Final April 22, 2019

Ohio Environmental Protection Agency

Surface Water Field Sampling Manual

for water quality parameters and flows

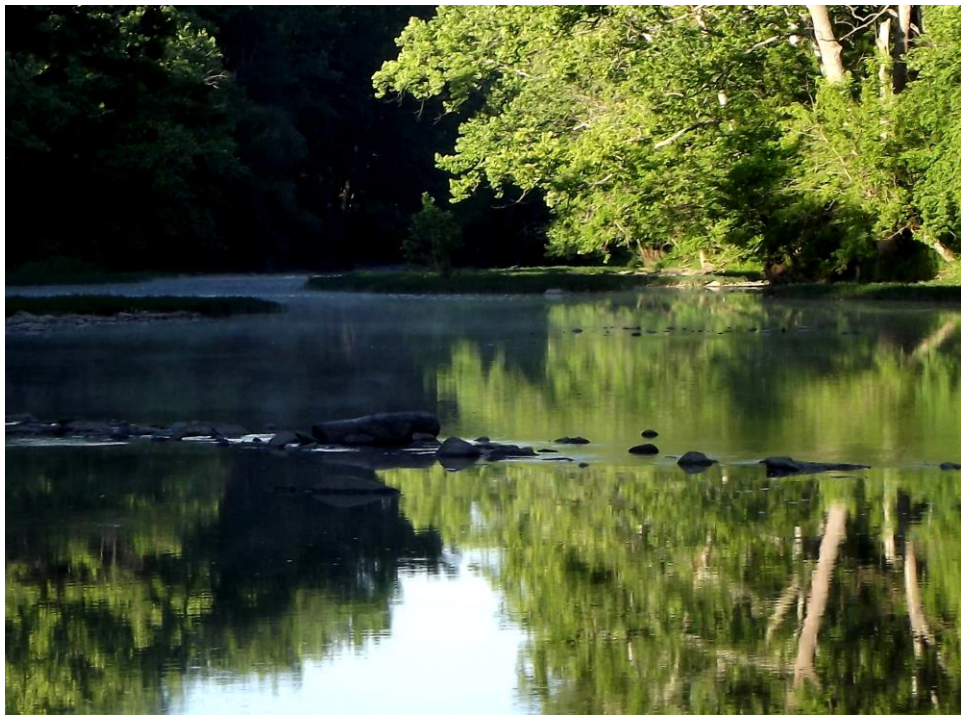

Photo Courtesy of Russ Gibson, Ohio EPA, DSW

April 22, 2019

Next Revision Due: April 22, 2021

Mike DeWine, Governor
John Husted, Lt. Governor
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Revision History

This table shows changes to this controlled document over time. The most recent version is presented in the top row of the table. Previous versions are maintained by the OEPA Division of Surface Water Modeling and Assessment Section Manager.

History	Effective Date
Ohio EPA Surface Water Quality Sampling Manual version 7.0 Table of Contents: Updated to include new Section G of Appendix II and removed Sections B, C and D of Appendix IV. The revision histories of the appendices are included in each appendix.	**April 22, 2019**
Ohio EPA Surface Water Quality Sampling Manual version 6.0 Table of Contents: Updated to Remove Subsection E.6, revised Section titles for Appendix II, add New Appendix IV Section A: Minor wording changes and title updates. Section B: Minor wording changes and title updates. Section C: Replaced CyberIntern references with Sample Master®. Section D: Remove note about field conductivity; remove information about collecting samples for methods 531 and 547; minor clarifications. Section E: Updated/revised QC samples subsection E5 to include previous E6, and renumbered remaining subsections; removed carbamate pesticide method paragraph; minor wording changes throughout. Section F: Minor edits/clarifications. Section G-H: Replaced CyberIntern references with Sample Master®, removed sample submission form information, minor edits/clarifications. Section I: Moved to Appendix IV Section A. Appendix II: Minor edits/clarifications to Section A. Moved EA3 Station Manual to Appendix IV and replaced it with Section C: Churn Splitter Protocol. Added Section D: Sampling Method for Documentation of Public Health Nuisances and Section E: Compliance and Whole Effluent Toxicity Sampling, and Section F: Water Quality Sonde Deployment. Appendix IV: Created Appendix with Section A: Data Management (moved from main manual Section I); Section B: EAS Station Manual (moved from Appendix II); Section C: EA3 Instruction Manual (Placeholder), and Section D: Sample Master® Instruction Manual.	**March 30, 2018**

History	Effective Date
Ohio EPA Surface Water Quality Sampling Manual version 5.0 Name changed slightly to reflect broader application Table of Contents: Updated to Include Appendix III, Sediment Data Collection and Analysis Section D: Flow measurement equipment terminology made more general. Section E: Low level phosphorus and Atrazine ELISA sampling information added, changes to samples sizes made, references corrected and typos corrected. Revisions to cyanide method. Table E2 updated for low level phosphorus and new cyanide method. Section I: Typos corrected, clarifications added to headers and footers of tables. Appendix II: Updated the chlorophyll-a sampling protocol and organized by sestonic and benthic sampling protocols. Appendix III: Added to link sediment documents to this manual.	**July 31, 2015**
Ohio EPA Surface Water Quality Sampling Manual version 4.0 replaces previous Manual of Ohio EPA Surveillance Methods and QAPs, April 2012 version General: Name changed, overall report format updated, Health and Safety section added, Pre-sampling Activities section added, some information re-organized; added Appendices. Section A: No significant revisions. Section B: Minor corrections. Section C: Replaced previous contract lab information with safety and field preparation information. Section D: Minor adjustments to record keeping Section E: Minor adjustments to sampling and preservation requirements, added reference to chlorophyll-a sampling procedure. Section F: Flow measurement section updated and references to equipment no longer used removed (e.g. Pygmy meters). Section G: Minor updates/revisions incorporated. Section H: No revisions. New Section I Data Management added. Appendix I and II added to link the documents within them to this manual	**January 31, 2013**

Manual of Ohio EPA Surveillance Methods and Quality Assurance Practices, April 2012 version replaces 2009 version Revision History page added, footer updated, page numbering changed, minor errors fixed throughout. Tables D1, D2, were updated. Subsections 5 and 6 of Section E regarding QC procedures were updated. A new Table E1 for Field QC was added, and existing Tables E1 and E2 were re-numbered to E2 and E3.	**April 13, 2012**
Manual of Ohio EPA Surveillance Methods and Quality Assurance Practices, 2009 version	**2009**

Contents

In Separate Appendix Documents:

DISCLAIMER:

The mention of trade names or commercial products in this manual does not constitute endorsement or recommendation for use by the Ohio Environmental Protection Agency.

INTRODUCTION

In response to the need for an overall program to coordinate the collection and reporting of water quality monitoring data, and to ensure the reliability of such data, the Ohio Environmental Protection Agency (Ohio EPA) Division of Surface Water (DSW) in conjunction with the Division of Environmental Services (DES) have developed these Surface Water Quality Sampling Procedures. This manual includes a statement of the Ohio EPA quality assurance policy, as well as a description of the management structure of the quality assurance program. Laboratory elements to be used in support of the various monitoring activities are defined.

This procedural manual covers the pre, post and in-field activities for collection and handling of water column chemistry and bacteriological samples, as well as flow measurements of surface waters.

Sediment collection and handling is also addressed in Appendix III of this manual. Quality assurance procedures for field operations, laboratory methods, data reporting, and chain of custody are defined.

SECTION A. QUALITY ASSURANCE POLICY

The general objective of this manual is to promote greater standardization of procedures for all facets of sample collection, data generation, and reporting used in support of Ohio EPA's efforts in water pollution control and abatement. Therefore, the methods and quality assurance practices defined in this manual shall be used by all Ohio EPA personnel when collecting data.

Specific objectives of this manual are to establish detailed and documented procedures for the collection and reporting of all water quality data and to define criteria for the acceptance or rejection of data generated by these methods. Where applicable, control limits on the precision and accuracy of these methods will be established and only data that falls within these limits will be reported without qualification. To achieve these goals, Ohio EPA will commit a minimum of 10% of its monitoring and assessment program to quality assurance activities.

Laboratory Quality Control Policy. Ten percent of the samples collected will be analyzed in duplicate to establish levels of precision or spiked and analyzed for recovery efficiency and accuracy. Control limits based on precision and accuracy will determine the acceptance or rejection of laboratory data on a daily basis. Quality control samples obtained from sources external to the laboratory will be analyzed daily. These samples are used to check laboratory performance. Annual intra-laboratory audits are also conducted, during which unknown proficiency testing samples are analyzed for a majority of the parameters that are tested.

Field Quality Control Policy. Ten percent of the samples collected will be used for quality control purposes. Duplicate samples will be used to determine laboratory method precision. Replicate samples will be used to determine representativeness of sampling. Field samples may be split for inter-laboratory comparisons. Field blanks consisting of distilled deionized water and preservative, where appropriate, will be submitted along with regular samples to establish practicable detection limits and to monitor for levels of contaminants to which field samples may be exposed. All field instruments used in the measurement of physical, chemical, or biological parameters shall be properly calibrated and maintained. Records will be kept of these operations for each instrument.

Inter-Laboratory Quality Control Policy. DES participates in several national inter-laboratory proficiency testing (PT) studies annually. These PT studies are administered by US EPA contractors and PT providers accredited by the National Institute of Standards and Technology (NIST). Participation in the studies satisfies some of the quality assurance requirements for waste water, drinking water, and air pollution monitoring programs. Participation is on a biannual basis for the waste water and drinking water programs, and quarterly for the air program.

SECTION B. MANAGEMENT STRUCTURE OF OEPA QUALITY ASSURANCE PROGRAM

Responsibility for the Ohio EPA surface water and effluent monitoring programs are divided among several semi-independent work sections. Field operations are conducted by various Ohio EPA District and Central Office personnel. DES is responsible for analyses of samples collected for routine monitoring programs and ambient and compliance monitoring, as well as intensive and TMDL water quality surveys. DSW staff collects samples for a variety of uses, including permit compliance, complaint response, in-stream chemical and biological monitoring programs and laboratory bioassays. Fecal coliform, *E. coli*, and fecal strep analyses are performed at the DES laboratory as well as at contract laboratories in some of the districts.

DES quality assurance staff will review and update the Manual of Laboratory Standard Operating Procedures, Volumes I, II and III, and the Quality Management Plan at the end of each year. The Quality Management Plan defines performance standards for all aspects of data collection activities. Laboratory quality control and method detection limits (MDLs) are updated annually or more frequently as is deemed appropriate. Reporting limits (RLs) are assessed annually to ensure programmatic data quality objects are being met.

SECTION C. GENERAL CONSIDERATIONS: HEALTH AND SAFETY AND PRE-SAMPLING ACTIVITIES

Subsection C1. Health and Safety

All samplers must comply with Ohio EPA Standard Safety Operating Procedures (SSOPs). In particular, the following SSOPs should be reviewed at least annually and adhered to:

SP10-13 Personal Protective Equipment,
SP10-15 Chemical Hazard Communication,
SP11-9 Working Alone,
SP11-3 First Aid Kits for Field Activities,
SP11-5 Work Zone Traffic Control, and
SP11-6 Seasonal Considerations for Field Work

Before they begin work, samplers must have received any mandatory health and safety training, as outlined by their supervisor in the Ohio EPA Safety Management System assessment worksheet.

Safety Equipment:

The sampler must have adequate protection, including protective clothing. They must wear gloves, as protection against chemical and/or bacteriological hazards, while they are sampling or handling samples that are known or suspected to be hazardous (e.g. visible solids or sheens, downstream from CSOs, etc), or if hands have open wounds. The type of gloves worn shall be determined by the sampling circumstance and type of pollutants expected – for instance longer gloves are needed when samples must be taken well below the surface.

When in a boat, a personal floatation device shall be worn at all times. Other protective measures shall be taken in accordance with the Ohio EPA Safety Management System assessment worksheet, or standard safety operating procedures. For sampling events on large bodies of water, daily field plans should be prepared that identify who is going out on the boat, anticipated times of departure and return, who is responsible for verifying that crew returns as expected, etc.

Upon arrival at a sampling site, safety equipment such as cones, lights, etc. shall be set out as appropriate. Vehicles shall be parked in locations and directions to minimize traffic disruption and avoid sample contamination (especially when sampling for organics).

Subsection C2. Pre-Sampling Considerations

Sample Master®

Sample container labels must be printed using Sample Master® if at all possible. The user's manual for Sample Master® is found in Appendix IV of the field manual.

Table C.1. Pre-sampling Activities and Checks

The following table describes activities that typically need completed prior to actually taking the samples. This table can also serve as a checklist for pre-sample preparation.

Pre-Run Preparation

___ hotel reservations
___ field work plan
___ sample tags
___ field report data forms
___ meter calibration log form/book
___ run directions and maps
___ cell phone(s) and charger
___ gas vehicle
___ check oil, wipers, etc.
___ GPS

Standards and Sampling Supplies

___ pH 7 and 10 buffers
___ pH probe filling solution
___ conductivity standards
___ foil packs (chlor-a)
___ deionized water
___ filters and/or syringes
___ preservatives
___ disposable gloves
___ extra batteries

Sampling Equipment

___ USGS or other keys
___ bucket sampler(s)
___ specimen sample bottles
___ filter apparatus/forceps/cylinder
___ cubitainers
___ ropes
___ tape measure
___ maps/gazetteer
___ boots, waders
___ rain gear
___ camera

Vehicle/Safety Equipment

___ hazard lights
___ cones
___ flashlight
___ tool chest
___ jumper cables
___ flares or reflectors
___ first aid kit
___ reflective vests
___ hard hats
___ drinking water
___ jack kit and inflated spare tire
___ safety glasses
___ throw ropes
___ face shields or goggles (e.g. acids)

Personal Gear

___ sunglasses, sunscreen
___ extra clothing
___ hat
___ bug spray
___ watch with timer

Meters/Instruments

___ multi-parameter meters
___ datasondes
___ temperature probes
___ level loggers
___ level recorders
___ flow meters

Pre-Departure Preparation

___ check road conditions, weather forecast and stream flow levels
___ calibrate instruments
___ critical clean sampling equipment
___ fill ice chests

SECTION D. INSTRUMENT CALIBRATION AND MAINTENANCE

Ohio EPA staff will be required to maintain a separate, up-to-date calibration and maintenance logbook for each piece of equipment. The logbook should be maintained to have consecutively numbered pages and shall contain at least the following: date, sonde ID#, description of field work (where they are headed that day), calibration comments (includes things like needs new DO membrane, changed DO membrane, etc.), and initials. Each instrument must be clearly identified (e.g. the make, model, serial and/or ID number) to differentiate among multiple meters.

The appropriate calibration procedure, as specified in the instruments user manual, must be followed. If the instrumentation does not have an electronic program that maintains a running calibration log, then the results must be recorded in the logbook each time a piece of field equipment is used, along with the date and name/initials of the person performing the calibration. Dissolved Oxygen sensors should always be calibrated the day of use. Other sensors do not always require calibration. If the sensor being calibrated is within 50% of the specified accuracy of the sensor it should not be recalibrated. This is a validation process. Most equipment types will not allow you to log sensor validations, therefore, it must be recorded in the calibration and maintenance logbook. The purpose of validation over calibration is to identify if a sensors calibration starts to drift more rapidly so sensors can be replaced in a timely fashion. If difficulty is encountered in calibrating an instrument, or if the instrument will not hold calibration, this information must also be recorded.

Malfunctioning equipment should not be used to collect data. Proper steps should be taken to correct the problem as soon as possible. All equipment maintenance should be recorded in the logbook indicating what was done to correct the problem, along with the date and signature/initials of the staff person that corrected the problem.

Subsection D1. Dissolved Oxygen Measurement

Maintain and operate the meter in accordance with the manufacturer's instructions. Record all calibration, use, and repair and maintenance information in the logbook including name/initials and date. If using an instrument with provided electronic calibration procedures, ensure that calibration data was logged.

Subsection D2. pH Measurement

Part a) Maintain and operate the meter in accordance with the manufacturer's instructions. Record all calibration, use, and repair and maintenance information in the logbook, including name/initials and date. If using an instrument with provided electronic calibration procedures, ensure that calibration data was logged.

Part b) At the start of each sampling day, calibrate (or validate) using two reference buffers. If the expected sample reading is alkaline, use pH 7 and pH 10 buffers. If the expected sample reading is acidic, use pH 7 and pH 4 buffers. The value of the sample should register within 2 pH units of the selected buffers. Sample results should be rejected if they are not within 2 units of the selected buffers.

Part c) Buffer solutions should not be used if they are past the expiration date. Date all buffer bottles with the expiration date when new buffer solutions are received and note the expiration date in the instrument logbook. Rotate stock as appropriate.

*NOTE: The response of a pH electrode is temperature dependent. If a temperature compensating pH probe is not used, the instrument should be calibrated under field conditions. It may be necessary to store buffers in insulated containers to prevent them from freezing. Therefore, it is important that buffer solutions and unknown solutions be at nearly the same temperature (*i.e. *within ±2˚C) prior to measurement. If this is not the case, the temperature of the buffer solution can be adjusted by submerging the closed bottle of buffer solution in the test water for several minutes prior to use. Since the actual pH of reference buffer solutions varies slightly with temperature, it will then be necessary to use the pH value of the buffer at the "adjusted" temperature when standardizing the instrument (see Table D-1). (A table of these values should also be printed on the bottle of buffer solution.) Use of temperature compensating pH probes should eliminate this variable.*

Table D-1. Variation of standard pH buffer with temperature

Temperature (˚C)	pH		
	4	7	10
0	4.00	7.12	10.31
10	4.00	7.06	10.17
20	4.00	7.02	10.05
25	4.00	7.00	10.00
30	4.01	6.99	9.95

Part d) Maintenance of Electrodes

The electrodes should be stored, cleaned and maintained according to manufacturer's recommendations. Storage solutions may include buffers or a solution of saturated KCl.

If the pH electrode becomes coated with deposits during use, it can be cleaned using a mild detergent and soft cloth, or by soaking for a short time in a weak acid such as 0.1 N hydrochloric acid, followed by a thorough rinse of distilled water.

Subsection D3. Conductivity Measurement

Maintain and operate the conductivity meter in accordance with the manufacturer's instructions. Record all calibration, use, repair and maintenance information in the logbook including name/initials and date. If using an instrument with provided electronic calibration procedures, ensure that calibration data was logged.

Table D-2. Variation of 0.01N KCl conductivity standard with temperature

Temperature (˚C)	Conductivity (µS/cm)	Temperature (˚C)	Conductivity (µS/cm)
15	1147	23	1359
16	1173	24	1386
17	1199	25	1413
18	1225	26	1441
19	1251	27	1468
20	1278	28	1496
21	1305	29	1524
22	1332	30	1552

Subsection D4. Flow Measurement

Acoustic Doppler Velocimeter (ADV)

Calibrate and operate the flow meter according to manufacturer's instructions. Consult the ADV Operation Manual for detailed operation and maintenance information. All velocimeters should be updated with the latest software and firmware available. About once per week (or prior to each field trip) perform a BeamCheck diagnostic test to verify ADV performance.

An automated field QC check should be performed at least once/day (or preferably every time a flow is measured). The results are automatically stored with each discharge measurement. This test does not replace the office BeamCheck.

SECTION E. SAMPLE COLLECTION AND PRESERVATION

The most precise and accurate analytical measurements are worthless and even detrimental if performed on a sample that was improperly collected and stored or was contaminated in the process. The purpose of sampling and analysis is to provide data that can be used to interpret the quality or condition of the water under investigation. For this reason, the sampling and testing program should be established in accordance with principles that will permit valid interpretation. Unfortunately, water quality characteristics are not spatially or temporally uniform from one sample to another. A sampling program must recognize such variations and provide a basis for compensations for their effects. The sample must be: (a) representative of the material being examined; (b) uncontaminated by the sampling technique or container; (c) of adequate size for all laboratory examinations; (d) properly and completely identified; (e) properly preserved, and (f) delivered and analyzed within established holding times. These six requirements are absolutely necessary for a proper water or wastewater survey. Additional aspects are discussed below.

Subsection E1. Where to Sample

It is impossible to establish hard and fast rules concerning sampling locations. However, the following general guidelines should be applied:

Part a) Sampling location should be selected based upon the specific information to be obtained.

Part b) Unless you are sampling an effluent or evaluating a mixing zone, the sampling location should be far enough upstream or downstream of confluences or point sources so that the stream and effluent is well mixed. Natural turbulence can be used to provide a good mixture.

Part c) Samples should be collected at a location where the velocity is sufficient to prevent deposition of solids, and to the extent practical, should be in straight reach having uniform flow. All flow in the reach should be represented, so divided flow areas should be avoided and samples should be taken towards the middle of the reach where feasible.

Part d) Sampler must always stand downstream of the collection vessel, and sample “into the current”. Care must be taken when sampling instream to avoid introducing re-suspended sediment into the sample.

Subsection E2. Sample Types

Part a) Grab Sample – A grab sample is defined as an individual sample collected over a period of time not exceeding 15 minutes. Grab samples represent only the condition that exists at the time the sample is collected (US EPA 1977).

1) Surface Grab Sample – a sample collected at the water surface (i.e., skimming) directly into the sample container or into an intermediate container such as a clean bucket. A single or discrete sample collected at a single location.

2) Subsurface Grab Sample –includes any sample that is not a surface sample and is the most frequently used. This includes samples taken from a bridge with a bucket or using a cubitainer and submerging slightly in the water column. A single or discrete sample collected at a single location.

3) Integrated Grab Sample - A sample comprised of more than one collected sub-samples from a water column or across a cross-section of a waterbody within a short period of time (generally less than 15 minutes). An example of the need for such sampling occurs in a river or stream that varies in composition across its width and depth (APHA 16th Edition 1985). Samples should be collected from several horizontal locations across the stream section and combined in one (set of) sample containers.

i) Vertical integration is accomplished by allowing the sampling container to fill continuously as it is dropped down through the water column and as it is pulled to the surface from the bottom or a specific depth.

ii) Vertical integration may also be accomplished using a tube sampler, an apparatus designed to take a sample of a column of water of designated depth and allow for the mixing of the water.

Part b) Composite Sample – A sample in one container comprised of several sub-samples collected over an extended period of time, usually 24 hours. Typically time proportioned, but may be flow proportioned in special circumstances. All composite samples should be identified as to the method of sampling collection, duration of composite (e.g., 24 hours), and frequency of the sampling (e.g., every 2 hours).

Subsection E3. Selection of Sampling Method

Part a) Grab samples are appropriate for the characterization of a stream at a particular time, to provide information about minimum and maximum concentrations, to allow for the collection of variable sample volume, to comply with the NPDES permit monitoring specifications, or to corroborate with a composite sample.

Grab samples may be collected directly into the sample container, or a clean decontaminated intermediate container may be used if a wading sample is not possible or safe. If an intermediate container is used, when in the field, double rinse the sampling device (bucket, automatic sampler) with sample water prior to collecting the sample and be sure to discard rinse water downstream of where sample will be collected. If samples are collected in a bucket and distributed to multiple cubitainers, use a churn splitter or similar device where practical, or at a minimum pour in back and forth pattern – e.g. 1-2-3-3-2-1. Do not pre-rinse sample containers.

1) Surface grab samples are to be used for stream sampling when collecting floating materials, such as oil and grease. Surface grab samples should be collected from enough horizontal locations to characterize the shore-to-shore distribution of the parameter(s) of interest.

2) Multiple subsurface grab samples may be appropriate to determine water quality at various discrete depths. A Kemmerer or VanDorn water sampler (Welch 1948) may be used for this type of sampling.

3) Integrated grab samples are to be used to collect stream grab samples when incomplete mixing exists. Conductivity, temperature, pH and dissolved oxygen measurements and visual observations can be utilized to determine if horizontal plumes and/or vertical stratification are present.

NOTE: Grab samples are also used for the collection of some special types of samples as described in part c) Parameters that Require Special Collection Techniques.

Part b) Composite samples are required when a widely variable flow, or parameter concentration, is being sampled and "average" concentrations, or loadings, are desired. Twenty-four hour composite samples are to be used in NPDES Compliance Sampling Inspections (except as noted in Part c below) to test compliance with concentration limits in NPDES Permits.

Part c) Parameters requiring special collection techniques:

1) Organics – Do not pre-rinse sample containers. All samples must be iced or refrigerated at less than or equal to 6˚C from the time of collection until analysis. Samples requiring analysis for purgeables -Volatile Organic Compounds (VOCs), USEPA method 624, must be collected as a GRAB sample in two 40 ml glass vials with Teflon-lined septum sealed caps. The sample vial must be filled (either directly or with an intermediate container) to form a meniscus, not overflowing the vial to avoid loss of preservative, and in such a manner that no air bubbles pass through the sample as the vial is being filled. If two drops of 1:1 HCl preservative have been added, the vial should be inverted multiple times for one minute. The addition of preservative extends the holding time from seven to 14 days. The hermetic seal on the sample vial must be maintained until the time of analysis. VOC samples containing residual chlorine must be treated with sodium thiosulfate. Use a spatula to add 3 mg of sodium thiosulfate per 40 ml of sample. All samples must be iced or refrigerated at less than or equal to 6˚C.

Samples requiring analysis of acid/base/neutral extractables (BNAs), USEPA method 625, should be collected in two non-preserved amber glass quart jars. The caps of sample containers must be Teflon-lined. All samples must be iced or refrigerated at less than or equal to 6˚C.

Samples for polychlorinated biphenyls (PCBs) and pesticide analyses require, USEPA method 608, the collection of two additional non-preserved amber glass quart jars with Teflon-lined caps. All samples must be iced or refrigerated at less than or equal to 6˚C.

Samples analyzed for the organic compounds Alachlor, Atrazine, Metolachlor, Simazine, and Metribuzin, using Ohio EPA Method 525.2, require two glass amber jars preserved in the field with 40-50 mg of sodium sulfite to reduce residual chlorine then 6 N HCl to adjust the pH to <2 are required. If Cyanazine is requested, an additional two glass amber jars that are non-preserved are required (for a total of 4 jars). For the two preserved jars, sodium sulfite should be added first to the sample, the lid re-applied, and the sample inverted a couple of times prior to adding the 6 N HCl.

All samples must be iced or refrigerated at less than or equal to 6˚C.

i) Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination. Teflon or Teflon-lined Tygon tubing is acceptable for use as organic sampling intake line. PVC/Tygon tubing is acceptable for use as conventional sampling intake line. The pump tubing can be organic chemical resistant Tygon peristaltic pump tubing or silicone tubing supplied by the manufacturer.

ii) VOC samples containing residual chlorine must be treated with sodium thiosulfate. Use a spatula to add 3 mg of sodium thiosulfate per 40 ml of sample.

2) Oil & Grease – The only acceptable method for collecting oil and grease samples is to collect the sample DIRECTLY into a one liter, laboratory issued clear glass jar. A Teflon-lined lid must be used. Two jars must be submitted to the laboratory.

3) Cyanide – Samples requiring analysis of cyanide should be collected in a quart cubitainer and preserved with 4-6 pellets (depending on pellet size) of sodium hydroxide (NaOH) transferred to the container without handling the preservative. The pH of the sample must be >10 but less than 12 S.U. Verify the sample pH is within the desirable range before departing from the sample site. Cyanide samples must be collected as GRAB samples. Samples should be iced or refrigerated at less than or equal to 6˚C.

Cyanide Interference

Carbonate: If a co-collected acid preserved sample effervesces when acid is added, it must be noted on the sample submission form.

Sulfide: If sulfide is suspected to be present in the sample (rotten egg odor), test by placing a drop of sample on a lead acetate test strip that has been previously moistened with acetate buffer. If the test strip turns black, sulfide is present, and treatment is necessary.

Sulfide treatment: diluting with reagent water until the test strip no longer turns black is the preferred method, with the dilution volume noted on the sample submission form.

If this will raise the reporting limit too high, instead add either powdered lead carbonate or lead acetate solution to the sample until no further black lead sulfide precipitates out. Retest with lead acetate paper, immediately filter the sample with coarse filter paper (5 um) and preserve with NaOH.

4) Phenols – Samples requiring analysis of phenols must be collected in glass laboratory issued containers. A white polypropylene cap with a foam polyethylene liner must be used. Black and green caps contain phenol and must be avoided. Also, avoid caps with cardboard liners. Phenols must be collected as GRAB samples.

Phenols for compliance monitoring require the collection of additional samples to meet the volume requirements of manual distillation. Sample volumes exceeding 125 ml should be collected in one-liter glass container(s) with white polypropylene cap(s) with a foam polyethylene liner. Two ml of H_2SO_4 should be added per liter of sample as a preservative. Samples must be iced or refrigerated at less than or equal to 6˚C.

5) Acidity/Alkalinity – Sample requiring analysis for acidity and alkalinity should be collected in cubitainers and must be iced or refrigerated to less than or equal to 6˚C. Samples for the analysis of these parameters should not be composited when sampling NPDES permit discharges whose effluent has a highly variable pH that might be expected to exceed the permit limits during a given 24-hour period.

6) pH (Hydrogen Ion) – pH must be collected as a GRAB sample and analyzed within 15 minutes of collection.

7) Dissolved Parameters – Samples should be collected as GRAB samples, filtered immediately using a 0.45-micron filter, and chemically preserved (if appropriate) within 15 minutes of collection. See Table E-2 for preservatives and amounts required. Some parameters must be iced or refrigerated to less than or equal to 6˚C. Note on cubitainer and the sample submission form that the sample has been filtered. Separate data sheets must be submitted for filtered samples. Samples can be collected directly from the stream or from an intermediate container.

i) Orthophosphate and dissolved phosphorus samples (note – see Paragraph 11 below for low level information) should be filtered in the field whenever possible, using a Whatman GMF 25 mm Luer-Lock 0.45-micron filter or equivalent. Use the syringe without the filter to draw the sample water from the top of the intermediate container or stream by pulling the plunger until at least 60 ml is in the syringe for orthophosphate, and 100 ml for dissolved phosphorus. Do not use syringes to draw sample water from a sample container that will be submitted to the lab. Attach the filter, and slowly and gently push the sample through the filter into a quart cubitainer. In samples that are sediment or algae laden, it is possible filter will clog prior to collecting sufficient sample – in that case twist off filter, discard it, and replace it with a new one. The syringe plunger will become difficult to push when the filter is clogged. Once you encounter moderate resistance, do not push harder or you may burst the filter and have to start all over.

ii) Orthophosphate samples must not be preserved with acid but must be iced or refrigerated to less than or equal to 6˚C. Note that there is a 48-hour maximum holding time for orthophosphate samples. Dissolved phosphorus samples must be preserved with 2 ml H_2SO_4 to pH <2 and there is a 28-day maximum holding time.

iii) Syringes and filters should be kept in clean containers or original packaging until ready for use to prevent contamination (e.g. keep both wrapped in original package or in new/clean plastic baggies until actually collecting and/or filtering the sample). Syringes may be reused AFTER cleaning in the field/office area following the Phosphorus Syringe Critical Cleaning Protocol found in Appendix II of this manual unless low level testing is needed (reporting levels of 1 µg/l or similar). For typical testing (reporting levels of 10 µg/l or greater), the syringes can be cleaned and reused up to three times before disposal.

8) Bacteria – Samples are to be collected directly into a sterilized glass or polypropylene (or other autoclavable plastic) bottle. Samples should be collected by hand according to the following procedure:

Sampler must stand downstream of collection bottle, and sample "into the current". The collection container should be submerged into the water carefully to avoid contamination from land and surface debris. This is accomplished by holding the container near the base with one hand and removing the cap with the other hand. The container is quickly pushed into the water to a depth of about six inches with the mouth of the collection container down. The mouth of the bottle is then tilted upward into the current and allowed to fill. If there is no current, move the container through the water in a continuous and unbroken movement. Bottles should be filled to between 2/3 and 3/4 full. Add sodium thiosulfate crystals or 0.1 ml of a 10% sodium thiosulfate solution to the sample if residual chlorine is suspected. NOTE THAT CAPS MUST BE SCREWED ON SECURELY TO AVOID LEAKAGE.

For safety reasons, it may be impossible to collect a bacteria sample directly into the sterile container. If samples must be collected remotely, a clean bucket may be used to collect the sample and then the sample transferred to the sterile container. An alternative method is to attach the sterile sample container to a string and lower into the stream. The collection method should eliminate any possibility of contamination of the sample. The sterile container should be filled to between 2/3 to 3/4 full.

Bacteria samples collected to document unsanitary conditions in water bodies that are not listed in the water quality standards rules should follow procedures in Section D of Appendix II. Bacteria samples must be maintained in the dark and iced or refrigerated at less than 6˚C but not frozen.

9) Metals– Serious errors may be introduced during sampling due to contamination from a metal sampling device and the failure to remove residues of previous samples from the sample container. To eliminate such errors, ensure that the sampling device and all materials coming into contact with the sample are glass or polyethylene plastic and have been properly cleaned (non-phosphorus detergent wash, tap water rinse, and distilled water rinse) prior to sampling. Samples for all metals but mercury should be collected in a 1-quart cubitainer and preserved with 5 ml HNO_3. Mercury samples must be collected in a 125 ml glass jar and preserved with 0.625 ml HNO_3. Samples do not require refrigeration once they are preserved with HNO_3.

10) Chlorophyll-*a* – See Appendix II, Section A - Chlorophyll-*a* Sampling Procedure

11) Low Level Phosphorus

i) Low Level Total Phosphorus: 125 ml glass jars with Teflon™ lined polypropylene cap are required sample containers. The jars need to be pre-rinsed 3 times with Nanopure™. This can be done in the office or field. The total-P sample is non-filtered and preserved with 0.25 ml H_2SO_4 per 125ml of sample. The preservative needs to be added within 15 minutes of collecting the sample. The jar can be pre-dosed with preservative after it has been rinsed.

Samples should be submitted to the laboratory as soon as possible and analyzed within 28 days.

Do not use plastic cubitainers. Precautions should be taken in handling and cleaning sampling equipment so that it does not become contaminated with phosphorus. Commercial detergents leave a phosphate residue that may be removed with a 1:4 hydrochloric acid rinse.

ii) Low level Orthophosphate: 125 ml glass jars with Teflon™ lined polypropylene cap are required sample containers. The jars need to be pre-rinsed 3 times with Nanopure™. This can be done in the office or field. The ortho-P sample is filtered and non-preserved. Use a 60 ml polypropylene syringe with Luer-Lock™ tip and Whatman™ 0.45µ GM/F to filter the sample. Use a new, unopened syringe for each sample. Draw 60 ml of Nanopure™ into the syringe and discard the rinsate a total of two times. On the third rinse attach the filter to the tip first and then discard the rinsate. Remove the filter, draw 60ml of sample into the syringe and re-attach the filter. Discarding the first few milliliters of sample is recommended before dispensing into the container.

Since commercial detergents leave a residue, it is imperative to not use washed/used syringes for low level samples. The filter and syringe must be discarded after each sample, if disposable. Samples are stored at 6° C with no preservatives added to the sample. Samples should be submitted to the laboratory as soon as possible and analyzed within 48 hours of collection. Do not use plastic cubitainers.

12) Atrazine - ELISA Method

i) Samples must be collected in glass vials, amber or clear, with Teflon-lined lids. A 40 ml VOA vial, unpreserved, is preferred. However, if the sample is above a pH of 9 it must be adjusted to <9, preferably to a pH range of 6-8. Use a drop of 0.008% sodium thiosulfate solution to dechlorinate if residual chlorine is present.

ii) Samples must be stored at 6°C and protected from light. All samples must be analyzed within 14 days of collection. However, the holding time can be increased by freezing the sample immediately after collection. If freezing, sample containers should be filled half full and placed on their side to prevent breakage.

NOTE: All samples for bacteria or demand parameters (including nutrients) must be iced and/or preserved within 15 minutes. If those times cannot be met, a note should be made on the sample submission form of what time the samples were iced and/or the preservative was added.

Subsection E4. Sample Volume

The size of the final sample is an important consideration. This must be more than required for all the tests to be made, thus providing for any duplicate or repeat examinations that may be necessary. In general, this should be from one to two liters in volume but will depend upon the number of parameters to be analyzed.

NOTE: Some analytical methods require that the entire sample be used so that separate samples are required for these tests (see Tables E-2 and E-3 for details).

Subsection E5. Quality Control Samples

All QC samples submitted to the Division of Environmental Services (DES) should use approved labeling and chain of custody methods described in Section H (and Sample Master® instructions in Appendix IV, Section D). All samples should be cooled on wet ice until delivered. Containers include both glass and plastic types. Glass containers are usually certified as clean by the manufacturer. The most commonly used plastic containers (Cubitainers®) are collapsible and made of low density polyethylene (LDPE). **Reagent water** used for blanks is distilled/de-ionized tap water that has been purified using a Nanopure® filtration system and is supplied by the DES. The reagent water can be stored for up to 28 calendar days in a clean container to facilitate transport.

E.5 a) Duplicate and Replicate samples are one of the two major types of field QC samples (blanks being the other). The overall QC sampling rates may be tracked by management in the district and/or Central Office, but each sampler is responsible for ensuring they are collecting QC samples at the required minimum frequencies. Duplicate and replicate QC samples are to be collected and submitted at a combined minimum frequency of 5% of the total number of field samples. Field blank and equipment blanks are also to be collected and submitted at a combined minimum frequency of 5% of the total number of field samples. This results in a minimum of 10% QC samples. Other types of QC samples, including those collected to resolve previous QC issues, do not count toward these percentages. QC sampling should be generally proportional to the types of samples (and parameters) collected by that sampler. For example, if a person collects roughly 50% ambient samples, roughly 50% of their QC samples should be taken from ambient sampling.

Field Duplicate Samples (also known as Field Splits) are used to assess the variance of the total method of sampling and analytical procedures. Duplicate samples demonstrate the precision of the sampling system, from initial sample collection through analysis at the laboratory. A field duplicate is done by thoroughly mixing one sample and dividing it into two separate sets of containers. The samples should be labeled and submitted to the laboratory as "blind" samples so their identity is unknown to the analysts. The samples are independently analyzed using the same laboratory analytical procedure. The sample with the actual correct location on the label should be considered the "real" sample to be used for project data analysis (the QC duplicate should be otherwise identified to the lab, see Data Management in Appendix IV).

Field Replicate Samples are used to measure sample representativeness and natural variability of the matrix sampled. The variability of replicates should be compared to duplicate variability (which is presumed to represent duplicate variability, i.e., precision). A field replicate is done by collecting two or more separate samples from the same site at approximately the same time using the same sampling method. The samples are labeled as Replicate A and Replicate B and independently analyzed using the same laboratory analytical procedure. Both sample results may be used for project data analysis in some situations since they are independent representatives of the sample population. Replicate data is often used to estimate heterogeneity of the media (e.g., sediment). *When collecting replicate samples, best practice may be to also collect duplicates at that site, to have a way to determine if replicate*

variability (which is an indicator of media heterogeneity) exceeds duplicate variability (which is an indicator of sampling/analytical precision).

Matrix Spikes/Matrix Spike Duplicates are a type of duplicate samples that are collected in the field but does not count as a field duplicate because they are laboratory QC samples. They are used to document the precision and bias of a method in a given sample matrix. Most DES internal QC analysis is performed by using aliquots from sample containers, as most containers hold adequate volume for multiple analyses. However, for some methods the entire sample container is used for one analysis. In these cases, DSW must collect MS/MSDs for use by DES. Laboratories need to demonstrate they can recover target compounds from actual water samples and not just reagent water. We help them by collecting samples from the surface water matrix for their QC. These samples are to be collected at a rate of 5% of organic samples only and do not count towards your duplicate sampling rate.

For VOC volatiles intended for use as MS/MSD, fill two extra 40 mL vials (4 total). For semi-volatiles, PCBs, or herbicides fill two extra amber jars (4 total). Four extra jars are needed if both PCB and BNA samples are submitted (8 total). The extra containers indicated are beyond the usual number of containers specified in Subsection 3, Part c of Section E.

Note: Oil and Grease samples were previously called out in this manual as needing monthly duplicate sample collection. However, DES has confirmed that collecting the two one-liter jars indicated by the DES Field Handbook gives them adequate volume to do their QC. Now, Oil and Grease samples are subject only to the 5% field duplicate collection rate.

Note: ***MATRIX SPIKE*** *is an aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.* ***MATRIX SPIKE DUPLICATES*** *are intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.*

E.5 b) Blanks are used to evaluate the potential for contamination of a sample by contaminants from a source not associated the water being tested. Blanks may be used to demonstrate that sample contaminants were not from equipment used, reagent water, preservatives, sample containers, ambient air, etc. QC sampling should be generally proportional to the types of samples (and parameters) collected by that sampler. For example, if a person collects roughly 50% ambient samples, roughly 50% of their QC samples should be taken from ambient sampling.

Note: Blank QC samples should be submitted at a rate of about 5% of all field samples. This 5% is a combined total for Field Blanks and Equipment Blanks. This should not include extra blanks collected to resolve previous contamination issues.

Field Blanks are used to evaluate the potential for contamination of a sample by site contaminants from a source not associated with the sample collected (i.e. air-borne dust, etc.). They should be collected at varying times throughout the day to represent different conditions (not always first thing in the morning or

last action of the day). Reagent water is taken into the field in a sealed container. The reagent water is then poured into the sample container and the chemical preservative is added if appropriate, while in the vicinity of a surface water being sampled. The containers are labeled as "Field Blank". The same template selected for the test samples should be used. Field blanks are subject to the same holding time limitations as samples.

Equipment Blanks are collected to verify that cleaning techniques are sufficient, and that cross contamination does not occur between sites if an intermediate container is re-used (e.g., bridge-sampling bucket). At least one equipment blank per equipment type per field season should be collected by each office using that equipment type. Equipment blanks for automatic samplers are collected after the completion of decontamination of sampling equipment and prior to sampling by running reagent water through the equipment. Equipment blanks for intermediate containers are collected between sites after they have been used by rinsing at least once and filling the vessel with reagent water. Equipment blanks can be prepared in the field or in the laboratory (after completion of field sampling). One equipment blank container must be prepared for each type of preservative used. Use the same parameter template as the test samples. Equipment blanks may also serve as field blanks since the same water is used - but be aware that sorting out the source of contamination problems is confounded with this approach, so you may wish to have some separate field blanks only.

Cubitainer Blanks Normally the laboratory purchases cubitainers and runs the blank tests. If for some reason cubitainers are obtained elsewhere, then blanks should be submitted when a new lot of containers are received from the manufacturer to verify that they are clean (prior to using any of the containers for field samples). A Cubitainer Blank is prepared by filling a randomly selected container from each lot with reagent water and adding a dose of preservative, if appropriate. Use "Equipment Blank" in the laboratory template section to automate the parameters analyzed. Non-preserved containers are tested for chloride, conductivity, nitrite, fluoride, dissolved solids, suspended solids and sulfate. Containers preserved with sulfuric acid are tested for chemical oxygen demand, nitrate-nitrite, ammonia, total Kjeldahl nitrogen and total phosphorus. Containers preserved with nitric acid are tested for ICP-1 metals (Al, Ba, Ca, Fe, Mg, Mn, Na, K, Sr, and Zn), ICP/MS-1 metals (As, Cd, Cr, Cu, Ni, Pb and Se) and mercury.

> *Note: If you receive your cubitainers from DES, they should handle the "cubie" blank. Otherwise, the sampling staff need to submit cubitainer blank samples to the lab for each lot # received.*

Acid Blanks are done to ensure that new lots of acid and units used to dispense nitric and sulfuric acid in the field are free of contamination (prior to using any of the preservatives for field samples. Use "Acid Blank" in the laboratory template section to automate the parameters analyzed. Sulfuric acid blanks are tested for chemical oxygen demand, nitrate-nitrite, ammonia, total Kjeldahl nitrogen and total phosphorus. Nitric acid blanks are tested for ICP-1 metals (Al, Ba, Ca, Fe, Mg, Mn, Na, K, Sr, and Zn), and ICP/MS-1 metals (As, Cd, Cr, Cu, Ni, Pb and Se).

> *Note: If you receive your acid from DES, they should handle the acid blank. Otherwise, the sampling staff needs to submit acid blank samples to the lab for each lot # received. Either way, staff need to verify a blank was done and results acceptable before using the data.*

Trip Blanks are used to determine if samples were contaminated during storage and/or transportation back to the laboratory. A trip blank is only required when conducting volatile organic compound (VOC) sampling but should accompany each cooler containing any VOC samples. A trip blank is prepared for field personnel by the laboratory staff prior to the sampling event and is stored in the same cooler with the investigative VOC samples throughout the sampling event. At no time after their preparation are trip blanks to be opened before they reach the laboratory. To obtain trip blanks, please contact the laboratory and inform them of the number needed. Trip blank VOC containers are labeled" Trip Blank ". Trip blanks should be kept on ice in the cooler along with the VOC samples during the entire sampling run. They must be stored in an iced cooler from the time of sample collection, while they are in the sampling vehicle, until they arrive at the laboratory. One VOC trip blank per cooler should be submitted. Trip blanks should be stored under refrigeration before use and should be submitted to the lab in time to allow for laboratory analysis within 30 days of being filled.

Table E-1. Quality Control Sampling Frequency for Water Matrix Sampling.

These apply to inorganic and organic samples except as noted (i.e., MS/MSD for organics and trip blanks only for VOCs)

QC Sample Type	QC Sample Rate or Frequency
Field Duplicates and Field Replicates	5% of total water samples (emphasizing duplicates, since the variability of duplicate data provides context for evaluating the variability of replicate data (i.e., is precision greater than with the duplicates?).
Field Blanks	5% of total water samples (may overlap with equipment blanks)
Trip Blanks (VOCs)	One per cooler with VOC samples
Equipment Blanks	Minimum of 1 per equipment
Acid Blanks	Once per acid lot (by DSW staff, unless DES tells them they have already done it).
Cubitainer Blanks	Once per lot (by DSW staff, unless DES tells them they have already done it).
MS/MSD (organics)	5% of organic samples only (track in each D.O., collected for lab QC, do not count as part of 10% minimum)

It is the responsibility of the project coordinator to track and ensure QC sample submission (however one QC coordinator per district/office may coordinate less frequent QC sample types, and sample results, as well as the overall district/office QC sample rates). It is suggested that QC samples be addressed in the study plan (type/frequency/who will track).

Subsection E6. Preparation of Sample Containers

Part a) Containers

1) Quart and gallon size disposable, soft, polyethylene cubitainers with disposable polypropylene lids should be used as sample containers for all samples not requiring special containers (see Tables E-2 and E-3).

2) Containers must be stored with lids on until sample is collected. Prepare and submit cubitainer blank QA/QC samples as directed by DES. When cubitainer blanks are submitted to DES, enter the lot number from the box containing the cubitainers onto the lab sheet.

Part b) Oil and Grease

1) Two one-quart glass jars with Teflon-lined screw caps should be used as sample containers for this parameter. No intermediate container is allowed for sampling this parameter.

2) Jars must be stored with the lids ON until the sample is collected.

Part c) Organics

1) Quart amber glass jars with Teflon-lined screw caps should be used as sample containers.

2) Glass jars must be stored with the lids ON until the sample is collected.

3) Volatile organic parameters must be collected in 40 ml glass vials with septum seals. Vials must be stored with lids ON until samples are to be collected.

Part d) Bacteria

1) Bacteria samples may be collected in commercially available disposable, sterile, four-ounce, polypropylene containers with polypropylene screw caps.

2) Immediately after collection, the samples should be placed in a dark, iced cooler or refrigerated at less than 6˚C.

3) If the collector determines the presence of chlorine in the sample, a 0.1 ml aliquot of 10% aqueous solution of sodium thiosulfate (100 g of $Na_2S_20_3$ per liter) is added to each sample immediately after collection, in a manner that does not introduce *E.coli* bacteria. The addition of thiosulfate should be documented on the field collection sheet ("Sample is chlorinated and preserved with sodium thiosulfate"). Some containers are pre-dosed with sodium thiosulfate. Commercial contract laboratories may provide their own reusable, sterile pre-dosed container. The sodium thiosulfate will not interfere with the test when chlorine is absent.

Part e) Automatic Sampler Cleanup Procedure

After each use, all sampler parts that contact the sample (sampler lines, bottles, etc.) should be thoroughly rinsed with:

1. Hot tap water.
2. Liquinox (low phosphorus) detergent solution.
3. Tap water.
4. 10% hydrochloric acid.
5. Distilled water.

For Toxic/Organic sampling, repeat above procedure and add additional rinses with:

6. Methanol.
7. Distilled deionized water.

NOTE: Stainless steel strainers should not have the 10% acid rinse but should be rinsed with methanol. When using acid or methanol to rinse, only use what is necessary to contact all surfaces.

Intake and pump tubing should be replaced at the discretion of the sampling team.

Subsection E7. Preservation and Holding Times

Part a) Recommended Preservatives

1. Re-distilled or spectrograde nitric acid (HNO_3).
2. Reagent grade or re-distilled sulfuric acid (H_2SO_4).
3. Sodium hydroxide (NaOH) as pellets stored in glass or polyethylene bottles.
4. Reagent grade or re-distilled hydrochloric acid (HCl).
5. Ascorbic Acid ($C_6H_8O_6$).
6. Sodium Thiosulfate ($Na_2S_2O_3$).
7. Sodium Sulfite (Na_2SO_3).

Part b) Preservation Techniques

1) Chemical preservation of manually collected samples should be performed as soon as practical after sample collection, but no longer than 15 minutes after sample collection. If the samples cannot be preserved immediately, they should be placed on ice until they are preserved, and the time of preservation noted on the paperwork in addition to the time of collection. Where appropriate, (see Tables E-2 and E-3) samples should be quickly cooled to less than or equal to 6˚C and maintained at that temperature until turned over to laboratory personnel. Samples for metals analyses do not require refrigeration after preservation with acid.

2) When automatic samplers are used, the chemical preservatives must be added to the sample bottle(s) after compositing. All samples must be kept at less than or equal to 6˚C during the compositing period. If there are special circumstances where only metals are to be analyzed (i.e. no demand pollutants or organics), then refrigeration is not necessary –check Tables E-2 and E-3 for parameter preservation requirements.

EXCEPTIONS: If the sample contains residual chlorine, it is necessary to de-chlorinate the sample prior to preservation. APHA, 20th Edition (1998) recommends the use of ferrous sulfate for phenolics and sodium thiosulfate for cyanide.

Part c) Holding Times

Tables E-2 and E-3 list the holding times permitted between sample collection and analysis.

Table E-2. Conventional Parameters Sample Preservation and Maximum Holding Times[1]

LDPE = low density polyethylene PPE = polypropylene

Parameter	Container Type(s)	Preservative(s)	Max Holding Time
Acidity	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	14 days
Alkalinity	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	14 days
Bacteria	4 oz sterile glass or PPE container	Cool to < 6 ˚C, $Na_2S_2O_3$, if chlorine suspected or present	6 hours[2]
BOD	1 gal LDPE cubitainer	Cool to ≤6˚C	48 hours
Bromide	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	28 days
COD	1 qt LDPE cubitainer	Cool to ≤6˚C, 2 ml H_2SO_4 to pH <2	28 days
Chloride	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	28 days
Conductivity, 25˚C	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	28 days
Cyanide, All	1 qt LDPE cubitainer	Cool to ≤6˚C, 4-6 pellets NaOH to pH>10 but less than 12 S.U.	14 days
Fluoride	1 qt LDPE cubitainer	Cool to ≤6˚C	28 days
Oil & Grease	1 liter clear glass, Teflon-lined cap	Cool to ≤6˚C, 2 ml H_2SO_4 to pH <2	28 days
Laboratory pH	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	Immediate upon receipt at lab
Field pH	None, probe, in-situ	Determine onsite	Immediate
Dissolved oxygen	None, probe, in-situ	Determine onsite	Immediate
Hardness (calc)	1 qt LDPE cubitainer	5 ml HNO_3 to pH <2	6 months
Organic Carbon – Total	1 qt LDPE cubitainer	Cool to ≤6˚C, 2 ml H_2SO_4 to pH <2	28 days
Organic Carbon – Dissolved	1 qt LDPE cubitainer (100 ml min)	Cool to ≤6˚C	7 days
Metals			
Dissolved	1 qt LDPE cubitainer	Filter onsite, 5 ml HNO_3 to pH <2	6 months
Suspended	1 qt LDPE cubitainer	Filter onsite, retain filter pad	6 months
Total	1 qt LDPE cubitainer	5 ml HNO_3 to pH <2	6 months
Chromium (VI)	1 qt LDPE cubitainer (100 ml min)	Filter onsite, cool to 4˚C	24 hours
Mercury, dissolved	125 ml glass jar	Filter onsite, 0.625 ml HNO_3 to pH <2	28 days
Mercury, total	125 ml glass jar	0.625 ml HNO_3 to pH <2	28 days
Nutrients			
Ammonia	1 qt LDPE cubitainer	Cool to ≤6˚C, 2 ml H_2SO_4 to pH <2	28 days
TKN	1 qt LDPE cubitainer	Cool to ≤6˚C, 2 ml H_2SO_4 to pH <2	28 days
Nitrite + Nitrate	1 qt LDPE cubitainer	Cool to ≤6˚C, 2 ml H_2SO_4 to pH <2	28 days
Nitrite	1 qt LDPE cubitainer	Cool to ≤6˚C	48 hours
Orthophosphate[3]	1 qt LDPE cubitainer (60 ml min)	Filter onsite. Cool to ≤6˚C	48 hours
Phosphorus, dissolved[3]	1 qt LDPE cubitainer (100 ml min)	Filter onsite. Cool to ≤6˚C, 2 ml H_2SO_4 to pH <2	28 days
Phosphorus, total[3]	1 qt LDPE cubitainer	Cool to ≤6˚C, 2 ml H_2SO_4 to pH <2	28 days
Residue			
Filterable	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	7 days
Nonfilterable	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	7 days
Total	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	7 days
Volatile	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	7 days
Organic Carbon	1 qt/gal LDPE cubitainer	Cool to ≤6˚C	7 days
Phenolics			
Survey	125 ml glass with white cap	1 ml H_2SO_4 to a pH <2, Cool to ≤6˚C	28 days
Compliance, manual distillation	1 qt clear glass jar with white cap	Cool to ≤6˚C, 2ml H_2SO_4 to pH <2	28 days

[1]A chain of custody form must accompany the transfer of any samples to the testing laboratory in order to get samples into evidence in a legal proceeding.

[2]The sample shall be cooled to <6 ˚C and delivered to the laboratory for analysis within six hours. Do not freeze. According to APHA *Standard Methods* 9060 A (2006), the maximum time from sample collection to laboratory analysis is eight hours. Make arrangements with your laboratory if transport time will exceed six hours to ensure that the eight hour ultimate holding time is not exceeded.

[3] See Subsection E3 for low level phosphorus collection method. Submit samples in a 125ml glass jar with Teflon™ lined polypropylene cap.

Table E-3. Organic Parameter Sample Preservation and Maximum Holding Times

Parameter	Container	Preservative	Hold Time
Acid Herbicides Method 515.1	(2) 1 L amber glass jars with Teflon lined cap	If chlorine is believed to be present, treat with 80 mg $Na_2S_2O_3$ or 50 mg of Na_2SO_3 , cool to ≤6˚C	14 day extraction 30 day analysis
Herbicides Method 525.2	(2) 1 L amber glass jars with Teflon lined cap	First preserve with 50 mg Na_2SO_3 (required regardless of the presence of chlorine) and then 6 ml. 6N HCL, Cool to ≤6˚C	14 day extraction 30 day analysis
Cyanazine Method 525.2	(2) 1 L amber glass jars with Teflon lined cap	Cool to ≤6˚C	14 day extraction 30 day analysis
Organo-chlorine Insecticides Method 608, 8081	(2) 1 L amber glass jars with Teflon lined cap	Cool to ≤6˚C	7 day extraction 40 day analysis
Polychlorinated biphenyl (PCB) Method 608, 8082	(2) 1 L amber glass jars with Teflon lined cap	Cool to ≤6˚C	7 day extraction 40 day analysis
Purgeable Aromatics Method 624, 8260	(2) 40 ml glass vials with Teflon lined septum seal	2 drops 1:1 HCL to pH<2, 3 mg $Na_2S_2O_3$ if chlorinated, cool to ≤6˚C	14 days
Purgeable Halocarbons Method 624, 8260	(2) 40 ml glass vials with Teflon lined septum seal	3 mg $Na_2S_2O_3$ if chlorinated, cool to ≤6˚C	14 days
Semi-Volatile Organics Method 625, 8270	(2) 1 L amber glass jars with Teflon lined cap	Cool to ≤6˚C	7 day extraction 40 day analysis

SECTION F. METHODS FOR CONDUCTING STREAM MEASUREMENTS

Subsection F1. Dissolved Oxygen (D.O.)

a) Measurement of D.O. shall be performed using a dissolved oxygen meter. Values should be reported to the nearest 0.1 mg/l unless calibrated to 0.01 mg/l.

b) It is important that a minimum water velocity of one foot per second be maintained across the surface of the D.O. probe. If the probe is used in slow-moving water, jiggling the probe cable will provide the needed agitation. However, some meters use a rapid pulse or optical oxygen sensor that does not require velocity.

c) A temperature measurement should accompany each D.O. measurement. Readings should be recorded to the nearest 0.1 ˚C.

d) Dissolved oxygen measurements should be taken at enough locations across the stream section and through the vertical water column to characterize the variation in D.O. concentration at a given site. Use best professional judgment.

e) Dissolved oxygen measurements may be collected from bridges by using a dissolved oxygen meter equipped with the appropriate probe cable.

Subsection F2. pH

a) The pH meter must be standardized as described in Section D.

b) The sample should be stirred for several seconds by gently moving the pH electrode back and forth through the sample prior to measurement. This will minimize the time needed for the equilibration of the electrode.

c) An integrated grab sample (see Section E, Subsection2, Part a-3), should be used to represent the "average" pH of the stream at any given time.

Subsection F3. Conductivity

The conductivity meter should be checked as described in Section D. Conductivity is generally reported in mS/cm (mS/cm =10^{-3} µmhos/cm). A temperature measurement should accompany each conductivity measurement (see Section D, Subsection 3). Conductivity measurements can be made in-situ, or remotely using a meter equipped with the appropriate length cable. Field conductivity measurement results can be reported as long as the appropriate STORET code is used.

Subsection F4. Temperature

Thermistors on D.O. and conductivity meters, or thermometers, can be used to measure water temperature. All field temperature measuring devices (thermistors and field thermometers) should be standardized at least once per year against a non-mercury NBS calibrated thermometer. Report temperature values to the nearest 0.1 ˚C.

Subsection F5. Current Measurement and Discharge Calculation

The accuracy of a water measurement system varies widely, depending principally upon the primary flow devices used. The total error inherent in a flow measuring system is, of course, the sum of each component part of the system. However, any system that cannot measure the water flow within ±10% is considered unacceptable for NPDES permit compliance purposes.

Flow Meters

The following procedures typically used for mechanical flow meters also apply to the use of the Sontek FlowTracker:

1) The measurement section should be within a straight stream reach, where streamlines are parallel. The streambed should be relatively uniform and free of numerous boulders, debris, and heavy aquatic growth. The flow should be relatively uniform and free of eddies, slack water, and excessive turbulence. The ideal section is perpendicular to the direction of the flow, with uniform bed and banks, a minimum velocity greater than 0.5 fps, and a depth adequate for use of the two-point method.

2) After selection of the reach, determine the width of the stream by stringing a tag line or measuring tape at right angles to the direction of flow.

3) Determine the spacing of the verticals.

i) Generally, use about 25 to 30 partial sections. (When there are smooth cross-sections and a good velocity distribution, fewer sections may be used).

ii) Space the sections so that any one section has no more than 10% (ideally 5%) of the total flow passing through it.

iii) Equal widths of partial sections are not recommended unless the discharge is well distributed. (Make the section width less, as depths and velocities become greater).

4) Velocity sample time: under normal measurement conditions, each point velocity measurement should be sampled for a minimum of 40 seconds. Under extreme flow conditions, such as rapidly changing state, a shorter sample time may be used to lessen the time needed to complete the discharge measurement.

5) Location of velocity observations in each vertical: at water depths of 1.5 feet or less, the 0.6 depth from surface method should be used; at depths between 1.5 and 2.0 feet, the two-point

(0.2/0.8) method should be used unless the 0.8 depth measurement is located less than two inches from a rock or other boundary. At depths greater than 2.0 feet, the two-point method should be used.

6) A flow data sheet should be completed every time a stream discharge measurement is made, specifying stream name, river mile, specific site description, latitude/longitude (including the method used, e.g. GPS), date and time, staff names, weather conditions, stream bottom description, the type of meter and the meter's serial number, and, if using the SonTek unit, the flowtracker data field name. Record the time the measurement began and ended. Record which bank of the stream that was the starting point (LEW or REW, i.e, left edge of water or right edge of water, when facing downstream).

7) FlowTracker flow data: All flow measurement data files should be saved. Recommended format for the field name: Filename.nnn, where "Filename" is an eight-digit stream and site ID. The "nnn" suffix serves to identify the date, with the first digit used for the month, and the other two digits for the day. The year cannot be specified in filename.nnn, so it is important to fill a field sheet with additional details for each filename used. See examples below:

FILENAME	STORET NUMBER	DATE
GMR 25_4.917	H09S13	September 17
OTTAW117.015	P04P16	October 15
R04S03.N13	R04S03	November 13

Date suffix (nnn): Use 1 through 9 for January through September; use O/0 for October; N for November; D for December. The station ID for the flow measurement site should be added into the FlowTracker file where prompted for "Name" (note that this is different than the file name).

8) Taking a Measurement:

Table F-1. Velocity Measurement Methods for Various Depths

WATER DEPTH FT.	VELOCITY METHOD
2.0 and >	Two-point method 0.2 and 0.8 depth from surface
1.5 – 2.0	Two-point method except as noted in paragraph 5 above, then use single-point method
0.3 – 1.5	Single-point method 0.6 depth from surface

Keep the wading rod in a vertical position and the meter parallel to the direction of flow while observing the velocity. If the flow is not normal to the tag line, measure the angle coefficient carefully and record the value.

When natural conditions for measuring the velocity are unsuitable, modify the cross-section to provide acceptable conditions, if practical. Often, it is possible to build dikes to cut off dead water and shallow flows in a cross section, or to improve the cross-section by removing the rocks and debris within the section and from the reach of stream immediately upstream.

After modifying a cross-section, allow the flow to stabilize before starting the velocity measurement. Stand in a position that least affects the velocity of the water passing the current meter. This position is usually obtained by facing the bank with the water flowing against the side of the leg. Holding the wading rod at the tag line, stand from one to three inches downstream from the tag line and 18 inches or more from the wading rod. In small streams where the width permits, stand on a plank, or other support, rather than in the water.

NOTE: A wading measurement is preferred, if conditions permit. The advantage is that it is usually possible to select the best of several available cross-sections for the measurement. Use the SAME meter for the entire measurement.

If conditions for wading measurements do not exist, the Modeling and Assessment Section can measure flows using the StreamPro and/or RiverRay. These units utilize Acoustic Doppler Current Profiler (ADCP) technology. The ADCP is mounted to a small boat which is guided across the stream to obtain measurements of depth and velocity. The StreamPro can work at about 0.5 feet water depth, while the RiverRay needs at least 2.5 feet water depth. The StreamPro maximum velocity is around 4 ft/sec, while the RiverRay can measure over 10 ft/sec. For streams/reaches with high velocity or depth, this equipment is available, and shall be used in accordance with the manufacturer's instructions by staff trained in the use of the equipment as well as the software.

9) Flow Tracker Directions

For more detailed information refer to the Flow Tracker Operating Manual, making sure the version is appropriate for your equipment.

Quick Start

Install the batteries (access the battery compartment from the back of the Flow Tracker). Turn the system on by holding the **On/Off** switch for 1 second; hold the switch for 4 seconds to turn the system off.

Explore the **Setup Parameters** menu by pressing **1** from the **Main Menu**.

-Press **Enter** to switch between the multiple display screens.

-Use the menu items to change the parameters that affect data collection.

Explore the **System Functions Menu** by pressing **2** from the **Main Menu.**

- Press **Enter** to switch between the multiple display screens.

-Use the menu items to access FlowTracker diagnostic procedures.

Collect a test data set.

-Select a data collection mode (general/discharge) from the **Setup Parameters Menu.**

-Start the data run by pressing **3** from the **Main Menu.**

-Follow the on-screen prompts. Use the **Next Station** and **Prev. Station** keys to scroll between stations. Use the **Set** keys to set various parameters.

-See Sections 4 and 5 of the *FlowTracker Operation Manual* for a description of the General Mode and Discharge Mode data collection procedures.

PC Software Installation

The PC software is used to download data from the FlowTracker, to extract data to ASCII-text data files, and to perform detailed system diagnostics. Insert the FlowTracker Software CD into your computer's CD-ROM driver. An installation menu should automatically appear after the CD has been inserted.

-If the installation window does not appear in a few seconds, click **Start/Run** and type d:\install.exe where d:\ is the letter of your CD-ROM drive.

On the menu, click the **FlowTracker Software Installation** button. Follow the on-screen installation instructions. See Section 6.1 of the *FlowTracker Operation Manual* for detailed instructions.

Downloading Data Files from the FlowTracker

Connect the power/communication cable from the FlowTracker to COM1 of your PC. Start the *FlowTracker* software using **Start/Programs/SonTek Software/FlowTracker.**

Click **SonRecW** to launch the data download software.

Click **Connect** to establish communication with the FlowTracker.

Select one or more files from the downloaded recorder directory.

Specify a destination directory for the downloaded files using the **Browse** button.

Click **Download** to retrieve the files from the FlowTracker to your PC.

See Section 6.4 of the *FlowTracker Operation Manual* for detailed instructions.

Extacting Data from FlowTracker Data files

Start the FlowTracker software using **Start/Programs/SonTek Software/Flow Tracker.**

Click **Data Export** to launch the data extraction software.

Click **Open** and select a Flow/Tracker file to access.

Click **Options** to specify the unit system to use.

Select a file type to output and click **Export Selected Variable** to create the specified file, or click **Export All Variables** to create all available output files.

See Section 6.5 of the *FlowTracker Operation Manual* for detailed instructions.

Basic FlowTracker data collection process, using the keypad interface

At the start of data collection, the user is prompted for a file name. For **Discharge** measurements, the user enters site-specific data before data collection: staff/gauge height (optional), rated flow (optional), and edge location data (required). At each measurement location, the user specifies location, water depth, and measurement depth data to document the data set. For **Discharge** measurements, these are used to calculate discharge in real-time.

A fixed-length burst of velocity data is recorded at each measurement location. Velocity data is recorded once per second during the burst; mean velocity and quality control data are recorded at the end of each burst. Summary velocity and quality control data are displayed at the end of each measurement.

The user is allowed to repeat individual measurements if desired. The user proceeds through a series of measurement locations (up to 100 stations can be recorded with each file.) The user can scroll through previous stations to view data and edit station information.

When done, the user presses **End Section** to close the file. For **Discharge** measurements, the user enters ending-edge information and is then shown the final discharge data.

SECTION G. OHIO EPA LABORATORY SAMPLE SUBMISSION/ FIELD PROCEDURES

Subsection G1. Sample Containers

Part a) All sample containers must be clearly labeled with the following information:

1) Sampling location (stream name and river mile or cross road, station number)

2) Type of sample preservation i.e., H_2SO_4 (sulfuric acid), HNO_3 (nitric acid), HCl (hydrochloric acid), NaOH (sodium hydroxide), $Na_2S_2O_3$ (sodium thiosulfate), Na_2SO_3 (sodium sulfite), or "NP" (no preservative).

3) Date and time of collection (military time).

4) VOC vials should also be labeled with the method of interest (e.g. VOC, or Atrazine (ELISA)).

NOTE: Whenever there are several trip blanks in the same cooler and sampling involved several individuals, the name of each sample collector must be written on each trip blank label.

Part b) The information above must be written on waterproof labels or on labels created using the Sample Master® application, which are then securely attached to all glass containers. The information may also be written on tape or duct tape that has been wrapped around the container, except for VOC vials, which require the use of labels rather than tape. When samples are collected in cubitainers, the information must be written directly on the sample containers with indelible ink or on labels created using the Sample Master® application.

Part c) All sample containers should be labeled as completely as possible before beginning the sample collection process to reduce probability of error and improve efficiency in the field.

Subsection G2. Sample Submission Forms

Ohio EPA staff will follow the instructions for sample submission found in the Sample Master® Instruction Manual in Appendix IV, Section D. Persons other than Ohio EPA staff should contact DES before submitting samples to confirm what information is needed and in what format.

SECTION H. OHIO EPA LABORATORY DOCUMENTED CUSTODY PROCEDURES

Subsection H1. General

Whenever samples are collected, formal documented procedures for sample handling MUST be followed. The primary objective of these procedures is to create an accurate, written record that can be used to trace the possession and handling of the sample from the moment of its collection through its introduction as evidence.

Subsection H2. Definitions

Part a) Sample custody – A sample is in your custody if:

1) It is in your physical possession; or

2) It is in your view, after being in your physical possession; or

3) It was in your physical possession and you locked it in a transfer-proof container or storage area. (U.S. EPA 1976)

Part b) Transfer of sample custody – A transfer of custody occurs whenever a sample, or group of samples:

1) Passes from the physical possession of one person to another; or

2) Is removed from a transfer-proof container, or storage area, by a person other than the person who put the sample(s) in said container or storage area.

Subsection H3. Transfer of Custody Procedures

Each time the custody of a sample or group of samples is transferred, the person relinquishing custody of the sample(s) must sign, date, and record the military time on a "transfer of custody" form. The form should also indicate the number of samples being transferred, the parameters to be analyzed, and a brief description of the origin of the sample(s). The person receiving custody of the samples must also sign, date, and record the military time on the DES Chain of Custody Report form. Both persons should keep a copy of the transfer form. The laboratory data sheets must be transferred with the samples.

SECTION I. LITERATURE CITED

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