEP XFB2470; EPA – several	12x3

Count	Station	Longitude	Latitude	Area	Ches. Bay Program Segment	Location/Depth	Sampling Coordination	Historical Station names	Annual Sample Freq. x No. Of Depth
41	TF2.2	-77.111107	38.69067	Potomac	POTTF	Buoy 67 off mouth of Dogue Creek; 8 m	Sampled in coordination with mainstem, plankton Jul- Sep-live surface	OEP XFB1433; USGS 3841360 77054600; EPA – Several	12x3
42	TF2.3	-77.173897	38.6082	Potomac	POTTF	Buoy N54 mid-channel off Indian Head; 15 m	Sampled in coordination with mainstem, VSS, plankton Mar-Nov whole water column composite live & fixed, DOC Mar-Sep	OEP XEA6596	12x3
43	TF2.4	-77.265404	38.5301	Potomac	POTTF	Buoy 44 between Possum Pt. And Moss Point; 9 m	Sampled in coordination with mainstem, plankton Jul- Sep-live surface	OEP XEA1840; USGS 06158710; EPA- Several	12x3
44	RET2.1	-77.269096	38.4035	Potomac	РОТОН	Buoy 27 SW of Smith Point; 8 m	Sampled in coordination with mainstem	OEP XDA4238; EPA – Several	12x2
45	RET2.2	-77.205101	38.3525	Potomac	РОТОН	Buoy 19 mid-channel off Maryland Point; 11 m	Sampled in coordination with mainstem, VSS, plankton Mar-Nov-whole water column composite live & fixed, DOC Mar-Sep	OEP XDA1177; EPA - Several	12x3
46	RET2.4	-76.990631	38.3626	Potomac	РОТМН	Mid-channel at Morgantown bridge (US Rt. 301); 19 m	Sampled in coordination with mainstem, VSS	OEP XDC1706; USGS 01660800; EPA - Several	12x4
47	LE2.2	-76.598	38.1576	Potomac	РОТМН	Potomac River off Ragged Point at Buoy 51B; 10 m	Sampled in coordination with mainstem, VSS, DOC Mar-Sep, plankton Jan- Dec live surface	OEP XBE9541	12x4
48	LE2.3	-76.347702	38.0215	Potomac	РОТМН	Mouth of Potomac River (1.6 nm from Pt Lookout on Hdg 240, 0.5 nm NW of Whistle A); 19.8 m	Sampled on mainstem cruise	OEP XBF0893	14x4
49	ET1.1	-75.967819	39.56976	Tributary	NORT.F	Northeast River at Day marker 12 off Hance Pt, mid-channel; 3 m		OEP XKI4220, XKI3717, XKI4523, XKI5025	12x2
50	ET2.1	-75.811348	39.5293	Tributary	C&DOH	C&D Canal E of Rt. 213 Bridge at Chesapeake City; 13 m		<b>OEP</b> XKJ1810, XKJ1811	12x2

Count	Station	Longitude	Latitude	Area	Ches. Bay Program Segment	Location/Depth	Sampling Coordination	Historical Station names	Annual Sample Freq. x No. Of Depths
51	ET2.2	-75.87368	39.46704	Tributary	вонон	Bohemia River off Hack Pt, 75 yards ENE of day marker R 4, mid- channel; 3 m		<b>OEP</b> XJI8076, XJI7678; <b>EPA</b> U9	12x2
52	ET2.3	-75.897827	39.50873	Tributary	ELKOH	Elk River SE of Old Cornfield Pt at G 21, mid-channel; 12 m		OEP XKI0661; EPA U10	12x2
53	ET3.1	-75.882034	39.36416	Tributary	SASOH	Sassafras R from end of pier at Georgetown Yacht Basin, NW side of MD. Rt. 213 bridge; 5 m		<b>OEP</b> XJI1970; <b>EPA</b> U1	12x2
54	ET4.1	-75.924896	39.2437	Tributary	CHSOH	Chester River at Rt. 290 bridge near Crumpton; 6 m		OEP CHE0367	12x2
55	ET4.2	-76.215096	38.99233	Tributary	СНЅМН	Lower Chester River South of Easter Neck Island 200 yards SW of buoy FL G 9; 16m	plankton Jan- Dec-above pycnocline composite; Jul- Sep-above pycnocline composite picoplankton, DOC Mar-Sep	OEP XGG9572; CBI CHO9C	12x4
56	EE1.1	-76.251503	38.88	Tributary	EASMH	Eastern Bay between Tilghman Pt and Parsons Island, N of buoy R4; 13m	Mar-Nov-live plankton at surface	<b>OEP</b> XGG2649; <b>CBI</b> 851N	12x4
57	ET5.1	-75.909706	38.80645	Tributary	СНООН	Upper Choptank River 200 yards upriver from Ganey's Wharf, downstream of confluence with Tuckahoe Creek; 6 m	Mar-Nov-whole water column composite -live & fixed plankton	<b>OEP</b> CHO0429	12x2
58	ET5.2	-76.058701	38.5807	Tributary	СНОМН2	Lower Choptank River, mid-river 50yards NNE of G I, W of Rt. 50 bridge at Cambridge; 11 m	Mar-Nov- above pycnocline composite-live & fixed. Jul- Sep-above pycnocline composite picoplankton, DOC Mar-Sep	<b>OEP</b> XEH4766	12x4
59	EE2.1	-76.264297	38.6549	Tributary	CHOMH1	Choptank embayment between Todd's Point and Nelson Pt; 8 m	·	<b>OEP</b> XEG9440, XEG9652	12x4
60	EE2.2	-76.304077	38.52609	Tributary	LCHMH	Little Choptank River mid-channel West of Ragged Point, W of Buoy Fl g 3, 14 m		OEP XEG1617	12x2
61	EE3.0	-76.01033	38.28093	Tributary	FSBMH	Fishing Bay at day marker 3, W of Roasting Ear Pt; 7 m	VSS, plankton Mar-Nov-live surface	OEP XCH6994, XCH5991	12x2
62	TRQ0088	-75.99345	38.41727	Tributary	FSBMH	Transquaking River, at bridge on Bestpitch Ferry Rd (Griffith Neck Rd), 2.5m	DNA probe Pfiesteria sampling 1998-2002 Continuous monitoring		12x1

Count	Station	Longitude	Latitude	Area	Ches. Bay Program Segment	Location/Depth	Sampling Coordination	Historical Station names	Annual Sample Freq. x No. Of Depths
63	TRQ0146	-76.0001	38.46566	Tributary	FSBMH	Transquaking River at DeCoursey Bridge, 2.5m	DNA probe Pfiesteria sampling 1998-2002		12x1
64	CCM0069	-75.9048	38.4423	Tributary	FSBMH	Chicamacomico River drawbridge & road crossing, 2.5m	DNA probe Pfiesteria sampling 1998-2002 Continuous monitoring 2000-2003		12x1
65	ET6.1	-75.703056	38.54833	Tributary	NANTF	Upper Nanticoke River at old Rt. 313 bridge (fishing pier,1987) in Sharptown; 5 m	VSS, Mar-Nov- live surface plankton	OEP NAN0302 1	12x2
66	ET6.2	-75.888336	38.34133	Tributary	NANMH	Lower Nanticoke River mid-channel near FI G 11; 3.5 m	VSS	Near OEP XDI0567, Near OEP XDI0567	12x2
67	XDJ9007	-75.82098	38.48375	Tributary	NANMH	Nanticoke River at Old Rt. 50 bridge in Vienna, 2m	DNA probe Pfiesteria sampling 1998-2002		12x1
68	EE3.1	-75.973206	38.19685	Tributary	TANMH	North Tangier Sound, NW of Haines Pt, 100 yards N of buoy R16; 13 m	Jan-Dec-above pycnocline composite plankton-live & fixed; Jul-Sep-above pycnocline picoplankton, DOC Mar-Sep	<b>OEP</b> XCI1717	12x4
69	EE3.2	-75.924232	37.98139	Tributary	TANMH	South Tangier Sound, mid-channel East of Smith Island, 500 yards NNW of buoy R8; 28 m	plankton Mar- Nov-live surface	OEP XAI8845, Near OEP XBI3003	12x4
70	WIW0141	-75.695686	38.34156	Tributary	WICMH	Wicomico River at upper ferry crossing on Upper Ferry Road	DNA probe, Pfiesteria sampling 1998-2002		12x1
71	ET7.1	-75.787933	38.26783	Tributary	WICMH	Lower Wicomico River at Whitehaven, 150 yards downriver of Ferry Road, mid- channel; 7m	VSS, plankton Mar-Nov-live surface	OEP WIW0050	12x2
72	XCI4078	-75.86963	38.23379	Tributary	WICMH	Wicomico River at Island Pt in channel at buoy FL14, 4.5m	DNA probe Pfiesteria sampling 1998-2002		12x1
73	ET8.1	-75.81411	38.13794	Tributary	MANMH	Manokin River at upper extent of channel; approx. 100 yards NNE of buoy R 8, mid- channel; 6 m	VSS	OEP XBJ8215	12x2
74	BXK0031	-75.75156	38.13563	Tributary	MANMH	Manokin River, Back Creek at Milliard Long Rd, 3m	DNA probe Pfiesteria sampling 1998-2002		12x1

Count	Station	Longitude	Latitude	Area	Ches. Bay Program Segment	Location/Depth	Sampling Coordination	Historical Station names	Annual Sample Freq. x No. Of Depths
75	MNK0146	-75.72235	38.17513	Tributary	MANMH	Manokin River at unnamed road off of Stewart. Neck Rd, 4.5m	DNR phytoplankton (live) DNA probe Pfiesteria sampling 1998-2002		12x1
76	ET9.1	-75.801666	38.055	Tributary	BIGMH	Big Annemessex River, NW of Long Pt in channel S of day marker G5; 5m	VSS	<b>OEP</b> XBJ3312	12x2
77	EE3.3	-75.801483	37.91455	Tributary	РОСМН	Pocomoke Sound, near buoy W S"A" midway between Oystershell Pt and Long Pt	Plankton Mar- Nov-live surface	Near OEP XAJ4719, Near VA EE3.1	12x2
78	WT1.1	-76.24205	39.43511	Tributary	BSHOH	Bush River E of Gum Point, E of Fl G9 on power line support; 2 m		OEP XJG6254	12x2
79	WT2.1	-76.334648	39.37747	Tributary	GUNOH	Gunpowder River, 200 yards E of Oliver Point at buoy G15; 2.5 m		OEP XJF2798	12x2
80	WT3.1	-76.409538	39.30538	Tributary	MIDOH	Middle River East of Wilson Point at channel junction day marker WP; 3 m	plankton Mar- Nov-live surface	OEP XIF5484; EPA M2	12x2
81	WT4.1	-76.44368	39.27755	Tributary	ВАСОН	Back River, East of Stansbury Point, East of day marker R12; 2 m		OEP XIF6633, Near OEP XIF6732	12x2
82	WT5.1	-76.522537	39.21309	Tributary	РАТМН	Patapsco River East of Hawkins Point at Buoy G3; 14 m	Plankton Mar- Nov-above pycnocline composite-live & fixed. Jul- Sep-above pycnocline composite picoplankton, DOC Mar-Sep	OEP XIE2885	12x4
83	WT6.1	-76.510048	39.07851	Tributary	MAGMH	Magothy River N of South Ferry Pt, mid- channel at buoy R12 and day marker G11; 5 m	plankton Mar- Nov-live surface; Jul- Sep picoplankton at surface	OEP XHE4794	12x2
84	WT7.1	-76.503502	39.00764	Tributary	SEVMH	Severn River, 200 yards upstream of Rt. 50/301 bridge and 150 yards off NE shore; 9 m	plankton Mar- Nov-live surface	OEP XHE0497	12x2
85	WT8.1	-76.546097	38.9496	Tributary	SOUMH	South River South of Poplar Point at day marker R16; 9m	plankton Mar- Nov-live surface; Jul- Sep picoplankton at surface	OEP XGE6972	12x2

Count	Station	Longitude	Latitude	Area	Ches. Bay Program Segment	Location/Depth	Sampling Coordination	Historical Station names	Annual Sample Freq. x No. Of Depths
86	WT8.2	-76.534904	38.88696	Tributary	RHDMH	Rhode River between Flat Island and Big Island; 3 m		OEP XGE3279	12x2
87	WT8.3	-76.534103	38.8425	Tributary	WSTMH	West River just upstream of day marker R6; 4 m		OEP XGE0579	12x2
88	POK0087	-75.65047	37.96396	Tributary	РОСОН	Pocomoke River off Rehoboth Rd in the Town of Rehoboth, 2m	DNA probe Pfiesteria sampling 1998-2002		12x1
89	XAK7810	-75.65047	37.96396	Tributary	РОСОН	Pocomoke River, mid mouth of the river, 3.5m	DNR phytoplankton (live) DNA probe Pfiesteria sampling 1998-2002		12x1
90	XGG8251	-76.14.840	38 58.267	Tributary	CHSMH	Chester River at Kent Narrows			12x1
91	ET10.1	-75.5663	38.0835	Tributary	POCTF	Pocomoke River on Alt US Rt. 13 (Market St.) an old drawbridge in Pocomoke City, 5m	Striped bass spawning	OEP POK0170	12x2

#### **KEY FOR Historical Stations:**

Abbreviation	Description
CBI	Chesapeake Bay Institute, Johns Hopkins University, 1949-1980
EPA/AFP	EPA, Annapolis Field Office studies, 1969-1970
EPA	EPA, Water Quality Office, Chesapeake Technical Support Laboratory, 1967-1969
USDI	U.S. Department of the Interior, Federal Water Pollution Control Administration, Chesapeake Technical Support Laboratory, 1965-1968
USGS	U.S. Geological Survey Water Quality of the Potomac River and Estuary Hydrologic Data Report, 1978-1981
OEP	Office of Environmental Programs, Maryland Department of Health and Mental Hygiene, 1984-1987; this program was moved to Maryland Department of the Environment 1987-1996 and to the Maryland Department of Natural Resources 1996-present; the current sampling site names were adopted in 2000 to conform to EPA Chesapeake Bay Program station names.

For logistical reasons, Potomac component station LE2.3 is sampled with mainstem stations and Mainstem component station CB5.1W is sampled during Patuxent boat cruises.

For analytical purposes, LE2.3 is often considered a tributary station because the water body is "Potomac River", and station CB5.1W is often considered a Mainstern station because the water body is "Chesapeake Bay". Care should be used when aggregating station water quality data by water body, or Chesapeake Bay segment. In cases where limits of detection are used in analyses, there may be challenges. (See Appendix 13 for yearly component detection limits).

NOTE: Refer to Appendix 1 for details on the physical/chemical parameter sampling. Refer to the following work plan/scope of work for details on the plankton monitoring component:

MD Department of Natural Resources. 2009. Quality Assurance Documentation Plan for the Phytoplankton Monitoring Component of the Chesapeake Bay Water Quality Monitoring Program. Annapolis, Maryland, 37 p.

## 2. MEASURED PARAMETERS

The Chemical and Physical Properties Component of the Chesapeake Bay Water Quality Monitoring Program measures a broad suite of physical and chemical parameters that are indicative of the Bay's eutrophication problem. Several "natural" properties such as salinity and temperature in the water column provide important information for interpretation of water quality indicators.

Some parameters, such as specific conductance, temperature, dissolved oxygen, and pH, are measured in situ using multi-parameter water quality instrumentation manufactured by Hydrolab or Yellow Springs Instruments (YSI). Salinity is calculated from conductivity and temperature. Photosynthetic Active Radiation (PAR) measurements are made in situ using a LI-COR® quantum meter and probe. Secchi depth is measured using a weighted 20 cm diameter limnological Secchi disc with alternating white and black quadrants. The disc is attached to a graduated line.

Several Series of Hydrolab multi-parameter instruments have been used by this monitoring program since 1984. Advances in sensor design and measurement technology, and the switch from analog to digital technology have been implemented in the newer Series. Beginning in February 2009, YSI Series 6 instruments were added to the field instrument inventory. Sensor differences on each Series of Hydrolab and YSI instruments are noted in Table 3 and Appendix 5, section III B, Routine Sensor Maintenance and Performance Verification.

Hydrolab Series 4041, 2, 3, 4a and 5 instruments had Standard Clark Polarographic Dissolved Oxygen Sensors. Beginning in 2009 all existing Hydrolab Series 5 instruments were converted from Standard Clark Polarographic Dissolved Oxygen Sensors to Optical Dissolved Oxygen Sensors known as Luminescent Dissolved Oxygen (LDO), but temperature, pH, specific conductance and depth sensors were not changed. Since then, Hydrolab Series 4a instruments were systematically replaced with Series 5 instruments equipped with LDO Sensors. In March 2015, all remaining Series 4a instruments equipped with Standard Clark Polarographic Dissolved Oxygen Sensors were replaced with Series 5 instruments equipped with LDO Sensors. Beginning in 2020, a new series of Hydrolab, the HL4, was also being used. Hydrolab Series 4041, 2, 3 and 4a instruments have not been in service for several years. Calibration logs for each instrument will list the date taken out-of-service. Sensor differences for each instrument Series are noted under Routine Sensor Maintenance (see App. 5 III B).

YSI instruments are equipped with an optical dissolved oxygen sensor (ROX) instead of the Standard Clark Polarographic sensor. YSI temperature, pH, specific conductance and depth sensors are different than their respective Hydrolab sensors but perform similarly. Both the Hydrolab and YSI optical dissolved oxygen sensors use similar luminescent technology to measure dissolved oxygen.

During 2014, YSI pH sensors in all YSI sondes were switched from Model 6561 to Model 6589. These sensors are identical to and perform exactly as Model 6561. Model 6561 were only lasting 6 to 9 months of field deployment before replacement was required. Model 6589 is amplified, responds faster and lasts up to two years of field deployment. Thus, compared to YSI pH sensor Model 6561, YSI pH sensor Model 6589 has greater longevity and reliability. Henceforth, all YSI Series 6 instruments will be equipped with YSI pH sensor Model 6589. These sensors will be replaced once per year.

Since February 2009, Mainstem and Patuxent River cruises have exclusively used YSI Series 6. Prior to February 2009, these cruises exclusively used various Series of Hydrolab instruments. Beginning in 2020

EXO2 instruments are being used for Mainstem and Patuxent River sampling. Whether Hydrolab or YSI, field sheets document which instruments were used on each Mainstem and Patuxent River cruises. All other sampling activities use Hydrolab or YSI instruments. Beginning in 2020, YSI EXO meters have been used.

This document may be amended when new Hydrolab and YSI instruments are purchased and instrument protocols changed, and their use and protocols receive approval from the Chesapeake Bay Program Quality Assurance Officer.

The other measured parameters – including nitrogen, 5-day biochemical oxygen demand, phosphorus, carbon and silicon species, total suspended solids, total alkalinity, volatile suspended solids, turbidity and chlorophyll a – are determined in the laboratory. Table 3 lists the parameters measured, their detection limits, methods references, and holding times and conditions. Details of sample collection, sample processing and storage, and analytical procedures are described in Appendices 1, 14 and 15.

The Chesapeake Biological Laboratory Nutrient Analytical Services Laboratory (NASL) has revised all Standard Operating Procedures (SOP) to reflect changes in procedures and instrumentation. These SOPs are reviewed annually and revised when needed. When made, revisions are documented, and EPA Chesapeake Bay Program is notified prior to the publication of the affected QAPP. All laboratory methods used by NASL for DNR analyses have been updated.

Maryland Department of Health, Division of Environmental Sciences, Inorganics Analytical Laboratory performs 5-day biochemical oxygen demand, total alkalinity and turbidity analyses. The Inorganics Analytical Laboratory methods and procedures are reviewed and updated annually.

All methods of both laboratories were written to comply with Methods and Quality Assurance for Chesapeake Bay Water Quality Monitoring Programs (2017) and National Environmental Laboratory Accreditation Conference (NELAC 2003) guidance and recommendations. Organization charts have been created. Documentation of procedures for logging-in and tracking samples, standards and reagents has been developed and are in place.

Appendix 14 aggregates Inorganics Analytical Laboratory methods. Appendix 15 is a copy of NASL website with links to method documents. Table 2 lists the documents in Appendix 14 and Appendix 15.

The most current versions of NASL methods documents and detection limits are maintained on-line by NASL and may be accessed at the following URL: <a href="https://www.umces.edu/nasl/methods">https://www.umces.edu/nasl/methods</a>

The Chesapeake Biological Laboratory, Nutrient Analytical Services Laboratory assumed responsibility in January 2009 for analyzing chlorophyll samples. Prior to year 2009, chlorophyll analyses were conducted by the Maryland Department of Health.

**Table 2. Nutrient Analytical Services Laboratory methods** 

Water Column Chemistry	Method	Revised	
Ammonium Method	Standard Operating Procedure for Determination of Dissolved Inorganic Ammonium (NH4) in Fresh/Estuarine/Coastal Waters (References Standard Methods 4500-NH3 G-1997)	1-May-2022	
Cadmium Nitrate Method	Standard Operating Procedure for Determination of Dissolved Inorganic Nitrate plus Nitrite (NO3+NO2) in Fresh/Estuarine/Coastal Waters Using Cadmium Reduction (References EPA 353.2)		
Enzyme Catalyzed Nitrate Method	Standard Operating Procedure for Determination of Dissolved Inorganic Nitrate plus Nitrite (NO3+NO2) in Fresh/Estuarine/Coastal Waters Using Enzyme Catalyzed Reduction (References EPA 353.2, Standard Methods #4500-N C, 4500-NO3 F)	1-May-2022	
Nitrite Method	Standard Operating Procedure for Determination of Dissolved Inorganic Nitrite (NO2) in Fresh/Estuarine/Coastal Waters (References EPA 353.2)	1-May-2022	
Orthophosphate Method	Standard Operating Procedure for Determination of Dissolved Inorganic Orthophosphate (PO4) in Fresh/Estuarine/Coastal Waters (References EPA 365.1)	1-May-2022	
Silicate Method	Determination of Silicate from Fresh, Estuarine, and Coastal Waters Using the Molybdosilicate Method (Reference Method: EPA Method 366.0)	1-May-2022	
Total Dissolved Nitrogen Enzyme Catalyzed Nitrate Method	Standard Operating Procedure for Determination of Total Dissolved Nitrogen (TDN) and Total Nitrogen (TN) in Fresh/Estuarine/Coastal Waters Using Alkaline Persulfate Digestion of Nitrogen to Nitrate and Measured Using Enzyme Catalyzed Reduction (References EPA 353.2, Standard Methods #4500-N C, 4500-NO3 F)	1-May-2022	
Total Dissolved Nitrogen Cadmium Nitrate Method	Standard Operating Procedure for Determination of Total Dissolved Nitrogen (TDN) and Total Nitrogen (TN) in Fresh/Estuarine/Coastal Waters Using Alkaline Persulfate Digestion of Nitrogen to Nitrate and Measured Using Cadmium Reduction (References EPA 353.2, Standard Methods #4500-N C, 4500-NO3 F)	1-May-2022	
Total Dissolved Phosphorus Discrete Photometric Analyzer Method	Standard Operating Procedure for Determination of Total Dissolved Phosphorus (TDP) and Total Phosphorus (TP) in Fresh/Estuarine/Coastal Waters Using Alkaline Persulfate Digestion of Phosphorus to Orthophosphate (PO4) with Colorimetric Analysis by Random Access Discrete Photometric Analyzer (References Standard Methods #4500-P.B.5, #4500 P.E, and EPA Method 365.1)	1-May-2022	
Total Dissolved Phosphorus Auto Analyzer II System Method	Standard Operating Procedure for Determination of Total Dissolved Phosphorus (TDP) and Total Phosphorus (TP) in Fresh/Estuarine/Coastal Waters Using Alkaline Persulfate Digestion of Phosphorus to Orthophosphate (PO4) (References Standard Methods #4500-P.B.5, #4500 P.E, and EPA Method 365.1)	1-May-2022	
Total and Dissolved Organic and Inorganic Carbon Method	Standard Operating Procedure for Determination of Dissolved Organic Carbon/Non-Purgeable Organic Carbon (DOC/NPOC), and Total Organic Carbon (TOC) in Fresh/Estuarine/Coastal Waters using High Temperature Combustion and Infrared Detection. (References: SM5310B)	1-May-2022	
Inorganic Carbon and Alkalinity Method	Standard Operating Procedure for Determination of Aqueous Inorganic Carbon and calculated Carbonate Alkalinity in waters of Fresh/Estuarine/Coastal Waters. (References: ASTM D7573-09)	1-May-2022	

Water Column Chemistry	Method	Revised	
Particulates & Sediments			
Chlorophyll Spectrophotometric Method	Standard Operating Procedure for Spectrophotometric Determination of Chlorophyll α in waters and sediments of Fresh/Estuarine/Coastal Areas. (References: SM10200H, EPA 446.0)	1-May-2022	
Particulate Carbon and Nitrogen Method	Standard Operating Procedure for Determination of Carbon and Nitrogen in Particulates and Sediments of Fresh/Estuarine/Coastal Waters, Plant and Animal Tissue, and Soils Using Elemental Analysis. (Reference Method: EPA 440.0)	1-May-2022	
Particulate Phosphorus Method	Determination of Total Particulate Phosphorus (TPP) and Particulate Inorganic Phosphorus (PIP) in Fresh/Estuarine/Coastal Waters (Reference Method: EPA 365.1, Rev. 2.0)	1-May-2022	
Total Suspended Solids and Total Volatile Solids Methods	Determination of Total Suspended Solids (TSS) and Total Volatile Solids (TVS) in Waters of Fresh/Estuarine/Coastal Waters. (Reference Method: EPA Method 160.2 and Standard Methods 208 E.)	1-May-2022	

**Table 3. Water Column Parameters, Detection Limits, References, Holding Times and Conditions.** 

IN SITU MEASUREMENTS				
Parameter (Units)	Instrument	Detection Limit (or Range)	Method Reference	Holding Time and Condition
Temperature (° C)	Hydrolab Series 4041 and 2	-5 to +45°C	Linear thermistor (HWQIUM-S4041, HWQIUM-S2)	- Not applicable <i>in situ</i>
	Hydrolab Series 3, 4a, and 5	-5 to +50°C	Linear thermistor (HWQIUM-S3, HWQIUM-S4a, HWQIUM-S5)	
	YSI Series 6	-5 to +50°C	Thermistor of sintered metallic oxide (YSIUM-S6)	
	YSI EXO2	-5 to +50°C	Thermistor	
Depth (m)	Hydrolab Series 3, 4a, and 5	0-100 m	Strain gauge pressure transducer, non-vented, stainless steel (HWQIUM-S3, HWQIUM-S4a, HWQIUM-S5)	

	YSI Series 6	0-61 m	Differential strain gauge transducer, non-vented (YSIUM-S6)	
	YSI EXO2	0 – 33 ft (S) 0 – 32 ft (M) 0 – 82 ft (D)	Stainless steel strain gauge	
	Hydrolab Series 4041, 2, 3, and 4a	0-20 mg/L	Standard Clark Au/Ag Polarographic Cell (HWQIUM-S4041, HWQIUM-S2, HWQIUM-S3, HWQIUM-S4a)	
	Hydrolab Series 5	0-50 mg/L	Standard Clark Au/Ag Polarographic Cell (HWQIUM-S5)	
Dissolved Oxygen (mg/L)	Hydrolab Series 5	0-20 mg/L	Optical Probe – Luminescent Dissolved Oxygen Probe (LDO) (HWQIUM-S5)	
	YSI Series 6	0-50 mg/L	Optical Sensor – ROX Optical Dissolved Oxygen (YSIUM-S6)	
	YSI EXO2	0-50 mg/L	Optical luminescence lifetime	
	Hydrolab Series 4041	0-200 mS/cm	Four nickel electrode cell with saltwater cell block (HWQIUM-S4041)	
	Hydrolab Series 2	0-150 mS/cm	Six nickel electrode cell with saltwater cell block (HWQIUM-S2)	
Charifia	Hydrolab Series 3	0-100 mS/cm	Six nickel electrode cell with saltwater cell block (HWQIUM-S3)	Not applicable <i>in situ</i>
Specific Conductance	Hydrolab Series 4a and 5	0-100 mS/cm	0.25" x 1" oval bore with four graphite electrodes (HWQIUM-S4a, HWQIUM-S5)	m situ
	YSI Series 6	0-100 mS/cm	Four electrode cell (YSIUM-S6)	
	YSI EXO2	0-200 mS/cm	Four electrode nickel cell	
рН	Hydrolab Series 4041 and 2	0-14 pH units	Paired bulb type Ag/AgCl glass <i>in situ</i> and rebuildable reference probes – reference probe in sleeve filled with saturated KCl/pH7 buffer and capped with replaceable porous Teflon™ junction (HWQIUM-S4041, HWQIUM-S2)	
	Hydrolab Series 3, 4a, and 5	0-14 pH units	Paired bulb type Ag/AgCl glass <i>in situ</i> probe and Silver pellet reference probe – reference probe in sleeve filled with 4M KCl saturated with AgCl and capped with replaceable porous Teflon™ junction (HWQIUM-S3, HWQIUM-S4a, HWQIUM-S5)	

	YSI Series 6	0-14 pH units	Combined glass bulb type electrode with Ag/AgCl reference electrode (YSIUM-S6)	
	YSI EXO2	0-14 pH units	Glass combination electrode	
Secchi Depth (m)		0.1 - 7.0 m	20 cm diameter disk with alternating black and white quadrants (Welch, 1948)	
Light Attenuation* (Photosynthetic Active Radiation) (two measurements - one from boat and one taken at depth with an up sensor)	LI-COR Model LI1400	400–700 nm	Parsons (1977); Smith (1969), CBP F01	Not applicable <i>in situ</i>

<sup>\*</sup> Light Attenuation is not measured by MD DNR on Tributary cruises except the Patuxent River. Light attenuation is measured on Mainstem cruises.

## Table 3 (continued)

#### **GRAB SAMPLES**

Parameter (Units)	Laboratory Detection Limit	Method (Reference)	Holding Time and Condition
Ammonium (mg/L as N)	0.009 mg N/L	Standard Methods 4500-NH3 G (2011)	Freezing-28 d
Biochemical Oxygen Demand (BOD5)	NA	Standard Methods 5210 B (2005)	4°C 48 hrs.
Chlorophyll <i>a</i> (µg/L)	0.62 <i>µ</i> g/L	Standard Methods 10200H, (2005) Arar, 446.0 (EPA 1997)	Freezing-28 d
Dissolved Organic Carbon (mg/L as C)	0.16 mg/L	Sugimura and Suzuki (1988), EPA method 415.1 (EPA 1971)	Freezing-28 d
Dissolved Silicate (mg/L as Si)	0.05 mg/L	EPA method 366.6 (EPA 1997), Zhang 366.0 (EPA 1997).	4°C - 28 d
Nitrite (mg/L as N)	0.0009 mg/L	EPA method 353.2 (EPA 1993)	Freezing-28 d
Nitrite + Nitrate (mg/L as N)	0.0015 mg/L	EPA method 353.2 (EPA 1993) and enzymatic nitrate method. Instrumentation used: Aquakem 250 (enzyme reduction) and AutoAnalyzer II (cadmium reduction), ASTM D7781	Freezing-28 d

Orthophosphate (mg/L as P)	0.0034 mg/L	EPA method 365.1 (EPA 1993)	Freezing-28 d
Particulate Carbon (mg/L as C)	0.0633 mg/L	EPA method 440.0 (EPA 1997)	Freezing-28 d
Particulate Nitrogen (mg/L as N)	0.0263 mg/L	EPA method 440.0 (EPA 1997)	Freezing-28 d
Particulate Phosphorus (mg/L as P)	0.0010 mg/L	Aspila et al. 1976, EPA 365.1 (EPA 1993).	Freezing-28 d
Pheophytin <i>a</i> (µg/L)	0.74 μg/L	Standard Methods 10200H (2005) Arar 446.0 (EPA 1997)	Freezing-28 d
Total Alkalinity (mg/L as CaCO3)	0.75 mg/L	Standard Methods 2320 B (2005)	4°C 14 d
Total Dissolved Nitrogen (mg/L as N)	0.05 mg/L	D'Elia et al. 1977; Valderrama 1981, Alkaline persulfate digestion. (Analysis by both by cadmium reduction and enzyme reduction post Alkaline persulfate digestion), EPA 353.2 (EPA 1993)	Freezing-28 d
Total Diss. Phosphorus (mg/L as P)	0.0015 mg/L	Valderrama 1981, Alkaline persulfate digestion, EPA 365.1 (EPA 1993)	Freezing-28 d
Total Suspended Solids (mg/L)	2.4 mg/L	Standard Method 2540 D (1998)	Freezing-28 d
Volatile Suspended Solids (mg/L)	0.9 mg/L	Standard Method 2540 E (1988)	Freezing-28 d
Turbidity (NTU)	0.1 NTU	EPA Method 180.1 (1993)	4°C 48 hrs.

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## 3. FIELD MEASUREMENTS AND SAMPLING

Sampling procedures have been formulated for each part of Maryland's Chemical and Physical Properties Component of the Chesapeake Bay Water Quality Monitoring Program to take measurements that meet the program objectives in an efficient, cost-effective, and logistically practical manner.

As defined in the Scope of Work, a total of 22 Mainstem stations and 69 tributary stations are included in the Chemical and Physical Properties Component of the monitoring program (see Figure 1 and Table 1 above in Section 1). Water column samples are collected once a month at most stations, for a total of twelve samplings per year. In the Chesapeake Mainstem, sampling will be conducted twice monthly in June, July and August of 2022 and 2023, and once monthly during the remaining months, for a total of fifteen samplings in the period of July 1, 2022- June 30, 2023. However, at eastern and western transect Mainstem stations, samples will not be collected from November through February, resulting in only eleven samplings a year. Nutrient samples will not be collected during the second survey in July. On the Potomac and Patuxent and smaller tributaries, twelve samplings will be conducted per year. The current frequency of sampling for each station is shown in Table 1 (provided above in Section 1).

The water column will be profiled for temperature, conductivity, dissolved oxygen, and pH using an *in-situ* probe that transmits data to a shipboard readout via cable. Profiling will be conducted at a minimum resolution of 2-meter sampling intervals. In strata where there is appreciable change in conductivity or dissolved oxygen (i.e., at the pycnocline), 1-meter intervals will be sampled. The protocols for determining profiling depths are detailed in Appendix 1.

Water column grab samples collected for subsequent analysis in the laboratory will be taken by submersible pump, bucket, Alpha or Kemmerer bottle. The number of depths sampled per station is listed in the last column of Table 1.

One or two depths will be sampled at stations that do not normally exhibit vertical density stratification. For stations where samples are collected at a single depth, the grab will be collected from depth of either 0.0 m or 0.5 m depending on the site. The depths of 0.5 meter and 1 meter above bottom will be sampled at sites where grabs are made at two depths.

Four depths will be sampled at stations that are normally density stratified: 0.5 m below the surface, 1.5 m above the upper limit of the pycnocline, 1.5 m below the lower limit of the pycnocline, and 1 m above the bottom. Grab sampling depths relative to the pycnocline will be determined according to the protocols described in Appendix 1.

Above pycnocline depth and below pycnocline depth grab samples are collected at the following stations: CB2.2, CB3.1, CB3.2, CB3.3C, CB4.1C, CB4.1E, CB4.2C, CB4.3C, CB4.3E, CB4.4, CB5.2, CB5.3, EE1.1, EE2.1, EE3.1, EE3.2, ET4.2, ET5.2, LE2.2, LE2.3, RET2.4 and WT5.1.

Four depth grab samples are also collected at seven other sites where mid-water sampling is conducted at fixed depths to maintain consistency with historical-station sampling depths. In addition to surface and bottom water samples at the six Patuxent boat survey stations, upper mid-water samples are collected at 3 meters depth. At stations CB5.1W, RET1.1 and TF1.5, lower mid-water samples are collected at 6 meters. Lower mid-water samples are collected at 9 meters at stations LE1.1 and LE1.4. At stations LE1.2 and LE1.3 lower mid-water samples are collected at the depth of 12 meters.

Grab samples on the Potomac boat survey are collected at three depths at five stations. In addition to surface and bottom water samples, to maintain consistency with historical-station sampling depths, mid-depth samples (M) are collected at 4.6 meters at stations RET 2.2, TF2.4, TF 2.3 and TF 2.2. The station TF 2.1 mid-depth sample is collected at 9.1 meters.

Details on filtration, containers, and storage techniques can also be found in Appendix 1. This sampling protocol provides one or two measurements of the water column in well-mixed non-stratified regions and two additional measurements - one in the surface mixed layer, and one in the bottom mixed layer - where the estuary is stratified into the typical two-layered flow pattern.

For the Mainstern stations only, when there is an odor of hydrogen sulfide present in the bottom sample or the below pycnocline sample, a Hach Kit test for hydrogen sulfide presence on the bottom and/or below pycnocline sample(s) will be performed.

Water transparency will be measured by Secchi depth, determined in meters using a 20 cm standard Secchi disc lowered into the water column with a calibrated rope. Observations will be made on the shady side of the boat.

## 4. LABORATORY ANALYSIS

All laboratory-measured parameters, with three exceptions, will be analyzed at the University of Maryland Center for Environmental Science (UMCES), Chesapeake Biological Laboratory (CBL), Nutrient Analytical Services Laboratory (NASL). See Appendix 15 for the list of NASL Standard Operating Procedures and analytical methods and weblinks. <a href="https://www.umces.edu/nasl/methods">https://www.umces.edu/nasl/methods</a>.

Maryland Department of Health, Division of Environmental Sciences; Inorganics Analytical Laboratory performs 5-day biochemical oxygen demand, total alkalinity and turbidity analyses. See Appendix 14 for the Inorganics Analytical Laboratory Standard Operating Procedures and analytical methods.

The NASL assumed responsibility for analyzing active chlorophyll *a* and pheophytin *a* in January 2009. See Appendix 15 for NASL chlorophyll analysis methods. Maryland Department of Health's (MDH) Environmental Chemistry Division analyzed chlorophyll and pheophytin samples prior to January 2009.

# 5. DATA MANAGEMENT, VERIFICATION AND DOCUMENTATION

Data collection for the Chemical and Physical Properties Component of the Chesapeake Bay Water Quality Monitoring Program will begin when measurements from field recording instruments are entered onto field data sheets. A field logbook will be used to document any problems encountered in the field that might affect the field parameters or samples brought back to the laboratory. The senior scientist, on board each cruise, will ensure that all measurements are taken properly. All data acquisition processes in the field and laboratory measurements will be recorded in the Cruise Report to ensure data quality. After field personnel complete data sheets for a given calendar month, they will make photocopies of the sheets to keep in the

Field Office and send the original field sheets to data management staff at the DNR Tawes Building. The Field Office will also generate a Cross Reference Sheet for each set of field sheets, which is sent to the DNR data management personnel along with the field data sheets. The Cross Reference Sheet allows data management personnel to know what field, nutrient, lab, and chlorophyll lab sheets to expect. See Appendix 2 for field sheets and associated documentation, Appendix 3 for a Cross Reference Sheet and documentation, and Appendix 4 for Cruise Report Documentation and Procedures.

Laboratory data sheets (nutrient volume sheets) will be initiated in the field. The analytical lab sheets will be used to record basic information about samples, such as station, date, depth, and volume filtered. The sheets will serve as sample transfer sheets, traveling with the samples to CBL's Nutrient Analytical Services Lab, or the MDH Inorganics Analytical Laboratory, for analysis. Both the sheets and the samples will be logged in at the respective labs.

At the labs, data generated from nutrient and chemical analyses will be recorded directly to an electronic file. The labs keep active control charts. Each instrument has an operator dedicated to that instrument. The dedicated operator is responsible for keeping track of the slopes of the regression analysis for that instrument to determine if the analyses are "in control." The analyst will review the data and, if the data exceed their control limits, the entire run will be re-analyzed. Re-analysis can occur for any number of reasons, such as a poor r squared (R²) on the standard curve, the wrong set of pump tubes (which would provide abnormally low peaks), or high blank values (in the case of DOC). See Appendix 15 for Chesapeake Biological Laboratory procedures and methods weblinks. See Appendix 14 for Inorganics Analytical Laboratory procedures and methods.

When laboratory staff members complete the nutrient lab sheets and chlorophyll lab sheets, the sheets will be sent to the DNR Tawes Building along with any electronic files that have been generated. During the pandemic, CBL and MDH laboratory results were also electronically shared on cloud drives with access limited to appropriate laboratory and DNR analytical personnel. See Appendix 2 for nutrient/chlorophyll lab sheets, and associated documentation. See Appendix 9 for a list of codes used on the sheets and to qualify analytical results when necessary.

Data review and verification will be conducted at four levels by DNR data management personnel.

At the first level, DNR data management personnel will review cross reference sheets and field data sheets: (1) comparing field sheets to cross reference sheets to ensure that all field sheets have been received; (2) reviewing all field sheets to check that they are filled out completely and legibly, and (3) sending the sheets to a data entry service for keypunch (see Appendix 6 for procedures). At the data entry service, the field sheet data values will be double entered to minimize errors at the keypunch stage. The entered field data will be sent back to DNR as electronic files for further processing.

At the second level, a Data Processing Programmer will generate reports and plots for data verification using the Water Quality Import v3 software. The WQ Import v3 software was designed in late 1998 and completely developed in 2000 in Microsoft Access. The WQ Import v3 software will be used to import data and cross reference files and to conduct data management activities, such as performing initial data checks, conducting major key field checks, performing parameter range checks (including measured and calculated parameters), conducting combination checks for specific parameters, generating error reports

and verification plots, generating a "data verified list," reformatting data, creating a database, and submitting data. Data checks are listed in Exhibit

Third, system printouts or PDF files of each data set will be sent to a biologist and the Quality Assurance Officer for verification and editing. The Quality Assurance Officer and DNR biologists will ensure that measured or calculated information for all types of data is correct and that the codes associated with parameters are properly established. In addition, the Quality Assurance Officer will identify data problems, provide data correction instructions, and coordinate data correction activities. Possible errors will be identified and sent to the laboratory or field office for verification or verified by phone or email. Any necessary corrections will be written on an edit form, which will be given to a programmer. The programmer will make changes to correct the electronic data set, re-run the verification programs, and update the verification reports and plots. This procedure will be repeated until a clean data set is produced. Sample verification reports and plots and an example of an edit request are provided in Appendix 11.

The fourth step will be for data management staff to ensure that the overall data verification processes are completed, all data errors are corrected, and that the finalized data sets are created and formatted to be consistent with historical data sets. The final data set combining the field, lab, and chlorophyll data is created as an "MDB file" after the completion of data verification processes. This final data set will be stored in the designated DNR data library subdirectory on Local Area Network server for data user access. A formatted submission data set and associated data documentation will also be transferred to the Chesapeake Bay Program Data Center on a monthly basis.

The data management process is diagrammed in Figure 2.

#### Exhibit 1. Data Verification Conducted on Water **Quality Data**

- (1) Individual Data Parameter Checks:
  - Range check for numeric data parameters (reports (a) error if data are outside the normal range for that parameter).
  - (b) Character validation check for character data parameters (reports error if the character data are not appropriate for that parameter).
- (2) Parameter Combination Checks:
  - Field Data:
    - Sample layer depth check (checks to make sure layer depths are appropriate, e.g., reports error if surface layer depth is greater than 1.0 m, surface depth is greater than bottom depth, etc.).
    - Upper and lower pycnocline check (reports error if pycnocline depths are outside expected range).
    - Maximum and minimum wind parameter check (reports error if minimum wind exceeds maximum wind).
  - (b) Laboratory Data:
    - APC code check for all laboratory related parameters (reports if APC code has been
    - G code (greater than or less than detection limit flag) check for all laboratory related parameters (reports if lab has flagged values as greater or less than the detection limit).
    - Parameter combination check for the following parameters:
      - Parameters PO4 and TDP (reports error if PO4 > TDP).
      - Parameters NO23, NH4, and TDN (reports error if NO23 + NH4 > TDN).
      - Parameters NO2 and NO23 (reports error if NO2 > NO23).
  - Chlorophyll Data: APC code checks with light path, extraction volume, and/or optical density parameters (reports error if values are outside expected range.
- (3) Verification Plots for Review: Sampling dates and times and values for all chemical and physical parameters are plotted by station for review by biologists and the Quality Assurance Officer (QAO). Biologists and the QAO look at patterns and identify any outliers or unusual values to be checked for errors.

# Data management flow chart Data Entry through production of Final Master Data Set

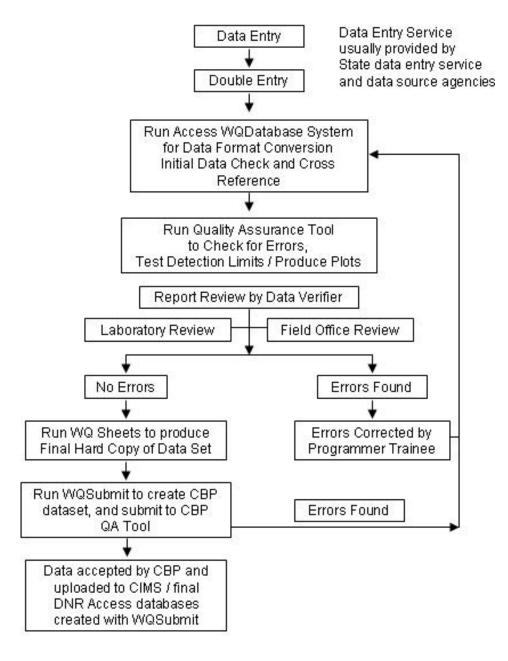


Figure 2. Data Management Flow Chart

A data tracking system has been designed and implemented to track the progress of data through the data management system. Data Status Forms will be assigned to all data files received (see Appendix 8 for example sheet and documentation). Data sheets and tracking sheets used in data management will be stored at the DNR Tawes Building for ten years. The data tracking system is diagrammed in Figure 3.

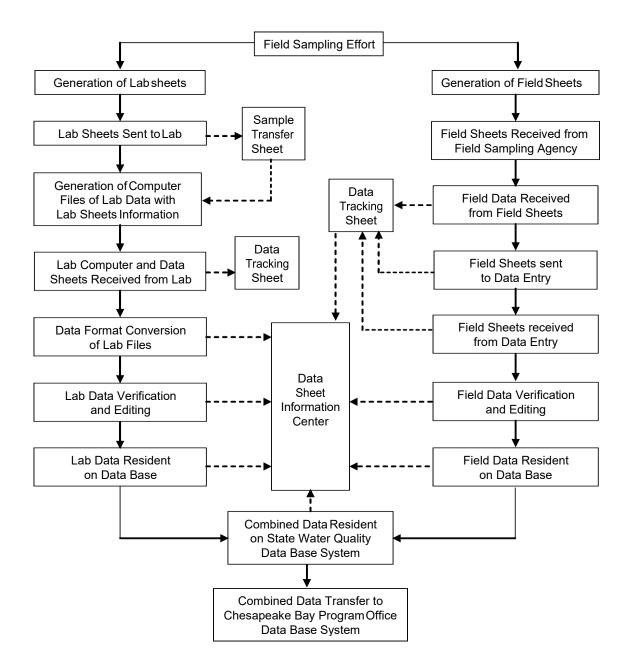


Figure 3. Data Tracking Flow Chart

Additionally, data from duplicate field samples will be reviewed by a data analyst.

# 6. PROJECT QUALITY ASSURANCE/QUALITY CONTROL

The data collected as part of the Chemical and Physical Properties Component of the Chesapeake Bay Water Quality Monitoring Program are used in making management decisions regarding Chesapeake Bay water quality as described in the Introduction. DNR will follow specific procedures to ensure that the design is properly implemented and that monitoring measurements are made and managed with sufficient accuracy, precision, and detection limits. General discussions of quality assurance and quality control aspects associated with accuracy, precision, data management, reporting, and audits are provided in the subsections below. For detailed descriptions of quality assurance and control procedures used in the field, the laboratories, and data management, see the attached appendices.

# 6.1. Accuracy

The accuracy (closeness to the true value) of the collected data will be controlled and assured by the proper use, calibration, and maintenance of both field and laboratory equipment for the measurement of physical and chemical parameters. All instruments are identified by a unique number, used as an index for documentation of calibration, repair, and preventive maintenance. Where possible, standards used for calibration purposes will be validated against a primary standard such as those available from the National Institute of Standards and Technology (NIST).

Daily quality control checks (including the running of blanks and standards) will be used to control and assure laboratory accuracy. See Appendix 15 weblinks for details on the frequency of running blanks and standards and for additional procedures for laboratory quality assurance and control.

Accuracy of laboratory results will also be assessed through DNR's participation in the Chesapeake Bay Coordinated Split Sample Program, a split sampling program in which the coordinated split samples are analyzed by five laboratories involved in Chesapeake Bay monitoring. CSSP was established in June 1989 to establish a measure of comparability between sampling and analytical operations for water quality monitoring throughout the Chesapeake Bay and its tributaries. DNR follows the protocols in the *Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines Rev. 4* (EPA 2010) and its revisions. Split samples are collected quarterly. Results are analyzed by appropriate statistical methods to determine if results differ significantly among labs. When a difference occurs, discussion begins regarding techniques and potential methods changes to resolve discrepancies. A summary of the coordinated split sample program and a copy of the split sample custody log are provided in Appendix 7.

Additionally, CBL's Nutrient Analytical Services Laboratory will participate two times per year in the United States Geologic Survey (USGS) reference sample program and will permit USGS to release the results to the Chesapeake Bay Program Quality Assurance Officer.

Procedures to control and assure the accuracy of field measurements involve the calibration of field instruments, the verification of these calibrations, equipment maintenance, and collection of filter blanks. These procedures are detailed in Appendices 5 and 6.

When field replicate control limits are exceeded, or when field blank values exceed lowest calibration standards, information about the issue is presented to the <u>Data Integrity Work Group</u> (DIWG). The DIWG may suggest corrective actions to field and laboratory procedures.

# 6.2. Precision

Precision (repeatability) of the chemical analytical methods will be determined and documented from duplicate analyses. Precision of the entire measurement system for laboratory-analyzed parameters, including field processing, storage, and chemical analysis, can be assessed from duplicate field samples. Duplicate field samples will be routinely collected approximately every 20 samples, as described in Appendix 1. The protocols for duplicate analyses in the laboratory are described in the Standard Operating Procedures for the Nutrient Analytical Services Laboratory in Appendix 15 weblinks.

# 6.3. Data Review and Data Verification

Data review and data verification ensure the quality assurance and quality control of data. Corrective actions routinely taken when data checks fail is detailed above in Section 5, DATA MANAGEMENT, VERIFICATION AND DOCUMENTATION.

## 6.4. Audits

#### The Chesapeake Bay Blind Audit Program

The CBP Blind Audit Program provides laboratory proficiency testing samples for dissolved and particulate nutrients and chlorophyll at the relatively low concentrations commonly found in estuarine systems. Prepared concentrates of dissolved and particulate substances, whose concentrations are unknown to the analysts, are distributed twice a year to multiple regional laboratories, as well as laboratories outside of the Chesapeake Bay area. The results provide a measure of laboratory accuracy as the samples are fully prepared prior to distribution and the errors associated with field filtering and subsampling are minimized. The Nutrient Analytical Services Laboratory at the UMCES Chesapeake Biological Laboratory is the sole provider of the Blind Audit samples.

Performance audits for chemical analyses conducted at the University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory, Nutrient Analytical Services Laboratory (NASL) are based on the results of samples distributed by the EPA Chesapeake Bay Program Blind Audit Program. These samples must fall within the 95% confidence interval for acceptance. If results fall outside this range, corrective actions for each parameter and measurement are taken. NASL prepares the blind audit samples for all participating laboratories and analyzes some of those samples. For dissolved nitrogen and dissolved phosphorus, a laboratory quality assurance officer determines the concentrations in the ampules, prepares the concentrates, and seals the ampules. A different person then analyzes the sample blindly. For the particulate fractions (particulate carbon, /particulate nitrogen, and particulate phosphorus), samples are filtered and then placed in pouches in the freezer until they are ready to be sent to the other CBP participating laboratories. For chlorophyll, samples are filtered and then placed in pouches in the freezer until they are ready to be sent to the other CBP participating laboratories. As of 2-May-2022 the following labs were participating in the Blind Audit program: College of William and Mary - Virginia Institute of Marine Science, Analytical Services Center; Delaware DNREC-DWR; Hampton Roads Sanitation District - CEL; Maryland Department of Health; Virginia Tech Occoquan Watershed Monitoring Lab; Division of Environmental Sciences, Inorganics Analytical Laboratory; Massachusetts Water Resource Authority; New Jersey Public Health, E&A Lab; New Jersey State Police HQ Campus; Old Dominion University, Water Quality Laboratory; Patrick Center for Environmental Research - Academy of Natural Sciences of Philadelphia; Pennsylvania Department of Environmental Protection - Bureau of Laboratories; Sprague River Water Quality Laboratory; University of Maryland, CES, Appalachian Laboratory; University of Maryland, CES, Chesapeake Biological Laboratory; Virginia Division of Consolidated

<u>Laboratory Services</u>; Anne Arundel County Community College Environmental Center; and the Interstate Environmental Commission (IEC/NY-NJ-CT).

Final annual audit reports can be viewed at <a href="https://www.umces.edu/blind-audit-results-nasl">https://www.umces.edu/blind-audit-results-nasl</a>

Once annually, the EPA Chesapeake Bay Program quality assurance officer will conduct an on-site audit of the Mainstem laboratory and field programs. The DNR Quality Assurance Officer will communicate on a weekly basis with the field program staff and confers with the laboratory quality assurance officers to ensure that all aspects of the program are being conducted properly.

# 6.5. Reporting

Quality assurance information for field duplicate samples in the Mainstem and tributaries will be stored within the routine computerized water quality data sets as replicate observations that can be used to assess precision. For both the tributary and Mainstem chemistry, laboratory quality assurance/control information on duplicates and spikes will be stored in a computerized data set as a companion to the regular data sets and submitted to the Chesapeake Bay Program Office (CBPO) quarterly. The DNR Quality Assurance Officer will provide a summary of any relevant quality assurance/control information in quarterly progress reports for the Mainstem program. The EPA Chesapeake Bay Program quality assurance officer will report on results of field and laboratory audits for the Mainstem program.

# 6.6. Data Quality Indicators

To ensure that data are of the quality required to support Chesapeake Bay Program management decisions, Maryland's Chesapeake Bay Water Quality Monitoring Program will strive to provide monitoring data of known and consistent quality to the CBPO by generally following the guidelines outlined in Chapter II, Section E of the *Recommended Guidelines for Sampling and Analysis in the Chesapeake Bay Monitoring Program, August 1996* (EPA 1996). These guidelines recommend precision goals of field and lab measurements of <20 percent of the coefficient of variation; accuracy goals within 80 to 120 percent, and the completeness goals of 100 percent. Detection limit ranges are provided in Table 3 above. Field measurement minimum detection limits are listed in Table 4.

**Table 4. Minimum Detection Limits for Field Measurements** 

PARAMETER	MINIMUM DETECTION LIMIT
Water Temperature	0.1 °C
Depth	0.5 m
Dissolved Oxygen	0.0 mg/L
Conductance, Specific	Down to 1 micromhos/cm at low levels (accurate to 3 significant digits)
pН	0.1 pH units
Secchi Depth	0.1 m
Salinity	0.1 ppt
Light Attenuation (PAR)	0.05% at 100% light

# 7. DATA ANALYSIS AND REPORTING

The key objectives of the Chesapeake Bay water quality monitoring program are to accurately describe the current state of the Bay Mainstem and tidal tributaries and to detect long-term trends. Trends are analyzed using techniques recommended by the Chesapeake Bay Program's Tidal Monitoring and Analysis Work Group (TMAW, formerly the Data Analysis Work Group—DAWG), including the *Guidance for the Analysis of Water Quality Trends in the Chesapeake Bay* (Eskin et al. 1993) developed by DAWG in 1993. This published guidance provides general discussion on developing analytical objectives, reviewing and assembling data, and interpreting results. Data analysis topics covered in the document include:

- Selecting appropriate spatial and temporal scales.
- Exploring data characteristics such as distribution, censoring, trend characteristics (step versus monotonic), variances, seasonality, persistence, and missing data.
- Adjusting for flow variability; and,
- Considering the power and robustness of the tests.

The document also briefly discusses specific statistical tests, such as the seasonal Kendall test, Van Belle and Hughes intra-block tests, and Mann-Kendall tests, and corrections for serial dependence. TMAW made recommendations and had a goal of updating the *Guidance for the Analysis of Water Quality Trends in Chesapeake Bay* to help analysts reach technically sound conclusions and interpretations and to foster a consistent approach to trend analysis among the various investigators and multiple jurisdictions involved in the monitoring and analysis of Chesapeake Bay water and habitat quality.

In 2014, the Scientific, Technical Assessment & Reporting (<u>STAR</u>) team formed the Integrated Trends Analysis Team (ITAT). Many TMAW goals have been subsumed by similar ITAT goals. ITAT goals are listed below.

- Gather researchers and analysts from various governmental, academic, non-profit, and private organizations for biannual meetings to identify the broad scope of on-going work related to trends and patterns of water quality in the Chesapeake watershed and estuary.
- Discover previously un-identified linkages among the ongoing research activities of participating individuals and organizations.
- Develop a standard set of analysis tools that can be applied in any relevant ecosystem within the Chesapeake watershed and estuary.
- Foster increased collaboration and awareness of ongoing research.
- Provide a forum for bringing findings to the broader Chesapeake Bay management community

Beyond analysis of the Maryland monitoring data, DNR staff members participate in Chesapeake Bay Program monitoring activities to produce Bay-wide analyses and reports with cooperating state, federal and local agencies. This activity leads to a better Bay-wide understanding of water and habitat quality and addresses the linkage between water quality and living resources. The Bay Agreement of 1987 also called for a re-evaluation of the nutrient strategies in 1991 and in 1997. Annual updates of water and habitat quality status and trends also were analyzed and summarized in *The State of the Chesapeake Bay and the Watershed: A Progress Report January 3, 2008*, the *Chesapeake Bay Nutrient Reduction Progress & Future Directions Nutrient Reduction Reevaluation Summary Report* (CBP 1997), *Bay Barometer: Health and Restoration in the Chesapeake Bay Watershed* (2018-2019), and Basin Summary Reports.

Beginning in 2011, water quality status and trends analytical results became available via an internet mapping application, rendered on MD DNR's Eyes on the Bay web site that allows users to select parameters and metrics. Detailed methods for Status and Trend calculations are available via the application.

The monitoring data also are used extensively in mathematical modeling efforts to project the water quality response of Chesapeake Bay to various management alternatives. Bay models are regularly updated and refined. The 2010 Chesapeake Bay Eutrophication Model combines interactive models. Additional related information may be accessed by downloading the Chesapeake Bay Program Environmental Modeling – Backgrounder. Results for earlier versions of the model have already been used to set nutrient reduction goals agreed to in the 1987 Bay Agreement and affirmed by the 1991 and 1997 Re-evaluations.

Other components of the DNR Chesapeake Bay Water Quality Monitoring Program are required to produce cumulative "Level I" data reports annually that describe the results of that component from the inception of the programs. These components include the Benthic, Ecosystem Processes, and River Input Programs. In addition to documenting the results of the individual monitoring components, these cumulative reports are intended to serve as "building blocks" for more integrated levels of analysis among the coordinated components.

# 8. PROJECT ORGANIZATION AND RESPONSIBILITY

This section lists the individuals responsible for the major aspects of the Chemical and Physical Properties Component of Maryland's Chesapeake Bay Water Quality Monitoring Program.

Director and Principal Investigator: Thomas Parham, Tidewater Ecosystem Assessment, DNR.

RESPONSIBILITIES: The director and principal investigator is responsible for overseeing the administrative aspects of the program including fiscal management, coordination among other DNR managers and coordination with cooperating agencies and institutions. This individual is also responsible for the technical design, conduct and data analysis of the program.

Quality Assurance Officer: David Goshorn, Senior Bay Restoration Coordinator, DNR.

RESPONSIBILITIES: The quality assurance officer is responsible for documenting and assuring the conduct of field, laboratory, and data management procedures that comprise this study.

Field Sampling Operations: Kristen Heyer, Monitoring Field Office, DNR.

RESPONSIBILITIES: This individual is responsible for administration of the field sampling activities including sample collection, sample storage and sample delivery to laboratories.

Field Sampling Quality Assurance Officer: Kristen Heyer, Monitoring Field Office, DNR.

RESPONSIBILITIES: This individual is responsible for assuring the quality of field procedures and equipment used in this study.

<u>Laboratory Analyses/Water Column Chemistry:</u> Jerry Frank, University of Maryland, Chesapeake Biological Lab, Nutrient Analytical Services Laboratory.

RESPONSIBILITIES: This individual is responsible for analysis of water samples collected in the Mainstern and tidal tributaries.

Communications - Field: Thomas Parham, Tidewater Ecosystem Assessment, DNR.

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RESPONSIBILITIES: This individual is responsible for communications with Field Supervisors.

Communications - Laboratory: Renee Karrh, Thomas Parham, Tidewater Ecosystem Assessment, DNR

RESPONSIBILITIES: These individuals are responsible for communications with Laboratory Supervisors.

Data Management: Mark Trice, Tidewater Ecosystem Assessment, DNR

RESPONSIBILITIES: This individual is responsible for overseeing the management of field and laboratory data collected under this program; managing historical field and laboratory data collected under this program; and maintaining existing data management software.

# 9. PROCEDURAL CHANGE PROTOCOL

The CBP Quality Assurance Coordinator must be notified of the intent to make any substantial or long-term change to a procedure or method, either in the field or laboratory. These changes include items such as instrument type and sampling stations.

The effects of any change in analytical instruments, reagents, calibration, digestion procedure, etc., should be quantified, documented and submitted to the CBP QA Coordinator prior to implementing.

All modifications should be documented using the Chesapeake Bay Monitoring Program Procedure Modification Tracking Form (PMTF). The completed PMTF should be submitted to the State agency Monitoring Coordinator, CBP Quality Assurance Coordinator and CBP Water Quality Database Manager.

Minor changes in field or laboratory procedures, including detection limit changes, should be documented in the CIMS metadata and data submission tables.

Minor events and problems encountered during Chesapeake Bay Mainstem cruises may be reported in the CBP Monitoring Cruise Report and submitted to the State agency, who will then forward the information to the Chesapeake Bay Program Office. For smaller sampling events, all remarks relating to field work may be reported in the CIMS WQ\_Cruise and WQ\_Event tables.

Modifications due to emergencies during a sampling cruise are authorized by the Chief Scientist with priorities for safety and completion of the cruise. The change should be documented within 30 days after the cruise, in either the PMTF or the Monitoring Cruise Report, depending on size or potential impact of the deviation on the data.

# 10. LOG OF SIGNIFICANT CHANGES

Procedural changes have been made over the years to address evolving water quality sampling program requirements, goals, budgetary changes, and recommendations of the Analytical Methods and Quality Assurance Work Group and other issues. (See Appendix 13, LOG OF SIGNIFICANT CHANGES).

The Change Log is a chronological list of changes to the monitoring program. The Log will be updated annually. The list is comprised of change implementation-dates and brief descriptive summaries of modified procedures. Additionally, changes in measured parameter analytical detection limits are summarized in tabular form.

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# MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

#### WATER COLUMN SAMPLING AND SAMPLE PROCESSING PROCEDURES

## I. DEPTH SAMPLING PROTOCOLS

- A. Hydrolab/YSI Depth Sampling Protocols (Mainstern and Tributary)
  - 1. Take readings of temperature, specific conductance, salinity, dissolved oxygen, and pH at 0.5 m, 1.0 m, 2.0 m and 3.0 m. Thereafter, take readings at a minimum of 2.0 m intervals (subject to conditions specified in A.2. below) and at the bottom sample depth. Mainstem bottom sample depth is equal to the nearest whole meter that is at least one meter above the total depth. Tributary bottom sample depth is equal to the total depth minus one meter (not rounded).
  - 2. If the change in DO exceeds 1.0 mg/l OR if the change in specific conductance equals or exceeds 1,000 micromhos/cm over any 2.0 m interval, take readings at the 1.0 m interval between these two readings. Take readings at 1.0 m intervals for total depths less than or equal to 10.0 m.
  - 3. If the above pycnocline (AP) or below pycnocline (BP) sample depth has not been sampled for *in situ* parameters, obtain readings at this depth.
  - 4. At a minimum, take readings at 0.5, 1.0, 2.0, 3.0 m, bottom, and every odd-numbered whole meter depth.

# B. Grab Sampling Depth Protocols

- 1. At stations where two depths are sampled, take collections at:
  - a. 0.5 m below surface.
  - b. 1.0 m above bottom (total depth) to nearest 1.0 m that is at least one full m from the bottom (Mainstem).
  - c. 1.0 m above bottom (tributaries).

NOTES: If total station depth is  $\leq$ 1.5 m, take bottom sample at 0.5 m. Exercise caution when taking bottom samples; if disturbed bottom sediments appear to have been included in a sample, resample after sediment has settled or take sample slightly higher in the water column. If resampling occurs, note this on the field sheet.

- 2. *Pycnocline Exists*: At stations where 4 depths are sampled and a pycnocline exists (see Section C, below), take collections at:
  - a. 0.5 m below surface.
  - b. 1.5 m above upper boundary of pycnocline.
  - c. 1.5 m below lower boundary of pycnocline.
  - d. 1.0 m above bottom to nearest 1.0 m that is at least one full m from bottom (Mainstem).
  - e. 1.0 m above bottom (tributaries).

NOTE: Above pycnocline depth and below pycnocline depth grab samples are collected at the following stations: CB2.2, CB3.1, CB3.2, CB3.3C, CB4.1C, CB4.1E, CB4.2C, CB4.3C, CB4.3E, CB4.4, CB5.1, CB5.2, CB5.3, EE1.1, EE2.1, EE3.1, EE3.2, ET4.2, ET5.2, LE2.2, LE2.3, RET2.4 and WT5.1.

Grab samples on the Patuxent Boat survey are collected at four depths at seven other sites. In addition to surface and bottom water samples, upper mid-water samples (designated as AP) are collected at 3 meters depth. At stations CB5.1W, RET1.1 and TF1.5, lower mid-water samples (designated as BP) are collected at 6 meters. Lower mid-water samples are collected at 9 meters at stations LE1.1 and LE1.4. At stations LE1.2 and LE1.3 lower mid-water samples are collected at the depth of 12 meters.

Grab samples on the Potomac Boat survey are collected at three depths at five stations. In addition to surface and bottom water samples, mid-depth samples (M) are collected at 4.6 meters at stations RET 2.2, TF2.4, TF 2.3 and TF 2.2. The station TF 2.1 mid-depth sample is collected at 9.1 meters.

- 3. *No Discernable Pycnocline*: At stations where 4 depths are sampled and there is no discernable pycnocline (see Section C, below), take collections at:
  - a. 0.5 m below surface.
  - b. at closest profile depth one third the distance from the surface to the bottom.
  - c. at closest profile depth two thirds the distance from the surface to the bottom.
  - d. 1.0 m above bottom (total depth) to nearest 1.0 m that is at least one full m from the bottom (Mainstem).
  - e. 1.0 m above bottom (tributary).
- C. Pycnocline Determination (Only for Stations Sampled at four depths)

The pycnocline is a region in which the water density changes appreciably with increasing depth and thus forms a layer of much greater stability than is provided by overlying surface waters.

1. The pycnocline Calculated Threshold Value (CTV) is used to determine the boundaries of the pycnocline and to calculate the depths at which grab samples should be

collected. The pycnocline Calculated Threshold Value (CTV) is derived using the equation below.

$$CTV = \frac{C_b - C_s}{D_b - D_s} \times 2$$

Where:

 $C_b$  = bottom conductivity (micromhos/cm),

 $C_s$  = surface conductivity (micromhos/cm),

 $D_b$  = depth of bottom conductivity measurement (m),

 $D_s$  = depth of surface conductivity measurement (m),

CTV = calculated threshold value (micromhos/cm)

ex. bottom conductivity: 15800 micromhos/cm surface conductivity: 9500 micromh0s/cm depth of bottom conductivity measurement: 14.6 m depth of surface conductivity measurement: 0.5 m

$$CTV = \frac{15800 - 9500}{14.6 - 0.5} \times 2 = 893.6 \,\text{micromhos/cm}$$

NOTE: micromhos/cm is equivalent to microSiemens/cm (µS/cm)

2. If the Calculated Threshold Value is greater than 500 micromhos/cm, a pycnocline exists with boundaries at the first and last depths where the change in conductivity is greater than the CTV. For example, continuing with the CTV value: 893.6 derived in the example calculation above, and evaluating conductivity readings moving up in the water column from the bottom (at 1-meter increments), the lower boundary of the pycnocline occurs at first depth where the change in conductivity from that measured at the preceding depth exceeds 893.6. Moving upward in the water column, the upper boundary of the pycnocline occurs at last depth where the change in conductivity from that measured at the preceding depth exceeds 893.6. Samples will be taken as described above in section B. 2.

NOTE: In the rare cases when the sample is theoretically 'below the bottom' or 'above the surface', use following procedures. If the below pycnocline (BP) sample is determined to be below the bottom sample, collect the BP sample at the bottom sample depth. If the above pycnocline (AP) sample is determined to be above the surface sample, collect the AP sample at 0.5 m.

3. Take samples as described in section B. 3. (No Discernable Pycnocline), above, if

either of the following two conditions are true:

a. the CTV is less than 500 micromhos/cm.

b. the CTV is equal to or greater than 500 micromhos/cm BUT no depth interval exceeds that CTV.

NOTES: Upper and lower boundaries of the pycnocline may be the same point. If this is the case, collect the Above Pycnocline sample 1.5 m above the upper pycnocline limit and collect the Below Pycnocline sample 1.5 m below the lower pycnocline limit.

# D. Hydrogen Sulfide (H<sub>2</sub>S) Protocols

- \* H2S was not sampled during the 2020-2021 sampling season due to staff shortage and COVID restrictions. H<sub>2</sub>S sampling is tentatively planned to resume in the 2022 sampling season.
- 1. For the Mainstem only, when there is an odor of hydrogen sulfide present in the bottom sample or the below pycnocline sample, perform a Hach Kit test for hydrogen sulfide presence on the bottom and/or below pycnocline sample(s).
- 2. Immediately upon collection of the sample that meets the requirements in D. 1. above, transfer a portion of sample from the sample bottle to the 25 ml Hach Test glass container (from the Hach Hydrogen Sulfide Test Kit, Model HS-6), for hydrogen sulfide determination.
- 3. Immediately perform test for H<sub>2</sub>S presence following instructions in Hach Hydrogen Sulfide Test Kit. Record results on the Cruise Report.

# E. Secchi Depth

Measure water transparency using Secchi disc. Determine Secchi depth in meters to the nearest 0.1 meter using a 20-cm standard Secchi disc lowered into the water column with a calibrated rope. Make observations on the shady side of the boat. Do not wear sunglasses while taking a Secchi reading.

# F. Photosynthetic Active Radiation (PAR)

PAR readings (in  $\mu$ Moles/square meter/second) are taken in the field in order to calculate a light attenuation coefficient. Take PAR measurements with a LICOR quantum meter (Model LI-1400 Data Logger) with an attached underwater probe (Model LI-192SA). The probe is a flat, upwardly directed probe. Each underwater reading is paired with a reading from a flat, upwardly directed ambient light probe (model LI-190SA).

Begin a vertical profile of light penetration by taking an initial reading with the underwater sensor just below the surface of the water (0.1 m). Take subsequent measurements at either 0.25-m or 0.50-m intervals depending on the turbidity of the water column, (taking shallower measurements in more turbid water). Continue to take

readings until a value less than ten percent (10 %) of the surface reading (0.1 m) is attained. Once the readings stabilize, allow at least five readings to flash on the display

before recording the data reading for a specific depth. Record in the data logger the mean of the previous five readings that appear on the instrument display. Alternatively, the mean value may be recorded on the field datasheet. Underwater water and ambient readings must be recorded simultaneously. Be sure to collect additional profile readings if the ambient readings decreased significantly from the starting ambient reading.

The light measurements made for each profile are log-scale regressed against depth to determine the compensation depth, i.e., the depth of penetration of one percent (1 %) of the surface PAR. The compensation depth is used in computing the integrated carbon production for that water column. When light profiles are not available, the secchi disk depth is used to calculate the compensation depth. Over the study period, 1984-1996, a regression has been made between the secchi depth and the compensation depth for the same water column (for those stations where both secchi data and LICOR data are taken). By using this regression, a compensation depth can be estimated from a secchi depth.

The following table lists the parameters measured and the associated qualifiers to be recorded for light attenuation:

FIELD	DESCRIPTION					
SOURCE (PK, FK)	Code identifying agency or contractor that measured the data					
PROJECT (PK, FK)	Agency monitoring project code					
STATION (PK, FK)	CBP station name					
SAMPLE_DATE (PK)	Date on which the PAR readings were taken					
SAMPLE_TIME (PK)	Time at which the PAR readings were taken					
DEPTH (PK)	Depth at which the PAR readings were taken (meters)					
EPAR_S	PAR reading (μM/m²/s) taken at the boat just before or during the measurement of PAR readings at depth					
EPARU_Z	PAR reading (μM/m²/s) taken at depth (up sensor)					
UNITS	Units for PAR (μM/m²/s)					
METHOD	Method code identifying the field measurement procedure					
COMMENTS	Comments related to the collection of PAR readings					

# II. SAMPLE COLLECTION

- A. Lower submersible pump to desired depth.
- B. Allow hose to flush completely before taking sample (flush time is pump dependent).
- C. Rinse pre-marked sample container (plastic bottle) and cap three times with sample water.
- D. Collect sample, cap the bottle, and begin water sample processing and appropriate storage/preservation.
- E. Any time a field duplicate is required (whenever indicated on the station lab data sheet), follow the procedures in the section "Split-sample collection method for field duplicates".
- F. Enter all identifying information pertinent to samples collected on the lab and field sheets.

## III. SPLIT-SAMPLE COLLECTION METHOD FOR FIELD DUPLICATES

- A. Samples for field duplicates are generated approximately one for every 20 samples collected.
- B. Collect sample as in section II. A and II. B above.
- C. Rinse duplicate collection container three times and fill with sample water.

NOTE: Collection container must be large enough to generate two complete samples. If more than one gallon of sample is needed for samples, fill a plastic bucket (2.5 to 5 gallon) with sample water and draw all samples from the bucket, taking care to maintain a homogeneous mixture as water is drawn from the duplicate container.

- D. Begin water sample processing and appropriate storage/preservation.
- E. Enter all identifying information pertinent to samples collected on lab and field sheets.

NOTE: Lab and field sheets must have a replicate number entered for each duplicate generated.

# IV. FILTRATION, PROCESSING AND STORAGE OF CHLOROPHYLL SAMPLES

A. For every depth sampled, clean bell and frit with deionized water (DI-water; stored in a high-density polyethylene container) generated at the Field Office. Set up bell and frit for filtering. Ensure that there is a trap in line between the manifold and the vacuum source.

- B. Place a Whatman GF/F glass fiber filter pad (pore size =  $0.7 \mu m$ ) on the filter frit. When handling the pad, use clean forceps.
- C. Mix sample thoroughly by agitating plastic sample container vigorously, then rinse graduated cylinder three times with sample.
- D. Fill graduated cylinder with sample and filter desired volume through filtration unit. Keep the vacuum below 10 inches of Hg. Filter sufficient volume of sample (100 1500 ml) so that you have sufficient color on the filter pad. Do not filter the filter pad dry. In order to avoid cell damage, decrease the amount of vacuum as the final volume approaches the level of the filter and release the vacuum as the last of the water is pulled through the pad. Record the total volume filtered.
- E. Add approximately 1 ml of MgCO<sub>3</sub> suspension (Laboratory grade from Fisher Scientific prepared in a 1.0 g MgCO<sub>3</sub> to 100 ml of DI-water ratio) to the last 50 ml of sample in the filtration bell. This is equivalent to less than 1 mg of MgCO<sub>3</sub> per 15 ml extract.

NOTE: Filtrate for nutrient analysis should not be saved from this filtration.

- F. Remove filter pad with forceps, fold filter in half with sample inside, and place in premarked foil square, and carefully fold square in thirds, horizontally and vertically, to seal filter inside. Be sure forceps do not touch sample residue on the filter pads, because the sample will adhere to the forceps.
- G. Be sure that foil square is marked with date, station, sample layer code, volume of sample filtered, sample number, and "CHLA".
- H. Place sample FOIL into pre-marked zip-lock plastic bag. Store bag of chlorophyll samples in Research Vessel freezer for Mainstem samples or an ice chest for tributary samples. If samples are stored on ice, place in freezer on return to Field Office.
- I. Record sample identifier, date, volume filtered (L), depth (m), layer, start time, end time, study code, submitter code, data category code, field scientist sign-off, and replicate number, if necessary, on chlorophyll volume sheet. This sheet is submitted to the laboratory with the samples.

NOTE: Filter pad with chlorophyll sample should be exposed to as little direct sunlight as possible. Store filter pad in foil as soon as possible.

NOTE: A lab replicate pad (different from the field replicate) is generated every 10 samples. Filter the exact same volume as the first pad. Place the second pad alongside the first pad into foil. The label on the foil will indicate "2 pads" to denote when to generate a replicate pad.

# V. FILTRATION, PROCESSING AND STORAGE FOR PARTICULATE FRACTIONS (PARTICULATE P, C, N AND TOTAL SUSPENDED SOLIDS)

# A. Processing and storage - PC, PN:

For each depth sampled, thoroughly clean all bells and frits with DI-water, set up filter apparatus, filters (two pre-combusted 25 mm GF/F filters, pore size =  $0.7~\mu m$ ), and bells for filtering. Filter 10-300 ml through each filter. Filter enough of the sample to leave noticeable color on the filter pad. Make sure filter pad is filtered dry. Using forceps, fold each filter in half. Place both filters in a foil square labeled with date, PC/PN-CBL sample number, station, sample layer, and volume filtered. Fold as described in IV.F. and then place folded foil in zip-lock bag and put in freezer (large boats) or on ice (small boats).

# B. Processing and storage - PP, TSS:

For each depth sampled, thoroughly clean all glassware with DI-water. Set up one flask, filter (one pre-weighed and numbered 47 mm GF/F filter placed with the pad number facing down), and bell for filtering. After rinsing a graduated cylinder three times with sample water, measure 50 - 300 ml of sample into the filter bell. Use the filtrate as an equipment rinse and discard. Note amount filtered through the filter. Then filter enough additional (another 50 -400 ml) to leave a noticeable color on the filter pad. Use this filtrate as required for filtered parameter analysis.

After collecting filtrate, make sure filter is filtered dry. Then rinse filter pad three times with 10 ml rinses of DI water, making sure filter pad is filtered dry after each rinse. Using forceps, fold filter in half. Make sure the pad number is clearly legible on one side only and not on the crease. Place filter in a foil square labeled with date, TSS/PP-CBL sample number, station, sample layer, and volume filtered. Fold as described in IV.F. Place foil square in zip-lock bag and put in freezer (large boats) or on ice in (small boats).

NOTE: A lab replicate pad (different from the field replicate) is generated every 10 samples. Filter the exact same volume as the first pad. Place the second pad alongside the first pad into foil. The label on the foil will indicate "2 pads" to denote when to generate a replicate pad.

Ten percent of the filters that CBL supplies for field filtering TSS must be prerinsed 3 times with deionized water, dried at 103-105 °C for 1 hour, then weighed, redried and reweighed until a constant weight is obtained.

# C. Processing and storage - VSS:

VSS samples are collected from the surface and AP samples at pre-determined stations. Thoroughly clean all glassware with DI-H<sub>2</sub>O. Set up one flask, filter (1 pre-weighed, pre-combusted and numbered 47 mm GF/F filter), and bell for filtering. The number for the pad is written on the individual Petri dish that the pad came in. You must write this number on the foil square label and volume sheet. Also, when done filtering place the

piece of tape with the pad number from the Petri dish on the volume sheet. After rinsing a graduated cylinder three times with sample water, measure 50 - 300 ml of sample into the filter bell. Use the filtrate as an equipment rinse and discard. Note amount filtered through the filter. Then filter enough additional (another 50 -400 ml) to leave a noticeable color on the filter pad. You may use this filtrate as required for filtered parameter analysis.

After collecting filtrate, make sure filter pad is filtered dry. Then rinse three times with 10 ml rinses of DI water and making sure filter pad is filtered dry after each rinse. Using forceps, fold each filter in half. Place the filter in a foil square labeled with date, VSS-CBL sample number, pad number, station, sample layer, and volume filtered. Fold as described in IV.F. Place foil square in the TSS/PP zip-lock bag and put in freezer (large boats) or on ice in (small boats).

# VI. FILTRATION, PROCESSING AND STORAGE FOR "DISSOLVED" FRACTIONS (NH<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub>, PO<sub>4</sub>, Si, TDN, TDP, DOC)

A. This filtrate for the dissolved fractions always comes from particulate phosphorus/TSS filters described in section V. It is acceptable to use the filtrate from the VSS filtration if more volume as needed. Use GF/F filters, and pre-rinse the filter and flask with at least 50 ml of sample water. The sample must be collected prior to rinsing the pads with DI-water.

# B. Processing and storage - NH<sub>4</sub>, NO<sub>2</sub> + NO<sub>3</sub>, NO<sub>3</sub>, PO<sub>4</sub>, Si:

Triple rinse, with filtrate, three like-numbered autoanalyzer (AA) vials and caps. Fill approximately 7/8 full, allowing for sample expansion upon freezing. Place the AA vials in a rack in the freezer. A fourth vial is collected for silica at a subset of stations. The silicate vial should be stored at 4 °C in the R/V refrigerator. On small boats, keep all samples iced in a cooler, and then freeze all but silica upon return to Field Office. Place the silica samples in the refrigerator upon return to the Field Office.

NOTE: The number on all vials and test tubes is the CBL sample number. This should match the number on TSS/PP and PC/PN foil pouches for each particular sample.

# C. Processing and storage - TDN, TDP:

Triple rinse test tube, cap, and 10 ml graduated cylinder with filtrate. Be sure the number on test tube corresponds to the number on the vials and sample number. Use 10 ml graduated cylinder to measure EXACTLY 10.0 ml of filtrate. Shake any remaining rinse water out of the test tube. Pour into pre-rinsed test tube and cap sample, then freeze sample in test tube rack on large boats. On small boats, keep sample on ice in cooler, then freeze upon return to Field Office.

D. Processing and storage - DOC (collected at subset of Bay Tributary and Mainstem

survey stations): Triple rinse 60 ml container and cap with filtrate. Fill the 60 ml bottle to the shoulder with filtrate and cap sample, then freeze in DOC rack. On small boats, keep sample on ice, then freeze at Field Office.

# VII. ROUTINE MAINTENANCE OF FILTRATION UNITS AND CONTAINERS FOR MAINSTEM CRUISES AND AFTER RETURNING FROM FIELD

A. After each day's sampling on Mainstem cruises, filtration units, flasks, frits and graduated cylinders should be cleaned with a non-phosphorus liquid soap, rinsed with tap water three times, then rinsed with 10% HCl (prepared from concentrated HCL from Fisher Scientific diluted with DI-water), tap rinsed, and finally rinsed three times with DI-water. All open flasks, filtration units and graduated cylinders should then be covered to prevent contamination if filtering is not to begin immediately. The filtration unit used for chlorophyll *a* filters should be washed with soap and rinsed with tap and DI-water and not be rinsed with 10 percent HCl.

B. Big boat units are cleaned at the end of each day's sampling. Small boat or land run units are rinsed with DI-water at end of each day's use and cleaned (with acid) weekly, or after processing 20 to 30 samples.

## VIII. FIELD FILTERED AND SOURCE WATER BLANKS

- A. Mainstem One field filtered equipment blank will be collected each day. One unfiltered (source water) blank will be collected each day. The filtered equipment blank and source water blank will be collected and submitted at the same time.
- B. Tributary- One field filtered equipment blank will be collected each month. One unfiltered (source water) blank will be collected each month. The filtered equipment blank and source water blank will be collected and submitted at the same time. The tributary field blanks will rotate through the sampling teams to ensure that all filtering equipment is being evaluated for contamination.
- C. Both the Mainstem and Tributary blanks will be analyzed by CBL. If any of the blanks show results greater than the Minimum Detection Limit, MDDNR Field Office staff members will investigate the potential sources of contamination and will assess the significance of the contamination.

# MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

## FIELD SHEET AND LAB SHEET- DOCUMENTATION AND PROCEDURES

The following words describe procedures Maryland Department of Natural Resources uses to fill out Field Data Sheets, and Lab Volume Sheets (nutrient, suspended solids and chlorophyll) used for the Chesapeake Bay Mainstem and Tributaries water quality monitoring programs.

Examples of Field Data Sheets: A, B and Patuxent River are located at the end of this appendix. Lab volume sheet, raw and processed Mainstem LiCor data are also shown.

Water quality data columns on field data sheets A and B are different from Patuxent Field Data Sheet water quality columns because of differences in how LiCor data are handled. LiCor data is logged on Patuxent Field Data Sheets. LiCor data collected on Mainstem surveys are downloaded, stored, processed and submitted separately. Differences between Patuxent Field Sheets and Field Sheets A and B are noted below.

Beginning in 2009, chlorophyll analysis by the Maryland Department of Health ceased and the Chesapeake Bay Laboratory, Nutrient Analytical Services Laboratory began analyzing chlorophyll samples.

Codes used for the water quality monitoring program are listed in Appendix 9.

NOTE: Leave blank any boxes on the Field Sheet for which data are not collected.

## **Field Sheet A:**

The Field Sheets are sent along with a Cross Reference Sheet from the Field Office to the Data Management Unit at the DNR Tawes Building. (See Appendix 3 for information on the Cross Reference Sheet.) The Field Office must provide the following information on the Field Sheet.

1. Sequence Number (boxes 3-9, upper right-hand corner)

The following convention has been used to designate the 7-digit sequence number for the Mainstem, where YY is last two digits of year, NNN is the cruise number (that year), and SS is the station order for that week's cruise:

MAINSTEM Convention YYNNNSS

For example, sequence number 8401204 is the 12th cruise in 1984 at station 4 for that week's cruise.

The following convention has been used to designate the 7-digit sequence number for the tributary sampling, where YY is last two digits of year, MM is month, T is for tributary, P is for Patuxent, M is for Potomac, C is for CORE, and XX is an arbitrary ordering number:

TRIB Convention	YYMMTXX			
PXT Convention	YYMMPXX			
POT Convention	YYMMMXX			
CORE Convention	YYMMCXX			

For example, 9603P05 is the fifth field sheet for a March Patuxent cruise in 1996.

## 2. Sampling Station Number (boxes 10-18)

Enter the appropriate Chesapeake Bay Program station location (e.g., WT5.1, ET5.2) beginning with the box numbered 10. Put only one character (including decimal points) per box.

#### 3. Start Date (boxes 20-25)

Enter the start date beginning with year, then month and then day. Use two numbers each for year, month and day. For example, March 2, 2017, would be entered 170302.

# 4. Start Time (boxes 27-30)

Enter the start time of the sampling effort at a station location in military time.

#### 5. End Date (boxes 32-37)

If the end date for a particular station is the same as the start date, the end date boxes can be left blank.

## 6. End Time (boxes 39-42)

Enter the end time of the sampling collection effort at a station location in military time. The end time is the time at the end of *in situ* data collection (meter readings).

#### 7. Number of Samples (boxes 44-45)

Enter the number of samples taken (including duplicates) at the station location. Routinely, there are two to five samples collected at stations for the Chesapeake Bay Monitoring program.

#### 8. Submitter Code (boxes 47-48)

The submitter codes specify the collection group and the lab that will perform the analyses.

## 9. Data Category Code (boxes 50-51)

The data category codes, which are listed in Appendix 9, specify the code for the type of sample being collected. For example, for the Chesapeake Bay Program Main Bay Sampling, the code is 'MB' - Chesapeake Bay Monitoring Sample- MD. Main Bay".

## 10. Total Depth (M) (boxes 53-55)

Enter the total depth at the station in meters to the nearest 0.1 m for tributary stations and to the nearest 0.5 m for Mainstern stations.

#### 11. Study Code (boxes 57-58)

The study codes, which are listed in Appendix 9, indicate the type of monitoring program. For example, '01' is the study code for the "Chesapeake Bay Monitoring Program - Main Bay".

#### 12. Sample Method (line #2, box 10)

The sample method codes, which are listed in Appendix 9, indicate the sample method used for the sampling effort. For example, '1' is the code for 'Grab Samples'.

Note: If no water samples are collected, the code is '7', (FIELD MEASUREMENTS ONLY).

# 13. Air Temperature degrees Celsius (line #2, boxes 11-14)

Air temperature is reported in degrees Celsius to the nearest 0.5 degrees. The value is recorded in boxes 12-14. Box 11 is used to indicate whether the temperature is above, below or exactly zero. If the temperature is above zero, write a plus (+) in box 11. If the temperature is below zero, write a minus (-) and leave box 11 blank if the temperature is 0 degrees. If the air temperature is a single digit (-/+ 4.0), a zero must be placed in box 12 of the field sheet for example: -04.0.

#### 14. Tide State (line #2, box 18)

Tide state codes are listed in Appendix 9. For example, the code 'E' specifies an ebb tide.

## 15. Weather Code Yesterday (line #2, boxes 20-21)

Enter the code for yesterday's weather in these boxes. The weather codes with their corresponding descriptions are listed in Appendix 9. Additional weather information can be included in the comments section if appropriate.

## 16. Weather Code Today (line #2, boxes 23-24)

Enter the code for current weather (while at station) in these boxes. Additional weather information can be included in the comments section if appropriate.

## 17. Percent Cloud Cover (line #2, boxes 25-27)

Enter the amount of cloud cover in these boxes. Percent Cloud Cover is reported as values from 000 to 100 percent. Numbers must be **right** justified, e.g., 5 (not 5 ).

## 18. Wind Direction (line #2, boxes 28-30)

Record wind direction using the codes:

- N Northerly direction
- S Southerly direction
- E Easterly direction
- W Westerly direction

Record wind direction in boxes 28-30 using up to three letters to designate the prevailing conditions. An example of wind direction would be 'north by north east' and the codes in boxes 28-30 would be 'NNE'. If only one or two letters are needed to designate the conditions, use the boxes beginning with box #28 for the codes. Letters must be **left** justified, e.g., <u>S W</u> (**not** <u>S W</u>)

## 19. Wind Velocity (knots) (line #2, boxes 31-32, 33-34)

Record wind velocity in knots in boxes 31-32, 33-34. Record the minimum (or lower range) velocity in boxes 31-32; record the maximum (or upper range) velocity in boxes 33-34. For example, if the wind is blowing from 7 to 10 knots, the minimum wind velocity is '07' and the maximum wind velocity is '10'. If only one number is needed to designate the wind velocity conditions, enter the identical numbers in both the boxes for minimum velocity as well as in the boxes for maximum velocity. Beaufort Wind Force Scale values may be used when recording wind velocity. 01-03, 04-06, 07-10, 11-16, 17-21, 22-27, and 28-33.

number	Wind speed			Mean wind speed (kt / km/h / mph) Descripti on on	Wave height		Sea conditions	Land conditions		
	kt	km/h	mph	m/s			m	ft		Calm. Smoke rises
0	0	0	0	0-0.2	0/0/0	Calm	0	0	Flat.	vertically.
1	1-3	1-6	1-3	0.3-1.5	2 / 4/ 2	Light air	0.1	0.33	Ripples without crests.	Wind motion visible in smoke.
2	4-6	7-11	4-7	1.6-3.3	5/9/6	Light breeze	0.2	0.66	Small wavelets. Crests of glassy appearance, not breaking	Wind felt on exposed skin. Leaves rustle.
3	7-10	12-19	8-12	3.4-5.4	9 / 17 /11	Gentle breeze	0.6	2	Large wavelets. Crests begin to break; scattered whitecaps	Leaves and smaller twigs in constant motion.
4	11-16	20-29	13-18	5.5-7.9	13 / 24 / 15	Moderate breeze	1	3.3	Small waves.	Dust and loose paper raised. Small branches begin to move.
5	17-21	30-39	19-24	8.0-10.7	19 / 35 / 22	Fresh breeze	2	6.6	Moderate (1.2 m) longer waves. Some foam and spray.	Smaller trees sway.
6	22-27	40-50	25-31	10.8-13.8	24 / 44 / 27	Strong breeze	3	9.9	Large waves with foam crests and some spray.	Large branches in motion. Whistling heard in overhead wires. Umbrella use becomes difficult.
7	28-33	51-62	32-38	13.9-17.1	30 / 56 / 35	Near gale	4	13.1	Sea heaps up and foam begins to streak.	Whole trees in motion. Effort needed to walk against the wind.

# 20. Secchi (M) (line #2, boxes 35-38)

Record Secchi depth in meters to the nearest 0.1 meter.

#### 21. Flow Value (line#2, boxes 39-46)

Note that flow is not recorded in regular scientific notation but is recorded as follows. Box #39 is the flow basis code, where:

- 1 = measured in cubic feet per second (CFS)
- 2 = estimated in cubic feet per second (CFS)
- 3 = measured in million gallons per second (MGS)
- 4 = estimated in million gallons per second (MGS)
- 5 = measured in gallons per day (GPD)
- 6 =estimated in gallons per day (GPD)

Boxes 40-44 are for the five-digit mantissa and box 45 is for the exponential value in base 10. These boxes are to be left blank at boat or other stations where flow is not recorded.

For example, estimated flow  $4.5_{cfs} = 2.450001$ , where "2" indicates that the flow is estimated in cubic feet per second, "45000" indicates that the mantissa is 4.5000, and "1" indicates multiply the mantissa by  $10^1$ .

The final box, #46, is for greater or less than (G or L).

Note: Flow value is not a required parameter and is seldom measured.

## 22. Senior Scientist (line #2, boxes 47-49)

The three initials of the senior scientist (the scientist in charge of the sampling effort for that day) are entered in these boxes. If the scientist has only 2 initials the letters are flush left with box 49 empty.

# 23. DO Method (line #3, box 50)

The codes for the dissolved oxygen (DO) methods are listed in Appendix 9. Method code values currently used are: 'H' for Hydrolab Clark Cell; 'L' for Hydrolab LDO; and 'R' for YSI ROX. A switch to YSI EXO began in 2020.

#### 24. Equipment Set Unit # (line #3, boxes 51-52)

The numbers assigned to equipment packages is recorded in these boxes.

# 25. Probe Number (line #3, boxes 53-54)

Enter the Hydrolab or YSI probe number in these boxes. If using spares, enter the same equipment letter in probe number box and record spare number in comments boxes.

The text of the label over boxes 53-54 on the field sheets used on Patuxent River project is "LiCor Number" instead of "Probe Number". (See Patuxent field sheet example at the end of this appendix).

# 26. Flow/Tide Unit Number (line #3, boxes 55-56)

Enter in boxes 55-56 the number of the meter used to measure the flow value. These boxes should be left blank if flow was not recorded for the station.

The text of the label over boxes 55-56 on the field sheets used on Patuxent River project is "LiCor Method" instead of "Flow/Tide Unit Number". (See Patuxent field sheet example at the end of this appendix).

# 27. Wave Height (M) (line #3, boxes 57-59)

Wave height is recorded in meters.

Values used for wave heights are

```
0.00 \text{ m}=flat calm 0.09 \text{ m}= slight ripple 0.20 \text{ m}= ripple-1 foot 0.40 \text{ m}= 1-2 feet 1.00 \text{ m}= 2-4 feet 1.5 \text{ m}= 4-6 feet
```

# 28. Upper Pycnocline Limit (M) (line #3, boxes 60-62)

The calculated value for the upper pycnocline limit is recorded in meters and is entered in these boxes. If no pycnocline exists, leave these boxes blank.

## 29. Lower Pycnocline Limit (M) (line #3, boxes 63-65)

The calculated value for the lower pycnocline limit is recorded in meters and is entered in these boxes. If no pycnocline exists, leave these boxes blank.

30. Scientist Signoff (line #3, boxes 66-68)

A DATA SHEET WITH NO SCIENTIST SIGNOFF WILL NOT BE SENT TO THE DATA ENTRY SERVICE.

The scientist who checked over the field sheet for:

- the correct codes
- the correct date
- the correct start time and end time
- the correct sampling station number
- reasonable values for the parameters

the values for the parameters are entered on the sheet properly enters his/her initials in these boxes.

Ideally, the individual who initiates the signoff is a separate individual from the one who enters the values on the data sheet. This process of using two separate individuals whenever possible, one to enter the values onto the sheet and one to check over the values that are entered, can help minimize transcription errors and correct aberrations in protocol. However, when a scientist works alone, the same scientist who enters the values checks the sheets before leaving the station.

# 31. Comments (beginning on line #3 - #5)

Any comments that are necessary to fully describe the sampling effort should be entered in the Comment section. Use one box for each character, decimal point, or period.

# 32. Replicate Number (line #6, box 11).

Patuxent River Survey Replicate Number (line #6, box 10)

If the values for specific conductance, water temperature, DO, etc. are repeated for a single depth and are entered on the field sheet, indicate this by entering the replicate number (from 2 to 9) in these boxes. A blank in line #6, box 11 defaults to 1. A blank in Patuxent River line #6, box 10 defaults to 1.

## 33. Depth (M) (line #6, columns 13-15)

Patuxent River Survey Depth (M) (line #6, columns 11-14)

Enter the depth at which the suite of parameters is measured (in meters).

# 34. Water Temperature degrees C (line #6, columns 17-20)

The water temperature is recorded in degrees Celsius. The value is recorded in columns 18-20; column #17 is to indicate a minus (-) value. Leave this column blank if temperature is greater than or equal to zero; write in a minus (-) sign if it is below zero.

Patuxent River Survey Water Temperature (line #6, columns 15-18).

On the Patuxent River Survey, the temperature value is recorded in columns 16-18; column #15 is used to indicate a minus (-) value. Leave this column blank if temperature is greater than or equal to zero; write in a minus (-) sign if it is below zero.

## 35. Field pH (line #6, columns 22-25)

Patuxent River Survey Field pH (line #6, columns 19-22)

Enter values for field pH in these columns (round pH to the nearest tenth).

## 36. Value Corrected (line #6, column 27)

Patuxent River Survey Value Corrected (line #6, column 23)

Use one of the three codes for DO correction in Appendix 9, (usually "C").

# 37. DO (mg/l) (line #6, columns 28-32)

Enter the DO value in columns 29-32. Column #28 is used to indicate greater than (G) or less than (L) values. A less than (L) in column #28 indicates that the value for DO in columns 29-32 is less than the detection limit for the DO probe. The code "C" may be used in the column designated for G/L if no value is recorded due to probe/ instrument failure. The code "F" may be used in the column designated for G/L if the data appear normal, but the probe/ instrument failed post calibration check due to damage after sampling. The code "V" may be used in the column designated for G/L if the probe post calibrated outside of QA guidelines.

Enter Patuxent River Survey DO value in columns 25-28. Column #24 is used to indicate greater than (G) or less than (L) values. A less than (L) in column #24 indicates that the value for DO in columns 25-28 is less than the detection limit for the DO probe. The code "C" may be used in the column designated for G/L if no value is recorded due to probe/ instrument failure. The code "F" may be used in the column designated for G/L if the data appear normal, but the probe/ instrument failed post calibration check due to damage after sampling. The code "V" may be used in the column designated for G/L if the probe post calibrated outside of QA guidelines.

38. Specific Conductance (microSiemens/cm) (line #6, columns 34-39)
Patuxent River Survey Specific Conductance (microSiemens/cm) (line #6, columns 29-34)

Enter the values for specific conductance in columns 35-39. Use column #34 to indicate greater than (G) or less than (L) values. The code "C" may be used in the column designated for G/L if no value is recorded due to probe/ instrument failure. The code "F" may be used in the column designated for G/L if the data appear normal, but the probe/ instrument failed post calibration check due to damage after sampling. The code "V" may be used in the column designated for G/L if the probe post calibrated outside of QA guidelines.

Enter Patuxent River Survey values for specific conductance in columns 30-34. Use column #29 to indicate greater than (G) or less than (L) values. The code "C" may be used in the column designated for G/L if no value is recorded due to probe/ instrument failure. The code "F" may be used in the column designated for G/L if the data appear normal, but the probe/ instrument failed post calibration check due to damage after sampling. The code "V" may be used in the column designated for G/L if the probe post calibrated outside of QA guidelines.

NOTE: Hydrolab reports microSiemens/cm.

39. Salinity (ppt) (line #6, columns 40-43) salinity values are rounded to the nearest tenth. Patuxent River Survey Salinity (ppt) (line #6, columns 35-38)

Enter a value for salinity in columns 40-43. Enter a value for Patuxent River Survey salinity in columns 35-38.

40. Lab Login Section (line # 6, columns 49-63) (See 40B below: Patuxent River Survey Layer Code and LiCor Section (line # 6, columns 39-49))

This section is used to record the number of replicate water samples which were collected, the depth at which the samples were collected, the layer from which the samples were collected, and the bottle numbers that the samples were assigned. (Note the designation AP and BP indicate above and below pycnocline only if a pycnocline actually was present. If no pycnocline they indicate below surface and above bottom at 1/3, 2/3 depths.)

A. Replicate (line #6, column 49)

If more than one sample is collected for analysis at an identical depth, indicate this by entering a 1, 2, 3, etc. to differentiate the replicates. Leaving this column blank results in a default to 1.

B. Sample Depth (M) (line #6, columns 50-52)

Record the depth in meters at which the samples were collected. Meter readings are required for this depth.

C. Layer Code (line #6, columns 53-54)

Indicate at which layer the samples were collected. The layer codes are listed in Appendix 9. Enter layer code (S=surface, B=bottom, AP=above pycnocline, BP=below pycnocline, M=mid water column). Left justify single-character codes (i.e., codes with only one letter).

D. Bottle Numbers (line #6, columns 55-63)

Enter the bottle numbers assigned to the samples. Up to nine alphanumeric characters can be used. If less than nine characters are used, left justify. These bottle numbers are the same as those indicated on lab sheets.

40B. Patuxent River Survey Layer Code and LiCor Section (line # 6, columns 39-49)

This section is used to record the layer from which the bottle samples were collected and Deck and Underwater LiCor readings.

A. Layer Code (line #6, columns 39 and 40)

Indicate at which layer the samples were collected. The layer codes are listed in Appendix 9. Enter layer code (S=surface, B=bottom, AP=above pycnocline, BP=below pycnocline). Left justify single-character codes (i.e., codes with only one letter).

B. LiCor Deck (micromols/m<sup>2</sup>) (line #6, columns 41-44)

Record the LiCor deck value in micromols/m<sup>2</sup> at depths where readings were taken.

C. LiCor Underwater (micromols/m<sup>2</sup>) (line #6, columns 41-44)

Record the LiCor underwater value in micromols/m<sup>2</sup> at depths where readings were taken.

NOTE: Bottle Numbers on Patuxent River Surveys are entered in an unnumbered column to the left of Patuxent River Survey Replicate Number (line #6, column 10).

41. Pycnocline Threshold Calculations

This section is used as a worksheet to calculate the pycnocline. The following symbols are used in the formula.

42. Date entered (entered by keypunch at bottom left of sheet)

Date returned from keypunching (entered by keypunch at bottom of sheet).

43. Page of (bottom right of sheet)

If only one sheet is generated at a station, leave this blank; the default value is 'page 1 of 1.' When two sheets are generated at one station, enter in this area 'page 1 of 2' for the first sheet generated, and 'page 2 of 2' for the second sheet generated. The second sheet generated at a sampling location is Field Sheet B, discussed next.

#### **Field Sheet B**:

Use Field Sheet B when two field sheets are generated at one sampling location.

#### 1. Sequence Number

Use the same convention (described above) for sequence number for this field sheet. The second sheet generated at one location must have the identical sequence number as the first sheet. The two sheets should not be stapled together.

# 2. Top Half of Form

The top of this form only has lines for Sampling Station Number, Date, Start Time, and End Time (the boxes have been replaced with lines). Enter this information to alleviate the problem of mismatched or unidentifiable sheets.

#### 3. Bottom Half of Form

The bottom half of this form is the same as the field sheet previously discussed. There is no need to enter information on the second sheet for the Lab Login or pycnocline calculation.

Lab Sheet (also called filtering volume sheet, for nutrient, suspended solids and chlorophyll analyses)

When nutrient, suspended solids and chlorophyll samples are collected, a lab sheet is generated, and serves as a Sample Transfer Sheet. The lab sheet lists multiple stations that contain information for several samples on one sheet. Information on the sheet includes the sample number, layer, depth, time, salinity, and volume sampled for each set of parameters (e.g., TSS/PP, PC/PN, CHLA). This sheet is filled out by field personnel and must accompany the samples to CBL. CBL produces electronic files which are for uploaded into MD DNR Water Quality Data Management system.

1. Cruise Identification Number (Mainstern stations only)

Enter the cruise identification number in the space provided (year and cruise number, e.g., 97018 for 1997, Cruise Number 18).

# 2. Date

Enter the date in the space provided. It does not need to be in any specific format.

## 3. Scientist Signoff

The scientist must check the sheet for completeness and accuracy, and then initial in the signoff space.

4. Station, Sample Number, Layer

Enter the station, sample number, and layer code (S=surface, B=bottom, AP=above pycnocline, BP=below pycnocline, M=mid water column), if not preprinted.

5. Sampling Time (column 5)

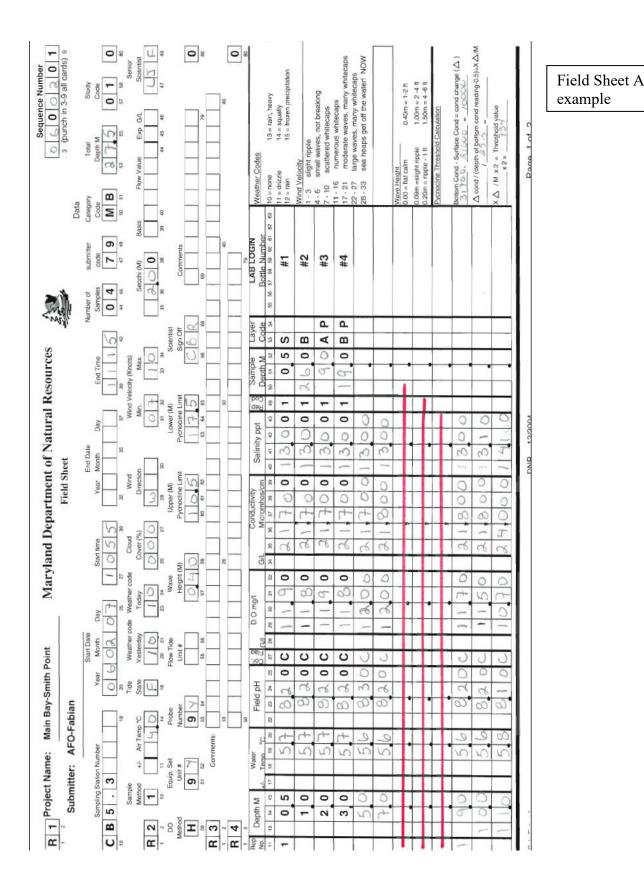
Enter the sampling time in military time in column 5.

6. Salinity (column 6)

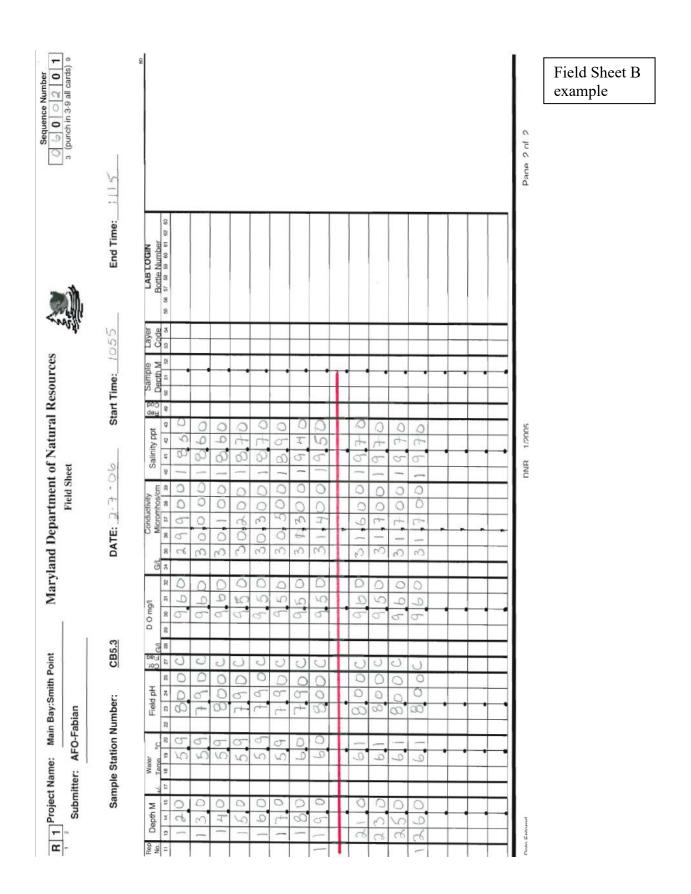
Enter the salinity in parts per thousand (ppt) in column 6.

7. Vol. (ml) (final 3 or 4 columns)

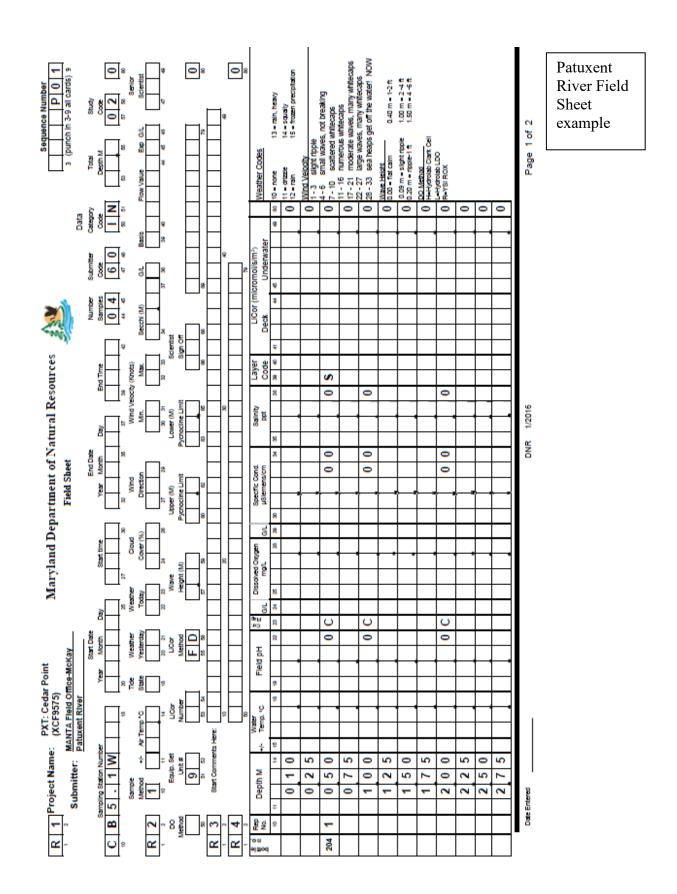
In the final 3 or 4 columns, enter the volume sampled for each set of sample parameters (e.g., TSS/PP, PC/PN, VSS, CHLA) in milliliters.



May 31, 2022, QAPP: Chemical & Physical Property Component



May 31, 2022, QAPP: Chemical & Physical Property Component



May 31, 2022, QAPP: Chemical & Physical Property Component

Bay Tributary Filtering Volume Sheet Example

# DEPARTMENT OF NATURAL RESOURCES Monitoring and Non-Tidal Assessment Bay Tributary Filtering Volume Summary CBL

RUN NAME_	<u>BT4</u>		
DATE		FIELD SIGNOFF	

STATION	SAMPLE TIME (mlty)	FILTER TIME (mlty)	SÄMPLE NUMBER	LAYER	DEPTH (M)	SALINITY (ppt)	TSS/PP (ml)	PC/PN (ml)	CHLA (ml)
ET 4.2			21	S	0.5				
			22	AP					
			23	BP					_
			24	В					
			* 150 T.day		AND THE STATE OF T				
EE 1.1			25	S	0.5				
			. 26	AP					
			27	BP					
			28	В					
*				V 88-28001-4					9797
XGG8251			145	S	0.3				
			_						
			R	DUP					

# MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

## CROSS REFERENCE SHEET DOCUMENTATION AND PROCEDURES

The following documentation outlines the conventions for filling out the Cross Reference Sheet.

(Note: Although the sheet has a subheading "Progress Report" or "Progress Report / Cross Reference Sheet", it is generally known as the Cross Reference Sheet and should not be confused with the "Cruise Reports/Quarterly Progress Report" described in Appendix 4.)

The Cross Reference Sheet is sent along with Field Sheets from the Field Office to the DNR Tawes Building, so that the DNR data management staff knows what data to expect in the form of field sheets and lab data.

The Cross Reference Sheet includes the name of the program, the sampling month and year, the name of the Field Office representative who originated the sheet. Columns with headings: Station, Day, Depth (m), Sequence #, Sample # list the samples and replicates that were collected. Columns with the headings: Nutrients (CBL), Chlorophyll (CBL), and Plankton are used to track whether DNR data management has received the analytical results. The Comments column is used to enter information explaining missing samples, stations, field abnormalities, or potential data problems.

The structure of the Mainstem and Bay Tributaries cross reference sheets are the same.

Examples of Mainstem and Patuxent River cross reference sheets are as followed: (labeled "Progress Report/Cross Reference Sheet") follow.

#### Maryland Department of Natural Resources RAS/MANTA

# Chesapeake Bay Mainstem

Month/ Year: April /2017

Progress Report / Cross Reference Sheet

Submitted by: <u>Laura Fabian</u>

Station	Day	Depth (M)	Sequence #	Sample #	Nutrients (CBL)	Chloro. (CBL)		Plankton (Wolny)		Comments
		3.3			130 0	1000	Live composite	Fixed Lugols composite	picoplankton	
		26.0		1				N/S		Run postponed 1 day due to
CB5.3	11	17.0	1700401	2				N/S		ill boat captain and wavy water
Smith Point	-11	6.0		3				N/S		
		0.5		4				N/S		
		19.0		5				N/S		
LE2.3	11	13.0	1700402	6			N/S		1	
Point Lookout	11	7.0		7			N/S		1	
		0.5		8				N/S		
		30.0	1700403	9			Bottom sa	mple discontinued	Nov 2016	
		19.0		10						1
CB5.2 Point No Point	11	3.0		11			AP and above	AP and above composite year round PAP and above composite year round		1
roun ro roun		0.5/1		12						
		0.5/2		13				100000000		
		34.0		14				N/S		
CB5.1	11	23.0	1700404	404 15				N/S		1
Cedar Point	11	9.0		16				N/S		1
		0.5	] ]	17				N/S		1

# Maryland Department of Natural Resources MANTA Chesapeake Bay Water Quality Monitoring Progress Report – Patuxent River

# Month/ Year: January 2015

Submitted by: Debbie McKay

Station	Day	Sample Depth	Sequence Number	Chloro (CBL)	Lab (CBL)	Plankton	Comments
CB5.1W		0.5				n/s	No Licor. Boat and Land stations sampled on different days due to a
CD3.1 W	06	3.0	1501P01			n/s	snowstorm.
(Cedar Pt.)		6.0				n/s	
		8.0				n/s	
		0.5				n/s	Boat and Land stations sampled or
LE1.4	06	3.0	1501P02			n/s	different days due to a snowstorm.
(Drum Pt.)	00	9.0	1501102			n/s	
(		16.0				n/s	
		0.5					Boat and Land stations sampled or
LE1.3 (Above Pt.	06	3.0	1501P03			n/s	different days due to a snowstorm.
Patience)		12.0				n/s	
,		22.0				n/s	
		0.5				n/s	Boat and Land stations sampled or different days due to a snowstorm.
		3.0/1				n/s	
LE1.2	06	12.0	1501P04			n/s	
(St. Leonard)	00	15.0	1301104			n/s	
		3.0/ 2				n/s	
LE1.1		0.5			+VSS		Boat and Land stations sampled or
(Jack Bay)		3.0				n/s	different days due to a snowstorm.
,	06	9.0	1501P05		,	n/s	Licor data incomplete.
		11.0				n/s	

# MARYLAND DEPARTMENT OF THE NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

# CRUISE REPORTS/QUARTERLY PROGRESS REPORT DOCUMENTATION AND PROCEDURES

The Cruise Report is filled out by Field Office personnel for each cruise and is provided to the Quality Assurance Officer at DNR. Every three months, the Quality Assurance Officer combines and summarizes the Cruise Reports, creating a Quarterly Progress Report to submit to the Chesapeake Bay Program Office.

The Cruise Report includes the following: cruise identification number, name of the water quality monitoring program, scheduled sampling date, name of the Field Office representative who submits the sheet, additional sampling activities, station names, sampling dates and times, filtration completion times, station departure time, the presence or absence of hydrogen sulfide odor and results of any Hach tests conducted, the research vessel name, the names of the captain, crew, and scientific party, the departure-from-dock time and location, the return-to-dock time and location, weather conditions, air temperature, barometric pressure, estimated wind speed and direction, equipment conditions, morning dissolved oxygen check, sample status and additional comments.

# **Information filled out by Field Personnel:**

Pa	age 1
1.	Cruise I.D. (top left of sheet) (Mainstem)
	Enter the cruise identification number in the space provided at top left of sheet.
2.	Pageof(top right of page)
	When more than one sheet is generated and sent with samples, enter this information in the area provided, 'Pageof'. If only one sheet is generated, indicate this by entering page 1 of 1.
3.	Day # (top right of page, under page number) (Mainstem)
	Provide the day number of the cruise (i.e., Day #1, Day #2, or Day #3)
4.	Study Location (top of sheet)
	If not preprinted, enter the name of the study location (e.g., Mainstem Cruise Report) at the

top center of the sheet.

# 5. Scheduled Sampling Date

Enter the scheduled sampling date in the space provided.

# 6. Submitted by

Enter the name of the field scientist who originates the sheet.

# 7. Station Sampled (1st column of sheet)

The station sampled should be preprinted in the first column of the sheet. If not preprinted, enter the station name. (For example, if the samples were collected from station CB5.3, the station sampled would be "CB5.3").

### 8. Date

Enter the actual date sampled in the space provided.

# 9. Time

Enter the time the samples are taken.

# 10. FF (finished filtering) (Mainstem)

Enter the time that filtering is finished.

# 11. LS (left station) (Mainstem)

Enter the time of leaving the station.

# 12. H<sub>2</sub>S odor (Mainstem)

For both below pycnocline (BP) and bottom (B) layer samples:

- If H<sub>2</sub>S odor is present (rotten egg smell), enter "+" and perform a Hach test for hydrogen sulfide. Record the Hach reading.
- If no H<sub>2</sub>S odor is present, enter "-".

# 13. Cruise I.D. (top left of sheet) (Mainstem)

Provide the cruise identification number in the space provided at top left of sheet. Cruise ID numbers consist of last 2 digits of year, 0, and cruise # of year. For example, the cruise ID for the third trip of 2008 would be 08003.

## 14. Date

Enter the actual sampling date in the space provided.

### 15. R/V Utilized

Enter the name of the research vessel in the space provided.

# 16. Captain, Crew and Scientific Party

Enter the names of the Captain, Mate, scientists and occasional collaborators or observers on board. Identify the agency/company that the scientists and observers represent (e.g., DNR, CBL, Baltimore Sun).

# 17. Departure Time and Location

Enter the departure time and location.

### 18. Return time and location

Enter the return time and location.

### 19. Weather conditions

- Enter the air temperature in degrees Celsius for the morning (AM) and afternoon (PM).
- Enter the barometric pressure in inches of mercury for the morning (AM) and afternoon (PM).
- Enter the estimated wind speed in knots and the direction from which the wind is blowing for the morning (AM) and afternoon (PM).

## 20. Equipment conditions

Enter the refrigerator (FRIDGE) temperature in degrees Celsius. January–June, August and November only (no Silicate samples in July, August, Sept. October, December). Enter the freezer temperature in degrees Celsius.

## 21. Morning Dissolved Oxygen (DO) Check (Mainstem)

Enter the meters checked, whether the meters were changed or not during the DO check and which meter is being used for the day. Meter readings are logged in Cruise Report when a sonde is changed during a survey.

# 22. Sample Status

Enter the status of the sample in cases when unusual events might affect a sample. For example, a refrigerator/freezer failure, or samples transported at odd times.

## 23. Additional Comments

Enter additional comments as needed.

Pages 3 and 5 are the same as Page 1 (for additional stations). Pages 4 and 6 are the same as Page 2 (for additional stations).

# See below for examples of Mainstem and Patuxent Cruise Reports

CRUISE I.D. 19002 Page 1 of 6 Day 1

# MARYLAND DEPARTMENT OF NATURAL RESOURCES WATER QUALITY MONITORING DIVISION MAINSTEM CRUISE REPORT- WINTER

Scheduled Sampling Date: Feb 12, 2019

Submitted by: L J Fabian

Additional Sampling Activities: Multi-laboratory split; phytoplankton

### TABLE OF STATIONS SAMPLED

STATION#	DATE	TIME	COMMENTS
LE2,3			FF 0952 LS 0943
Point Lookout	2-11-19	0930	H <sub>2</sub> 5 odor BP (-) B (-)
			55 1011
CB5.3			FF 1044 LS 1039
Smith Point	2-11-19	1018	H <sub>2</sub> S odor BP (-) B (-)
CB5.2			FF 1204 LS 1153
Point No Point	2-11-19	1126	H <sub>2</sub> S odor BP (-) B (-)
FOIRT NO FOIRT			Phyto. depths 0,5, 4, 7, 14, 12 m
CB5.1			FF 1300 LS 1254
Cedar Point	2-11-19	1232	H <sub>2</sub> S odor BP (-) B (-)
Cedal. Folial			
CDAA			FF 1355 LS 1350
CB4.4 Cove Point	2-11-19	1315	H <sub>2</sub> S odor BP (-) B (-)
COVE FOIRI			Split collected @ 1340

\*FF: FINISHED FILTERING; LS: LEFT STATION; H≥S ODOR: (-) ABSENT, (+)

CRUISE I.D. 19002 Page 2 of 6 2-11-19 Day 1

Vessel Utilized: RV Kerhin

PERSONNEL:

DNR:

Captain: Rick Younger Meter: Debbie McKay

Mate: Eric Montgomery TSS/PP: Amy Imirie

Chla/PC/PN: Lauren Cunningham

Others: none

Hosing: Kerry Maguire

LOCATION & TIMES

Depart dock: 0800 Calvert Marina, Dowell, MD AM fuel dock----

Arrived @ dock: time not listed- Calvert Marina, PM fuel dock- 1425-1451

Dowell, MD

### WEATHER CONDITIONS

	AM	PM	Please give a general description of the days
			weather
Air Temp (°C)	+4	+ 2	rain
Barometer (in/hg)	30,40	30,40	
Wind Speed &	calm	calm	
Direction (knots)			

# EQUIPMENT CONDITIONS

	AM	PM	Problems?
Freezer temp (°C)		- 17	
Fridge Temp (°C)		- 1.0	

### MORNING DO CHECK

meter#	У	changed?	no	Used	У	today	
meter#	Z	changed?	no				

SAMPLE

STATUS:

ADDITIONAL Split delivered to Port Royal by ALI & DSM

COMMENTS:

# MARYLAND DEPARTMENT OF NATURAL RESOURCES WATER QUALITY MONITORING DIVISION PATUXENT CRUISE REPORT

Scheduled Sampling Date:	1/7/2020	_Submitted by	Debbie McKay
Additional Sampling Activities:	Phytoplankton		

TABLE OF STATIONS SAMPLED							
STATION	DATE	TIME	COMMENTS				
CB5.1W	1/6/2020	0904	Live S Plankton.				
LE1.4	1/6/2020	0940	Live S Plankton.				
LE1.3	1/6/2020	1018	Live S Plankton.				
LE1.2	1/6/2020	1055	Live S Plankton.				
LE1.1	1/6/2020	1129	Composite plankton sample 0.5, 3.0, 5.0, 7.0, and 10.0 meters. Live S Plankton.				
RET1.1	1/6/2020	1207	Live S Plankton.				
TF1.7	1/6/2020	1259					
TF1.6	1/6/2020	1330					
TF1.5	1/6/2020	1020	Station sample from land-too shallow for the R/V Rachel Carson.				

R/V UTILIZED <u>Rachel Carson</u>

PERSONNEL:

CPT: Michael Hulme Guests: DNR: Hunter Horn

CREW: Rob Nilsen Holly Caroline Harper Graf Kerry Maguire

Debbie McKay

**LOCATION & TIMES** 

DEPARTED DOCK: 0850 Calvert Marina, Dowell, MD

FUEL DOCK: Arrival: Departure:

ARRIVED AT DOCK: 1510 Calvert Marina, Dowell, MD

**WEATHER CONDITIONS:** 

AM PM General description (e.g., nice)

Air Temp.  $+6.0 \quad \circ_{\text{C}} \quad +12.0 \quad \circ_{\text{C}}$ 

Barometer <u>30.01</u> <u>29.92</u>

Wind Speed & Direction <u>calm</u> kts <u>W 4-6</u> kts

SAMPLE STATUS:

ADDITIONAL Patuxent sampling day was switched to 1/6/2020 due to high winds.

COMMENTS: 1/7/2020 was a better day to sample BT 10/11 from the Rachel Carson.

# MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

# FIELD INSTRUMENT QUALITY ASSURANCE/QUALITY CONTROL

# I. MULTIPARAMETER WATER QUALTIY INSTRUMENTS

These procedures refer to Hydrolab Series 5 and Yellow Springs Instrument (YSI) Series 6 and EXO instruments. Detailed calibration procedures are performed as described in their respective operating manuals.

## NOTE:

In March 2015, all remaining Series 4a instrument equipped with Standard Clark Polarographic Dissolved Oxygen Sensors were replaced with Series 5 instruments equipped with optical dissolved oxygen sensors (Luminescent Dissolved Oxygen Sensor - LDO). Calibration logs for each instrument will list specific replacement dates. Sensors for temperature, specific conductance, pH and depth are identical for Series 4a and 5 instruments.

Beginning in February 2009, YSI Series 6 instruments were added to the field instrument inventory. YSI instruments are equipped with optical dissolved oxygen sensors (Reliable Oxygen Sensor - ROX). YSI temperature, specific conductance, pH and depth sensors are different than their respective Hydrolab sensors but perform similarly.

Both the Hydrolab and YSI optical dissolved oxygen sensors use similar luminescent technology to measure dissolved oxygen.

Mainstem and Patuxent River cruises will exclusively use YSI instead of Hydrolab instruments. All other sampling activities will use Hydrolab or YSI instruments.

Beginning in 2021, YSI EXO instruments were added to the field instrument inventory. These instruments are equipped with optical dissolved oxygen, temperature, specific conductance, pH, and depth sensors. These sensors use similar technology and data are comparable with YSI 6 series and Hydrolab sensors.

### A. Calibration

# 1. Hydrolab Series 5 Instruments

- a. Set up a calibration logbook for each instrument with make, model, serial numbers and first-in-service date. Assign a letter for DNR use as required. Calibrations are best done in the field office instrument lab which is kept at a stable temperature of 20-25°C.
- b. Calibrate instruments on Friday for use the next week. If possible, calibrate instrument within 24 hours of first field deployment. After one to four days of field deployment, post-calibrate instruments after last use to determine if calibration of any parameter drifted (see App V, Section I.C.1.c and d for procedure). If possible, post-calibrate instrument within 24 hours after last field deployment.
- c. Calibrate specific conductance sensor with standards generated by the field office from dry KCl and deionized water with specific conductance equal to 0 μS/cm. Standards are 147, 292, 718, 1413, 2767, 6668, 12900, 24820 and 58640 microSiemens/cm (μS/cm) (microSiemens/cm is equivalent to micromhos/cm at 25°C). Respective concentrations are 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 molar KCl. Calibrate specific conductance sensors of Series 5 instruments following a two-point linear protocol. Calibrate the zero point with the sensor dry and the slope with one of the above standards.
- d. Calibrate pH sensor with premixed standards of pH 4.00, pH 7.00 and pH 10.00 purchased from Fisher Scientific. Standards are color coded (red for pH 4.00, yellow for pH 7.00 and blue for pH 10.00) and certified as accurate at 25°C (pH 4.00 ± 0.01, pH 7.00 ± 0.01, pH 10.00 ± 0.02) and used before their labeled expiration dates. Calibrate pH sensor with these standards using a two-point linear protocol. First, calibrate the zero point with pH 7.00 standard buffer. Then, calibrate slope with either pH 4.00 or 10.00 standard buffer. The slope buffer is selected so that pH measurements anticipated during field deployment are between the zero point and slope buffer values. The pH value of each buffer is adjusted for instrument temperature before calibration. A pH calibration value vs. temperature table (pH Calibration Table) is supplied by the buffer manufacturer for each standard buffer. This value is the pH calibration point.
- e. Calibrate the optical dissolved oxygen sensor (LDO) using a 1-point percent saturation protocol in the common standard of air saturated water. The volume of water must have a specific conductance less than 100 μS/cm. Determine the oxygen saturation calibration point in air-saturated water from theoretical DO saturation tables using the temperature from the instrument and local barometric

pressure from a standard Fortner Mercury Barometer. A specific notation on the field data sheet shows that Hydrolab instruments are equipped with LDO sensors.

- f. Temperature sensor is calibrated by the manufacturer and cannot be adjusted by the user.
- g. Calibrate depth sensor by submerging it to a known depth at the field sampling station and calibrating to this known depth.
- h. Record all calibration and post-calibration information (e.g., barometric pressure, calibration values and instrument readings), maintenance procedures and repairs in the instrument specific calibration logbook. An example of this log is included.
- i. During calibration, post-calibration and field deployment, record in the calibration logbook any unusual circumstances that may affect instrument readings.

## 2. YSI EXO1 and EXO2 Instruments

These procedures refer to Yellow Springs Instrument (YSI) EXO1 and EXO2 instruments. Detailed calibration procedures are performed as described in the operating manual.

### Basic Notes:

- It is recommended to use a new clean sensor guard exclusively for calibration to minimize contamination of calibration standards.
- When filling calibration cup with standards, fill to the first line
  when a full payload of sensors are installed and fill to second line
  when less sensors are installed to ensure that sensors are fully
  immersed in calibration standard.
- Be sure to thoroughly rinse sensors with DI water between calibration standards to reduce contamination.
- Remove the wiper brush during calibration as it can trap residual standard and affect calibration accuracy.
- Never accept a calibration that displays an error message.

- a. Set up a calibration logbook for each instrument with make, model, serial numbers and first-in-service date. Assign a letter for DNR use as required. Calibrations are best done in the field office instrument lab which is kept at a stable temperature of 20-25°C.
- b. Calibrate instruments on Friday for use the next week. If possible, calibrate instrument within 24 hours of first field deployment. After one to four days of field deployment, post-calibrate instruments after last use to determine if calibration of any parameter drifted (see App V, Section I.C.1.c and d for procedure). If possible, post-calibrate instrument within 24 hours after last field deployment.
- c. Calibrate specific conductance sensor with standards generated by the field office from dry KCl and deionized water with specific conductance equal to 0 μS/cm. Standards are 147, 292, 718, 1413, 2767, 6668, 12900, 24820 and 58640 microSiemens/cm (μS/cm) (microSiemens/cm is equivalent to micromhos/cm at 25°C). Respective concentrations are 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 molar KCl. Calibrate specific conductance sensor following a two-point linear protocol with one of the above standards as the slope standard. The zero point is factory calibrated and cannot be adjusted by the user.
- d. Calibrate pH sensor with premixed standards of pH 4.00, pH 7.00 and pH 10.00 purchased from Fisher Scientific. Standards are color coded (red for pH 4.00, yellow for pH 7.00 and blue for pH 10.00) and certified as accurate at 25°C (pH 4.00 ± 0.01, pH 7.00 ± 0.01, pH 10.00 ± 0.02) when used before their labeled expiration dates. Calibrate pH sensor with these standards using a two-point linear protocol. First, calibrate the zero point with pH 7.00 standard buffer. Then, calibrate slope with either pH 4.00 or 10.00 standard buffer. The slope buffer is selected so that pH measurements anticipated during field deployment are between the zero point and slope buffer values. The pH value of each buffer is adjusted for instrument temperature before calibration. A pH calibration value vs. temperature table (pH Calibration Table) is supplied by the buffer manufacturer for each standard buffer. This value is the pH calibration point.
- e. Calibrate the optical dissolved oxygen sensor (ROX) using a 1-point percent saturation protocol in the common standard of air saturated water. The volume of water must have a specific conductance less than 100 µS/cm. Check and calibrate, if necessary, the YSI EXO Handheld Display Unit barometer to local barometric pressure in mm Hg as measured from a standard Fortner Mercury Barometer. Determine the oxygen saturation calibration point in air-saturated water from theoretical DO saturation tables using the temperature from the instrument and local barometric pressure from a standard Fortner Mercury Barometer or display unit barometer. Note in the calibration if the display unit barometer was calibrated and reading used to calibrate the dissolved oxygen

- sensor. A specific notation on the field data sheet shows that YSI instruments are equipped with ROX sensors.
- f. Temperature sensor is calibrated by the manufacturer and cannot be adjusted by the user.
- g. Calibrate depth sensor by submerging to a known depth at the field sampling station and calibrating to this known depth.
- h. Record all calibration and post-calibration information (e.g., barometric pressure, calibration values and instrument readings), maintenance procedures and repairs in the instrument specific calibration logbook. An example of this log is included.
- i. During calibration, post-calibration and field deployment, record in the calibration logbook any unusual circumstances which may affect the instrument readings.

## 3. YSI EXO2

These procedures refer to Yellow Springs Instrument (YSI) EXO2 instruments. Detailed calibration procedures are performed as described in the operating manual.

### **Basic Notes:**

- It is recommended to use a new clean sensor guard exclusively for calibration to minimize contamination of calibration standards.
- When filling calibration cup with standards, fill to the first line
  when a full payload of sensors are installed and fill to second line
  when less sensors are installed to ensure that sensors are fully
  immersed in calibration standard.
- Be sure to thoroughly rinse sensors with DI water between calibration standards to reduce contamination.
- Remove the wiper brush during calibration as it can trap residual standard and affect calibration accuracy.
- Never accept a calibration that displays an error message.
- a. Set up a calibration logbook for each instrument with make, model, serial numbers and first-in-service date. Assign a letter for DNR use as required. Calibrations are best done in the field office instrument lab which is kept at a stable temperature of 20-25°C.
- b. Calibrate instruments on Friday for use the next week. If possible, calibrate instrument within 24 hours of first field deployment. After one to four days of field deployment, post-calibrate instruments after last use to determine if calibration of any parameter drifted (see App V, Section I.C.1.c and d for procedure). If possible, post-calibrate instrument within 24 hours after last field deployment.
- c. Calibrate specific conductance sensor with standards generated by the field office from dry KCl and deionized water with specific conductance equal to 0 μS/cm. Standards are 147, 292, 718, 1413, 2767, 6668, 12900, 24820 and 58640 microSiemens/cm (μS/cm) (microSiemens/cm is equivalent to micromhos/cm at 25°C). Respective concentrations are 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 molar KCl. Calibrate specific conductance sensor following a two-point linear protocol with one of the above standards as the slope standard. The zero point is factory calibrated and cannot be adjusted by the user.

- d. Calibrate pH sensor with premixed standards of pH 4.00, pH 7.00 and pH 10.00 purchased from Fisher Scientific. Standards are color coded (red for pH 4.00, yellow for pH 7.00 and blue for pH 10.00) and certified as accurate at 25°C (pH 4.00 ± 0.01, pH 7.00 ± 0.01, pH 10.00 ± 0.02) when used before their labeled expiration dates. Calibrate pH sensor with these standards using a two-point linear protocol. First, calibrate the zero point with pH 7.00 standard buffer. Then, calibrate slope with either pH 4.00 or 10.00 standard buffer. The slope buffer is selected so that pH measurements anticipated during field deployment are between the zero point and slope buffer values. The pH value of each buffer is adjusted for instrument temperature before calibration. A pH calibration value vs. temperature table (pH Calibration Table) is supplied by the buffer manufacturer for each standard buffer. This value is the pH calibration point.
- e. Calibrate the optical dissolved oxygen sensor (ROX) using a 1-point percent saturation protocol in the common standard of air saturated water. The volume of water must have a specific conductance less than 100 µS/cm. Check and calibrate, if necessary, the YSI 650 MDS Display Unit barometer to local barometric pressure in mm Hg as measured from a standard Fortner Mercury Barometer. Determine the oxygen saturation calibration point in air-saturated water from theoretical DO saturation tables using the temperature from the instrument and local barometric pressure from a standard Fortner Mercury Barometer or display unit barometer. Note in the calibration if the display unit barometer was calibrated and reading used to calibrate the dissolved oxygen sensor. A specific notation on the field data sheet shows that YSI instruments are equipped with ROX sensors.
- f. Temperature sensor is calibrated by the manufacturer and cannot be adjusted by the user.
- g. Calibrate depth sensor by submerging to a known depth at the field sampling station and calibrating to this known depth.
- h. Record all calibration and post-calibration information (e.g., barometric pressure, calibration values and instrument readings), maintenance procedures and repairs in the instrument specific calibration logbook. An example of this log is included.
- i. During calibration, post-calibration and field deployment, record in the calibration logbook any unusual circumstances which may affect the instrument readings.

# B. Field Deployment and Verification of Instrument Performance

- 1. Before daily field deployment and, if possible, before deployment at each sample station, inspect sensors for damage. If damaged, do not use instrument and deploy second instrument. Teams carry two calibrated instruments in case one instrument fails or gives suspect measurements. Readings from the instrument in use are compared to those from the second instrument only when the field scientist recording measurements observes readings (a) that are outside reasonably expected values, (b) that are variable or erratic, or (c) if the instrument displays an error message. If these instruments do not agree within QA/QC guidelines and the field scientist reasonably believes that the primary instrument is not working correctly, the second instrument is used. This is noted on the field sheet, cruise report, and instrument calibration log. The instrument supervisor is also informed. The suspect instrument should not be used until its performance is evaluated during post-calibration.
- 2. Before each day of a Mainstem Cruise both instruments receive a morning-of-use dissolved oxygen validation check. Set up the instruments for a dissolved oxygen calibration as appropriate for the type of sensor. Follow procedures for the dissolved oxygen validation check to adjust the calibration only if the reading is greater than  $\pm$  0.20 mg/L from the saturation calibration point. If the reading is greater than  $\pm$  0.50 mg/L, the instrument is not used for field measurements until evaluated by the instrument supervisor.

### C. Maintenance

- 1. Post Field Deployment Maintenance and Performance Verification
  - a. Daily: At the end of each day of use inspect all sensors for damage and record any damage in cruise report, monthly report, calibration log, and affected field data sheet(s). Then rinse sensors with de-ionized or tap water and install the storage cup filled with sufficient tap water so the pH and reference sensors are not submerged.
  - b. Weekly: At the end of each week, rinse instrument (sonde and cable) and basket carrier with tap water. Wipe display with paper towel made wet with tap or deionized water. Rinse sensors with de-ionized or tap water and install the storage cup filled with sufficient tap water so the pH and reference sensors are not submerged.
  - c. Post-calibrate dissolved oxygen, pH and specific conductance for each instrument weekly on Friday after one to four days of field sampling. If

possible, post-calibrate instrument within 24 hours after last use. Before postcalibrating, inspect all sensors for damage and record any damage in the calibration log, cruise report, monthly reports, and affected field data sheets. If there is sensor damage, post-calibrate instrument as is to evaluate sensor and instrument performance. Post-calibrate instrument only after sensors stabilize to room temperature (20-25°C). Post-calibrate instruments using the same standards and procedures as were used during calibration except the calibration settings are not adjusted. For instruments with an optical DO sensor, visually inspect the luminescent material before post-calibration. If DO sensor is damaged, describe the damage in the calibration log and post-calibrate the sensor as is. Damage to DO sensor is repaired before next calibration and field deployment. If during field deployment, instrument readings of pH and specific conductance fall outside the range of the zero and slope calibration standards, make additional post-calibration readings of appropriate pH and specific conductance standards so that field readings fall within the range from the zero calibration point to the additional post-calibration standard. All post-calibration standards and instrument readings are recorded in the calibration log.

d. If readings of a parameter during post-calibration are outside quality guidelines, note this in the calibration log and inform the field quality assurance supervisor. The supervisor will determine if the instrument is operating correctly and if associated field data are reliable.

Data Quality Guidelines During Post-calibration:

pH Sensor reads  $\pm 0.20$  pH units of standard

Dissolved Oxygen Optical dissolved oxygen sensor reads  $\pm 0.50$  mg/L of calibration dissolved oxygen value

Specific Conductance

Standard µS/cm	Threshold ±5% of Standard μS/cm
147	8
292	15
718	36
1413	71
2767	139
6668	334
12900	645
24820	1241
58640	2932

Instrument parameter readings that are outside quality guidelines during post-

calibration are flagged on field data sheets with the Analytical Problem Code (APC) value 'F'. The description of APC 'F' is: "Field data instrument post calibration failed but data within theoretical limits, (e.g., post cal. failed but data kept)" see Appendix 9.

All field data, including instrument data, are re-evaluated during quality assurance, (see step 3 of DATA MANAGEMENT, VERIFICATION AND DOCUMENTATION). If the analyst/biologist and Quality Assurance Officer determine that the data are not usable, values are flagged with the APC code 'V'. The definition for APC code 'V' is: "Sample results rejected due to quality control criteria", see Appendix 9.

- 2. Routine Sensor Maintenance and Performance Verification: sensor and overall instrument maintenance is conducted at approximately 8–12-week intervals based on instrument usage and performance.
  - a. Hydrolab Series 5 Instrument
    - (1). Optical Dissolved Oxygen Sensor (LDO): Remove plastic LDO cap on end of sensor. Inspect cap for integrity of luminescent material, optical path for water, area under optical glass for condensation, and integrity of o-ring seals. Water or condensation interferes with the optical path. If cap will be reused, replace o-rings if damaged and reinstall cap on sensor. Replace cap and o-rings if damaged. First, gently wipe plastic cap exterior surface with cotton swab soaked with laboratory soap, then rinse cap with deionized water. Second, gently wipe cap exterior surface with new cotton swab soaked with Simple Green<sup>TM</sup>, then rinse cap with deionized water. Replace the cap once per year because luminescent material and zero dissolved oxygen performance degrade with age. Organic solvents, such as, methanol and acetone, should never contact any part of this sensor.
    - (2). Specific Conductance Sensor (graphite sensor): First, wipe all surfaces of sensor with cotton swab soaked with laboratory soap, then rinse with deionized water. Second, wipe sensor with new cotton swab soaked with Simple Green<sup>TM</sup>, then rinse with deionized water. Do not use any organic solvents, such as methanol or acetone, to clean this sensor.
    - (3). pH System (paired sensors *in situ* and reference): *in situ* sensor is bulb type Ag/AgCl₂ glass sensor. Reference sensor is a pellet of silver inside a sleeve capped with a porous Teflon<sup>™</sup> junction and filled with electrolyte (4M KCl aqueous solution saturated with AgCl₂). First, wipe *in situ* glass sensor with cotton swab soaked with laboratory soap, then rinse with de-

ionized water. Second, wipe glass sensor with new cotton swab soaked with Simple Green<sup>TM</sup>, then rinse with deionized water. Soak sensor in 0.1 N HCl for no more than 30 minutes, then rinse sensor with deionized water. Do not use any organic solvents, such as methanol or acetone, to clean this sensor. Remove junction sleeve assembly from reference sensor. Remove and discard porous Teflon<sup>TM</sup> reference junction and associated o-ring from junction sleeve assembly. Inspect junction sleeve and silver pellet for integrity and replace if damaged. Do not clean pellet of silver. Remove and discard o-ring from reference sensor post. Lightly grease new o-ring with silicone grease and install on reference sensor post. Install new junction and associated o-ring on sleeve. Firmly tighten junction on sleeve to compress o-ring seal but do not overtighten. Fill sleeve with fresh electrolyte, add two KCl pellets in sleeve, and reinstall sleeve on reference sensor so that no air bubbles are inside sleeve.

- (4). Depth Sensor (stainless steel differential strain gauge transducer): Inspect sensor port and remove any obstructions. No further maintenance is required.
- (5). Temperature Sensor (stainless steel thermistor): First, wipe with cotton swab soaked with laboratory soap, then rinse with deionized water. Second, wipe with new cotton swab soaked with Simple Green<sup>TM</sup>, then rinse with deionized water. Do not use any organic solvent, such as methanol or acetone, to clean this sensor.

### b. YSI Series 6 Instrument

(1). Optical Dissolved Oxygen Sensor (ROX): Remove membrane assembly on end of sensor. Inspect membrane for integrity of luminescent material, optical path for water, area under optical glass for condensation, and integrity of assembly o-ring seals. Water or condensation interferes with the optical path. If necessary, carefully clean optical glass with cotton swab moistened with deionized water. Gently remove any residual moisture from optical glass with dry cotton swab. Reinstall luminescent membrane assembly. Replace membrane assembly if damaged. First, gently wipe membrane exterior surface with cotton swab soaked in laboratory soap, then rinse with deionized water. Second, gently wipe membrane exterior surface with new cotton swab soaked in Simple Green<sup>TM</sup>, then rinse with deionized water. Replace the membrane assembly once per year because luminescent material and zero dissolved oxygen performance degrade with age. Do not use any organic solvents, such as methanol or acetone, to clean this sensor.

- (2). Specific Conductance Sensor (four nickel electrode array): First, soak small nylon bristle brush in laboratory soap and gently push back and forth multiple times through both channels. Rinse with deionized water. Second, soak small nylon bristle brush in Simple Green<sup>TM</sup> and gently push back and forth multiple times through both channels. Rinse with deionized water.
- (3). pH System: Model 6561 System is a glass bulb type combination electrode consisting of a proton selective glass bulb reservoir filled with buffer at approximately pH 7 and Ag/AgCl<sub>2</sub> reference electrode. First, gently wipe glass bulb with cotton swab soaked with laboratory soap, then rinse with deionized water. Second, gently wipe glass bulb with new cotton swab soaked with Simple Green<sup>TM</sup>, then rinse with deionized water. If required, soak glass bulb in 1 M HCl for 30 60 minutes, then rinse with deionized water. Do not use any organic solvents, such as methanol or acetone, to clean this sensor.

Note: During 2014 YSI pH sensors in all YSI sondes were switched from Model 6561 to Model 6589 (amplified). The Model 6589 sensor has identical glass bulb type combination electrodes and will perform similarly as the Model 6561 but last longer. The Model 6589 is serviced the same as the Model 6561 sensor.

- (4). Depth Sensor YSI Model 6820 Sonde (differential strain gauge transducer): Ensure that access ports are clear of debris. Using a plastic syringe flush deionized water through one port and out the others. Repeat flush through each port.
  - Depth Sensor YSI Model 6920 Sonde (differential strain gauge transducer): Inspect access tunnel for debris and remove. Clean tunnel by first gently pushing new cotton swab soaked with laboratory soap through tunnel, then rinse tunnel with deionized water. Second, gently push new cotton swab soaked with Simple Green<sup>TM</sup> through tunnel, then rinse tunnel with deionized water.
- (5). Temperature Sensor YSI Model 6820 and 6920 Sondes (stainless steel thermistor): First, wipe sensor with cotton swab soaked with laboratory soap, then rinse with deionized water. Second, wipe sensor with new cotton swab soaked with Simple Green<sup>TM</sup>, then rinse with deionized water. Do not use any organic solvents, such as methanol or acetone, to clean this sensor.

## c. YSI EXO1 and EXO2

- (1). Optical Dissolved Oxygen Sensor (ODO): Inspect membrane for integrity of luminescent material. (Only remove membrane if there are issues or suspected issues with readings. Remove membrane and inspect optical path for water, area under optical glass for condensation, and integrity of assembly o-ring seals. Water or condensation interferes with the optical path. If necessary, carefully clean optical glass with cotton swab moistened with deionized water. Gently remove any residual moisture from optical glass with dry cotton swab. Reinstall luminescent membrane assembly.) Replace membrane assembly if damaged. First, gently wipe membrane exterior surface with cotton swab soaked in laboratory soap, then rinse with deionized water. Second, gently wipe membrane exterior surface with new cotton swab soaked in Simple Green<sup>TM</sup>, then rinse with deionized water. Replace the membrane assembly once per year because luminescent material and zero dissolved oxygen performance degrade with age. Do not use any organic solvents, such as methanol or acetone, to clean this sensor.
- (2). Specific Conductance Sensor (four nickel electrode array): First, soak small nylon bristle brush in laboratory soap and gently push back and forth multiple times through both channels. Rinse with deionized water. Second, soak small nylon bristle brush in Simple Green™ and gently push back and forth multiple times through both channels. Rinse with deionized water.
- (3). pH System: EXO unguarded pH System is a glass bulb type combination electrode consisting of a proton selective glass bulb reservoir filled with buffer at approximately pH 7 and an Ag/AgCl<sub>2</sub> reference electrode. First, inspect glass bulb for cracks or breakage. Second, gently wipe glass bulb with cotton swab soaked with laboratory soap, then rinse with deionized water. Third, gently wipe glass bulb with new cotton swab soaked with Simple Green<sup>TM</sup>, then rinse with deionized water. If required, soak glass bulb in 1 M HCl for 30 60 minutes, then rinse with deionized water. Do not use any organic solvents, such as methanol or acetone, to clean this sensor. The pH sensor tip is user replaceable. Replace tip if sensor is out of range or broken. Record date and serial number of new sensor tip in calibration log.
- (4). Depth Sensor YSI EXO Sonde (differential strain gauge transducer): Ensure that access to four ports are clear of debris. Using a plastic syringe flush deionized water through one port and out the others. Repeat flush through each port.

- (5). Temperature Sensor YSI Model EXO (stainless steel thermistor): First, wipe sensor with cotton swab soaked with laboratory soap, then rinse with deionized water. Second, wipe sensor with new cotton swab soaked with Simple Green<sup>TM</sup>, then rinse with deionized water. Do not use any organic solvents, such as methanol or acetone, to clean this sensor.
- d. Sensor Performance Verification: After routine sensor maintenance, the performance of Hydrolab and YSI instruments are verified as follows before assignment to field surveys. Instruments that do not satisfy these criteria are repaired in house or returned to the manufacturer for repair. Performance verification is documented in the calibration log for each instrument.
  - (1). Temperature: Submerge sensor and traceable standard mercury thermometer in freshwater at room temperature (20° 25°C). Sensor reading must be stable and within 0.20°C of the standard thermometer reading observed over a 2-minute interval.
  - (2). Dissolved Oxygen: Calibrate optical sensor in the standard of air saturated water. (See App V, Section I.A.1.e for Hydrolab, App V, Section I.A.2.e for YSI 6 series, and App V, Section I.A.3.e for YSI EXO2). Sensor reading before calibration must be stable (within 0.05 mg/L of reading) over a 2-minute interval. Sensor must calibrate to the saturation standard value and remain stable (within 0.05 mg/L of standard value) observed over a 2-minute interval.
  - (3). pH: Calibrate system using the two-point linear protocol (see App V, Section I.A.1.d for Hydrolab, App V, Section I.A.2.d for YSI 6 series, and App V, Section I.A.3.d for YSI EXO2). Calibrate zero point with pH 7 standard buffer. Calibrate slope with pH 10 standard buffer. Check response of system to pH 4 standard buffer but do not calibrate. Sensor should read stable pH values (within 0.01 pH units of reading) within 2-minutes or less of immersion in standard buffer before and after calibration. Sensor readings of pH 4 standard buffer should be stable (within 0.01 pH units of reading) and within 0.20 units of standard value as determined from pH Calibration Table.

During calibration, YSI pH 6561 and 6589 sensors must have stable millivolt (mV) readings in standard buffers within the following ranges:

```
pH 7 buffer -30 to +30 mV
pH 10 buffer -210 to -150 mV
pH 4 buffer +150 to +210 mV
```

If mV readings are not within these ranges, pH sensor must be replaced.

# (4). Specific Conductance

For Hydrolab Series 5 instruments calibrate in any of three autoranges (0 –  $1500~\mu\text{S/cm}$ ,  $1500~-15,000~\mu\text{S/cm}$ , and  $15,000~-150,000~\mu\text{S/cm}$ ) using a two-point linear protocol (see App V, Section I.A.1.c). Sensor reading before calibration should be stable (within 1% of reading) over a 2-minute interval. Sensor reading after calibration should be stable and within 1% of standard over a 2-minute interval. Select a standard in another autorange and check linearity response. Sensor reading should be stable (within 1% of reading) and within 5% of standard value over a 2-minute interval.

For YSI Series 6 instruments calibrate with a standard from one of the three Hydrolab autoranges above using a two-point linear protocol (see App V, Section I.A.2.c). Sensor reading before calibration should be stable (within 1% of reading) over a 2-minute interval. Sensor reading after calibration should be stable and within 1% of standard over a 2-minute interval. Select a standard in another Hydrolab autorange and check linearity response. Sensor reading should be stable (within 1% of reading) and within  $\pm 5\%$  of standard value over a 2-minute interval.

For YSI EXO instruments calibrate with a standard from one of the three Hydrolab autoranges above using a two-point linear protocol (see App V, Section I.A.3.c). Sensor reading before calibration should be stable (within 1% of reading) over a 2-minute interval. Sensor reading after calibration should be stable and within 1% of standard over a 2-minute interval. Select a standard in another Hydrolab autorange and check linearity response. Sensor reading should be stable (within 1% of reading) and within  $\pm 5\%$  of standard value over a 2-minute interval.

(5). Depth: Calibrate zero point in air. Sensor should calibrate and read stable value.

### II. LI-COR® INSTRUMENTATION MAINTENANCE:

Photosynthetic Active Radiation (PAR) is measured using LI-COR® Bioscientific equipment. Each LI-COR® setup is comprised of an LI-1400 display unit, an LI-

190SA ambient light sensor, and an LI-192SA underwater light sensor, an underwater leveling frame, and an underwater cable attached to a calibrated lowering-line.

The following factory-maintenance procedure ensures compliance with the manufacturer's required maintenance schedule. Each winter half of the ambient and underwater sensors are shipped to LI-COR® Bioscientific for re-calibration. The next year, the remaining ambient and underwater sensors are sent to the factory for re-calibration. Upon return from the factory, updated, sensor specific, correction values are entered into the displays before the equipment is deployed.

The LI-1400 display units are battery powered. Twice each year, the four AA batteries in each of the display units are replaced with new AA batteries.

Lowering lines are evaluated yearly to ensure depth markings are correctly located. Troubleshooting is performed as necessary before sending PAR measurement components to the factory for repair.

A LI-COR equipment tracking maintenance log is used to document which instrumentation components are attached to specific display units. As well as provide a permanent record of all re-calibrations, battery replacements, lowering-line checks and equipment repairs.

## IV. SECCHI DISK

Each year the Secchi disk line is calibrated by comparing its 0.2m marks to a metal meter stick. Each mark is a small piece of colored flat synthetic webbing pulled through the line and sewn for security. Marks are moved if the webbing does not line up with the corresponding line on the meter stick.

### V. AUDITS

Annual audits of all field equipment logbooks, maintenance records and field procedures will be conducted by the field quality assurance officer. This information will be reported to the DNR Quality Assurance Officer. (See Quality Assurance Project Plan, Section 8: Project Organization and Responsibility).

The following pages contain examples of calibration logs for Hydrolab Series 5, YSI Series 6, and YSI EXO instruments.

Note: The example Hydrolab Calibration log form and instructions are in use as of November 1, 2016. Revisions are planned. References to deprecated equipment and procedures will be removed and guidance for temperature thermistors will be added.

# VI. INSTRUMENT CALIBRATION LOGS

The following pages are calibration logs and their documentation for Hydrolab Series 5, YSI Series 6, and YSI EXO instruments. These revisions have been used since July 2009.

HYDROLAB IN STRUMENT CALIBRATION LOG SERIES 4a/5 METER PAGE NO. (July 2008)					GE NO		
DATE	: MM/DD/YYYY						
TIME:	: HHMM (MILITARY TIME)						
LOCA	TION: OFFICE, HOME, FIELD, MOTEL						
CALIE	BRATION TYPE: CAL, POST CAL, CHECK, TEST	ELD, MOTEL  ET CAL,  ED OXYGEN - CLARK POLAROGRAPHIC CELL (water saturated air  IHg  YES ND YES NO YES NO  YES NO  YES NO  YES NO  YES NO  YES NO  YES NO  YES NO  YES NO  YES NO  YES NO  YES NO  YES NO  YES NO  YES NO					
PROJECT							
CHEC	CKED BY: INITIALS						
DISSOLVED OXYGEN – CLARK POLAROGRAPHIC CELL (water saturated air – mg/L protocol)							
TEMP	PERTURE: *C						
BARC	OMETRIC PRESSURE: mm Hg						
CALIE	BRATION D. O.: mg/L						
D. O.	READING: mg/L						
ADJU	8TED: CIRCLE ONE	YE3 NO	YES NO	YE8 NO	YES NO	YES NO	
	DI\$SOLVED OXYGEN	I – OPTICAL SENS	3OR (air saturated	d water – percent	saturation protoco	ol)	
TEMP	PERTURE: 10						
BARC	OMETRIC PRESSURE: mm Hg						
CALIE	BRATION D. O.: % sat / mg/L	I	1	1	I	I	
D. O.	READING: % sat / mg/L	I	1	1	I	I	
ADJU	8TED: CIRCLE ONE	YES NO	YE8 NO	YES NO	YES NO	YES NO	
	SPECIFIC CONDUCTANCE (u.Siemens/cm)						
ZERO	POINT: READING / ADJUSTED	YES NO	YES NO	YES NO	YES NO	YES NO	
[	TEMPERATURE: °C						
SLOPE	8TANDARD: 48/cm						
ಪ	METER READS: µ8/cm						
	ADJUSTED: CIRCLE ONE	YE8 NO	YE8 NO	YE8 NO	YE8 NO	YE8 NO	
			pH.				
Ę	TEMPERATURE: °C						
PH 7 ZERO POINT	CHART pH: pH units						
F 62	METER READ 8: pH units						
2	ADJUSTED: CIRCLE ONE	YES NO	YE8 NO	YE8 NO	YES NO	YES NO	
	TEMPERATURE: °C						
pH 4/10	CHART pH: pH units						
포글	METER READ 8: pH units						
	ADJUSTED: CIRCLE ONE	YE3 NO	YE8 NO	YE8 NO	YES NO	YE8 NO	
				_			
ВАТТ	ERY: BATTERY/VOLTS	l	ı	ı	Ì		
QA/Q	C SIGN OFF: INITIALS						
DATE: MW/DDYYYY COMMENT8 (NITIALED)							

# HYDROLAB INSTRUMENT CALIBRATION LOG DOCUMENTATION SERIES 4a/5 JULY 2009

PAGE HEADER INFORMATION – row of information at top of page.

- 1. METER record letter identifier, in upper case, for instrument on this log page.
- 2. PAGE NUMBER record next page number in sequence; pages numbered sequentially from first use of letter identifier.

LOG ENTRY – one column is one log entry.

### **HEADER INFORMATION**

- 1. DATE record date with month and day as two-digit fields each and year as four-digit field. Separate fields with slash.
- 2. TIME record time in military format (hours and minutes as two-digit fields each) when beginning work.
- 3. LOCATION record place where work performed as one of four choices (office, home, field, or motel); if not one of four choices, be as specific as possible.
- 4, CALIBRATION TYPE record type of work performed as one of these choices:
  - CAL calibration performed before field deployment; calibration adjusted if necessary.
  - POST CAL post-calibration performed as calibration check after field deployment, no calibration adjustments.
  - CHECK check calibration of specific parameter(s); calibration adjustments possible.
  - TEST instrument performance test performed for maintenance or repair reasons.
- 5. PROJECT record project(s) on which instrument intended to be used or was used.
- 6. CHECKED BY record initials of person(s) performing work; initials are three-character field. Separate multiple persons with slash.

### DISSOLVED OXYGEN – CLARK POLAROGAPHIC CELL

- 1. TEMPERATURE record temperature in degrees centigrade as displayed on the instrument. Reading used to determine "CALIBRATION D. O." entry.
- 2. BAROMETRIC PRESSURE record temperature corrected local barometric pressure in millimeters of mercury from a Fortin mercury barometer. Reading used to determine "CALIBRATION D. O." entry.
- 3. CALIBRATION D. O. record dissolved oxygen concentration in milligrams per liter from calibration chart or calculation.
- 4. D. O. READING record dissolved oxygen concentration in milligrams per liter as displayed on the instrument before making calibration adjustments.
- 5. ADJUSTED circle "yes" or "no" if calibration setting was changed or not changed, respectively.

# DISSOLVED OXYGEN – OPTICAL SENSOR

- 1. TEMPERATURE record temperature in degrees centigrade as displayed on the instrument. Reading used to determine "CALIBRATION D.O." entry.
- 2. BAROMETRIC PRESSURE record temperature corrected local barometric pressure in millimeters of mercury from a Fortin mercury barometer. Reading used to determine "CALIBRATION D.O." entry.
- 3. CALIBRATON D.O. record dissolved oxygen concentration as percent saturation and milligrams per liter from calibration chart or calculation.
- 4. D. O. READING record dissolved oxygen concentration as percent saturation and milligrams per liter as displayed on the instrument before making calibration adjustments.
- 5. ADJUSTED circle "yes" or "no" if calibration setting was changed or not changed, respectively.

### SPECIFIC CONDUCTANCE

A. ZERO POINT – record "zero" reading from instrument display before making calibration adjustments. Circle "yes" or "no" if calibration setting was changed or not, respectively.

### B. SLOPE

- 1. TEMPERATURE record temperature in degrees centigrade as displayed on the instrument.
- 2. STANDARD record specific conductance of standard in microSiemens per centimeter as written on the bottle of standard.
- 3. METER READS record specific conductance of standard in microSiemens per centimeter as displayed on the instrument before making calibration adjustments.
- 4. ADJUSTED circle "yes" or "no" if calibration setting was changed or not changed, respectively.

pН

# A. pH 7 – ZERO POINT

- 1. TEMPERATURE record temperature in degrees centigrade as displayed on the instrument.
- 2. CHART pH record pH in pH units from calibration chart.
- 3. METER READS record pH in pH units as displayed on the instrument before making calibration adjustments.
- 4. ADJUSTED circle "yes" or "no" if calibration setting was changed or not changed, respectively.

# B. pH 4/10 BUFFER – SLOPE

- 1. TEMPERATURE record temperature in degrees centigrade as displayed on the instrument.
- 2. CHART pH record pH in pH units from calibration chart.
- 3. METER READS record pH in pH units as displayed on the instrument before making calibration adjustments.
- 4. ADJUSTED circle "yes" or "no" if calibration setting was changed or not changed, respectively.

### **BATTERY**

Record letter or number identity of battery connected to instrument (record internal battery as letter or number identity of display). Record voltage reading of this battery as displayed on the instrument. Separate each field with a slash.

# QA/QC SIGN OFF

Scientist who verified completeness and accuracy of log entry records his/her initials.

# **COMMENTS**

- 1. DATE record date of entry with month and day as two-digit fields each and year as four-digit field. Separate fields with slash.
- 2. COMMENTS comments should be long enough to cover the subject but short enough to be interesting. Initials of person making entry should be at end of comments.

NOTE: to facilitate matching comments with log entry, a circled number should appear both at the top of appropriate log entry column and preceding the date in the comments section. This circled number should be unique and sequential to each log page.

HYDROLAB INSTRUMENT CALIBRATION LOG SERIES 5 METER PAGE NO.															
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$\vdash$	DATE: MM/DD/YYYY														
		MM (MILITARY T		├──									-		
_			E, FIELD, MOTEL	₩											
	CHEC	ION TYPE: CAL CK, TEST	, POST CAL,	<u> </u>											
_	OJECT:			├──									-		
СН		BY: INITIALS													
TE		DISSOLVE	D OXYGEN -	OPTICA	AL SE	NSOR (a	air satu	ırated v	vater -	- percer	t satu	ration p	orotoc	ol)	
_			E88URE: mm Hg	+											
		CONDUCTANCE	$\vdash$												
			$\vdash$												
_	CALIBRATION D. O.: mg/L. METER READ8: mg/L.														
	DJUSTED TO CALIBRATION D.O.		YE8	NO	YE8	NO	YE8	NO	YE8	NO	YE8	NO	YE3	NO	
				SPECI	IFIC C	ONDUC	TANC	Ε (μSie	mens	(cm)					
ZE	ERO POINT: READING   ADJUSTED TO ZERO		YE8 NO		YE8 NO		YE8 NO		YE8 NO		YE8 NO		YES NO		
ļ,	TEMPERATURE: °C			<del>                                     </del>											
3LOPE	CAI		NDARD: μS/cm	₩											
-	$\vdash$	TER READ8: μ		₩											
	AD.	JUSTED TO CAL	L. 8TANDARD	YE8	NO	YE8	NO	YE8	NO	YE8	NO	YE8	NO	YE8	NO
							рΗ								
	a F	TEMPERATUR	RE: °C	Τ											
7	STANDARD ZERO POINT		N pH: pH units	$\vdash$											
픙	NA PE		ETER READS: pH units												
	2E ZE		ADJUSTED TO CAL pH		NO	YE8	NO	YE8	NO	YE8	NO	YE8	NO	YE8	NO
			EMPERATURE: °C												
10	A BB			+									-		
4	PH 4710 STANDARD SLOPE		CALIBRATON pH: pH units METER READ 8: pH units										-		
-	E	ADJUSTED TO CAL pH		YE8	NO	YE8	NO	YE8	NO	YE8	NO	YE8	NO	YE8	NO
		A2000112011	ADSUSTED TO CAL PH			1.25		123							
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QA/QC 8/9N OFF: NITIALS															
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## YSI INSTRUMENT CALIBRATION LOG DOCUMENTATION SERIES 6/ EXO JULY 2009

PAGE HEADER INFORMATION – row of information at top of page.

- 1. METER record letter identifier, in upper case, for instrument on this log page.
- 2. PAGE NUMBER record next page number in sequence; pages numbered sequentially from first use of letter identifier.

LOG ENTRY – one column is one log entry.

### **HEADER INFORMATION**

- 1. DATE record date with month and day as two-digit fields each and year as four-digit field. Separate fields with slash.
- 2. TIME record time in military format (hours and minutes as two-digit fields each) when beginning work.
- 3. LOCATION record place where work performed as one of four choices (office, home, field, or motel); if not one of four choices, be as specific as possible.
- 4, CALIBRATION TYPE record type of work performed as one of these choices:

CAL – calibration performed before field deployment; calibration adjusted if necessary.

POST CAL – post-calibration performed as calibration check after field deployment, no calibration adjustments.

CHECK – check calibration of specific parameter(s); calibration adjustments possible.

TEST – instrument performance test performed for maintenance or repair reasons.

- 5. PROJECT record project(s) on which instrument intended to be used or was used.
- 6. CHECKED BY record initials of person(s) performing work; initials are three-character field. Separate multiple persons with slash.

### DISSOLVED OXYGEN – OPTICAL SENSOR

- 1. TEMPERATURE record temperature in degrees centigrade as displayed on the instrument. Reading used to determine "CALIBRATION D.O." entry.
- 2. BAROMETRIC PRESSURE record temperature corrected local barometric pressure in millimeters of mercury from a Fortin mercury barometer. Reading used to determine "CALIBRATION D.O." entry.
- 3. CALIBRATON D.O. record dissolved oxygen concentration as percent saturation and milligrams per liter from calibration chart or calculation.
- 4. D. O. READING record dissolved oxygen concentration as percent saturation and milligrams per liter as displayed on the instrument before making calibration adjustments.
- 5. ADJUSTED circle "yes" or "no" if calibration setting was changed or not changed, respectively.

### SPECIFIC CONDUCTANCE

### A. SLOPE

- 1. TEMPERATURE record temperature in degrees centigrade as displayed on the instrument.
- 2. STANDARD record specific conductance of standard in microSiemens per centimeter as written on the bottle of standard.
- 3. METER READS record specific conductance of standard in microSiemens per centimeter as displayed on the instrument before making calibration adjustments.
- 4. ADJUSTED circle "yes" or "no" if calibration setting was changed or not changed, respectively.

### A. pH7 - ZERO POINT

- 1. TEMPERATURE record temperature in degrees centigrade as displayed on the instrument.
- 2. CHART pH record pH in pH units from calibration chart.
- 3. METER READS record pH in pH units as displayed on the instrument before making calibration adjustments.
- 4. ADJUSTED circle "yes" or "no" if calibration setting was changed or not changed, respectively.

### B. pH 4/10 BUFFER – SLOPE

- 1. TEMPERATURE record temperature in degrees centigrade as displayed on the instrument.
- 2. CHART pH record pH in pH units from calibration chart.
- 3. METER READS record pH in pH units as displayed on the instrument before making calibration adjustments.
- 4. ADJUSTED circle "yes" or "no" if calibration setting was changed or not changed, respectively.

### QA/QC SIGN OFF

Scientist who verified completeness and accuracy of log entry records his/her initials.

### **COMMENTS**

- 1. DATE record date of entry with month and day as two-digit fields each and year as four-digit field. Separate fields with slash.
- 2. COMMENTS comments should be long enough to cover the subject but short enough to be interesting. Initials of person making entry should be at end of comments.

NOTE: to facilitate matching comments with log entry, a circled number should appear both at the top of appropriate log entry column and preceding the date in the comments section. This circled number should be unique and sequential to each log page.

# MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

### FIELD PROCEDURES QUALITY ASSURANCE / QUALITY CONTROL

- I. Cleaning procedures (A-D are performed by Chesapeake Biological Lab staff members):
  - A. Autoanalyzer (AA) cups and caps: Cups and caps are used only one time and then are discarded.
  - B. DOC tubes: Place tubes in 10 % HCl bath for approximately 24 hours; follow by rinsing tubes several times in deionized water.
  - C. DOC caps: Place caps in 10 % HCl bath for approximately 24 hours; follow by rinsing tubes several times in deionized water.
  - D. TDN/TDP tubes: new tubes are digested using potassium persulfate followed by multiple deionized water rinses. Tubes that are "in-the-cycle" are cleaned by emptying old contents, rinsing the tubes and caps with 3-4 tap water rinses followed by 6 rinses with deionized water.
- II. Review of procedures for field and lab sheets in the field

### A. "Scientist signoff" duties

The field scientist is responsible for recording values on the field data sheets and on the lab sheets. This includes entering all Hydrolab/YSI *in situ* values, calculating the pycnocline, and ensuring that the field data sheet is complete. This individual is also responsible for transcribing necessary header information onto the lab sheets.

### B. "Senior scientist" duties

The individual who enters their initials in the 'senior scientist' boxes is the scientist who is officially designated as being in charge of the cruise.

### Mainstem Cruises:

- 1. The senior scientist, as field quality assurance officer on cruise, should ensure that:
- a. Thermometers are placed in refrigerator and freezer to monitor daily temperatures (4 °C for refrigerator and -10 to -20 °C for freezer) and record data on cruise report.

(The refrigerator is used January-June and August and November for the Split, to keep silicate samples cool). If the temperatures are too high; they should be set lower if possible and if not possible, the Captain of the research vessel should be notified.

- b. Check with Captain of the research vessel to ensure that weather and location instruments used onboard the ship (e.g., Raytheon factory calibrated barometer, anemometer, or GPS) are functioning properly and, if not, record it in the Cruise Report.
- c. Check to make sure all equipment necessary to accomplish sampling is on board and functioning before leaving dock.
- d. Document and report back to the field quality assurance officer any deviations from existing protocol or problems that have arisen during the cruise.

### III. Dissolved Oxygen Calibrations and Checks

Dissolved Oxygen calibration checks shall be done every morning for Mainstem Monitoring. Typically, the instruments used on Mainstem employ optical DO probes and are checked using the common standard of air-saturated water. After correcting for the barometric pressure and temperature, the oxygen content of air saturated water can be checked against standard D.O. tables.

### IV. Spare Instrument

As discussed in Appendix 5 (Field Instrument Quality Assurance/Quality Control), teams carry two calibrated Hydrolab/YSI meters in case of failure. The meter in use is compared to the reserve meter any time (a) the field scientist recording measurements observes values outside the "typically expected range"; (b) the meter generates variable or erratic values; or, (c) the meter in use displays an error message. If the meters do not agree within acceptable limits, the reserve meter is used. This is noted under the additional comments section.

### V. Deionized water

The deionized water at the Field Office is generated from tap water using a Thermo Scientific Barnstead DIamond TII RO/DI system with a GE SmartWater external pre-filter. The RO/DI system is linked to a Thermo Scientific Barnstead DIamond TII 60L storage reservoir. The system uses a thin film composite reverse osmosis membrane with pretreatment to produce RO water. This water is then put through a two-stage deionization process combined with UV oxidation and a 0.2-micron final filter. The reagent grade water provided by this system exceeds ASTM Type II and NCCLS/CAP Type I standards. All manufacturer recommendations are followed regarding cartridge replacement and system sanitation (Refer to Thermo Scientific. 2007. Barnstead DIamond TII Type II Water System Operation Manual

and Barnstead DIamond TII Type II Storage Reservoir Operation Manual). The GE SmartWater pre-filter was placed in-line to improve the integrity of feedwater going into the Barnstead DIamond System. The pre-filter is changed at least every three (3) months or more frequently during periods of heavy use. A log is kept at the front of the DI System Manual to document all changes and updates made to the system.

### VI. Transfer of nutrient samples/sheets to laboratory

All samples are delivered to CBL at the end of the sampling week. The samples are placed in the freezer at the Field Office until delivery. The silicate samples that are collected at a subset of stations are stored in the Field Office refrigerator. The samples are packed with dewatered ice in a cooler. Do not place the silicates directly in the ice as this may cause them to freeze. The volume sheets for each sampling run are placed in a bin marked "CBL" on the side of the Field Office freezer at the end of the field day. The laboratory (volume) sheets must be collected from the bin and accompany all samples to CBL.

# MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

### **SPLIT SAMPLE PROGRAM**

The following summarizes the split sample program and is excerpted from the <u>Recommended Guidelines</u> for <u>Sampling and Analysis in the Chesapeake Bay Monitoring Program</u>. (EPA 1996). Information about the Split Sample and Blind Sample Programs program is available on-line at the EPA Chesapeake Bay Program web site: http://www.chesapeakebay.net/about/programs/qa.

### **Background and Objectives**

The Chesapeake Bay Coordinated Split Sample Program (CSSP) was established in June 1989 by recommendation of AMQAW [the Chesapeake Bay Program Analytical Methods and Quality Assurance Workgroup], to the Monitoring Subcommittee. The major objective of this program is to establish a measure of comparability between sampling and analytical operations for water quality monitoring basin-wide. A secondary objective is to evaluate the in-matrix dilution of standard U.S. Environmental Protection Agency (EPA) reference materials. These standard reference materials are analyzed in appropriate matrix, fresh to saline, and concentration level to match the sample. All laboratories participating in basin-wide data collection programs are also required to participate in the CSSP.

Early in 2015, the Data Integrity Work Group (DIWG) was formed. The DIWG replaced the AMQAW. The goals and objectives of the DIWQ are similar to those of the AMQAW. The Data Integrity Work Group plans to complete the document "Methods and Quality Assurance for Chesapeake Bay Water Quality Monitoring Programs" and publish it on the Chesapeake Bay Program website.

For additional information on the program, please consult <u>Chesapeake Bay Coordinated Split Sample</u> <u>Program Implementation Guidelines Rev. 4</u>, (EPA Dec. 2010), <u>2015 Work Plan for the Chesapeake Bay Program Data Integrity Workgroup</u>, <u>Data Integrity Workgroup</u> (formerly AMQAW).

### **Summary of Criteria**

(1) The Participant will participate in the applicable component(s) of the CSSP.

- (2) The Standard Operating Procedures (SOPs) that are developed and used should be in accordance with the <u>Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines CBP/TRS 58/91, May 1991</u> plus any revisions specified by the CBP Quality Assurance Officer.
- (3) For each of the Virginia and Maryland CSSP stations and on a quarterly basis, the Participant will receive and analyze four sub-samples. Since 1998, Maryland DNR has performed the sample split at one station and depth, (usually the surface sample at station CB4.4C). In recent years, the August split samples has been collected from the bottom as doing so often provides measurable P values for comparison.

Four sub samples will be collected for each participating laboratory. Samples to be analyzed at Virginia Labs will be delivered to Port Royal, VA, the afternoon of the day they are collected and processed the following morning. The samples that are collected for Horn Point Laboratory and South River Federation are picked up from the Annapolis Water Quality Field Office the afternoon of the day of collection and are also process the following morning. In order to treat all of the samples uniformly, the MD DNR field team will also wait until the next morning to process their split samples.

Laboratories currently participating in the CCSP program Mainstem sample analyses are: University of Maryland Chesapeake Biological Laboratory Nutrient Analytical Services Laboratory (CBL), University of Maryland Horn Point Laboratory (HPL), Old Dominion University College of Sciences Water Quality Laboratory (ODU), Virginia Division of Consolidated Laboratory Services (VADCLS), Virginia Institute of Marine Science (VIMS), South River Federation (SRF), and Delaware Department of Natural Resources and Environmental Control (DNREC).

Tributaries project CSSP samples are also analyzed by CBL, ODU and VADCLS as well as, the following list of laboratories: Delaware Department of Natural Resources-DNREC and Environmental Control-DSL, District of Columbia Department of the Environment, Fairfax County Department of Public Works (FCDPW), Maryland Dept. of Health (MDH), National Water Quality Laboratory (twice a year), Pennsylvania Department of Environmental Protection - Bureau of Laboratories (twice a year), Susquehanna River Basin Commission (SRBC), Appalachian Lab-UMCES (twice a year), United States Geological Survey (USGS, twice a year) and Virginia Polytechnic Institute - Occoquan Laboratory. VIMS does not currently participate in tributaries sampling.

The Tributaries project CSSP sample is collected by the District Department of Environment, DC.

Treating each sub-sample as a discrete sample, participating laboratories are generally required to perform only those analyses which they routinely perform in support of basin-wide data collection program. One of the three sub-samples should be used to generate laboratory duplicates and a laboratory spike. These quality control (QC) samples should be analyzed concurrently with the associated CSSP sub-samples.

- (4) The routine submission of split sample data is the responsibility of each laboratory and its inhouse data management organization.
- (5) To supplement the analyses of the three sub-samples and the respective QC sample, EPA standard reference materials provides a strong measure of comparability between all laboratories and within one laboratory's analytical system over time. Quarterly analysis of Standard Reference Materials (SRMs) is the most independent evaluation of laboratory performance available at this time. It is a critical element of any diagnostic efforts associated with the CSSP.

## **Examples of Split Sample information sheets and Custody Logs**

An example of the field sheet used to record sample number, time of collection and salinity when split sample water is collected follows. Volumes are filled in the next morning when samples are processed for the Laboratories.

An example of a log sheet used to document the split sample Chain of Custody follows.

### **REFERENCES:**

U.S. Environmental Protection Agency (EPA). 1996. <u>Recommended Guidelines for Sampling and Analysis in the Chesapeake Bay Monitoring Program</u>. Chesapeake Bay Program, August 1996. CBP/TRS 148/96; EPA 903-R-96-006.

U.S. Environmental Protection Agency (EPA). 2010. <u>Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines Rev. 4</u> Chesapeake Bay Program, December 2010.

<u>2015 Work Plan for the Chesapeake Bay Program Data Integrity Workgroup,</u> Chesapeake Bay Program, January 2015.

Website: Data Integrity Workgroup (formerly AMQAW).

# MAIN BAY SPLIT SAMPLE CUSTODY LOG

				BOTTLE N	NUMBERS: <u>f</u>	1,F2,F3,F4,
LOCATION: CB4.4			COLLECT	ED FOR: Sc	outh River	Federation
COLLECTION DETAILS: COMMENTS: (unusual c						T: PPT
	,	1		,	,	
SPLITTING DETAILS: COMPOSITE CONTAINER FILLED BY: subme				ial bottle		e=====================================
Splitting Sequence	order # Ac	tency or	der # Agency	, orde	er # Agenc	757
	9 B2 C 10C2 C 11D2 V 12E2 I 13F2 S	DDU 16 CBL 17 7IMS 18 HP 19	B3 ODU C3 CBL D3 VIMS E3 HP F3 SRF	23 24 25 2 2	3 B4 OE 4 C4 CE 5 D4 VI 6 E4 H 7 F4 SF	DU BL EMS P RF
TRANSFER SEQUENCE: Composite collected & split	DATE	TIME		WHOM?	(circ	DF SAMPLE le one) bient
Subsample picked up					0°C	4°C ambient
Subsamples delivere to lab	d 	<del></del>			0°C	4°C ambient
FIELD PROCESSING IN BOTTLE # FIELD P	-	DONE	Σ	ATE/TIME		BY WHOM?
NOTE: PLEASE SEND	A COPY OF	THIS COMPLE	TED FORM TO:	Main Bay	 Split, Le	enora

Dennis, Maryland Dept of Natural Resources, TEA/C-2, 580 Taylor Avenue, Annapolis

May 31, 2022, QAPP: Chemical & Physical Property Component

MD, 21401, (410) 260-8647.

Collected for: MD/MDHMH+DSL Bottle No.(s): A1, A2, A3, J1, J2, J3

POTOMAC COMPONENT S	PLIT SAMPLE	CUSTODY I	OG			
COLLECTION DETAILS: WTEMP4.9 PH 8.27	DATE:/2////C					
DO 13.   COMMENTS: (unusual					×	
SPLITTING DETAILS: COMPOSITE CONTAINER FILLED BY: multiple grabs pump other		BPLITTING  bottl  bottl	e e e e e e e e e e e e e e e e e e e		DCLS CRL FCDPW ODU OL USGS SRBC OSL HDHMH DCLS CRL FCDPW ODU OL USGS SRBC QSL HDHMH DCLS CRL FCDPW ODU OL USGS SRBC CRL FCDPW ODU OL USGS SRBC CRL FCDPW ODU OL SRBC CRL FCDPW ODU OL USGS SRBC	B1 - C1 - D1 - E1 F1 H1 J1 - A2 - B2 - C2 - B2 - F2 - H2 - J2 - A3 - C3
TRANSFER SEQUENCE:	Date	Time	By V	Whom		f Sample le one)
Composite collected Composite split Subsamples picked up Subsamples delivered to lab	-	W   12/1   125		EO GH		Cambien
mbal All s	Processing  AmpleS processing  A	Done on S OCLSSED PP CHL WITH DONE S complete	A PC/PN	17/12/17 12/12/17 to: is, MD 21	60635 60710 80735	y Whom DSM DSM DSM

# MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

### DATA STATUS FORM DOCUMENTATION AND PROCEDURES

The Data Status Form is used for all monthly water quality data for all monitoring projects. The form is designed to facilitate data management by tracking data management activities and identifying potential problems for remedy early in the process. Upon receiving the data sheets or files from the data source agencies (e.g., the Field Office and the laboratories), the data clerk initiates a Data Status Form, which then accompanies the data sheets/files. When all of data have been processed for that month, the Data Status Form is stored with the data sheets and other computer-generated information at the DNR Tawes Office Building in Annapolis.

This sheet was developed in 1986 and updated in 1995. An updated web-based data status tracking form is being designed and will be implemented in the future. Note that many of the columns on the form are no longer actively used. The necessary information in the sheet is described in the following paragraphs. An example Data Status Form is attached for reference.

### I. COMPLETE THE FOLLOWING WHEN THE FORM IS ISSUED:

### 1. DATE INITIATED (UPPER RIGHT-HAND CORNER)

Indicate the date when the form is issued. In general, issue the form upon receiving the first group of data sheets and/or data files from data source agencies for a given month.

#### 2. DATA SET NAME

Enter the data set name with the project abbreviation, data sampling month, year, and data type (e.g., TJAN98FD for tributary field data for January 1998). Refer to the detailed description of naming conventions at the end of this appendix.

### 3. DATA RECEIVED

Upon receiving the first group of data sheets and/or data files, enter the date and initial in this field.

# II. COMPLETE THE FOLLOWING UPON FINISHING THE DATA MANAGEMENT PROCESS

### 1. DATA REVIEWED

Once all monthly data sheets and/or data files have been received and the data have been reviewed, enter completion date. Initial in this field.

#### 2. CROSS REFERENCE

If the completed cross reference sheets are included with the incoming data sheets, enter the date and initial in this field. If, for some reason, cross reference sheets are not included, the Quality Assurance Officer would be notified, and s/he would contact the field office.

#### 3. XEROXING

Before sending field data sheets to the data entry service agency, copy data sheets and send originals to the data entry service agency. Enter the completion date and initial in this field.

### 4. DATA ENTRY - SENT

Enter the date data sheets are sent to data entry service in this field. Initial.

### 5. DATA ENTRY – RETURNED

Enter the date that data sheets and data diskette are received from data entry service in this field. Initial.

- 6. INITIAL DATA CHECK
- 7. DATA VERIFICATION
- 8. TEMPORARY MERGE(S)

### **BIO CHECK** (#9 - #13)

- 9. VERIFICATION(S)
- 10. EDIT(S) IDENTIFIED
- 11. DATA CORRECTION(S)
- 12. TEMPORARY MERGE(S)
- 13. BIOLOGIST SIGN OFF
- 14. FINAL DATA CORRECTION
- 15. MERGE COMPLETED
- 16. GENERATE MS ACCESS DATA SET

- 17. GENERATE EPA MS ACCESS DATA (This field generally is left blank—this step is included under "PRODUCE CBP DATA TRN FILE.")
- 18. SUBMISSION DOCUMENT (This field generally is left blank-this step is included under "PRODUCE CBP DATA TRN FILE.")
- 19. SUBMISSION LETTER (This field generally is left blank—this step is included under "PRODUCE CBP DATA TRN FILE.")

#### 20. FINAL SIGN-OFF

Upon verifying all of the above data management processes and ensuring that all corrections have been made, finalize the data set in the state data base system by running permanent merge process in the EZMERGE system, enter the completion date and initial in this field.

### 21. SUBMISSION TO CBP (PRODUCE CBP DATA TRN FILE)

Upon successfully creating data submission file, report, and document for the monthly data submission process, enter the completion date in this field and initial.

### 22. CBP ACCEPTS / SIGN OFF

After receiving the checklist and ACCEPTS/SIGN OFF form from CBP and upon completing all the necessary data verification actions (e.g., double checking errors), put the completion date in this field and initial.

NOTE: Any special comments can be entered in the COMMENTS column during the data management activities.

### CONVENTIONS FOR NAMING THE DATA SET

An eight-character text string is used for this data set name. This section contains the naming conventions for data set names for all monitoring projects. Any new sampling monitoring and data collection projects must follow these conventions.

### 1. CHESAPEAKE BAY MAINSTEM MONITORING PROJECT

Data Set Name: MMMYYDDD

<u>Description</u>: The data set name contains the data sampling month, year, and data type only. The first three characters of the data set name (MMM) stand for the sampling month. The next two characters (YY) of the data set name are the last two digits of the sampling year. The last three characters of data set name (DDD) stand for sample collection type. The following types are available for this project:

DATA TYPE DATA DESCRIPTION

FLD Field Data
LAB Laboratory Data
CHL Chlorophyll Data

<u>Example of Mainstem Data Set Name</u>: For field data sheets for January 1998 data, the data set name is 'JAN98FLD'.

### 2. MARYLAND TRIBUTARY MONITORING PROJECT

Data Set Name: TMMMYYDD

<u>Description:</u> The data set name begins with the project initial 'T', followed by the data sampling month (MMM), year (YY), and data type (DD). The last two characters of the data set name (DD) stand for data type. The following types are available for this project:

DATA TYPE DATA DESCRIPTION

FD Field Data
LB Laboratory Data
CH Chlorophyll Data

Example of a Tributary Data Set Name: For field data sheets for January 1998 data, the data set name is 'TJAN98FD'.

# 3. MARYLAND PATUXENT RIVER INTENSIVE SURVEY (PART OF MARYLAND TRIBUTARY MONITORING PROJECT)

Data Set Name: PTMMMYYD

<u>Description:</u> The data set name begins with the project initials 'PT', followed by the data sampling month (MMM), year (YY), and data type (D). The last character of data set name (D) stands for data type. The following types are available for this project:

DATA TYPE DATA DESCRIPTION

F Field Data L Laboratory Data

[Note: Chlorophyll data for the Patuxent is included in the tributary data set.]

<u>Example of a Patuxent Data Set Name</u>: For field data sheets for January 1998 data, the data set name is 'PTJAN98F'.

# Example of Monitoring Data Status Form

	MARYLAND DEPARTMENT OF NATURAL RESOURCES DATA STATUS FORM  DATA STATUS FORM  DATE Initiated: 2/22/04				
*	Data Set Name: FEBO				
	///////////////////////////////////////		Initials	Comments	
•	Data Received	2 22 06	RVR		
•	Data Reviewed	2/22/06	RVR		
**	Cross Reference				
•	Xeroxing Field sheets				
**	Data Entry   Sent Field/Lab/	3/16/06	RYR		
	Patuxent Returned	3/23/06	RUR		
*	Initial Data Check				
	- Data Verification				
	Temporary Merge(s)				
	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	Check Records (Date 1   2   3	4	///////////////////////////////////////	
B I	Verification(s)			·	
o *	Edit(s) Identified				
c *	Data Correction(s)				
C +	Temporary Merge(s)				
ĸ	Biologist Sign Off				
•	Final Data Correction				
*	Merge Completed				
•	Generate FLC Data Set				
	Generate EPA FLC Data				
•	Submission Document				
•	Submission Letter				
	Final Sign Off				
	Submission to CBP				
	CBP Data Check List(s)				
	CBP Accepts / Signoff				

# MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

### **OUTLINE OF CODES FOR FIELD AND LABORATORY DATA SHEETS**

This file contains the computer codes for water quality data that will be used for field and laboratory data sheets. The computer codes are listed with their corresponding descriptions.

### **OUTLINE OF CODES**

### **FIELD DATA SHEETS**

Submitter Codes
Data Category Codes
Study Codes
Sample Method Codes
Tide State Codes
Weather Codes
Percentage Cloud Cover Codes
Dissolved Oxygen Method Codes
'Value Corrected' Codes
Sample Layer Codes
Wind Direction Codes

### LABORATORY DATA SHEETS

### COMPUTER CODES FOR NUTRIENT PARAMETER ANALYSES SHEET

Submitter Codes
Data Category Codes
Sample Method Codes
Sample Layer Codes
Study Codes
Parameter Codes
Analytical Problem Codes
Detection Limit Codes
Method Codes

### COMPUTER CODES FOR CHLOROPHYLL PARAMETER ANALYSES SHEET

Submitter Codes
Data Category Codes
Sample Layer Codes
Study Codes
Analytical Problem Codes

### **DETAILED DESCRIPTION OF CODES**

THE FOLLOWING LISTS ONLY THE MOST COMMONLY USED COMPUTER CODES IN THE DATA PROCESSING SYSTEM.

### FIELD DATA SHEETS

### **Submitter Codes:**

Code	Data collection agency	Analytical lab
28	CBL/FIELD	CHEMICAL – CBL/LAB
		CHLOROPHYLL – DHMH through 12/31/2008
		TURBIDITY - DHMH
60	DNR/TEA	CHEMICAL – CBL, DHMH
		CHLOROPHYLL – DHMH through 12/31/2008
		CHLOROPHYLL – CBL beginning 1/1/2009
79	DNR/TEA	CHEMICAL – CBL
		CHLOROPHYLL – DHMH through 12/31/2008
		CHLOROPHYLL – CBL beginning 1/1/2009

# Data Category Codes: These codes are designed to indicate the type of data collected

Code	Description
AA	PRIMARY MONITORING SAMPLE - LAND
AB	PRIMARY MONITORING SAMPLE – BOAT
IN	WATER QUALITY INTENSIVE SURVEY DATA
NR	NON-POINT SOURCE/RUN-OFF SAMPLING DATA
MB	CHESAPEAKE BAY MONITORING WATER QUALITY SAMPLE MAIN BAY
MN	AUTOMATED MONITORING STUDY
MT	CHESAPEAKE BAY MONITORING WATER QUALITY SAMPLE MARYLAND
	TRIBUTARY
ST	SEDIMENT DATA SAMPLE
WQ	WATER QUALITY SAMPLE, UNSPECIFIED PROGRAM

# **Study Codes**

Code	Description	Lab details
01	CHESAPEAKE BAY MONITORING PROGRAM – MAIN BAY	CHEMICAL – CBL CHLOROPHYLL – DHMH through 12/31/2008 CHLOROPHYLL – CBL beginning 1/1/2009
02	CHESAPEAKE BAY MONITORING PROGRAM – TRIBUTARY (includes PATUXENT)	CHEMICAL (PATUXENT) – DHMH through 6/1990 CHEMICAL (PATUXENT) – CBL beginning 7/1990 CHEMICAL (NON-PATUXENT) – DHMH through 4/1998 CHEMICAL (NON-PATUXENT) – CBL beginning 5/1998 CHLOROPHYLL – DHMH through 12/31/2008 CHLOROPHYLL – CBL beginning 1/1/2009
04	CORE/TREND MONITORING PROGRAM	CHEMICAL – DHMH (Whole Water) Through 6/2005 CHEMICAL – DHMH (Filtered Water) beginning 7/2005 CHLOROPHYLL – DHMH through 12/31/2008 CHLOROPHYLL – CBL beginning 1/1/2009
06	POTOMAC COORDINATED MONITORING PROGRAM - COG	CHEMICAL Tidal – DHMH though 4/1998 CHEMICAL Tidal – CBL beginning 5/1998 CHEMICAL Freshwater – DHMH (Whole Water) Through 6/2005 CHEMICAL Freshwater – DHMH (Filtered Water) beginning 7/2005 CHLOROPHYLL – DHMH through 12/31/2008 CHLOROPHYLL – CBL beginning 1/1/2009
08	COASTAL BAYS PROGRAM	CHEMICAL – CBL CHLOROPHYLL – DHMH through 12/31/2008 CHLOROPHYLL – CBL beginning 1/1/2009
09	ROUTINE FISH WATER QUALITY	CHEMICAL – CBL CHLOROPHYLL – DHMH through 12/31/2008 (last samples collected in 2002)
21	WATER QUALITY MAPPING (DATAFLOW)	CHEMICAL – CBL CHLOROPHYLL – DHMH through 12/31/2008 CHLOROPHYLL – CBL beginning 1/1/2009
22	CONTINUOUS MONITORING	CHEMICAL – CBL CHLOROPHYLL – DHMH through 12/31/2008 CHLOROPHYLL – CBL beginning 1/1/2009
97	ROUTINE PFIESTERIA WATER QUALITY	CHEMICAL – CBL CHLOROPHYLL – DHMH through 12/31/2008 (last samples collected in 2002)
99	RAPID RESPONSE PFIESTERIA WATER QUALITY	CHEMICAL – CBL CHLOROPHYLL – DHMH through 12/31/2008 (last samples collected in 2002)

# **Sample Method Codes**

Code	Description
1	GRAB SAMPLE
7	FIELD MEASUREMENTS ONLY

### **Tide State Codes**

Code	Description	Comment
Е	EBB TIDE	STAGE OF WATER MOVEMENT FROM A HIGHER TO A
		LOWER LEVEL.
F	FLOOD TIDE	STAGE OF WATER MOVEMENT FROM A LOWER TO A
		HIGHER LEVEL.
L	LOWER SLACK	STAGE OF WATER WHERE THE LEVEL IS BELOW MEAN
	TIDE	AND VELOCITY APPROACHES ZERO
Н	HIGH SLACK TIDE	STAGE OF WATER WHERE THE LEVEL IS ABOVE MEAN
		AND VELOCITY APPROACHES ZERO
BLANK	NOT RECORDED	NOT APPLICABLE

### **Weather Codes**

Code	Description
10	NONE
11	DRIZZLE
12	RAIN
13	HEAVY RAIN
14	SQUALLY
15	FROZEN PRECIPITATION
16	MIXED RAIN AND SNOW
BLANK	NOT RECORDED, OR NOT APPLICABLE

# **Percentage Cloud Cover Codes**

PERCENTAGE CLOUD COVER IS REPORTED AS VALUES FROM 0 –100 %

# **Dissolved Oxygen Method Codes**

Code	CBP_code	Description
Н	F01	HYDROLAB
M	F02	YSI METER
W	F03	WINKLER METHOD
R	F04	YSI METER – RDOX; HYDROLAB - LDO
BLANK		NOT RECORDED, OR NOT
		APPLICABLE

**'Value Corrected' Codes:** These codes are designed to specify whether corrections have been made by the instrument calculation for the dissolved oxygen value.

Code	Description
N	NO CORRECTION
T	TEMPERATURE CORRECTION ONLY
С	TEMPERATURE AND CONDUCTIVITY CORRECTION

## **Sample Layer Codes**

Code	Description
S	SURFACE SAMPLE
AP	ABOVE PYCNOCLINE
BP	BELOW PYCNOCLINE
В	BOTTOM SAMPLE
M	MID-DEPTH SAMPLE
BLANK	NOT RECORDED, OR NOT APPLICABLE

### **Wind Direction Codes**

Code	Description
E	FROM THE EAST (90 DEGREES)
ENE	FROM THE EAST NORTHEAST (67.5 DEGREES)
ESE	FROM THE EAST SOUTHEAST (112.5 DEGREES)
N	FROM THE NORTH (0 DEGREES)
NE	FROM THE NORTHEAST (45 DEGREES)
NNE	FROM THE NORTH NORTHEAST (22.5 DEGREES)
NNW	FROM THE NORTH NORTHWEST (337.5 DEGREES)
NW	FROM THE NORTHWEST (315 DEGREES)
S	FROM THE SOUTH (180 DEGREES)
SE	FROM THE SOUTHEAST (135 DEGREES)
SSE	FROM THE SOUTH SOUTHEAST (157.5 DEGREES)
SSW	FROM THE SOUTH SOUTHWEST (202.5 DEGREES)
SW	FROM THE SOUTHWEST (225 DEGREES)
W	FROM THE WEST (270 DEGREES)
WNW	FROM THE WEST NORTHWEST (292.5 DEGREES)
WSW	FROM THE WEST SOUTHWEST (247.5 DEGREES)
NR	NOT RECORDED, OR NOT APPLICABLE

### **LABORATORY DATA SHEETS**

### COMPUTER CODES FOR NUTRIENT PARAMETER ANALYSES SHEET

Submitter Codes: The codes are the same as for field data sheets

Data Category Codes: The codes are the same as for field data sheets

**Sample Method Codes**: The codes are the same as for field data sheets

Sample Layer Codes: The codes are the same as for field data sheets

**Study Codes**: The codes are the same as for field data sheets

## Parameter Codes:

Code	Description	Unit
BIOSI	PARTICULATE BIOGENIC SILICA	mg/L
BOD5W	FIVE DAY BIOLOGICAL OXYGEN DEMAND	mg/L
CHLA	ACTIVE CHLOROPHYLL A	μg/L
DOC	DISSOLVED ORGANIC CARBON AS C	mg/L
DON	DISSOLVED ORGANIC NITROGEN AS N	mg/L
DOP	DISSOLVED ORGANIC PHOSPHORUS AS P	mg/L
TDS	DISSOLVED SOLIDS if on filtered water sample	mg/L
FCOL_M	FECAL COLIFORM	MPN/100ml
FE_M	TOTAL IRON	mg/L
NH4F	AMMONIA AS N (FILTERED)	mg/L
NH4W	AMMONIA AS N (WHOLE)	mg/L
NO2F	NITRITE AS N (FILTERED)	mg/L
NO2W	NITRITE AS N (WHOLE)	mg/L
NO23F	NITRITE + NITRATE AS N (FILTERED)	mg/L
NO23W	NITRITE + NITRATE AS N (WHOLE)	mg/L
NO3F	NITRATE AS N (FILTERED)	mg/L
NO3W	NITRATE AS N (WHOLE)	mg/L
PC	PARTICULATE ORGANIC CARBON AS C	mg/L
PHEO	MONOCHROMATIC PHEOPHYTIN A	μg/L
PIP	PARTICULATE INORGANIC PHOSPHORUS	mg/L
PN	PARTICULATE ORGANIC NITROGEN AS N	mg/L
PO4F	DISSOLVED ORTHOPHOSPHATE AS P (FILTERED)	mg/L
PO4W	DISSOLVED ORTHOPHOSPHATE AS P (WHOLE)	mg/L
PP	PARTICULATE PHOSPHORUS AS P	mg/L
SIF	REACTIVE SILICA AS SI (FILTERED)	mg/L
SIW	REACTIVE SILICA AS SI (WHOLE)	mg/L
SO4F	SULFATE (FILTERED)	mg/L
SO4W	SULFATE (WHOLE)	mg/L
TALK	TOTAL ALKALINITY	mg/L
TCOLI_M	TOTAL COLIFORM	MPN/100ml
TDN	TOTAL DISSOLVED NITROGEN AS N (FILTERED)	mg/L
TDP	TOTAL DISSOLVED PHOSPHORUS AS P (FILTERED)	mg/L
TKNF	TOTAL KJELDAHL NITROGEN AS N (FILTERED)	mg/L
TKNW	TOTAL KJELDAHL NITROGEN AS N (WHOLE)	mg/L
TN	TOTAL NITROGEN	mg/L
TOC	TOTAL ORGANIC CARBON	mg/L
TP	TOTAL PHOSPHORUS	mg/L
TSS	TOTAL SUSPENDED SOLIDS	mg/L
TURB_NTU	TURBIDITY	NTU

## **Detection Limit Codes:**

Code	Description
BLANK	NORMAL
G	GREATER THAN THE UPPER METHOD DETECTION LIMIT (MDL)
L	LESS THAN THE LOWER METHOD DETECTION LIMIT (MDL) AND STORED LOWER DETECTION LIMIT
U	VALUE LESS THAN LOWER METHOD DETECTION LIMIT (MDL) AND STORED IN REAL VALUE

## **Method Codes:**

Code	Method title	Unit	Method	Cbp mthd_id
BOD5W	5-DAY BIOCHEMICAL OXYGEN DEMAND	mg/L	L01	23
CHLA	MONOCHROMATIC; SPECTROPHOTOMETRIC	μg/L	L01	108
DOC	COMBUSTION INFRARED METHOD	mg/L	L01	42
FE_M	TOTAL IRON; PHENANTHROLINE METHOD	mg/L	L01	87
	COLORIMETRIC; AUTOMATED PHENATE			
NH4F	(INDOPHENOL)	mg/L	L01	76
NO23F	ENZYME CATALYZED NITRATE REDUCTION	mg/L	L03	471
NO2F	AUTOMATED; COLORIMETRIC; DIAZOTIZATION	mg/L	L01	44
NO3F	CALCULATED NO3F (SUBMITTED TO CBPO)	mg/L	C01	110
PC	PARTICULATE CARBON (inorganic + organic)	mg/L	L01	51
PHEO	MONOCHROMATIC; SPECTROPHOTOMETRIC	μg/L	L01	71
PN	PARTICULATE NITROGEN	mg/L	L01	52
PO4F	ORTHOPHOSPHATE; AUTOMATED; ASCORBIC ACID	mg/L	L01	48
PP	PARTICULATE PHOSPHORUS; SEMI- AUTOMATED; DIRECT	mg/L	L01	11
SIF	COLORIMETRIC; AUTOMATED; MOLYBDENUM BLUE	mg/L	L01	53
SO4F	SULFATE; TURBIDIMETRIC METHOD	mg/L	L01	106
TALK	ALKALINITY; TITRIMETRIC; pH 4.5	mg/L	L01	16
TDN	ALKALINE PERSULFATE WET OXIDATION + ENZYME CATALYZED NITRATE REDUCTION	mg/L	L02	55
TDP	ALKALINE PERSULFATE WET OXIDATION + EPA365.1OR EPA 365	mg/L	L01	56
TDS	TOT. DISSOLVED SOLIDS; GRAVIMETRIC; DRIED AT 180 C	mg/L	L01	107
TKNF	SEMI-AUTOMATED BLOCK DIGESTOR; COLORIMETRIC; NITRO	mg/L	L02	60
TKNW	SEMI-AUTOMATED BLOCK DIGESTOR; COLORIMETRIC; NITRO	mg/L	L02	2
TSS	GRAVIMETRIC; DRIED AT 103-105 C	mg/L	L01	10
TURB_NTU	NEPHELOMETRIC	NTU	L01	24

### COMPUTER CODES FOR CHLOROPHYLL PARAMETER ANALYSIS SHEET

**Submitter Codes**: The codes are the same as field data sheets

Data Category Codes: The codes are the same as field data sheets

Sample Layer Codes: The codes are the same as field data sheets

**Study Codes**: The codes are the same as field data sheets

Analytical Problem Codes: The codes are the same as laboratory data sheets

## **Analytical Problem Codes (APC):**

TEA Maryland Department of Natural Resources Tidal Ecosystem Assessment
CBP Environmental Protection Agency Chesapeake Bay Program Office

CBL University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory,

Nutrient Analytical Services Laboratory

# Converting CBL lab error codes to CBP APC codes

(DKD, February 2022)

Note: CBP codes printed in RED are no longer valid. CBP code "none" means that no APC code is needed.

CBL Error Description	CBL CODE	Keep Value?	CBP CODE	CBP Error Description
Laboratory accident, sample damaged during processing	1	no	Α	Laboratory Accident
			AA	Field Accident
			В	Chemical Matrix Interference
			ВВ	("Torn filter pad". No longer a valid code. Use <b>TP</b> instead - see CBL code #19)
Insufficient sample - typically inadequate liquid volume or sediment mass required for requested analysis	2		D	Insufficient Sample
Analysis conducted by another laboratory	3			
Sample frozen when received (should have arrived un-frozen)	4	yes	X	Sample not preserved properly
Sample received thawed (should have arrived frozen)	5	yes	X	Sample not preserved properly
Sample not received, sample received in condition that prevents analysis	6	no	RR	No sample received by lab from field office
Lost results	7	no	Α	Laboratory Accident
Sample contaminated	8	no	R	Sample Contaminated
Sample results rejected due to quality control criteria	9	no	V	Sample results rejected due to QC criteria  (May appear as the incorrect and outdated CBL code W "Duplicate results for all parameters". All W codes should be changed to V.)
Sample not preserved properly	10	yes	X	Sample not preserved properly
Analyzed in duplicate, results below detection limit	11			
Instrument failure	12	no	С	Instrument Failure
			CC	Cannot Calculate Given Available Data
			F	Post-Calibration Failure Likely Due To Equipment Damage After Sampling; Data Appear Normal

Foil pouch very wet (salty) when	13			
received from field; mean reported	13			
Poor replication between pads, mean reported.	14	yes	FF	Mean Reported Due To Poor Replication between Pads
Poor replication between pads, mean reported. Difference is within 50%.	14A <sup>1</sup>	yes	FF	Mean Reported Due To Poor Replication between Pads
Poor replication between pads. Sample rejected because the difference is greater than 50%	14B <sup>1</sup>	no	٧	Sample results rejected due to QC criteria
Sample size not reported - either mass or volume	15	yes	DD	Sample Size Not Reported (Assumed)
			LL	("Sample mislabeled". No longer a valid code. Use <b>RR</b> instead - see CBL code #16.)
Sample mislabeled	16	no	RR <sup>2</sup>	No sample received by lab from field office
Over 20% of sample adhered to pouch and outside of pad	17	Yes <sup>3</sup>	ММ	(Substitute for outdated CBP code LL.)  Over 20% of Sample Adhered To  Pouch And Outside Of Pad
Sample not collected	18	no	RR	No sample received by lab from field office
Torn filter pad	19	yes	TP	Torn filter pad  (Substitute for outdated CBP code BB.)
Pad unfolded in foil pouch	20 <sup>4</sup>	yes	none	
Particulates found in filtered sample	21	yes	NN	Particulates Found In Filtered Sample
			- 1	Suspect Value Has Been Verified Correct
			IQ	Cannot Determine If Part Exceeds Whole Value and Whether Or Not Difference Is Within Analytical Precision
			J	Incorrect Sample Fraction for Analysis
Assumed sample volume, usually based on COC (pouch vol used if different from COC) and only when verification with sampler is not possible	22	yes	IJ	Volume Filtered Not Recorded (Assumed)  (Substitute for outdated code PP.)
vermeation with sampler is not possible			L	LICOR Calibration Off By >= 10% per Year. Use with Calculated KD Where Prob Of LU, LS, LB Exist In Raw
			LB	LICOR Calibration Off By >= 10% per Year for Both Air And Upward Facing Sensors
			LS	LICOR Calibration Off By >= 10% per Year for Air Sensor

			l	LICOR Calibration Off Days = 400/ man
			LU	LICOR Calibration Off By >= 10% per
				Year for Upward Facing Sensor
				Part Exceeds Whole Value and
			NQ	Difference Is Not Within Analytical
				Precision
				Negative Calculated Value Is Valid
				Given Precision of Measured Water
			NIV/	Quality Parameters; Actual Calculated
			NV	Concentration Likely Is Low; Possibly
				Less than PQLS of Measured Water
				Quality Parameters
			Р	Provisional Data
			•	("Assumed sample volume". No longer
			PP	a valid code. Use <b>JJ</b> instead – see CBL
			PP	
				code #22.)
				Part Exceeds Whole Value Yet
				Difference Is Within Analytical
				Precision
Value exceeds a theoretical equivalent,				
but is within analytical precision	23	yes	QQ	(If any value in an inconsistent
but is within analytical precision				relationship is below the detection limit,
				do NOT assign the QQ error codes.
				Keep all the values and do NOT use
				error codes.)
Is greater than the acid persulfate total				
phosphorus by less than or equal to	24			
0.01 MG P/L				
If NO2 > NO23 by = 0.0019 MG N/L</td <td></td> <td></td> <td></td> <td></td>				
at STD. CAL of 9.0 for both, or =</td <td></td> <td></td> <td></td> <td></td>				
0.0030 MG N/L at a STD. CAL of 9.0	27			
for NO2 and a STD CAL of 6.0 for				
NO23				
11020				Part Exceeds Whole Value Yet
				Difference Is Within Analytical
				Precision
Dissolved organic carbon > total				FIECISIOII
organic carbon, Total Dissolved	20		00	(If any value in an inconsistant
Phosphorus > Total Phosphorus, Total	28	yes	QQ	(If any value in an inconsistent
Dissolved Nitrogen > Total Nitrogen				relationship is below the detection limit,
				do NOT assign the QQ error codes.
				Keep all the values and do NOT use
				error codes.)
				Part Exceeds Whole Value Yet
				Difference Is Within Analytical
				Precision
TVS > TSS, PIP > PP	29	yes	QQ	(If any value in an inconsistent
				relationship is below the detection limit,
				do NOT assign the QQ error codes.
				Keep all the values and do NOT use
				error codes.)
	l	l	l	0.7.07.00000./

Samples received more than 28 days				
from date of collection	30	yes	E	Sample Received After Holding Time
Samples received within 28 days of collection, but not within 7 days of collection, thus analysis within 28 days of collection not practical	31	yes	GG	Sample Analyzed After Holding Time
Samples not analyzed within 28 days of collection	32	yes	GG	Sample Analyzed After Holding Time
Original analysis performed within 28 days of collection, but reanalysis/reported results performed after 28 days of collection due to instrument failures, concentration range changes, QA/QC failures, or time constraints.	33	yes	GG	Sample Analyzed After Holding Time
BOD final readings not taken at the 5 day ± 3 hour threshold.	34	yes	GG	Sample Analyzed After Holding Time
			SS	Sample rejected due to high suspended sediment concentration
			U	Matrix problem resulting from the interrelationship between variables such as pH and ammonia
			UN	For DCDOH data, these values are issues or are nulls with no assigned problem codes. 8/27/2008
			W	("Duplicate results for all parameters".  No longer a valid code. Use <b>V</b> instead  – see CBL code #9).
			ww	High optical density (750 nm); actual value recorded
			N	None
Sample collection data (such as collection date and time) omitted by client. As a result NASL not responsible for method specified holding times.	35			
Sample diluted or standard calibration range changed to bring concentration/sample within linear range	<b>36</b> <sup>5</sup>	yes	none	
Value below method detection limit (MDL). Actual observed value reported.	U	yes	none	(Note: Qualifiers (< method detection limit) get assigned during data processing)
Value below method detection limit (MDL). Method detection limit reported.	L			
Value below method reporting limit (RL). Actual observed value reported.	BR	yes	none	

- 1) Following a lab audit, CBL started reporting samples with "poor replication between pads" using new codes to note how far off the values were. For CBP, this translates to either an FF code (Difference is within 50%) or a V code (Difference is greater than 50%)
- 2) There is no valid CBP code for "Sample mislabeled". Without proper labeling, there is no way to be sure that the sample is correct. Delete any reported values and use code RR for "No sample received by lab".
- 3) Code 17 is used by the lab to identify a problematic sample. A reported value indicates that the analyst was confident in the laboratory result, and the value should be kept. A missing value indicates that the sample was so compromised that the analyst could not report a value.
- 4) There is no CBP code for "Pad unfolded in pouch". Code 20 identifies a problematic sample, but a reported value indicates that the analyst was confident in the laboratory results.
- 5) Code 36 relates to sample processing by the lab (dilution). CBL did not use code 36 until recently. In the past, samples that were diluted for lab analysis were not identified as such.

Chesapeake Bay Program codes and University of Maryland, Chesapeake Bay Laboratory codes follow:

### **Chesapeake Bay Laboratory Data Qualifiers and Description**

- 1 Laboratory accident, sample damaged during processing
- 2 Insufficient sample typically inadequate liquid volume or sediment mass required for requested analysis
- 3 Analysis conducted by another laboratory
- 4 Sample frozen when received (should have arrived un-frozen)
- 5 Sample received thawed (should have arrived frozen)
- 6 Sample not received; sample received in condition that prevents analysis
- 7 Lost results
- 8 Sample contaminated
- 9 Sample results rejected due to quality control criteria
- 10 Sample not preserved properly
- Analyzed in duplicate, results below detection limit
- 12 Instrument failure
- Foil pouch very wet (salty) when received from field; mean reported
- 14A Poor replication between pads, mean reported. Difference is within 50%.
- Poor replication between pads. Sample rejected because the difference is greater than 50%
- Sample size not reported either mass or volume
- 16 Sample mislabeled
- 17 Over 20% of sample adhered to pouch and outside of pad
- 18 Sample not collected
- 19 Torn filter pad
- 20 Pad unfolded in foil pouch
- 21 Particulates found in filtered sample
- Assumed sample volume, usually based on COC (pouch vol used if different from COC) and only when verification with sampler is not possible
- Value exceeds a theoretical equivalent, but is within analytical precision
- Is greater than the acid persulfate total phosphorus by less than or equal to 0.01 MG P/L
- 27 If NO2 > NO23 by </= 0.0019 MG N/L at STD. CAL of 9.0 for both, or </= 0.0030 MG N/L at a STD. CAL of 9.0 for NO2 and a STD CAL of 6.0 for NO23
- Dissolved organic carbon > total organic carbon, Total Dissolved Phosphorus > Total Phosphorus, Total Dissolved Nitrogen > Total Nitrogen

- 29 TVS > TSS, PIP > PP
- 30 Samples received more than 28 days from date of collection
- 31 Samples received within 28 days of collection, but not within 7 days of collection, thus analysis within 28 days of collection not practical
- 32 Samples not analyzed within 28 days of collection
- Original analyses performed within 28 days of collection, but reanalysis/reported results performed after 28 days of collection due to instrument failures, concentration range changes, QA/QC failures, or time constraints.
- BOD final readings not taken at the 5-day  $\pm$  3 hour threshold.
- 35 Sample collection data (such as collection date and time) omitted by client. As a result, NASL not responsible for method specified holding times.
- 36 Sample diluted or standard calibration range changed to bring concentration/sample within linear range
- U Value below method detection limit (MDL). Actual observed value reported.
- L Value below method detection limit (MDL). Method detection limit reported.
- BR Value below method reporting limit (RL). Actual observed value reported.

### **CBL QC Data Qualifiers & Description**

- QC1 Spike recovery is outside method specified criteria
- QC2 Duplicates are outside method specified criteria
- QC3 CRM value is outside method specified criteria
- QC4 CCV value is outside method specified criteria
- QC5 Calibration point is outside method specified criteria

### Chesapeake Bay Program Results Status & Description

- A Laboratory Accident
- AA Field Accident
- B Chemical Matrix Interference
- C Instrument Failure
- CC Cannot Calculate Given Available Data
- D Insufficient Sample
- DD Sample Size Not Reported (Assumed)
- E Sample Received After Holding Time
- F Post-Calibration Failure Likely Due To Equipment Damage After Sampling; Data Appear Normal
- FF Mean Reported Due To Poor Replication between Pads
- GG Sample Analyzed After Holding Time
- I Suspect Value Has Been Verified Correct
- IQ Cannot Determine If Part Exceeds Whole Value and Whether Or Not Difference Is Within Analytical Precision
- J Incorrect Sample Fraction for Analysis
- JJ Volume Filtered Not Recorded (Assumed)
- L LICOR Calibration Off By >= 10% per Year. Use with Calculated KD Where Prob Of LU, LS, LB Exist InRaw
- LB LICOR Calibration Off By >= 10% per Year for Both Air and Upward Facing Sensors
- LS LICOR Calibration Off By >= 10% per Year for Air Sensor
- LU LICOR Calibration Off By >= 10% per Year for Upward Facing Sensor
- MM Over 20% of Sample Adhered To Pouch And Outside Of Pad
- NN Particulates Found In Filtered Sample
- NQ Part Exceeds Whole Value and Difference Is Not Within Analytical Precision
- NV Negative Calculated Value Is Valid Given Precision of Measured Water Quality Parameters; Actual Calculated Concentration Likely Is Low; Possibly Less Than PQLS of Measured Water Quality Parameters
- P Provisional Data
- QQ Part Exceeds Whole Value yet Difference Is Within Analytical Precision
- R Sample Contaminated
- RR No sample received by lab from field office

SS Sample rejected due to high suspended sediment concentration

TP Torn filter pad

Matrix problem resulting from the interrelationship between variables such as PH and ammonia U

UN For DCDOH data, these values are issues or are nulls with no assigned problem codes.

V

Sample results rejected due to QC criteria High optical density (750 nm); actual value recorded WW

X Sample not preserved properly

N None

Analyte present: Reported value is estimated; CONC is below the range for quantitation Q

# MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

## DATA ENTRY REQUEST FORM DOCUMENTATION AND PROCEDURES

When submitting a job for data entry service, a data entry request form must be completed with the information specified below. A sample data entry request form is attached to the end of this appendix for reference.

# RESOURCE ASSESSMENT ADMINISTRATION DATA ENTRY REQUEST FORM 1. AGENCY CONTROL NO: \_\_\_\_\_ The agency control number is be used by the Data Processing Department (D.P.D.) to track keypunch jobs. Then number is assigned by the Maryland Department of Natural Resources (MDDNR) Data Processing Programmer Trainee when preparing the request form. 2. D.P.D. CONTROL NO: The D.P.D. control number field is optional and can be used by the Department of Data Processing for tracking. 3. APPLICATION REQUESTED ID (JOB ID) The application Requested ID is an eight-character alphanumeric value followed by a water quality monitoring project data type description enclosed in parentheses. Three different request IDs are used for Maryland Mainstem and tributary water quality monitoring field data sets: A34202CB (Main Bay field), A34200CB (Patuxent field) and A34205CB (Tributaries field). 4. Requested By: The name of the MDDNR Data Processing Programmer Trainee is used to identify the person submitting the data entry request form to the Data

Processing Department.

5	5.	Date Sent:
		Date sent is optional and may be used to document when the date the request form was sent to the Data Processing Department. The MDDNR Data Processing Programmer Trainee maintains a log of this information separately.
$\epsilon$	5.	Date Originals Returned:
		Date originals returned is optional and may be used to document the date the field sheet originals were returned to MDDNR. The MDDNR Data Processing Programmer Trainee maintains a log of this information separately.
7	7.	Agency:
		Agency is the agency submitting the data entry request to the Department of Data Processing. The abbreviation "DNR" for Department of Natural Resources is used in the agency field.
8	3.	Telephone:
		The telephone number is the voice contact number of the Data Processing Programmer Trainee who submitted the data entry request.
Ģ	€.	Email received:
		The email received field is optional and may be used to indicate whether an electronic mail message was received by the Data Processing Programmer Trainee. The MDDNR Data Processing Programmer Trainee maintains this information in the form of email messages.
SPECIAL II	NS'	TRUCTIONS TO D.P.D.
Cont	trol	Information
1	10.	Deliver Documents To:

The deliver documents to information is: DNR, Tawes State Office

Bldg., D-2, 580 Taylor Ave, Annapolis, MD 21401.

The DVD containing electronic files produced by the Data Processing Department, and the original field data sheets that were sent to the Data Processing Department with the data entry request should be delivered to DNR at the address specified above.

11. Dataset Name:			
		G file. For example scription 'MAY07	e, for Patuxent November LAB.ORG'.
12. REMARKS:			_
Comments may	be entered	in the remarks fie	ld.
Example of Data Entry Reques	t form		
RES		SMENT ADMINISTRATION Y REQUEST FORM	I
AGENCY CONTR	ROL NO: <u>0043</u>	D.P.D. CONTROL NO:	
	APPLICATION	REQUESTED ID (JOB ID)	
	A3	34200CB atuxent Field)	
Requested By: <u>Le</u>	enora Dennis	Agency: <u>DNR</u>	
Date Sent:		Telephone: 410-260-8	647
Date Originals Re	turned:	Email Received:	
	ODEOLAL INIO	TRUCTIONS TO D.D.D.	
Control Information		TRUCTIONS TO, D.P.D  Data Set Name	
Deliver Documen		PTNOVISF. ORG-	
DNR			
Tawes State Office	e Bldg., D-2		
580 Taylor Ave.	1101		
Annapolis, Md. 2	1401	- Ogn	45 - A
		REMARKS	2000
			TE SO

Note: The Date Received stamp in the example was applied when the original field sheets were received by the Department of Data Processing.

# APPENDIX 11.

# Sample Verification Reports and Plots and Edit Form

							- 8	Field :	Sheet						
Contraction of the last	n Name 085.3	Pro	ject Code	,								Sequence	Number		0600201
	mple Date	Arrival Time	Departure Time	Nun	nber	easured Depth	100	rature	Tid Cod	ie	Weather Yesterday	Weather Today	Clou		Wave Height
2/7	2006	10:55	11:15		•	27.5	4		F		10	10			0.4
	w	ind W	ind Min.	Wind Max.	Equi	pment	Probe	Photo	meter		Pycnoclin	e			
	Dire	ction	Velocity	Velocity		nit No.	Number	Unit N	umber	Low		Upper	Sec	ochi G/	L
	ame				SECOND	Callain	Cala	Des	Cample	1					
Rep	Sample depth	Wate Tem	г РН	DO	SPCOND	Salinity	Calc. Salinity	Rep Code	Sample depth	Layer Code	INSDEC	INSUW	EPAR_S I	EPARU	z
Rep	Sample depth 0.5	Wate Tem 5.7	r PH P 8.2	11,9	21700	13	Salinity 12.86	Code	depth 0.5	Code	INSDEC	INSUW	EPAR_S I	EPARU,	1
Rep 1	Sample depth 0.5	Wate Tem 5.7 5.7	r PH 9 82 82	11.9	21700 21700	13 13	Salinity 12.85 12.86	Code	depth 0.5	Code S M	INSDEC	INSUW	EPAR S E	EPARU	ı
Rep	Sample depth 0.5 1	Wate Tem 6.7 6.7	8.2 8.2 8.2	11,9 11,8 11,9	21700 21700 21700	13 13 13	Salinity 12.86 12.86 12.98	Code 1 1	0.5 1 2	Code S M	INSDEC	INSUV	EPAR_S I	EPARU.	z
Rep	Sample depth 0.5	Wate Tem 5.7 5.7	r PH 9 82 82	11.9	21700 21700	13 13	Salinity 12.85 12.86	Code	depth 0.5	Code S M	INSDEC	INSUW	EPAR_S I	EPARU	z
Rep	Sample depth 0.5 1 2 3	Wate Tem 5.7 5.7 5.7	8.2 8.2 8.2 8.2 8.2	11,9 11,8 11,9 11,8	21700 21700 21700 21700	13 13 13	\$alinity 12.86 12.86 12.91 12.86	Code 1 1 7	0.5 1 2 3	Code S M 14	INSDEC	INSUW	EPAR_S I	EPARU,	z
1 1 1 1 1 1	Sample depth 0.5 1 2 3 5	Wate Tem 5.7 5.7 5.7 5.7	8.2 8.2 8.2 8.2 8.3	11,9 11,8 11,9 11,8	21700 21700 21700 21700 21700	13 13 13 13	\$alinity 12.86 12.86 12.96 12.86 12.86	1 1 1 1	0.5 1 2 3 5	Code S M N M M	INSDEC	INSUW	EPAR_S E	EPARU	ı
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Rep	Sample death 0.5 1 2 3 5 7 9 10 11 12 13 14	Wate Tem 5.7 5.7 6.7 6.8 6.8 6.8 6.8 6.8 6.9 6.9	8.2 8.2 8.2 8.3 8.3 8.2 8.2 8.2 8.2 8.1 8	11.9 11.8 11.9 11.8 12 12 11.7 11.5 10.7 9.6 9.6	21700 21700 21700 21700 21700 21800 21800 21800 24800 24900 30000 30100	13 13 13 13 13 13 13 13 13,1 14,1 18 18,6	Salinity 12.86 12.86 12.93 12.86 12.86 12.86 12.83 12.93 12.93 14.4 18.41 18.49	Cocle 1 1 7 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	depth 0,5 1 2 3 5 7 9 10 11 12 13	Code S M M M M M M M M M M M M M M M M M M	INSDEC	INSUW	EPAR_S I	EPARU	Z
Rep	Sample depth 0.5 1 2 3 5 7 9 10 11 12 13 14 15	Wate Tem 6.7 6.7 6.7 6.6 6.8 6.8 6.8 6.8 6.9 6.9 6.9	R PH P 8.2 6.2 6.2 6.2 6.3 8.3 6.2 8.2 8.1 8.9 7.9	11.9 11.8 11.9 11.8 12 12 11.7 11.5 10.7 9.6 9.6 9.5	21700 21700 21700 21700 21700 21700 21800 21800 24000 29000 30100 30200	13 13 13 13 13 13 13 13 13.1 14.1 18.6 18.6	Salinety 12.86 12.86 12.96 12.96 12.96 12.93 12.93 12.93 14.4 18.41 18.41 18.55	Cocie 1 1 7 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	depth 0.5 1 2 3 5 7 9 10 11 12 13 14	Code S M W M M M M M M M M M M M M M M M M M	INSDEC	INSUW	EPAR_S I	EPARU	I
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Maryland Department of Natural Resources

								Chlorophyll Sheet	phyll S	heet				4 5	9		Chi Sequence No	nce No
roject Code MAIN	z						Samp	SampleDate:		277/2006	9						3-460	
Paramete	ers:																	
Station Name	SEO	# Beb	Code	Sample Depth	EXVOL	APC	LIPAT_CM	SAMVOL	OD630 B	00645 B	0D647 B	ODEE3B	006648	ODGGGB ODGGSA OD750A	ODTSOA	00750 B	PHEO	CHLA
385.2	3.460	-	69	0.5	ž		50	0.50	0.038	0.035	0.039	0,135	0.136	0.085	9000	0.005	000.748	007.626
385.2	3-460	~	US.	0.5	14		vr.	050	0.037	0.035	0.039	0.132	0.132	0.082	0.005	0.005	000.583	007.476
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385.3	3.450	-	AP	6	14		8	020	0.058	0.054	0.062	0.218	0.218	0.134	0.007	0.007	000.733	012.500
385.3	3-450	-	86	61	41		10.	0.40	0.042	0.039	0.045	0.152	0.152	8600	0.005	0.005	002.075	010.003
385.3	3.450	-	89	56	41		9	0.40	0.047	0.045	0.051	0.169	0.169	0.115	800.0	900.0	003.532	010,466
.E2.3	3-460	-	sa	0.5	17		v	050	0.052	0.048	0.054	0.192	0.192	0.117	900'0	9000	900.404	011214
.E2.3	3-460	-	AP	1	4		S	050	690'0	0.064	0.073	0.263	0.264	091 0	0.007	0.005	900.164	015.849
E2.3	3-450	-	ВР	13	27		w	0.40	0.059	0.054	0.062	0.227	0.227	0.136	0.005	0.005	000.131	017.008
E2.3	3-400	-	8	19	4		'n	0.40	0.121	901.0	0.120	0.432	0.434	0.272	2000	9000	004.205	030.465

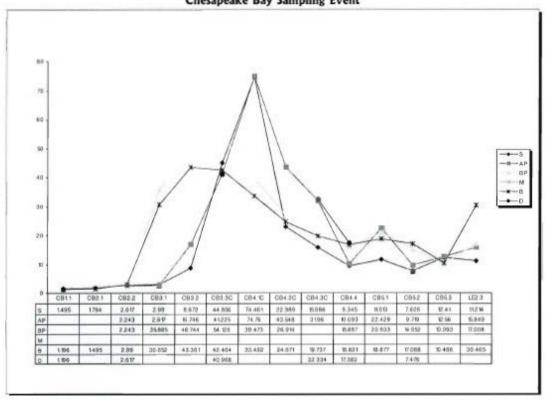
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## Maryland Department of Natural Resources

				Lab Sh	eet				
Station Name 35.3		Project MAIN	Sample Date 2/7/2006	Arrival Time 10:56	Sample Depth 0.5	Layer Code S	Replicate 1 Number 1	Sumple 5	equence Numbe 200602070001
Sample Descrip	ition :								
LAB Description	n:								
Sale La			APC						
NH4	E	L01	e. Code	< 0.00		Visible	e Enabled	Pseudo	
NO2	F	L01		0.006		₹	2	- 17	- 12
NO23	F	L01		0.15		~	~	n	- 6
PC	N	L01		1.14		₩.	Ž	- 17	
PN	N	LOT		0.18		×	8	17	- B
P04	F	L01		0.000		₩.	-	H	- 1
pp	N	L01		0.009		V	~	- 6	0
Si	F	L01		0.4		¥	7	- 6	(7)
TDN	N	L01		0.5		¥	~	- 0	- 6
TDP	N	L01		0.009	6	V	2	0	0
TSS	N	L01		3.7		- 2	×	n	- 0
Actual		W WAR	APC	W 400	100	7(000)	Same Property	U 1028 W	102000000000000000000000000000000000000
		Method Cod	e Code	OL Value		Visibl	e Enable	d Pseudo	Calculated
NH4	F	L01		< 0.00			*	- 0	

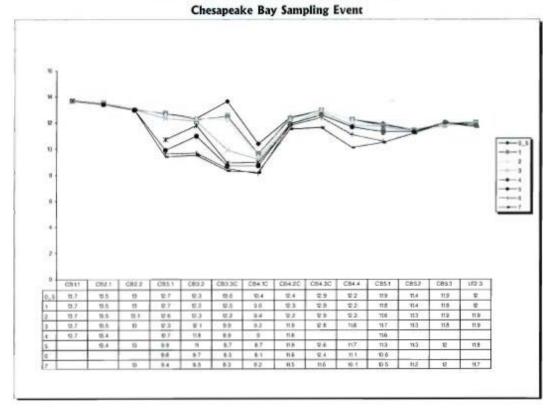
CHLA\_N RESULTS FOR CRUISE 200602A

## Chesapeake Bay Sampling Event



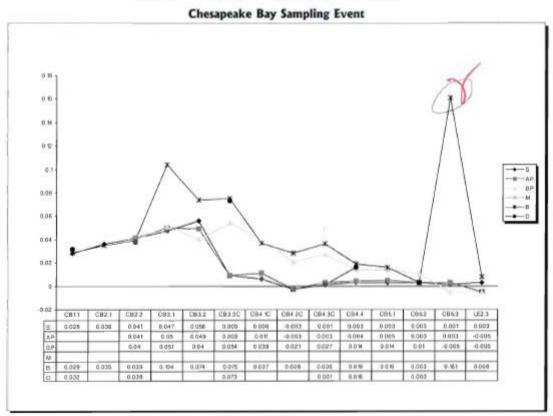


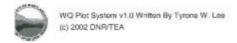
## DO\_N RESULTS FOR CRUISE 200602A





NH4\_F RESULTS FOR CRUISE 200602A





e00206	CB4.3C	MAIN	200602A	2	8/2006	0.5	S		1	EQ NUM
0600207	C84.2C	MAIN	200602A		8/2006	0.5	8		1	EQ NUM
0600208	CB4.1C	MAIN	200602A		8/2006	0.5	S		1	EQ NUM
0600209	OB3.3C	MAIN	200602A		8/2008	0.5	5		1	EQ_NUM
0600210	CB3.2	MAIN	200602A		8/2006	0.5	5		1	EQ NUM
0600211	C83.1	MAIN	200602A		9/2006	0.5	5		1	EQ_NUM
0600212	C82.2	MAIN	200602A	5.5	9/2006	0.5	8		1	EQ NUM
0600213	C82.1	MAIN	200602A		9/2006	0.5	6		1	EQ_NUM
0600214	C81.1	MAIN	200602A		/9/2006	0.5	8		1	EQ_NUM
Branch Control of the	Parameter Val	ues are falling	outside of a	reason	able ran	ge				
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Field Seq No	StationName	Project Code		-	Layer	Rep. No	Parameter	Value	Lower DL	
0600201	CB5.3	MAIN	2/7/2006	0.5	S	1	WTEMP	5.7	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	1	M	1	WIEMP	5.7	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	2	М	1	WTEMP	5.7	-0.5	5
0500201	CB5.3	MAIN	2/7/2006	3	M	1	WTEMP	5.7	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	5	M	1	WIEMP	5.6 V	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	7	M	1	WIEMP	5.6	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	9	AP	1	WTEMP	5.6	-0.5	5
0600201	CB5.3	MAIN	3/7/2006	10	M	1	WTEMP	5.6	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	11	M	1	WTEMP	3.8	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	12	M	1	WTEMP	5.9	-0.5	5
0600200	CB5.3	MAIN	2/7/2006	13	M	1	WTEMP	59/	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	14	M	1	WTEMP	5.5	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	15	M	1	WIEMP	5.9	-0.5	5
0600201	C85.3	MAIN	2/7/2006	16	M	1	WIEMP	5.9 V	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	17	M	1	WTEMP	5.9 -	-0.5	5
D600201	CB5.3	MAIN	2/7/2006	18	м	1	WTEMP	6	-0.5	5
0600201	CB5.3	MAIN	2/7/2006	19	BP	1	WTEMP	6 4	-0.5	5
10600201	CB5.3	MAIN	2/7/2006	28	M	1	WIEMP	6.1	-0.5	5

Column Chec	k: ParameterA	PCodes migl	ht not appro	priate and n	eed to	erify				
		ar cours mag		p						
Chi Seq No	StationName	Project Code	Cruise Name	SampleDate	Depth	Layer	Rep. #	Parameter	Value	Problem
5-460B	CB4.3C	MAIN	200602A	2/8/2006	13	BP	1	CHILA	0	A
3-460B	CB4.3C	MAIN	200602A	2/8/2006	13	BP	1	EXVOL_ML	14	A
3-460B	CB4.3C	MAIN	200602A	2/8/2006	13	BP	1	LIPAT_CM	5	A
3-460B	CB4.3C	MAIN	200602A	2/8/2006	13	BP	1	OD630B	0.127	A
3-460B	CB4.3C	MAIN	200602A	2/8/2006	13	BP	I.	OD645B	0.107	A
3-460B	CB4.3C	MAIN	200602A	2/8/2006	13	BP	1	OD647B	0.121	A
I-460B	CB4.3C	MAIN	200602A	2/8/2006	13	BP	1	OD663B	0.437	A

#### 2005 CMON - May

- Field (see changes written on sheets)

  Sequence Number: RHO0521 (Page 68 of 79)

  No Plots For:

  Cruise D = Eastern Shore: EPAR\_S\_N

  Cruise D = Potomac River: EPARU\_Z\_N

  Cruise D = RWS: SALINITY\_N

  Cruise D = Western Shore: SALINITY\_N

  Cruise D = Western Shore: SALINITY\_FLD\_N

- Laboratory (see changes written on sheets)

  Sequence Number: 200505100832 (Page 29 of 83)

  Sequence Number: 200505170852 (Page 45 of 83)

  Sequence Number: 200505240100 (Page 59 of 83)

  Sequence Number: 200505240101 (Page 60 of 83)

  Sequence Number: 200505240102 (Page 61 of 83)

  Sequence Number: 200505310103 (Page 77 of 83)

### APPENDIX 12

## **Chesapeake Bay Monitoring Program Procedure Modification Tracking Form**

METHODS AND QUALITY ASSURANCE FOR CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAMS, May 2017, CBP/TRS-319-17, Chapter 2, Figure 2.1 <a href="https://www.chesapeakebay.net/documents/CBPMethodsManualMay2017.pdf">https://www.chesapeakebay.net/documents/CBPMethodsManualMay2017.pdf</a>

Figure 2.1 CHFSAPFAKF BAY MON	UTORING PROGRAM P	ROCEDURE MODIFICAT	CHAPTER 2 QUALITY ASSURANCE PROGRAM JAN. 31, 2017 (Rev. 2)
PMTF * This form is used to request approval:	for modifications and to document titute for timely contact with the C	□ APPROVED □ DE approved modifications made to Che BPO Quality Assurance Officer or hi	NIED sapeake Bay Program Office s/her designee, who may be reached at
DATE SUBMITTED		DATE APPROVED	
REQUESTOR NAME		ORGANIZATION	
NEWLY PROPOSED [ ] MODIFICATION	FIELD-APPROVED [ MODIFICATION	] APPROVED BY: DATE:	
TYPE OF PROCEDURE / METHOD		ANALYTICAL[]	REPORTING [ ]
	FIELD [ ] MEASUREMENT	OTHER [] SPECIFY:	
DURATION	PERMANENT [ ] TEMPORARY [ ]	EFFECTIVE DATE: START DATE: END DATE:	
PROCEDURE/METHOD DESCRIPTION			
MODIFICATION DESCRIPTION			
JUSTIFICATION FOR MODIFICATION			
ANALYTICAL PARAMETERS THAT MAY BE AFFECTED BY THIS CHANGE			
AFFECTED QA PLAN(S) (TITLE, REVISION, & DATE)			
AFFECTED CRUISE(S)		_	_
PMTF COMPLETED BY	NAME:		DATE:
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## MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

## **Log of Significant Changes**

Date Initiated	Procedural Changes
See Tables 1-6 at the end of this Log	<ul> <li>NOTE Changes in Measured Parameters and in Detection Limits are detailed in the following tables:</li> <li>Table 1 - Tributary Detection Limit</li> <li>Table 2 - Patuxent Detection Limits</li> <li>Table 3 - Potomac Detection Limits</li> <li>Table 4 - LE2.3 and Mainstem Detection Limits.</li> <li>Table 5 - Light Attenuation - Mainstem and Patuxent Sampling Sites and Dates</li> <li>Table 6 - Light Attenuation - Other Maryland Tributaries Sampling Sites and Dates</li> </ul>
March 1, 1985 May 1, 1987	The EPA Central Regional Laboratory (CRL) in Annapolis processed Mainstem cruises water quality samples collected in July-December of 1984. CRL processed most Mainstem samples in 1985 and 1986. However, the beginning 1-Mar-1985 Chesapeake Biological Laboratory began analysis of dissolved constituents (Si, DOC, TDN and TDP). In May of 1987 water quality lab work was switched to Chesapeake Biological Laboratory
April 1, 1989	Dropped Patuxent River station XCG8613
July 1, 1990	Nutrient analysis of Patuxent River samples switched from State lab at Department of Health and Mental Hygiene (DHMH) to University of Maryland Chesapeake Biological Laboratory
October 1, 1990	Switch to filtering samples for PO4, NH4, NO23, NO2 in Potomac instead of analyzing whole water sample
December 10, 1990	A data quality assurance issue titled "Adjusting Maryland Department of Health and Mental Hygiene (MDHMH) total phosphorus (TP) and total dissolved phosphorus (TDP) data," was entered into the Data Analysis Issues Tracking System 10-Dec-1990. MDHMH was not using calibration data or blank data in calculating TP and TDP from 1984 through 1989. Most of the

## Date Initiated Procedural Changes

data affected by this problem were re-calibrated and re-submitted to the Chesapeake Bay Program. Samples analyzed in 1984 were not re-calculated. Some samples analyzed between 1985 and 1990 were also not re-calibrated due to missing blank data and other problems. As a result, there may be a mix of uncorrected and corrected TP and TDP data in the data base.

January 28, 1992

A report titled "Adjusting helix Kjeldahl nitrogen results: Maryland Chesapeake Bay Mainstem water quality monitoring program, 1984-1985" was produced by Computer Sciences Corporation under contract to the U.S. Environmental Protection Agency, contract number 68-WO-0043. The report examined the effects of helix digestion on Kjeldahl nitrogen, which is biased low relative to other digestion methods, and presented the equations used to adjust 1984 and 1985 data. The report was approved by Chesapeake Bay Program Analytical Methods and Quality Assurance Workgroup 12-Nov-1991 and by the Chesapeake Bay Program Monitoring Subcommittee 22-Jan-1992.

January 1996 TOC and DOC was dropped from Mainstern sampling

May 1, 1998 Nutrient analysis of Potomac and Minor Tributary samples switched from State lab at Department of Health and Mental

Hygiene (DHMH) to University of Maryland Chesapeake

**Biological Laboratory** 

March 2003 Addition of ten new long-term stations previously part of the

Pfiesteria special project sampling BXK0031, CCM0069, MNK0146, POK0087, TRQ0088, TRQ0146, WIW0141,

XAK7810, XCI4078, XDJ9007

July 1, 2005 Sampling TF1.0 on the Patuxent was dropped from the

CORE/Trend program, which had samples analyzed at DHMH. The station is now sampled only under the Patuxent tributary

program, which has samples analyzed at CBL

January 2007 Starting in July 2007, silica (SIF) will no longer be collected at

any of the Mainstem stations during the

months of July-December, and will only be collected from the

surface layer at the five mainstem stations

that correspond with phytoplankton program sampling (CB1.1,

CB2.2, CB3.3C, CB4.3C and CB5.2) in

the months January-June. Tributary collection of silica samples

will also change, beginning July 2007, as

Date Initiated	Procedural Changes
	follows: no samples July-December, and silica only from surface sample at the following stations January-June: TF2.3, RET2.2, LE2.2, TF1.5, TF1.7, LE1.1, ET5.1, WT5.1.
January 2009	Beginning in January 2009, chlorophyll analysis by the Maryland Department of Health and Mental Hygiene ceased and the Chesapeake Bay Laboratory, Nutrient Analytical Services Laboratory began analyzing chlorophyll samples.
January 2009	NO2 detection limit change was 0.0006 mg/L, updated to 0.0001 mg/L
January 2009	NH4 detection limit change was 0.003 mg/L updated to 0.006 mg/L $$
February 2009	Beginning in February 2009, YSI Series 6820 instruments were added to the field instrument inventory. YSI instruments are equipped with an optical dissolved oxygen sensor (ROX) instead of the Standard Clark Polarographic Sensor. Temperature, pH, specific conductance and depth sensors perform similarly to respective Hydrolab sensors.
	Both the Hydrolab and YSI optical dissolved oxygen sensors use similar luminescent technology and phase shift techniques to measure dissolved oxygen.
	Mainstem and Patuxent River cruises will exclusively use YSI instead of Hydrolab instruments. All tributary sampling activities will use either Hydrolab or YSI instruments.
January 2010	Mainstem stations: CB3.3 E CB3.3W, CB4.1E, CB4.1W, CB4.2E, CB4.2W, CB4.3E, CB4.3W will be sampled 10 times per year instead of 12 times per year.
	Patuxent River stations: CB5.1W, LE1.1, LE1.2, LE1.3, LE1.4, RET1.1, TF1.0, TF1.2, TF1.3, TF1.4, TF1.5, TF1.6, TF1.7 and WXT0001 will be sampled 12 times per year instead of 20 times per year.
	Potomac River stations: LE2.2, MAT0016, MAT0078, PIS0033, RET2.1, RET2.2, RET2.4, TF2.1, TF2.2, TF2.3, TF2.4 and XFB1986 will be sampled 12 times per year instead of 20 times per year. Potomac River station: LE2.3, which is sampled on Mainstem cruises, will be sampled 12 times per year instead of 20 times per year.

20 times per year.

Date Initiated	Procedural Changes
	Chester River stations: ET4.1 and ET4.2 and Choptank River stations: ET5.1 and ET5.2 and station WT4.1 in the Back River will be sampled 12 times per year instead of 16 times per year.
January 2011	CBL NASL NO2 detection limit change was $0.0001~\text{mg/L}$ , updated to $0.0002~\text{mg/L}$
January 2011	CBL NASL NH4 detection limit change was $0.006\ mg/L$ updated to $0.001\ mg/L$
January 2012	CBL NASL NO2 detection limit change was $0.0002\ mg/L$ , updated to $0.0007\ mg/L$
January 2012	CBL NASL SI detection limit change was 0.01 mg/L, updated to 0.06 mg/L $$
January 2013	CBL NASL SI detection limit change was 0.06 mg/L, updated to 0.002 mg/L $$
January 2014	CBL NASL SI detection limit change was 0.002 mg/L, updated to 0.01 mg/L $$
January 2014	Due to funding cutbacks sample collection ended at nine tributary stations in December 2013, Chicamacomico River: CCM0069; Manokin River: BXK0031, MNK0146; Nanticoke River: XDJ9007; Pocomoke River: POK0087, XAK7810; Transquaking River: TRQ0088, TRQ0146; and Wicomico River: XCI4078.
January 2016	CBL NASL PP detection limit change was 0.0021 mg/L, updated to 0.0035 mg/L
December 2016	Table 5 – Light Attenuation - Sampling Sites and Dates – Mainstem and Patuxent R.
December 2016	Table 6 – Light Attenuation - Sampling Sites and Dates – Other MD Tributaries – Data not collected or submitted by MD DNR
January 2017	CBL NASL Si detection limit change was 0.01 mg/L, updated to 0.0536 mg/L
January 2018	CBL NASL PN detection limit change was 0.0105, updated to 0.0263. PP detection limit change was 0.0035, updated to 0.0021

January 2019 CBL NASL NH4 detection limit change was 0.002, updated to 0.013. PO4 detection limit change was 0.0006, updated to 0.0034

January 2020

CBL NASL NH4 detection limit change was 0.013, updated to 0.009.

NO23 detection limit change was 0.0007, updated to 0.0015

PP detection limit change was 0.0021, updated to 0.001

Error code 14 was split into A and B codes where 14A = poor replication between pads, mean reported. Difference is within 50%. Code 14B = poor replication between pads. Sample rejected because the difference is greater than 50%.

Due to restrictions related to COVID-19, sampling was not conducted main stem bay stations in March and April. Sampling was conducted through the first third of March for tributary stations. March tributary field data were completed and submitted to the Chesapeake Bay Program, but chlorophyll and laboratory samples were held beyond acceptable analysis times. April and May tributary was not conducted. Main bay sampling resumed in May 2020, and tributary sampling resumed in June 2020.

April 2021 CBL NASL NO2 detection limit change was 0.0007, updated to 0.0009.

lab	DHMH	DHMH	DHMH	DHMH	DHMH	DHMH	CBL																	
parameter	1/1/85-5/31/86	6/1/86-12/31/88	1/1/89-4/30/90	5/1/90-6/30/94	7/1/94-7/12/95	7/13/95-4/30/98	5/1/98-12/31/99	1/1/00-12/31/03	1/1/04-12/31/05	1/1/06-12/31/06	1/1/07-12/31/07	1/1/08-12/31/08	1/1/09-12/31/09	1/1/10-12/31/10	1/1/11-12/31/11	1/1/12-12/31/12	1/1/13-12/31/13	1/1/14-12/31/15	1/1/16-12/31/16	1/1/17-12/31/17	1/1/18-12/31/18	1/1/19-12/31/19	1/1/20-12/31/20	1/1/21-12/31/21
CHLA				DHMH d	id Chloro	hylls unt	til Decem	ber 2008	no DL v	vere dete	rmined		0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	
DIN	0.04	0.028	0.028	0.028	0.028	0.01	0.0032	0.0037	0.0037	0.0037	0.0037	0.0037	0.0067	0.0067	0.0017	0.0017	0.0017	0.0017	0.0017	0.0027	0.0027	0.0137	0.0105	0.0105
DOC	1	1	0.8	0.5	0.5	0.5	0.24	0.24	0.15	0.15	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.16	0.16	0.16	0.16	0.16
DON	0.08	0.092	0.092	0.092	0.092	0.092	0.0168	0.0163	0.0163	0.0163	0.0163	0.0463	0.0433	0.0433	0.0483	0.0483	0.0483	0.0483	0.0483	0.0473	0.0473	0.0363	0.0395	0.0395
DOP	0	0.006	0.006	0.006	0.006	0.006	0.0004	0.0004	0.0004	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	-0.0019	-0.0019	-0.0019
NH4	0.02	0.008	0.008	0.008	0.008	0.008	0.003	0.003	0.003	0.003	0.003	0.003	0.006	0.006	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.013	0.009	0.009
NO2	0.002	0.002	0.002	0.002	0.002	0.002	0.0002	0.0002	0.0002	0.0002	0.0006	0.0006	0.0001	0.0006	0.0002	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0009
NO23	0.02	0.02	0.02	0.02	0.02	0.002	0.0002	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0015	0.0015
PC	0	0	0	0	0	0	0.0633	0.0633	0.0633	0.0759	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633
PHEO				DHMH d	id Pheopi	gments i	intil Dece	ember 200	)8; no Dĺ	_ were de	termined		0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
PN	0	0	0	0	0	0	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0263	0.0263	0.0263	0.0263
PO4	0.01	0.004	0.004	0.004	0.004	0.004	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0034	0.0034	0.0034
PP	0	0	0	0	0	0	0.0012	0.0024	0.0024	0.0024	0.0054	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0035	0.0035	0.0021	0.0021	0.001	0.001
SI	0.1	0.1	0.1	0.1	0.1	0.1	0.01	0.01	0.01	0.01	0.08	0.01	0.01	0.01	0.01	0.06	0.0022	0.01	0.01	0.0536	0.05	0.05	0.05	0.05
TDN	0.12	0.12	0.12	0.12	0.12	0.102	0.02	0.02	0.02	0.02	0.02	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
TDP	0.01	0.01	0.01	0.01	0.01	0.01	0.001	0.001	0.001	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015
TKNF	0.1	0.1	0.1	0.1	0.1	0.1																		
TKNW	0.1	0.1	0.1	0.1	0.1	0.1																		
TN	0.12	0.12	0.12	0.12	0.12	0.102	0.0305	0.0305	0.0305	0.0305	0.0305	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0763	0.0763	0.0763	0.0763
TOC	1	1	0.8	0.5	0.5	0.5	0.3033	0.3033	0.2133	0.2259	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.2233	0.2233	0.2233	0.2233	0.2233
TON	0.08	0.092	0.092	0.092	0.092	0.092	0.0273	0.0268	0.0268	0.0268	0.0268	0.0568	0.0538	0.0538	0.0588	0.0588	0.0588	0.0588	0.0588	0.0578	0.0736	0.0626	0.0658	0.0658
TOP	0	0.006	0.006	0.006	0.006	0.006	0.0016	0.0028	0.0028	0.0033	0.0063	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.0044	0.0044	0.003	0.0002	-0.0009	-0.0009
TP	0.01	0.01	0.01	0.01	0.01	0.01	0.0022	0.0034	0.0034	0.0039	0.0069	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.005	0.005	0.0036	0.0036	0.0025	0.0025
TSS	1	1	1	1	1	1	1.5	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
VSS							1.98	1.98	1.98	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

**Table 13-1 Tributary Detection Limits** 

	DHMH	DHMH	DHMH	DHMH	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL
parameter	1/1/85-5/31/86	6/1/86-12/31/88	1/1/89-4/30/90	5/1/90-6/30/9 <mark>0</mark>	7/1/90-12/31/99	1/1/00-12/31/03	1/1/04-12/31/05	1/1/06-12/31/06	1/1/07-12/31/07	1/1/08-12/31/08	1/1/09-12/31/09	1/1/10-12/31/10	1/1/11-12/31/11	1/1/12-12/31/12	1/1/13-12/31/13	1/1/14-12/31/15	1/1/16-12/31/16	1/1/17-12/31/17	1/1/18-12/31/18	1/1/19-12/31/19	1/1/20-12/31/20	1/1/21-12/31/21
CHLA	DHMH d	id Chloro	phylls un	til Decem	ber 2008	; no DL v	vere dete	rmined			0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
DIN	0.04	0.028	0.028	0.000	0.0032	0.0037	0.0037	0.0037	0.0037	0.0037	0.0067	0.0067	0.0017	0.0017	0.0017	0.0017	0.0017	0.0027	0.0027	0.0137	0.0105	0.0105
DOC	1	1	0.8	0.5	0.24	0.24	0.15	0.15	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.16	0.16			0.16
DON	0.08	0.092	0.092	0.092	0.0168	0.0163	0.0163	0.0163	0.0163	0.0463	0.0433	0.0433	0.0483	0.0483	0.0483	0.0483	0.0483	0.0473	0.0473	0.0363	0.0395	0.0395
DOP	0	0.006	0.006	0.006	0.0004	0.0004	0.0004	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	-0.0019	-0.0019	-0.0019
NH4	0.02	0.008	0.008		0.003	0.003	0.003	0.003	0.003	0.003	0.006	0.006	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.013	0.009	0.009
NO2 NO23	0.002	0.002	0.002	0.002	0.0002	0.0002	0.0002	0.0002	0.0006 0.0007	0.0006	0.0001 0.0007	0.0006 0.0007	0.0002 0.0007	0.0007 0.0007	0.0007	0.0007	0.0007	0.0007	0.0007 0.0007	0.0007 0.0007	0.0007 0.0015	0.0009 0.0015
PC	0.02	0.02	0.02	0.02	0.0002	0.0633	0.0633	0.0007	0.0007	0.0633	0.0007	0.0633	0.0007	0.0007	0.0007	0.0633	0.0633	0.0007	0.0007	0.0007	0.0633	0.0633
	DHMH 4	id Pheon	iamente i	ıntil Dece	mber 200					0.0033	0.0033	0.0033	0.0033	0.0033	0.0033	0.0033	0.0033	0.0033	0.0033	0.0033	0.0033	0.0033
PN	0	0	0	0	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0263	0.0263	0.0263	0.0263
PO4	0.01	0.004	0.004	0.004	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006		0.0034	0.0034
PP	0	0	0	0	0.0012	0.0024	0.0024	0.0024	0.0054	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0035	0.0035	0.0021	0.0021	0.001	0.001
SI	0.1	0.1	0.1	0.1	0.01	0.01	0.01	0.01	0.08	0.01	0.01	0.01	0.01	0.06	0.0022	0.01	0.01	0.0536	0.05	0.05	0.05	0.05
TDN	0.12	0.12	0.12	0.12	0.02	0.02	0.02	0.02	0.02	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
TDP	0.01	0.01	0.01	0.01	0.001	0.001	0.001	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015
TKNF	0.1	0.1	0.1	0.1																		
TKNW	0.1	0.1	0.1	0.1																		
TN	0.12	0.12	0.12		0.0305	0.0305	0.0305	0.0305	0.0305	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0763	0.0763	0.0763	0.0763
TOC	1	1	0.8	0.5	0.3033	0.3033	0.2133	0.2259	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.2233	0.2233	0.2233	0.2233	0.2233
TON	0.08	0.092	0.092	0.092	0.0273	0.0268	0.0268	0.0268	0.0268	0.0568	0.0538	0.0538	0.0588	0.0588	0.0588	0.0588	0.0588	0.0578	0.0736	0.0626	0.0658	0.0658
TOP	0	0.006	0.006	0.006	0.0016	0.0028	0.0028	0.0033	0.0063	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.0044	0.0044	0.003	0.0002	-0.0009	-0.0009
TP	0.01	0.01	0.01	0.01		0.0034	0.0034	0.0039	0.0069	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.005	0.005	0.0036	0.0036		0.0025
TSS	1	1	1	1	1.5	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
VSS					1.98	1.98	1.98	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

**Table 13-2 Patuxent Detection Limits** 

	DHMH	DHMH	DHMH	DHMH	DHMH	DHMH	CBL																	
parameter	1/1/85-5/31/86	6/1/86-12/31/88	1/1/89-4/30/90	5/1/90-6/30/94	7/1/94-7/12/95	7/13/95-4/30/98	5/1/98-12/31/99	1/1/00-12/31/03	1/1/04-12/31/05	1/1/06-12/31/06	1/1/07-12/31/07	1/1/08-12/31/08	1/1/09-12/31/09	1/1/10-12/31/10	1/1/11-12/31/11	1/1/12-12/31/12	1/1/13-12/31/13	1/1/14-12/31/15	1/1/16-12/31/16	1/1/17-12/31/17	1/1/18-12/31/18	1/1/19-12/31/19	1/1/20-12/31/20	1/1/21-12/31/21
CHLA	DHMH di	d Chlorop	hylls unt	il Decem	ber 2008	; no DL v	were dete	rmined					0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
DIN	0.04	0.028	0.028	0.028	0.028	0.01	0.0032	0.0037	0.0037	0.0037	0.0037	0.0037	0.0017	0.0017	0.0017	0.0017	0.0017	0.0017	0.0017	0.0027	0.0027	0.0137	0.0105	0.0105
DOC	1	1	8.0	0.5	0.5	0.5	0.24	0.24	0.15	0.15	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.16	0.16	0.16	0.16	0.16
DON	0.08	0.092	0.092	0.092	0.092	0.092	0.0168	0.0163	0.0163	0.0163	0.0163	0.0463	0.0483	0.0483	0.0483	0.0483	0.0483	0.0483	0.0483	0.0473	0.0473	0.0363	0.0395	0.0395
DOP	0	0.006	0.006	0.006	0.006	0.006	0.0004	0.0004	0.0004	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	-0.0019	-0.0019	-0.0019
NH4	0.02	0.008	0.008	0.008	0.008	0.008	0.003	0.003	0.003	0.003	0.003	0.003	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002	0.013	0.009	0.009
NO2	0.002	0.002	0.002	0.002	0.002	0.002	0.0002	0.0002	0.0002	0.0002	0.0006	0.0006	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0009
NO23	0.02	0.02	0.02	0.02	0.02	0.002	0.0002	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0015	0.0015
PC	0	0	0	0	0	0	0.0633	0.0633	0.0633	0.0759	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633
PHEO	DHMH di	d Pheopi	gments ι	ıntil Dece	mber 200	)8; no DI	L were de	termined					0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
PN	0	0	0	0	0	0	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0263	0.0263	0.0263	0.0263
PO4	0.01	0.004	0.004	0.004	0.004	0.004	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0034	0.0034	0.0034
PP	0	0	0	0	0	0	0.0012	0.0024	0.0024	0.0024	0.0054	0.0021	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0035	0.0021	0.0021	0.001	0.001
SI	0.1	0.1	0.1	0.1	0.1	0.1	0.01	0.01	0.01	0.01	0.08	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.0536	0.05	0.05	0.05	0.05
TDN	0.12	0.12	0.12	0.12	0.12	0.102	0.02	0.02	0.02	0.02	0.02	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
TDP	0.01	0.01	0.01	0.01	0.01	0.01	0.001	0.001	0.001	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015
TKNF	0.1	0.1	0.1	0.1	0.1	0.1																		
TKNW	0.1	0.1	0.1	0.1	0.1	0.1																		
TN	0.12	0.12	0.12	0.12	0.12	0.102	0.0305	0.0305	0.0305	0.0305	0.0305	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0763	0.0763	0.0763	0.0763
TOC	1	1	0.8	0.5	0.5	0.5	0.3033	0.3033	0.2133	0.2259	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.2233	0.2233	0.2233	0.2233	0.2233
TON	0.08	0.092	0.092	0.092	0.092	0.092	0.0273	0.0268	0.0268	0.0268	0.0268	0.0568	0.0588	0.0588	0.0588	0.0588	0.0588	0.0588	0.0588	0.0578	0.0736	0.0626	0.0658	0.0658
TOP	0	0.006	0.006	0.006	0.006	0.006	0.0016	0.0028	0.0028	0.0033	0.0063	0.003	0.0044	0.0044	0.0044	0.0044	0.0044	0.0044	0.0044	0.0044	0.003	0.0002	-0.0009	-0.0009
TP	0.01	0.01	0.01	0.01	0.01	0.01	0.0022	0.0034	0.0034	0.0039	0.0069	0.0036	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.0036	0.0036	0.0025	0.0025
TSS	1	1	1	1	1	1	1.5	2.4	2.4	2.4	2.4	2.4	2.4		2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
VSS							1.98	1.98	1.98	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

**Table 13-3 Potomac Detection Limits** 

	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBL	CBI	CBI	CBL
parameter	1/1/85-2/28/85	3/1/85-5/15/85	5/16/85-9/30/86	10/1/86-9/31/87	10/1/87-9/19/88	9/20/8812/31/99	1/1/00-12/31/03	1/1/04-12/31/05	1/1/06-12/31/06	1/1/07-12/31/07	1/1/08-12/31/08	1/1/09-12/31/09	1/1/10-12/31/10	1/1/11-12/31/11	1/1/12-12/31/12	1/1/13-12/31/13	1/1/14-12/31/15	1/1/16-12/31/16	1/1/17-12/31/17	1/1/18-12/31/18	0.000000000000000000000000000000000000		1/1/21-12/31/21
CHLA	DHMH d	id Chloro	ohylls unt	til Decem	ber 2008	; no DL v	vere dete	rmined				0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
DIN	0.08	0.0039	0.0039	0.0039	0.0032	0.0032	0.0037	0.0037	0.0037	0.0037	0.0037	0.0067	0.0067	0.0017	0.0017	0.0017	0.0017	0.0017	0.0027	0.0027	0.0137	0.0105	0.0105
DOC	1	1	0.5	0.5	0.5	0.24	0.24	0.15	0.15	0.24	0.24	0.24	0.24	0.24	0.24			0.24	0.16	0.16		0.62	
DON	0.335	0.372	0.0261	0.197	0.0168	0.0168	0.0163	0.0163	0.0163	0.0163	0.0463	0.0433	0.0433	0.0483	0.0483	0.0483	0.0483	0.0483	0.0473	0.0473	0.0363	0.0395	0.0395
DOP	0.005	0.0034	0.0034	0.0104	0.0004	0.0004	0.0004	0.0004	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009		-0.0019	-0.0019
NH4	0.04	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.006	0.006	0.001	0.001	0.001	0.001	0.001	0.002	0.002		0.62 0.62 0.62 0.0137 0.0105 0.16 0.16 0.0363 0.0395 0.0623 0.0263 0.034 0.0024 0.005 0.05 0.05 0.05 0.05 0.063 0.2233 0.2233 0.2233 0.2233 0.0626 0.0658 0.0009 0.0036 0.0025 0.0036 0.0025 0.0036 0.0025 0.0099 0.0036 0.0025 0.0099 0.0036 0.0025 0.0099 0.0036 0.0025 0.0099 0.0036 0.0025 0.0099 0.0036 0.0025 0.0099 0.0036 0.0025 0.0099 0.0036 0.0025 0.0099 0.0036 0.0025 0.0099 0.0036 0.0025 0.0025 0.0025 0.0099 0.0036 0.0025 0.	
NO2	0.01	0.0005	0.0005	0.0005	0.0002	0.0002	0.0002	0.0002	0.0002	0.0006	0.0006	0.0001	0.0006	0.0002	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.62 0.62 0.0137 0.0105 0.16 0.16 0.0363 0.0395 -0.0019 -0.0019 0.013 0.009 0.0007 0.0007 0.0007 0.0015 0.0633 0.0633 0.74 0.74 0.0263 0.0263 0.0034 0.0034 0.0021 0.001 0.05 0.05 0.05 0.05 0.05 0.05 0.05 0.05 0.05 0.05 0.0015 0.0015 0.0763 0.2233 0.2233 0.2233 0.0266 0.0658 0.0002 -0.0009 0.0036 0.0025 2.4 2.4		0.0009
NO23	0.04	0.0009	0.0009	0.0009	0.0002	0.0002	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007		0.62 0.62 0.015 0.0015 0.0034 0.0021 0.0015 0.005 0.05 0.005 0.005 0.005 0.0023 0.2233 0.2233 0.2233 0.0026 0.0026 0.0036 0.0025 0.0025 0.0025 0.0036 0.0025 0.0025 0.0036 0.0025 0.0025 0.0036 0.0025 0.0025 0.0036 0.0025 0.0025 0.0036 0.0025	
PC	0	0	0.001	0.5	0.001	0.0633	0.0633	0.0633	0.0759	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633	0.0633		0.62 0.62 0.0137 0.0105 0.16 0.16 0.0363 0.0395 0.0019 -0.0019 -0.0019 0.013 0.009 0.0007 0.0015 0.0633 0.0633 0.74 0.74 0.0263 0.0263 0.0034 0.0034 0.0021 0.001 0.05 0.05 0.05 0.05 0.0015 0.0015 0.0763 0.0763 0.2233 0.2233 0.0626 0.0658 0.0002 -0.0009 -0.0009 -0.0036 0.0036 0.0025 2.4 2.4	
PHEO	DHMH d		gments u	until Dece	ember 200	)8; no DL	_ were de	termined				0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74		0.62 0.62 0.015 0.0019 0.0007 0.0007 0.0007 0.0005 0.05 0.05 0	
PN	0.068**	0.068**	0.001	0	0.001	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0105	0.0263			0.0263
PO4	0.007	0.0016	0.0016	0.0016		0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006	0.0006		0.0006		0.0006	0.0006			0.0034
PP	0	0	0.0013	0	0.0012	0.0012	0.0024	0.0024	0.0024	0.0054	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0021	0.0035	0.0035	0.0021			0.001
SI	0.1	0.012	0.012	0.012	0.01	0.01	0.01	0.01	0.01	0.08	0.01	0.01	0.01	0.01	0.06	0.0022	0.01	0.01	0.0536	0.05			0.05
TDN	0.415	0.3759	0.03	0.2009	0.02	0.02	0.02	0.02	0.02	0.02	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05			0.05
TDP	0.012	0.005	0.005	0.012	0.001	0.001	0.001	0.001	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015
TKNF	0.375	0.375		0.2																			
TKNW	0.443	0.443		0.2																			0.0700
TN	0.483	0.4439	0.031	0.2009	0.021	0.0305	0.0305	0.0305	0.0305	0.0305	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0605	0.0763			0.0763
TOC	1	1	0.501	1	0.501	0.3033	0.3033	0.2133	0.2259	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.3033	0.2233	0.2233	2 0.62 0.62 7 0.0137 0.0105 6 0.16 0.16 3 0.0363 0.0395 9 -0.0019 -0.0019 2 0.013 0.0007 7 0.0007 0.0007 7 0.0007 0.0007 3 0.0633 0.0633 4 0.74 0.74 3 0.0263 0.0263 6 0.0034 0.0034 1 0.0021 0.001 5 0.05 0.05 5 0.05 0.05 6 0.0015 0.0015 3 0.0763 0.0763 3 0.0763 0.0763 3 0.0763 0.0763 6 0.0626 0.0658 6 0.0626 0.0658 6 0.0036 0.0025		0.2233
TON	0.403	0.44	0.0271	0.197	0.0178	0.0273	0.0268	0.0268	0.0268	0.0268	0.0568	0.0538	0.0538	0.0588	0.0588	0.0588	0.0588	0.0588	0.0578	0.0736			0.0658
TOP	0.005	0.0034	0.0047	0.0104	0.0016	0.0016	0.0028	0.0028	0.0033	0.0063	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.0044	0.0044	0.003			-0.0009
TP	0.012	0.005	0.0063	0.012	0.0022	0.0022	0.0034	0.0034	0.0039	0.0069	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.005	0.005	0.0036			0.0025
TSS VSS	4	4	1	7	1.98	1.5 1.98	2.4 1.98	2.4 1.98	2.4 0.9			2.4 0.9	2.4 0.9	2.4 0.9			0.9						
V 3 3						1.98	1.98	1.98	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9

**Table 13-4** Chesapeake Bay Mainstem Detection Limits

NOTE: Due to logistical considerations, samples for the Tributaries station LE2.3 are collected during Mainstem cruises.

CBTF:1	CB1.1																										1						
CBTF1																	X	X		X	X	X	X	X	X		X			X	X	X	X
CB2OH																	X	X	х	x	X	X	X	X	х		Х			x	X	x	X
CB2OH																	X	X	X	X X	x	X X	X	X	X	x	x			X	X	x x	X
CB3MH																	х	X	х				Х	X	х					X	X		x
	CB3.2 CB3.3C																x x	x	X	x	X	X	X	x	X		X			x	x	x	
	CB3.3E																		_ ^		X		Х				X						X
	CB3.3L																X	X	X	X	X	X	X	X	X		X			X	X	X	X
	CB4.1C																х	х	х	х	x	X	X	х	х	X	Х			х	х	X	Х
	CB4.1C																X	X	X	X	X	X	X	X	X		X			X	X	x	X
	CB4.1E																X	X	х	x	X	X	Х	X	х		Х			X	X		x x
	CB4.1W																х	х	х	х	х	х	х	х	х		х			х	х	х	
	CB4.2C																X	X	X	x	X	X	X	X	х	X	X	X		x	X	X	X
	CB4.2E CB4.2W																X	X	X	X	X	X	X	X	X		X			X	X	X	X
	CB4.2W																X	X	X	x	X	X	X	X	х		Х			X	X	x	X
	CB4.3C CB4.3E																X	X	X	X	X	X	X	X	X		X			X	x	X	X
	CB4.3E																X	X	Х	x	X	X	X	X	х	X	Х			X	X	x	X
СВ4МН																	X	X	X	X	X	X	X	X	X		X			X	X	X	X
																	Х	х	х	х	х	х	х	Х	х	х	х			х	Х	х	Х
CB5MH CB5MH																	Х	х	х	х	х	х	Х	х	х		×			х	х	х	Х
CB5MH																	Х	х	Х	х	х	Х	х	Х	х		х			х	Х	х	Х
PAXMH																	Х	х	х	х	х	х	х	х	х		×			х	х	х	х
																	Х	х	х	х	х	х	х	Х	х	х	х			х	Х	х	Х
CHOOH	CB5.1W	х	х	х	Х	Х	х	х	х	х	х	Х	х	х	Х	х											×	х		х	х	х	х
CHOMH																	Х	х	Х	х	х	Х	х	Х									
																	х	х	х	х	х	х	Х	х									
PAXMH		Х	х	X	х	х	Х	Х	Х	Х	Х	х	х	Х	Х	х	Х	х	Х	Х	Х	X	х	Х			х	X		Х	Х	х	Х
PAXMIH		х	х	х	х	х	х	Х	х	х	х	х	х	х	Х	х											х			х	х	х	Х
PAXMH PAXMH		х	х	Х	х	Х	Х	Х	Х	Х	х	х	х	Х	х	х											х			х	х	х	Х
		х	х	х	х	х	х	х	х	х	х	х	х	х	х	х											×	х		х	х	х	х
PAXMH	RET1.1																Х	х	Х	х	х	х	х	Х						-	77		
		х	х	х	Х	х	х	х	х	х	х	Х	х	х	Х	х											х	×		х	х	х	х
	RET2.2																Х	х	Х	х	х	Х	х	Х							77		
PAXTF WRBTF	TF1.0	X				х																					X						
		Х																									х				77		
PAXTE	TF1.3	х	х																								х						
PAXTE	TF1.4	х																									х				7		
PAXT	TF1.5	х	х	х	х	Х	Х	Х	Х	Х	х	х	х	Х	х	х	х	х	х	х	х	х	х	х			х			х	x	х	Х
PAXOH		х	х	Х	х	Х	Х	Х	Х	Х	х	х	х	Х	х	х											х			х	х	х	Х
PAXOH		х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х	х			х	х	_	х	x	х	х
POTTF																	Х	х	х	х	х	х	х	Х									
PATMIH																	х	х	х	х	х	х	х	х					_				
	WXT0001																										х						
CB5MH	XCG8613	х	х	х	х	х	х	х	х																								

Table 13-5 Light Attenuation – Mainstem and Patuxent River Sampling Sites and Dates

Waterbody	Station	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
Manokin R, Back Cr	BXK0031																
Susquehanna R	CB1.0																
Chicamacomico R	CCM0069																
Eastern Bay	EE1.1								X								X
Choptank	EE2.1									X				X	X		
Little Choptank	EE2.2												X				X
Fishing Bay	EE3.0																
Tangier Sound, N	EE3.1	X	X					X					X				
Tangier Sound, S	EE3.2					X											
Pocomoke Sound	EE3.3						X		X	X			X		X		
Northeast R	ET1.1									X					X		
Pocomoke R	ET10.1										X					X	
C&D Canal	ET2.1								X			X					
Bohemia R	ET2.2																
Elk R	ET2.3						X					X		X			
Sassafras R	ET3.1						X									X	
Chester R	ET4.1								X					X	X		
Chester R	ET4.2	X	X				X				X				X		
Nanticoke	ET6.1	71	21				11				21			X	X	X	
Nanticoke	ET6.2												X				
Wicomico R	ET7.1																
Manokin R	ET8.1		X											X			
Big Annemessex R	ET9.1		21		X									71	X		
Mattawoman R - Pot	MAT0016				- 21				X		X	X		X	X		
Mattawoman R - Pot	MAT0078								X		21	21		X	2 1		X
Manokin R	MNK0146								11					71			11
Piscataway Cr - Pot	PIS0033														X		X
Pocomoke R - Shelltown	POK0014														X		X
Potomac R	RET2.1														71		21
Potomac R	RET2.4																
Piscataway Cr - Pot	TF2.1									X	X			X			X
Dogue Cr - Pot	TF2.2									X	71			1			71
Potomac R	TF2.4								X	21							
Transquaking R	TRQ0088								71								
Transquaking R Transquaking R	TRQ0086																
Transquaking R Transquaking R	TRQ0224																
Wicomico R - ferry	WIW0141																
Bush R	WTW0141	X															
	WT2.1	Λ		X													X
Gunpowder R Middle R	WT3.1			Λ					v								
Back R	W13.1 WT4.1								X						X		X
															Λ		v
Magothy R Severn R	WT6.1 WT7.1																X
South R												V		V			
Rhode R	WT8.1 WT8.2											X		X		X	
							v	V				Λ	V			Λ	
West R	WT8.3						X	X					X				
Pocomoke R	XAK7810																
Wicomico R	XCI4078																
Nanticoke	XDJ9007		37												37		
Chester R	XGG8251		X												X		
Corsica R	XHH4742				Atton												

**Table 13-6 Light Attenuation Maryland Tributary Sites** 

## APPENDIX 14

## Maryland Department of Health Inorganics Analytical Laboratory Standard Operating Procedures and Methods

- 1. Alkalinity
- 2. Biological Oxygen Demand (BOD)
- 3. Total Suspended Sediments

## MDH- Laboratories Administration DIVISION OF ENVIRONMENTAL SCIENCES

**Effective:** 5/1/2022

Date

Determination of Alkalinity by Titrimetry (Standard Method 2320 B)

Replaces: 4.3

Inorganics Analytical Laboratory

CHEM-SOP-SM 2320 B

Jacob Kilczewski

4.4

SOP Title:

SOP No.:

Revision:

POC:

Laboratory:

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Laboratory Supervisor:	Lora Phillips	4/25/2022
	Signature	Date
QA Officer:	Molly Mollay	4/25/2022
	Signature	Date
Manager:	<u>Cynthia Stevenson</u> Signature	4/25/2022 Date
	Signature	Date
Division Chief:	- fiftia	04/25/2022

## Standard Method 2320 B Sop No.: CHEM-SOP-SM 2320 B

## **REVISION RECORD**

Revision	Date	Changes	Made By	Effective Date
0.0	6/3/08	N/A	Taiyin Wei	6/2/08
1.0	12/09/09	Screen snapshots added to procedure, new Sample Run Log, tracking IDs for standards and reagents	Taiyin Wei	1/10
2.0	1/11	New SOP tracking number	Asoka Katumuluwa	1/11
3.0	4/12/12	Editorial and technical changes- Checklist update	S. Ameli J. Freeman-Scott	9/17/12
3.0	4/16/13	Reviewed The SOP	S. Ameli J. Freeman-Scott	6/16/13
4.0	10/31/14	Changed the format	A. Hamilton S. Ameli L. Phillips	12/01/14
4.1	6/1/15	Reviewed document, updated section 9.4	L. Phillips S. Ameli	7/1/15
4.1	5/2/16	Reviewed Document	L. Phillips S. Ameli	7/1/16
4.2	6/2/17	Reviewed Document and made organizational name changes	L. Phillips S. Ameli	7/1/17
4.3	6/4/18	Reviewed Document and updated section 13.5	L. Phillips S. Ameli	7/1/18
4.3	3/1/19	Reviewed Document	L. Phillips S. Ameli	3/4/19
4.4	4/22/20	Reviewed Document, updated run log	L. Phillips S. Ameli	5/1/20
4.4	4/9/21	Reviewed Document	L. Phillips C. Stevenson	5/1/21
4.4	4/22/21	Reviewed Document	J. Kilczewski L. Phillips	5/1/22

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# STANDARD OPERATING PROCEDURE DETERMINATION OF ALKALINITY BY TITRIMETRY

Standard Method 2320 B

#### 1.0 SCOPE AND APPLICATION

- 1.1 This method is applicable to drinking, surface, saline, domestic and industrial waters.
- 1.2 This method is suitable for all concentrations of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 mL. The sample must not be filtered, diluted, concentrated, or altered in any way.
- 1.3 Alkalinity is the acid-neutralizing or buffering capacity of a water body. The alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content; it is taken as an indication of the concentration of these constituents.
- 1.4 Measuring alkalinity is important in determining a stream's ability to neutralize acidic pollution from rainfall or wastewater. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of water for irrigation.

#### 2.0 SUMMARY OF METHOD

- **2.1** An unaltered sample is titrated to an electrometrically determined end-point of pH 4.5 using an automated system. The sample must not be filtered, diluted, concentrated, or altered in any way.
- 2.2 Alkalinity as CaCO<sub>3</sub> is determined from the volume required of a 0.02 N sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to titrate 50 mL of the sample. For samples with high alkalinities that require more than 50 mL of titrant, smaller sample volumes are used.
- 2.3 For samples of alkalinities less than 20 mg/L, the amount of the acid required to reduce the pH exactly 0.30 pH units below pH 4.5 is measured and an extrapolation technique is used to determine the equivalence point.

#### 3.0 INTERFERENCES

Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Clean the electrode occasionally. Do not filter, dilute, concentrate, or alter sample.

#### 4.0 HEALTH AND SAFETY

- **4.1** Good laboratory practices should be followed during reagent preparation and instrument operation.
- 4.2 The use of a fume hood, protective eyewear and clothing and proper gloves are recommended when handling acids.
- **4.3** Each employee is issued a *Laboratory Safety Manual* and a *Quality Assurance plan* and is responsible for adhering to the recommendations contained therein.
- **4.4** Each chemical should be regarded as a potential health hazard. A reference file of material safety data sheet (MSDS) is available in the lab.

### 5.0 EQUIPMENT AND SUPPLIES

- **5.1** Equipment
  - 5.1.1 Mantech PC Titration system, consisting of
    - 5.1.1.1 PC-Titrator with Auto-Sampler
    - 5.1.1.2 System Controller with monitor
    - 5.1.1.3 Printer
    - 5.1.1.4 Electrode Sure-Flow Combination pH electrode, glass body, with BNC connector, Man-Tech#PCE-80-PH1200 or equivalent.
  - 5.1.2 Analytical balance Mettler Toledo AG204 or equivalent
- **5.2** Supplies

- 5.2.1 Glass beakers 100 mL
- 5.2.2 Graduated cylinder class A, 50 mL
- 5.2.3 Volumetric flasks class A, 50 mL, 100 mL, 500 mL, and 1000 mL
- 5.2.4 Pipetters  $100 1000 \mu L$ ,  $500 5000 \mu L$ , and 1 10 mL
- 5.2.5 Carboy 5 L, with spigot, Nalgene
- 5.2.6 Transfer pipettes Samco, cat. #231
- 5.2.7 pH Electrode filling solution follow manufacturer's recommendations

#### 6.0 REAGENTS AND STANDARDS

- **6.1** Reagents
  - 6.1.1 Deionized water
  - 6.1.2 H<sub>2</sub>SO<sub>4</sub>, 0.02N Fisher, cat. # SA 226-4
- 6.2 Standards
  - 6.2.1 pH 4.0 buffer solution Fisher, cat. #SB 101-500
  - 6.2.2 pH 7.0 buffer solution Fisher, cat. #SB 107-500
  - 6.2.3 pH 10.0 buffer solution Fisher, cat. # SB 115-500
  - 6.2.4 Stock standard, 25,000 mg/L CaCO $_3$  (0.5N) 10 mL/ 16 voluette ampoules, Hach, product # 14278-10
  - 6.2.5 Intermediate standard, 5000 mg/L CaCO<sub>3</sub> Pipet 5 mL of the stock standard (6.2.4) into a 25 mL volumetric flask. Bring to volume with deionized water. Prepare every two weeks.
  - 6.2.6 Check standard, 50 mg/L CaCO<sub>3</sub> Pipet 5 mL of intermediate standard (6.2.5) into a 500 mL volumetric flask. Bring to volume with deionized water. Prepare every two weeks.

#### 7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 7.1 Samples are collected in 1 liter polyethylene cubitainers and iced or refrigerated to 4 °C. The holding time is 14 days
- 7.2 The sample must not be filtered, diluted, concentrated or altered in any way.

#### 8.0 QUALITY CONTROL

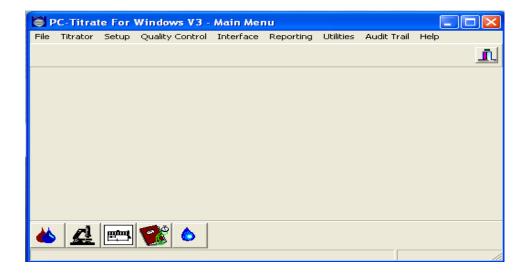
- 8.1 The acceptable range for the slope of the calibration curve is -65 mV to -53 mV. Calibration must be repeated if the slope falls outside this range.
- 8.2 A blank and a blank spike are analyzed at the beginning of the run. Blank concentration must be less than the reporting level of 1 ppm and the acceptable

- value for the spike recovery is 90 110%. Blank, blank spike or sample spike not meeting the criteria is reanalyzed.
- 8.3 Every tenth sample is duplicated and spiked. The acceptable values for the relative percent difference (RPD) are  $\pm$  10 and for the spike recovery (SR) are 90 110%. If these do not fall within the accepted ranges, the corresponding analyses are repeated.
- **8.4** A check standard is run after every ten samples.
- **8.5** A QC sample is analyzed at the beginning and the end of each analytical run.
- **8.6** Data acceptance criteria are listed on the data review checklist. (Appendix A).
- 8.7 Laboratory participates in yearly ERA WatR Supply (WS) and WatR Pollution (WP) Proficiency Tests.
- **8.8** An initial demonstration of capability study is performed by each analyst performing the test.

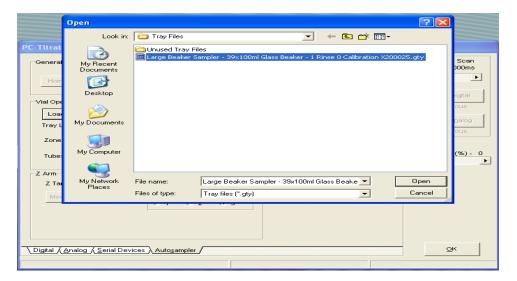
#### 9.0 PROCEDURE

- **9.1** Sample preparation
  - 9.1.1 Prepare a list of samples to be analyzed on a Sample Run Log (Appendix B).
  - 9.1.2 Pour approximately 60 mL of the pH 4, pH 7 and pH 10 buffers into each of the labeled 100 mL beakers.
  - 9.1.3 Pour 50 mL portions of each well mixed sample, measured using a class "A" graduated cylinder, into labeled 100 mL beakers. Pour a duplicate of every tenth sample.
  - 9.1.4 Spike blank and every tenth sample, or one sample per batch if analyzing less than 10 samples, by adding 1 mL of Intermediate standard solution (6.2.5) to 49 mL of deionized water and samples respectively.
- **9.2** Daily electrode preparation
  - 9.2.1 Rinse the electrode with deionized water to remove crystal residue that may have formed on the surface during storage.
  - 9.2.2 Check the electrolyte level in the reference cavity, which should be approximately ½ inch below the fill-hole. If the electrolyte level is too

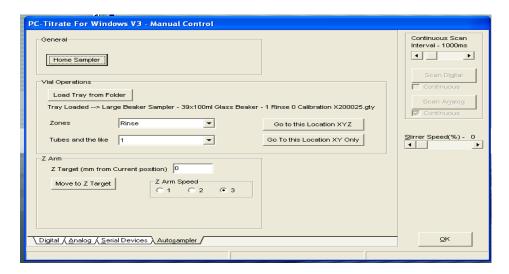
- low, add filling solution (5.2.7) with a transfer pipet. Replace the cap, and rinse clean the electrode.
- 9.2.3 Remove fill-hole cover during calibration and measurement to ensure uniform flow of filling solution.
- **9.3** Weekly electrode maintenance
  - 9.3.1 Disconnect the electrode from the unit. Empty the electrode with a transfer pipet. Rinse with deionized water and then, fill up with filling solution. Connect the electrode.
  - 9.3.2 Soak electrode in pH 4 buffer for a minimum of one hour.
    - 9.3.2.1 Follow the steps in 9.4.1 to 9.4.3
    - 9.3.2.2 Place a beaker with pH 4 buffer in the # 1 position.
    - 9.3.2.3 Select "Tubes" from "Zones", select "l" as the beaker number for "Tubes & the like". Click on "Go to this location XYZ" to send the probe to "l" position.
- **9.4** Instrument preparation
  - 9.4.1 Check and fill the deionized water bottle and acid bottle.
  - 9.4.2 Turn on the computer and the autosampler. Double click on "PC-Titrate V3".



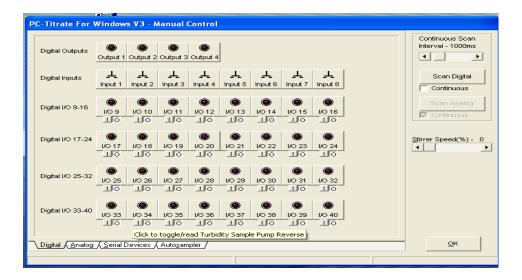
9.4.3 Click on "Titrator" and select "Manual control" from the pull down list. Select "Autosampler", "Load tray from folder", Automax beaker, Open



- 9.4.4 Click on "Home sampler" to send the probe to home position.
- 9.4.5 Select "Rinse" from "Zones" and "l" as the beaker number for "Tubes & the like". Click on "Go to this location XYZ" to send the probe to the rinse beaker.



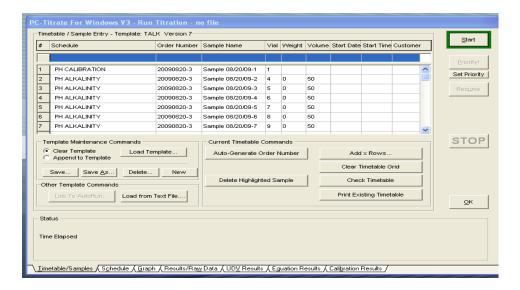
9.4.6 Click on "Digit" tab and "Output 4" to rinse the probe and fill up the beaker. Click "Output 4" again to turn it off.



## **9.5** Buret preparation

- 9.5.1 Remove the titrant delivery line from the electrode block on the autosampler and place it into a waste beaker.
- 9.5.2 Check and fill the acid bottle.
- 9.5.3 Go to the "Serial devices".
- 9.5.4 Click on button labeled "Dispense 10%" to dispense the 0.02 N H<sub>2</sub>SO<sub>4</sub> through the titrant delivery line. Repeat 2 more times or until no bubbles are observed in the flow.
- 9.5.5 Fill up the syringe by clicking on "Syringe full down".
- 9.5.6 Remove the dispenser tip from the waste beaker and return it to its position in the probe holder.
- **9.6** Daily electrode calibration and sample analysis
  - 9.6.1 Place pH 4.0, 7.0 & 10.0 buffers into autosampler tray using position # 1, 2 & 3.
  - 9.6.2 Click on the PC Titrate V3 tab.
  - 9.6.3 Click on the book tab at the bottom labeled "pH cal 4-7-10" tab to call up the sample table.
  - 9.6.4 Place the samples after the calibration: The template will have "4-7-10" under sample name at the first row reserved for a schedule of "pH calibration" with a 1 in the vial number box. Enter sample names

according to the sample run log (9.1.1) starting with the second row (vial # 4) a check standard, a blank, a blank spike, a QC, and samples to be analyzed. Enter a check standard, a blank, and a QC again at the end of the run. All other samples and checks are to be run with a "pH Alkalinity" schedule chosen.



- 9.6.5 Highlight each excess line, and then click on "Delete Highlighted Sample" to remove all unused sample information.
- 9.6.6 Highlight a line and click on "Add x lines" to add additional lines. Left click on the mouse to relocate the lines.
- 9.6.7 Click "Check Timetable" to verify information entered are valid. Roll down the table to make corrections if needed. Click "OK".
- 9.6.8 Load the samples according to the run list with the last sample followed by a beaker with the solution recommended by the probe's manufacturer.
- 9.6.9 Click on "Start".
- 9.6.10 To run a second tray using the same calibration: Double click on "pH Calibration" and replace it with "pH Alkalinity". Fill in sample names starting with the first row (vial #1). Make sure a set of the quality control samples: check standard, blank, and external QC is also being run at the beginning and at the end in the second tray.
- 9.6.11 Print the *Calibration Report* and a custom report of *Alkalinity Results* at the end of the run.

- 9.6.12 Recall each titration curve by clicking on "Titrator", "Titration Replay", "Load", and then, selecting date and sample name. Click on "Select" to observe the titration curve. Click "OK" to return to the main menu.
- 9.6.13 Results can also be printed out by clicking on "Equation results" tab, "Print", and then "OK".
- 9.6.14 Go to "Manual control" and select "Autosampler" tab. Select "tubes" from "Zones" and "l" as the number for "Tubes & the like". Click on "Go to this location XYZ" to send the probe to the #1 beaker with the solution recommended by the probe's manufacturer.
- 9.6.15 Shut down the computer and turn off the autosampler.

#### 10.0 DATA ANALYSIS AND CALCULATIONS

- Alkalinities are calculated automatically by the PC-Titrate V.3 software based on 1 mL of  $0.1N H_2SO_4 = 5.0 mg CaCO_3$ 
  - 10.1.1 Potentiometric titration to an end point of pH 4.5

Alkalinity, mg CaCO<sub>3</sub>/L = 
$$\frac{\text{titrant dispensed, mL x 0.02N (H}_2\text{SO}_4\text{) x 50,000}}{\text{sample volume, mL}}$$

10.1.2 Potentiometric titration of low alkalinity

Total Alkalinity, mg CaCO<sub>3</sub>/L = 
$$\frac{(2 \text{ B - C}) \times 0.02 \text{N} (\text{H}_2\text{SO}_4) \times 50,000}{\text{sample volume, mL}}$$

where:

B = mL titrant to first recorded pH

C = total mL titrant to reach pH 0.3 unit lower

10.2 Calculate the percentage spike recovery of the laboratory fortified blanks and samples as follows:

$$%SR = \frac{\text{spiked sample conc. - sample conc., ppm}}{\text{amount of spike added to sample, ppm}} \times 100$$

10.3 Calculate the relative percentage difference of the duplicated samples as follows:

$$RPD = \frac{difference between the duplicates}{average of the duplicates} \times 100$$

#### 11.0 DATA AND RECORDS MANAGEMENT

- 11.1 Instrument maintenance, instrument calibration, and quality control data are kept in binders and test results are kept in the file cabinet.
- 11.2 Normal turnaround time for samples submitted to this lab will be 2 to 10 days from receipt. Results are reported in writing on a sample analysis request form.
- 11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five years custody period.

#### 12.0 WASTE MANAGEMENT

- 12.1 Excess reagents, samples and method process waste are poured into the sink with running water.
- **12.2** Actual reagent preparation volumes are to reflect anticipated usage and reagent stability.

#### 13.0 REFERENCES

- **13.1** American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, Method Number 2320B, 21<sup>st</sup> Edition, 2005
- **13.2** Man-Tech Associates inc., *PC-Titrate Windows Software Manual*, version 3.0, November 2004.
- 13.3 U.S. Environmental Protection Agency, Monitoring and Assessing Water Quality, 5.10 Total Alkalinity, November 2006
- 13.4 Division of Environmental Chemistry, Maryland Department of Health, *Quality Assurance Plan*, SOP No. CHEM-SOP-QAP
- Division of Environmental Chemistry and Division of Microbiology, Maryland Department of Health, *Quality Manual*, SOP No. QA-SOP-QM

## APPENDIX A

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

## Data Review Checklist - Alkalinity Standard Methods 2320 B

ate Collected:	Date Analyzed:	Analyst:	
Procedure	Acceptance Criteria	Status*	Comments
Holding Time	14 days @ 4°C		
Calibration Results	Slope = $-65.00 \text{ to } -53.00 \text{ mV}$		
External QC <sup>2</sup>	Beginning and end of each run Within acceptable range		
Reagent Blank	< Reporting level (1 mg/L)		
Blank Spike	1 per batch Recovery = 90 - 110%		
Check Standard	After every 10 <sup>th</sup> sample and at the end of the run  Concentration within 90 to 110% of the true value		
Duplicates/Replicates	Every 10 <sup>th</sup> and the last sample or 1/batch, if less than 10 samples RPD:S 10%		
Matrix Spike	Every 10 <sup>th</sup> and the last sample or 1/batch, if less than 10 samples  Recovery = 90 - 110%		
Decimal Places Reported	0		
Changes/Notes	Clearly stated		
* Check (□) if criteria are me		er's Signature &	Data
laryst's Signature & Date	Keview	er's Signature &	Date
pervisor's Signature & Date			
	Identification	2 <u>F</u>	External QC
	True Value	;=	
	Range	: = <u> </u>	

CONTROLLED DOCUMENT - Do Not Copy

Analyst:

## APPENDIX **B**

## Division of Environmental Sciences INORGANICS ANALYTICAL LABORATORY

## Sample Run Log -Alkalinity

Date:

Standard Method 2320 B

Tray 1 Cup #	Sample ID	Dilution	Tray 1 Cup #	Sample ID	Dilution
1	pH 4		21		
2	pH 7		22		
3	pH 10		23		
4	Blank		24		
5	Ck Std		25		
6	QC		26		
7	Blank		27		
8	Blank -Spike		28		
9			29		
10			30		
11			31		
12			32		
13			33		
14			34		
15			35		
16			36		
17			37		
18			38		
19			39		
20					

Tray 2 Cup #	Sample ID	Dilution
1		
2		
3		
4		
5		
6		
7		
8		
9		
10		
11		
12		
13		
14		
15		
16		
17		
18		
19		
20		

Sample Name	Tracking ID
pH 4 Buffer	
pH 7 Buffer	
pH 10 Buffer	
H <sub>2</sub> SO <sub>4</sub> , 0.02N	

Lab#	Average	RPD	% Spk Rec

Sample Name	Prep Log ID
Intermediate Std, 5,000 ppm	
Ck Std, 50 ppm	
QC:	

### DES-FORM-IAL-002 (05/20)

Title:

SOP No.:

Revision:

Laboratory:

# MDH- Laboratories Administration DIVISION OF ENVIRONMENTAL SCIENCES

CHEM-SOP-SM 5210 B

3.5

Replaces: 3.4

Inorganics Analytical Laboratory

Signature

POC:	Jacob Kilczewski jacob.kilczewski@maryland.gov	
Laboratory Supervisor:	Low Phillips	4/25/2022
·	Signature	Date
QA Officer:	Molly Mollay	4/25/2022
	Signature	Date
Manager:	<u>Cynthia Stevenson</u> Signature	4/25/2022 Date
Division Chief:		04/25/2022

Determination of 5-Day Biochemical Oxygen Demand (Standard Method 5210 B)

Effective: 5/1/22

Date

## CHEM-SOP-SM 5210 B SOP N0.: CHEM-SOP-SM 5210 B

## REVISION RECORD

Revision	Date	Changes	Made By	Effective Date
0.0	6/4/08	N/A	Taiyin Wei	6/5/08
1.0	12/09	Tracking IDs for standards and reagents	Taiyin Wei	1/10
2.0	1/11	New SOP tracking number	Asoka Katumuluwa	1/11
3.0	2/12	New Procedure for new BOD analyzer	Cynthia Stevenson	12/12/12
3.1	10/31/14	Changed format	C. Stevenson S. Ameli	12/01/14
3.1	6/1/2015	Reviewed document	L. Phillips Y. Simms S. Ameli	7/1/15
3.1	5/31/2016	Reviewed document	L. Phillips Y. Simms S. Ameli	7/1/16
3.2	6/05/2017	Reviewed document and made organizational name changes, Updated 5.1.4, 9.3.2-9.3.3, 9.6.1, 9.11.1, 9.11.2.6 to 9.11.2.8 and Run Log	L. Phillips Y. Simms S. Ameli	7/1/17
3.3	6/4/18	Reviewed document added 9.10, updated section 13.7	L. Phillips Y. Simms S. Ameli	7/1/18
3.3	3/1/19	Reviewed document	L. Phillips Y. Simms S. Ameli	3/4/19
3.4	4/21/20	Reviewed document and updated contact information	Jacob Kilczewsk L. Phillips	5/1/20
3.4	4/9/21	Reviewed document	Jacob Kilczewsk L. Phillips	5/1/21
3.5	4/21/21	Reviewed document, updated 6.3.2, 6.5.7	J. Kilczewski L.Phillips	5/1/22

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#### STANDARD OPER ATING PROCEDURE

# DETERMINATION OF 5 - Day Biochemical Oxygen Demand Standard Method 5210 B

#### 1.0 SCOPE AND APPLICATION

- 1.1 The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirement of wastewaters, effluents, polluted waters, and streams. The test has its widest application in measuring waste loadings to treatment plants and in evaluating the BOD-removal efficiency of such treatment system. The application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water.
- 1.2 The BOD determination is an empirical test which measures the dissolved oxygen utilized during a specified incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous irons. It also may measure the amount of oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. The standard test conditions include dark incubation at 20 °C for five days. The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be actually reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

#### 2.0 SUMMARY OF METHOD

2.1 Appropriate dilutions of each sample and the quality control samples are incubated for 5 days (BOD<sub>5</sub>) at 20 °C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

#### 3.0 INTERFERENCES

- 3.1 Residual chorine can interfere in this determination and it is neutralized with Na<sub>2</sub>SO<sub>3</sub>, if present. Hach's USEPA-accepted DPD (N, N-diethyl-p-phenylenediamine) colorimetric method is used to detect any free chlorine in the sample.
- 3.2 The source water used for BOD sample dilution must be free of heavy metals, specifically copper, and toxic substances such as chlorine that can interfere with BOD measurements. Protect source water quality by using clean glassware, tubing, and bottles. Storage of prepared dilution water for more than 24 h after adding nutrients, minerals, and buffer is not recommended unless dilution water blanks consistently meet quality control limits.

- 3.3 Oxidation of reduced forms of nitrogen, mediated by micro-organisms, has been considered interference in the determination of BOD and can be prevented by an inhibitory chemical and reported results as carbonaceous biochemical oxygen demand (CBOD).
- Exclude all light during the 5 day incubation period to prevent the possibility of photosynthetic production of dissolved oxygen (DO).

#### 4.0 HEALTH AND SAFETY

- **4.1** Good laboratory practices should be followed during reagent preparation and instrument operation.
- **4.2** Each employee is issued a *Laboratory Safety Manual* and is responsible for adhering to the recommendations contained therein.
- 4.3 Use absorbent towels if material is spilled and wash residual into drain.
- **4.4** Each chemical should be regarded as a potential health hazard. A reference file of material safety data sheet (MSDS) is available in lab.

#### 5.0 EQUIPMENT AND SUPPLIES

- 5.1 Equipment
  - 5.1.1 YSI Model 5100 dissolved oxygen meter
    - 5.1.1.1 Dissolved oxygen (DO) probe
    - 5.1.1.2 Membrane replacement kits for DO probe
    - 5.1.1.3 Mantech AutoMax 122 Autosampler with pumps
    - 5.1.1.4 Computer and printer
  - 5.1.2 Incubator, thermostatically controlled at  $20 \pm 1^{\circ}$ C
  - 5.1.3 pH meter Accumet pH meter 15, Fisher Scientific or equivalent
  - 5.1.4 Magnetic stirrer or automatic stirrer
  - 5.1.5 Buret 50 mL
  - 5.1.6 Drying oven isotemp, gravity flow convection, 103 °C to 105 °C
  - 5.1.7 Air compressor 135 psi, Westward

# **5.2** Supplies

- 5.2.1 BOD bottles 300 mL disposable bottles (cat. # D1001), bottle stoppers (cat. # D1025), and overcaps (cat. # D1050), Environmental Express
- 5.2.2 Carboy with spigot 20 Lcapacity
- 5.2.3 Graduated Cylinders 25, 50, 100, and 250 mL
- 5.2.4 Micropipetter adjustable volume ranges from 1.0 to 5.0 mL
- 5.2.5 Pipet tips  $5000 \,\mu$ L
- 5.2.7 Plastic beakers polypropylene, 1000 mL,
- 5.2.8 Membrane kit for BOD probe cat. # 5906, YSI
- 5.2.9 Filter Unit, 0.45  $\mu$ m Nalgene disposable sterilization filter unit, cat. # 09-740-25B, Fisher
- 5.2.10 Tubes polypropylene with snap caps, sterile, 14 mL, cat. # 14-959B, Fisher
- 5.2.11 Glass pipettes volumetric, class A, 5 mL
- 5.2.12 Flasks volumetric, class A, 500 mL and 1000 mL
- 5.2.13 Glass rods
- 5.2.14 Stirring bars with stir plate or automatic stirrer
- 5.2.15 Weighing pans aluminum, cat. #D57-144, Labsources, Inc.

#### 6.0 REAGENTS

#### **6.1** Dilution water

- 6.1.1 Aerate 19 liters (5 gallons) of deionized water in a 20 L carboy for a minimum of 30 minutes. The dissolved oxygen concentration of water used for BOD test must be at least 7.5 mg/L. Following aeration, leave carboy to sit overnight or longer in 20 °C incubator with the cap loosened to allow water to equilibrate.
- Prepare dilution water one hour before use by emptying one premixed pillow of BOD Nutrient Buffer (Hach cat. # 14863-98) into aerated water (6.1.1) at 20 °C. Mix well. Place in incubator until ready to use.
- **6.2** Glucose-Glutamic acid (GGA) solution

- Dry a few grams each of glucose or dextrose and glutamic acid in aluminum weigh pans for 1 hour at 103 °C. Cool to room temperature in a dessicator.
- Weigh out 0.15 g each of dextrose and glutamic acid and dissolve in 800 mL of deionized water in a 1 L volumetric flask. Dilute to mark and mix well. Prepare fresh immediately before use.
- Instead of preparing fresh GGA solution each time, the solution prepared in 6.2.2 can be sterilized by filtering through a disposable sterilization filter unit, divided and stored in small volumes. If this procedure is followed, pour about 12 mL aliquots into each sterile 14 mL polystyrene tube, snap cap back on the tube, label, and store in the refrigerator. Prepare every two months.
- Premade GGA is also commercially available. To prepare the standards, simply add the content of the 6 mL vial into each of the two BOD bottles marked for GGA.

# **6.3** Seeding material, prepare daily

- One bottle of wastewater from the Cox Creek Wastewater Treatment Plant is delivered to the laboratory every Tuesday. Store the wastewater in the incubator.
- Shake the sample, let settle and then pour the supernatant into an Erlenmeyer flask about an hour before beginning the run to allow solids to settle to the bottom of the flask. The amount of supernatant to be added to each BOD bottle is between 1.0 mL to 3.0 mL depending on the color, odor and density of the wastewater.

## **6.4** Sample pH

- 6.4.1 Calibration buffers pH 4.0, pH 7.0, and pH 10.0 Fisher cat. # SB105,
- Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), 1M Slowly and while stirring, add 2.8 mL of conc. H<sub>2</sub>SO<sub>4</sub> to 80 mL of deionized water. Dilute to 100 mL. Mix well, label and store for up to a year.
- 643 Sodium hydroxide (NaOH), 1N Dissolve 4 g of NaOH in 80 mL of deionized water. Dilute to 100 mL. Mix well, label and store for up to a year.

#### **6.5** Dechlorination

- DPD free chlorine reagent power cat. # 14070-99, Hach
- Starch soluble for iodometry cat. # 516-100, Fisher

- Sodium sulfite solution (Na<sub>2</sub>SO<sub>3</sub>) Dissolve 0.157 g of Na<sub>2</sub>SO<sub>3</sub> in 100 mL of deionized water. This solution is not stable; prepare fresh daily.
- Potassium iodide (KI) solution Dissolve 10 g of KI in 100 mL deionized water. Mix well.
- Acetic acid (CH<sub>3</sub>COOH), 1:1 Mix 20 mL deionized water with 20 mL glacial acetic acid.
- Nitrification inhibitor 2-chloro-6-(trichloro methyl) pyridine (TCMP), cat. # 2533, Hach
- 65.7 External Quality Control Sample WatR Pollution Demand (ERA) or equivalent.

#### 7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Keep samples at or below 4 °C from the time of collection and analyze within 48 hours after collection.

#### 8.0 QUALITY CONTROL

- 8.1 Dilution water quality check: The dilution water blank, prepared in 6.1, serves as a check on quality of unseeded dilution water and cleanliness of incubation bottles. The DO uptake in 5 days must not be more than 0.20 mg/L. If this value exceeds 0.20 mg/L, then evaluate the cause and make appropriate corrections.
- 8.2 Glucose-glutamic acid check: The glucose-glutamic acid check solution is the primary basis for establishing precision and accuracy and is the principal measure of seed quality and analytical technique. For the 300 mg/L mixed primary standard, the average 5 days BOD must fall within the range of 198 ± 30.5 mg/L. If the average value falls outside this range, evaluate the reason and take appropriate actions. Consistently high values can indicate the use of too much seed suspension, contaminated dilution water, or the occurrence of nitrification. Consistently low values can indicate poor seed quality, use of insufficient quantity of seed suspension, or the presence of toxic materials. If low values persist, prepare a new mixture of glucose and glutamic acid and check the sources of dilution water and the seed.
- 8.3 Minimum residual DO and minimum DO depletion: Only the dilutions resulting in a DO depletion of at least 2.0 mg/L and a residual DO of at least 1.0 mg/L after 5 days of incubation are considered to produce valid data.
- 8.4 Seed Control: The DO uptake attributable to the seed should be between 0.6 -1.0 mg/L. The volume of seed added should be adjusted in order to meet the required range of  $198 \pm 30.5$  mg/L for glucose-glutamic acid check.

- 8.5 An external quality control sample with a known BOD value is analyzed each quarter.
- 8.6 The YSI dissolved oxygen meter is calibrated in air (water saturated), i.e. the probe is parked in a BOD bottle containing 1" of water.
- 8.7 Data acceptance criteria are listed in the data review checklist (Appendix A).
- **8.8** Laboratory participates in ERA WatR Pollution (WP) Proficiency Testing annually.

#### 9.0 PROCEDURE

- **9.1** Sample preparation:
  - 9.1.1 Prepare the sample run list for checking color, odor, pH and chlorine and for dilutions. (Appendix B)
- **9.2** Check samples for residual chlorine.
  - 9.2.1 Using the Hach Swiftest dispenser, insert DPD free chlorine reagent powder into each test tube, add about 10 mL of sample and observe for any color change occurring within a few seconds. A pink color indicates presence of chlorine and therefore the samples(s) must be dechlorinated.
  - 9.2.2 Determine the required volume of Na<sub>2</sub>SO<sub>3</sub> needed to dechlorinate on a 50 mL portion of the pH adjusted sample. Add 0.5 mL of 1:1 acetic acid (6.5.5), 0.5 mL of KI solution (6.5.4) and a few drops of starch solution to sample. Using a 50 mL buret, titrate with Na<sub>2</sub>SO<sub>3</sub> (6.5.3) solution to the starch-iodine (blue) end point. Record the volume used. Calculate and add the required volume of Na<sub>2</sub>SO<sub>3</sub> solution to the pH adjusted portion of the sample (9.3.3).

#### 9.3 Check sample pH

- 9.3.1 Label 1 L polypropylene beakers with the sample numbers. Pour about 500 mL of samples into 1 L beakers. Pour 100 mL of sample if it has strong sewage odor.
- 9.3.2 Calibrate the pH meter as stated in the meter directions. Standardize the pH meter using pH 4, 7 and 10 buffers. Record the slope and temperature in the logbook. Read each buffer after the calibration and record the results in the pH meter log.
- 9.3.3 Read the pH of each sample making sure they are stirred during the measurement. Adjust the pH of each sample to a final reading between 6.5 to 7.5. with 1N NaOH or 1M H<sub>2</sub>SO<sub>4</sub>. Record the final pH. Leave the pH meter on standby until the completion of the entire run for that day.

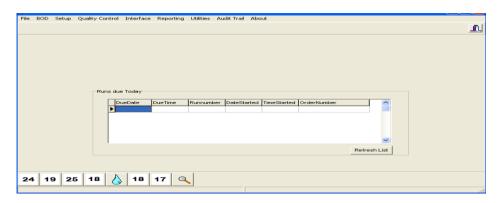
#### **9.4** Sample dilution:

9.4.1 Bring samples to BOD room temperature (20 °C) before making dilutions.

- 9.4.2 Check samples for color and odor.
- 9.4.3 Dilutions are prepared directly in BOD bottles. Transfer 200 and 100 mL aliquots of each prepared stream sample, 50, 25, 10 and 5 mL aliquots of each prepared sewage sample, and 10, 5, 1 and 0.5 mL aliquots of each prepared strong industrial wastes, as appropriate, into labeled BOD bottles using class A graduated cylinders and volumetric pipets. Rinse the cylinder between samples. Dilutions may need to be adjusted to reflect the qualities of the sample. Place the bottles in the correct order in the rack.
- **9.5** Nitrification inhibition:
  - 9.5.1 If nitrification inhibition is desired add 3 mg of TCMP (6.5.6) to each 300 mL bottle before capping.
  - 9.5.2 Note the use of nitrification inhibition in the reporting results.
- **9.6** Prepare autosampler using the "PC-BOD" software:
  - 9.6.1 Push the bottle containing 1" of water up to the probe to create a seal. Warm up YSI 5100 for at least 30 minutes. Calibrate the probe. Ensure that it is set in **REMOTE** mode.
  - 9.6.2 On the computer desktop locate the software icon.



Double click on the icon and the software will open to the main screen. If the icon is not present, open the software by clicking on the desktop 'Start' menu, followed by 'All Programs' and select 'PC-BOD'.

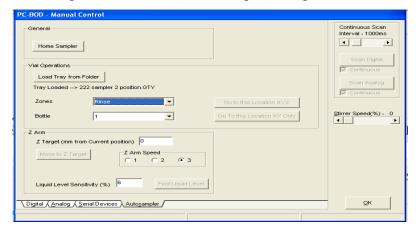


9.6.3 Under BOD select MANUAL.

- 9.6.3.1 Click on the 'Load Tray from Folder' button. The window shown at right will appear.
- 9.6.3.2 Click on the tray file named 271 sampler. and then click on the 'Open' button.



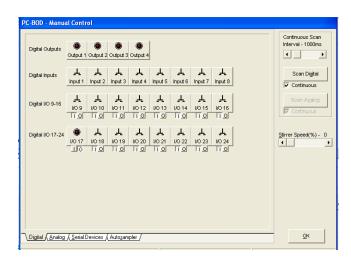
- 9.6.3.3 The **Home Sampler** button will become active and the 'zones' and 'bottle' windows will be filled in.
  - 9.6.3.4 Click on the 'Home Sampler' button. The sampler will move to the home position and the buttons to the right of zones' & 'bottles' will become active. If the sampler is already in the home position, it will appear that nothing is happening but within a few seconds the two buttons will become active. Remove the rack and place a waste beaker in bottle position 3.
  - 9.6.3.5 To move the autosampler to a specific location first select the following zone: -Bottle: allows DO probe to go into a bottle



- 9.6.3.6 Select the bottle location to move to by using the drop down menu. For example selecting 'Bottle' and '3' will allow the DO probe to go to the 3<sup>rd</sup> bottle position.
- 9.6.3.7 To move the autosampler to the specified location click on 'Go to this location XV only' to move above the bottle position.
- 9.6.3.8 To move the autosampler only in the Z direction (up and down), enter the number of millimeters to move in the box next to 'Z Target (mm from current position)'. Use a '-' sign before the number of millimeters to indicate moving in a downward direction. Click 'Move to Z Target' to move the sampler. For example, entering -43 will move the Z arm down 43mm.

- 9.6.3.9 Move the autosampler to bottle location **3** and lower it into a waste collection beaker by moving the autosampler down the Z axis by three **-43mm** increments.
- 9.6.4.0 Prime the pumps with the seed, nutrient water and rinse water.9.6.4.1 Open 'Digital' Tab: This tab allows the pumps and stirrer to be turned on or off. Click on the button listed below to turn the device on or off.

Output 1 - dilution pump Output 2 - seed pump Output 3 - inhibitor pump Output 4 - DO probe stirrer Output 17 - rinse pump



9.6.4.2 Turn on the seed pump,(**Output2**),

ensuring that all the rinse water left in the line has been emptied into the waste beaker and the seed is being drawn completely through the line. Turn it off when the seed is dripping into the waste beaker.

- 9.6.4.3 Turn on the dilution pump, (**Output 1**), ensuring that all the rinse water left in the line has been emptied into the waste beaker and the nutrient water is being drawn through the line. Turn it off.
- 9.6.4.4 Return the Autosampler to the home position.
  - 1. Open the **Autosampler** tab.
  - 2. Click on 'home sampler'
  - 3. Click '**OK**'.
- 9.7 If there are no excessive delays in executing steps 9.6.3 to 9.6.4.4 continue to 9.8 in order to start the run. An example of a delay would be, if dilution water is too high and needs to be degassed or the instrument malfunctions and needs to be restarted. In the case of significant delays, it is best to recalibrate the probe after the problems are resolved and running conditions are favorable and then proceed to section 9.8
- **9.8** Setting up a run manually.
- 9.8.1 From the run screen (**BOD/Run BOD**), click on the '**Edit'** followed by the '**Add X Rows**' button. Enter the number of rows that need to be added to the one

- already on the grid to give one row per bottle in the run. Click 'OK' and the rows will be added.
- 9.8.2 Build the batch starting with one stabilizing water blank, two duplicated water blanks, three seeds at 10, 15 and 20 mL, two duplicated mixtures of 5 mL of G/G with 2-3 mL of seeds followed by 2 to 5 different dilutions of each sample plus 2-3 mL of seeds. See appendix C for an example run and enter as shown.
- 9.8.3 Fill in the columns on the template. To remove extra lines, click the 'Delete Highlighted Sample' button. Do not leave blank lines in the template.
- 9.8.4 Click '**Done Edit**' and the batch will be setup.
- 9.8.5 Click the 'Auto-Generate Order Number' button. Enter operator's initials in the box in the upper left corner of the screen.
- 9.8.6 Load marked bottles into the autosampler racks.
- 9.8.7 Place the rack containing the first samples onto the autosampler.
- 9.8.8 Press the '**Start**' button to begin calibration and sample analysis. When prompted enter the rack number currently on the autosampler and press '**OK**'.
- 9.8.9 Following the screen prompts with regard to calibrating the autosampler and recording the results in the book.
- 9.8.10 Continue following the screen prompts to allow the auto dilutor to seed, dilute and take an initial D.O. reading of all the samples in the rack. If there are multiple racks the program will prompt for insertion of them at the correct time.
- **9.9** When a sample is supersaturated.
  - 9.9.1 Stop, delete initial DO readings higher than 9.2.
  - 9.9.2 Shake the diluted, seeded sample in the designated container to remove excess DO
  - 9.9.3 Restart the run and the autosampler will begin with the first sample without a reading.
- **9.10** Using the manual BOD probe
  - 9.10.1 In the case of instrumental error or malfunction that cannot be resolved, the sample can be run manually using the stand alone BOD probe. Calibrate probe as in 9.12.1 then press mode button to place in read mode.

- 9.10.2 Add required amount of seed and dilution water to the sample. Turn on timer and stirrer for 30s. Then hit the read button on the meter and record the DO reading. Follow this step for each sample.
- 9.11 Incubation: After all the samples in a rack have been diluted, seeded and had an initial DO reading taken, remove the rack from the autosampler. Place a stopper and cap on each bottle before incubating the sealed bottles for 5 days in the 20°C incubation room with the lights turned off.

#### **9.12** Read final DO:

- 9.12.1 Turn on the YSI 1500, push the bottle up to seal it to the probe and allow to meter to warm up for 30 minutes. On the DO meter, press **Calibrate** and then press **Autocal**. Note the readings in the log book. Press the '**Mode**' button then choose '**Remote**' from among the options.
- 9.12.2 Loading an Existing Run in the computer.
- 9.12.2.1 Open the 'PC BOD' program.
  - 9.12.2.2 On the main screen click on 'BOD' and then select 'Run BOD'
  - 9.12.2.3 Choose the 'Load Existing Runs' tab. On this screen there are 4 buttons which indicate runs in various stages of completion. Choose 'Finals Due Today' and highlight the row containing the appropriate run.
  - 9.12.2.4 Click on 'Load Selected' Enter the operators initials in upper right window.
  - 9.12.2.5 Place the rack with the samples to be run onto the autosampler.
  - 9.12.2.6 Check instrument tubing is free from pinching and that rack is seated properly.
  - 9.12.2.7 Make sure all caps are removed from BOD bottles.
  - 9.12.2.8 To begin the run click on the '**Start**' button and enter the number of the rack currently on the autosampler when prompted.

#### **9.13** Regular maintenance of BOD probe

- 9.13.1 Prepare the oxygen probe electrolyte by filling the bottle included with the kit to neck with deionized water. Shake well until crystals are dissolved.
- 9.13.2 Remove the old membrane cap assembly from the probe. Wipe clean the metal tip of the probe.

- 9.13.3 Take a new membrane cap assembly and fill in with the fresh electrolyte solution and then screw the cap assembly onto the probe.
- 9.13.4 Always park the probe in a BOD bottle containing one inch of D.I. water when not in use.

#### 10.0 DATA ANALYSIS AND CALCULATIONS

- 10.1 All the calculations are preformed automatically by BOD Analyst software using the following equations:
  - 10.1.1 Amount of dissolved oxygen consumed during the incubation period:

 $O_2$  Depletion (mg/L) = Initial DO - Final DO

10.1.2 Seed factor used for correcting the BOD test for oxygen depletion resulting from the presence of seed:

Seed

Factor (mg/L) = 
$$\frac{O_2 \text{ Depl in seed control}}{\text{Vol seed in seed control}} \times \text{Vol seed in sample}$$

10.1.3 BOD of the samples:

$$BOD (mg/L) = \frac{O_2 Depl in sample - Seed Factor}{Model Model Mod$$

- 10.2 If more than one sample dilution meets the acceptance criteria, report the average calculated by the software program.
- 10.3 If the O<sub>2</sub> depletion is less than 2 mg/L with 200 mL portion (maximum sample volume) of the sample, report the result from this dilution.
- 10.4 If all the sample dilutions produce a final DO of less than 1.0 mg/L, report the result from the highest dilution with a > sign.

#### 11.0 DATA AND RECORDS MANAGEMENT

- 11.1 All Quality Control data are kept in a binder labeled as "Quarterly QC for BOD".
- 11.2 Normal turnaround time for BOD samples submitted to this lab is 7 to 10 days from receipt with a sample holding time of 2 days. Results are reported in writing on a sample analysis request form.
- 11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the CONTROLLED DOCUMENT Do Not Copy

option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five years custody period.

#### 12.0 WASTE MANAGEMENT

- 12.1 It is laboratory's responsibility to comply with all state, federal and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions, and to protect the air, water and land buy minimizing and controlling all releases from fume and bench operation.
- 12.2 Samples and standards are poured down the drain while large amount of water is running.

#### 13.0 REFERENCES

- **13.1** United States Environmental Protection Agency, *Methods for Chemical Analysis of Water and Waste*, Method Number 405.1, August, 1993.
- 13.2 American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 21st Edition, Method 5210 B, 2005.
- 13.3 YSI BODANALYST Operations Manual, 1999.
- **13.4** YSI 5905/5010 BOD Probe Instruction Manual, 1999.
- 13.5 PC-BOD Operator's Manual Man Tech 2009
- 13.6 Division of Environmental Chemistry, Maryland Department of Health and Mental Hygiene, *Quality Assurance Plan*, SOP No. CHEM-SOP-QAP
- 13.7 Division of Environmental Chemistry and Division of Microbiology, Maryland Department of Health and Mental Hygiene, *Quality Manual*, SOP No. QA-SOP-QM

# APPENDIX A

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

# Data Review Checklist -BOD5

Date Collected:	Date Analyzed:	Analyst:	
Procedure	Acceptance Criteria	Status*	Comments
Holding Time	48 hours @ 4 °C		
Chlorine	Neutralized if present		
рН	Between 6.5 to 7.5; adjusted if out of range		
Initial DO	< 9.20 mg/L at 20 °C		
Incubation Period	5 days		
DO uptake of dilution water	< 0.20 mg/L		
DO uptake of seeded dilution water (seed factor)	0.60 to 1.00 mg/L		
BOD <sub>5</sub> for Glucose/Glutamic Acid (G/GA) solution	198 <u>+</u> 30.5 mg/L		
Sample dilutions	Meet the requirements: Final DO 2' 1.00 mg/L and DO depletion 2' 2.00 mg/L		
•	Decide on the value to be reported if requirements are not met.		
External QC <sup>2</sup>	Last date analyzed		
Analyzed quarterly	Within acceptable range		
Decimal Places Reported	1		
Reported Values	2' 2 mg/L; concentrations below this value reported with < sign for Chesapeake Bay samples; as < 2 mg/L for all other samples.		
Changes/Notes	Clearly stated		
nclude beginning and ending numbers, accou	nt for gaps by bracketing.		
Analyst's Signature & Date	Reviewer's Signat	ure & Date	

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# Division of Environmental Sciences INORGANICS ANALYTICAL LABORATORY

### Sample Run Log -BOD<sub>5</sub> Standard Method 5210 B

Date:	Collection Date:	Analyst:
Datc	Collection Date:	Allalyst.

Lab #	Sample Type	Dilution	Color	Odor	Cl	Chl. Neutr	pН	pH Adj. to
1.								
2.								
3.								
4.								
5.								
6.								
7.								
8.								
9.								
10.								
11.								
12.								
13.								
14.								
15.								
16.								
17.								
18.								
19.								
20.								
21.								
22.								
23.								
24.								
25.								
26.								

Sample Name	Tracking ID
pH 4 Buffer	
pH 7 Buffer	
pH 10 Buffer	
Seeds	

Sample Name	Prep Log ID
H <sub>2</sub> SO <sub>4</sub> , 1M	
NaOH, 1N	
Dilution water	
G/GA	

# APPENDIX C

Division of Environmental Chemistry
INORGANICS ANALYTICAL LABORATORY

# **EXAMPLE OF BATCH**

Bottle#	Sample name	Sample Volume (mL)	Seed Volume(mL)
1	Calib		
2	Blank		
3	Blank		
4	Blank		
5	Seed		10
6	Seed		15
7	Seed		20
8	BOD GGA	5	3
9	BOD GGA	5	3
10	WW 1111	100	3
11	WW 1111	200	3
12	WW E12001111001	50	3
13	WW E12001111001	100	3
14	WW E12001111001	200	3
15			

# APPENDIX D

Division of Environmental Sciences
INORGANICS ANALYTICAL LABORATORY

# **Troubleshooting**

PROBLEM	CAUSE	SOLUTION
Autosampler jam.	Tangled lines.	Straighten the lines. Exit the Run. Home the Sampler. Reload the Run.
D.O. readings inconsistent/ unexpected.	Probe membrane no longer intact.	Change membrane.
Initial Blank readings too high.	Dilution water supersaturated.	Degas carboy with Helium gas for 30 seconds.
Initial Sample readings too high.	Sample is supersaturated.	Stop the Run. Pour diluted sample into a shaker and shake for 30 seconds. Return to BOD bottle and replace in rack. Delete the D.O. reading in EDIT mode. Restart the run.

SOP Title: Determination of Turbidity by Nephelometry

(EPA Method 180.1)

SOP No.: CHEM-SOP-EPA 180.1

Revision: 3.5 Replaces: 3.4 Effective: 5/1/22

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4/25/2022

Signature

Date

OA Officer:

Manager:

Cynthia Stevenson

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O4/25/2022

Date

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SOP No.: CHEM-SOP-EPA 180.1

EPA Method 180.1

Revision	Date	Changes	Made By	Effective Date
0.0	6/3/08	N/A	Taiyin Wei	6/2/08
1.0	12/09	Tracking IDs for standards and reagents	Taiyin Wei	1/10
2.0	1/11	New SOP tracking number	Asoka Katumuluwa	1/10
2.0	6/13	Reviewed SOP	S. Ameli	6/13
3.0	10/20/14	Changed format	L. Phillips/J. Fernandez S. Ameli	12/1/14
3.0	6/1/15	Reviewed	L. Phillips S. Ameli	7/1/15
3.1	5/3/16	Reviewed and updated formatting and checklist	L. Phillips S. Ameli	7/1/16
3.2	5/2/17	Reviewed and updated formatting and checklist	L. Phillips/J. Fernandez S. Ameli	7/1/17
3.3	6/4/18	Reviewed SOP, updated section 8.6 and 13.6	L. Phillips/J. Fernandez S. Ameli	7/1/18
3.3	3/1/19	Reviewed SOP	L. Phillips/J. Fernandez S. Ameli	3/4/19
3.4	4/21/20	Reviewed SOP and edited for clarity.	L. Phillips J. Fernandez	5/1/20
3.4	4/9/201	Reviewed SOP	L. Phillips J. Fernandez	5/1/21
3.5	4/21/22	Reviewed SOP, update 5.2, 6.2 and sample run log	L. Phillips J. Fernandez	5/1/22

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#### STANDARD OPERATING PROCEDURES

# DETERMINATION OF TURBIDITY BY NEPHELOMETRY EPA Method 180.1

#### 1.0 SCOPE AND APPLICATION

- 1.1 Turbidity is a principal physical characteristic of water and is an expression of the optical property that causes light to be scattered and absorbed by suspended matter or impurities that interfere with the clarity of the water.
- 1.2 Determination of turbidity is a common component of water quality assessments. This method is applicable to drinking, ground, waste and saline waters.
- 1.3 The applicable range of Hach 2100AN Turbidimeter is 0 to 4000 nephelometric turbidity units (NTU). Drinking water samples with turbidity values greater than 40 NTU are diluted and re-analyzed.

#### 2.0 SUMMARY OF METHOD

- 2.1 This method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of light scattered, the higher the turbidity.
- 2.2 Readings in NTUs are made using a nephelometer. Detectors of the nephelometer are in place to measure the 90° scattered light, the forward scattered light, the back scattered light and the light transmitted through the sample. The laboratory measures the value in the "Ratio On" mode, in which the instrument's microprocessor uses a mathematical calculation to ratio signals from each detector. The benefits of applying "ratio" on measurements include better linearity, calibration stability, wide measurement range, and the ability to measure turbidity in the presence of color.

#### 3.0 INTERFERENCES

- **3.1** Etched, scratched, or dirty sample vials or dust contamination within the sample cell compartment and optical compartment scatter light and give inaccurate readings.
- **3.2** Samples containing air bubbles, coarse debris, or floating sediments can cause erroneous readings.

#### 4.0 HEALTH AND SAFETY

- 4.1 Good laboratory practices should be followed during inversion of sample and reading of sample result. Use absorbent towels if material is spilled and wash residual into drain.
- **4.2** Each employee is issued a *Laboratory Safety Manual* and is responsible for adhering to the recommendations contained therein.
- 4.3 Use absorbent towels if material is spilled and wash residual into drain.
- **4.4** A binder of MSDS is available.

#### 5.0 EQUIPMENT AND SUPPLIES

- **5.1** Equipment
  - 5.1.1 Hach Model 2100AN Laboratory Turbidimeter or equivalent- consisting of a nephelometer with a tungsten-filament lamp for illuminating the sample and detectors to measure scattered light.
  - 5.1.2 Computer
  - 5.1.3 Printer

# 5.2 Supplies

- 5.2.1 Sample cells 30 mL capacity, item # 20849-00, Hach Co.
- 5.2.2 Pipettes plastic, graduated and glass, class A, various sizes as needed.
- 5.2.3 Flasks Volumetric, class A, 50 mL, 100 mL and 200 mL
- 5.2.4 Cylinder plastic, graduated, various volumes as needed.
- 5.2.5 Gloves Powder-free, nitrile, item #FF-700, Micro Flex.
- 5.2.6 Kimwipes 14.7 x 16.6", item #34721, Kimberly-Clark.
- 5.2.7 Carboy  $2^{1}_{2}$  gal, with spigot, item # 23210020, Nalgene.
- 5.2.8 Container Plastic, for liquid waste, 1 or 2 liter size.

#### 6.0 REAGENTS AND STANDARDS

- **6.1** Reagents
  - 6.1.1 Deionized water.
  - 6.1.2 Hydrochloric acid, 6N Fisher Scientific #LC15370-Z.

#### **6.2** Standards

- 6.2.1 AMCO CLEAR Calibration Kit, for Hach 2100N/AN: 0, 20, 200, 1000, and 4000 NTU Item # 85525, GFA Chemical or equivalent calibration kit. Use freshly poured portions for calibrating the turbidimeter and discard the used standards prior to each new calibration. Rinse with DI water and new standard before pouring fresh standards.
- 6.2.2 AMCO CLEAR Sealed Standards: 0.5, 1.0, 2.0, 5.0, 20, 50, 100, and 200 NTU Item # 86180, 86443, 86534, 86492, 86122, 85385, 86124, and 86123 respectively, GFA Chemicals or equivalent standards. Read these standards at the beginning of each analytical run.
- 6.2.3 Quality Control Sample ERA WatR Supply Turbidity or equivalent QC sample. Follow manufacturer's directions.

#### 7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 7.1 Samples are collected in liter polyethylene cubitainers and refrigerated or iced to 4 °C until analysis to minimize microbiological decomposition of solids.
- 7.2 The holding time is 48 hours when preserved at 4 °C.

#### 8.0 QUALITY CONTROL

- **8.1** Instrument Calibration
  - 8.1.1 Primary standards (6.2.1) with concentrations ranging from 0 to 4000 NTU are used to calibrate the turbidimeter every two months.
  - 8.1.2 Sealed secondary standards (6.2.2) with concentrations ranging from 0.5 to 200 NTU are analyzed before each day's run of samples. The instrument check is considered valid when each measured NTU value is within 90 110% of its true value. If the values do not fall within the acceptable range the instrument has to be recalibrated using the primary standards (6.2.1) or new standards should be ordered.
  - 8.1.3 AMCO Clear standards are guaranteed to maintain the certified value for 1 year from ship date.

- **8.2** A mid-range check standard is analyzed after every ten samples and at the end of each run. If a check standard fails, the samples between the last satisfactory check standard and the unsatisfactory standard are re-analyzed.
- 8.3 Every tenth sample is analyzed in duplicate. The accepted value for the relative percent difference (RPD) is  $\pm$  10 %. If the reading does not fall within the accepted ranges, the corresponding analysis is repeated.
- 8.4 Deionized water is run at the beginning, after every ten samples, and at the end of the run. The accepted value for the blank is less than 0.07 NTU. Routine maintenance includes periodically clean sample cells. Also see Section 9.5.3.
- **8.5** A quality control sample is analyzed quarterly. Results are kept in a binder next to the instrument.
- 8.6 The U.S. EPA MDL40 procedures CFR Part 136, Appendix B) including the EPA Definition and Procedure for the Determination of the Method Detection Limit, Revision (2016); EPA Methods Update Rule (Final rule August 28, 2017); EPA Method Detection Limit Frequent Questions; and EPA Part 136 Method Update Rule Revisions to Appendix B MDL Procedure as Applied to Drinking Water (October 2017), are used for carrying out the method detection limit studies as calculated annually. The acceptance criteria as stated in the CFR document and revision are those used to determine the demonstration of capability and performance of an analytical method, as applicable.
- 8.7 Data acceptance criteria are listed on the data review checklist (Appendix A).

#### 9.0 PROCEDURE

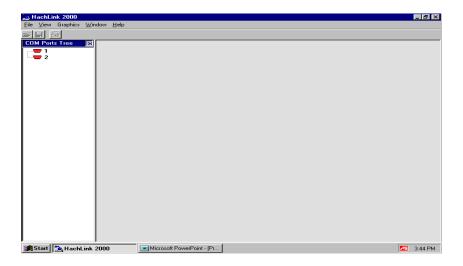
- **9.1** Sample Cell Preparation
  - 9.1.1 Clean the samples cells meticulously, both inside and out, and the caps.
  - 9.1.2 Wash the sample cells with soap and rinse with deionized water.
  - 9.1.3 After rinsing, immediately soak the sample cells in a 6N hydrochloric acid solution for a minimum of one hour.
  - 9.1.4 After soaking, immediately rinse the sample cells with deionized water. Rinse a minimum of 15 times.
  - 9.1.5 Immediately after rinsing the sample cells, cap the cells to prevent contamination from the air, and to prevent the inner cell walls from drying out.
  - 9.1.6 Sample cells that are nicked or scratched must be replaced.

## 9.2 Index New Sample Cells

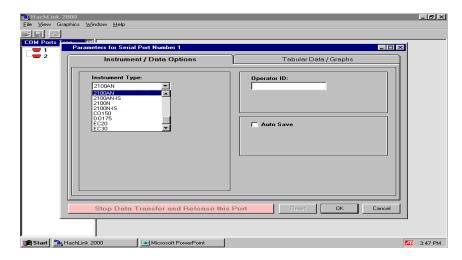
- 9.2.1 Fill clean sample cells with deionized water to the fill ring mark. Let samples stand for 30 seconds to allow bubbles to rise.
- 9.2.2 Measure the turbidity at several points of rotation, or as many points as needed, starting with placing the sample cell into the holder with the diamond mark at 6 o'clock position. Mark the orientation where the turbidity reading is the lowest. Use this orientation to perform all sample measurements.
- 9.2.3 Use the same indexed sample cell, if possible, to measure all the samples.

### 9.3 Instrument Start-up

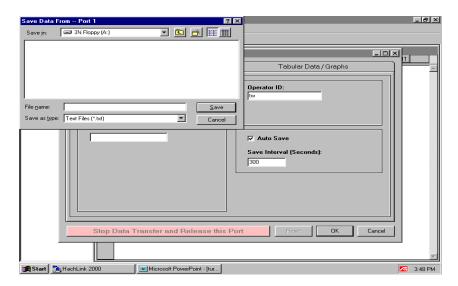
9.3.1 Leave the turbidimeter on 24 hours a day if the instrument is used daily. Make sure "Ratio", "Sample" and "Signal Average" keys are in "ON" mode displayed by a green light. Maintain "Range" key in "Auto" mode. Select "NTU" from "Units/Exit" key. Turn on the computer. Insert the disk marked as "Turbidity Data". Click on "Hachlink" on the desktop.



- 9.3.3 Select "COM Port 1" as the port type by clicking on "1".
- 9.3.4 Select "2100AN" from the pull down menu of instrument types.

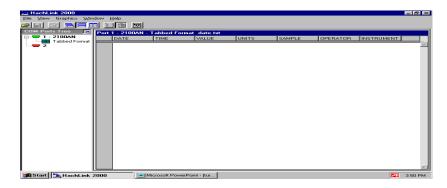


9.3.5 Enter operator I.D. and select "Auto Save".



# **9.4** Instrument Calibration

9.4.1 Select "Free Format" for calibration. Enter Date (Cal MM-DD-YY) as file name and click on "Save".



- 9.4.2 Press "Cal Zero". When 00 flashes in green display proceed. Do not shake or mix standards.
- 9.4.3 Place the "0" NTU standard into the cell holder, align the mark, then close the cell cover.
- 9.4.4 Press "Enter". The instrument display counts down from 60 to 0, and then makes a measurement.
- 9.4.5 The instrument automatically increments to the next standard, 01, as shown on screen in green display. Repeat steps 9.4.3 and 9.4.4 with the rest of the standards: 200, 1000 and 4000 NTU (When the instrument asks for 7500 NTU, press "Cal" to end it.)
- 9.4.6 Press "Cal Zero" again to store calibration information into memory. Press "Print". The instrument returns to the sample measurement mode.
- 9.4.7 Press "Cal" key to review Calibration Data. Use "L" key to scroll through the standards. Press the "Print" key prints all of the calibration data in effect. Press the "Units Exit" key to return to the operating mode.
- 9.4.8 Read sealed secondary standards
  - 9.48.1 Follow step 9.3. Select "Tabled Format" for sample reading. Enter date as file name. Start with the deionized water as the blank. Thoroughly clean the outside of the sample cell and place it in the sample compartment. Close the sample holder cover.
  - 9482 Press "Enter", then press "Print" to save the reading.
  - 9483 Thoroughly clean each of the standard vials. Repeat steps 9.3.8.1 and 9.3.8.2 for all the standards: 0.5, 1.0, 2.0, 5.0, 20.0, 50.0, 100, and 200 NTU.
- 9484 Press "Print". Keep the printouts in the binder marked "Instrument calibration data".
  - 9.4.9 Check and fill the carboy with deionized water for rinsing the sample cell when performing sample measurements.

#### **9.5** Sample Analysis

9.5.1 Prepare the list of samples for turbidity on the sample run log sheet (Appendix B) starting with blank, the daily check standards of 0.5, 1.0, 2.0, 5.0, 20, 50, 100, and 200 NTU, the deionized water, then enter each sample

- number. Measure one replicate, one check standard and one blank for every ten samples. Read check standards again at the end of the run.
- 9.5.2 Follow step 9.3. Select "Tabled Format" for sample reading. Enter date as file name.
- 9.5.3 Fill the clean and dry glass cell with deionized water. Wipe dry, then insert the cell. If the reading is greater than 0.07 NTU, the cell should be cleaned with detergent and the process repeated. Press "Enter" to clear all previous data, and then press "Print" to transmit data to computer and printer.
- 9.5.4 Place the 0.5 NTU sealed standard in the sample compartment. Close the cover. Press "Enter" and then press "Print".
- 9.5.5 Repeat for the rest of the standards.
- 9.5.6 Allow samples to reach room temperature to prevent fogging of the cell. Thoroughly mix the sample by gentle inversion. Do not shake. Quickly remove cap and pour approximately 20 ml of sample into the cell for rinse. Immediately fill cell with sample to volume line, wipe dry and insert into turbidimeter. Align the index mark (9.2) on the cell with the raised mark on the spill ring around the cell holder opening. Be sure the cell has been pushed down completely and is held in place by the spring clip. Close the cover.
- 9.5.7 Wait for 30 seconds. Check the turbidity reading of the sample from the digital display. Press "Enter", then press "Print" to save the first stable reading at approximately 15 seconds. If the turbidity reading fluctuates, take the cell out, invert to mix well and measure again. Observe the results in the display for accuracy.
- 9.5.8 Read the rest of the samples according to the run log sheet following step 9.5.6 and 9.5.7. Rinse the cell with deionized water, then rinsed with some of the sample before each sample measurement.
- 9.5.9 For drinking water sample with turbidities exceeding 40 NTU, dilute the sample with turbidity-free water until turbidity falls below 40 NTU.
- 9.5.10 After reading all samples, double click the blank area outside the table to go to "Microsoft Excel" table. Enter all sample identifications according to the run log sheet into the sample column. Print out the results.

#### 10.0 DATA ANALYSIS AND CALCULATIONS

- **10.1** Calculate and report the average for the duplicated samples.
- Multiply sample reading by the dilution factor to obtain the final result for diluted samples.
- 10.3 Calculate the relative percent difference for the duplicated samples as follows:

# RPD =

# differencebetweenthe duplicates average of the duplicates x 100

10.3 All results are reported to one decimal place. The reporting level (RL) is 0.5 NTU. All sample concentrations below this value are recorded as less than 0.5 NTU (< 0.5 NTU).

#### 11.0 DATA AND RECORDS MANAGEMENT

- 11.1 Normal turnaround time for samples submitted to this lab will be 2 to 10 days from receipt. Results are reported in writing on a sample analysis request form.
- 11.2 Instrument maintenance, instrument calibration, and quality control data are kept in binders and test results are kept in the file cabinet.
- 11.3 The Division shall retain all pertinent laboratory records for each sample for a period of five years. At the conclusion of this period, clients shall be given the option to take custody of their sample records. The Division shall not be responsible for retrieving, copying, or transferring laboratory records exceeding the five years custody period.

#### 12.0 WASTE MANAGEMENT

- 12.1 It is laboratory's responsibility to comply with all state, federal and local regulations governing waste management, particularly the hazardous waste identification rules and disposal restrictions, and to protect the air, water and land buy minimizing and controlling all releases from fume and bench operation.
- 12.2 Samples and standards are poured down the drain while large amount of water is running.

#### 13.0 REFERENCES

- **13.1** United States Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes*, Method 180.1 Revision 2.0, August, 1993.
- 13.2 Hach Company, Model 2100AN Laboratory Turbidimeter Instruction Manual, 1993.
- 13.3 Hach Company Technical Information Series Booklet No. 11, *Turbidity Science*, 1998.
- 13.4 The American Public Health Association, *Standard Methods for the Examination of Water and Wastewate*, Method, 21<sup>th</sup>Edition, 2005.
- 13.5 Division of Environmental Chemistry, Maryland Department of Health and Mental Hygiene, *Quality Assurance Plan*, SOP No. CHEM-SOP-QAP
- 13.6 Division of Environmental Chemistry and Division of Microbiology, Maryland Department of Health and Mental Hygiene, *Quality Manual*, SOP No. QA-SOP-QM.
- 13.7 EPA 'Definition and Procedure for the Determination of the Method Detection Limit, Revision 2. Dec 2016.

# APPENDIX A

Division of Environmental Sciences INORGANICS ANALYTICAL LABORATORY

Date Collected:	Date Analyzed:	Analy	st:
Procedure	Acceptance Criteria	Status*	Comments
Holding Time	48 hours @ 4 °C		
Instrument Calibration <sup>2</sup> (0 - 4000 NTU)	Every two months		
Daily Calibration Checks <sup>3</sup> (0 - 200 NTU)	Within 90 to 110% of true values		
Blank	< 0.07 NTU		
Check Standards	After every 10 <sup>th</sup> sample and at the end of the run		
Check Standards	Concentrations within 90 to 110% of the true values		
Duplicates/Replicates	Every 10 <sup>th</sup> and the last sample or 1/batch of drinking water samples and 1/batch of wastewater samples, if less than 10 samples of each kind		
	RPD :: 10 %		
External QC <sup>4</sup>	Within acceptable range		
Every two months	Last date analyzed:		
Decimal places reported			
Reporting Level	0.5 NTU; concentrations below this value reported as < 0.5 NTU		
Measured Values	Within range of 0 to 40.0 NTU for drinking water and 0 to 4000 NTU for others		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		
Check (□) if criteria are met.			
analyst's Signature& Date	Review	wer's Signature	& Date
upervisor's Signature & Date			
Include beginning and ending i	numbers; account for gaps by bracketing.		
Sample Name: AMCO CLEAR Ca	alibration kit Tracking ID:		

# APPENDIX B

# Division of Environmental Sciences INORGANICS ANALYTICAL LABORATORY

# Sample Run Log - Turbidity EPA Method 180.1

Date:	Analyst:
2	111111 500

Sample #	Sample ID	Dilution	Conc. NTU
1	0.0 NTU		
2	0.5 NTU		
3	1.0 NTU		
4	2.0 NTU		
5	5.0 NTU		
6	10.0 NTU		
7	20.0 NTU		
8	50.0 NTU		
9	100 NTU		
10	200 NTU		
11	DI Water		
12			
13			
14			
15			
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21			
22			
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24			
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26			
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28			
29			
20	İ		

	1		I
Sample #	Sample ID	Dilution	Conc. NTU
31			
32			
33			
34			
35			
36			
37			
38			
39			
40			
41			
42			
43			
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57			
58			
59			

QC Name	Prep Log ID

Lab #	Average	RPD

# MARYLAND DEPARTMENT OF NATURAL RESOURCES CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

University of Maryland, Chesapeake Bay Laboratory - Nutrient Analytical Services Laboratory <a href="https://www.umces.edu/nasl/methods">https://www.umces.edu/nasl/methods</a>

Visit the website and click on any of the parameters to download the SOP

## **Water Column Chemistry**

- Ammonium Method
- Cadmium Nitrate Method
- Enzyme-Catalyzed Nitrate Method
- Nitrite Method
- Orthophosphate Method
- Silicate Method
- Total Dissolved Nitrogen and Total Nitrogen Enzyme-Catalyzed Method Total
- Dissolved Nitrogen and Total Nitrogen Cadmium Nitrate Method
- Total Dissolved Phosphorous and Total Phosphorous Discrete Photometric Analyzer Method
- Total Dissolved Phosphorous and Total Phosphorous Auto Analyzer II Method
- Total and Dissolved Organic Carbon Method

#### **Particulates and Sediments**

- Particulate Carbon and Nitrogen Method
- Particulate Phosphorous and Particulate Inorganic Phosphorous Method Particulate
- Biogenic Silica Method
- Total Suspended Solids and Total Volatile Solids Methods
- Chlorophyll Fluorometric Method
- Chlorophyll Spectrophotometric Method

#### **Other Chemistries**

- Hardness Method
- Inorganic Carbon and Alkalinity Method
- Biochemical Oxygen Demand (BOD) Method
- Dissolved Metals
- Ion Chromatography Anions Method
- Specific Conductance Method