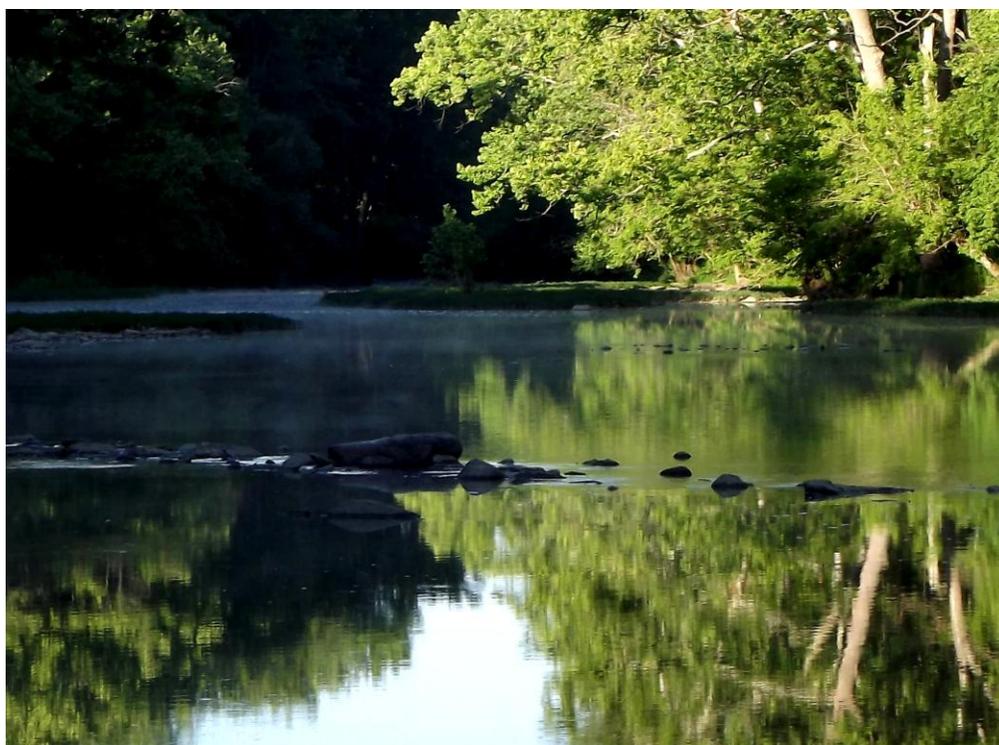


# Surface Water Field Sampling Manual

for water column chemistry, bacteria and flows



*Photo Courtesy of Russ Gibson, Ohio EPA, DSW*

Final Manual  
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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
<p><b>Ohio EPA Surface Water Quality Sampling Manual version 4.0 replaces previous Manual of Ohio EPA Surveillance Methods and QAPs, April 2012 version</b></p> <p>General: Name changed, overall report format updated, Health and Safety section added, Pre-sampling Activities section added, some information re-organized; added Appendices.</p> <p>Section A: No significant revisions.</p> <p>Section B: Minor corrections.</p> <p>Section C: Replaced previous contract lab information with safety and field preparation information.</p> <p>Section D: Minor adjustments to record keeping</p> <p>Section E: Minor adjustments to sampling and preservation requirements, added reference to chlorophyll-a sampling procedure.</p> <p>Section F: Flow measurement section updated and references to equipment no longer used removed (e.g. Pygmy meters).</p> <p>Section G: Minor updates/revisions incorporated.</p> <p>Section H: No revisions.</p> <p>New Section I Data Management added.</p> <p>Appendix 1 and 2 added to link the documents within them to this manual</p>	<p><b>January 31, 2013</b></p>
<p><b>Manual of Ohio EPA Surveillance Methods and Quality Assurance Practices, April 2012 version replaces 2009 version</b></p> <p>Revision History page added, footer updated, page numbering changed, minor errors fixed throughout.</p> <p>Tables D1, D2, were updated.</p> <p>Subsections 5 and 6 of Section E regarding QC procedures were updated.</p> <p>A new Table E1 for Field QC was added, and existing Tables E1 and E2 were re-numbered to E2 and E3.</p>	<p><b>April 13, 2012</b></p>
<p><b>Manual of Ohio EPA Surveillance Methods and Quality Assurance Practices, 2009 version</b></p>	<p><b>2009</b></p>

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**In Separate Appendix Documents:**

- APPENDIX I. LAKES SAMPLING MANUAL
- APPENDIX II. Section A. CHLOROPHYLL-A SAMPLING PROTOCOL
- Section B. CRITICAL CLEANING OF ORTHO-P SAMPLING SYRINGES
- Section C. EA3 STATION MODULE MANUAL

## 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 addressed in the document “Sediment Sampling Guide and Methodologies, 3<sup>rd</sup> Edition, March 2012” which can be found at:

<http://www.epa.ohio.gov/portals/35/guidance/sedman2012.pdf>

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. Ten percent of the chemistry samples will be spiked and analyzed for recovery efficiently 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. Quarterly 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 Assurance Plan at the end of each year. The Quality Assurance 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 SMS 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***

#### **Cyberintern**

Sample container labels must be printed using Cyberintern if at all possible. The user's manual for Cyberintern is available to agency employees through the DSW Web Applications Portal.

## 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.
- soak probes
- 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

- pH/temp/cond meters
- DO 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**

Each Ohio EPA monitoring crew 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 must be followed and 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. 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 using two reference buffers. If the expected reading is alkaline, use pH 7 and pH 10 buffers. If the expected 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.

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  $\pm 2^{\circ}\text{C}$ ) 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.

*NOTE: Field conductivity measurements are only to be used for the purposes of delineating mixing zone boundaries and identifying sources of high dissolved solids. When highly accurate conductivity values are desired, i.e. for input to the US EPA’s STORET Data System, laboratory analysis at 25°C should be performed. However, a functional check of all field conductivity meters must be performed according to the manufacturer’s instructions with the results noted in the meter logbook. Table D-2 shows the relationship between conductivity and sample temperature. NOTE: There is a STORET parameter code for field conductivity (P00094), which is separate from the STORET parameter code for laboratory conductivity (P00095). Both values can be entered into STORET.*

**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***

#### SonTek FlowTracker

Calibrate and operate the flow meter according to manufacturer's instructions. Consult the SonTek FlowTracker 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 FlowTracker 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 effluent 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 (OEPA 1978).”

### ***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 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 16<sup>th</sup> 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 swirl the contents of the bucket as it is being poured into containers to avoid settling of solids (and 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. Twenty-four hour composite samples shall also be used to determine if any effluent toxicity exists, when collecting effluent samples for bioassays.

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.

Samples analyzed for CARBAMATE pesticides (Aldicarb, Aldicarb Sulfone, Aldicarb Sulfoxide, Carbaryl, Carbofuran, 3-Hydroxycarbofuran, Methiocarb, Methomyl, Oxamyl, Propoxur) using Ohio EPA Method 531.1 require two 40 ml glass vials with Teflon-lined septum sealed caps. Do not pre-rinse the vials. Add 4 mg of sodium thiosulfate for 40 ml of sample if chlorine is present or suspected. Fill vials approximately 1/2 to 3/4 full, add 1.2 ml of monochloroacetic acid buffer then top with additional sample (meniscus is not necessary). Invert vial multiple times to mix preservatives. Samples analyzed for GLYPHOSATE herbicides (Glialka, Roundup, Sting, Rodeo, Spasor, Muster, Tumbleweed, Sonic, Glifonox, Glycel, Rondo) using Ohio EPA Method 547 require two 40 ml glass vials with Teflon-lined septum sealed caps. Add 4 mg of sodium thiosulfate for 40 ml of sample if chlorine is present or suspected. Leave no headspace in the vial. Invert vial multiple times to mix preservative. All samples must be iced or refrigerated at less than or equal to 6°C. Keep samples away from light until analysis.

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 quart, laboratory issued 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 quart cubitainers and preserved with 6-10 pellets (depending on pellet size) of sodium hydroxide (NaOH) transferred to the container without handling the preservative. The pH of the sample must be >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 must be iced or refrigerated at less than or equal to 6°C.

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<sub>2</sub>SO<sub>4</sub> 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 must be filtered in the field, 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. 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<sub>2</sub>SO<sub>4</sub> 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 A 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 is 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 the *Water Quality Standards Guidance #3, Sampling Methods for Documentation of a Public Health Nuisance Under OAC 3745-1-04 (F) & (G)* (Ohio EPA 1998). This guidance document is available at: [www.epa.state.oh.us/dsw/guidance/wqs3.pdf](http://www.epa.state.oh.us/dsw/guidance/wqs3.pdf).

Bacteria samples must be maintained in the dark and iced or refrigerated at less than 8°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 should be collected in a 1 quart cubitainer and preserved with 5 ml. HNO<sub>3</sub>. Samples do not require refrigeration once they are preserved with HNO<sub>3</sub>.

10) Chlorophyll-a – See Appendix A, Collection of Chlorophyll-a Samples.

*NOTE: All samples for bacteria or demand parameters (including nutrients) must be iced and 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. Duplicate Samples***

Field Sample Duplicates collected for laboratory Matrix Spike Duplicate (MSD) QC samples are to be collected and submitted at a minimum frequency of 5% of the total number of organic field samples (for a total of 10% QC samples in typical practice). Oil and Grease is the exception, a duplicate for O & G is collected and submitted monthly (in any month the parameter is collected), regardless of sample numbers. The frequency of these samples should be tracked in each DSW office (by a WQ Supervisor or Designee).

Most DES internal QC analysis is performed by splitting the contents of a field sample's containers, as most containers are large enough to hold enough matrix for multiple analyses. However, there are some special containers for parameters which do not contain enough matrix for internal sample splitting (*i.e.*, the whole container is used for analysis). DSW must collect Matrix Spike/Matrix Spike Duplicate samples in these cases. If DSW has not collected enough Matrix Spike/Matrix Spike Duplicate samples for the lab's QC needs, DES may request the sampler to fill extra containers for laboratory QC assessment. For oil and grease fill one extra jar. For VOC volatiles fill two extra 40 mL vials (4 total). For semi-volatiles, pesticides, PCBs, or herbicides fill two extra amber jars. Four extra jars are needed if both PCB and BNA samples are submitted (8 total). The extra containers indicated are beyond the usual numbers of containers specified in Subsection 3, Part c of Section E. Write "MATRIX SPIKE" on top of the laboratory sample submission sheet or type in the field comments if using Cyber Intern Software. Mark the appropriate FIELD QC box on the sample submission form.

*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.*

### ***Subsection E6. Field QC: Field Blanks/VOC Trip Blanks/ Equipment Blanks/Matrix Spike Duplicates/Acid Banks***

Field Duplicates, Field Replicates, Field Blanks and Equipment Blanks combined should comprise about 10% of the total number of field samples. Other less frequent types of QC samples do not count against this 10% (*i.e.*, acid blanks, cubitainer blanks, VOC trip blanks, Oil + Grease blanks, etc.). Any extra QC samples collected to resolve previous contamination issues, other special case QC concerns, etc. also do not count as part of the 10%. The frequency of these samples and the completeness of less frequent samples like cubitainer and acid blanks should be tracked in each DSW office.

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

QC Sample Type	QC Sample Rate or Frequency
<b>Field Duplicates and Field Replicates</b>	5% of total water samples (emphasizing duplicates, since the variability of duplicate data provides context for evaluating the variability of replicate data ( <i>i.e.</i> , is precision greater than with the duplicates?).
<b>Field Blanks</b>	5% of total water samples (may overlap with equipment blanks)
<b>Trip Blanks (VOCs)</b>	One per cooler with VOC samples
<b>Equipment Blanks</b>	Minimum of 1 per equipment type, combined with field blanks
<b>Acid Blanks</b>	Once per acid lot or dispenser cleaning
<b>Cubitainer Blanks</b>	Once per lot (by D.O., unless the lab tells them they have already done it).
<b>MS/MSD (organics)</b>	5% of organic samples only (track in each D.O., collected for lab QC)

VOC Trip blanks must accompany each batch of VOC test samples, Cubitainer® Blanks should be submitted for each new lot of containers, and Acid Blanks are submitted for new lots of acid received and after bulk dispensers are cleaned. 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).

All QC samples submitted to the Division of Environmental Services (DES) should use approved labeling and chain of custody methods described in Section G. 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). **Stock 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 stock water can be stored for up to 28 calendar days in a clean container to facilitate transport.

Part a) **Field Duplicates** (also known as Field Split) are used to measure laboratory method precision. 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 should be considered the “real” sample to be used for project data analysis (the QC duplicate **should** be otherwise identified to the lab).

*Note: Duplicate and Replicate QC samples should be submitted at a rate of about 5% of all field samples. This 5% is a combined total for both types. When collecting replicate samples, best practice may be to also collect duplicates at that site, in order to have a way to determine if replicate variability (which is an indicator of media heterogeneity) exceeds duplicate variability (which is an indicator of laboratory precision).*

Part b) **Field Replicates** 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 laboratory 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).

Part c) **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.). Stock water is taken into the field in a sealed container. The stock water is then poured into the sample container and the chemical preservative is added if appropriate. The containers and sample submission forms 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. The appropriate FIELD QC box on the sample submission form should be checked.

*Note: Blank QC samples should be submitted at a rate of about 5% of all field samples. This 5% is a combined total for all blank types. Generally Field Blanks and Equipment Blanks will comprise the bulk of this 5%.*

Part d) **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 and sample submission forms 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.

Part e) **Equipment Blanks** are done 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). Equipment blanks for automatic samplers are collected after the completion of decontamination

of sampling equipment and prior to sampling by running stock 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 stock 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. Label the containers and laboratory sheet "EQUIPMENT BLANK ". Mark the appropriate FIELD QC box on the sample submission form. 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.

Part f) **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. Dispenser units should be cleaned a minimum of every 6 months by emptying their contents and soaking in deionized water for 20 minutes. The date of last cleaning should be recorded in a logbook and marked on the dispenser. Each district/office should designate an individual to be responsible for this. An Acid blank is prepared by filling a quart cubitainer with stock water and adding a dose of acid from the newly cleaned dispenser. On the sample submission form the location should be listed as "Acid Blank". Mark the appropriate FIELD QC box and 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), ICP/MS-1 metals (As, Cd, Cr, Cu, Ni, Pb and Se) and mercury.

Part g) **Cubitainer Blanks** should be submitted when a new lot of containers are received from the manufacturer to verify that they are clean. A Cubitainer Blank is prepared by filling a randomly selected container from each lot with stock water and adding a dose of preservative, if appropriate. On the sample submission form the location should be listed as "Cubitainer Blank" and include the manufacturer's lot number. Use a separate sample submission form for each lot number. Mark the appropriate FIELD QC box and use "Cubitainer 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.

## ***Subsection E7. 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 8°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<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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.*

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

## ***Subsection E8. Preservation and Holding Times***

### Part a) Recommended Preservatives

1. Re-distilled or spectrograde nitric acid (HNO<sub>3</sub>).
2. Reagent grade or re-distilled sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).
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<sub>6</sub>H<sub>8</sub>O<sub>6</sub>).
6. Sodium Thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>).
7. Magnesium Carbonate (MgCO<sub>3</sub>) - chlorophyll A.
8. Sodium Sulfite (Na<sub>2</sub>SO<sub>3</sub>).

### 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, 20<sup>th</sup> 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<sup>1</sup>**

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 < 8 °C, Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , if chlorine suspected or present	6 hours <sup>2</sup>
BOD	1 gal LDPE cubitainer	Cool to ≤6°C	48 hours
COD	1 qt LDPE cubitainer	Cool to ≤6°C, 2 ml H <sub>2</sub> SO <sub>4</sub> 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, 6-10 pellets NaOH to pH<12	14 days
Fluoride	1 qt LDPE cubitainer	Cool to ≤6°C	28 days
Oil & Grease	1 qt clear glass, Teflon-lined cap	Cool to ≤6°C, 2 ml H <sub>2</sub> SO <sub>4</sub> 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 <sub>3</sub> to pH <2	6 months
Metals			
Dissolved	1 qt LDPE cubitainer	Filter onsite, 5 ml HNO <sub>3</sub> 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 <sub>3</sub> to pH <2	6 months
Chromium (VI)	1 qt LDPE cubitainer	Filter onsite, cool to 4°C	24 hours
Mercury, dissolved	1 qt LDPE cubitainer	5 ml HNO <sub>3</sub> to pH <2	28 days
Mercury, total	1 qt LDPE cubitainer	5 ml HNO <sub>3</sub> to pH <2	28 days
Nutrients			
Ammonia	1 qt LDPE cubitainer	Cool to ≤6°C, 2 ml H <sub>2</sub> SO <sub>4</sub> to pH <2	28 days
TKN	1 qt LDPE cubitainer	Cool to ≤6°C, 2 ml H <sub>2</sub> SO <sub>4</sub> to pH <2	28 days
Nitrite + Nitrate	1 qt LDPE cubitainer	Cool to ≤6°C, 2 ml H <sub>2</sub> SO <sub>4</sub> to pH <2	28 days
Nitrite	1 qt LDPE cubitainer	Cool to ≤6°C	48 hours
Orthophosphate	1 qt LDPE cubitainer (60 ml min)	Filter onsite. Cool to ≤6°C	48 hours
Phosphorus, dissolved	1 qt LDPE cubitainer (100 ml min)	Filter onsite. Cool to ≤6°C, 2 ml H <sub>2</sub> SO <sub>4</sub> to pH <2	28 days
Phosphorus, total	1 qt LDPE cubitainer	Cool to ≤6°C, 2 ml H <sub>2</sub> SO <sub>4</sub> 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 <sub>2</sub> SO <sub>4</sub> 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 <sub>2</sub> SO <sub>4</sub> to pH <2	28 days

<sup>1</sup>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.

<sup>2</sup>The sample shall be cooled to <8 °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.

**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	80 mg Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> if chlorinated, cool to ≤6°C	14 day extraction 30 day analysis
Herbicides Method 525.2	(2) 1 L amber glass jars with Teflon lined cap	50 mg Na <sub>2</sub> SO <sub>3</sub> , 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
Carbomate Insecticides Method 531.1	(2) 40 ml glass vials with Teflon lined septum seal	1.8 ml chloroacetic acid buffer, 4 mg Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> if chlorinated, cool to ≤6°C	28 days
Glyphosate Method 547	(2) 40 ml glass vials with Teflon lined septum seal	4 mg Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> if chlorinated, cool to ≤6°C	14 days
OrganoChlorine 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 <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 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 <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 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 oxygen sensor that does not require stirring.
- c) A temperature measurement should accompany each D.O. measurement. Readings should be recorded to the nearest .01 °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, Subsection 2, 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 =  $10^{-3}$  umhos/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) must be standardized monthly 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  $\pm 10\%$  is considered unacceptable for NPDES permit compliance purposes.

### Part a) Flow Meters

The following procedures typically used for mechanical (Pygmy and AA) 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 depths of 1.5 feet or less, the 0.6 depth method should be used; at depths between 1.5 and 2.5 feet, the 2 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 2.5 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	SITE DESCRIPTON	DATE
GMR 25_4.917	Great Miami R at RM 25.4	September 17
OTTAW117.015	OttawaR at Route 117	October 15
R04S03.N13	Storet station #R04S03	November 13

Date suffix (nnn): Use 1 through 9 for January through September; use O/O 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).

### 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 units 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.

**Table F-1. Velocity Measurement Methods For Various Depths**

DEPTH FT.	VELOCITY METHOD
2.5 and >	Two-point method 0.2 and 0.8 $d_x$
1.5 – 2.5	Single-point method 0.6 $d_x$
0.3 – 1.5	Single-point method 0.6 $d_x$

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.

#### Part b) Weirs

Weirs are obstructions built across an open channel, or in a pipe through which water flows. The water usually flows through an opening or notch, but may flow over the entire weir crest. Weirs are normally incorporated into hydraulic projects as overflow structures. However, they can be used to measure flow. The equation for weir takes the following form:

$$Q = CLH^{3/2}$$

where

Q = discharge.

C = Coefficient depending on the shape of the crest and the head.

L = Length of the weir crest.

H = Head of the weir crest, and

Values of the coefficient for various shapes of weirs are given in the hydraulic handbook (USGS 1971). When these structures are used to measure waste water flow, they should be calibrated using independent flow measurements. The most convenient method for translating weir head measurements to flow is a set of weir tables. The use of weir formulas and curves in the field is not recommended, since this is a cumbersome procedure and leads to numerous computational errors. Excellent weir tables are included in USGS (1971) and Stevens. The explanatory material accompanying these tables should be read thoroughly before they are used.

#### Part c) Flumes

Flumes are widely used to measure waste water flow in open channels. They are particularly useful for measuring large flow rates. A set of flume tables is necessary for calculating flows.

Both the USGS (1971) and Stevens contain a complete set of tables for measuring flows from flumes.

# 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<sub>2</sub>SO<sub>4</sub> (sulfuric acid), HNO<sub>3</sub> (nitric acid), HCl (hydrochloric acid), NaOH (sodium hydroxide), Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (sodium thiosulfate), Na<sub>2</sub>SO<sub>3</sub> (sodium sulfite), MgCO<sub>3</sub> (magnesium carbonate), 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. 608, or 625).

*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 CYBERINTERN 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 CYBERINTERN 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***

Part a) A separate sample submission form must be filled out for each sampling location and for each QC sample (*i.e.*, blanks, duplicates, replicates)

Part b) The sample submission form must contain all the information recorded on the corresponding sample containers (see Section G, Subsection 1, Part a above) plus the following:

- 1) All categories in the **Sample Information Section** must be completed and only one circle should be selected for each category.
- 2) The **Client** (bill to) line must always be completed.
- 3) The type of sample collected “grab” or “composite” must be indicated.
- 4) The sample **Collection Date** and time should be completed using military time format.
- 5) The frequency and duration of composite sample (where applicable), or the number of grab sub-samples/composite.
- 6) The **Container Information** subsection enables DES to verify that the correct containers were submitted for each parameter requested so this subsection should be accurately completed.
- 7) When applicable, the appropriate **Field QC** should be checked.
- 8) The **Customer ID** is an internal code provided by DES to each sample collector. It enables the collector to collocate inorganic and organic samples from the same site. This ID should be recorded on both inorganic and organic sample submission forms.
- 9) The **Station ID** field should be used to record the Ohio set STORET code.
- 10) The information in the **Sample Location** section should correspond to what was recorded on the sample container.
- 11) The **Template** name should be indicated or parameters may be selected from the list (parameters in the template should not be selected twice). If parameters are to be deleted from the template for a particular site, the parameter should be crossed out on the sample submission form and initialed by the staff member making the change.

The back page of the sample submission form and the “Ohio EPA Field Sampling Handbook” may be consulted for additional information.

Part c) All sample submission forms should be filled out as completely as possible before beginning the sample collection process in order to minimize confusion and clerical work in the field.

# **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 “Chemistry Laboratory 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. DATA MANAGEMENT

## *Subsection I1. Data Validation Guidelines for QC and Field Samples*

For most DSW chemical water quality data, data validation is generally confined to evaluation of Blank results, Duplicate results, sample holding times, paired parameter results (defined below) and confirming that samples were properly preserved/prepared (including filtration, *etc.* - if indicated by the method). Standards for evaluation of analytical results of those QC sample types and general field samples are described below.

Data can be qualified using the standard qualifiers available as defined by DES (in their field handbook) such as “J” for an estimated concentration or “R” for rejected result as well as one additional qualifier, “Trend.” Some results may be too uncertain for some data uses but potentially useful for more general data trend applications.

Data qualifiers should be added by samplers to EA3 as part of their data review process. This will ensure the qualifier remains with the sample result. We want to be sure that valid conclusions can be made using our data for any current and future data uses.

### **Data Qualifiers**

All sample results have some amount of uncertainty surrounding the quantification of analyte in a given sample. Data qualifiers are used to indicate that extra uncertainty is present surrounding a given result (*e.g.*, “J” for estimated or “Trend” to indicate more uncertainty). The data qualifier “R”, Rejected, is used to indicate that too much uncertainty is present to consider the result quantitatively (for most data applications). “Trend” is a new qualifier used by DSW to indicate when data is considered to have less quantitative significance but enough for assessing data trends.

**Blanks** – Blank contamination can result in qualification of other results that were in the same field batch as that blank. In some cases these other results may still be useable and other times the sample results should not be considered valid, largely depending on the concentration in the sample vs. the concentration in the blank.

Laboratories often use a factor of three to differentiate a detected compound from background “noise” present in the system (analytical instrument, *etc.*). When a result exceeds three times the background noise, it is considered to be positively identified in the sample. We can consider blank contamination as extra “noise” in the system, since we don’t know the source of the contamination, and use this factor of three to help us assess our data. To do so, the sample concentration must be at least three times the blank concentration for us to be confident that analyte is truly present in the sample.

**Sample Result**

Sample ≤ 3x Blank

3x Blank &lt; Sample ≤ 5x Blank

&lt; 5x Blank &lt; Sample ≤ 10x Blank

&lt; 10x Blank

Blank qualification examples:

**Interpretation**

Reject sample results in this range as insufficiently different from blank results

Likely indication that the analyte is present but poor confidence in the numerical result - generally limit data use to data “trend” applications

Consider the sample result to be an estimated concentration (qualified “J”) but still suitable for most data uses

Do not qualify data (blank contamination does not significantly change the result within the uncertainty of the value reported)

<u>Blank Result</u>	<u>Detect. Level</u>	<u>Sample Result</u>	<u>Qualifier</u>	<u>Reason</u>
8	5	7	“R”	Result ≤ 3x Blank
8	5	16	“R”	Result ≤ 3x Blank
8	5	29	“Trend”	< 3x Result ≤ 5x Blank
8	5	79	“J”	< 5x Result ≤ 10x Blank
8	5	81	No qualifier	Result > 10x Blank

**Field Duplicates** – Laboratories analyze and evaluate duplicates for their own internal procedures but DSW staff collect field duplicates to evaluate variability in regards to sampling precision for field QC. Duplicates must be submitted “blind” to the laboratory in order to properly assess precision. The duplicate sample results are compared using a statistic called Relative Percent Difference (RPD).

RPD - Relative Percent Difference: 
$$\% Diff. = \left| \frac{x_1 - x_2}{\frac{(x_1 + x_2)}{2}} \right| \times 100$$

In the %RPD example below one sample result/ concentration is substituted in the equation for  $x_1$  (6) and the other for  $x_2$  (10 - it doesn't matter which is which in this equation - but traditionally the duplicate will be  $x_2$ ). Example RPD calculation:

$$\frac{|(6-10)|}{|(6+10)/2|} \times 100 = \frac{|-4|}{|8|} \times 100 = 0.5 \times 100, \text{ (positive since it's an absolute value)}$$

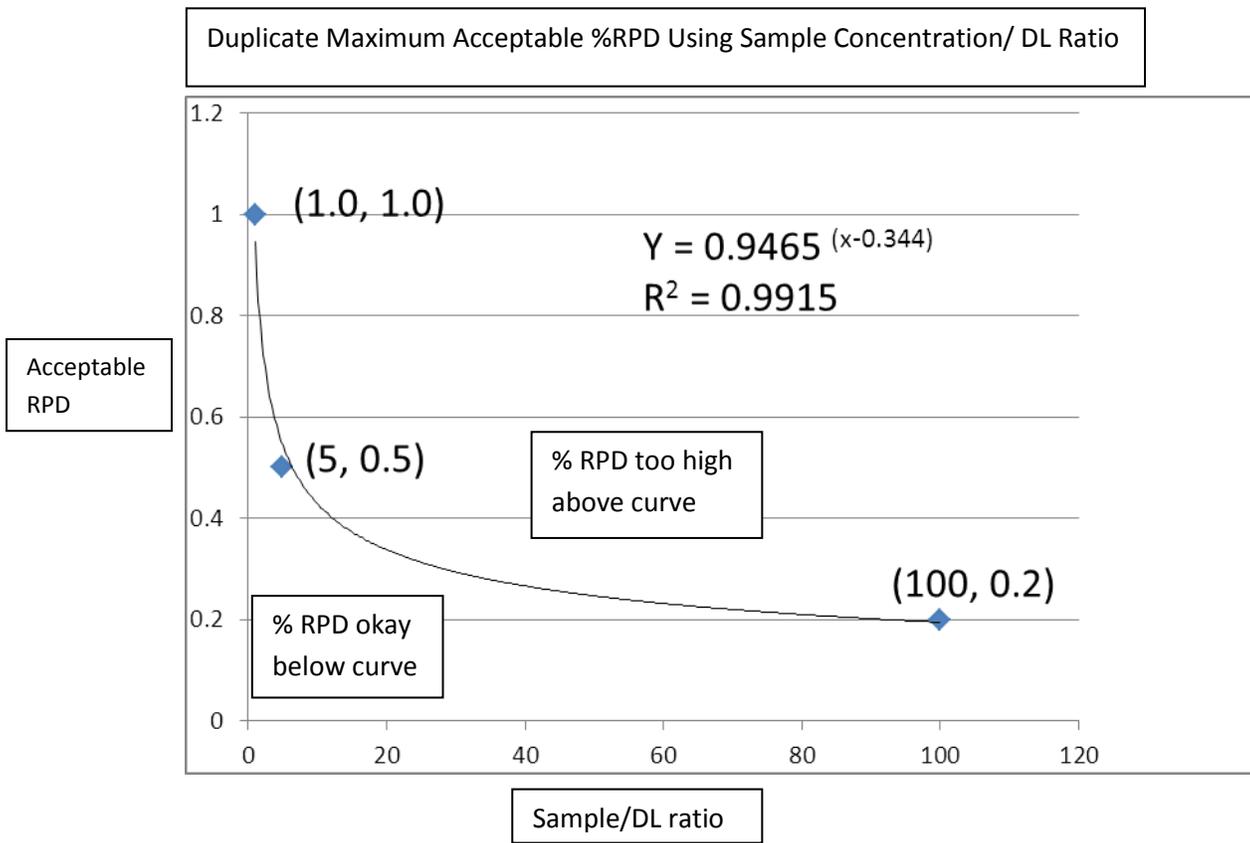
RPD = 50%

We allow a higher %RPD at lower concentrations, since there is a greater percent uncertainty closer to the detection level, and allow a lower %RPD at higher concentrations, since analytical results should be more consistent at higher concentrations. To account for this varying acceptable %RPD, we assess our duplicate samples using a curved line.

By starting with three points based on the ratio of the sample concentration to the detection limit and the %RPD we are willing to accept, we can use Excel to generate the equation of a line. The three points used were:

- (1, 1.0) – At the detection limit, we are willing to accept approximately 100% RPD
- (5, 0.5) – at 5x the detection limit (often near the RL), we are willing to accept approximately 50% RPD
- (100, 0.2) – at 100x the detection limit, we are willing to accept approximately 20% RPD

The graph (taken from Excel, using the “Power” option from the “Trendline” function) shown below illustrates the curve of best fit for these three points. The resulting R<sup>2</sup> value confirms a good fit of our line to our points.



Using “Trendline” in Excel we are able to generate an equation with a very good fit to these three points. With additional tweaking of the equation (adding 5% to each result,) we get a result that gives us almost exactly 100% RPD when the sample concentration equals the detection limit and puts us back up above 10% RPD for high concentration samples (see the table below).

The resulting final equation is  $Y = [(0.9465x^{-0.344}) * 100] + 5$

where x = Sample/DL ratio and y = acceptable %RPD

At first take, this approach might seem somewhat arbitrary, but we have to remember that all approaches have some arbitrary component and what we need is to be consistent and to define an approach that we are comfortable with. Using the above equation, we get acceptable %RPDs at the following levels:

### Determine Maximum Acceptable %RPD (based on sample concentration to DL ratio)

Sample* Conc./DL (x)	“Trendline” equation from Excel $Y = (0.9465x^{-0.344}) * 100$	$y' = [(0.9465x^{-0.344}) * 100] + 5$ (add 5% to baseline eqn.)
1	94.65	99.65
2	74.57	79.57
5	54.41	59.41
10	42.87	47.87
50	24.64	29.64
100	20.41	24.41
200	15.30	20.30
1000	8.79	13.79

\*Not the duplicate sample concentration

This leaves us with a two-tiered system for duplicates. If our %RPD is below the values from our equation (*i.e.*, below the curve), we accept both data points as valid. If the %RPD exceeds the %RPD from the equation, we don’t know which value to believe is correct, the sample or the duplicate value, so we must reject (“R” qualify) both data points. At that point, particularly if multiple duplicate pairs have been rejected, the sampler(s) should look into possible causes for the disagreement and work to minimize those causes for future sampling.

**Paired Parameters** – There are some parameter pairings that DES evaluates (using %RPD) in tandem, since they are related. We can make use of these assessments too. Some parameters are fractions or subsets of others, such as nitrate being part of nitrate/nitrite, so that the one parameter should, in theory, never have a higher concentration than the other parameter. Examples of paired parameters are below:

**TOC ≥ DOC**

**Nitrate/Nitrite ≥ Nitrate**

**Total P ≥ orthophosphate (or dissolved reactive phosphorus)**

**Total Cr ≥ Hexavalent Cr**

**TKN ≥ Ammonia**

**BOD ≥ Dissolved BOD (or other dissolved parameter pairings)**

It’s theoretically possible that the subset analyte could be 100% of the total (or larger) analyte, but any result where that compound exceeds the total (or larger compound) should be considered an estimated concentration (qualified with a “J”). Results that are quite close may be essentially the same number and valid for most data uses. Similar to how we evaluated duplicate samples above, we will use the same equation to determine the acceptable %RPD for “Paired Parameters” analytical results within the same sample.

For “Paired Parameters” with a %RPD less than the equation amount (using an average Detection Limit this time, since they may be different), we will simply acknowledge the difference with a “J” qualifier, leaving both data points as useable for most applications. However when the %RPD exceeds the amount from the equation, we will generally not use the two data points and reject (qualify with an “R”) the results. In this situation we don’t know which result to believe and they are too different for us to be comfortable with the variability

present. This all applies only when the subset parameter has a higher concentration than the expected larger/parent parameter. If the subset parameter has a lower concentration, then no evaluation/qualifiers are needed.

Example data for “Paired Parameters” assessed using the maximum %RPD equation:

$$Y = [(0.9465x^{-0.344}) * 100] + 5 \text{ (where } x \text{ is the sample concentration/DL and } Y \text{ is the max. \%RPD).}$$

Subset parameter – example concentration	Parent (larger) parameter –example concentrations	Subset DL (DES webpage*)	Parent DL (DES webpage*)	Average DL	%RPD (Parent and Subset)	Max. Allowed %RPD (from the eqn.)	Data Qualifier
Cr +6 – 3.6	Tot. Cr – 3.5	3.4 ug/L	0.28 ug/L	1.8 ug/L	2.82	75.87	“J”
Cr +6 – 7.5	Tot. Cr – 3.5	3.4 ug/L	0.28 ug/L	1.8 ug/L	72.73	75.87	“J”
Cr +6 – 7.8	Tot. Cr – 3.5	3.4 ug/L	0.28 ug/L	1.8 ug/L	76.11	75.87	“R”
Cr +6 – 24	Tot. Cr – 16	3.4 ug/L	0.28 ug/L	1.8 ug/L	40.0	44.98	“J”
Cr +6 – 26	Tot. Cr – 16	3.4 ug/L	0.28 ug/L	1.8 ug/L	47.62	44.98	“R”
Cr +6 – 16	Tot. Cr - 26	3.4 ug/L	0.28 ug/L	1.8 ug/L	47.62	38.06	None (par>sub)

*\* Detections limits may change annually - check the current DES intranet page for current values associated with your data.*

**Sample Holding Time** – This is an important QC item that is easily checked on any data set. Generally, DES will note any holding time discrepancy but it’s still worth some discussion. With some parameters, like a total result for a metal, slightly exceeding the holding time may make little or no difference (and would likely result in only a “J” qualifier being added to the result in the reported concentration. But for other parameters missing the holding time would generally lead to complete rejection (“R”) of that data.

The amount of the holding time exceedance can be evaluated relative to the total holding time, shorter times lead to lower tolerance of exceedances (as a result of less stable analytes). It can also be situation dependent – in some cases a one day exceedance for a 28 day holding time may be acceptable and other times, not so. Alternately a one day exceedance for a metals sample would likely make no difference (but we’d likely “J” qualify it as an acknowledgement of the exceedance – and for most situations we will use “J” qualified data anyway).

***Subsection I2. Reserved for other Data Management Topics in the future.***

## SECTION J. LITERATURE CITED

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