MARYLAND DEPARTMENT OF NATURAL RESOURCES

SECTION 106

AMBIENT WATER QUALITY MONITORING

(CORE/TREND MONITORING)

QUALITY ASSURANCE PROJECT PLAN

MARYLAND
DEPARTMENT OF
NATURAL RESOURCES

CHESAPEAKE BAY AND WATERSHED PROGRAMS
MONITORING AND NON-TIDAL ASSESSMENT
CBWP-MANTA-MN-09-2

Martin O'Malley
Governor

Anthony G. Brown
Lt. Governor

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The Maryland Department of Natural Resources (DNR) seeks to preserve, protect and enhance the living resources of the state. Working in partnership with the citizens of Maryland, this worthwhile goal will become a reality. This publication provides information that will increase your understanding of how DNR strives to reach that goal through its many diverse programs.

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SECTION 106
AMBIENT WATER QUALITY MONITORING
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QUALITY ASSURANCE PROJECT PLAN

March 15, 2009

MARYLAND DEPARTMENT OF NATURAL RESOURCES
RESOURCE ASSESSMENT SERVICE
MONITORING AND NON-TIDAL ASSESSMENT DIVISION

Maryland Department of Natural Resources
Section 106 - Ambient Water Quality Monitoring
(Core/Trend Monitoring)
Quality Assurance Project Plan
July 1, 2008 – June 30, 2009

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ACRONYMS AND ABBREVIATIONS

AMQAW	Analytical Methods and Quality Assurance Workgroup (a workgroup of the Chesapeake Bay Program's Monitoring Subcommittee)
C	Carbon
CBP	EPA's Chesapeake Bay Program
CBPO	EPA's Chesapeake Bay Program Office
CBL	University of Maryland's Chesapeake Biological Laboratory
cm	Centimeter
CSSP	Coordinated Split Sample Program
DHMH	Maryland Department of Health and Mental Hygiene
MDNR	Maryland Department of Natural Resources
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EPA	U.S. Environmental Protection Agency
g	Gram
H_2O	Dihydrogen oxide (water)
L	Liter
m	Meter
MDE	Maryland Department of the Environment
min.	Minute
mg	Milligram
ml	Milliliter
mm	Millimeter
N	Nitrogen
NIST	National Institute of Science and Technology
NO_2	Nitrite
$NO_{2,3}$	Nitrate + nitrite
NO_3	Nitrate
P	Phosphorus
PC	Particulate carbon
PN	Particulate nitrogen
PO_4	Phosphate
PP	Particulate phosphorus
QAO	Quality Assurance Officer (unless otherwise noted, this refers to the DNR QAO)
QAPP	Quality Assurance Project Plan
RP	Replicate
TDN	Total dissolved nitrogen
TDP	Total dissolved phosphorus
TSS	Total suspended solids
USGS	U.S. Geological Survey
^oC	Degrees Celsius

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PROJECT MANAGEMENT

A4 Project/Task Organization

This section lists the individuals responsible for the major aspects of Maryland's Ambient Water Quality Monitoring Program. The flow of project tasks is indicated in Figure 1.

Director and Principal Investigator: Bruce Michael, Resource Assessment Service, MDNR. 410-260-8627, bmichael@dnr.state.md.us

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, management and data analysis of the program.

Quality Assurance Officer: Bruce Michael, Resource Assessment Service, MDNR. 410-260-8627, bmichael@dnr.state.md.us

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

Field Sampling Operations: Sally Bowen, Project Chief. Monitoring and Non-tidal Assessment Division, MDNR. 410-990-4528, sbowen@dnr.state.md.us and Laura Fabian, Monitoring and Non-tidal Assessment Division, MDNR. 410-990-4524, lfabian@dnr.state.md.us

Responsibilities: These individuals are responsible for administration of the field sampling activities including sample collection, sample storage and sample delivery to laboratories.

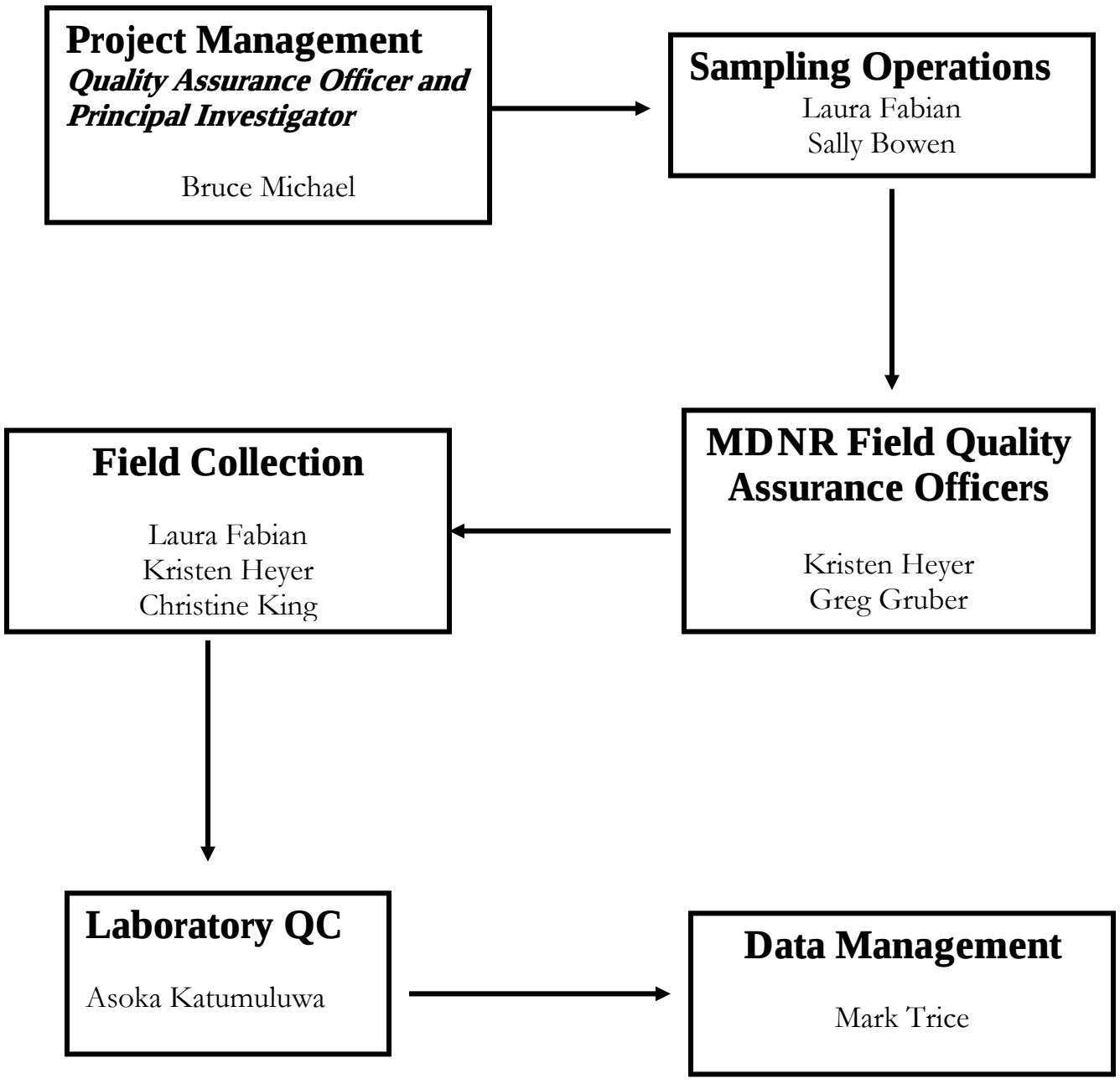
Laboratory Analyses/Water Column Chemistry: Asoka Katumuluwa, Program Director, Division of Environmental Chemistry, DHMH. 410-767-5034, katumuluwaa@dhmh.state.md.us

Responsibilities: This person oversees the laboratory that does all of the nutrient analysis and water chemistry for the Ambient Water Quality Monitoring Program.

Data Management; Mark Trice, Program Chief of Water Quality Informatics, Tidal Ecosystem Assessment, MDNR. 410-260-8642, mtrice@dnr.state.md.us

Responsibilities: This person 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.

Figure 1. Project Organization for Maryland's 106 Ambient Water Quality Monitoring Program



A5 Problem Definition/Background

Maryland DNR's Ambient Water Quality Monitoring Program (Core/Trend Monitoring) is part of a nationwide ambient monitoring effort designed to measure progress towards achieving EPA's national water quality goals. This program was initiated in 1974 to meet an EPA-mandated monitoring requirement for the State of Maryland to collect data that can be used to detect status and trends in the quality of the State's waters. To detect status and trends in Maryland's waters, ambient fixed stations were located in water use areas, problem areas, land use areas and in areas where future development may impact water quality. As of 1 July 1995, responsibility for Maryland's Ambient Water Quality Monitoring Program was transferred from the Maryland Department of the Environment to the Maryland Department of Natural Resources.

A6 Project/Task Description

Maryland's portion of this national ambient monitoring effort includes 37 Core stations located in non-tidal and tidal freshwater and estuarine areas and 25 Trend stations located on larger, non-tidal streams and rivers (4^{th} order and larger). A map of station locations is presented in Figure 2 and a description of each station is presented in Table 1. The 62 stations that comprise this monitoring program are sampled monthly, year-round, for physical and chemical parameters.

A6.1 Core Stations

Core Station selection was based upon EPA's Basic Water Monitoring Program (BWMP) manual (EPA 1976). The selection of stations for the Core network was guided primarily by the need to assess conditions in water use areas. These included recreational areas, surface water supply areas, land use areas and potential areas of development. Since these data are used in the national assessment program, both impacted and non-impacted areas were included in the network to ensure that the evaluation would not be biased. Sampling stations were also selected to be representative of various regions in Maryland. Where consistent with the aforementioned criteria, stations were located to maintain continuity with existing sites. Overall, the locations of the 37 stations cover the major freshwater rivers of the State that flow into the Chesapeake Bay and also bracket major population centers.

Water quality data are collected monthly from each of the 37 Core stations located throughout the State. Surface samples are collected at 29 freshwater Core stations, but at various depths at the 8 estuarine stations. Seventeen sampling stations in the western part of the State (located in the Youghiogheny, North Branch Potomac, or Upper Potomac River) are sampled for additional water quality parameters (sulfate and total dissolved solids) to monitor for the impacts of acid mine-drainage. For logistical reasons, samples for the 8 estuarine Core stations are collected during sampling for other Maryland DNR monitoring programs. Samples for stations CB2.1, CB3.3C, and CB5.1 are collected during Bay mainstem cruises, while ET5.2, XGG 8251, WT5.1, RET2.4 and TF2.3 are collected during tributary sampling (see Figure 2, estuarine Core stations are presented in orange). Sampling protocols for these 8 stations are outlined in this Quality Assurance Project Plan (QAPP). Sample analysis is conducted by the University of Maryland, Chesapeake Biological Laboratory, Nutrient Analytical Services Laboratory (NASL). The analytical methods utilized by NASL are detailed in Appendix VII of the Quality Assurance Project Plan for

Maryland DNR's Chesapeake Bay Water Quality Monitoring Program – Chemical and Physical Properties Component. The latest version of this Plan is available at: http://mddnr.chesapeakebay.net/eyesonthebay/documents/MainstemTributaries2008-2009QAPP.pdf.

Eleven stations (identified with an asterisk in Table 1) are also sampled separately as part of the Chesapeake Bay Program's Non-tidal Network (117(d)). For additional information on this monitoring program, please see Maryland DNR's Non-tidal Network, Quality Assurance Project Plan. The latest version of this QAPP is available at: http://www.dnr.state.md.us/streams/pubs/117_QAPP.pdf

A6.2 Trend Stations

In addition to the Core stations, water samples are also collected monthly, year-round, at an additional 25 freshwater Trend stations. These stations are sampled to enhance the amount of water quality information available for status and trends assessments in the freshwater portions of Maryland's larger streams and rivers.

Both Core and Trend water quality samples are collected and analyzed in the exact same manner and follow the same quality assurance and quality control protocols. Parameters and analytical methods are listed in Table 2.

A6.3 Schedule of Tasks and Projects

Maryland DNR's Ambient Water Quality Monitoring Program was initiated in its present form. Since this is an ongoing effort, the schedule and time required to complete each of the tasks (from sampling to data verification) associated with monthly collections are presented below.

Schedule for Monthly Sampling and Data Processing

Task	Time Required	Cumulative Time
Sample Collection	20 person days	3 weeks
Laboratory Analysis	1 week	4 weeks
Data Verification	1 week	5 weeks
Data Keypunching	1 week	6 weeks
Final Data Verification	2 weeks	8 weeks

Data analysis to determine status and trends in water quality are calculated after the data has undergone the quality assurance process. Status and trends have been calculated annually through 2006. Following this period, status and trends will now be calculated every 4 years (2010). Appendix I provides a complete description on how status and trends are calculated. Results will continue to be provided on the Internet at (http://www.dnr.state.md.us/streams/status_trend/index.html) as well as provided directly to Tributary Strategy workgroups. The primary reporting mechanism for this program is the State's integrated 305b/303d report. This report provides a comprehensive assessment of Maryland's waters incorporating MDNR's Ambient Water Quality Monitoring Program results with other intensive or routine water quality surveys within Maryland. The integrated report is submitted to EPA's regional office for review and approval. Draft and final versions are posted on Maryland Department of the Environment's website

(www.mde.state.md.us) for access by federal, state, and local agencies as well as other officials and the public.

A7 Quality Objectives and Criteria

Maryland DNR's Ambient Water Quality Monitoring Program is designed to provide laboratory and field data that will help the State of Maryland to detect status and trends in the quality of its' waters. Assessments of the quality of the data collected through this program can be expressed in terms of representativeness, comparability, completeness, accuracy and precision.

A7.1 Representativeness

Representativeness is the degree to which the sample data represent the actual conditions or concentrations present in the sampled population or area. Representativeness can be affected by experimental design and sample collection and handling. The experimental design (described in section A6) for this monitoring program requires monthly sampling (12 collections/year) for physical and chemical parameters on a pre-determined date, which is adequate for capturing long-term annual trends in concentration (Alden et al. 1994).

A7.2 Comparability

Comparability refers to the confidence with which one data set can be compared with another. Comparability must be ensured so that the results for one station are of comparable quality to other stations. In addition, the data generated by Maryland's Ambient Water Quality Monitoring Program must also be of comparable quality to the data generated by other states and laboratories. Comparability among data sets is assured through the use of consistent field methods and protocols, participation in the Analytical Methods and Quality Assurance Workgroup (AMQAW) and the use of field splits and blind audit samples. Comparability of monitoring data is achieved as a result of quality assurance procedures at each phase of data gathering and processing. It includes representative sampling and sample handling procedures, uniform laboratory methods and validation of laboratory data and procedures for reduction, validation and reporting of environmental data.

A7.3 Completeness

Completeness is a measure of the amount of valid data obtained compared to the amount that was expected under normal conditions. Completeness is a condition to be achieved in order to meet the data requirements of the program. Factors that can affect completeness include problems encountered by the field crews such as adverse weather conditions or equipment failures and laboratory-related issues such as sample preservation, exceeding holding times and accidents. To ensure that data are of the quality required to aid and support management decisions, Maryland's Ambient Water Quality Monitoring Program strives to provide monitoring data of known and consistent quality by generally following the guidelines outlined in 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 laboratory measurements of < 20 percent of the coefficient of variation; accuracy goals within 80 to 120 percent, and the completeness

goals of 90 percent.

A7.4 Accuracy

The accuracy (closeness to the true value) of the collected data is 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 preventative maintenance. Multiparameter field instruments are calibrated prior to field sampling to ensure accuracy. Where possible, standards used for calibration purposes are validated against a primary standard such as those available from the National Institute of Science and Technology (NIST). Daily quality control checks (including the running of blanks and standards) are used to control and assure laboratory accuracy.

Accuracy of laboratory results is also assessed through MDNR's participation in the Chesapeake Bay Coordinated Split Sample Program (CSSP), a split sampling program in which five laboratories involved in Chesapeake Bay monitoring analyze quarterly, coordinated split samples. 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. MDNR follows the protocols in the Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines (EPA 1991) and its revisions. Split samples are collected quarterly. Results are analyzed by appropriate statistical methods to determine if results differ significantly among laboratories. When a difference occurs, discussion begins regarding techniques and potential methods changes to resolve discrepancies and identify potential problems. Additionally, DHMH participates biannually in the USGS reference sample program and permits USGS to release the results to the Chesapeake Bay Program Quality Assurance Officer. Laboratory accuracy is 90-110% recovery.

A7.5 Precision

Precision (repeatability) measures the closeness of values for a parameter within a data set. Quality control samples along with appropriate statistical techniques are used to ensure precision in the production of laboratory data. Precision of the chemical analytical methods is determined and documented from duplicate analyses. DHMH performs precision calculations for laboratory duplicates. Every tenth sample is analyzed in duplicate. The acceptable value for the relative percent difference (RPD) is +/- 10%. If the calculated RPD does not fall within the acceptable range, the corresponding analysis is repeated. Precision of the entire measurement system for laboratory-analyzed parameters, including field processing, storage, and chemical analysis, can be assessed from duplicate field samples. Maryland DNR data analysts responsible for quality assurance checks examine field duplicate data. Based on preliminary analysis, there can be relatively large differences in measured values for certain water quality parameters. Maryland DNR's data management section is currently devising more robust procedures to address this issue in a statistically quantifiable manner.

A8 Special Training / Certification

Maryland DNR field personnel are required to demonstrate proficiency in all aspects of sample collection to the Chesapeake Bay Program Quality Assurance Coordinator, who conducts annual site visits to assure the continued proficiency of field personnel and adherence to the procedures specified in the Department's SOP. Training for field personnel who collect samples for the Ambient Water Quality Monitoring Program is provided by experienced field staff and the field Quality Assurance Officers (Greg Gruber and Kristen Heyer). All training and procedures adhere to the Standard Operating Procedures developed for the Ambient Water Quality Monitoring Program.

Like DNR field personnel, analysts working for DHMH are required to demonstrate proficiency in laboratory procedures. New analysts are trained by an experienced analyst on the laboratory procedures he/she will be assigned to perform. Training is documented using the Division's training forms and signed by the Supervisor and the Division Chief.

A9 Documentation and Records

Documenting sampling events is an important component of the Ambient Water Quality Monitoring Program. Field crews document all data obtained in the field on field sheets. Examples of the field sheets are provided in the Standard Operating Procedures #PR-03: Maryland Core/Trend Monitoring Program (Appendix II). Since the data generated by this program are not used for legal purposes, a formal chain-of-custody sheet is not required. Field sheets and any information regarding a specific problem and/or event during a sampling run, as well as modifications to the sampling program are maintained by MDNR field office staff.

A water quality monitoring field sheet is completed on arrival at each station. This form is used to record field measurements and other data pertinent to the collection of samples, including sample type and date and time of collection. An instrument specific calibration logbook is also used to record instrument calibration data, notes on instrument testing, and notes on instrument performance, problems and repairs.

Critical project personnel receive copies of the QAPP (please see distribution list on page vii). The QAPP and all associated SOPs referenced herein will be updated annually by June 30th. Any modifications to the QAPP will be reviewed and approved by personnel conducting the sampling, the principal investigators and MDNR's Quality Assurance Officer. Once approved, the final version will be made available to all interested parties by placing downloadable copies on the CBP's and MDNR's websites. Project reporting to management will be accomplished by quarterly progress reports of activities. Electronic summaries of provisional instantaneous water quality data will be provided on an annual basis. The final data set is stored in a local designated DNR database directory for data user access. Data requests should be directed to Mark Trice, Program Chief of Water Quality Informatics (410-260-8630). Data are also entered into the CIMS database and are available to the public via the Bay Program web site at http://www.chesapeakebay.net/dataandtools.aspx.

Figure 2. Maryland Department of Natural Resource's Ambient Water Quality Monitoring Stations

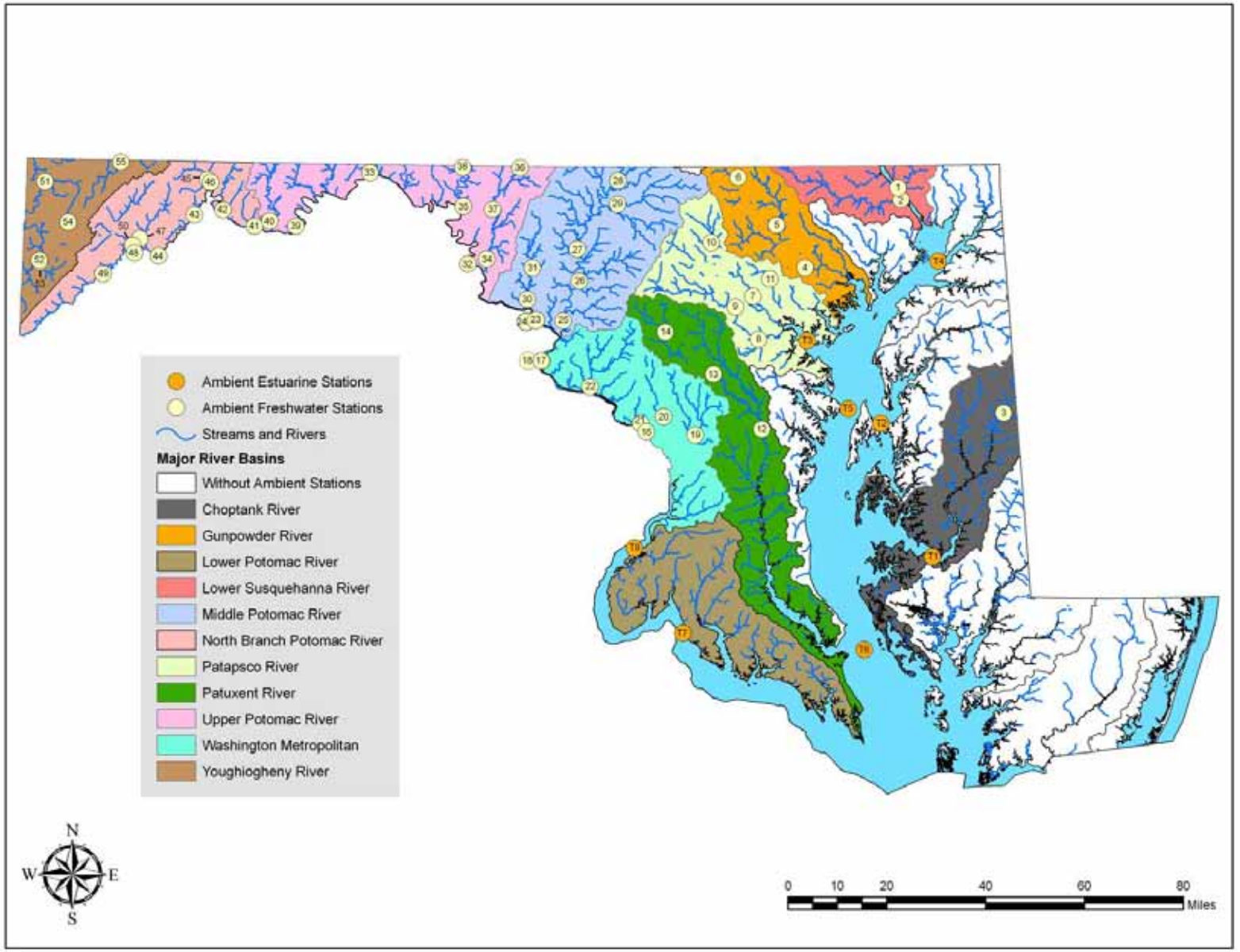


Table 1. Maryland Department of Natural Resource's Ambient Water Quality Monitoring Station Information.

Map #	Station I.D.	Stream Name	River Mile	Longitude (NAD 83)	Latitude (NAD 83)	Description and Site Type (Core or Trend)
02-12-02 SUSQUEHANNA RIVER BASIN						
1	CB1.0 (SUS 0109)	Susquehanna River	10.90	076 10.5023788	39 39.3729986	Below Conowingo Dam at boat ramp - gaging station USGS-01578310 - C
2	DER 0015*	Deer Creek	1.50	076 09.8863318	39 37.4085651	Bridge on Stafford Bridge Road - Tr
02-13-04 CHOPTANK RIVER BASIN						
T1	ET5.2 (XEH 4766)	Choptank River		076 03.5202530	38 34.8394323	At drawspan on U.S. Rt. 50 bridge - C
3	ET5.0 (CHO 0626)	Choptank River	62.60	075 47.1864631	38 59.8311087	At Red Bridges near Sewell Mills USGS-01491000 - C
02-13-05 CHESTER RIVER BASIN						
T2	XGG 8251	Kent Island Narrows		076 14.8401240	38 58.2675736	At drawspan on Route 50 bridge - C
02-13-08 GUNPOWDER RIVER BASIN						
4	GUN 0125	Gunpowder Falls	12.50	076 31.7336277	39 25.5375149	At bridge on Cromwell Bridge Road - C
5	GUN 0258*	Gunpowder Falls	25.80	076 38.1520258	39 33.0386351	End of Glencoe Road at old bridge crossing USGS – 01582500 - C
6	GUN 0476	Gunpowder Falls	47.60	076 46.8285205	39 41.3615564	Bridge at Gunpowder Road - C
02-13-09 PATAPSCO RIVER BASIN						
7	GWN 0115*	Gwynns Falls	11.50	076 43.5833003	39 20.5671785	At bridge on Essex Road in Villa Nova near gaging station USGS-01589300 - C

Table 1. Maryland DNR's Ambient Water Quality Monitoring Sampling Locations (cont.)

Map #	Station I.D.	Stream Name	River Mile	Longitude (NAD 83)	Latitude (NAD 83)	Description and Site Type (Core or Trend)
02-13-09 PATAPSCO RIVER BASIN (cont.)						
8	PAT 0176	Patapsco River	17.60	076 42.3202382	39 13.0687759	At bridge on Washington Boulevard (U.S. Rt. 1) - C
9	PAT 0285	Patapsco River	28.50	076 47.5345192	39 18.7467204	At bridge on Md. Rt. 99 near Hollofield gage USGS-01589000 (discontinued 2004) - Tr
10	NPA 0165*	North Branch Patapsco River	16.50	076 52.9250807	39 28.9671330	Bridge at Md. Route 91 near gage USGS-01586000 - C
11	JON 0184	Jones Falls	10.8	076 39.68155	39 23.0730508	Falls Road (Md. Rt. 25) at Sorrento – sampled at USGS-01589440 - C
T3	WT5.1 (XIE 2885)	Patapsco River	5.31	076 31.3521434	39 12.7856735	At buoy 5M, Hawkins Point - C
02-13-11 PATUXENT RIVER BASIN						
12	TF1.0 (PXT 0603)	Patuxent River	61.58	076 41.6465749	38 57.3343692	At bridge on U.S. Route 50 USGS-01594440 - C
13	PXT 0809	Patuxent River	81.91	076 52.4958913	39 07.0081428	At the gaging station just below Rocky Gorge Dam USGS-01592500 - C
14	PXT 0972*	Patuxent River	102.22	077 03.3713472	39 14.3584868	At bridge on Md. Route 97 near Unity gage USGS-01591000 - C
02-13-99 CHESAPEAKE BAY MAINSTEM						
T4	CB2.1 (XJH 6680)	Chesapeake Bay		076 01.5594740	39 26.4894865	200 yds. northeast of buoy RBA, mid-bay, south of Turkey Point, 15' depth - C
T5	CB3.3C (XHF 1373)	Chesapeake Bay		076 22.1808	39 00.84772	2100 yds., NE of Sandy Point, 55' depth - C
T6	CB5.1 (XCG 8613)	Chesapeake Bay	94	076 18.6833820	38 18.6510555	Off Patuxent River near mid-channel - depth 55 - 100' - C

Table 1. Maryland DNR's Ambient Water Quality Monitoring Sampling Locations (cont.)

Map #	Station I.D.	Stream Name	River Mile	Longitude (NAD 83)	Latitude (NAD 83)	Description and Site Type (Core or Trend)
02-14-01 LOWER POTOMAC RIVER BASIN						
T7	RET2.4 [a] (XDC 1706)	Potomac River		076 59.4376865	38 21.7559638	In mid-channel at Morgantown Bridge (U.S. Route 301), 58' depth - C
T8	TF2.3 [a] (XEA 6596)	Potomac River		077 10.4383095	38 31.8040859	Buoy N54 off Indian Head, 44' depth - C
02-14-02 WASHINGTON METROPOLITAN AREA						
16	POT 1184 [a]	Potomac River	118.40	077 07.6400929	38 56.8928182	At gaging station just above Little Falls Dam USGS-01646500 - C
17	POT 1471 [a]	Potomac River	147.10	077 31.2750641	39 09.2651668	At Eastern Terminus off Whites Ferry - C
18	POT 1472 [a]	Potomac River	147.0	077 31.3390209	39 09.3307768	At Western Terminus of Whites Ferry - Tr
19	ANA 0082 [a]	Anacostia River	8.20	076 56.6068030	38 56.3360716	At bridge on Bladensburg Road - C
20	RCM 0111 [a]	Rock Creek	11.10	077 03.7817405	38 59.5812919	At bridge on Md. Route 410 - Tr
21	CJB 0005 [a]	Cabin John Branch	0.50	077 08.9301668	38 58.4069338	At bridge on MacArthur Boulevard - Tr
22	SEN 0008 [a]	Seneca Creek	0.80	077 20.3781583	39 04.7749739	At bridge on Md. Route 112 - Tr
02-14-05 UPPER POTOMAC BASIN						
23	POT 1595 [a]	Potomac River	159.50	077 32.6203211	39 16.4085768	MD side of U.S. Rt. 15 near Pt. of Rocks USGS-01638500 - Tr
24	POT 1596 [a]	Potomac River	159.55	077 32.8740048	39 163250283	VA side of U.S. Rt. 15 near Pt. of Rocks - Tr
25	MON 0020 [a]	Monocacy River	2.00	077 26.4946321	39 16.3025469	Bridge on MD 28 - C
26	MON 0155 [a]	Monocacy River	15.50	077 22.8656221	39 23.2669471	Pine Cliff Park ramp upstream of bridge - C

Table 1. Maryland DNR's Ambient Water Quality Monitoring Sampling Locations (cont.)

Map #	Station I.D.	Stream Name	River Mile	Longitude	Latitude	Description and Site Type (Core or Trend)
02-14-05 UPPER POTOMAC BASIN (cont.)						
27	MON 0269 [a]	Monocacy River	26.90	077 23.3631412	39 28.8165566	Bridge on Biggs Ford Rd. - C
28	MON 0528* [a]	Monocacy River	52.80	077 14.0929806	39 40.7500155	At gage house in Bridgeport near Md. Rt. 140 – USGS – 1639000 - C
29	BPC 0035 [a]	Big Pipe Creek	3.50	077 14.2924934	39 36.7306812	Bridge on Md. Rt. 194 USGS gaging station USGS – 1639500 - Tr
30	CAC 0031 [a]	Catoctin Creek	3.10	077 34.8107379	39 19.9069327	Near mouth at bridge on Md. Route 464 - Tr
31	CAC 0148* [a]	Catoctin Creek	14.80	077 33.5401108	39 25.5468858	At bridge on Md. Route 17 at gaging station USGS-01637500 - Tr
32	POT 1830 [a]	Potomac River	183.00	077 48.1594887	39 26.1046394	At gaging station below bridge on Md. Rt. 34 USGS-01618000 (discontinued 2004) - C
33	POT 2386	Potomac River	238.60	078 10.5781510	39 41.4671425	At gaging station 0.5 mile below bridge on U.S. Rt. 522 USGS-0161300 - C
34	ANT 0044* [a]	Antietam Creek	4.40	077 43.8991688	39 27.0219634	Downstream of Sharpsburg gage house, streamside – USGS-01619500 - Tr
35	CON 0005	Conococheague Creek	0.50	077 49.2963323	39 36.1943845	Md. 68 bridge - C
36	ANT 0366	Antietam Creek	20.30	077 36.4935486	39 42.9592863	At gaging station west of MD 60 at Rocky Forge – USGS – 01619000 - Tr
37	ANT 0203	Antietam Creek	20.30	077 42.6475848	39 35.6775584	At bridge on Poffenberger Rd. near Funkstown - C
38	CON 0180	Conococheague Creek	18.00	077 49.5032338	39 42.9627173	At gaging station on Wishard Rd. USGS-01614500 - Tr
39	POT 2766 [+]	Potomac River	276.60	078 27.2695565	39 32.3189316	At bridge on Md. Rt. 51 near Paw Paw, W. Va. USGS-01610000 - Tr
40	TOW 0030 [+]	Town Creek	3.00	078 33.2032866	39 33.1821660	At gage on Pack Horse Road USGS-01609000 - C
02-14-10 NORTH BRANCH POTOMAC RIVER BASIN						
41	NBP 0023 [+]	North Branch Potomac	2.30	079 39.3300605	37 58.4618290	Toll bridge at Oldtown - Tr
42	NBP 0103 [+]	North Branch Potomac	10.30	078 43.8873501	39 34.9607011	Boat ramp off Rt. 51 in Spring Gap - C

Table 1. Maryland DNR's Ambient Water Quality Monitoring Sampling Locations (cont.)

Map #	Station I.D.	Stream Name	River Mile	Longitude	Latitude	Description and Site Type (Core or Trend)
02-14-10 NORTH BRANCH POTOMAC RIVER BASIN (cont.)						
43	NBP 0326 +	North Branch Potomac	32.60	078 50.3348823	39 34.0064182	USGS gaging station near W. Md. RR bridge at Pinto USGS-01600000 - C
44	NBP 0461 +	North Branch Potomac	46.10	078 58.3048527	39 26.6943955	At bridge on U.S. Route 220 - Tr
45	BDK 0000 +	Braddock Run	0.01	078 47.4487205	39 40.2286587	Braddock Run just above its mouth near junction U.S. 40 and Md. 36 - Tr
46	WIL 0013* +	Wills Creek	1.38	078 46.8174564	39 39.7110428	Locust Grove Road bridge crossing near gaging station USGS-01601500 - Tr
47	GEO 0009* +	Georges Creek	0.90	079 02.6819423	39 29.6183080	Victory bridge in Westernport next to Town Hall - near USGS – 01599000 - C
48	NBP 0534 +	North Branch Potomac	53.48	079 04.0814362	39 28.7536221	North Branch at Bloomington just upstream of confluence with Savage River USGS-01596000 - C
49	NBP 0689 +	North Branch Potomac	68.90	079 10.7614696	39 23.3607386	Rt. 38 bridge over North Branch USGS – 01595500 - C
50	SAV 0000 +	Savage River	0.02	079 04.0838436	39 28.8359583	Savage River at Md. 135 - Tr
05-02-02 YOUGHIOGHENY RIVER BASIN						
51	YOU 0925 +	Youghiogheny River	94.00	079 24.5074447	39 39.1739972	Bridge Crossing in Friendship on Main street near USGS – 03076500 - Tr
52	YOU 1139 +	Youghiogheny River	115.91	079 25.3143438	39 25.4158776	Liberty Street/Herrington Manor Bridge crossing near USGS – 03075500 - Tr
53	LYO 0004 +	Little Youghiogheny R.	0.38	079 25.1550365	39 25.1060846	Bridge Crossing at Oakland/Rosedale Rd. - Tr
54	CCR 0001 +	Cherry Creek	0.15	079 18.9509986	39 32.2335135	Bridge Crossing on State Park Road - Tr
55	CAS 0479 +	Casselman River	47.92	079 08.1846184	39 42.1242778	Casselman River where crossed by River Road at USGS – 03078000 - Tr

* Ambient Water Quality Monitoring Stations that are also sampled separately as part of the Chesapeake Bay Program's Non-tidal Network – 117(d). For additional information on this monitoring program, please see Maryland DNR's Non-tidal Network, Quality Assurance Project Plan, March 2009.

+ Western Maryland stations sampled for additional water quality parameters - sulfate and total dissolved solids

[a] Potomac River Basin Ambient Water Quality Monitoring Stations sampled for an additional water quality parameter – 5-day biochemical oxygen demand

( ) = Original Station Name

Table 2. Water Quality Parameters, Methods, Preservation/Holding Times and Method Detection Limits for MDNR's Ambient Water Quality Monitoring Program.

Parameter (units)	Method/Reference	Condition/ Holding Time	Method Detection Limits
Field (In situ)			
Temperature (^{o}C)	N.B.S. calibrated EPA 1979 #170	< 5 min.	0.1°C
Dissolved Oxygen (mg/L)	Membrane Probe EPA 1979 #360	< 5 min.	0.2 mg/L
pH	Glass Probe EPA 1979 #50	< 5 min.	0.1 units
Specific Conductance (umhos/cm)	Conductivity Bridge APHA #205	< 5 min.	% of calibration standard
Secchi Disc (cm) *estuarine stations*	8-inch Black/White	< 5 min.	0.1 meter
Laboratory			
Dissolved Organic Carbon (mg/L)	EPA Method 415.1	Frozen, 28 days/ 4 ^{o}C, 48 hrs	0.14 mg/L
Particulate Carbon (mg/L)	Exeter Analytical Model CE-440 Elemental analyzer	Frozen 28 days	0.006 mg/L
Ammonium (mg/L)	EPA Method 350.1	Frozen, 28 days/ 4 ^{o}C, 48 hrs.	0.004 mg/L
Particulate Nitrogen (mg/L)	Exeter Analytical Model CE-440 Elemental analyzer	Frozen 28 days	0.003 mg/L
Total Dissolved Nitrogen (mg/L)	alk. Persulfate then EPA 353.2	Frozen, 28 days/ 4 ^{o}C, 48 hrs.	0.034 mg/L
Nitrate + Nitrite (mg/L)	EPA Method 353.2	Frozen, 28 days/ 4 ^{o}C, 48 hrs.	0.003 mg/L
Nitrite (mg/L)	EPA Method 353.2	Frozen, 28 days/ 4 ^{o}C, 48 hrs.	0.002 mg/L
Orthophosphate (mg/L)	EPA Method 365.1	Frozen, 28 days/ 4 ^{o}C, 48 hrs.	0.002 μg/L
Particulate Phosphorus (mg/L)	Combustion, HCl extraction, then EPA Method 365.1	Frozen 28 days	0.003 mg/L
Total Dissolved Phosphorus (mg/L)	alk. Persulfate then EPA 365.1	Frozen, 28 days/ 4 ^{o}C, 48 hrs.	0.006 mg/L
Biochemical Oxygen Demand (BOD)	EPA Method 5210 B	4 ^{o}C 48 hrs.	NA
Total Suspended Solids (mg/L)	EPA Method 160.2	4 ^{o}C 7 days	1.88 mg/L
Total Dissolved Solids ppm	EPA Method 160.1	4 ^{o}C 7 days	2 ppm
Turbidity (NTU)	EPA Method 180.1	4 ^{o}C 48 hrs.	0.1 NTU
Chlorophyll “a” (μg/L)	Spectrophotometric SM 20th Ed. #10200 H	Frozen 28 days	0.62 μg/L
Phaeophytin “a” (μg/L)	Spectrophotometric SM 20th. Ed. #10200 H	Frozen 28 days	0.74 μg/L
Sulfate (mg/L)	EPA Method 375.4	4 ^{o}C 28 days	2 mg/L
Alkalinity, Total (mg/L)	EPA Method 310.1	4 ^{o}C 14 days	1 mg/L

MEASUREMENT/DATA ACQUISITION

B1 Program Design

Table 1 on pages 9-13 provides the station location descriptions for Maryland DNR's Ambient Water Quality Monitoring Program. Water quality data are collected at select stations in tributaries of the Choptank, Gunpowder, Patapsco, Patuxent, Susquehanna, Potomac and Youghiogheny Rivers. The selection of stations for this monitoring program was guided primarily by the need to assess conditions in water use areas. These included recreational areas, surface water supply areas, land use areas and potential areas of development. All ambient stations are sampled monthly (12 collections/year) on a pre-determined date. This sampling design allows the collection of data over a wide range of stream/river flows and provides adequate data for capturing long-term annual trends.

B2 Sampling Methods

Maryland DNR staff obtains field data and water quality samples (grab samples) from all stations by land (freshwater stations) or boat (8 estuarine stations). Bucket sampling is used on all land runs to collect samples from bridges, weirs, and stream banks. Bridge sampling is the preferred sample method and is used whenever possible. For the tidal stations, a submersible pump is used to collect a surface sample (depth of 0.5 m) and several depth samples from a boat. Appendix II provides the Standard Operating Procedures for Maryland DNR's Ambient Water Quality Monitoring Program (referred to as #PR-03: Maryland Core/Trend Monitoring Program).

B2.1 Field Measurements

Maryland DNR personnel obtain field data with the use of multi-parameter instruments (e.g., Hydrolab or YSI). The operation and calibration protocols are outlined in Section 6.0 in MDNR's Standard Operating Procedures #PR-03: Maryland Core/Trend Monitoring Program (Appendix II). The instruments are maintained according to the operating manuals provided by the manufacturers for each instrument. Field measurements include dissolved oxygen, temperature, specific conductance and pH. These parameters are currently measured with instruments manufactured by Hydrolab (except in 1974-1982, when YSI meters were utilized). At the estuarine stations, secchi depth is measured with an 8 inch black and white secchi disc. Table 2 provides the methods and detection limits for the field measurements.

B2.2 Water Quality Samples

Grab samples for each station are collected by MDNR personnel utilizing methods dependent on the physical conditions of the station location. Estuarine stations (8) are sampled by boat, whereas the land run stations are sampled from a bridge, weir, or streamside. At each land run station, a surface grab sample is collected, if possible, at mid-channel. For a complete description of the collection methods utilized under each condition please refer to Section 8.0 in MDNR's Standard Operating Procedures #PR-03: Maryland Core/Trend Monitoring Program (Appendix II). Both whole water and filtered water samples for each freshwater station are provided to the Maryland Department of Health and

Mental Hygiene's (DHMH), Environmental Chemistry Division for analysis. A complete list of the physical and analytical parameters obtained, holding times, methods, and method detection limits is provided in Table 2 (page 14).

B3 Sample Handling and Custody

Laboratory samples are placed on ice (i.e., stored at 4°C) in a large cooler and transported by Maryland DNR field personnel to Annapolis. Iced samples are then shipped overnight directly to DHMH. Frozen samples are placed in a freezer in Annapolis and delivered weekly to DHMH. Table 2 provides the holding times for each water quality parameter. For a complete description of sample handling and the procedures utilized to label and track all samples, please see Sections 9 and 10 in MDNR's Standard Operating Procedures #PR-03: Maryland Core/Trend Monitoring Program (Appendix II). Because the data generated by MDNR's Ambient Water Quality Monitoring Program is not used for legal purposes, formal chain-of-custody procedures are not required.

B4 Analytical Methods

Table 2 provides a list of analytical methods for all water quality parameters utilized by MDNR's Ambient Water Quality Monitoring Program. All analysis (except chlorophyll "a" and phaeophytin "a") is conducted by the State of Maryland, DHMH Laboratories. The Standard Operating Procedures for all water quality parameters utilized by DHMH are detailed in Appendix III. For each water quality parameter, scope of application, methods, equipment and supplies, reagents and standards, sample collection, quality control, procedures, data analysis and calculations, and data management are detailed. Starting in January 2009, chlorophyll "a" and phaeophytin "a" is analyzed by the University of Maryland, Chesapeake Biological Laboratory, Nutrient Analytical Services Laboratory (NASL). These parameters were originally measured by DHMH. The analytical methods utilized by NASL are identical to the ones that were utilized by DHMH and are detailed in Appendix VIII of the Quality Assurance Project Plan for Maryland DNR's Chesapeake Bay Water Quality Monitoring Program – Chemical and Physical Properties Component. The latest version of this Plan is available at:
http://mddnr.chesapeakebay.net/eyesonthebay/documents/MainstemTributaries2008-2009QAPP.pdf.

B5 Quality Control

The data collected as part of the Ambient Water Quality Monitoring Program are used in making management decisions regarding Chesapeake Bay water quality as described in section A5. DNR follows 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. Section 11.0 in Appendix II provides a list of quality control and quality assurance procedures that are utilized for this monitoring program. General discussions of quality assurance and quality control aspects associated with accuracy, precision, and audits are provided in the subsections below.

B5.1 Accuracy

The accuracy (closeness to the true value) of the collected data is 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. Daily quality control checks (including the running of blanks and standards) are used to control and assure laboratory accuracy. Accuracy of laboratory results is also assessed through DNR's participation in the Chesapeake Bay Coordinated Split Sample Program (CSSP), a split sampling program in which five laboratories involved in Chesapeake Bay monitoring analyze the coordinated split samples.

B5.2 Precision

Precision of the chemical analytical methods is determined and documented from duplicate analyses. Every tenth sample is analyzed in duplicate at DHMH. 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 are routinely collected approximately every 10 to 20 samples.

B5.3 Audits

Performance audits for chemical analyses 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. The DNR Quality Assurance Officer communicates 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.

B6 Instrument/Equipment Testing, Inspection, and Maintenance

Field crews carry two calibrated Hydrolab 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 on the field data sheet (the field sheet is illustrated in MDNR's Standard Operating Procedures #PR-03: Maryland Core/Trend Monitoring Program (Appendix II)). All equipment repairs are handled by Greg Gruber, MDNR's Field Quality Assurance Officer for this monitoring program. All parts are ordered directly from the manufacturer. If the repairs cannot be performed by the Field Quality Assurance Officer, the instrument is sent to the manufacturer for repairs.

The water quality instrument to be used each day for stations in Western Maryland receives a dissolved oxygen validation check to allow for barometric pressure corrections.

Laboratory instrument standard operating procedures include preventive maintenance procedures as well as performance checks and calibration procedures. Appropriate maintenance is scheduled based on the results of performance checks or after a specified number of hours of operation. Instrument preventive maintenance, repairs, and analytical corrective actions are

documented on laboratory notebooks or on DHMH's Divisional Analytical Corrective Actions forms (Appendix IV).

B7 Instrument/Equipment Calibration and Frequency

As mentioned previously, Section 6.0 in MDNR's Standard Operating Procedures #PR-03: Maryland Core/Trend Monitoring Program provides detailed information regarding Hydrolab calibration. The following information provides general procedures that should be followed while utilizing Hydrolab units for this monitoring program.

Calibration and Frequency

A. Set up a calibration logbook for each unit, with make, model, and serial number and purchase date. Assign a letter for MDNR use as required.

B. Calibrate meters on Friday for use the next week. After one to four days of field use, post calibrate equipment to determine if parameters have drifted.

C. Specific conductance calibration shall be made using standards generated by the field office from dry KCl and deionized water. Standards used are 294, 720, 2767, 6668, 12950, and 24820 microsiemens/cm (microsiemens=microS=μS); or 0.002, 0.005, 0.02, 0.05, 0.1, and 0.2 molar KCl, respectively. (At 25 °C microsiemens/cm = micromhos/cm.)

D. A pH calibration shall be made using premixed standards of color-coded pH 4.00, pH 7.00 and pH 10.00 purchased from Fisher Scientific. Standards are specifically labeled (contain expiration dates) and color coded - red for pH 4.00, yellow for pH 7.00 and blue for pH 10.00.

E. Dissolved Oxygen calibration shall be done on the common standard of water-saturated air. After correcting for the barometric pressure and temperature the oxygen content of water-saturated air can be checked against standard DO tables. The DO membrane is also visually checked every time the meter is pre- or post-calibrated. If the membrane appears damaged, the meter is posted as is. Then the membrane and electrolyte are replaced and the meter is calibrated after 24 hours.

F. Record all pre-calibration, post-calibration, and maintenance procedures in the log book, including any values (e.g. barometric pressure) that are used in the calibration procedures. An example of the equipment calibration log is included.

G. Record any unusual circumstances that may affect the Hydrolab unit readings in the logbook.

B8 Inspection/Acceptance of Supplies and Consumables

From 1974 to September 2007, the deionized water used at the MDNR Annapolis field office was generated from Annapolis City water passed through a non-pressurized Barnstead cartridge system equipped with two Ultrapure mixed bed cartridges and one organic removal

cartridge. This produced ASTM Type III water. Starting on September 10, 2007, the MDNR field office switched to a system that produces ASTM Type II water. The deionized water 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 *Apr 17, 2008, Revision 14, QAPP: Chemical & Physical Property Component Page VI-3* 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 inline to improve the integrity of feed-water 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.

The Maryland Department of Health and Mental Hygiene produces deionized water by utilizing a water system provided and serviced by SIEMENS. In this system, tap water is passed through a 1 micron filter, a carbon tank, and two mix bed ion exchange resin columns. The water is then subjected to UV oxidation and passed through a 0.2 micron filter Appendix III (DHMH's Standard Operating Procedures for Water Quality Parameters) lists all supplies and consumables utilized by the analytical laboratory for sample analysis.

B9 Non-direct Measurements

No data are needed for implementation or decision making that are obtained from non-direct measurement sources.

B10 Data Management

Data collection for the Ambient Water Quality Monitoring Program begins when measurements from field recording instruments are entered onto field data sheets. A section on the field sheet is used to document any problems encountered in the field that might affect the field parameters or the samples brought back for the laboratory analysis. A senior field scientist ensures that all measurements are taken and recorded properly. After field personnel have completed data sheets for a given calendar month, they make a photocopy of the sheets to keep in the Field Office, and send the original field sheets to data management staff at the MDNR Tawes State Office Building in Annapolis. The Field Office also generates 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 provides the data management personnel with the documentation to determine what field and laboratory results to expect. The Cross Reference Sheet is illustrated in Appendix III contained in MDNR's Standard Operating Procedures #PR-03: Maryland Core/Trend Monitoring Program (Appendix II).

Laboratory analysis sheets are also initiated in the field (laboratory sheets are illustrated in Appendix V and Appendix VI in MDNR's Standard Operating Procedures #PR-03: Maryland

Core/Trend Monitoring Program (Appendix II)). These laboratory sheets list each parameter requested for analysis and include basic information about the sample, such as station, date, time, depth, and volume filtered. The sheets serve as sample transfer sheets, traveling with the samples to the Maryland Department of Health and Mental Hygiene laboratory (DHMH) for analysis. Both the sheets and the samples are logged in at the laboratory.

The laboratory analyst reviews the data and, if the data exceed their control limits, the entire run is re-analyzed. Re-analysis can occur for any number of reasons, such as, a poor r-squared 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). Once laboratory staff has completed the laboratory sheets, they are sent to the DNR data management at the Tawes Building.

Data review and verification are conducted at four levels by DNR data management personnel. At the first level, DNR data management personnel 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. At the data entry service, the field sheet data are double-entered to minimize errors at the keypunch stage. The entered field data are sent back to DNR as an electronic file on a diskette for further processing.

At the second level, a Data Processing Technician generates 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 is used to conduct data management activities, such as performing an initial data check, conducting major key field checks, performing a parameter range check (including measured and calculated parameters), conducting combination checks for specific parameters, generating an error report and verification plots, generating a "data verified list," reforming data, creating a database, and submitting data.

Third, system printouts or PDF files of each data set are sent to a biologist and the Quality Assurance Officer for verification and editing. The Quality Assurance Officer and DNR biologists ensure that measured or calculated information for all types of data are correct and that the codes associated with parameters are properly established. In addition, the Quality Assurance Officer identifies data problems, provides data correction instructions, and coordinates data correction activities. Possible errors are identified, and sent to the laboratory or field office for verification or verified over the phone. Any necessary corrections are written on an edit form, which is given to a Data Processing Technician. The technician makes changes to correct the electronic data set, re-runs the verification programs, and updates the verification reports and plots. This procedure is repeated until a clean data set is produced.

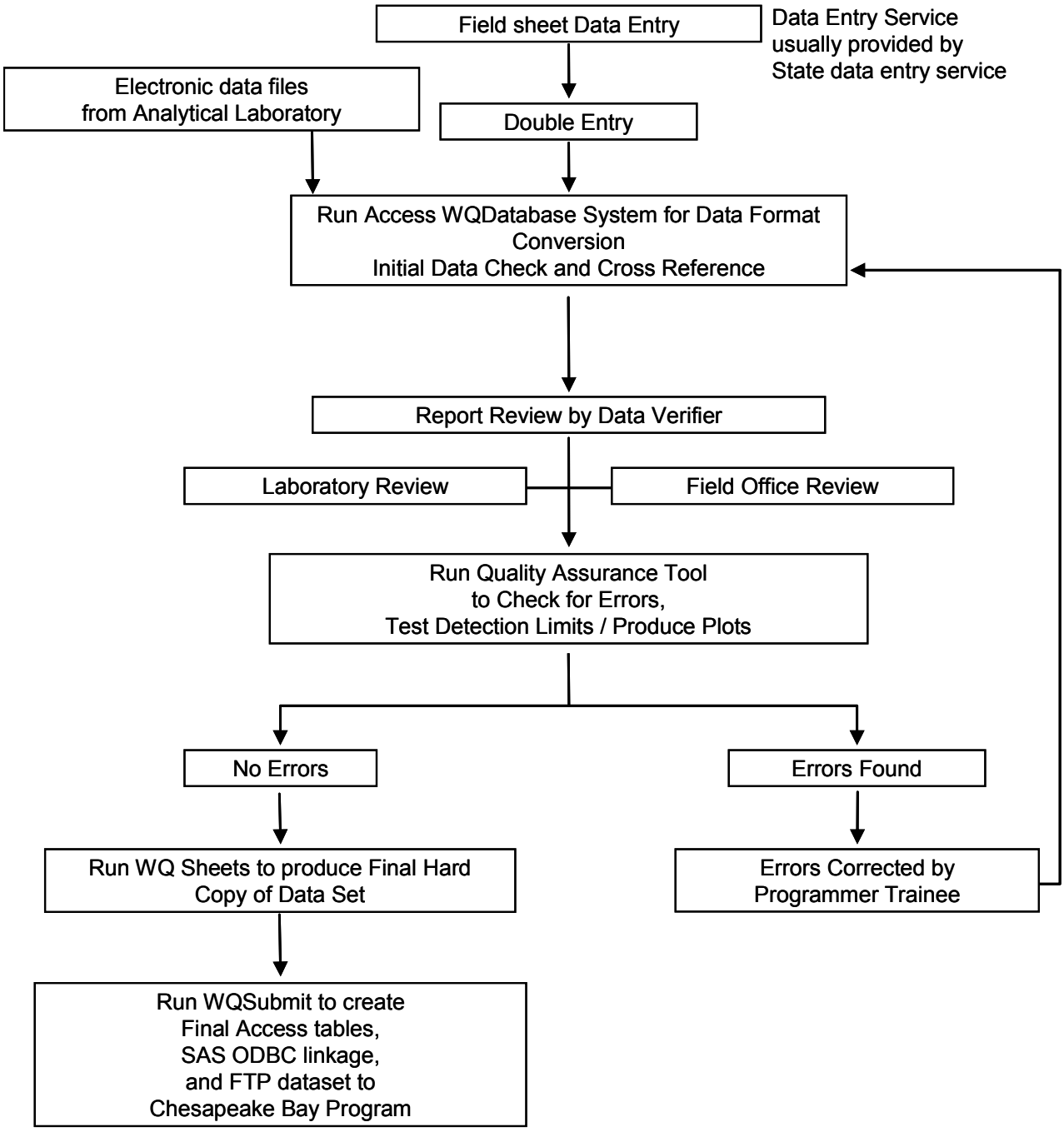
The fourth step is for data management staff to ensure that the overall data verification processes are completed, all data errors are corrected, and that the finalized data sets are created and formatted to be consistent with historical data sets.

The final data set combining the field and laboratory data is created as an Access “MDB file" after the completion of data verification processes. This final data set is stored in a local designated DNR database directory for data user access. Data requests should be directed to Mark Trice,

Program Chief of Water Quality Informatics (410-260-8630). A formatted submission data set and associated data documentation is also transferred to the Chesapeake Bay Program Data Center on a monthly basis.

Files submitted by DNR are further screened by the Bay Program's Quality Assurance Tool (QAT). The QAT generates a Chesapeake Information Management System (CIMS) Water Quality Data Quality Assurance Report for each file submitted. The Report identifies fatal errors for records that are incompatible with the CIMS database and prevents files that have fatal errors from being entered into CIMS. Nonfatal errors, such as those with values falling out of a historical range are reviewed and accepted or rejected. Once data are entered into the CIMS database, they are available to the public via the Bay Program datahub at: www.chesapeakebay.net. The data management process is diagramed in Figure 3.

Figure 3. Data Management Flow Chart: Data Entry through Production of Final Master Data Set



ASSESSMENT AND OVERSIGHT

Program and performance audits verify that procedures specified in the Project Plan are being followed throughout the entire MDNR Ambient Water Quality Monitoring Program. These audits ensure the integrity of the reported data so it can be used for its intended purpose.

C1 Assessments and Response Action

C1.1 Field Activities

If a station or specific sample cannot be collected, it is noted on the cross-reference sheet. Specific problems associated with field collection of a site are also noted on the field sheet. Conditions that may affect data results are included in the comments section of the field sheet so that they are available to each data analyst. If post calibration results are outside acceptable limits, the individual calibrating notifies the Field QA Officer who decides if data should be deleted or flagged. If split sample results suggest that there is a problem with the data, the issue is thoroughly discussed by laboratory and field representatives at AMQAW and possible solutions are offered. The Field QA Officer regularly reviews Equipment Log Books to ensure that all staff is following QC procedures. Standard maintenance recommended by Hydrolab is performed at six-week intervals. All serious Quality Control issues are reported directly to the Field Office Project Chief. Audits of the field staff are conducted as needed.

C1.2 Laboratory Activities

Corrective actions are initiated by the analyst, with the input of the Lead Scientist of the Laboratory Section, if necessary. The Lead Scientist and the Supervisor review corrective actions. A copy of the completed form is submitted to the division QA officer, and the original is kept in the laboratory. The DHMH Division of Environmental Chemistry is audited approximately every three years by EPA Region III or Chesapeake Bay Program Office staff.

C1.3 Data Management Activities

The Data Input Editor is the first line of defense for data correction. Maryland DNR data management personnel review all incoming data and compare the data to the cross-reference file. Data management personnel verify the submitted data and apply corrections to the physical datasheet if errors are identified. During the data-import process, a Data Processing Technician makes all corrections to the data and key fields as they are imported into the WQ Database System. The Data Processing Technician assists where needed in constructing better tools to edit and apply to large quantities of data corrections if necessary. Documenting the correction is handled within WQ Maintenance process. If the correction is fairly generic, edits to the changes are logged. There is no formal documentation for editing data sheets. These tasks are considered extreme and performed only when confirmed by field office or laboratory personnel.

C2 Reports to Management

Maryland DNR provides four quarterly progress reports (January, April, July and November) that indicate the number of Ambient Water Quality Stations that were sampled and an update on the status of water clarity assessments, efforts to acquire and assess data for the Integrated Report and a copy of the State 305(b) update. Status reports also provide explanations, if needed, for why accomplishments fell short of the projections. In addition, any changes to the Quality Assurance Project Plan or the SOPs referenced herein are documented and approval is required for all of those involved in project management (i.e., the individuals responsible for the major aspects of this monitoring program).

DATA REVIEW AND USABILITY

D1 Data Review, Verification, and Validation

Field: Described in C1.1 above.

Laboratory: The DHMH Environmental Chemistry Division uses data review checklists for data validation (example provided in Figure 4). Appendix III provides copies of each data review checklist for all water quality parameters.

Data Management: The data-management group validates key fields. The key fields ensure that the data are accurate and will not be lost or duplicated within the system. After the key fields are validated, the values are plotted to discover any anomalies. The scientists/project managers review the reports and determine if any additional edits are needed to data values. These edits are reported to the Data Processing Technician who makes the changes (Figure 3).

D2 Verification Validation Methods

Maryland DNR data management personnel conduct data review and verification at four levels: At the first level, DNR data management personnel 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. At the data entry service, the field sheet data are double-entered to minimize errors at the keypunch stage. The entered field data are sent back to DNR as an electronic file on a diskette for further processing.

At the second level, a Data Processing Technician generates reports and plots for data verification using the Water Quality Import v3 software.

At the third level, system printouts of each data set are sent to a biologist and the Quality Assurance Officer for verification and editing. The Quality Assurance Officer and DNR biologists ensure that measured or calculated information for all types of data are correct and that the codes associated with parameters are properly established.

At the fourth level, data management staff ensure that the overall data verification processes are completed, all data errors are corrected, and that the finalized data sets are created and are formatted to be consistent with historical data sets. The final data set combining the field and laboratory data is created as an Access database file after completion of data verification processes. This final data set is stored in a local designated DNR database directory for data user access. A formatted submission data set and associated data documentation is also transferred to the Chesapeake Bay Program Data Center on a monthly basis.

D3 Reconciliation with User Requirements

The data generated by Maryland DNR's Ambient Water Quality Monitoring Program are utilized to calculate relative status and long-term linear and non-linear trends (Appendix I describes methods). These calculations are performed for MDNR under contract by a statistical consultant.

The experimental design of this program requires monthly collections of water quality data (i.e., 12 collections per year) which are adequate for capturing long-term annual trends (Alden et al., 1994). As a result, the data generated by this program directly meet the objectives for which it is collected.

Figure 4. Data Review Checklist

State of Maryland
DHMH - Laboratories Administration
DIVISION OF ENVIRONMENTAL CHEMISTRY

Nutrients Section

LL Orthophosphate/EPA Method 365.**1**
LL Ammonia/ EPA Method 350.1

Lab Numbers[1]:_____
_____

Date Collected: _____ Date Analyzed: _____ Analyst: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	48 hours @ 4°C; 28 days @ –20°C		
Samples Analyzed	Within 5 working days		
Calibration Curve	Corr. Coeff. ≥ 0.9950		
Reagent Blank	< Reporting Level (0.004 ppm for OP; 0.008 ppm for NH_3)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10 samples		
	Recovery = 90–110%		
External QC[2]	Beginning and end of each run		
	Within acceptable range		
Check Standard	After every 10th sample and at the end of the run		
	Concentration = 90–110% of the true value		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples		
	RSD ≤ 10%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.004–0.250 ppm for OP; 0.008–0.500 ppm for NH_3)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

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Appendix I: Methods for Calculating Status and Trends at Maryland DNR's Ambient Water Quality Monitoring Stations

Status and trend analyses are performed at all CORE/Trend monitoring stations for nutrients (nitrogen and phosphorus), field-measured parameters such as conductivity, pH, and water temperature, and total suspended solids, total alkalinity, and total organic carbon. Trends in chlorophyll and sulfate are also assessed at stations where those parameters are measured.

Water quality status is a measure of the current water quality condition compared to some benchmark. Trends are measured to assess changes in water quality over time. For the CORE/Trend stations increasing trends are generally associated with degrading water quality and decreasing trends are generally associated with improving water quality conditions. Linear and non-linear trend analyses are performed on "long-term" data (1986 to present) and "short-term" data (1995 to present). Trends for both long- and short-term periods are deemed significant if the probability value (p-value) is less than or equal to 0.01, a level which was chosen to reduce the Type I error rate (i.e., reduce the chance of stating that there is a trend when in fact there is no trend).

Relative Status

In the absence of water quality reference levels or restoration targets, members of the Data Analysis Workgroup (DAWG), which was a workgroup of the U.S. Environmental Protection Agency Chesapeake Bay Program Monitoring Subcommittee, developed a method of comparing stations in similar salinity zones (Aden and Perry, 1997). The first version of the relative status method was developed and implemented for the 1997 Re-evaluation effort of the Chesapeake Bay Program to assess progress in meeting nutrient reduction goals established in 1987.

The relative status method compares the median of the most recent three years of data for a specific parameter at a particular station to all stations in the same salinity regime using "cut-points" in a benchmark data set. The most recent three years of data are used in the status data set to even out year-to-year climatic variation. The benchmark data set consists of water quality data that were collected between January 1985 and December 1990 to establish a Bay-wide baseline against which to score water quality at each station. Data in the benchmark data set were partitioned using a beta cumulative distribution function to establish the "cut-points" for individual parameters in a particular salinity zone; in this case non-tidal, fresh water systems.

The status data set is scored using the logistic probability integral transform, and the score is adjusted based on sample size to account for the inter-dependence of observations. The lack of independence in observations at a site tends to result in too many observations in the ends of the distribution, i.e., in the "good" and "poor" categories. The adjustment results in a more even distribution of scores. Both the benchmark and status data sets are log transformed prior to analysis to meet the distributional assumptions of the procedure.

It is important to note that this is a relative ranking procedure. Just because a parameter at a station is scored as "good" does not mean that water quality is acceptable. It is only a relative indication that the station scored better than other stations rated as "fair" or "poor" based on a comparison to cut-points in the benchmark data set for similar stations.

Linear Trend Analysis

A combination of statistical procedures is used to calculate the significance of linear trends and the percent change in a water quality parameter over time. First, the seasonal Kendall test, which is a generalization of the Mann-Kendall test, is used to assess the presence of a trend in time

in seasonal data (Hirsh, et al., 1982). The seasonal Kendall test was proposed by Hirsh for use in data with 12 seasons (months). Basically, the Mann-Kendall "S" statistic and its variance VAR(S) are computed for each month (season) for data collected over a number of years. The seasonal statistics are then summed over the years and an overall Z statistic is then calculated, which is compared to standard normal tables to assess significance (Gilbert, 1987). The seasonal Kendall test is particularly useful for water quality trend assessment because it is non-parametric (i.e., does not assume any particular distribution in the data), and is not affected by missing, tied, or below detection limit values.

The magnitude of change in the data over time, for trends that are significant, is calculated using the seasonal Kendall slope estimator, which is a generalization of Sen's estimator of slope (Sen, 1968). The seasonal Kendall slope estimator is calculated from the median of all possible differences in the data. The magnitude of change is expressed as the percent change since the beginning of the period of record. Percent change is calculated by multiplying the Sen's slope estimator times the number of years of the study period, and dividing by the initial median:

$$\text{Percent change} = [(\text{slope}*\text{nyrs})/\text{base median}] * 100$$

The base median is calculated from the first two years of data. For most stations that period is January 1986 to December 1987.

Non-linear Trend Analysis

As the monitoring timeline has lengthened, non-linear trend analyses have been added. The utility of identifying non-linear trends was investigated by Alden (Alden et al., 2000). Non-linear trends provide a picture of how a parameter has changed within the period of evaluation and can serve as early warning signals for managers. These analyses identify whether a trend is primarily linear (generally unidirectional), U-shaped (decreasing early in the time series, increasing later in the time series), or the reverse (inverse U-shaped). They can also determine where the critical point (change in direction of trend), if any, is located (either within or outside the period of evaluation).

Non-linear trends are assessed using a general linear model with a linear TIME term and a quadratic ($TIME^2$) term. Data are log-transformed prior to the analysis in an effort to conform to the distributional requirements of the general linear model. A MONTH term is included in the model to account for seasonal effects. The TIME and $TIME^2$ terms are first standardized to a mean of zero to ensure that the TIME and $TIME^2$ terms are orthogonal (uncorrelated), thus reducing the chances of misinterpretation of correlated regression terms (E. Perry, personal communication).

The log of the water quality parameter in question is then regressed on TIME and $TIME^2$ using SAS® PROC GLM (SAS, 1989) with the following statements:

```
PROC GLM;
  CLASS MONTH;
    MODEL log(WQ variable) = TIME TIME2 MONTH;
```

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Appendix II: Maryland Department of Natural Resources: Standard Operating Procedures #PR-03: Maryland Core / Trend Monitoring Program

Standard Operating Procedure # PR-03
MARYLAND CORE/TREND MONITORING PROGRAM
Revision 1: February 2009

Prepared by: Kristen Heyer
Reviewed by: Laura Fabian
Approved by: Sara Bowen

Table of Contents

1.0 Scope and Application

1.1 This Standard Operating Procedure is applicable to the collection of water quality samples for the Maryland Core/ Trend Program (Section 106).

1.2 The water samples are collected for physical and chemical analysis.

2.0 Summary of Method

2.1 Stations sampled for the Core/ Trend Monitoring Program are mostly sampled by land. A few Core/Trend stations are sampled in conjunction with other programs: Chesapeake Bay Mainstem (refer to SOP# PR-01); Chesapeake Bay Tributary (refer to SOP# PR-02); and Potomac River Program (refer to SOP# PR-05). These samples are collected at depth, aboard a research vessel and follow the respective program Standard Operating Procedure.

2.2 Whole water samples are collected at every station for the Core/ Trend Program. The following equipment are used for collection of water samples depending on the station description and conditions:

- Bucket
- Submersible pump

2.3 The whole water samples are collected and analyzed for both physical and chemical properties; whole water nutrients and dissolved fractions.

3.0 Health and Safety Warnings

3.1 When sampling from boats and piers, wear appropriate safety gear and follow appropriate safety procedures for working around the water and under slippery conditions.

3.2 When sampling from road bridges, wear appropriate safety gear and follow appropriate safety procedures for working around high speed traffic.

3.3 When sampling along the stream bank, care should be exercised in areas with slippery and uneven terrain.

3.4 Proper methods for lifting and moving equipment and samples should be exercised to avoid bodily injury.

3.5 Any water sample collected could contain a potentially harmful algae species. If the presence of a toxic species is suspected, protective equipment **must** be used. Protective gear must include gloves and raingear. Respirators and goggles must be used when sampling a bloom

suspected of containing algae species that can produce toxic aerosols such as *Pfiesteria sp.*

4.0 Interferences

4.1 Contamination of samples can be minimized or eliminated by following the procedure for cleaning of sampling equipment. Equipment is washed on a regular basis to include acid rinsing. Refer to SOP # MC-01: *Cleaning and decontamination of sampling equipment*.

4.2 Improper sample collection can be avoided by following the guidelines in this SOP and taking care not to disturb the substrate of the area being sampling.

4.3 Care should be exercised to avoid collecting debris in the sample when it is present in the body of water being sampled.

4.4 Inaccessibility to sampling stations may occur due road and/or bridge construction, maintenance or closure. Inaccessibility can also be caused by boat ramp closure, homeowner denial of access to the site and overgrowth of brush.

4.5 Weather conditions may interfere with the collection of samples. High winds and ice cover are examples of interferences that may occur. Sample collection should be rescheduled if possible.

4.6 Insufficient water volume would interfere with the collection of grab samples. This problem could manifest itself as an inaccessibility problem (i.e. there is not enough water to reach the station) or there is not sufficient volume to grab a sample.

4.7 Malfunctioning sampling equipment, i.e. submersible pumps, etc. will interfere with the collection of grab samples. Malfunctioning or missing filtration equipment, i.e. electric vacuum pumps or filter funnels, will interfere with the generation of particulate and dissolved samples. Having spare filtration equipment and/ or a hand pump could solve this problem. If too many samples need to be processed by hand, the whole water sample used for filtering can be preserved in ice and filtered as soon as you return to the office. Be sure to note the time the sample was filtered on the volume sheet.

4.8 Contamination can occur from dirt and debris near the processing area. This can be minimized by maintaining clean vehicles, vessels and lab areas. Filtration equipment is placed on clean lab towels during processing to further maintain a clean working environment. The boat

and/ or vehicle engines should not be running while processing samples if the fumes could accumulate in the processing area.

4.9 Insufficient lab supplies would also interfere with collection of particulate and dissolved nutrient samples. This problem can be solved by maintaining a back-up supply of necessary items.

5.0 Equipment and Supplies

5.1 A bucket is typically the equipment used for collection of water samples for the Core/ Trend Program. For bucket sampling, we use a square 3 gallon bucket (Rubbermaid, model #2964). The bucket is then tied to a line long enough to reach the water surface. The bucket should be cleaned periodically (refer to SOP # MC-01: *Cleaning and decontamination of sampling equipment*). Each van is equipped with its own sampling buckets. Bucket sampling will be described in this SOP.

5.2 A submersible pump is used for Core/ Trend stations that are sampled in conjunction with another program, i.e. Chesapeake Mainstem or Potomac. Submersible pump sampling uses either a well pump (Dayton, ½ HP, 230 V, model # D10KS05221) or a bilge pump (Rule, 2000 gph, 12 V, model # 10). Refer to the Standard Operating Procedure for the Field Collection of Grab Water Samples (SOP # SC-01) for sample collection details.

5.3 The whole water samples collected for the Water Quality Monitoring Program are collected in new HDPE (plastic milk jug) bottles. These may include, but are not limited to, half- gallon (2 qt. bottles), quart, 16 oz. and 8 oz. bottles. Ice-filled coolers labeled for courier delivery to the Baltimore Lab are necessary for transporting the whole water samples.

5.4 Any or all of the following equipment is used to collect and record data on the field sheets:

- pencils, pens & sharpies
- watch, clock or instrument that displays the current time
- thermometer (readings in Celsius)
- water quality instrument (Hydrolab) with stirrer and/ or probe guard
- calculator (for boat stations sampled where there is a pycnocline)
- compass & secchi disk (for tidal stations)

5.5 Any or all of the following equipment is used for collection of particulate and dissolved samples.

- 25mm filter funnel, 200ml; polysulfone (Pall Corp.# 4203)
- 47mm filter funnel, 300 ml; magnetic (Pall Corp.# 4242)
- Filter funnel manifold; polyurethane (Pall Corp.# 4205) with trap
- 47mm filter funnel & base; Millipore

- Filter flasks, 1000ml/ 500 ml (Fisher# 10-181F; 10-180E)
- Graduated Cylinders; 10ml, 50ml, 100ml, 250ml
- Forceps
- DI squirt bottles
- Adjustable vacuum pump (115V AC or 12 V DC Air Cadet) with pressure gage and trap

5.6 Any or all of the following supplies are used for collection of particulate and dissolved samples. When sampling Core/ Trend stations that are sampled in conjunction with another program, i.e. Chesapeake Mainstem or Potomac additional supplies may also be used. Refer to the Standard Operating Procedure for the Field Filtration for Particulate and Dissolved Nutrient Constituents (SOP # SC-03) for full filtration details for other programs within the Water Quality Monitoring Program.

- Pads
  - CHLA & PP: 47mm GF/F Whatman glass fiber filter (#1825-047, Fisher # 09-874-71); pore size 0.7 µm.
  - PC/ PN: 25mm GF/F Whatman glass fiber filter, pre-combusted at 490^{o}C; pore size 0.7 µm. Direct from lab.
- 8 oz. or 16 oz. HDPE bottles
- DI water
- Sample water
- Freezer or cooler with ice for sample storage and/ or transport

6.0 Hydrolab Calibration

6.1 Model 4041 Instrument, Series 2 Instrument & Series 3 Instrument Calibration

1. Temperature – temperature is measured with a stainless steel thermistor. Calibration is not required because it is factory set and not user adjustable. During periodic routine servicing, temperature is checked at one temperature against a standard mercury thermometer. The multiprobe is returned to the manufacturer if test results are not within 0.2°C of standard thermometer.

2. Dissolved Oxygen – dissolved oxygen is measured with a Standard Clark Polarographic cell and corrected to standard temperature and pressure and for specific conductance. The probe is calibrated using a 1 point mg/L linear protocol in water saturated air. Calibration dissolved oxygen concentration is determined from a table of saturation concentrations in mg/L as calculated from the instrument temperature and local barometric pressure measured with a Standard Fortin Mercury Barometer.

3. Specific Conductance – conductivity is measured with a probe having an array of 6 nickel electrodes oriented in two vertical rows of three with each row inside adjacent parallel channels of a standard plastic block. Individual electrodes are oriented horizontally. The conductivity reading is corrected to standard temperature (25°C). The probe is calibrated with a standard potassium chloride solution using a 1 point linear protocol. These standard solutions are made in house. The zero point is factory set and cannot be calibrated. The slope is calibrated with a standard potassium chloride solution. The slope standard is selected so that field measurements fall between zero and the specific conductance of this standard, but as close to the specific conductance of this standard as possible.

4. pH – pH is measured with a two probe system (*in situ* pH and reference probes) and corrected to standard temperature. The *in situ* pH probe is a standard silver/silver chloride glass probe and the reference probe is a pellet of silver inside a hollow plastic sleeve containing 4 M potassium chloride solution saturated with silver chloride. This sleeve has a porous Teflon™ junction at one end to connect this probe to the environment. The pH system is calibrated with standard pH buffers using a two point linear protocol. The zero point is first calibrated with a pH 7.00 standard buffer. The slope is calibrated with either pH 4.00 or 10.00 standard buffer. The slope buffer is selected depending on pH measurements anticipated during field deployment.

6.2 Series 4a Instrument Calibration

1. Temperature – temperature is measured with a stainless steel thermistor. Calibration is not required because it is factory set and not user adjustable. During periodic routine servicing, temperature is checked at one temperature against a standard mercury thermometer. The multiprobe is returned to the manufacturer if test results are not within 0.2°C of standard thermometer.

2. Dissolved Oxygen – dissolved oxygen is measured with a Standard Clark Polarographic cell and corrected to standard temperature and pressure and for specific conductance. The probe is calibrated using a 1 point mg/L linear protocol in water saturated air. Calibration dissolved oxygen concentration is determined from a table of saturation concentrations in mg/L as calculated from the instrument temperature and local barometric pressure measured with a Standard Fortin Mercury Barometer.

3. Specific Conductance – conductivity is measured with a probe having two opposing graphite electrodes oriented horizontally inside a vertical plastic channel. The conductivity reading is corrected to standard temperature (25°C). The probe is calibrated with a standard potassium chloride solution using a 2 point linear protocol. These standard solutions are made in house. The zero point is calibrated in air with the probe dry. The slope is calibrated with a standard potassium chloride solution. The slope standard is selected so that field measurements fall between zero and the specific conductance of this standard, but as close to the specific conductance of this standard as possible.

4. pH – pH is measured with a two probe system (*in situ* pH and reference probes) and corrected to standard temperature. The *in situ* pH probe is a standard silver/silver chloride glass probe and the reference probe is a pellet of silver inside a hollow plastic sleeve containing 4 M potassium chloride solution saturated with silver chloride. This sleeve has a porous Teflon™ junction at one end to connect this probe to the environment. The pH system is calibrated with standard pH buffers using a two point linear protocol. The zero point is first calibrated with a pH 7.00 standard buffer. The slope is calibrated with either pH 4.00 or 10.00 standard buffer. The slope buffer is selected depending on pH measurements anticipated during field deployment.

6.3 Series 5 Instrument Calibration

1. Temperature – temperature is measured with a stainless steel thermistor. Calibration is not required because it is factory set and not user adjustable. During periodic routine servicing, temperature is checked at one temperature against a standard mercury thermometer. The multiprobe is returned to the manufacturer if test results are not within 0.2°C of standard thermometer.

2. Dissolved Oxygen – dissolved oxygen is measured with a Standard Clark Polarographic cell and corrected to standard temperature and pressure and for specific conductance. The probe is calibrated using a 1 point mg/L linear protocol in water saturated air. Calibration dissolved oxygen concentration is determined from a table of saturation concentrations in mg/L as calculated from the instrument temperature and local barometric pressure measured with a Standard Fortin Mercury Barometer.

3. Specific Conductance – conductivity is measured with a probe having two opposing graphite electrodes oriented horizontally inside a vertical plastic channel. The conductivity reading is

corrected to standard temperature (25°C). The probe is calibrated with a standard potassium chloride solution using a 2 point linear protocol. These standard solutions are made in house. The zero point is calibrated in air with the probe dry. The slope is calibrated with a standard potassium chloride solution. The slope standard is selected so that field measurements fall between zero and the specific conductance of this standard, but as close to the specific conductance of this standard as possible.

4. pH – pH is measured with a two probe system (*in situ* pH and reference probes) and corrected to standard temperature. The *in situ* pH probe is a standard silver/silver chloride glass probe and the reference probe is a pellet of silver inside a hollow plastic sleeve containing 4 M potassium chloride solution saturated with silver chloride. This sleeve has a porous Teflon™ junction at one end to connect this probe to the environment. The pH system is calibrated with standard pH buffers using a two point linear protocol. The zero point is first calibrated with a pH 7.00 standard buffer. The slope is calibrated with either pH 4.00 or 10.00 standard buffer. The slope buffer is selected depending on pH measurements anticipated during field deployment.

6.4 Frequency of Calibration

- All instruments are calibrated prior to field use. Calibration is typically completed the Friday before the sampling week. If office time is available on a closer day preceding the run, then the calibration will be completed at that time.
- If large adjustments to the DO value were necessary during calibration, the DO should be checked prior to taking the instrument in the field.
- The DO is checked in the morning prior to sampling, when large changes in barometric pressure have occurred. This is typical of the Western Maryland Core run.
- Instrument calibrations may be rechecked in the calibration lab any time the field readings seem suspect.
- Instruments are post-calibrated (checked) after use. Typically the post-calibration occurs on the Friday after the sampling week. After post-calibration, the instrument is ready to be calibrated for field sampling the following week.

7.0 Preparation for Sampling

1. When preparing for a Core/ Trend sampling run the first step is to get the field pack for the specific run you are doing. The packs are distributed to one member of the field team prior to the scheduled sampling date. The field packs contain all information to complete the run: field sheets, chemistry sheets, volume sheets, directions to all of the stations with maps, list for

samples being collected, foils squares, baggies, PC/PN pads, lab towels, and extra sheets. When the run is complete, everything (except for the volume & chemistry sheets which accompany the samples) should be returned to the field pack and turned in to Laura Fabian.

2. Ensure that the field van has necessary supplies for safe collection of the sample. Each van should have buckets with line, orange cones and safety vests.
3. Ensure that the field van has the necessary supplies for processing the sample. Make sure there are enough quart, two quart and 16 oz. bottles for the whole and filtered samples. Check for a WORKING vacuum pump and appropriate filtration supplies: forceps, $MgCO_3$, Whatman pads.
4. Just prior to leaving for the run, the following equipment should be loaded into the van: fully charged & calibrated Hydrolab meters (294 µs/cm for specific conductance); filter unit, courier cooler big enough for all of the sample bottles, another small cooler for bringing pads back to the office after delivery to the courier and ice.
5. Before you arrive on station, turn on the Hydrolab so that it can warm up for 15 minutes before recording the readings.

8.0 Sample Collection

8.1 Bucket Sampling

Bucket sampling is used on all land runs, including Core/ Trend sampling. Bucket samples are taken from bridges, weirs and stream banks. However, bridge sampling is the preferred sample method and should be used whenever possible. Below, the steps to be taken for each type of bucket sampling are listed.

8.1.1 Bridge Sampling

NOTE: When sampling from bridges, always make sure you have the appropriate lengths of rope before leaving for your run. Once you arrive at the station:

1. Select the appropriate length of rope for the bridge from which you will be sampling. You may need to tie 2 or more ropes together to reach the water surface at some stations. Secure the rope to the bucket, making sure that it will not come loose while retrieving the sample. Most sample buckets already have the ropes tied on to ensure that the bucket “hangs” properly.
2. Sample on the upstream side of the bridge (if possible) and as close to the center of the stream/river as possible, where the majority of flow is located.
3. Lower the bucket to the water.
4. Tip the bucket and fill with enough water to rinse the bucket (at least a few inches). Depending on the height of the bridge, you

may want to shake the rope to expel the rinse water from the bucket, or pull the bucket back up to dump the rinse water out of the bucket. Follow this procedure 3 times; making sure the bucket is properly rinsed.
5. Fill the bucket as full as possible.
6. Pull the bucket back up, making sure the rope does not rub against the side of the bridge. This can sometimes cause dirt, rust, paint, etc. to fall into the sample.
7. Carry the bucket back to the van.

8.1.2 Weir Sampling

NOTE: You may want to wear waterproof boots or water shoes when sampling from weirs or stream banks. Depending on the depth of the water, you may need to walk into the stream to collect a sample.

1. Select the shortest length of rope, and secure to the bucket.
2. Depending on the water level, you may be able to walk out onto the weir to get closer to the center of the stream. If the water level is too high, sample from the stream bank close the weir.
3. Always sample just upstream of the weir. Holding onto the rope, throw or drop the bucket into the water and fill with enough water to rinse without disturbing or touching the bottom of the stream with the bucket.
4. Dump the rinse water downstream of the sampling area.
5. Repeat steps 3 & 4 two more times.
6. Once the bucket is properly rinsed, throw or drop the bucket into the water and fill to the lip of the bucket.
7. Pull the bucket from the water, and carry it back to the van.

8.1.3 Stream Bank Sampling

1. Select the shortest length of rope, and secure to the bucket..
2. Try to get as close to the center of the stream as possible when it is safe to do so (using rocks, etc.). If it is shallow near the sample area, do your best to get a sample without touching or disturbing the bottom of the stream with the bucket. At times, you may have to walk out farther into the stream.
3. Holding the rope, throw or drop the bucket into the water and fill with enough water to rinse.
4. Dump the rinse water downstream of the sampling area.
5. Repeat steps 3 & 4 two more times.
6. Once the bucket is properly rinsed, throw or drop the bucket into the water and fill to the lip of the bucket.
7. Pull the bucket from the water, and carry the sample back to the van.
8.

8.2 Recording the physical data

After the bucket has been collected, the next step is to take readings of physical parameters and record them on the field sheet.

8.2.1 Completing the Field Sheet

For complete details, see Standard Operating Procedure # DR-01: *Recording Physical Data on Field Sheets*. For an example Core/ Trend field sheet, see Appendix IV.

1. The start date is recorded as YYMMDD (2 digit year, 2 digit month, 2 digit day). Do not record an end date, it is assumed that it is a one day sampling period.
2. The start and end times are recorded in military time (4 digits). The start time is when you start sampling the station (collecting the bucket) and the end time is when you finish with the readings and whole water sample collection.
3. The two digit number of samples reflects the number of water samples collected at individual, discrete depths. It also denotes if there was a duplicate sample taken.
4. The total depth is only recorded on tidal stations. This is the depth, in meters, to the bottom.
5. Air temperature is recorded in Celsius to the nearest 0.5 degree. The thermometer should be hung out when you arrive on station to allow it to equilibrate to the current temperature. The thermometer should be placed approximately 3-4 feet from the ground and in the shade. Hanging the thermometer on the van in times of weather extremes may skew the reading.
6. Weather codes recorded on the field sheet are as follows:

10- no precipitation	11- drizzle
12- rain	13-heavy rain
14- squally	15- frozen precipitation

   Yesterday's weather code is recorded as the predominate weather the day prior to sampling for the station being sampled. Today's weather code is the weather conditions at or near the time of sampling. If a weather condition had occurred that will affect the water quality sample, but does not represent today or yesterday's weather it can be noted in the comment section of the field sheet: e.g. 2 feet of snow covering the ground or hurricane 2 days ago.
7. Percent cloud cover is reported as a value from 0% to 100%. Numbers are three digits and are right justified on the field sheet: e.g. 005 would be 5% cloud cover. Thin clouds and haziness may be noted in the comment section of the field sheet.
8. Wind direction & velocity, wave height, secchi, tide state, pycnocline limits are only collected at tidal stations.

9. The flow value is recorded by Laura Fabian after the sampling run if the station is associated with a USGS Gaging Station. The flow value box is 8 boxes long. The basis, flow value, exponent, & G/L boxes are included.
   a. The basis number refers to whether a flow value is measured or estimated. If the flow value was measured then a 1 goes in the basis box. A 2 is used when the flow value was estimated.
   b. The flow value is a five digit number in cfs (cubic feet per second). If the value given less than five digits then zeros are added following the value to fill all boxes. For example, if the flow value is 261 cfs, then you would enter 26100.
   c. The exponent box denotes the placement of the decimal point for the flow value in the preceding boxes. Following the example above of a flow value of 26100 (for 261 cfs), the exponent would be 3. This exponent denotes moving the decimal three place from the left, i.e. 261.00 giving the flow value as 261 cfs (the original value).
   d. The G/L box is for noting if a value is greater or less than the reported value.
   e. For most sampling, the flow values are currently taken from the USGS real-time data website, http://waterdata.usgs.gov/md/nwis/current?type=flow . These values are recorded in 15 minute increments. The increment that most closely matches the sampling time is entered on the field sheet. Note that all data on the website are timed in Eastern Standard Time all year long.
10. The equipment & probe numbers correspond to the number or letter associated with the water quality instrument used to record data. Currently, the Hydrolab instruments have an individual letter associated with them. The instrument is recorded as 9 and then its assigned letter, i.e. 9L.
11. The scientist and senior scientist sign-offs are places for the sampling team to initial, denoting the fact that they collected and verified the data. The spaces are three boxes long. All letters are left justified. If someone only has 2 initials, then they would be placed in the first 2 boxes and the third is left blank.
12. Any comments pertinent to the station or collection of data or samples should be placed in the comments section of the field sheet.

8.2.2 Recording Hydrolab Readings

1. Remove the storage cup from the sonde.
2. Check the DO membrane to make sure that it looks good. It should not be wrinkled, dented, torn or have any bubbles beneath the surface.

3. Install the probe guard.
4. Swirl the Hydrolab in the bucket until the readings stabilize. The water should be moving past the DO membrane at 1 ft/sec to obtain an accurate reading.

- Record the water temperature is degrees Celsius. The temperature should be recorded to the nearest tenth.
- Record the pH to the nearest tenth. Place a zero in the hundredths place following the reading.
- Record the dissolved oxygen in mg/L to the nearest tenth. Place a zero in the hundredths place following the reading. The G/L box is available for instances when the DO is reaching its upper or lower limit.
- Record the specific conductance in µS/cm to three significant figures.
- Salinity is not recorded on the typical non-tidal Core/ Trend station. It is only recorded at tidal stations in ppt to the nearest tenth.

8.3 Collecting the whole water sample

1. Whole water samples for the Core/ Trend program are collected directly from the bucket. Whole water samples from tidal stations are collected according to the specific SOP for the program being sampled. The sample will either be a one quart or a two quart sample that is sent to DHMH for analysis. One quart is collected for all stations. A second quart is collected for stations sampling for BOD (Potomac core stations). Whole water for the stations including BOD analysis can either be collected in two 1-quart bottles or one 2-quart bottle.
2. Bottles sent to DHMH for analysis must have the station name, date and sample number, e.g. C-12, on the bottle. It is recommended to add “CORE” on the bottle also since some of the same stations are sampled for the Non-Tidal Network Program. Bottles must be labeled legibly with a permanent marker (sharpie). Add depth if multiple depths are being collected at a single station (tidal stations). Do not write on the caps of bottles being sent to the DHMH lab.
3. Stir the water in the sampling bucket (without introducing bubbles) to create a homogeneous sample. Rinse the pre-labeled collection bottle(s) and cap(s) with the sample water 3 times. Fill the bottle(s) and cap tightly.
4. Place the bottle in ice in the sample cooler.
5. The following parameters are analyzed from the whole water bottle: total suspended solids, total alkalinity and turbidity. A second quart is collected to analyze for 5-day BOD on the Potomac core runs (Monocacy, Mid-Potomac & Lower Potomac runs).
6. Whole water samples for Western Maryland Core follow the above collection procedure, but are analyzed by the Western Maryland

Regional Laboratory. The Western Maryland Core stations are analyzed for the following parameters: total alkalinity, dissolved solids, sulfate, turbidity and suspended solids.

8.4 Collecting the filtered and particulate samples

8.4.1 Follow the above instructions for filling a bottle for filtration of the sample. Usually a 2- quart bottle or a one quart "plankton" bottle is used.

8.4.2 Chlorophyll (CHLA)

Chlorophyll samples are not collected for the Western Maryland Core.

1. For each sample, clean a 47mm bell with deionized (DI) water. Set up unit for filtering. Be sure that there is a trap in line between the manifold and the vacuum source.
2. Place a Whatman 47mm GF/F glass fiber filter pad on the filter frit. Always use clean forceps when handling the filter pads.
3. Mix sample thoroughly by agitating and shaking the sample bottle vigorously, then rinse graduated cylinder three times with sample.
4. Agitate the sample again before measuring in the graduated cylinder. Fill graduated cylinder with sample and filter desired volume through filtration unit. Be sure to use a graduate that is close to the volume being filtered (ex: if you are only filtering 80 ml of sample use a 100 ml graduate). Keep the vacuum pressure below 10 inches of Hg (around 8" Hg is good).
5. Filter sufficient volume of sample (20 - 2000 ml) to leave **noticeable color** on the filter pad.
6. Record the total volume filtered on the foil square.
7. Agitate the squirt bottle of $MgCO_3$, as it settles rapidly. Add approximately 1 ml of $MgCO_3$ suspension (1.0 g $MgCO_3$ in 100 ml of DI water) to the last 25 ml of sample in the filtration bell.

NOTE: Samples for dissolved parameters are not to be collected from this filtrate.

8. The pad should be removed as soon as the sample is completely filtered. The pad should not be left on the frit under vacuum. If you are unable to remove it immediately, be sure to release the vacuum to avoid damaging the sample.
9. Using forceps (1 or 2 pair), fold filter in half with sample inside and remove filter pad.
10. Place pad in pre-marked foil square, and carefully fold foil square in thirds, horizontally. Then fold the ends in to seal the filter inside. Be sure forceps do not touch sample residue on the filter pads, because the sample will adhere to the forceps.
11. Be sure that foil square is marked with the date, station, volume of sample filtered, and sample number.

12. Place foil packet into the labeled zip-lock plastic bag and place in the sample cooler on ice.

NOTE: The filter pads for chlorophyll analysis should not be exposed to direct sunlight. Store as soon as possible.

8.4.3 Particulate Carbon/ Particulate Nitrogen (PC/PN)

1. For each sample, clean two 25 mm filter bells with deionized (DI) water.
2. Place a pre-combusted 25 mm GF/F filter (direct from the lab) on each filter frit. Always use clean forceps when handling the filter pads.
3. Mix sample thoroughly by agitating and shaking the sample bottle vigorously, then rinse graduated cylinder three times with sample.
4. Agitate the sample again before measuring in the graduated cylinder. Fill graduated cylinder with sample and filter desired volume through filtration unit.
5. Filter 10-800 ml through each filter. Filter enough sample to leave **noticeable color** on the filter pad.
6. Make sure filter is sucked dry and the **same volume is filtered for both pads**.
7. Record the volume filtered (total volume through one pad - do not add the volumes for the 2 pads together) on the foil square.

NOTE: Samples for dissolved parameters are not to be collected from this filtrate.

8. Using forceps, fold each filter in half.
9. Place both filters in a foil square labeled with date, sample number, station, PC/PN, and volume filtered. Be sure that the pads are not overlapping in the foil square to keep them from freezing together. Fold foil square as described above.
10. Place the folded foil in the labeled zip-lock bag and place in the sample cooler

8.4.4 Particulate Phosphorus (PP)

1. Follow steps above setting up and rinsing two 47 mm filter bells and flasks. The filters used are two Whatman 47 mm GF/F filters (same pads we use for chlorophyll).
2. Filter 50 ml of sample through each filter pad. If 50ml will not go through one pad then filter a smaller volume through multiple pads to attain 50ml of filtrate.
3. Use the filtrate as an equipment rinse and discard.
4. Then filter enough additional (another 20 - 950 ml) to leave **noticeable color** on the filter pad.
5. Record the **total** volume filtered through each pad being sure to add the 50 ml rinse water (total volume through one pad – do not add the volumes for the 2 pads together) on the foil square.

6. **Use this filtrate to fill up the filtrate bottle for the dissolved parameter analysis.**
7. After collecting filtrate, make sure filter is sucked dry.
8. Rinse the filter pad using at least three - 10 ml rinses of DI water, sucking the pad dry after each rinse.

NOTE: If the volume filtered through one pad is ≤ 100 ml, you may want to collect all filtrate in one flask. To do this, filter 50ml to rinse one flask. Collect the remaining volume being filtered in this rinsed flask. Move the filter bell with the unused pad atop the flask containing the filtrate from the first pad (collection flask). Filter and collect the entire volume through the second pad. You may use the second flask as the "pad rinse flask". Place the bell with the already filtered sample pad atop this second flask. Use deionized water to rinse each sample pad 3 times, sucking dry after each rinse.

9. Using forceps, fold each filter in half.
10. Place both filters in a foil square labeled with station, date, PP, sample number, and volume filtered (this is the total volume of sample through each pad, including the initial 50 ml rinse). Be sure that the pads are not overlapping in the foil square to keep them from freezing together.
11. Fold the foil square as described above. Place foil square in labeled zip-lock bag and place in the sample cooler on ice until you return to the field office.

8.4.5 Filtrate collection (for the dissolved parameters TDN, TDP, NH_4, NO_2+ NO_3, NO_2, PO_4 & DOC)

1. A bottle of filtrate is collected for submission to the DHMH lab for the analysis of dissolved parameters. A 16 oz. bottle is typically used for this purpose. The bottle should be labeled with the station name, date, sample number, e.g. C-12, "CORE" and "filtrate". Bottles must be labeled legibly with a permanent marker (sharpie). Do not write on the caps of bottles going to the DHMH lab.
2. The filtrate should be collected from the PP filtration described in 7.4.4 above.
3. Rinse the labeled bottle and cap 3 times with filtrate.
4. Fill the bottle at least ¾ full with filtrate. Do not fill the bottle above the shoulder.
5. Place the bottle in ice in the sample cooler.

8.5 Completing the Laboratory Sheets

8.5.1 DHMH Chemistry Sheet

1. The chemistry sheets should already be labeled with the station numbers. There should be a separate sheet for each station.

The type of sample (whole, filtered, etc) and bottle number should also be pre-filled in. See Appendix V for an example.

2. The following items will need to be filled in:
   - Collector (last names of scientists)
   - Date
   - Start time
   - Salinity (place a line here since for non-tidal core stations where we don't record salinity. Fill in the salinity for the tidal core stations)
   - Field scientist sign-off
   - Start depth (always 0.0 m for bucket samples, but need to be to be filled in at tidal core stations)

8.5.2 Western Maryland Chemistry Sheet

1. The chemistry sheets for Western Maryland Core are also pre-labeled with the station number, bottle number and other header information (river & location, county, type of water sample).
2. The following items will need to be filled in:
   - Date
   - Time (start time in military time)
   - Collector (last name of scientists)
   - pH
   - Specific conductance

8.5.3 DHMH volume Sheet

1. The DHMH volume sheet should have the run name, station names, sample numbers, layer codes and depths all pre-filled in. Depths may need to be added on the volume sheets for the tidal core stations.
2. The following items will need to be filled in
   - Date
   - Time (start time in military time)
   - PP volume filtered, in ml
   - PC/PN volume filtered, in ml
   - Scientist sign-off

8.5.4 CBL Volume Sheet

1. The CBL volume sheet should have the run name, station names, sample numbers, layer codes and depths all pre-filled in. Depths may need to be added on the volume sheets for the tidal core stations.
2. The following items will need to be filled in
   - Date
   - Time (start time in military time)
   - CHLA volume filtered, in ml
   - Scientist sign-off

9.0 Sample Handling and Preservation

1. All samples (whole water, filtrate & pads) must be iced immediately after collection.
2. The whole water and filtrate samples are typically sent to DHMH via a courier. If courier service is used, drain all ice melt water from the cooler and repack, filling with ice up to the necks of the bottles before leaving the cooler at the courier. Be sure that the cooler reads "Baltimore Lab, Water Chemistry, 7th Floor" and "Return to Anne Arundel Health Dept." All lab sheets must accompany the samples in the cooler. Place the completed sheets in the zip-loc bag provided in the field pack.
3. The pads collected should be kept on ice and placed in the freezer in the bin marked "DHMH" upon return to the Field Office. The volume sheet for the particulate samples should be folded and placed in one of the bags of pads. If you are delivering directly to the DHMH lab then the pads may be given to the lab tech along with the whole water and filtrate bottles and they will store them properly. Samples that have been stored frozen at the Field Office are delivered to DHMH at the end of the sampling week. Use enough ice in the delivery cooler to ensure that the samples stay frozen.
4. The Western Maryland Core samples are delivered to the Western Maryland Regional Laboratory in Cumberland. The whole water and filtrate bottles are delivered to DHMH in Baltimore via courier. The filtered pads can be left in the freezer overnight at the lab at the end of the day. The pads must be brought back to the Field Office in a frozen state. On the last day of sampling get dry ice (Wilson Supply, Inc. 15401 McMullen Hwy, Cumberland (301) 729-2515; acct # 7724) to bring the samples back to Annapolis. Place the samples in the freezer immediately after returning to the Field Office.

10.0 Data and Records Management

10.1 All samples collected are labeled and recorded on the field sheet. The field sheets are reviewed for accuracy and completeness and then submitted to the Principal Investigator and Quality Assurance Officer (RAS/TEA). A progress report/ cross reference sheet accompanies the original field sheets. The progress report/ cross reference sheet tracks which samples were taken at each site. Any comments or additional samples are noted on this sheet. Notes about instrumentation problems, etc are included with the report. For more information refer to SOP # DR-05: *QA/QC and submission of field data*. An example of a cross reference sheet can be found in Appendix III. Copies of all field sheets, with their attached progress report/ cross reference sheets, are kept on file at the Field Office.

10.2 The whole water and filtered samples submitted to DHMH also have laboratory sheets associated with them. The sheets are submitted with the samples at the time of delivery, by either direct delivery to DHMH or in the cooler via courier. The laboratory data are reported on the lab sheet and sent directly to MDNR, TEA. No copies of the DHMH lab sheets remain at the Field Office.

10.3 A separate laboratory sheet accompanies the whole water samples collected for Western Maryland Core to the Western Maryland Regional Lab. Laboratory results are sent directly to MDNR, TEA. An additional copy of the results is sent to Laura Fabian and the copies are placed in the file with the packet of field sheet copies.

10.4 The filter pads have a volume sheet associated with them. There is one volume sheet for the particulate pads (PC/PN & PP) that are sent to DHMH. The results for these parameters are submitted to TEA at the bottom of the whole and filtered water sample laboratory sheet. A second volume sheet accompanies the chlorophyll samples to CBL and the results are sent directly to TEA in a data report. No results or lab sheets are kept on file at the Field Office.

11.0 Quality Control and Quality Assurance

11.1 Samples are collected by properly trained staff to ensure continuity of high quality samples. Field staff must adhere to all Standard Operating Procedures.

11.2 Field duplicates (replicates) are collected every 20 samples to check for accuracy of field collection and preparation of the samples.

11.3 Quality control and quality assurance are maintained by proper cleaning and decontamination of sampling gear. Refer to SOP # MC-01: *Cleaning and decontamination of sampling equipment*.

11.4 Equipment blanks of deionized water are submitted monthly to catch any possible contamination. Refer to SOP MC-02: *Deionized water, blank sample checks*.

11.5 If contamination occurs, every effort is made to pinpoint the source of the contamination and eliminate it.

12.0 References

1. Maryland Department of Natural Resources. 2008. *Quality Assurance Project Plan. Chesapeake Bay Water Quality Monitoring Program- Chemical and Physical Properties Component, 2008-2009.*

2. Maryland Department of Natural Resources. *Standard Operating Procedures Manual.* Water Quality Monitoring Program. WQMP Field Office, 1919 Lincoln Drive, Annapolis, MD 21401.

    1. Standard Operating Procedure # SC-01: *Field Collection of Grab Water Samples*

    2. Standard Operating Procedure # SC-02: *Collection of Whole Water Samples*

    3. Standard Operating Procedure # SC-03: *Field Filtration for Particulate and Dissolved Nutrient Constituents*

    4. Standard Operating Procedure # SC-04: *Pycnocline Calculation*

    5. Standard Operating Procedure # SC-05: *Collection of Live Plankton Samples*

    6. Standard Operating Procedure # MC-01: *Cleaning and Decontamination of Sampling Equipment*

    7. Standard Operating Procedure # MC-02: *Deionized Water, Blank Sample Checks*

    8. Standard Operating Procedure # DR-05: *Quality Assurance/ Quality Control and Submission of field data*

Appendix I.: Station List for Core/ Trend

BALTIMORE CORE

DATA CODE	NEAREST TOWN	COUNTY	BODY OF WATER	STATION #	STATION LOCATION
1B	ELKRIDGE	HOWARD	PATAPSCO RIVER	PAT 0176	U.S. ROUTE 1
1D	HOLLOFIELD	HOWARD	PATAPSCO RIVER	PAT 0285	MD ROUTE 99
1B	VILLA NOVA	BALTIMORE	GWYNNS FALLS	GWN 0115	ESSEX ROAD
1B	FINKSBURG	CARROLL	N.BR.PATAPSCO	NPA 0165	MD ROUTE 91, GAGE
1B	SORRENTO	BALTIMORE	JONES FALLS	JON 0184	FALLS ROAD GAGE
1B	TOWSON	BALTIMORE	GUNPOWDER FALLS	GUN 0125	CROMWELL BRIDGE

SUSQUEHANNA CORE

DATA CODE	NEAREST TOWN	COUNTY	BODY OF WATER	STATION #	STATION LOCATION
1D	DARLINGTON	HARFORD	DEER CREEK	DER 0015	STAFFORD BRIDGE
1B	CONOWINGO	HARFORD	SUSQUEHANNA	CB1.0	BELOW CONOWINGO DAM,
1B	HOFFMANVILLE	BALTIMORE	GUNPOWDER FALLS	GUN 0476	GUNPOWDER ROAD
1B	GLENCOE	BALTIMORE	GUNPOWDER FALLS	GUN 0258	GLENCOE ROAD BRIDGE,GAGE

HAGERSTOWN CORE

DATA CODE	NEAREST TOWN	COUNTY	BODY OF WATER	STATION #	STATION LOCATION
1B	FUNKSTOWN	WASHINGTON	ANTIETAM CREEK	ANT 0203	POFFENBERGER ROAD
1D	LEITERSBURG	WASHINGTON	ANTIETAM CREEK	ANT 0366	MILLER CHURCH RD
1D	FAIRVIEW	WASHINGTON	CONOCOCHEAGUE	CON 0180	GAGE NEAR FAIRVIEW
1B	WILLIAMSPORT	WASHINGTON	CONOCOCHEAGUE	CON 0005	MD ROUTE 68 BRIDGE
1B	HANCOCK	WASHINGTON	POTOMAC RIVER	POT 2386	GAGE NEAR RT 522

MONOCACY CORE

DATA CODE	NEAREST TOWN	COUNTY	BODY OF WATER	STATION #	STATION LOCATION
1D	TANEYTOWN	CARROLL	BIG PIPE CREEK	BPC 0035	BRUCEVILLE GAGE
1B	EMITTSBURG	FREDERICK	MONOCACY RIVER	MON 0528	BRIDGEPORT BRIDGE, GAGE
1D	FREDERICK	FREDERICK	MONOCACY RIVER	MON 0269	BIGGS FORD ROAD
1D	MIDDLETOWN	FREDERICK	CATOCTIN CREEK	CAC 0148	MD ROUTE 17, GAGE
1B	SHEPHERDSTOWN	WASHINGTON	POTOMAC RIVER	POT 1830	SHEPHERDSTOWN W.V. WEST VIRGINIA
1D	SHARPSBURG	WASHINGTON	ANTIETAM CREEK	ANT 0044	BURNSIDE BRIDGE, gage

PATUXENT LAND CORE

DATA CODE	NEAREST TOWN	COUNTY	BODY OF WATER	STATION #	STATION LOCATION
1B	UNITY	HOWARD	PATUXENT RIVER	PXT 0972	MD ROUTE 97 GAGE
1B	LAUREL	ANNE ARUNDEL	PATUXENT RIVER	PXT 0809	BELOW ROCKY GORGE DAM

LOWER POTOMAC CORE

DATA CODE	NEAREST TOWN	COUNTY	BODY OF WATER	STATION #	STATION LOCATION
1D	CABIN JOHN	MONTGOMERY	CABIN JOHN BR.	CJB 0005	MACARTHUR BLVD.
1B	BROOKMONT	MONTGOMERY	POTOMAC RIVER	POT 1184	LITTLE FALLS GAGE
1D	CHEVY CHASE	MONTGOMERY	ROCK CREEK	RCM 0111	MD ROUTE 410
1B	BLADENSBURG	PR. GEORGES	ANACOSTIA R.	ANA 0082	BLADENSBURG ROAD

MID POTOMAC LAND CORE

DATA CODE	NEAREST TOWN	COUNTY	BODY OF WATER	STATION #	STATION LOCATION
1B	FREDERICK	FREDERICK	MONOCACY RIVER	MON 0155	PINE CLIFF PARK, REELS MILL ROAD
1D	BRUNSWICK	FREDERICK	CATOCTIN CREEK	CAC 0031	MD ROUTE 464,
1B	DICKERSON	FREDERICK	MONOCACY R.	MON 0020	ROUTE 28
1E	PT. OF ROCKS	FREDERICK	POTOMAC RIVER	POT 1595	EAST BANK ROUTE 15
1E	PT. OF ROCKS	FREDERICK	POTOMAC RIVER	POT 1596	WEST BANK ROUTE 15
1B	POOLESVILLE	MONTGOMERY	POTOMAC RIVER	POT 1472	WEST BANK WHITES
1B	POOLESVILLE	MONTGOMERY	POTOMAC RIVER	POT 1471	EAST BANK WHITES FERRY
1B	SENECA	MONTGOMERY	SENECA CREEK	SEN 0008	MD ROUTE 112

WESTERN MARYLAND

DATA CODE	BOT #	NEAREST TOWN	COUNTY	CO. CODE	BODY OF WATER	STATION	STATION LOCATION
DAY 1							
1D	C-7	GRANTSVILLE	GARRETT	11	CASSELMANS R.	CAS0479	RIVER ROAD GAGE
1D	C-8	FRIENDSVILLE	GARRETT	11	YOUGHIOGHENY R.	YOU0925	FRIENDSVILLE
1D	C-9	DEEP CREEK	GARRETT	11	CHERRY CREEK	CCR0001	STATE PARK
1D	C-9 dup						ROAD
1D	C-10	OAKLAND	GARRETT	11	YOUGHIOGHENY R.	YOU1139	RT 20, GAGE
1D	C-11	OAKLAND	GARRETT	11	LITTLE YOUGHIOGHENY R	LYO0004	OAKLAND
1B	C-12	KITZMILLER	GARRETT	11	N. BR.POT. R.	NBP0689	MD 38, GAGE
1D	C-14	BLOOMINGTON	GARRETT	11	SAVAGE RIVER	SAV0000	Rt 135
1B	C-13	BLOOMINGTON	GARRETT	11	N. BR. POT. R.	NBP0534	BLOOMINGTON

1B	C-15	WESTERNPORT	ALLEGANY	01	GEORGES CREEK	GEO0009	WESTERNPORT, GAGE
1D	C-16	KEYSER WV	ALLEGANY	01	N.Br.Potomac R.	NBP0461	RT 220
1B	C-17	PINTO	ALLEGANY	01	N.Br.Potomac R.	NBP0326	RT. 956, GAGE

DAY 2

1D	C-5	CUMBERLAND	ALLEGANY	01	WILLS CREEK	WIL0013	LOCUST GROVE RD, GAGE
1D	C-6	CUMBERLAND	ALLEGANY	01	BRADDOCK RUN	BDK0000	OLD MT SAVAGE Rd
1B	C-1	CUMBERLAND	ALLEGANY	01	N.Br.Potomac R	NBP0103	SPRING GAP
1D	C-2	OLDTOWN	ALLEGANY	01	N.Br.Potomac R	.NBP0023	OLDTOWN
1D	C-4	PAW PAW WV	ALLEGANY	01	POTOMAC RIVER	POT2766	PAW PAW WV, Rt. 51,GAGE
1B	C-3	OLDTOWN	ALLEGANY	01	TOWN CREEK	TOW0030	PACK HORSE RD

PARAMETERS CHECKED ON THE ALLEGANY LAB SHEET ARE
ALKALINITY (TOTAL), SULFATE, DISSOLVED SOLIDS, TURBIDITY
PARAMETER ADDED TO THE SHEET IS: SUSPENDED SOLIDS.
IRON no longer sampled as of 6/30/02, bactis no longer sampled after 11/03, all whole water to WMRL and only 16 ounce filtrate to DHMH as of 10/05. **SUBMITTER IS 52**

POTOMAC BOAT CORE

DATA CODE	NEAREST TOWN	COUNTY	BODY OF WATER	STATION #	STATION LOCATION
1B	-----	CHARLES	POTOMAC RIVER	XDC 1706	MORGANTOWN BRIDGE
1E	-----	CHARLES	POTOMAC RIVER	XDA 1177	BUOY C19 OF MD POINT
1E	-----	CHARLES	POTOMAC RIVER	XDA 4238	BUOY 27 OFF SMITH POINT
1E	-----	CHARLES	POTOMAC RIVER	XEA 1840	BUOY 44 OFF POSSUM POINT
1E	-----	CHARLES	MATTAWOMAN CR.	MAT 0016	DAYMARKER 5 OFF SWEDAN PT.
1B	-----	CHARLES	POTOMAC RIVER	XEA 6596	BUOY N54 OFF INDIAN HEAD
1E	-----	PR. GEORGES	POTOMAC RIVER	XFB 1433	BUOY 67 OFF DOGUE CREEK
1E	-----	PR. GEORGES	POTOMAC RIVER	XFB 2470	BUOY 77 OFF PISCATAWAY CR.
1E	-----	PR. GEORGES	POTOMAC RIVER	XFB 1986	OFF FT. WASHINGTON MARINA
1E	INDIAN HEAD	CHARLES	MATTAWOMAN CR.	MAT 0078	MD ROUTE 225
1E	ACCOCEEK	PR. GEORGES	PISCATAWAY CR.	PIS 0033	MD ROUTE 210

Appendix II: Core/ Trend Program History

Core History Feb 25. 2009

1974-1997 Bacteriological samples collected all core stations and Potomac Boat.

April 1997 Turkey Pt – CB2.1 (XJH6680) & Sandy Pt – CB3.3C (XHF1373) now being sampled on Main Bay. 15 ft plankton for XHF1373 now sampled @ 5 meters.

May 1998 Bacteriological Labs @ Frederick & Cheverly closed. Monocacy, Mid Potomac, Lower Potomac/ Patuxent and Potomac Boat runs bacti samples dropped.
Bactis still collected for Baltimore, Susquehanna, Hagerstown & Western MD.

April-December 1999 and April, May & September 2000
Only WMD core (no trend) stations sampled due to body shortage at field office.

October 2000
Extra bactis collected @ CCR0001, NBP0103, NBP0534 and NBP0689 for bucket vs. direct stream comparison.

June 2001 name change CHO0626 to ET5.0 (Red Bridges)

July 2002 Western MD samples no longer tested for iron.

November 2003
WMD bacteriological samples no longer submitted. Whole water to WMRL and only filtrate plus pc/pn/pp filter pads to DHMH as of October 2005. Prior to that we were submitting a second quart of water to DHMH that was acid fixed by WMRL and shipped to DHMH via courier.

2004 Remaining Core runs dropped bacteriological sampling.

October & November 2004
Laboratory comparison. Collected regular sampling and 16 ounce filtrate and pc/pn pads at all stations.

July 2005 Began PC/PN/PP & filtered nutrient sampling for all core stations in addition to whole water and chlorophyll pads. Whole water to WMRL and only 16 ounce filtrate and PC/PN/PP pads to DHMH. Prior to that we were submitting 2 quarts

of whole water to DHMH, one of which was acid fixed by WMRL and both were shipped to DHMH via courier

July 2005 PXT0603 (TF1.0). and Kent Narrows (XGG8251) were no longer submitted with the core paperwork. TF1.0 submitted with Patuxent and XGG8251 submitted with Tributary data.

November and December 2008

Extra TSS pads generated with a churn splitter for Monocacy, Susquehanna, Baltimore, Lower Potomac Patuxent and the 2nd day of Western MD core.

January 2009

Chlorophylls now being processed by CBL due to budget cuts and people shortages @ DHMH. Equipment used @ DHMH will be given to CBL to process samples.

Appendix III: Progress Report/ Cross Reference Sheet

Maryland Department of Natural Resources
Chesapeake Bay Water Quality Monitoring

Progress Report / Cross Reference Sheet - CORE

Month/ Year: January/ 2009 **Submitted by: Laura Fabian**

Station	Day	Sequence #	Depth (M)	Sample #	Lab (DHMH)	Chloro. (CBL)	Comments
ET5.0 Red Bridges		0901C01	0.0	ET5.0			
Patuxent Land Core							
PXT0809 Rocky Gorge	7	0901C02	0.0	C-34			
PXT0972 Unity	7	0901C03	0.0	C-35			
Susquehanna Core							
DER0015 Deer Creek	6	0901C04	0.0	C-24			
GUN0258 Glencoe	6	0901C05	0.0	C-27			
GUN0476 Above Prettyboy	6	0901C06	0.0	C-26			
CB1.0 Below Conowingo Dam	6	0901C07	0.0/1	C-25			
			0.0/2	C-25 dup			

Appendix IV: Field Sheet

Maryland Department of Natural Resources

Field Sheet

R 1 **Project Name:** Core-Western MD

Submitter: AFO-Fabian

Sequence Number C 3 8 (punch in 3-9 all cards)

Data

Sampling Station Number	Start Date Year	Month	Day	Start time	End Date Year	Month	Day	End Time	Number of Samples	submitter code	Category Code	Total Depth M	Study Code
POT2766									01	80	AA		040

R 2

Sample Method	+/-	Air Temp °C	Tide State	Weather code Yesterday	Weather code Today	Cloud Cover (%)	Wind Direction	Wind Velocity (Knots) Min.	Max.	Secchi (M)	Basis	Flow Value	Exp	G/L	Senior Scientist
1															

DO Method	Equip. Set Unit #	Probe Number	Flow Tide Unit #	Wave Height (M)	Upper (M) Pycnocline Limit	Lower (M) Pycnocline Limit	Scientist Sign Off	gage height
H	9	9						0

R 3 begin comments here

R 4 0

Rep No.	Depth M	Water +/- Temp. °C	Field pH	Cor. Flag	D O mg/l G/L	Conductivity G/L Micromhos/cm	Salinity ppt	Rep Code	Sample Depth M	Layer Code	LAB LOGIN Bottle Number
1	00		0	C	0			1	00	S	C-4

other information

Weather Codes
10 = none
11 = drizzle
12 = rain
13 = rain, heavy
14 = squally
15 = frozen precipitation

pc/pn volume _____ml
pp/tss volume _____ml

USGS # 01610000
Potomac River @ Paw Paw, WV

Date Entered _____

DNR 2/2008

Page 1 of 1

Appendix V: DHMH Chemistry Sheet

R 5 study code: 0 4 Replicate:
1 2 3 4 5

Maryland Department of Natural Resources

Sequence Number
6 (punch in 6-13 all cards) 13

Survey: Core: Western MD

Collector: _____
AFO-410-990-4524/L. Fabian

Laboratory Analysis Sheet (Core/Trend Program)

Data Code 1D

Sample Station Number: P O T 2 7 6 6
17 25

Date (Year Month Day) 27 32 | Submitter

Start Depth M: 0 0 (33 35) | End Depth M (36 38) | Start Time (39 42) | Code: 8 0 (43 44)

Bottle Numbers:

Type of Sample: Filtered (2-8 oz. bottles) | Salinity: ppt

C - 4 (45 53) | C - 4 (56 64) | (68 76) | 0 (80)

R 6

Sample Method	Data Category Code	Sample Layer	Field Scientist Sign Off	Date received by Lab (Year Month Day)	Time Received by Lab	Batch Number	
1 (14)	A A (15 16)	S (17 18)	(19 21)	(22 27)	(28 31)		0 (80)

R 7

Check test Required	Parameter Description / Units	Parameter Code (14 17)	Method Code (18 20)	Analysis Problem Code (22 23)	G/L (25)	Results Record Decimal in a Box (26 31)	Percent Recovery (33 35)	Standard Deviation (37 41)	Number in Sample (43 44)	Analyst Sign Off (46 48)	
X	TDN as N (F) mg/l	T D N									0
X	Ammonia as N (F) mg/l	N H 4									
X	$NO_2 + NO_3$ as N (F) mg/l	N O 2 3									
X	Nitrite as N (F) mg/l	N O 2									
X	PO_4 as P (F) mg/l	P O 4									
X	Total Dissolved P (F) mg/l	T D P									
X	Dissolved Organic C (F) mg/l	D O C									
	Sulfate as SO_4 mg/l	S O 4									
	Turbidity NTU (W)	T U R B									
	Total Alkalinity (W) mg/l	T A L K									
	Total Susp. Solids (W) mg/l	T S S									
	Dissolved Solids mg/l	D S O L									
X	Part. Phosphorus as P mg/l	P P									
X	Part. Carbon as C mg/l	P C									
X	Part. Nitrogen as N mg/l	P N									

R 8 (1 2)

Date Reported (Year Month Day) 14 19 | Final Lab sign off (20 22) | QA/QC sign off (23 25) | Transcriber sign off (26 28)

Send Results To:

Bruce Michael
DNR D-2 Tawes Building
Annapolis, MD 21401
bmichael@dnr.state.md.us
410-260-8627

0 (80)

Date Entered: _____

DNR 5/2005

Appendix VI: Western Maryland Chemistry Sheet

SEND REPORT TO:
DEPT. OF NATURAL RESOURCES
MANTA
1919 LINCOLN DRIVE
ANNAPOLIS, MD 21401
ATTN: LAURA J. FABIAN

DEPARTMENT OF HEALTH AND MENTAL HYGIENE
Laboratories Administration
201 W. Preston St.
P.O. Box 2355, Baltimore, Maryland 21203

WATER ANALYSIS

Lab No. Date Received

Do not write above this line.

SAMPLE ID

Bottle Number C-7 Name CAS0479 County Garrett County Code 11

Source Casselman R @ Rive Road Data Category Code 1D

Collected: Date 4- -09 Time Collector & Phone 410 9904524 Submitter Code 52

CHECK (one per box)

Drinking Water / Landfill / Stream / Other	Community / Non-community / Private / Other	Source (raw water) / Distribution (treated) / MCL	Emergency / Routine / Recheck / Special	Federal Project
	X	X		

FIELD

Plant No. Sampling Station CAS 0479 Preservation: Iced X Acid Type of Acid

pH Chlorine: Free Total Specific Conductance

Notes to Lab/Remarks: CORE

CHECK TESTS	TESTS	ERROR CODE	RESULTS
✓	Alkalinity (Total)		
	Ammonia - N		
	Chloride		
	Color*		
	Conductance*, Spec.		
✓	Dissolved Solids		
	Hardness		
	Fluoride		
	Nitrite, N		
	Nitrate - Nitrite, N		
✓	Sulfate		
	Total Solids		
✓	Turbidity*		
	Other:		
✓	Suspended Solids		

* Results reported in Units, all others in milligrams per liter (ppm)

Number of Tests Requested

Section Chief

Date Reported

DHMH 80-A 7/04

ORIGINAL LABORATORY

Appendix VII: Particulate Sample Labels

DNR 3/ /2009 DHMH
CAS0479 S
C-7

PP_____ML

DNR 3/ /2009 DHMH
CAS0479 S
C-7

PC/PN_____ML

DNR 1/ /2009 Western MD
PC/PN Blank Core
Place 2 (if you have them left over) pads in foil & submit with rest of samples.

DNR 3/ /2009 DHMH
PAT0176 S
C-18

PP_____ML

DNR 3/ /2009 CBL
PAT0176 S
C-18

CHLA_____ML

DNR 3/ /2009 DHMH
PAT0176 S
C-18

PC/PN _____ML

Appendix VIII: DHMH Volume Sheet

Baltimore Core DNR-MANTA
DHMH

DATE_____ **SCIENTIST SIGNOFF_____**

STATION	SAMPLE #	LAYER CODE	DEPTH (M)	TIME (MLTY)	PP Vol. Filtered. (ml) Big pads	PC/PN Vol. Filt (ml) Little pads
PAT0176 Patapsco	**C-18**	**S**	**0.0**			
PAT0285 Patapsco	**C-19**	**S**	**0.0**			
GWN0115 Gwynns Falls	**C-20**	**S**	**0.0**			
NPA0165 N BR Patapsco	**C-21**	**S**	**0.0**			
JON0184 Jones Falls	**C-22**	**S**	**0.0**			
GUN0125 Gunpowder Falls	**C-23**	**S**	**0.0**			

Appendix IX: CBL Volume Sheet

Baltimore Core DNR-MANTA

CBL

DATE _____ **SCIENTIST SIGNOFF**_____

STATION	SAMPLE #	LAYER CODE	DEPTH (M)	TIME (MLTY)	Chlorophyll volume (ml)
PAT0176 Patapsco	C-18	S	0.0		
PAT0285 Patapsco	C-19	S	0.0		
GWN0115 Gwynns Falls	C-20	S	0.0		
NPA0165 N BR Patapsco	C-21	S	0.0		
JON0184 Jones Falls	C-22	S	0.0		
GUN0125 Gunpowder Falls	C-23	S	0.0		

Appendix III: Maryland Department of Health and Mental Hygiene, Environmental Chemistry Division: Standard Operating Procedures for Water Quality Parameters

Table of Contents – Appendix III

Standard Operating Procedures

Determination of Total Alkalinity by Titrimetry

Standard Method 2320B

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to drinking, surface, saline, and waste waters.

1.2 Alkalinity of water is its acid-neutralizing capacity. It is the sum of all the titratable bases, such as carbonate, bicarbonate, hydroxide, etc. The measured alkalinity may vary significantly with the end-point pH used.

1.3 This method is suitable for all concentration ranges of alkalinity. However, an appropriate aliquot should be used to avoid titration volumes greater than 45 mL.

2.0 SUMMARY OF METHOD

Alkalinity is determined from the volume of a standard acid required to titrate a portion of the sample to an electrometrically determined endpoint of pH 4.5 by an automated system. When the endpoint is from pH 4.3 – 4.9, the total alkalinity is due entirely to the measure of carbon dioxide evolving from carbonates and bicarbonates. The sample must not be filtered, diluted, concentrated or altered in any way.

3.0 INTERFERENCES

Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrode occasionally.

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 color reagent is prepared.

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 Computer and software

5.1.1.2 Interface module

5.1.1.3 Burivar-1/2 buret module

5.1.1.4 Beaker autosampler

5.1.1.5 Combination pH electrode – Mantech model # PC-PH1105

5.1.1.6 Temperature probe

5.1.1.7 Stirrer

5.1.1.8 Dispense tip

5.1.1.9 HP Laser Jet 1320 printer

5.1.2 Analytical balance – Mettler Toledo AG204

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 Volumetric pipette – 1 mL

5.2.5 Glass bottle – 1 liter size, for 0.02N H_2SO_4 (sect. 6.1.2)

5.2.6 Carboy – 5 L size, for deionized water pumped to rinse beaker in autosampler tray

5.2.7 Transfer pipettes – Samco, cat. # 231

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Deionized water

6.1.2 Sulfuric acid (H_2SO_4), 0.02N – Fisher, cat. # SA 226-4

6.1.3 Reference electrode filling solution, 4M KCl – Fisher, cat. # SP138-500

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 # 1427810

6.2.5 Intermediate standard, 5000 mg/L $CaCO_3$ – 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 $CaCO_3$ – 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.

6.2.7 Quality control (QC) Sample, QC-MIN-WP – Add approximately 900 mL of deionized water to a 1000 mL volumetric flask. Transfer exactly 10.0 mL of the concentrate from each ampule into the flask. Fill to mark with deionized water. Mix thoroughly. Transfer to a reagent bottle, label, and store at 4 ^{o}C. Prepare every 6 months. If a different QC is used, follow the sample preparation instructions given in the accompanying paper work.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in 1 liter polyethylene cubitainers and iced or refrigerated to 4 ^{o}C.

7.2 The holding time is 14 days when refrigerated at 4 ^{o}C. The analysis is performed on un-acidified and unfiltered samples.

8.0 QUALITY CONTROL

8.1 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%. Blanks and blank spikes not meeting these criteria are reanalyzed.

8.2 The acceptable window for the slope of the calibration curve is -61 mV to -57 mV. Calibration is repeated if the slope falls outside this range.

8.3 Every tenth sample is duplicated (analyzed from two different beakers) and spiked. The acceptable values for the relative percent difference (RPD) are ± 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 QC sample with known alkalinity is analyzed at the beginning and the end of each analytical run.

8.5 Data acceptance criteria are listed on the data review checklist. (Appendix B).

8.6 Laboratory participates in yearly ERA WatR Supply (WS) and WatR Pollution (WP) Proficiency Tests.

8.7 A demonstration of capability study is performed by each analyst performing the test by analyzing four replicates of an external quality control samples during one or two analytical runs.

9.0 PROCEDURE

9.1 Sample preparation

9.1.1 Prepare a list of samples to be analyzed on a Sample Run Log. (Appendix A).

9.1.2 Pour approximately 60 mL of the pH 4, pH 7 and pH 10 buffers into separate, 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 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 Electrode preparation

9.2.1 Disconnect the electrode from the unit. Empty the electrode with a plastic disposable pipet. Rinse with deionized water. Rinse with and then, fill up with 4 M KCl.

9.2.2 Connect the electrode. Soak electrode in pH 4 buffer for a minimum of one hour. Then, return it to the position in the probe holder.

9.3 Buret preparation

9.3.1 Turn the computer on. Double click on “PC Titrate” and enter user name and password to open the main menu.

9.3.2 Remove the titrant delivery line from the electrode block on the autosampler and place it into a waste beaker.

9.3.3 Check buret for bubbles by raising it up by hand after unscrewing bolt and lowering it to its original position. Screw bolt back.

9.3.4 Select “Titrator” and select “Manual Control” from the pull down list. Wait for buret to reset. Click on “Buret” tab.

9.3.5 Click on button labeled “10%” to dispense 10% of the volume of the buret through the titrant delivery line. Repeat until no bubbles are observed in the flow.

9.3.6 Refill the buret by clicking on “Full Down”.

9.3.7 Remove the dispenser tip from the waste beaker and return it to its position in the probe holder.

9.4 Electrode calibration

9.4.1 Turn on autosampler. Wait for probe holder to go up.

9.4.2 With the electrode, the dispense tip, and the temperature probe all aligned on the holder, click on “Digital” tab. Click on “Run”, then “OK”. On the top row of digital outputs, check the system by clicking on “4”, “2”, “2” again, then “4” again to wash dispense line, to home the probe holder and lower it into the rinse beaker. Click “OK” to return to the “Manual Control”.

9.4.3 Place pH 4.0, 7.0 & 10.0 buffers into autosampler tray using position # 1, 2 & 3.

9.4.4 Click on the “Book” tab. Enter pH 4, pH 7 and pH 10 under sample name. Press “Start”.

9.5 Sample analysis

9.5.1 Click on the “Water Drop” tab to call up the sample table.

9.5.2 Run samples with calibration: Enter “4-7-10” under sample name at the first row reserved for pH calibration. Fill in sample names starting with the second row.

9.5.3 Run samples only: Double click on “pH Calibration” and replace it with “pH Alkalinity”. Fill in sample names starting with the first row.

9.5.4 For a new run, the next six entries are TAP, TAP Dupl, TAP Sp, DEMIN, reagent water, and QC. After samples are entered, enter reagent water and QC again at the end of the run (Appendix A).

9.5.5 Highlight each excess line, and then click on “Delete Highlighted Sample” to remove all unused sample information.

9.5.6 Click “Time Table” to make sure the time table is valid. Click “OK”. Roll down the table to check that all information entered is correct.

9.5.7 Click on “Start”.

9.5.8 *Calibration Report* and *Total Alkalinity Results* will be printed out automatically at the end of the run.

9.5.9 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.

9.5.10 “Equation Results” can be printed out by clicking on “Print” and “OK”.

9.5.11 When finished fill buret up to 25 mL by clicking on Syringe “Full Down”, rinse the line by clicking on “Output 4”, and send probe back by clicking on “Output 2” twice. Click “OK”.

9.5.12 Store the electrode in pH 4 buffer.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Calculations are performed automatically by the "PC-Titrate Windows software (version 2.5). Based on 1 mL of 0.1N H_2SO_4 = 5.0 mg $CaCO_3$, the formula used to calculate total alkalinity, in mg $CaCO_3$/L is:

$$\text{Alkalinity, mg } CaCO_3/L = \frac{\text{titrant dispensed (mL) x 0.02N } (H_2SO_4) \text{ x 50,000}}{\text{sample volume (mL)}}$$

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

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

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

$$\%\ RPD = \frac{\text{difference between the duplicates}}{\text{average of the duplicates}} \text{ x } 100$$

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 Results are first reviewed by a second scientist using the data review check list, and then, reported on sample analysis request forms. The normal turnaround time for samples submitted to this lab for analysis is 2 to 10 days from receipt.

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 United States Environmental Protection Agency, *Methods for Chemical Analysis of Water and Wastes.* EPA 600/4-79-020, Method Number 310.1, August, 1993.

13.2 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater,* Method Number 2320B, 21st Edition, 2005.

13.3 Man-Tech Associates inc., *PC-Titrate Windows Software Manual,* version 2.5.

13.3 Division of Environmental Chemistry, Maryland Department of Health and Mental Hygiene, *Quality Assurance Plan,* Revision 8.0, 2007.

APPENDICES

Appendix A – Total Alkalinity Run Log
Appendix B – Data Review Checklist

APPENDIX A

State of Maryland
DHMH – Laboratories Administration
Division of Environmental Chemistry

GENERAL CHEMISTRY SECTION

Sample Run Log – Total Alkalinity

Standard Method 2320B

Date: _____ Analyst: _____ Analyte: _____

Cup #	Sample ID	dilution	ppm
1	pH 4		
2	pH 7		
3	pH 10		
4	Ck Std		
5	Blank		
6	Blank Spike		
7	QC		
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			

Cup #	Sample ID	dilution	ppm
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			
31			
32			
33			
34			
35			
36			
37			
38			

Sample Name	Prep Log ID
pH 4 buffer	
pH 7 buffer	
pH 10 buffer	
QC:	
H_2SO_4, 0.02N	
Na_2CO_3, 25,000 ppm	
Na_2CO_3, 1000 ppm	
Na_2CO_3, 50 ppm	

Lab #	Average (ppm)	% RPD	% Spk Rec

APPENDIX B

State of Maryland
DHMH Laboratories Administration
Division of Environmental Chemistry

GENERAL CHEMISTRY SECTION

Data Review Checklist – Total Alkalinity

Standard Methods 2320B

Lab Numbers[1]:_____

Date Collected: _____ Date Analyzed: _____ Analyst: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	14 days @ 4°C		
Samples Analyzed	Within 5 working days		
Calibration Results	Slope = –61.00 to –57.00 mV		
External QC[2]	Beginning and end of each run		
	Within acceptable range		
Reagent Blank	< Reporting level (1 mg/L)		
Blank Spike	1 per batch		
	Recovery = 90 – 110%		
Duplicates/Replicates	Every 10th and the last sample or 1/batch, if less than 10 samples		
	RPD ≤ 10%		
Matrix Spike	Every 10th and the last sample or 1/batch, if less than 10 samples		
	Recovery = 90 – 110%		
Decimal Places Reported	0		
Measured Values	Within limits of titration (1 to 900 ppm)		
Samples > 900 ppm	Use sample volume between 40 to 50 mL to reduce titrant used to ≤ 45 mL		
	Correct final calculations		
Changes/Notes	Clearly stated		

* Check (√) if criteria are met.

_____ Date Reported: _____
Reviewer's Signature & Date

[1]Include beginning and ending numbers, account for gaps by bracketing.

[2]QC Sample: _____ Tracking ID: _____

True Value = _____ Acceptable Range = _____

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 reference file of MSDS is available in room 7D1.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Hach Model 2100AN Laboratory Turbidimeter – consisting of a nephelometer with a tungsten-filament lamp for illuminating the sample and detectors to measure scattered light.

5.1.2 Computer – Dell, Microsoft Windows 98

5.1.3 Printer – Hewlett-Parker Deskjet 722C.

5.2 Supplies

5.2.1 Sample cells – 30 mL capacity, item # 20849-00, Hach Co.

5.2.2 Pipettes – Volumetric, class A, 5, 10, 20, and 25 mL.

5.2.3 Flasks – Volumetric, class A, 50 mL, 100 mL and 200 mL

5.2.4 Flasks – Erlenmyer, 50 mL and 100 mL

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 $\frac{1}{2}$ 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 Chemicals. Use freshly poured portions for calibrating the turbidimeter and discard the used standards when calibration is complete.

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. Read these standards at the beginning of each analytical run.

6.2.3 Quality Control Sample – QC-TUR-WS, Spex Certiprep Inc. Empty the entire contents into a small beaker and gently swirl to mix thoroughly. Do not rinse the ampule. Immediately transfer 10.0 mL of the concentrated solution into a 200 mL volumetric flask and bring to volume with deionized water. Mix well and use within 24 hours.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in liter polyethylene cubitainers and refrigerated or iced to 4 ^{o}C until analysis to minimize microbiological decomposition of solids.

7.2 The holding time is 48 hours when preserved at 4 ^{o}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 ± 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 A method detection limit (MDL) study is performed once a year by analyzing seven or more replicates of the 0.5 NTU standard spread out through three or more consecutive analytical runs. An MDL study is also performed by each new analyst and when any changes in the analytical procedure are made.

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

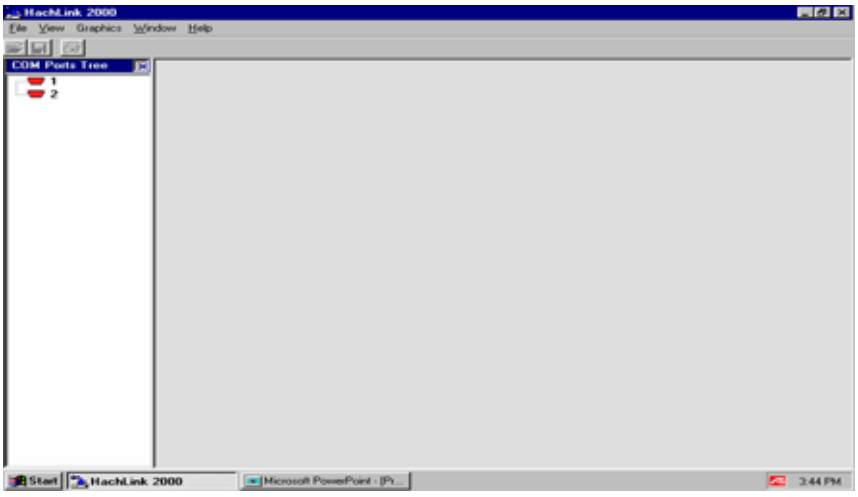
9.2.1 Fill clean sample cells with deionized water to the fill ring mark. Let samples stand for 30 seconds to allow bubbles to rise.

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.

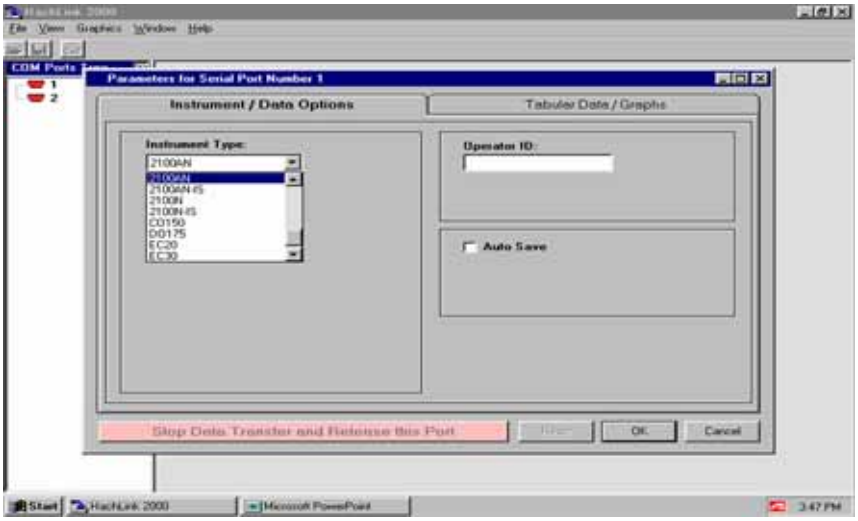
9.3 Instrument Start-up

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.

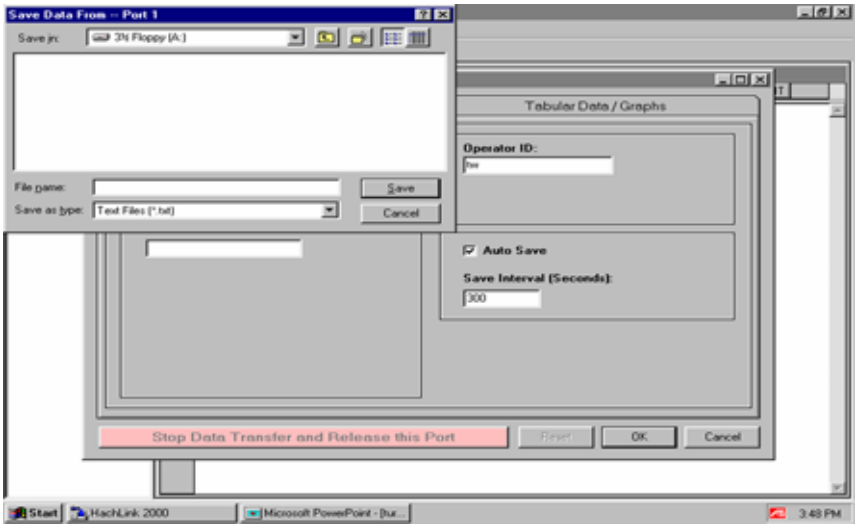


9.3.3 Select "COM Port 1" as the port type by clicking on "1".

9.3.4 Select “2100AN” from the pull down menu of instrument types.

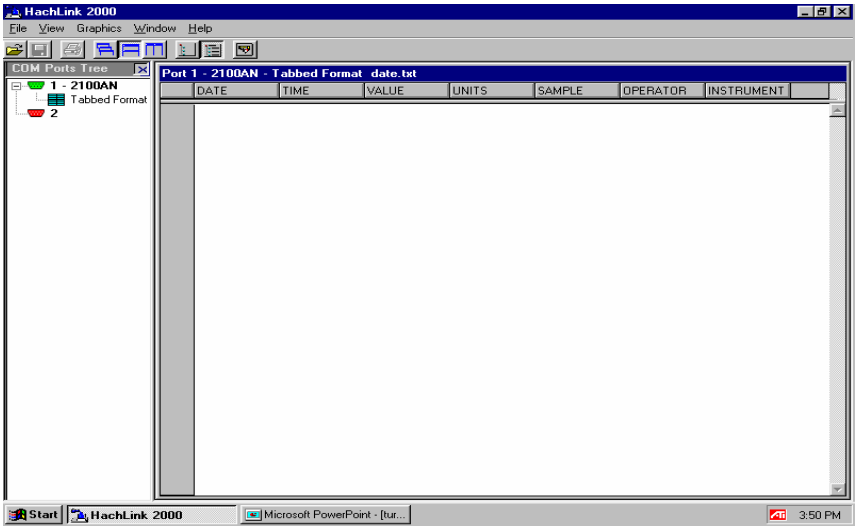


9.3.5 Enter operator I.D. and select “Auto Save”.



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”.

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, 20 NTU, as shown on screen. 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 “Δ” 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

9.3.8.1 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.

9.3.8.2 Press “Enter”, then press “Print” to save the reading.

9.3.8.3 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.

9.3.8.4 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.

10.2 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:

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

10.4 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 in Room 7-D4.

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 Number 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 Number 2130, 21thEdition, 2005.*

13.5 Division of Environmental Chemistry, Maryland Department of Health and Mental Hygiene, *Quality Assurance Plan, DECQA1, Revision 8.0*, 2007.

APPENDICES

Appendix A – Data Review Checklist
Appendix B – Turbidity Run Log

APPENDIX A

State of Maryland
DHMH - Laboratories Administration
DIVISION OF ENVIRONMENTAL CHEMISTRY
GENERAL CHEMISTRY SECTION

DATA REVIEW CHECKLIST

Turbidity/EPA Method 180.1

Lab Numbers[1]: _____
Date Collected: _____ Date Analyzed: _____ Analyst: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	48 hours @ 4 °C		
Calibration of Turbidimeter (0 – 4000 NTU)	Every two months		
Daily Calibration Checks (0 – 200 NTU)	Within 90–110% of true values		
Deionized Water Blank	< 0.07 NTU		
Check Standards	Every 10th sample or 1/batch, if less than 10 samples		
	values within 90-110% of the true values		
Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples		
	RSD ≤ 10 %		
External QC[2] Analyze Quarterly	Within acceptable range		
	Last date analyzed:		
Decimal places reported	1		
Reporting Level	0.5 NTU; concentrations below this value reported as < 0.5 NTU		
Measured Values	Within range 0– 40.0 NTU for drinking water		
	Within range 0-4000 NTU for others		
Diluted Samples	Proper dilutions		
	Correct final calculations		
Changes/Notes	Clearly stated		

* Check (√) if criteria are met

_____ Date Reported: _____
Reviewer's Signature & Date

[1]Include beginning and ending numbers; account for gaps by bracketing.

[2]QC Identification: _____ True Value = _____
Acceptable Range = _____

APPENDIX B

State of Maryland
DHMH - Laboratories Administration
DIVISION OF ENVIRONMENTAL CHEMISTRY
GENERAL CHEMISTRY SECTION

TURBIDITY RUN LOG
EPA Method 180.1

Analyst: _____ Date: _____

Sample No.	Sample ID	Dilutions	Sample No.	Sample ID	Dilutions
1			31		
2			32		
3			33		
4			34		
5			35		
6			36		
7			37		
8			38		
9			39		
10			40		
11			41		
12			42		
13			43		
14			44		
15			45		
16			46		
17			47		
18			48		
19			49		
20			50		
21			51		
22			52		
23			53		
24			54		
25			55		
26			56		
27			57		
28			58		
29			59		
30			60		

Standard Operating Procedures

Chlorophyll a and Pheophytin a

Standard Method 10200H (Spectrophometric, Beckman DU-650)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of chlorophyll *a*, *b*, *c* and pheophytin *a* in fresh and marine waters.

1.2 The concentrations are reported in SI units of mg/m^3.

2.0 SUMMARY OF METHOD

The chlorophyll and related compounds are extracted from the algae collected on glass fiber filters with aqueous 90% acetone solution. Light absorption of the extract is measured at selected wavelengths and the concentrations of the pigments of interest are calculated using the equations as in 10.0.

3.0 INTERFERENCES

3.1 Pheophytin *a* is a common degradation product of chlorophyll *a*. Pheophytin *a* is similar in structure to chlorophyll *a*, but lacks the magnesium atom (Mg) in the porphyrin ring. The magnesium can be removed from chlorophyll in the presence of acid.

3.1.1 Field Samplers can prevent this degradation by the addition of magnesium carbonate to the plankton sample prior to filtration.

3.1.2 When a solution of pure chlorophyll *a* is converted to pheophytin *a* by acidification, the absorption peak is reduced to approximately 60% of its original value and shifts from 664 to 665 nm. For pure chlorophyll this before/after acidification absorption peak ratio (OD_{664}/OD_{665}) is 1.7. Solutions of pure pheophytin show no reduction at OD_{665} upon acidification and have 664/665 ratio of 1.0. The *acid ratio* should fall between 1.0 and 1.7. If it is not within this range, the data are not valid and will be discarded. Sample submitter is immediately notified if more than 10% of the data will be rejected.

$$\frac{(OD_{664} - OD_{750})b}{(OD_{665} - OD_{750})a} = \text{acid ratio}$$

b = before acidification
a = after acidification

3.2 Chlorophyll solutions degrade rapidly in strong light. Work with these solutions should be carried out in subdued light, and all vessels, tubes, etc. containing the pigment should be covered with aluminum foil.

3.2.1 Naturally occurring, structurally related chlorophyll precursors and degradation products, such as the chlorophyllides, pheophytins and pheophorbides, commonly occur in pigment extracts and may absorb light in the same region of the spectrum as the chlorophylls.

3.2.2 Ground samples should be covered by aluminum foil and steeped in the refrigerator not less than 15 minutes or more than 24 hours. After clarification decant the extract directly into the cuvette for analysis or a screw cap tube and put in the freezer. The extract can be stored for one year.

4.0 HEALTH AND SAFETY

4.1 Good laboratory practices should be followed during reagent preparation and instrument operation. Use of gloves and eye protection is recommended when preparing solutions.

4.2 Each chemical should be regarded as a potential health hazard. A reference file of MSDS is available in lab.

4.3 Inhalation of acetone should be minimized by performing all operations in a well-ventilated hood.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Beckman DU-65 and DU-650 UV/V/S spectrophotometers, Beckman Instruments Inc.

5.1.1 Tissue Grinder – Con-Torque power-unit, Cat. # 7265, Eberbach Corp.

5.1.2 Centrifuge – Megafuge 2.0, Heraeus Instrument.

5.1.3 Magnetic Stirrer

5.2 Supplies

5.2.1 Centrifuge tubes - 15 ml graduated conical polypropylene tubes with screw caps, Catalog No. 05-538-43D, Fisher Scientific.

5.2.2 Cuvettes with 1 cm, 2 cm, 5 cm path length, catalog nos. 14-385-932 C-E, Fisher Scientific.

5.2.3 Repipet Dispensers – 5 and 10 ml volume, Fisher catalog no. 13-687-54 and 13-687-55.

6.0 REAGENTS AND STANDARDS

6.1 Acetone –Spectranalyzed, catalog no. A19-4, Fisher Scientific

6.2 Acetone solution, 90% – Add 900 ml of acetone to 100 ml of distilled water and mix well. The final volume will be less than 1 liter.

6.3 Hydrochloric Acid, 1N – Certified, catalog no. SA48-4, Fisher Scientific

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected and filtered in the field. Filters sealed in aluminum foil are cooled to – 4^{o}C on ice and transported to the laboratory by collection staff or courier service.

7.2 All samples must be delivered to the laboratory as soon as possible after collection.

7.3 The holding time between sample collection and extraction is 28 days at – 20^{o}C .

7.4 The acetone extracts can be stored in the dark at – 20^{o}C for one year (generally analyzed within 28 days) without appreciable chlorophyll degradation.

8.0 QUALITY CONTROL

8.1 90% acetone solution is measured as blank controls for every 10 samples

8.2 A reference sample, dried Chlorophyll a from spinach, ordered from Sigma Chemical Co., catalog no. C5753, is analyzed once every three months.

8.2.1 Prepare 10 mg/L solution by dissolving the 1 mg of dried chlorophyll a spinach in a small amount of 90% acetone in a 100ml volumetric flask and bring to volume with 90% acetone. Prepare 1 mg/L and 0.1 mg/L solutions by serial dilutions.

8.2.2 Analyze the 10 mg/L, 1 mg/L, and 0.1 mg/L solutions as regular samples on the spectrophotometer using a 1 cm cell cuvette and adding 1 drop of HCl.

8.2.3 Calculate chlorophyll a concentration following the steps listed below (equation to calculate chlorophyll a from 10.1 is entered in Quatro Pro):

8.2.3.1 Go to Main menu, press 9, <enter>

8.2.3.2 Type 'cd qpro', <enter>

8.2.3.3 Type 'q', <enter>

8.2.3.4 Using the mouse, click on File.

8.2.3.5 Click on Open.

8.2.3.6 Click on Judith 6.WQ1.

8.2.3.7 Enter data points from lab report.

8.2.3.8 Click on Print.

8.2.3.9 Click on Print to Fit; data will be printed.

8.2.3.10 Click on File/ Save/ Replace. Click on File/ Exit.

8.2.3.11 Type 'cd..' , then 'db' to get back to main chlorophyll menu.

9.0 PROCEDURE

9.1 Log in Samples in Sample Receiving Book

9.1.1 Open the envelope containing the samples. Check the name of the survey written on the plastic bag of the sample against that listed on the Analysis Request Sheet. If this information is not the same, contact the collector immediately for verification.

9.1.2 Arrange samples in numerical sequence as they appear on the Analysis Request Sheet and paper clip them together. Replace the samples in the storage envelope.

9.1.3 One lab number is assigned only to samples collected in the same month with same study code. Using the hand stamp (duplicate setting), stamp the

Analysis Request Sheet and the envelope (Post-it pad if envelope is plastic). Return envelope to the freezer.

9.1.4 Enter the lab number and sample information on the Analysis Request Sheet in the computer log book.

9.2 Grinding

9.2.1 Remove samples from freezer and warm up for 10 minutes at room temperature.

9.2.2 Number centrifuge tubes in numerical sequence. After every ten samples, insert a tube filled with 90% acetone for use as a sample blank.

9.2.3 Check and fill the two repipetors with 90% acetone.

9.2.4 Place the filter pad in the tissue grinder. With a pair of forceps stick the filter 2/3 down to the side of the grinding tube.

9.2.5 Turn on the switch of the tissue homogenizer.

9.2.6 Add in 4 ml of the 90% acetone to wet the filter. Move tube up and down with the filter tightly against the pestle. Macerate until all of the pad is completely ground up (looks like mush with no pieces of intact pad). A chlorophyll result is only as good as the way it is ground. To avoid spillage, hold tube firmly and move tube slowly.

9.2.7 Add in 4 ml of the 90% acetone to wash down thoroughly the paper pulp and continue to macerate for 30 second.

9.2.8 Pour the homogenate into a 15 ml conical centrifuge tube.

9.2.9 Rinse the pestle and grinding tube three times each with 2 ml of 90% acetone and add all the rinse into the 15 ml centrifuge tube. The final volume should be close to 14.5 ml.

9.2.10 Cap the tubes to prevent evaporation of the acetone and store the samples overnight at 4□C in refrigerator. Cover the tubes with aluminum foil to avoid light exposure.

9.2.7 Ground samples, prior to centrifugation, are not allowed to stay more than 24 hours.

9.3 Centrifugation

9.3.1 Take out the overnight samples from refrigerator. Clarify the samples by centrifuging the capped tubes for 30 minutes at 3000 rpm.

9.3.2 Number another set of centrifuge tubes in the same numerical sequence.

9.3.3 Carefully pour the clear liquid into a clean numbered centrifuge tube for reading and throw away the old centrifuge tube with filter paper residue.

9.3.4 If it is not possible to read the samples immediately, keep the tubes in the – 20^{o}C freezer for at most one year(generally read within 28 days). Centrifuge samples 10–15 minutes before reading.

9.4 Log -in Samples on the Chlorophyll Measurement Computer

9.4.1 Turn on the computer and wait for Main Menu to appear.

9.4.2 Select "1" – Log in Samples.

.

9.4.3 Type the information on the Analysis Sheet into the computer. If a mistake is made while logging the individual sample, it can be corrected on the same line. When data entry goes to another line (a new record) , the prior record cannot be corrected until data for all other records (samples) are entered.

9.4.4 Press [Enter] key down when all sample data have been logged in this survey. The computer screen will automatically change to another prompt.

9.4.5 When asked "Are you aware of any entry errors you made for this sample that are not already corrected in the individual filter lines? (Y or N?)", answer 'Y' if corrections are needed, and give the number. The computer screen will automatically change to vertical (dBase Edit Screen) format and allow you to edit. When finished, press [CTRL-W] to return to horizontal (dBase Browse Screen) format.

9.5 Log in samples on any other computer that has dBase

9.5.1 Turn on computer. If a menu comes up, exit on DOS.

9.5.2 Put the disk labeled □CHLOROPH in Drive A.

9.5.2.1 Type □:CHLOROPH, [Enter] then the screen will show the menu of chlorophyll.

9.5.2.2 When all data have been logged, put this disk into the Drive A of the computer. At the Main Menu, select "8" – Miscellaneous Utility option. Select "8" - Merge the information of the disk to the computer.

9.5.3 Use □:UPDATE disk to log-in some surveys which contain a long list of samples but for which most of the demographic information remains unchanged.

9.5.3.1 When menu comes hit 9, screen will show C:> Type A:UPDATE <Enter>.

9.5.3.2 The screen will show a list of surveys options.

9.5.3.3 Press the number that stands for the survey you want. The computer will retrieve the respective demographics for the samples. Type in the information that is changed or lacking. Keep the information that remains the same. (This program saves a lot of time and effort.)

9.5.3.4 When one lab number is logged in, it must be merged into the computer. If it is not merged and second survey is logged in, the second one replaces the first. Thus the former logged data are lost when a second survey is logged-in by using UPDATE disk. But this not true with the more general program like CHLOROPH.

9.6 Reading the samples

9.6.1 Turn on the spectrophotometer (by pressing the vis key), computer and the two printers. Let the spectrophotometer warm up for 30 minutes.

9.6.2 Select "3" at the Main Menu; read samples that have been logged in.

9.6.3 The spectrophotometer should be calibrated with a blank before scanning any samples. That is, fill the 5 cm cuvette with 90% acetone solution (the blank solution kept when grinding the samples). Place the cuvette into the spectrophotometer cell holder in the cell compartment. Press [Enter]; the printer attached to spectrophotometer will print out the result, which should also appear on the screen of the computer. Write down the line number
on the "blank" column of the Work Sheet. Accept or reject (than rescan) the data presented on the computer screen.

9.6.4 Rinse the 5 cm cuvette three times with distilled water. Then rinse with 90% acetone solution. Transfer sample extract into the rinsed cuvette using disposable pipette. If schleren (wavy lines when

looking through cell) appear, shake cell well until solution is homogeneous. Place cuvette into the spectrophotometer cell holder in the cell compartment. Type in the tube number and press [Enter]. Computer will count 30 seconds to allow particle settling in the sample, then the computer will command the spectrophotometer to begin to scan the required wavelengths. When the scan is complete, the data will appear on the computer screen, and the results will be printed out by the printer.

9.6.4.1 If data is satisfactory (absorption at 750 nm is less than 0.007 for DNR samples and less than 0.01 for MDE samples), press [Enter]. Write down the line number in the Work Sheet "line number" column.

9.6.4.2 If the absorption reading at 750 nm is unsatisfactory, press any key, then [Enter], then select from options presented. Write down the line numbering the Work Sheet "line number" column with an indication that the readings are not to be used.

9.6.5 Remove cuvette from spectrophotometer cell compartment. Remove stoppers and add 3 drops of 1N HCl into mouth of the cuvette. As soon as the acid is added, press [Enter] to start the reaction timer. Stopper, then shake well but quickly to mix for about 20 seconds. Place cuvette back into cell compartment and close lid securely. Computer timer will allow 90 seconds for the acid to react with the sample before starting the wavelength scan. When the screen shows the result, write down the line number on Work Sheet "line number" column and acid ratio in the "comments" column. If the ratio is out of the range, there will be a warning sound.

9.6.6 If the absorbance of the extract is greater than 0.8 at 664 nm (the computer will give a warning sound), transfer the sample to 2 cm or 1 cm cuvette and re-analyze the sample.

9.6.7 If absorbance at 750 nm appears to be a negative value (less than -0.000), for more than two successive scans, spectrophotometer drift has become excessive. To correct this drift, recalibrate the spectrophotometer with 90% acetone solution as in 9.6.3.

9.6.8 Recalibrate the spectrophotometer every ten samples with an extraction solvent "acetone solution blank" as in 9.6.3

9.7 Verification/Validation

9.7.1 Select "4" on the Main Menu. Approve completed work before printing.

9.7.2 Write the lab no., sample no., and tube no. from the worksheet onto the spectrophotometer printer output sheet.

9.7.3 Carefully check every item from the Analysis Request Sheet with screen data for the respective sample. If any item is incorrect, at the computer prompt indicate N and the dBase Edit screen will appear and let you edit. When editing is complete, press [CTRL-W] to return to a data screen.

9.8 Reports

9.8.1 To print reports for completed work, select "5" from Main Menu. Enter one lab number at a time and print reports; it will print one copy to send out, one copy in-house for reference, for each lab number entered.

9.8.2 If printing additional copy, choose "8" on menu,miscellaneous utility program.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 The chlorophyll a and pheophytin a concentrations in samples are calculated as follows:

First, 750 nm OD value is subtracted from the reading before and after acidification. Then, corrected values are used in the following equations:

$$\text{Chlorophyll a, } {}^{mg}/_{m^3} = \frac{26.7\,(OD_{664}b - OD_{665}a)}{V2 \times L} \times V1$$

$$\text{Pheophytin a, } {}^{mg}/_{m^3} = \frac{26.7\,[1.7\,(OD_{665}a) - (OD_{664}b)]}{V2 \times L} \times V1$$

Where V1 = volume of extract in liters
V2 = volume of sample in liters
L = light path length or width of cell in cm

$OD_{664}b$, $OD_{665}a$ = optical density of 90% acetone extract before and after acidification, respectively. These calculations are done using a dBase program. In sample reports, both calculated results are printed in the right most column for each sample line.

10.2 For reference samples, chlorophyll a concentrations are calculated using Quatro Pro as in 8.2.3.

10.3 Calculate the relative percent difference for the duplicated samples as follows:

$$\%\,\mathrm{RPD} = \frac{\text{difference between the duplicates}}{\text{average of the duplicates}} \times 100$$

11.0 DATA AND RECORDS MANAGEMENT

11.1 Copy results for DNR and MDE samples for each month to two separate floppy disks.

11.2 Instrument maintenance log is located near the instrument.

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

The solvent, acetone, is poured into a labeled waste container. Safety officer will arrange periodic pick-up and disposal.

13.0 REFERENCES

13.1 United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Chlorophyll – Spectrophotometric, March, 1991

13.2 American Public Health Association, Standard Methods for the Examination of Water and Wastewater, Method Number 10200H, 21st Edition, 2005

13.3 Chesapeake Bay Program, *Greenland: A Tool For Processing Chlorophyll Samples, 2005*

13.4 DEC, Maryland State Department of Health and Mental Hygiene, *Quality Assurance Plan*, May, 2007.

Standard Operating Procedures

Ammonia

EPA Method 350.1 (Flow Injection Colorimetric Analysis)

1.0 SCOPE AND APPLICATION

1.1 This method determines ammonia in drinking, surface, and saline waters.

1.2 The applicable range of this method is 0.008 mg P/L to 0.500 mg N/L.

2.0 SUMMARY OF METHOD

Alkaline phenol and sodium hypochlorite react with ammonia to form indophenol blue. Sodium nitroprusside is added to enhance sensitivity. The absorbance of measured at 630 nm, and is directly proportional to the ammonia concentration in the sample.

3.0 INTERFERENCES

3.1 Sufficient concentration of Calcium and magnesium ions can precipitate if they are present in sufficient concentrations. Tartrate or EDTA addition to the sample can prevent this problem.

3.2 Color, turbidity and certain organic species may interfere. Turbidity is removed by filtration and sample color can be corrected by running the samples through the manifold without color formation.

3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that can bias analyte response especially in low level detection of ammonia. To eliminate this problem wash glassware with 1:1 HCl and rinse with DI water.

4.0 HEALTH AND SAFETY

4.1 Accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Use of gloves and eye protection is recommended.

4.2 The following chemicals have the potential to be highly toxic or hazardous.

4.2.1 Phenol

4.2.2 Sodium nitroprusside
4.2.3 Sulfuric acid

4.3 A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in the chemical analysis.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Lachat Quick Chem FIA 8500 series consisting of the following:

5.1.1.1 XYZ Auto sampler ASX-520 series with sample, standard and dilution racks

5.1.1.2 Manifold or reaction unit

5.1.1.3 Multi-channel Reagent Pump RP-100 series

5.1.1.4 Colorimetric Detector

5.1.1.4.1 Flowcell, 10 mm, 80µL, glass flow cell

5.1.1.4.2 630 nm interference filter

5.1.1.5 Computer, monitor, printer, and Flow Solution software.

5.2 Supplies

5.2.1 13x100 mm test tubes, Fisher # 14-961-27

5.2.2 16x125 mm test tubes, Fisher # 14-961-30

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Sodium Phenolate- In a 1 L volumetric flask, dissolve 88 ml of 88% liquefied phenol. While stirring, slowly add 32g sodium hydroxide (NaOH). Cool and invert to mix. Do not degas this reagent. Prepare fresh every 3 to 5 days and save in amber container. Discard when the reagent turns brown. Always prepare this reagent under the hood.

6.1.2 Sodium Nitroprusside- In a 1 L volumetric flask, dissolve 3.5 g sodium nitroprusside. Mix and dilute to the mark with DI water. Prepare fresh every 1 to 2 weeks.

6.1.3 1 M Sodium Hydroxide Solution- In a 1L volumetric flask, dissolve 40.0 g sodium hydroxide in approximately 900 mL DI water. Dilute to the mark after it is all dissolve.

6.1.4 Buffer for non acidified samples- In a 1 L volumetric flask dissolve 50.0 g sodium ethylenediamine tetraacetic acid (Na_2EDTA) and 225 ml 1M sodium hydroxide in approximately 700 mL DI water. Mix well and dilute to the mark. Prepare fresh monthly.

6.1.5 1M HCl- Add 83 ml HCl to about 700 mL DI water and bring up to mark. Use this reagent to rinse the phenol lines that become brownish color after many runs.

6.1.6 Sodium Hydroxide – EDTA Rinse - Dissolve 65 g sodium hydroxide (NaOH) and 6 g tetrasodium Ethylenediamine tetraacetic acid (Na_4EDTA) in 1.0 L DI water.

6.2 Standards

6.2.1 Ammonia Stock Standard (1000) mg N/L - Dissolve 0.3819g ammonium chloride that has been (NH_4Cl) that has been dried in the oven for two hours at 105^oC in about 80 mL of DI water. Bring up to mark with DI water and store at 4^oC. Prepare this reagent monthly.

6.2.2 Intermediate Standard (100 mg N/L) - Pipette 10 mL of standard 6.2.1 into a 100 mL volumetric flask. Bring up to mark with DI water. Store at 4^oC. Prepare weekly.

6.2.3 Spiking Solution - Pipette 30 µL of standard 6.2.2 into 10 mL of DI water or 10 mL of sample. The known concentration of spike is 30 mg/L.

6.2.4 Working Standards - The working standards are prepared weekly in class A volumetric flasks by diluting intermediate standards with DI water according to the following table:

Standard	Conc. of Ammonia ppm N/L	Volume of Intermediate Standard	Final Volume mL
Std1	**0.000**	**0**	**100**
Std2	**0.008**	**2 ml of Std 6**	**100**
Std3	**0.020**	**10 ml std 4**	**100**
Std4	**0.100**	**100 µl**	**100**
Std5	**0200**	**200 µl**	**100**
Std6	**0.300**	**300 ul**	**200**
Std7	**0.400**	**400 µl**	**100**
Std8	**0.500**	**500 µl**	**100**

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in plastic cubitainers or bottles.

7.2 Samples are cooled to 4^{o}C at the time of collection. Alternatively, they can be frozen at - 20^{o}C as soon as possible after collection.

7.3 Samples cooled to 4^{o}C at the time of collection are analyzed within 48 hrs. of collection. Frozen samples must be analyzed within 28 days.

8.0 QUALITY CONTROL

8.1 A standard calibration curve is prepared with each analytical run.

8.2 A mid-range check standard and a blank are analyzed at the beginning, end and after every ten samples (or more frequently, if required) and at the end of the 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 duplicated (analyzed from two different tubes) and spiked. The accepted value for the relative standard deviation (RSD) or spike recovery is ± 10 %. If these do not fall within the accepted ranges, the corresponding analyses are repeated.

8.4 An external QC sample is analyzed at the beginning and the end of each analytical run.

9.0 PROCEDURE

9.1 Prepare a list of samples to be analyzed and pour into labeled tubes (16mm x 125 mm test tubes).

9.2 Turn on the instrument and enter the laboratory numbers for the samples and the identifications for the quality control samples using the template tray.

9.3 Degas all reagents, except those specified with helium in order to prevent bubble formation. Use helium at 140 Pa (20lb/in2) through a helium degassing tube or a pipette for a minimum of one minute. Pump DI water through all reagent lines and check for leaks and a smooth flow. Switch to reagents and allow enough time for the system to equilibrate and a stable baseline is established.

9.4 Start the run after all sample tubes, standards, check standard and dilution tubes are placed on the auto sampler.

9.5 All the samples greater than the highest standards will be automatically diluted and the run will stop.

9.6 Remove the reagent lines and place them in DI water and rinse for about 15 minutes. For extra rinse a reagent of 1N HCl can be used followed by DI rinse. Then all the reagent lines should be air dried and released from the pump.

10. DATA ANALYSIS AND CALCULATIONS

All calculations are performed automatically by the instrument. A calibration curve is established by plotting peak areas versus the concentration of standards. Sample concentrations are calculated from the calibration curve.

11.0 DATA AND RECORDS MANAGEMENT

11.1 Report only those results that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard are manually diluted and reanalyzed.

11.2 Sample results for samples are reported in mg N/L. Report results to three decimal places. Report results below the lowest calibration standard as <0.008. For the Chesapeake Bay Program only, report all calculated results with a "L " sign for concentrations less than that of the lowest standard.

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. Ammonia waste containing phenol is collected in a waste drum under the hood and handled according to the laboratory and state's regulations. For more information consult the "Waste Management manual for Laboratory Personnel", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 Street N. W., Washington D. C. 20036, (202) 872-4477.

13.0 REFERENCES

13.1 American Public Health Association, Standard Methods for the Examination of Water and Wastewater, Method 4500 NH_3 H, 20th Edition, 1998

13.2 United States Environmental Protection Agency, Methods for the Determination of Inorganic Substances in Environmental Samples, Method 350.1, August 1993

13.3 Lachat Instruments, Determination of Ammonia by Flow Injection Analysis, QuickChem Method 10-107-06–1-J, August 2003

Standard Operating Procedures

Nitrate / Nitrite and Nitrite (Low Level)

EPA Method 353.2 (Flow Injection Colorimetric Analysis)

1.0 SCOPE AND APPLICATION

1.1 This method determines nitrite, or nitrate/nitrate in drinking, ground, surface, domestic waters and industrial waste.

1.2 The range of this method is from 0.020 mg/L to 2.00 mg/L for nitrate–nitrite and 0.002 mg/L to 0.200 mg/L for nitrite.

1.3 Nitrate is found only in small amounts in domestic wastewater, but in the effluent of nitrifying biological treatments nitrate may be found in concentrations up to 30 mg/L.

2.0 SUMMARY OF METHOD

Nitrate is reduced quantitatively to nitrite by passage through a copperized cadmium column. The reduced nitrate plus original nitrite is further determined by coupling with N-(naphthyl) ethylenediamine dihydrochloride. The dye produced has magenta color and is read at 520nm, and is directly proportional to the concentration of analyte. Determination of nitrite takes place through the same procedure as Nitrate/Nitrite without a cadmium column.

3.0 INTERFERENCES

3.1 Interference from iron, copper or other metals is eliminated by addition of EDTA to the ammonium chloride buffer.

3.2 Suspended matter in the column will restrict sample flow. Remove suspended solids by filtration.

3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that can bias analyte response.

4.0 HEALTH AND SAFETY

4.1 Accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Use of gloves and eye protection is recommended.

4.2 The following chemicals have the potential to be highly toxic or hazardous.

4.2.1 Cadmium

4.2.2 Phosphoric acid

4.2.3 Hydrochloric acid

4.3 A reference file of Material Safety Data Sheet (MSDS) is available to all personnel involved in the chemical analysis.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Lachat Quick Chem FIA 8500 series

5.1.1.1 XYZ Auto sampler ASX-500 series with sample, standard and dilution racks

5.1.1.2 Manifold or reaction unit

5.1.1.3 Multichannel Reagent Pump RP-100 series

5.1.1.4 Colorimetric Detector

5.1.1.4.1 Flowcell, 10 mm, 80uL, glass flow cell

5.1.1.4.2 520 nm interference filter

5.1.1.5 Computer, monitor, printer and The Flow Solution software

5.2 Supplies

5.2.1 13x100 mm test tubes, Fisher # 14-961-27

5.2.2 16x125 mm test tubes, Fisher # 14-961-30

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Ammonium Chloride buffer, pH 8.5, 2 L - Dissolve 170 g of NH_4Cl and 2.0 g of disodium ETDA (Na2EDTA'2H2O) in about 1600 ml DI water in a 2 L beaker. Mix using a stir bar. Adjust the pH to 8.5 with 15N sodium hydroxide solution and bring up to volume. Use filter paper to remove all the small particles from the reagent and refrigerate.

6.1.2 Sulfanilamide color Reagent, 1 L - Add carefully, while mixing, 100 ml 85% phosphoric acid (H_3PO_4) to 700 ml DI water in a 1 L volumetric flask. Add 40 mg sulfanilamide and 1g N-1-naphthyl ethylenediamine dihydrochloride (NED) and stir to dissolve. Bring up to 1 L with DI water. Filter, store in amber bottle and refrigerate. This solution is stable for one month.

6.1.3 15N Sodium Hydroxide – Add 150g NaOH very slowly to 180 mL DI water in a 250 ml volumetric flask. CAUTION: The solution will get very hot! Mix until dissolved. Cool and store in a PLASTIC bottle.

6.2 Standards

6.2.1 Nitrate Stock Standard (900 mg /L of nitrate nitrogen) - Dissolve 0.6496 of dried potassium nitrate, KNO_3, in approximately 80 ml of deionized water in a 100 ml volumetric flask. Bring up to mark with DI water and store at 4^oC. Prepare this reagent monthly.

6.2.2 Nitrite Stock Standard (1000 mg/L of nitrite nitrogen) - Dissolve 0.6072g of potassium nitrite , KNO_2, dried at 110^oC, in 80 ml of deionized water in a 100 ml volumetric flask. Bring up to mark with water. Store at 4^oC. Prepare monthly.

6.2.3 Intermediate Nitrate Solution, 100 mg/L - Dissolve 0.0722 g of KNO_3 in 80 ml water in a 100 ml volumetric flask. Dilute to mark with water.

6.2.4 Intermediate Nitrite Solution - 100 mg/L of nitrite nitrogen: Dilute 10 ml of Nitrite Stock Standard (6.2.2) to 100 ml with water in a volumetric flask.

6.2.5 Combined Intermediate Standard, 90 mg/L nitrate nitrogen and 10 mg/L nitrite nitrogen - Use 10 ml volumetric pipettes to add 10 ml of Nitrate Stock Standard, 900 ppm (6.2.1) and 10 ml of Intermediate Nitrite Solution, 100 ppm (6.2.4) to approximately 60 ml of deionized water in a 100 ml volumetric flask. Bring up to mark with DI water.

6.2.6 Nitrate Cadmium check 0.5 ppm – Dilute 1 ml of reagent 6.2.3 to 200 ml DI water.

6.2.7 Nitrite Cadmium check 0.5 ppm – Dilute 1 ml of reagent 6.2.4 to 200 ml DI water.

6.2.8 Working Standards - The working standards are prepared weekly according to the following table:

Standard	Concentration of NO_2+NO_3 ppm N/L	Concentration of NO_2 ppm N/L	Volume of Combined Intermediate Std	Final Volume mL
S1	**0.020**	**0.002**	**10 ml of S3**	**100**
S2	**0.080**	**0.008**	**80 ul**	**100**
S3	**0.200**	**0.020**	**200 µl**	**100**
S4	**0.400**	**0.040**	**400 µl**	**100**
S5	**0.800**	**0.080**	**800 ul**	**100**
S6	**1.200**	**0.120**	**1200 µl**	**100**
S7	**2.000**	**0.200**	**2000 µl**	**100**

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in plastic bottles or cubitainers, and are preserved by cooling to 4^{o}C. .

7.2 Samples are analyzed within 48 hours after collection. If they can not be analyzed within this time period, they should be frozen at –20^{o}C on the first day they arrive to lab. The holding time for frozen samples is 28 days.

8.0 QUALITY CONTROL

8.1 All the standards are run in duplicates: that is, two analyses from each tube. A linear calibration is performed daily before the sample run.

8.2 A mid-range check standard and a calibration blank is analyzed following daily calibration, after every ten samples (or more frequently, if required) and at the end of the sample 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 duplicated (analyzed from two different tubes) and spiked. The accepted value for the relative standard deviation (RSD) or spike recovery is ± 10 %. If these do not fall within the accepted ranges, the corresponding analyses are repeated.

8.4 An external quality control is analyzed at the beginning and at the end of each analytical run.

8.5 A deionized water blank is run in the beginning and after every ten samples. Results for blanks should be <0.002 for NO2 and <0.02 for NO2+NO3 mg N/L.

9.0 PROCEDURE

9.1 Prepare a list of samples to be analyzed and pour samples into labeled tubes (16mm x 125 mm test tubes).

9.1.2 Turn on the instrument and enter all the samples using the template tray.

9.1.3 To prevent bubble formation, degas all reagents, except those specified with helium. Use He at 140 Pa (20lb/in2) through a helium degassing tube or a pipette for one minute or longer if necessary. Pump DI water through all reagent lines and check for leaks and a smooth flow. Switch to reagents and allow enough time for the system to equilibrate and a stable baseline is established.

9.1.4 Turn on the Cadmium switching valve on and allow the buffer to rinse it for 5-10 minutes.

9.1.5 Start the run after all sample tubes, standards, check standard and dilution tubes are placed on the auto sampler.

9.1.6 All the samples greater than the highest standards will be automatically diluted and the run will stop.

9.1.7 Let the column to rinse for about 5 minutes with buffer, then turn off the switching valve. Remove the reagent lines and place them in DI water and rinse for about 15 minutes. For extra rinse a reagent of Disodium EDTA can be used followed by DI rinse. Then all the reagent lines should be air dried and released from the pump.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 All calculations are performed automatically by the instrument. A calibration curve is established by plotting peak areas versus the concentration of standards. Sample concentrations are calculated from the calibration curve.

10.2 Calculate the reduction efficiency of the cadmium coil is calculated by analyzing NO_3 and NO_2 standards with the same concentration (0.5 ppm N/L) and using the following equation:

$$\frac{NO_3 \text{ (peak height)}}{NO_2 \text{ (peak height)}} \text{ X } 100$$

10.2 Calculate % of spike recovery of the laboratory fortified samples as follows:

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

10.3 Calculate the % of relative standard deviation for the duplicated samples as follows:

$$\%\ RSD = \frac{\text{SD of the duplicates}}{\text{average of the duplicates}} \times 100$$

11.0 DATA AND RECORDS MANAGEMENT

11.1 Report only those results that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard are manually diluted and reanalyzed.

11.2 Sample results for samples are reported in mg N/L. Report results to three decimal places. Report results below the lowest calibration standard as <0.02 for $NO_3 + NO_2$ and <0.002 for NO_2. For the Chesapeake Bay Program only, report all calculated results with a "L " sign for concentrations less than that of the lowest standard.

12.0 WASTE MANAGEMENT

12.1 Compliance with state's sewage discharge permits and regulations is required. For more information consult the "Waste Management manual for Laboratory Personnel", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 Street N. W., Washington D. C. 20036, (202) 872-4477.

13.0 REFERENCES

13.1 United States Environmental Protection Agency, Methods for the Determination of Inorganic Substances in Environmental Samples, Method 353.2.1, August 1993

13.2 American Public Health Association, Standard Methods for the Examination of Water and Wastewater, Method 4500 NO_3^- I, 20th Edition, 1998

13.3 Lachat Instruments, Determination of Ammonia by Flow Injection Analysis, QuickChem Method 10-107-06–1-J, August 2003

Standard Operating Procedure

Orthophosphate (Low Level)

EPA Method 365.1 (Flow Injection Colorimetric Analysis)

1.0 SCOPE AND APPLICATION

1.1 This method determines orthophosphate (PO_4^{3-}) in drinking, surface, and saline waters.

1.2 The applicable range of this method is 0.004 mg P/L to 0.250 mg P/L.

2.0 SUMMARY OF METHOD

The orthophosphate ion (PO_4^{3-}) reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex which is further reduced by ascorbic acid to form a blue complex, which absorbs light at 880 nm. The absorbance is directly proportional to the concentration of orthophosphate present in the sample.

3.0 INTERFERENCES

3.1 Silica forms a pale blue complex, which also absorbs at 880 nm. This interference is insignificant for silica concentration up to about 1 mg SiO_2/L. If the silicate concentration is higher than 1 ppm, the sample result will not be reliable within the calibration range of the method.

3.2 Concentrations of ferric iron (Fe^{3+}) greater than 50 mg/L will cause a negative error due to precipitation of and subsequent loss of orthophosphate.

3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that can bias analyte response especially in low level detection of orthophosphate. To eliminate this problem wash glassware with 1:1 HCl and rinse with DI water.

4.0 HEALTH AND SAFETY

4.1 Accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Use of gloves and eye protection is recommended.

4.2 The following chemical has the potential to be highly toxic or hazardous.

4.2.1 Sulfuric Acid

4.3 A reference file of Material Safety Data Sheet (MSDS) is available to all personnel involved in the chemical analysis.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Lachat Quick Chem FIA 8500 series consisting of the following:

5.1.1.1 XYZ Auto sampler ASX-520 series with sample, standard and dilution racks

5.1.1.2 Manifold or reaction unit

5.1.1.3 Multi-channel Reagent Pump RP-100 series

5.1.1.4 Colorimetric Detector
5.1.1.4.1 Flowcell, 10 mm, 80µL, glass flow cell
5.1.1.4.2 880 nm interference filter

5.1.1.5 Computer, monitor, printer, and Flow Solution software

5.2 Supplies

5.2.1 13x100 mm test tubes, Fisher # 14-961-27

5.2.2 16x125 mm test tubes, Fisher # 14-961-30

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Stock Ammonium Molybdate Solution - In a 1 L volumetric flask, dissolve 40.0 g ammonium molybdate tetrahydrate [$(NH_4)6Mo7O_{24}.4H_2O$] in approximately 800 mL DI water. Dilute to the mark and let stir for 4 hours. Store in a plastic and refrigerate. This solution may be stored up to two months when kept refrigerated.

6.1.2 Stock Antimony Potassium Tartrate Solution - In a 1 L volumetric flask dissolve 3.0 g antimony potassium tartrate hemihydrate $K(SbO)C_4H_4O_6.1/2H_2O$) in approximately 800 mL DI water. Dilute to the

mark and let stir for few minutes. Store in a dark bottle and refrigerate. This solution may be stored up to two months when kept refrigerated.

6.1.3 Molybdate color Reagent, 1 L - Add carefully, while mixing, 35 mL sulfuric acid to about 500 mL DI water in a 1 L volumetric flask. When the temperature is cool add 72.0 mL stock antimony potassium tartrate and 213 mL stock ammonium molybdate solution. Dilute to the mark and invert three times to mix. Degas with helium. Prepare fresh weekly.

6.1.4 Ascorbic Acid Reducing Solution, 0.33 M - In a 500 mL volumetric flask dissolve 30.0 g granular ascorbic acid in about 400 mL DI water. Add 0.5 g dodecy sulfate (CH_3 $(CH_2)_{11}OSO$ 3Na) and dissolve. Dilute to make and mix. Prepare fresh weekly. Discard if the solution becomes yellow.

6.1.5 Sodium Hydroxide - EDTA Rinse - Dissolve 65 g sodium hydroxide (NaOH) and 6 g tetrasodium Ethylenediamine tetraacetic acid (Na_4EDTA) in 1.0 L DI water.

6.2 Standards

6.2.1 Orthophosphate Stock Standard (1000 mg P/L) - Dissolve 0.4393g of primary standard grade anhydrous potassium phosphate monobasic (KH2PO4) that has been dried in the oven for one hour at 105^{o}C in about 50 ml of DI water. Bring up to 100 mL mark with DI water and store at 4^{o}C. Prepare this reagent monthly.

6.2.2 Intermediate Standard (50 mg P/L) - Pipette 10 ml of standard 6.2.1 into a 200 ml volumetric flask. Bring up to mark with DI water. Store at 4^{o}C. Make weekly.

6.2.3 Spiking Solution (50 mg P/L) - Pipette 30 µL of standard 6.2.2 into 10 mL DI water or 10 mL of sample. The known value for spiking solution is 0.150 mg/L

6.2.4 Working Standards - The working standards are prepared weekly in class A volumetric flasks by diluting intermediate standard with DI water according to the following table:

Standard	**Conc. of Orthophosphate ppm N/L**	**Volume of Intermediate Standard**	**Final Volume mL**
Std1	0.000	0	100
Std2	0.004	2 ml of Std 6	100
Std3	0.010	10 ml std 4	100
Std4	0.050	100 µl	100

Std5	0.100	200 µl	100
Std6	0.150	300 ul	200
Std7	0.200	400 µl	100
Std8	0.250	500 µl	100

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected in plastic cubitainers or bottles.

7.2 Samples are cooled to 4^{o}C at the time of collection. Alternatively, they can be frozen at - 20^{o}C as soon as possible after collection.

7.3 Samples cooled to 4^{o}C at the time of collection are analyzed within 48 hrs. of collection. Frozen samples must be analyzed within 28 days.

8.0 QUALITY CONTROL

8.1 A standard calibration curve is prepared with each analytical run.

8.2 A mid-range check standard and a blank are analyzed at the beginning, end and after every ten samples (or more frequently, if required) and at the end of the 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 duplicated (analyzed from two different tubes) and spiked. The accepted value for the relative standard deviation (RSD) or spike recovery is ± 10 %. If these do not fall within the accepted ranges, the corresponding analyses are repeated.

8.4 An external QC sample is analyzed at the beginning and the end of each analytical run.

9.0 PROCEDURE

9.1 Prepare a list of samples to be analyzed and pour into labeled tubes (16mm x 125 mm test tubes).

9.2 Turn on the instrument and enter the laboratory numbers for the samples and the identifications for the quality control samples using the template tray.

9.3 Degas all reagents, except those specified with helium in order to prevent bubble formation. Use helium at 140 Pa (20lb/in2) through a helium degassing tube or a pipette for a minimum of one minute. Pump DI water through all reagent lines

and check for leaks and a smooth flow. Switch to reagents and allow enough time for the system to equilibrate and a stable baseline is established.

9.4 Start the run after all sample tubes, standards, check standard and dilution tubes are placed on the auto sampler.

9.5 All the samples greater than the highest standards will be automatically diluted and the run will stop.

9.6 Remove the reagent lines and place them in DI water and rinse for about 15 minutes. For extra rinse a reagent of 1N HCl can be used followed by DI rinse. Then all the reagent lines should be air dried and released from the pump.

10. DATA ANALYSIS AND CALCULATIONS

All calculations are performed automatically by the instrument. A calibration curve is established by plotting peak areas versus the concentration of standards. Sample concentrations are calculated from the calibration curve.

11.0 DATA AND RECORDS MANAGEMENT

11.1 Report only those results that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard are manually diluted and reanalyzed.

11.2 Sample results for are reported in mg N/L. Report results to three decimal places. Report results below the lowest calibration standard as <0.004. For the Chesapeake Bay Program only, report all calculated results with the ” L “ sign for concentrations less than that of the lowest Standard.

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. For more information consult the “Waste Management manual for Laboratory Personnel”, available from the American Chemical Society’s Department of Government Regulations and Science Policy, 1155 Street N. W., Washington D. C. 20036, (202) 872-4477.

13.0 REFERENCES

13.1 American Public Health Association, Standard Methods for the Examination of Water and Wastewater, Method 4500 P G, 20th Edition, 1998

13.2 United States Environmental Protection Agency, Methods for the Determination of Inorganic Substances in Environmental Samples, Method 365.1, August 1993

13.3 Lachat Instruments, Determination of Orthophospate by Flow Injection Analysis, QuickChem Method 10-115-01–1-A, August 2003

Standard Operating Procedures

Particulate Carbon & Particulate Nitrogen

(CE-440 CHN Analyzer)

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the carbon and nitrogen content in organic and inorganic compounds in surface and saline waters.

1.2 This instrument performs elemental analysis of material retained on membranes used in water filtration application.

2.0 SUMMARY OF METHOD

Particulate material on a pre-ignited glass fiber filter is combusted in oxygen helium atmosphere at 900^{o}C. The products of combustion are passed over suitable reagents to assure complete oxidation and removal of undesirable by-products. The mixture then proceeds to a mixing chamber and the uniform gas mixture passes through a series of traps each bracketed with a pair of thermal conductivity detector. The difference in the signals from each of these pairs of detectors is proportional to the amount of hydrogen (H in H_2O) and carbon (C in CO_2) present in each sample. The only remaining sample gas, nitrogen (N in N_2), is measured against the pure helium carrier gas.

3.0 INTERFERENCES

3.1 Sampling is the single largest determination of data quality. Duplicates or even triplicates sampling is recommended.

3.2 Filter blanks should be treated the same as filter samples in all respects.

4.0 HEALTH AND SAFETY

4.1 Good laboratory practices should be followed during instrument operation.

4.2 Combustion and reduction tubes are heated to 900^{o}C and 700^{o}C respectively. Wear heat resistant gloves and work on heat resistant bench top when changing these two tubes.

4.3 Use insulated gloves and tongs to remove hot crucibles from the furnace, and have a metal tray ready to place them on.

4.4 Each employee is issued a *Laboratory Safety Manual* and a *Quality Assurance plan* and is responsible for adhering to the recommendations contained therein.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 CE-440 Elemental Analyzer

5.1.2 CEC-490 Interface Unit

5.1.3 PC Computer with Windows XP

5.1.4 Drying Oven, 45^{o}C

5.1.5 Muffle furnace, Lindberg

5.1.6 Microbalance, Sartorius ME 5

5.2 Supplies

5.2.1 Filters – Whatman GF/F glass fiber, 24 mm diameter, 0.7 µm particle retention

5.2.2 Nickel sleeves – 7 x 5 mm,

5.2.3 Tin capsules – smooth, 6 x 2.9 mm.

5.2.4 Desiccator

5.2.5 Compressed oxygen gas

5.2.6 Compressed helium gas

5.2.7 Microspectula – Hayman style, meets ASTM E 124, Fisher cat. no. 21-401-25A

5.2.8 Microforceps – smooth tips

5.2.9 Pinning forceps

5.2.10 Silver Tungstate-Magnesium Oxide on Chromosorb-A

5.2.11 Silver Oxide-Silver Tungstate on Chromosorb-A

5.2.12 Silver Vanadate on Chromosorb

5.2.13 Copper Wire

5.2.14 Quartz Wool

5.2.15 Vacuum Grease

5.2.16 Gloves – heat resistant

5.2.17 Crucible Dishes – 3" diameter

5.2.18 Crucible Tongs

6.0 REAGENTS AND STANDARDS

6.1 Standard

6.1.1 Primary standard – Acetanilide ($C_6H_5NHCOCH_3$), Acros Organics

6.1.2 Domestic Sludge – Standard Reference Material 2781, National Institute of Standards & Technology

6.1.3 Marine Sediment Reference materials (PACS-2) – National Research Council Canada

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample is filtered onto each muffled filter either in field or in the lab. The filter pads must stay frozen until analyzed.

8.0 QUALITY CONTROL

8.1 The calibration series must be placed at the beginning of the wheel. (9.3.1)

8.2 Continue the sample run only after the calibration standards have been analyzed and confirmed that the calculated K_C and K_N are acceptable. ($18 \leq K_C \geq 25$, $7 \leq K_N \geq 10$)

8.3 An acetanilide standard and/or a blank should follow each series of ten samples.

8.4 All samples are duplicated. The accepted value for the relative percent difference (RPD) is ± 10 %.

8.5 A standard series (blank, standard, blank) should also be placed at the end of the wheel.

8.6 Samples containing different particle sizes should be run in triplicate.

8.7 Data acceptance criteria are listed on the data review checklist.

9.0 PROCEDURE

9.1 Preparation for Analysis

9.1.1 Filters – Place the filters in crucible dishes, combust at a temperature of 450 – 500^{o}C for one hour, and store in a closed container.

9.1.2 Nickel sleeves – Place the nickel sleeves in stainless cups, muffle at 900^{o}C for one hour, cool down, and store in a capped glass jar.

9.2 Sampling Procedure

9.2.1 Place a piece of the pre-combusted filter pad, with rough side up, in a vacuum filtration assembly.

9.2.2 Agitate before each pour a known volume of water (anywhere from10 to 500 ml depending on where the sample was taken) vigorously and quickly pour sample into the filtration assembly.

9.2.3 Filter at a low pressure (15 in Hg) vacuum to dryness and break the seal.

9.2.4 Fold the filter in half (exposed surface inside), wrap in aluminum foil and labeled the sample with the date, ID, and volume filtered.

9.2.5 Freeze at –10 ^{o}C until analysis.

9.2.6 Prior to analysis, samples should be placed in a drying oven at 45 ^{o}C for at least 12 hours. Ensure temperature never goes above 50 ^{o}C. Once dried, leave samples in a desiccator until ready to use.

9.3 Sample Measurements

9.3.1 Prepare a sample run log starting with a calibration series that is consisting of 1 nickel sleeve blank, 1 conditional, 1 tin capsule blank, 1 conditional, and then followed with 3 acetanilide standards.

9.3.2 Standard Preparation

9.3.2.1 Weigh out 1200 to 1500 µg of acetanilide into a tin capsule for each standard. For low level samples, choose to use a smaller amount (as low as 500.0 µg) of acetalinide.

9.3.2.2 Weigh out 200 to 250 µg of domestic sluge into a pre-weighed tin capsule as the reference standard for particulate nitrogen (PN).

9.3.2.3 Weigh out about 1000 µg of PACS-2 into a pre-weighed tin capsule as a reference standard for particulate carbon (PC).

9.3.3 Sample Preparation

9.3.3.1 On a clean surface, place a 7 x 5 mm nickel sleeve into the filter loading die with a plastic loading funnel.

9.3.3.2 Fold the filter and squeeze it into the sleeve with a microforceps. Carefully pull out the microforceps. Use the 4 mm loading plunger to force the compressed filter into the nickel sleeve. Make sure no excess filter protrudes above the lip of the sleeve.

9.3.3.3 Transfer the standards and samples into the 64 sample wheel according to the run log (9.2.1).

9.3.4 Instrument Operation

9.3.4.1 On the main menu, click "**Run**" and select "**Cabon, Hydrogen, Nitrogen**" in the pull down list. Enter date (**ddmmyy**) as the run name, then click "**Run**" to open the sample information box.

9.3.4.2 Enter sample name and sample weight according to the run log. Enter 100 for the weight of the filter samples. Double check all entries.

9.3.4.4 Click "**Run**" to open the list of instructions.

9.3.4.5 Installation of the sample wheel

9.3.4.5.1 Open the manual purge valve on the injection box. Loosen the 4 cover screws and lift the lid. Remove the empty wheel if necessary.

9.3.4.5.2 Insert the loaded sample wheel with the locking pin in place. Tilt the wheel slightly, line up the scribe mark on the wheel with the ratchet in the housing, lower the wheel, and make sure that it is properly seated. Place the locking pin in the center hole.

9.3.4.5.3 Close the cover, and tighten equally on all four screws.

9.3.4.5.4 Open and remove any spent capsules in the capsule receiver. Re-install the cover.

9.3.4.5.5 Check the helium pressure is at 16 psi, oxygen Pressure at 25 psi, combustion temperature at 900 ^{o}C, and reduction temperature at 700 ^{o}C.

9.3.4.5.6 Close the valve. Click "**OK**" to start the run.

9.4 Data Export

9.4.1 Go to "**Calculate**" and click "**Recalculate Data and Statistics**". Search the samples by run numbers (available in the auto printouts) or by date of the run.

9.4.2 Select "**CHN**" in analysis and fresh data in "**Data**". Click "**OK**".

9.4.3 A new dialogue box called "**Recalculate Data and Statistics**" opens. Confirm that ID is "**ALL**", Dates are correct and run numbers are accurate.

9.4.4 Click on "**Results**" to open a new dialogue box and select "**Export**".

9.4.5 In the new dialogue box, called "**Export Data**" Type, in "**Alternative Export**" select "**Export as CSV**" and in "**Options**" select "**All Records**".

9.4.6 Click "**Continue**" and enter file name (**ddmmyy**) and click "**OK**".

9.4.7 Go to desk top and open the folder "**Shortcut to Export Data**" and save the file in a portable drive for your computer.

9.5 Data Transfer

9.5.1 Open the Excel work book template.

9.5.2 Copy the first nine C, H, N results and copy in first part of PC/PN calculation template file.

9.5.4 Copy the C Result and paste under the PC (µg) and do the same for N Result under the PN (µg).

9.5.5 Double check all entries and print out the results.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Calculate the concentrations of PC or PN using the following formula:

$$\text{PC/PN, ppm} = \frac{\text{PC/PN, ug}}{\text{sample volume filtered, mL}}$$

10.2 Calculate the % of relative standard deviation for the duplicated samples as follows:

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

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 for analysis 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

All spent capsules are disposed of as regular trash.

13.0 REFERENCES

13.1 Exeter Analytical, Inc., *Model 440 CHN/O/S Elemental Analyzer Manual,* 1994

13.2 Division of Environmental Chemistry, Maryland Department of Health and Mental Hygiene, *Quality Assurance Plan, DECQA1,* Revision 8.0, 2007.

Standard Operating Procedures

Particulate Phosphorus

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of particulate phosphorus in surface and saline waters.

1.2 The applicable range is 0.01 to 0.5 mg P/L.

2.0 SUMMARY OF METHOD

2.1 Samples for particulate phosphorus are collected by filtering known volumes of water samples through the filters in the field. The filters are folded, placed in aluminum foil pouches, and kept frozen until analysis.

2.2 Filters are combusted at 550^{o}C for 1.5 hrs., and treated with 1 N hydrochloric acid for 24 hrs.

2.2 The supernatant is analyzed for orthophosphate using Lachat Method 120115, where ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

3.0 INTERFERENCES

3.1 High iron concentrations (Fe^{3+} greater than 50 mg/L) can cause precipitation of, and subsequent loss, of phosphorus.

3.2 Silica forms a pale blue complex, which also absorbs at 880nm. This interference is generally insignificant as a silicate concentration of approximately 1 mg/L SiO_2/L would be required to produce a 0.3 µg P/L positive error in orthophosphate.

3.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus.

3.4 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other processing apparatus that bias analyte response.

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.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Flow injection analysis equipment (Lachat 8000 series, QuikChem FIA +), consisted of the following modules, designated to deliver and react sample and reagents in the required order and rations:

5.1.1.1 Sampler

5.1.1.2 Multi-channel proportioning pump

5.1.1.3 Reaction unit or manifold

5.1.1.4 Colorimetric detector with a 10 mm, 800 µL glass flow cell and a 880 nm interference filter

5.1.1.5 Data system

5.1.2 Isotemp Muffle Furnace (Fisher Scientific cat. no. 10-505-10)

5.1.3 Analytical Balance

5.2 Supplies

5.2.1 Glass calibration vials (Lachat part no. 21304)

5.2.2 Test tubes, 13 x 100 mm (Fisher Scientific cat. no. 14-961-27)

5.2.3 Volumetric flasks, Class A

5.2.4 Volumetric pipettes, Class A

5.2.5 Centrifuge tubes, 50 mL, with caps (Fisher Scientific cat. no. 14-432-22)

5.1.8 Test tubes, 16 x 125 mm (Fisher Scientific cat. no. 14-961-30)

5.1.9 Sera filters (TeckniServe cat. no. 510-4055-P01)

5.1.10 Aluminum weighing pans (Fisher Scientific cat. no. 08-732)

5.1.11 Glass Microfiber Filters, Whatman GF/F; 47 mm, 0.7 μm pore size (Fisher Scientific cat. no. 1825-047)

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Reagent Water – Use deionized (18 megohm) water when preparing all reagents and standards. Degas deionized water and all reagents, except standards, to remove dissolved gases.

6.1.2 Stock Ammonium Molybdate Solution – Dissolve 40.0 g ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$) in about 800 mL deionized water in a 1 L volumetric flask. Dilute to the mark and stir for at least 4 hours. Store in plastic bottle and refrigerate.

6.1.3 Stock Antimony Potassium Tartrate Solution – Dissolve 3.0 g antimony potassium tartrate ($K(SbO)C_2H_4O_6.1/2H_2O$) in about 600 mL of deionized water in a 1 L volumetric flask. Dilute to mark, mix, store in a dark bottle and refrigerate.

6.1.4 Molybdate Color Reagent – Add 213 mL stock ammonium molybdate and 72.0 mL stock antimony potassium tartrate to about 500 mL of deionized water in a 1 L volumetric flask.. Dilute to the mark with deionized water and invert to mix. Degas with helium.

6.1.5 Ascorbic Acid Reducing Solution – Dissolve 60.0 g ascorbic acid in about 800 mL deionized water in a 1 L volumetric flask. Mix on a magnetic stirrer and dilute to the mark with deionized water. Prepare fresh weekly.

6.1.6 1.0 M Hydrochloric Acid (Carrier/Diluent for Standards) – Add 83.0 mL of concentrated hydrochloric acid (37%, ACS Reagent Grade, d=1.200) to about 800 mL of deionized water in a 1L volumetric flask. Dilute to mark with deionized water after cooling to room temperature. Mix well.

6.1.7 Sodium Hydroxide - EDTA Rinse Solution – Dissolve 65.0 g sodium hydroxide and 6 g tetrasodium ethylenediamine tetraacetic acid (Na_4EDTA) in about 800 deionized water in a 1 L volumetric flask. Mix on a magnetic stirrer until it is completely dissolved. Dilute to the mark with deionized water and mix.

6.2 Standards

6.2.1 Stock Standard 100 mg P/L in 1.0 M Hydrochloric Acid – Dissolve 0.4394 g primary standard grade anhydrous potassium dihydrogen phosphate (KH_2PO_4) that has been dried for two hours at 110^{o}C in about 800 mL of 1 M hydrochloric acid (6.1.6) in a 1 L volumetric flask. Dilute to the mark with 1.0M hydrochloric acid and mix.

6.2.2 Intermediate Standard Solution (1 mg P/L) – Add 10 mL of stock standard (6.2.1) to 800 mL of 1 M hydrochloric acid (6.1.6) in a 1L volumetric flask and dilute to 1000 mL mark and mix

6.2.3 Working standards – Add 1, 2, 5,10, 20, and 50 mL of the intermediate standard (6.2.2) into six 100 mL volumetric flasks. Dilute to 100 mL with1.0 M hydrochloric acid (6.1.6) and mix. This will prepare 0.01. 0.02. 0.05, 0.10, 0.20, and 0.50 mg P/L standards respectively. Use the intermediate standard prepared in 6.2.1 (1 mg P/L) as the seventh working standard.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are collected by the field personnel on Whatman GF/F filters (47 mm; 0.7 μm pore size) by filtering known volumes of water samples through the filters. The filters are folded, placed in aluminum foil pouches, and kept frozen until analysis.

8.0 QUALITY CONTROL

8.1 In the analytical run, every tenth sample is duplicated followed a blank. The accepted value for the relative standard deviation (RSD) is ± 10%.

8.2 Blank filters are processed and analyzed when provided by the field personnel.

8.3 One mid-range standard (0.10 mg/L P) is analyzed for every 10 samples.

8.4 An external quality control sample is analyzed at the beginning and at the end of each analytical run.

8.5 Acidified deionized water blank is analyzed at the beginning of each analytical run and after every 10 samples

9.0 PROCEDURE

9.1 Sample Preparation

9.1.1 Place filters (samples and blanks, if provided) in labeled aluminum weighing pans and combust in a muffle furnace at 550^{o}C for 1.5 hours

.

9.1.2 Cool to ambient temperature, then transfer the combusted filters into labeled 50 mL screw cap centrifuge tubes.

9.1.3 Add 10 mL 1N hydrochloric acid to each tube.

9.1.4 Cap tubes and let stand for a minimum of 24 hours. Shake tubes several times during the 24 hour period.

9.1.5 Pour samples into 16 x 125 mm tubes and filter using Sera filters.

9.1.6 Transfer the filtrate to autosampler tubes with Pasteur pipettes.

9.2 Instrument Calibration and Sample Analysis

9.2.1 Set up manifold as shown in the manifold diagram in Appendix A.

9.2.2 Pump deionized water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to stabilize and a stable baseline is achieved.

9.2.3 Place standards, blanks, samples, etc. in the autosampler. Input the information required be the data system, such as standard concentration, sample identification (laboratory numbers), replicates, spikes, etc.

9.2.4 Begin the analysis.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 All calculations are performed automatically by the data system. Calibration is performed by analyzing a set of standards. The data will then prepare a calibration curve by plotting peak areas versus standard concentration. The acceptable values for the correlation coefficients are $\geq$ 0.9950. Sample concentrations are calculated from the regression equation.

10.2 Samples exceeding the concentration of the highest standard are diluted and reanalyzed.

10.3 Results are reported in mg P/L.

11.0 DATA AND RECORDS MANAGEMENT

11.1 Hard copies of all results are kept in the laboratory in a binder labeled "Particulate Phosphorus".

11.2 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 Samples and standards are poured down the drain while flushing with large amounts of cold water.

12.2 Waste line from the instrument is placed in the sink with cold water running.

13.0 REFERENCES

13.1 United States Environmental Protection Agency, *Methods for Chemical Analysis of Water and Waste, EPA/600/R-93/100, Method 365.4, May 1993.*

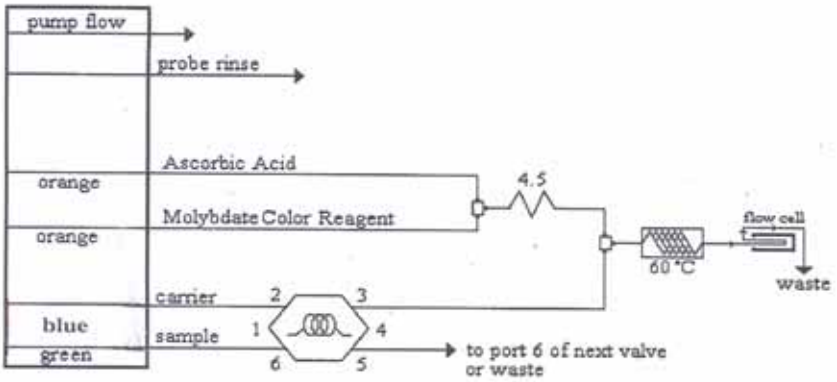
13.2 Lachat Instruments, *Determination of Total Phosphate in Ashed Soil Samples by Flow Injection Analysis, Method 12-115-01-1-F, September 2003.*

13.3 Chesapeake Biological Laboratories, *Particulate Phosphorus Method, February 2004.*

APPENDICES

Appendix A - Manifold Diagram
Appendix B - Data system parameters
Appendix C - Sample Run List
Appendix D – Data Review Checklist

Appendix A - MANIFOLD DIAGRAM FOR PARTICULATE PHOSPHORUS METHOD



Carrier: **Reagent 10**
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm.**

QC8000 Sample Loop: 150 cm

Interference Filter: 880 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  shows 650 cm of tubing wrapped around the heater block at the specified temperature.

4.5: **70** cm of tubing on a 4.5 cm coil support

Appendix B - DATA SYSTEM PARAMETERS FOR THE QC 8000

QC 8000 Parameter

Sample throughput:	65 samples/hr, 55 s/sample
Pump Speed:	35
Cycle period:	85

Analyte Data

Concentration Units:	mg P/L
Chemistry	Direct
Inject to Start of Peak Period:	23 s
Peak base width:	35s
% Width Tolerance:	100
Threshold:	3000

Calibration Data

Level	1	2	3	4	5	6	7	8
Concentration, mg P/L	0.00	0.01	0.02	0.05	0.10	0.20	0.50	1.00

Calibration fit type:	1st order poly
Calibration Rep. Handling:	Average
Weighing Method:	None
Force through zero:	No

Sampler Timing

Min Probe in Wash Period:	10.0 s
Probe in sample period:	30.0 s

Valve Timing

Sample reaches valve:	30.0 s
Load time:	0.0 s
Load Period:	22.5 s
Inject Period:	62.5 s

Appendix C - SAMPLE RUN LIST

State of Maryland
DHMH – Laboratories Administration
Division of Environmental Chemistry
INORGANICS SECTION – ***Nutrients Laboratory***

Particulate Phosphorus using Lachat QuickChem FIA +

Date: _____ **Analyst: _____**

TRAY POSITION	*SAMPLE IDENTIFICATION*	*TRAY POSITION*	*SAMPLE IDENTIFICATION*	*TRAY POSITION*	*SAMPLE IDENTIFICATION*	*TRAY POSITION*	*SAMPLE IDENTIFICATION*
1	***Blank***	**26**		**51**		**76**	
2	Blank Spike	**27**		**52**		**77**	
3	Blank	**28**	R1	**53**		**78**	
4	QC	**29**	R2	**54**	R1	**79**	
5	Blank	**30**	Blank	**55**	R2	**80**	R1
6		**31**		**56**	Blank	**81**	R2
7		**32**		**57**		**82**	Blank
8		**33**		**58**		**83**	
9		**34**		**59**		**84**	
10		**35**		**60**		**85**	
11		**36**		**61**		**86**	
12		**37**		**62**		**87**	
13		**38**		**63**		**88**	
14		**39**		**64**		**89**	
15	R1	**40**		**65**		**90**	
16	R2	**41**	R1	**66**		**91**	
17	Blank	**42**	R2	**67**	R1	**92**	
18		**43**	Blank	**68**	R2	**93**	R1
19		**44**		**69**	Blank	**94**	R2
20		**45**		**70**		**95**	Blank
21		**46**		**71**		**96**	QC
22		**47**		**72**		**97**	
23		**48**		**73**		**98**	
24		**49**		**74**		**99**	
25		**50**		**75**		**100**	

QC: _____ ***True Value:*** **_____**; ***Range:*** _____

Appendix D – DATA REVIEW CHECKLIST

State of Maryland
DHMH - Laboratories Administration
DIVISION OF ENVIRONMENTAL CHEMISTRY
Nutrients Section

Data Review Checklist

Particulate Phosphorus (PP)/Chesapeake Bay Program Method

Lab Numbers[1]:_____ Analyst: _____
Date Collected: _____ Date Digested: _____ Date Analyzed: _____

Procedure	Acceptance Criteria		Comments
Holding Time	28 days @ – 20°C		
Samples Analyzed	Within 5 working days		
Calibration Curve	Corr. Coeff. ≥ 0.9950		
Reagent Blank	< Reporting level (0.010 ppm)		
Blank Spike	1 per batch		
	Recovery = 90–110%		
Matrix Spike	Every 10th sample or 1/batch, if less than 10 samples	N/A	
	Recovery = 90–110%	N/A	
External QC[2]	Beginning and end of each run		
	Within acceptable range		
Check Standard	After every 10th sample and at the end of the run		
	Recovery = 90–110%		
Field Duplicates/Replicates	Every 10th sample or 1/batch, if less than 10 samples Every		
	RSD ≤ 10%		
Decimal Places Reported	3		
Measured Values	Within calibration range (0.010 – 1.00 ppm)		
Diluted Samples	Correct final calculations		
Changes/Notes	Clearly stated		

* Check (√) if criteria are met.

_____ Date Reported: _____
Reviewer's Signature & Date

[1]Include beginning and ending numbers, account for gaps by bracketing.

[2]QC Identification: _____ True Value = _____

Standard Operating Procedures

Total Dissolved Nitrogen in Alkaline Persulfate Digests

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to seawater, brackish water, and non-saline water.

1.2 The applicable range is 0.1 to 5.0 mg N/L.

1.3 The method detection limit is 0.006 mg N/L.

1.4 Approximately 55 samples per hour can be analyzed.

2.0 SUMMARY OF METHOD

Water samples are digested for one hour with alkaline persulfate to oxidize all the nitrogen compounds present in the sample to nitrate (NO_3^-). The nitrate is then quantitatively reduced to nitrite by passing the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide under acidic conditions followed by coupling with N-(1-naphthyl) ethylene diamine dihydrochloride (Marshall's reagent) to form a reddish-purple azo dye which is measured colorimetrically at 520nm.

3.0 INTERFERENCES

3.1 Total carbon concentrations in excess of 20 mg C/L or COD concentrations in excess of 50 mg/L will result incomplete oxidation of nitrogen compounds.

3.2 The presence of sulfide and chloride produced by seawater oxidation reduce the column life as compared to non-saline samples.

3.3 Colored samples that absorb at 520 nm and turbidity will interfere in the colorimetric determination. Turbidity of the samples can be removed by filtration prior to analysis.

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 preparing reagents.

4.3 Sodium hydroxide, ammonium hydroxide, hydrochloric acid, and phosphoric acid used in this determination have the potential to be highly toxic or hazardous. Consult MSDS for detailed explanations.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Lachat 8000 series, QuikChem FIA+ Automated Ion Analyzer, consists of auto-sampler, multi-channel proportioning pump, chemistry manifold, colorimetric detector, and data system.

5.1.2 Analytical balance, capable of accurately weighing to the nearest 0.0001g.

5.1.3 Autoclave capable of producing 15 psi (121^{o}C)

5.2 Supplies

5.2.1 Class A volumetric flasks and pipettes

5.2.2 Digestion tubes – 40 mL vials (Fisher 14-959-37C or equivalent) with autoclavable caps lined with Teflon liners (Kimble Caps Cat # 03-340-77E).

5.2.3 16 x 125 mm test tubes

5.2.4 13 x 100 mm culture tubes

5.2.5 Cadmium Reduction Column (Lachat Part No. 50237A).

5.2.6 Helium gas for degassing

6.0 REAGENTS AND STANDARDS

6.1 Reagents

Use deionized water (DI) for preparing all solutions. Prevent the bubble formation by degassing deionized water and all reagents except the standards with helium.

6.1.1 15 N Sodium Hydroxide - Dissolve 150 g NaOH in about 200 mL DI water. Mix well, let the solution get cooled to room temperature, and store in a plastic container**.**

6.1.2 Ammonium Chloride Buffer, pH 8.5 - In a 1L volumetric flask, dissolve 85.0 g ammonium chloride (NH_4Cl) and 1.0g disodium

ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA.2H_2O$) in about 800 mL DI water. Mix well and dilute to the mark. Adjust pH to 8.5 with 15N sodium hydroxide solution and then filter the reagent.

6.1.3 Sulfanilamide Color Reagent – Add about 600 mL of DI water into a 1 L volumetric flask. Then add 100 mL 85% phosphoric acid (H_3PO_4), 40.0 g sulfanilamide, and 1.0 g N- (1-naphthyl) ethylenediamine dihydrochloride (NED). Stir for about 30 minutes until dissolved. Dilute to the mark, filter and store in a dark bottle.

6.1.4 Digestion Solution – Add about 600 mL DI water into a 1 L volumetric flask. Then, add 20.1 g potassium persulfate ($K_2S_2O_8$), and 3 g sodium hydroxide (NaOH). Dilute to mark. Prepare fresh at least twice a week.

6.1.5 Borate Buffer, 1.0 M, pH 7.5 - dissolve 61.8 g boric acid and 8.0 g sodium hydroxide in about 800 DI water in a 1 L volumetric flask. Mix on a magnetic stirrer for about four hours until it is completely dissolved. Dilute to the mark with DI water and mix.

6.2 Standards

6.2.1 Stock Nitrate Standard Solution (1000 mg N/L) - Dissolve 0.722g of potassium nitrate in about 60 mL of DI water in a 100 mL volumetric flask. Dilute to mark and mix. Store in a dark bottle.

6.2.2 Mixed Intermediate Standard Solution (1 mg P/L and 10 mg N/L) – Add 10 mL of 100 mg P/L (stock standard solution for total dissolved phosphorus determination) and 10 mL of stock nitrate standard solution (6.2.1) to about 800 mL DI water in a 1L volumetric flask. Dilute to mark and mix.

6.2.3 Mixed Working Standard Solutions - Add 1, 2, 5, 10, 20, and 50 mL of intermediate standard (6.2.2) into six 100 mL volumetric flasks. Dilute to mark and mix.

6.2.4 Stock Nitrite Standard Solution (100 mg N/L) - Dissolve 0.049 g potassium nitrite in about 80 mL of DI water in a 100 mL volumetric flask. Dilute to mark and mix.

6.2.5 Nitrite Standard for Checking Cadmium Column (5.0 mg N/L) - Add 10 mL stock nitrite standard (6.2.4) to about 180 ml of DI water in a 200 mL volumetric flask. Dilute to mark and mix.

6.2.6 Nitrate Standard for Checking Cadmium Column (5.0 mg N/L) - Add 5 mL of stock nitrate standard solution (6.2.1) to about 800 mL DI water in a 1L volumetric flask. Dilute to mark and mix.

6.2.7 Spiking Solution - Use the mixed intermediate standard (6.2.2) as the spiking solution. Spike 10 mL of blanks and samples with 50 µl of this solution.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are filtered in the field, collected in plastic bottles or cubitainers, and are preserved by cooling to 4°C.

7.2 Samples are analyzed within 48 hrs after collection. If they cannot be analyzed within this time period, they may be frozen at -20°C as soon as possible at the laboratory. The holding time for frozen samples is 28 days.

8.0 QUALITY CONTROL

8.1 Every tenth sample is duplicated and spiked and is followed by a check standard and two blanks. The acceptable range for relative standard deviation (RSD) is ≤ 10%, and it is 90 – 110% for spike recovery. If these do not fall within the acceptable ranges, the correspondence analyses are repeated.

8.2 A deionized water blank is run at the beginning and after every ten samples. Results for the blanks must be < 0.010 mg P/L.

8.3 An external quality control is analyzed at the beginning and at the end of each analytical run.

8.4 The efficiency of the cadmium column before and after sample run is calculated by running 5 ppm NO_2-N (6.2.5) and 5 ppm NO_3-N (6.2.6) standards and using the formula (NO_3-N/NO_2-N) x 100. The accepted range for the cadmium column efficiency is 86%-114%. If the efficiency is out of this range, new standards are prepared and efficiency is re-evaluated. If the efficiency is still out of range then the column is replaced.

9.0 PROCEDURE

9.1 Sample Preparation

9.1.1 Make a list of samples to be analyzed and pour the samples into labeled 16mm x 125 mm test tubes.

9.1.2 Pipet 10 mL of each standard or sample into digestion tubes.

9.1.3 Pipet 10 mL of a mid-range (0.1 mg P/L and 1.0 mg N/L) standard, a blank, a blank spike, and an external quality control sample into digestion tubes with each tray of 24 samples. Prepare a duplicate and a spike of every 10th sample.

9.1.4 Pipet 10 mL of the nitrate and nitrite standards for cadmium column check (6.2.5 and 6.2.6) into digestion tubes.

9.1.4 Add 5 mL of digestion solution to each tube, screw the caps on loosely, and mix by vortexing. Digest the standards, samples, and all the quality control samples in the autoclave for 60 min. at 121 ^{o}C (250 ^{o}F) @ 17 psi.

9.1.5 After one hour, turn off the autoclave and let the digests cool for 5 minutes. Remove the tubes from the autoclave and let the digests come to room temperature. Add 1 mL of borate buffer, vortex, and pour into 13 x 100 mm culture tubes analyze them as soon as possible.

9.1.6 Refrigerate the digests at 4^{o}C, if they cannot be analyzed immediately. If the digests are refrigerated, warm them to room temperature, and add 1 mL borate buffer (6.1.7) to each tube and vortex.

9.1.7 Analyze the digests using the procedure described in 9.2.

9.2 Instrument Calibration and Sample Analysis

9.2.1 Set up manifold according to the manifold diagram.

9.2.2 Pump deionized water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to stabilize and a stable baseline is achieved.

9.2.3 Enter sample information required by the data system.

9.2.4 Place standards, blanks, samples, quality controls, etc. in the autosampler according to the run table.

9.2.5 Initiate the analytical run.

9.2.6 At the end of the run, review the calibration curve statistics and the results for the quality control samples. Acceptable values for the correlation coefficient are $\geq$ 0.9950. Other quality control criteria are described in 8.0.

9.2.7 Get the data reviewed by a designated scientist, and then, report the results on the Analysis Request Forms.

10.0 DATA ANALYSIS AND CALCULATIONS

All calculations are performed automatically by the instrument. Calibration curve is established by plotting peak areas versus concentration of the standards. Sample concentrations are calculated from the calibration curve.

11.0 DATA AND RECORDS MANAGEMENT

11.1 Report only those results that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard are manually diluted and reanalyzed.

11.2 Sample results for total dissolved nitrogen are reported in mg N/L. Report results to three decimal places. Report results below the lowest calibration standard as < 0.10. For the Chesapeake Bay Program only report all calculated results, with a < sign for those concentrations that are less than 0.10 mg N/L.

12.0 WASTE MANAGEMENT

12.2 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume and bench operation.

12.3 Samples and standards are poured down the drain while flushing with large amount of cold water.

13.0 REFERENCES

13.2 Lachat Instruments QuickChem Method 31-107-04-4-A, *Determination of Total Nitrogen in Brackish or Seawater by Flow Injection Analysis*.

13.3 Methods for Determination of Inorganic Substances in water and Fluvial Sediments. Book 5. Chapter A1. U. S. Geological Survey.

Standard Operating Procedures

Total Dissolved Phosphorus in Alkaline Persulfate Digests

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to seawater, brackish water, and non-saline water.

1.2 The applicable range is 0.01 to 0.5 mg P/L.

1.3 The method detection limit is 0.006 mg P/L.

1.4 Approximately 55 samples per hour can be analyzed.

2.0 SUMMARY OF METHOD

Water samples are digested for one hour with alkaline persulfate to convert all of the phosphorus present in the sample to orthophosphate (PO_4^{3-}). Approximately 1.3 mL of this digest is injected onto the manifold, where orthophosphate reacts with ammonium molybdate and antimony potassium tartrate under acidic condition and then reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. The absorbance is directly proportional to the concentration of phosphorus in the sample.

3.0 INTERFERENCES

3.1 Silica forms a pale blue complex which also absorbs at 880 nm. A silica concentration of 4000 ppm would produce a 1 ppm positive error in orthophosphate.

3.2 Glassware should be washed with 1:1 HCl and rinsed with deionized water in order to prevent possible contamination problems in low level phosphorus determinations.

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 preparing reagents.

4.3 Sodium hydroxide, hydrochloric acid, and sulfuric acid used in this determination have the potential to be highly toxic or hazardous. Consult MSDS for detailed explanations.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Lachat 8000 series, QuikChem FIA+ Automated Ion Analyzer, consists of auto-sampler, multi-channel proportioning pump, chemistry manifold, colorimetric detector, and data system.

5.1.2 Analytical balance, capable of accurately weighing to the nearest 0.0001g.

5.2 Supplies

5.2.1 Class A volumetric flasks and pipettes

5.2.2 Digestion tubes – 40 mL vials (Fisher 14-959-37C or equivalent) with autoclavable caps lined with Teflon liners (Kimble Caps Cat # 03-340-77E).

5.2.3 16 x 125 mm test tubes

5.2.4 13 x 100 mm culture tubes

5.2.5 Helium gas for degassing

6.0 REAGENTS AND STANDARDS

6.1 Reagents

Use deionized water (DI) for preparing all solutions. Prevent the bubble formation by degassing deionized water and all reagents except the standards with helium.

6.1.1 Alkaline Persulfate Oxidizing Reagent - In a 1L volumetric flask, dissolve 20.1 g potassium persulfate ($K_2S_2O_8$), and 3g sodium hydroxide (NaOH) in about 600 mL DI water. Dilute to mark and mix. Prepare fresh at least twice a week.

6.1.2 Hydrochloric Acid, 1.0 N – Add 83.3 mL concentrated hydrochloric acid (37%, ACS Reagent Grade, d = 1.200) to about 800 mL of DI water in a 1L volumetric flask in a fume hood. Dilute to mark and mix well.

6.1.3 Stock Ammonium Molybdate Solution – Dissolve 40.0 g ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24},4H_2O$) in about 800 mL DI water in a 1 L volumetric flask. Dilute to the mark and stir until completely dissolved; this may take about 4 hours. Store in plastic and refrigerate.

6.1.4 Stock Antimony Potassium Tartrate Solution – Dissolve 3.0 g antimony potassium tartrate ($K(SbO)C_2H_4O_6.1/2H_2O$) in about 600 mL DI water in a 1L volumetric flask. Dilute to mark and mix. Store in a dark bottle and refrigerate.

6.1.5. Molybdate Color Reagent – In a hood, carefully add 70.0 mL concentrated sulfuric acid to about 500 mL water in a 1 L volumetric flask and mix well. Then, add 72.0 mL stock antimony potassium tartrate (6.1.4) and 213 mL stock ammonium molybdate (6.1.3). Dilute to the mark with DI water. Degas with helium.

6.1.6 Ascorbic Acid Reducing Solution – Dissolve 75.0 g ascorbic acid in about 800 DI water in a 1 L volumetric flask. Mix on a magnetic stirrer and dilute to the mark with DI water. Prepare fresh weekly.

6.1.7 Borate Buffer, 1.0 M, pH 7.5 - Dissolve 61.8 g boric acid and 8.0 g sodium hydroxide in about 800 DI water in a 1 L volumetric flask. Mix on a magnetic stirrer until it is completely dissolved. Dilute to the mark with DI water.

6.1.8 Carrier Solution - Combine 300 mL of oxidizing reagent (6.1.1), 60.0 mL 1 N hydrochloric acid (6.1.2), and 60.0 mL borate buffer (6.1.7) in a 1 L volumetric flask, dilute to volume, and stir well. Degas the solution with helium. It is recommended that the carrier is degassed within 4 hours of use.

6.1.9 Sodium Hydroxide – EDTA Rinse - In a 1L flask, dissolve 65.0 g sodium hydroxide (NaOH) and 6 g tetrasodium ethylenediamine tetraacetic acid (Na_4EDTA) in about 800 deionized water. Mix on a magnetic stirrer until it is completely dissolved. Dilute to the mark with deionized water.

6.2 Standards

6.2.1 Stock Standard Solution (100 mg P/L) - Dissolve 0.4394 g of anhydrous potassium dihydrogen phosphate (KH2PO4) which has been dried for two hours at 110^{o}C in about 800 mL deionized water. Dilute to the mark and invert to mix.

6.2.2 Mixed Intermediate Standard Solution (1 mg P/L and 10 mg N/L) - Add 10 mL of stock standard, (6.2.1) and 10 mL of 1000 mg N/L (stock

standard solution for total dissolved nitrogen determination) to one liter of demineralized water in a 1L volumetric flask and dilute to 1000 mL mark.

6.2.3 Mixed Working Standard Solutions - Add 1, 2, 5, 10, 20, and 50 mL of intermediate standard (6.2.2) into six 100 ml volumetric flasks. Dilute to100 mL.

6.2.4 Spiking Solution - Use the mixed intermediate standard (6.2.2) as the spiking solution. Spike 10 mL of blanks and samples with 50 µl of this solution.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Samples are filtered in the field, collected in plastic bottles or cubitainers, and are preserved by cooling to 4^{o}C.

7.2 Samples are analyzed within 48 hrs after collection. If they cannot be analyzed within this time period, they may be frozen at -20^{o}C as soon as possible at the laboratory. The holding time for frozen samples is 28 days.

8.0 QUALITY CONTROL

8.1 Every tenth sample is duplicated and spiked and is followed by a check standard and two blanks. The acceptable range for relative standard deviation (RSD) is $\leq$ 10%, and it is 90 – 110% for spike recovery. If these do not fall within the acceptable ranges, the correspondence analyses are repeated.

8.2 A deionized water blank is run at the beginning and after every ten samples. Results for the blanks must be < 0.010 mg P/L.

8.3 An external quality control is analyzed at the beginning and at the end of each analytical run.

9.0 PROCEDURE

9.1 Sample Preparation

9.1.1 Make a list of samples to be analyzed and pour the samples into labeled 16mm x 125 mm test tubes.

9.1.2 Pipet 10 mL of each standard or sample into digestion tubes.

9.1.3 Pipet 10 mL of a mid-range (0.1 mg P/L and 1.0 mg N/L) standard, a blank, a blank spike, and an external quality control sample with each tray of 24 samples. Prepare a duplicate and a spike of every 10th sample.

9.1.4 Add 5 mL of digestion solution to each tube, screw cap the tubes, and mix by vortexing. Digest the standards, samples, and all the quality control samples in the autoclave for 60 min. at 121 ^{o}C (250 ^{o}F) @ 17 psi.

9.1.5 After one hour, turn off the autoclave and let the digests cool for 5 minutes. Remove the tubes from the autoclave and let the digests come to room temperature. Add 1 mL of borate buffer, vortex, and pour into 13 x 100 mm culture tubes analyze them as soon as possible.

9.1.6 Refrigerate the digests at 4^{o}C, if they cannot be analyzed immediately. If the digests are refrigerated, warm them to room temperature, and add 1 mL borate buffer (6.1.7) to each tube and vortex.

9.1.7 Analyze the digests using the procedure described in 9.2.

9.2 Instrument Calibration and Sample Analysis

9.2.1 Set up manifold according to the manifold diagram.

9.2.2 Pump deionized water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to stabilize and a stable baseline is achieved.

9.2.3 Enter sample information required by the data system.

9.2.4 Place standards, blanks, samples, quality controls, etc. in the autosampler according to the run table.

9.2.5 Initiate the analytical run.

9.2.6 At the end of the run, review the calibration curve statistics and the results for the quality control samples. Acceptable values for the correlation coefficient are $\geq$ 0.9950. Acceptable results for the quality control samples are as indicated in 8.0.

9.2.7 Get the data reviewed by a designated scientist, and then, report the results on the Analysis Request Forms.

10.0 DATA ANALYSIS AND CALCULATIONS

All calculations are performed automatically by the instrument. Calibration curve is established by plotting peak areas versus concentration of the standards. Sample concentrations are calculated from the calibration curve.

11.0 DATA AND RECORDS MANAGEMENT

11.1 Report only those results that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard are manually diluted and reanalyzed.

11.2 Sample results for total dissolved phosphorus are reported in mg P/L. Report results to three decimal places. Report results below the lowest calibration standard as < 0.01. For the Chesapeake Bay Program only report all calculated results, with a < sign for those concentrations that are less than 0.01 mg P/L.

12.0 WASTE MANAGEMENT

12.1 It is the laboratory's responsibility to comply with all federal, state and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume and bench operation.

12.2 Samples and standards are poured down the drain while flushing with large amount of cold water.

13.0 REFERENCES

13.1 Lachat Instruments QuickChem Method 10-107-04-A, *Determination of Total Nitrogen in Brackish or Seawater by Flow Injection Analysis*.

13.2 Methods for Determination of Inorganic Substances in water and Fluvial Sediments. Book 5. Chapter A1. U. S. Geological Survey.

Standard Operating Procedures

Total Organic Carbon/Dissolved Organic Carbon

EPA Method 415.1 (Combustion or Oxidation)

1.0 SCOPE AND APPLICATION

1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes.

1.2 The fraction of TOC that passes through a 0.45 μm pore diameter filter is defined as dissolved organic carbon (DOC).

1.3 The method is applicable to measurement of organic carbon above 0.5 mg/L

2.0 SUMMARY OF METHOD

Organic carbon in a sample is converted to carbon dioxide by catalytic combustion at 680^{o}C. The carbon dioxide formed is measurement using a non-dispersive infrared gas analyzer (NDIR). The amount of carbon dioxide is directly proportional to the concentration of carbonaceous material in the sample.

3.0 INTERFERENCES

3.1 Carbonate and bicarbonate carbons represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

3.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe. The opening of the syringe limits the maximum size of particles which may be included in the following measurements

4.0 HEALTH AND SAFETY

4.1 Good laboratory safety practices should be followed during reagent preparation and instrument operation.

4.2 Use of gloves and eye protection is recommended when working with Sodium Hydroxide which can cause severe burns.

4.3 Gloves and protective eyewear must be used when removing the cover from the furnace and replacing the combustion tube.

5.0 EQUIPMENT AND SUPPLIES

5.1 Equipment

5.1.1 Shimadzu 5000 TOC Analyzer

5.1.2 Shimadzu ASI 5000 Autosampler

5.2 Supplies

5.2.1 5 ml glass vials

5.2.2 50 ml glass vials for standards

5.2.3 High purity air, made of pure nitrogen and pure oxygen and contains no more than 1 ppm of CO_2, CO and HC, respectively.

6.0 REAGENTS AND STANDARDS

6.1 Reagents

6.1.1 Deionized water free with analyte of interest is used to prepare all the reagents and the standards to reduce the carbon concentration of the blank

6.1.2 2N Hydrochloric Acid – Dilute 166 ml of concentrated Hydrochloric Acid to 1 liter with deionied water.

6.1.3 TIC/TOC Standard - Shimadzu custom made standard containing 10 mg/L of total organic carbon and 10 mg/L of total inorganic carbon.

6.2 Standards

6.2.1 1000 ppm Potassium Hydrogen Phthalate (KHP) stock standard solution – Stir to dissolve 2.12 gm of KHP in distilled water and dilute to 1000 ml in a volumetric flask.

6.2.2 Potassium Hydrogen Phthalate (KHP) working standards

6.2.2.1 10 ppm - Dilute 10 ml of KHP 1000 ppm stock solution to 1 liter in a volumetric flask and mix well.

6.2.2.2 5 ppm - Dilute 100 mL of 10 ppm standard solution to 200 ml

in a volumetric flask.

6.2.2.3 1 ppm - Dilute 20 mL of 10 ppm standard solution to 200 ml in a volumetric flask.

6.2.2.4 0.5 ppm - Dilute 10 ml of 10 ppm standard solution to 200 ml in a volumetric flask.

6.2.2.5 0.0 ppm - Ultra pure deionized water.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Refrigeration at 4^{o}C prior to analysis is required to minimize microbiological decomposition of solids. The holding time is 48 hours for unacidified samples or 28 days if sample is acidified at the time of collection.

8.0 QUALITY CONTROL

8.1 Reagent grade water is run as the blank control.

8.2 Replicates and spike are performed on every tenth sample or one replicate per run. Duplicated determinations should agree within 10% of their average.

8.3 Spike the sample with 5 ppm KHP by adding 100 µl of 1000 ppm stock solution into 20 ml of the sample. The acceptable spike recovery should be within 10% of the concentration added.

8.4 Quality control samples including check standard, spiked blank and external QC are run at the beginning and at the end of each run. Each value should be within 10% of its true value.

8.5 Instrument check solution, TIC/TOC, is run at the beginning of each run. A reading of 10 ppm of TOC indicates the sample had been properly acidified and inorganic carbon had been successively removed.

8.6 All the standards and sample are run at least three analyses from each tube. The concentrations reported for the samples are the mean of the triplicates, calculated by the computer program.

8.7 Every tenth sample is duplicated (analyzed from two different tubes) and spiked. The accepted value for the relative standard deviation (RSD) or spike recovery is ± 10 %.

8.8 Data acceptance criteria are listed on the Data Review Checklist.

8.9 Laboratory participates in ERA WatR Pollution (WP) Proficiency Test.

9.0 PROCEDURE

9.1 Instrument Warm Up

9.1.1 Switch on TOC-5000, which undergoes the initialization sequence, so does the ASI when power is supplied.

9.1.2 Go to Main Menu and select #6 Monitor: TOC 5000 automatically turns on carrier gas, heats oven and starts drawing the base line.

9.1.3 Check that the temperature is reaching 675C and humidifier temperature is < 2C. Check base line, which at range setting x30 should be between +/- 20% and as close to zero as possible. Using a screwdriver to turn the knob on the top of the instrument to adjust the base line position, if necessary.

9.2 Instrument Check

9.2.1 Select #8 Maintenance from the Main Menu. Then select Mechanic Check and open the front panel of the instrument. Press IC On button on the panel and lowering tubing to release excess liquid. Press Off button when finish.

9.2.2 Select #8 Maintenance from the Main Menu. Then select Mechanic Check and open the front panel of the instrument. Press IC On button on the panel and lowering tubing to release excess liquid. Press Off button when finish.

9.2.3 Press ASI, wait until the turntable stops moving, then press IC to check that liquid flows through the front tubing and press TC to check that liquid flows through the back tubing.

9.2.4 Check and top off outside water bottle.

9.2.5 Check the water levels at least ¾ full in the two inside reagent bottles (i.e. IC reagent container and humidifier bottle)

9.2.6 Check gas leaking by pinching the S tubing of the CO2 absorber jar and watch any bubbling in the drain bottle.

9.2.7 Check and make sure that there is enough paper on the roll for printing.

9.3 Sample Loading

9.3.1 Place the standard solution vials in positions S1 to S8 of the turntable corresponding to the position specified in the ASI condition; i.e. vial S1-10ppm, S2-5ppm, S3-0.5ppm, S4-0ppm. When automatic injection of acid is specified for NPOC measurement, the vial containing 2N HCl must be placed in position S8.

9.3.2 Make a sample run list that starts with the 5 calibration check standards, a blank, the TIC/TOC check, and a QC. Followed by sample names with replicates and spikes for every ten samples. A blank, and a check standard are run after every 10 samples. A blank, a check standard and a QC should also be run at the end of each run.

9.3.3 Load sample vials starting with position #1 on the turntable in the sequence as assigned in the sample worksheet. However, the position #43 is designated for a blank vial.

9.3.4 Press Return and End to go back to the Main Menu.

9.4 Sample measurement

9.4.1 Go down to #9 Autosampler, select NPOC and enter to change the initial and last/total sample number under IS and FS.

9.4.2 Enter and check C1 (Calibration Curve 1) condition. Check and set the range as follows: Injection Volume: 53 μl; No. of Injection: 3; Maximum No. of Injection: 5; Sparging Time: 3 minutes; Shift to Origin: On; Acid Addition: On.

9.4.3 Press Return to get back to Sample Measurement (ASI)/Condition.

9.4.4 Select F1 for the saved higher range calibration curve. Make sure that 5 has been entered for Maximum number of Injections.

9.4.5 Press Next to go to ASI condition. Move down and select Auto Start Time and change the date to one month from now to defer its function if it is necessary

9.4.6 Press Next to go to Measurement Start , press “START” button to begin the measurement.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 The instrument uses a multiple point calibration and uses the least square method to calculate the sample results. Standard curve of 0.0 ppm to 10.0 ppm is established daily in the sample run. A high level standard curve of 10.0 ppm to 50.0 ppm is renewed quarterly.

10.2 Calculate % of spike recovery of the laboratory fortified samples as follows

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

10.3 Calculate the % of relative standard deviation for the duplicated samples as follows:

$$\% \text{ RSD} = \frac{\text{SD of the duplicates}}{\text{average of the duplicates}} \text{ x } 100$$

11.0 DATA AND RECORDS MANAGEMENT

11.1 The detection limit for this method is the concentration of the lowest standard, which is 0.5 ppm of TOC.

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 Samples and standards are poured down the drain while flushing with large amount of cold water.

12.2 Actual reagent preparation volumes are to be reflected anticipated usage and reagent stability.

13.0 REFERENCES

13.1 United States Environmental Protection Agency, *Methods for Chemical Analysis of Water and Waste, Method Number 415.1and 415.2, August 1993*

13.2 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater, 18th Edition*, 1992

13.3 Shimadzu Corporation, *Instrument Manual for Total Organic Carbon Analyzer Model TOC-5000*

Standard Operating Procedures

Total Suspended Solids

EPA Method 160.2 (Gravimetric, Dries at 103−105^{O}C)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to drinking, surface and saline waters, domestic and industrial wastes.

1.2 The practical range of the determination is 4 mg/L to 20,000 mg/L. This laboratory reports all values greater than 1 mg/L.

2.0 SUMMARY OF METHOD

A well mixed sample is filtered through a Gooch Crucible containing a glass-fiber filter with 2.0 um (or smaller) nominal pore size and the residue retained on the filter is dried at 103^{o}C to 105^{o}C. The increase in weight of the filter represents the total suspended solids.

3.0 INTERFERENCES

3.1 Samples high in dissolved solids, such as saline water, brines and some wastes, may be subject to a positive interference. For such samples, the filter with sample should be washed thoroughly to ensure removal of dissolved solids from the filter.

3.2 Large floating particles, submerged agglomerates of non-homogeneous materials from the sample or excessive residue on the filter may form a water-entrapping crust; limit the sample size to that yielding no more than 200 mg residues on the filter pad.

3.3 Prolonged filtration times resulting from filter clogging may produce high results due to increased colloidal materials captured on the clogged filter.

3.4 For residues high in oil and grease, it may be difficult to dry the residue to a constant weight in a reasonable amount of time.

4.0 HEALTH AND SAFETY

There is no apparent safety hazard associated with this analysis. However, it is advisable to wear disposable gloves and protective laboratory clothing when handling the samples and to wear autoclave gloves when taking metal trays in or out of the oven.

5.0 EQUIPMENT AND SUPPLIES

5.1 Glass fiber discs - without organic binder, such as Millipore AP-40, Gelman type A/E or equivalent. This laboratory uses 24 mm Whatman 934-AH microfiber filters with a porosity of 1.5μm.

5.2 Gooch crucibles - 40 ml capacity, are used in this laboratory as the filter support.

5.3 Suction flask – 1000 ml, with Gooch crucible holder.

5.4 Drying oven - isotemp, gravity flow convection, set at 103^{o}C to 105^{o}C.

5.5 Desiccator - with Drierite (anhydrous $CaSO_4$) or silica gel

5.6 Analytical balance – Mettler Toledo, AG 204, with the capability to accurately weigh to 0. 1 mg.

5.7 Autoclave gloves and tongs.

6.0 REAGENTS AND STANDARDS

Deionized water is used for blanks.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 Non-representative matter such as large floating particles or submerged agglomerates of non-homogeneous materials should be excluded from the sample if it is determined that their inclusions are not desired in the final result.

7.2 Refrigeration or icing at 4^{o}C prior to analysis is required to minimize microbiological decomposition of solids. The holding time is 7 days at 4^{o}C. However, it is recommended to begin the analysis as soon as possible.

8.0 QUALITY CONTROL

8.1 Deionized water is run as the blank control.

8.2 Replicates are performed on every tenth sample or one replicate per run.

8.3 There are no logical spiking protocols for this analysis.

8.4 A QC sample with known concentration of non-filterable residue from Spex Certiprep Inc. is run quarterly.

8.5 Data acceptance criteria are listed on the data review checklist.

8.6 Balance is professionally serviced and calibrated once a year and is checked with external weights by user once a month.

8.7 Laboratory participates in ERA WatR Pollution (WP) Proficiency Test.

9.0 PROCEDURE

9.1 Preparation of glass fiber filter disc

9.1.1 Insert the glass-fiber filter into the bottom of a Gooch crucible with wrinkled side up.

9.1.2 Apply vacuum and wash filter with three successive 20 mL of deionized water. Continue suction to remove all traces of water.

9.1.3 Remove crucible with filter in place.

9.1.4 Dry in an oven at 103^{o} to 105^{o}C for at least one hour.

9.1.5 Remove Gooch crucibles containing filters from oven and place in a desiccator to cool.

9.1.6 Weigh Gooch crucibles to four decimal places and record the weight and the Gooch label or designation in the Total Suspended Solids sample run sheet.

9.1.7 Repeat the cycle of drying, cooling, desiccating and weighing until a constant weigh is obtained or until the weight change is less than 4% of the previous weight or 0.5 mg.

9.1.8 After weighing, handle the crucible/filter with tongs only and store weighed Gooch crucibles in a desiccated cabinet in the same order in which they appear in the sample run sheet.

9.2 Sample Analysis

9.2.1 Prepare sample list with replicates for every tenth samples or one per batch and record sample number to be run next to the crucible number with the recorded weight in the Total Suspended Solids sample run sheet.

9.2.2 Carefully match Gooch crucible number with sample/laboratory number and place the Gooch crucible in the filter apparatus and check for secure fit. Do not pour sample into Gooch crucible before starting suction.

9.2.3 Wet the filter with a small volume of reagent grade water to seal it against the frittered holder. Turn on the vacuum pump.

9.2.4 Thoroughly mix sample by shaking and/or inversion and measure 50, 100 mL or up to 300 mL in a graduated cylinder. Immediately fill the Gooch crucible with the sample from the cylinder, then gradually pour the remainder into the Gooch crucible as room allows. Mixing thoroughly before pouring each time.

9.2.5 Pour additional measured aliquots through the filter until the flow rate slows to individual drops or a maximum of 300 ml is reached. Record the total volume filtered

9.2.6 Rinse the graduated cylinder, filter, non-filterablr residue and crucible wall with three to five times of reagent grade water and add to the Gooch. Allowing complete drainage between washings. The total volume of wash water should not be over 9 mls.

9.2.7 After all liquid has passed through the Gooch crucible, disconnect the suction flask from the pump tubing first to release the pressure. Then turn off the vacuum. Remove Gooch crucible and filter from crucible adaptor and place on a metal pan that will fit in the drying oven

9.2.8 Dry for at least one hour at 103^{o} to 105^{o}C, cool in a desiccator to room temperature and weigh.

9.2.9 Repeat the cycle of drying, cooling, desiccating and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight or 0.5 mg.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 Enter the data in the Microsoft Excel table, which is formulated according to the following equation:

$$\text{TSS, ppm} = \frac{(\text{wt. of filter \& residue, g} - \text{wt. of filter, g}) \times 1000 \text{ ml}}{\text{Vol. of water sample, L}}$$

10.2 Calculate the % of relative standard deviation for the duplicated samples as follows:

$$\% \text{ RSD} = \frac{\text{SD of the duplicates}}{\text{average of the duplicates}} \text{ x } 100$$

10.3 The detection limit for this method is 1 ppm.

11.0 DATA AND RECORDS MANAGEMENT

11.1 All daily run sheets are kept in a binder labeled as "TSS".

11.2 All quality control data are kept in a binder labeled as "Quarterly Quality Control".

11.3 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.

11.4 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. Wastewater Laboratory keeps all original copies of the data records

12.0 WASTE MANAGEMENT

Samples are poured down the drain while flushing with large amount of cold water. Filters are disposed of as regular trash.

13.0 REFERENCES

13.2 United States Environmental Protection Agency, *Methods for Chemical Analysis of Water and Waste, Method Number 160.2 August, 1993*

13.3 American Public Health Association, *Standard Methods for the Examination of Water and Wastewater, Method Number 2540 D, 18th Edition, 1992*

Standard Operating Procedures

Sulfate Analysis

Western Maryland Regional Lab
Cumberland, Maryland
Environmental Chemistry Unit

Method Summary

Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a spectrophotometer and compared to a curve prepared from standard sulfate solutions. This method is applicable to drinking and surface waters, domestic and industrial wastes. The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO4/L. The minimum detectable limit is 2 mg/L sulfate.

Procedure

Samples for sulfate analysis are collected by certified collectors, refrigerated (iced), and transported along with a completed laboratory report sheet to the laboratory within 24 hours of sample collection. After registration on the lab worksheet, a 50 ml. aliquot of sample is placed into a labeled 100 ml glass beaker to which 2.5 milliliters of conditioning reagent have been added. If necessary, the sample is filtered through a Whatman #1 filter paper to remove suspended materials. The samples are then covered and refrigerated at 0 to 4.5 degrees centigrade until sample analysis. Samples are held for a maximum of 28 days before analysis.

Standards Preparation

A 1000 ppm stock sulfate solution is prepared in-house and is used to prepare daily working standard solutions for instrument calibration. First, an intermediate 100 ppm stock solution is prepared by performing a 1:10 dilution of the 1000 ppm solution. Using this 100 ppm stock solution, the following standards are prepared:

5.0 ppm (1:20 dilution)

10.0 ppm (1:10 dilution)

20.0 ppm (1:5 dilution)

40.0 ppm (1:2.5 dilution)

As with the samples, 2.5 milliliters of conditioning reagent is added to each 50 ml.standard after preparation.

All solutions and standards are prepared using class A pipets, volumetric flasks and reagent-grade laboratory water. The standards are prepared day-of-use and then discarded.

Instrument Set-Up and Sample Processing

On the day of analysis, samples are allowed to warm to room temperature. The laboratory spectrophotometer, running at a wavelength of 420 nm, is turned on and allowed to warm up. The standards are analyzed first, starting with a laboratory blank made from lab quality water, using the following procedure:

1. While the solution is being stirred, a spoonful of BaCl2 crystals is added to the sample and timing commences.

2. The sample is stirred for exactly 1 minute at a constant speed.

3. Immediately after the stirring period has ended, the solution is poured into a clean spectrophotometer cell, which is wiped dry, and then placed into the instrument.

4. Timing commences and the instrument's absorbance reading is recorded at 30 second intervals for 4 minutes.

Data Manipulation

A standard curve of sulfate concentration versus absorbance is plotted using the data created from the analysis of the sulfate standards. From this curve, absorbance readings created by the analysis of the samples are used to determine sulfate concentrations.

Quality Control

Both duplicate samples and commercially-prepared quality control samples are analyzed during every analysis session to verify proper instrument response and analytical technique.

Reference Method

EPA 375.4
Sulfate SOP
3/16/99 MLR

Reviewed 4/05 MLR
Reviewed 2/07 MLR
Reviewed 8/08 MLR
Reviewed 2/09 MLR

Standard Operating Procedures

Total Dissolved Solids

(Residue, Filterable)

Western Maryland Regional Lab
Cumberland, Maryland
Environmental Chemistry Unit

Method Summary

A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C. If Total Suspended Solids are being determined, the filtrate from that method may be used for Total Dissolved Solids determinations.

Procedure

Samples for total dissolved solids analysis are collected by certified collectors, refrigerated (iced), and transported along with a completed laboratory report sheet to the laboratory within 24 hours of sample collection. After registration on the lab worksheet, the samples are refrigerated at 0 to 4.5 degrees centigrade until sample analysis. Samples are held for a maximum of 7 days before analysis.

Gooch filtration crucibles are prepared prior to sample analysis by placing a 24 mm glass fiber filter into each crucible and rinsing three times with ~20 ml. of lab quality water under vacuum pressure. The crucibles are then allowed to dry overnight in a 180 degree C oven.

On the day of analysis, the crucibles are allowed to cool to room temperature for two hours in a dessicator. At that time, each crucible is labeled with a sample's lab number and is weighed to the fourth decimal place using an analytical balance. In addition, clean, labeled, 100 ml. beakers which have been oven-dried and cooled in a dessicator are also weighed to the fourth decimal place. The corresponding laboratory sampled is mixed thoroughly and a 50 milliliter aliquot is then measured via a graduated cylinder and poured through the crucible and into the corresponding beaker while under vacuum pressure. After filtration is completed, the beaker is transferred to a 180 degree C oven and allowed to dry overnight. The following day, the beakers are allowed to cool to room temperature for two hours in a dessicator and then reweighed to the fourth decimal place.

Data Manipulation

The difference in weights before and after filtration is used to determine the total dissolved solids concentration of each sample:

Example - After Filtration Weight = 50.0403 grams
Initial Beaker Weight = 50.0311 grams
Residue Weight .0092 grams

.0092 grams per 50 ml. sample = 9.2 milligrams per 50 ml. sample =

184 milligrams per 1000 ml sample = 184 ppm Total Dissolved Solids

Reference Method

EPA 160.1

Total Dissolved Solids SOP

2/22.1999
Reviewed 4/05 MLR
Reviewed 2/07 MLR
Reviewed 8/08 MLR
Reviewed 2/09 MLR

Standard Operating Procedures

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 ^{o}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

2.2 Appropriate dilutions of each sample and the quality control samples are incubated for 5 days (BOD_5) at 20 ^{o}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_2SO_3, 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).

3.4 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 Bar code scanner & label set

5.1.1.4 Computer and printer

5.1.2 Incubation room, thermostatically controlled at 20 ± 1°C

5.1.3 pH meter – Accumet pH meter 15, Fisher Scientific

5.1.4 Magnetic 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), botttle stoppers (cat. # D1025), and overcaps (cat. # D1050) Environmental Express

5.2.2 Carboy with spigot – 20 L capacity

5.2.3 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 µL

5.2.6 Bottle-top dispenser – adjustable volume ranges from 2 to 10 mL with 1 L reservoir bottle

5.2.7 Plastic beakers – tricornered, polyprolene, 1000 mL, cat. # 02-593-50F, Fisher

5.2.8 Membrane kit for BOD probe – cat. # 5906, YSI

5.2.9 Filter Unit, 0.45 µm – Nalgene disposable sterilization filter unit, cat. # 09-740-25B. Fisher

5.2.10 Tubes – polyprolene 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

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 in the 20 ^{o}C room for at least 5 hours. The dissolved oxygen concentration of water used for BOD test must be at least 7.5 mg/L.

6.1.2 Empty one premixed pillow of BOD Nutrient Buffer (Hach cat. # 14863-98) into aerated water (6.1.1) at 20 ^{o}C. Mix well. Prepare dilution water immediately before use.

6.2 Glucose-Glutamic acid (G/G) solution

6.2.1 Dry few grams each of glucose or dextrose and glutamic acid in aluminum weigh pans for 1 hour at 103 ^{o}C. Cool to room temperature in a dessicator.

6.2.2 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.

6.2.3 Instead of preparing the G/G solution fresh 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.

6.3 Seeding material, prepare daily

6.3.1 Empty one seeds capsule (Hach cat. # 2471200, blends of microbial strains) into a 500 mL volumetric flask and add dilution water (6.1) to mark.

6.3.2 Mix and immediately pour the whole content into a plastic jar before any settlement happens. Aerate for at least one hour in the 20 ^{o}C room. Let settle for 15 minutes and pour the supernatant into the dispenser.

6.4 Sample pH

6.4.1 Calibration buffers – pH 4.0, pH 7.0, and pH 10.0, cat. # SB105,

Fisher

6.4.2 Sulfuric acid (H_2SO_4), 1M – Slowly and while stirring, add 2.8 mL of conc. H_2SO_4 to 80 mL of deionized water. Dilute to 100 mL. Mix well, label and store.

6.4.3 Sodium hydroxide (NaOH), 1N – Dissolve 4 g of NaOH in 80 mL of deionized water. Dilute to 100 mL.

6.5 Dechlorination

6.5.1 DPD free chlorine reagent power – cat. # 14070-99, Hach

6.5.2 Starch soluble for iodometry – cat. # 516-100, Fisher

6.5.3 Sodium sulfite solution (Na_2SO_3) – Dissolve 0.157 g of Na_2SO_3 in 100 mL of deionized water. This solution is not stable; prepare fresh daily.

6.5.4 Potassium iodide (KI) solution – Dissolve 10 g of KI in 100 mL deionized water. Mix well.

6.5.5 Acetic acid (CH_3COOH), 1:1 – Mix 20 mL deionized water with 20 mL glacial acetic acid.

6.5.6 Nitrification inhibitor – 2-chloro-6-(trichloro methyl) pyridine (TCMP), cat. # 2533, Hach

6.5.7 External Quality Control Sample – QC-DEM-WP, Spex Certiprep Inc.

7.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Keep samples at or below 4 ^{o}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 d must not be more than 0.20 mg/L. If this value is exceeded evaluate the cause and make appropriate corrections.

8.2 *Glucose-glutamic acid check:* The glucose-glutamic acid check solution is the primary basis form 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-d BOD must fall into the range of 198 ± 30.5 mg/L. If the average value falls outside this range, evaluate the cause and make appropriate corrections. 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 amount of seed suspension, or the presence of toxic material. If low values persist, prepare a new mixture of glucose and glutamic acid and the check the sources of dilution and source of seed.

8.3 *Minimum residual DO and minimum DO depletion:* Only bottles, including seed controls, giving a minimum DO depletion of 2.0 mg/L and a residual DO of at least 1.0 mg/L after 5 d of incubation are considered to produce valid data.

8.4 *Seed Control:* The DO uptake attributable to the seed added to each bottle generally should be between 0.6 and 1.0 mg/L, but the amount of seed added should be adjusted from this range, to that required to provide glucose-glutamic acid check results of 198 ± 30.5 mg/L.

8.5 An external quality control sample with a known BOD value is analyzed with each run.

8.6 The YSI dissolved oxygen water is calibrated in air (water saturated), i.e. the probe is kept 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 Test.

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)

9.1.2 Check sample pH

9.1.2.1 Standardize the pH meter using pH 4, 7 and 10 buffers. Press “Std”, press “2” to clear previous set of data; press “Std”, press “1” to add new; check all 3 standard buffers and record the readings in the pH log book. To

read sample pH: press “pH”. Read pH of all the samples making sure they are stirred during the measurement. Leave the pH meter on standby when finished. The pH of the samples out of the range of 6.5 to 7.5 must be adjusted to this range.

9.1.2.2 Label beakers with sample numbers needed to be pH adjusted. Pour about 500 mL of samples into 1 L beakers. Pour 100 mL if has strong sewage odor.

9.1.2.3 Stir while checking the pH. Adjust each sample to pH 6.5 to 7.5 with 1N NaOH or 1M H_2SO_4 and record the final pH.

9.1.3 Check samples for residue chlorine

9.1.3.1 Empty one pouch of the DPD free chlorine reagent powder into each test tube, add about 10 mL of sample and observe for any color change within a few seconds. A pink color indicates presence of residual chlorine and the samples(s) must be dechlorinated.

9.1.3.2 Determine the required volume of Na_2SO_3 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_2SO_3 (6.5.3) solution to the starch-iodine (blue) end point. Record the volume used. Calculate and add the required volume of Na_2SO_3 solution to the pH adjusted portion of the sample (9.1.2.3).

9.2 Sample dilution technique

9.2.1 Bring samples to room temperature before making dilutions.

9.2.2 Check samples for color and odor.

9.2.2 Make 200 and 100 mL aliquots of each prepared stream sample, make 50, 25, 10 and 5 mL aliquots of each prepared sewage sample, or make 10, 5, 1 and 0.5 mL aliquots of each prepared strong industrial wastes as appropriate.

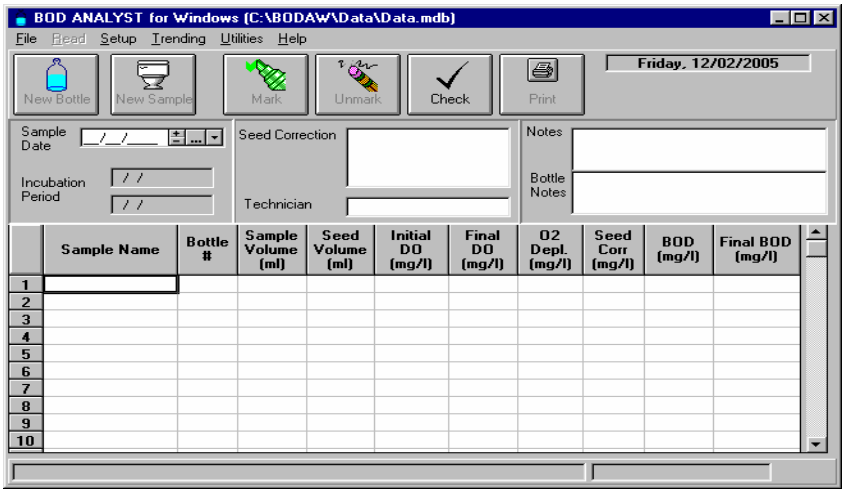
9.3 Nitrification inhibition

9.3.1 If nitrification inhibition is desired add 3 mg of TCMP (6.5.6) to each 300 mL bottle before capping.

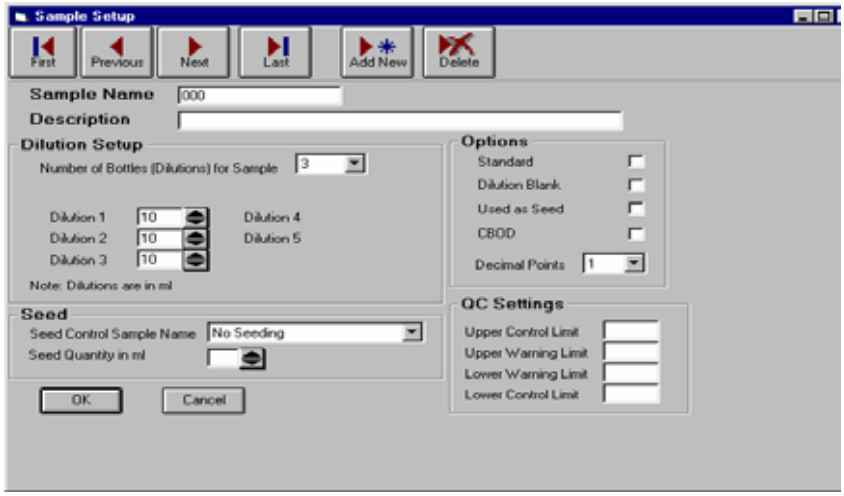
9.3.2 Note the use of nitrification inhibition in the reporting results.

9.4 Setup samples in the “BOD Analyst” software

9.4.1 Click on the “BOD Analyst” software icon. The bench sheet screen will be displayed.

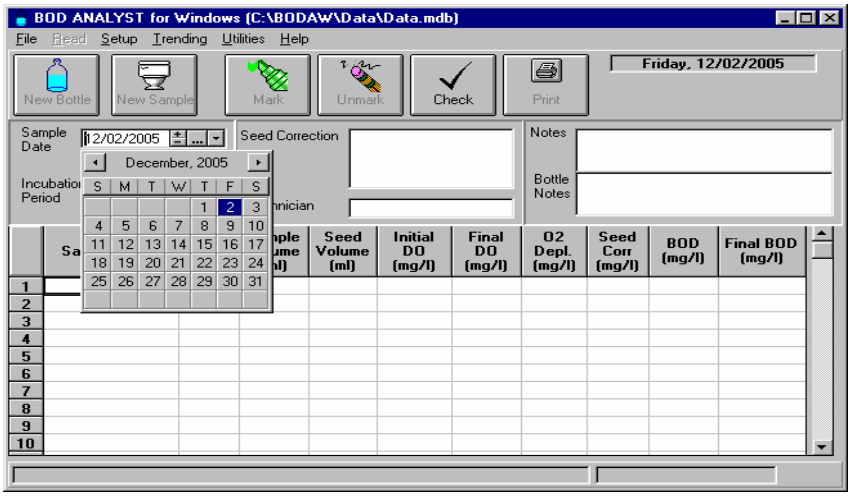


9.4.2 Click on “Setup” and **“**Sample” to open the Sample Setup screen.

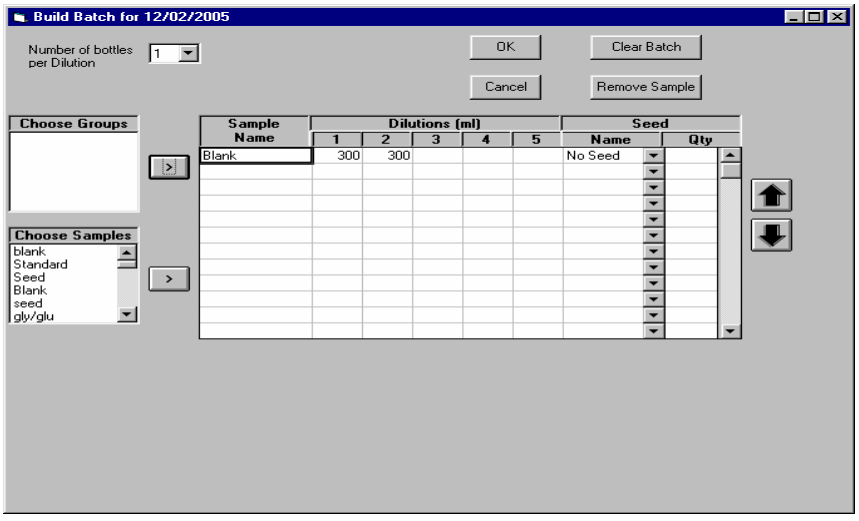


9.4.3 Click on “Add New”, then enter sample name, number of bottles, dilutions, and seed name and seed volume. Click on “Add New” again to enter information for all the rest samples. Click “OK” when finish.

9.4.4 From the bench sheet, enter a sample date or use the pull down menu to assign a date to open the build batch form.



9.4.5 Select the sample you want for the batch by selecting the sample from the “Choose Sample List” box and use the > button to build up the sample run list.



9.4.6 Build the batch starting with two duplicated water blanks, three seeds at 5, 10 and 20 mL and two duplicated mixtures of 5 mL of G/G and 3 mL of seeds and following by 2 to 5 different dilutions of each sample plus 3 mL of seeds. Click “OK” and the batch will be setup. Press “Print”.

9.5 Sample preparation

9.5.1 Label the incubation bottles with bar code and descriptions.

9.5.2 Pipet 5, 10, and 20 mL of seeds into 3 seeds bottles. Pipet 5 mL of G/G and 3 mL of seeds into each of the two bottles labeled G/G.

9.5.3 Measure and add sample into each pre-labeled bottle. Rinse the cylinder between samples. Set the dispensing volume and dispense 3 mL of seeds into each bottle.

9.6 Sample measurement

9.6.1 Warm up YSI 5100 for at least 15 minutes. Wipe clean the probe. Press “Calibrate”, then, “Auto Cal”. Saturation value for dissolved oxygen in fresh water in equilibrium with air at room temperature is 8.5 to 9.0 with 0 chlorinity. Press “Mode”, and then, “Mode” again. Select **“**Remote”.

9.6.2 Read initial DO

9.6.2.1 Fill up the first blank bottle to the rim with the aerated dilution water. Select “Read”, then “Initials” from the main menu. Follow the prompts on the YSI 5100 instrument or the PC to read the initial values. If the initial DO is more than 9.2 mg/mL. Reduce DO by vigorous shaking the carboy a few times. All the data is automatically saved. Stopper tightly, water-seal, and cap the bottle.

9.6.2.2 Fill up each bottle to the rim with the dilution water (9.6.2.1) right before taking its initial reading. For samples containing more than 9.2 mg/L, reduce DO by vigorous shaking or transferring a few times between two large beakers.

9.6.2.3 Rinse DO electrode between determinations to prevent cross-contamination of samples.

9.6.2.4 Press “Print” after reading DO of all the samples.

9.6.3 Incubation

Incubate sealed bottles for 5 days in the 20 ^{o}C incubation room with lights turned off.

9.6.4 Read final DO

Five days later, restart the BOD Analyst software. Select sample date to load the batch. Select “Read”, and then, “Finals” from the

main menu. Follow the prompts on the YSI or the PC to read the final DO values.

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:

$$O_2 \text{ Depletion (mg/L)} = \text{Initial DO} - \text{Final DO}$$

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

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

10.1.3 BOD of the samples:

$$\text{BOD (mg/L)} = \frac{O_2 \text{ Depl in sample} - \text{Seed Factor}}{\text{Sample Volume, ml}} \text{ x Bottle Volume, mL}$$

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_2 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 will be 7 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 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 Division of Environmental Chemistry, Maryland Department of Health and Mental Hygiene, *Quality Assurance Plan, DECQA1, Revision 8.0,* 2007

APPENDICES

Appendix A – Data Review Checklist
Appendix B – BOD Run Log

APPENDIX A

State of Maryland
DHMH - Laboratories Administration
DIVISION OF ENVIRONMENTAL CHEMISTRY
GENERAL CHEMISTRY SECTION

DATA REVIEW CHECKLIST

5 Day Biochemical Oxygen Demand (BOD_5)/SM 5210 B

Lab Numbers[1]:_____ Analyst: _____

Date Collected: _____ Date Analyzed: _____

Procedure	Acceptance Criteria	Status*	Comments
Holding Time	48 hours @ 4 ^oC		
Chlorine	Neutralized if present		
pH	Between 6.5 – 7.5; adjusted if out of range		
Initial DO	< 9.20 mg/L at 20 ^oC		
Incubation Period	5 days		
DO uptake of dilution water	< 0.20 mg/L		
DO uptake of seeded dilution water	0.60– 1.00 mg/L		
BOD_5 for Glucose/Glutamic Acid (G/G) solution (QC)	198 $\pm$ 30.5 mg/L		
Sample dilutions	Meet the requirements: Final DO ≥ 1.00 mg/L and DO depletion ≥2.00 mg/L		
	Decide on the value to be reported if Requirements are not met.		
External QC[2]	Within acceptable range		
Decimal Places Reported	1		
Reported Values	> 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		

* Check (√) if criteria are met.

_____ Date Reported: _____ Reviewer's
Signature & Date

[1]Include beginning and ending numbers, account for gaps by bracketing.

[2]QC Identification = _____ True Value = _____
Acceptable Range = _____

APPENDIX B

State of Maryland
DHMH - Laboratories Administration
DIVISION OF ENVIRONMENTAL CHEMISTRY
GENERAL CHEMISTRY SECTION

BOD Run Log

Analyst: _____ **Date**: _____

Lab #	Sample Type	Dilutions	Color	Odor	pH	pH adjusted to	Chlorine	Chlorine Neutralized

Appendix IV: Maryland Department of Health and Mental Hygiene: Divisional Analytical Corrective Action Form

State of Maryland
DHMH - Laboratories Administration
Division of Environmental Chemistry

DIVISIONAL ANALYTICAL CORRECTIVE ACTION FORM

Quality Assurance Program

■ NONCONFORMANCE

Customer:		Samples(s):	
Test:	Method:	Instrument:	Date of Occurrence:

☐ Failed Tuning ☐ Failed Calculation ☐ Instrument Instability ☐ Instrument Malfunction ☐ Other	☐ Power Failure ☐ Broken or Lost Aliquot ☐ Insufficient Volume ☐ Poor Aliquot Preservation	☐ Exceeded Holding Time ☐ Matrix Interference ☐ Out-of-Control QC Parameters

Detailed Description:	
Signature of Originator:	Date:

■ CORRECTIVE ACTION TAKEN

☐ Instrument Returned ☐ Instrument Recalibrated ☐ Instrument Serviced	☐ Sample(s) Re-poured ☐ Sample(s) Reanalyzed ☐ Lab. Management Notified ☐ Other

Detailed Description:	
	Date of Completion:
Signature of Person responsible	Date:

■ VERIFICATION OF NONCONFORMANCE AND CORRECTIVE ACTION

Signature of Supervisor:	Date:

■ NOTIFICATION

Customer Contact Required? ☐ Yes ☐ No	SMA: Date of Contact:
Detailed Description:	
Signature of Notifier:	Date:

■ ACKNOWLEDGEMENT

Signature of Division QA Officer:	Date:

Copies: Division QA Officer
Laboratory File

DEC/QA9
8/2007