# WATER QUALITY PROGRAM

# STANDARD OPERATING PROCEDURES

# FOR WATER QUALITY SAMPLING

Revision V

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November 2025

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## WATER QUALITY PROGRAM DESCRIPTION

This document outlines standard operating procedures (SOP) for field water quality sampling conducted by the Water Quality Program (WQP).

The WQP standards team routinely monitors South Dakota rivers and streams through the Ambient Water Quality Monitoring (WQM) network. The standards team may also collect water samples and data during Use Attainability Analyses (UAAs), fish kill investigations, complaint investigations, and special short-term monitoring projects. The WQP permit team may also collect water samples during routine facility inspections, compliance sampling, and complaint investigations.

Environmental data collected by the WQP may be used to determine 1) trends in water quality, 2) support of beneficial uses and water quality standards, 3) compliance with permit conditions, and/or 4) causes/sources of pollution. More information regarding WQP sampling activities is available in the Quality Assurance Project Plan for the Water Quality Program (WQP QAPP).

## PRE-SAMPLING PROCEDURES

WQP personnel conduct sampling work to meet a variety of goals, each requires pre-planning to ensure the data is appropriate and useful. The planning phase involves refining the sampling scope to meet specific objectives. Common pre-sampling steps include:

1. Identify the objectives for sampling.
2. Review any existing data for the site/waterbody to be sampled.
3. Identify additional data requirements, such as sample types, parameters, and frequency.
4. Examine maps and diagrams of the area to be sampled.
5. Make a list of proposed sampling sites.
6. Check the operation of all required sampling equipment.
7. Gather all required sampling equipment, sample bottles, forms, documents, field books & apps.
    a. Sample bottles may be obtained from the lab that does the analysis. It is usually best to use the “A bottle” or a triple rinsed “field bottle” to fill pre preserved bottles.
    b. Deionized (DI) and “Polished” water may also be sourced from the lab.
8. Notify relevant parties such as landowners, businesses, city, state, federal, or tribal agencies.
9. Secure permission to access private property if you need to work outside the road right-of-way.
10. Check out the sites and general area/waterbody to be sampled before collecting samples.
11. Determine if the plan for sampling requires revision; and
12. Conduct sampling activities.

## DOCUMENTATION AND REPORTING

### A. Documentation

Accurate field documentation is essential. WQP personnel must record sampling activities using the Survey123 App, a field notebook and/or pre-printed project forms. It is recommended that all field notebooks and preprinted project forms be waterproof. A standard format for field notebook recordkeeping is not required. All field records should include the following:

#### 1. Survey123 App/Field notebook

a. Date and time.
b. Station ID (unique identification).
c. Station location (street #, avenue #, driving directions, WQM number, or GPS location).
d. Types of meters being used.

e. Enter meter calibration readings into Survey123 App. If Survey123 isn't working enter data in a field notebook so it can be entered into App later.
f. Comments regarding meter maintenance, damage or difficulty in operation/calibration.
g. Conditions that could impact water quality (high wind, rainfall, runoff, temperature).
h. Velocity or discharge measurements (if flow measurements are taken).
i. The following field measurements are recorded for every sample site based on equipment used (if not recorded, the rationale should be documented):
    i. water temperature
    ii. pH
    iii. specific conductance
    iv. dissolved oxygen
j. Fish size, length, species, number and photo vouchers for iNaturalist (when collected).
k. Fish collection method (equipment used, date/time set, length of stream segment, etc.).
l. Method of biological sample collection (net type, sampling equipment, depth, etc.).
m. Upstream and downstream photos. Discuss and identify all photographs (Take extra photos as needed or necessary for documentation).
n. Document site conditions/visual observations (riparian vegetation, bank and stream bottom, stream incision and definition, water appearance, flow, public access).
o. Document the name of any individual encountered during sampling and summarize the conversation along with any pertinent information.

2. Pre-printed project sheets

a. Completely fill out all applicable "blanks" on any pre-printed project forms.
b. Information discussed in section (1. Survey123 App/Field notebook) should be gathered for each project as needed.

3. Laboratory sheets and bottle labels

A DANR Water Quality Data Sheet (see Figure 6. Page 15) must be filled out completely and submitted with all laboratory samples. This provides the laboratory with information about the water sample and directs the laboratory on which analyses are requested. All bottles must be labeled prior to sample collection. At a minimum, the label must include the station identification, sample date, sample time, and bottle identification (Bottle "A"). The bottle will get wet, so ensure that bottle labels and marking pen or pencil are water resistant so the label stays affixed, and the ink does not run (see Figure 7. Page 15). To print lab sheets and labels go to: R:\Work\DENR WQ Lab Sheets\ DENR_HL_Datasheets.mdb

## B. Reporting

Data collected because of sampling is recorded in the following ways:

1. Recorded in proper database, hardcopy or electronic copies of data are also maintained.
2. Recorded in reports.
3. Hard copies or electronic hardcopies filed.

## INSTRUMENT/EQUIPMENT CALIBRATION, CARE, AND OPERATION

All field instruments must be inspected and calibrated prior to use. Operate instruments according to manufacturer specifications. If problems with any field instrument are encountered, the user should consult the manufacturer's manual, the project manager, and/or call the manufacturer. Calibrations and instrument observations must be recorded in the calibration logbook or Survey123 App prior to field use. The following is calibration procedures and operating instruction information.

## A. Multimeter – YSI ProQuatro

**Record each step of calibration in the Survey 123 App under Probe Calibration.**
Always calibrate the multimeter in the following order, Specific Conductance, pH, ORP (if needed), and DO. The meter should always stay connected to the probe bulkhead. Use fresh calibration solutions with each calibration. Do not leave meter in vehicle as exposure to extreme heat and freezing will wreck electronics and probes.
YSI ProQuatro User Manual at: 606962-ProQuatro-User-Manual-English.pdf

### To Begin Calibration

1. Turn the meter on using the green button located on the bottom right of keypad (hold button in for a few seconds).
2. Open Survey123 app on iPhone. Open Probe calibration, Press Collect, press Probe and check the Probe ID of the meter you are using and Sampler.

### Specific Conductance Calibration

1. Press the Cal key.
2. Arrow down to highlight Conductivity and press enter. Next menu, the option highlighted, Specific Conductance is the one needed, so press enter. Another sub-menu will require you to select the calibration units. Microsiemens per centimeter or uS/cm is the unit needed and is already highlighted so press enter.
3. Triple rinse meter probes using conductivity standard in the calibration cup.
4. Fill the calibration cup approximately ¾ full of conductivity standard. This way when the probes are placed in the calibration cup it will be full. The port on the side of the probe must be completely submerged in conductivity standard to function correctly.
5. Enter the calibration solution value by highlighting Calibration Value, press enter, then using the alpha/numeric keypad to enter the known value. Once you have entered the value of the calibration standard, highlight <<ENTER>> and press enter.
6. When temp is stable, highlight Accept Calibration and press enter to calibrate. Enter the Post-Specific Conductance value (should be the same as the calibration solution used).
7. To get Cell constant, press the File button and scroll down to View Calibration Records, press enter. Now highlight Conductivity, press enter. Scroll down a few lines to find it.

### pH Calibration (2 point)

1. Press the Cal key. Arrow down to ISE1 (pH), press enter (always start with pH 7).
2. Triple rinse meter probes using pH 7 buffer solution in the calibration cup.
3. Fill the calibration cup approximately half full of pH 7 buffer.
4. Insert probe into the pH 7 solution, making sure the pH sensors glass bulb is submerged. Allow temperature and mV readings to stabilize.
5. The YSI should automatically recognize the buffer value, compensate for temp, and display it at the top of the screen. The pH solution should include a chart of solution values per temperature. Confirm the automatic value is correct from this chart. If not correct enter the pH buffer value by highlighting Calibration Value, pressing enter, and then using the alpha/numeric keypad to enter the known value. Once you have entered the value of the calibration standard, highlight <<ENTER>> and press enter.
6. Wait for the pH and pH mV readings to stabilize (normally 20-30 seconds, can take a couple minutes as probe gets older). Enter pre, post, and mV readings in Survey123. When the readings stabilize, highlight Accept Calibration and press enter to calibrate.
7. Triple rinse meter probes using pH 10 buffer solution in the calibration cup.

8. Fill the calibration cup approximately half full of pH 10 buffer.
9. Insert probe into the pH 10 solution, making sure the pH sensors glass bulb is submerged. Allow temperature to stabilize.
10. The YSI should again recognize the buffer, compensate for temp, and display it at the top of the screen. The pH solution should include a chart of solution values per temperature. Confirm the automatic value is correct from this chart. If not correct enter the pH buffer value by highlighting Calibration Value, pressing enter, and then using the alpha/numeric keypad to enter the known value. Once you have entered the value of the calibration standard, highlight <<ENTER>> and press enter.
11. Wait for the pH and pH mV readings to stabilize (normally 20-30 seconds, up to a couple minutes as probe gets older). Enter pre, post, and mV readings in Survey123. Once stable, press Accept Calibration followed by Finish Calibration to complete calibration.

## Oxidation-Reduction Potential (ORP) Calibration

1. Press the Cal key. Arrow down to highlight ISE2 (ORP), press enter.
2. Triple rinse meter probes using ORP calibration solution in the calibration cup.
3. Fill the calibration cup so that the ORP sensor tip is submerged in solution.
4. The ORP solution should include a chart of solution values per temperature. Enter the correct ORP mV value from the chart by highlighting Calibration Value, pressing enter, and then using the alpha/numeric keypad to enter the known value. Once you have entered the value of the calibration standard, highlight <<ENTER>> and press enter.
5. Wait for the readings to stabilize. Enter ORP pre and post values in the Survey123 app. Then press enter to accept the calibration.

## Dissolved Oxygen (DO) Calibration

1. Press the Cal key.
2. DO is highlighted so press enter. Next menu, the option highlighted DO% is the one needed so press enter. The galvanic DO sensor does not need a warm-up time.
3. Triple rinse meter probes using water in the calibration cup.
4. Place a small amount of water (1/8 inch) in the calibration cup and loosely screw the cup on the probe to ensure atmospheric venting. This creates a saturated environment which should be close to 100%. Do not submerge DO and temperature probes in water.
5. Verify the barometric pressure and salinity displayed are accurate. Salinity should be 0.00 ppt and if not rinse the probes and calibration chamber again. Once DO and temperature stabilize, enter all required data in the Survey123 app.
6. Highlight Accept Calibration and press enter. Calibration is complete. Don't forget to submit Survey123 app calibration.

## Taking a Measurement

After calibration, the meter is ready for use. Do the following to collect water quality data:

1. Screw on the weighted probe guard to protect probes from damage. Place in the water to be sampled. Be careful the probe does not get in mud and flow of water is sufficient to overcome oxygen consumption by the DO probe (swirl the probe in the water if flow is inadequate). Allow the meter sufficient time for the readings to stabilize, especially ORP.
2. Log One Sample is already highlighted after calibration or when you turn on the meter.
3. Allow the meter readings time to stabilize in water. Electronically record the measurements by pressing "ENTER" once, bringing up a submenu, and then pressing "ENTER" on Log Now. The measurement is stored in a data file in the YSI ProQuatro.

4. To find logged data press File, then highlight View Data, press enter. Scroll down to Show Data, press enter. Then scroll down to the sample date, toggle arrow to the right to see logged data. Record the measurements in Survey123 App, field logbook, or datasheet. If a water quality sample is also being submitted, record the measurement information on the lab sheet. Hold power button down for a few seconds to power off.

### B. Flow meter – SonTek FlowTracker

This flow meter is used to calculate stream flow or discharge. This meter uses sonar to detect water velocity. The operator inputs the location (on the tape line) and depth so the unit may calculate discharge. For best results and to reduce errors, select an area of the stream with minimal water turbulence and minimal underwater obstacles (rocks, algae, plants). A slower, less turbulent segment of the stream with a flat bottom is ideal. Take care to minimize disturbing sediment on the bottom of the stream bed as this can cause sonar errors. Refer to Figure 1. SonTek/YSI FlowTracker Handheld ADV Technical Manual (uvm.edu)

1. Attach the sonar probe to the wading rod and tighten the set screw.
2. Set up a tape line. While standing in the water facing downstream, the “right bank” is on your right side. This is the side where you will start.
3. On the right bank, use a stake to place the start of the tape line. Stake the tape line high enough up the bank so that the tape does not get in the stream and place in soil secure enough so that the line may be taut.
4. Cross the stream to the left bank allowing tape to reel out. Secure the end of the tape line to the left bank with a stake. Note the measurement of the tapeline at the edge of the left bank. Subtract the measurement of the starting edge on the right bank to determine the stream width. It is ideal to measure 10 to 20 stations (locations) at equal intervals so that no more than 10% of stream discharge is represented at any one stream location. This may not be possible on very narrow streams. At a minimum, measurements may be made every 3 inches. For example, the tape line measures 6.5 feet at the right bank shore and 32 feet at the left bank shore. Subtracting 6.5 from 32 results in a stream width of 25.5 feet. To prevent greater than 10% stream discharge in any one stream location, at least 10 stations should be measured. 25.5 feet divided by 10 stations would result in increments of 2.5 feet. However, to prevent greater than 10% discharge in any one station measurement, increments of 1.5 or 2 feet may be more appropriate. Determine the station intervals based on stream width.
5. Turn on the FlowTracker meter. The startup screen will appear.
6. Press the “ENTER” button. The Main Menu will display.
7. Press the “3” button to start the data run. This will take you to the data file name screen.
8. Press the “1” button to input the station name (StationID if it fits). Input a unique name. The name can only be 8 characters maximum, so you may need to abbreviate. Press the “ENTER” button once the name is input.
9. Press the “9” button to accept the name.
10. Press the “9” button again to start the data run. At this time the display message will read “Press QC Menu at any time for Gauge data Enter to continue.” Press “ENTER.”
11. The Automatic QC Test will appear. A QC test must be conducted once each day that the flow meter is used. Press “1” to run test or “2” to skip the test. If running the test, a message will display to “Put probe in moving water away from any underwater objects. Press Enter to start. Following those instructions, place the probe/wading rod in the water so that the direction of the flowing water is perpendicular to the direction of the

sonar. Make sure there are no underwater objects such as plants, rocks, or debris. Hold probe/wading rod still and upright. Press the "ENTER" button. The meter will begin a self-diagnostic QC test. Only proceed if the QC test passes the self-diagnosis.

12. The Starting Edge screen will appear. At the right bank, locate the measurement on the tapeline of the edge of the water. Press the blue "Set Location" button and use the numeric keys to enter the measurement of the tapeline at the edge of the water.
13. Press the gray "Next Station" button. This will take you to Station 1 – which correlates with the location on the tape line. The location of Station 1 may need to be adjusted based on the stream width. The first station (Station 1) and the last station measured on the left bank must be half the interval of the rest of the stations. This is to accommodate for slope of the stream from the stream edge to the first and last station. To adjust the location of Station 1, Press the blue "Set Location" button and manually enter the appropriate location. Go to that location on the tape line.
14. Press the blue "Set Depth" button and use the numeric keys to enter the depth of the water based on the stream depth measurement on the wading rod at Station 1.
15. Holding the meter still and upright, press the blue "Measure" button. The meter will begin taking measurements or "pings." If there are any errors, correct the source of the error if possible and repeat the measurement. It may take several attempts per station. Press "1" to accept the measurement or "2" to repeat the measurement.
16. Once you accept the measurement, the meter will go to Station 2 and so forth. At each station, you must verify you are at the appropriate location on the tape line and enter the appropriate depth based on the measurement on the wading rod.
17. After the last station has been recorded, press the gray "End Section" button. The screen will display a prompt to press "End Section" again to end the section. The Ending Edge screen will display. Press the blue "Set Location" button and key in the corresponding location of the left edge on the tapeline.
18. Press the gray "Calculate Disch." button. The screen will display a prompt to press the Calculate Discharge button again to confirm. Press the "Calculate Disch." button again.
19. The meter will display information. Press the "Enter" button to continue viewing data. Press the "0" button to exit. Important: After viewing the data, you must press the "0" button to exit for your data to be saved.
20. Record the flow discharge measurement in cubic feet per second in Survey123 app, field logbook, or pre-printed data sheet.

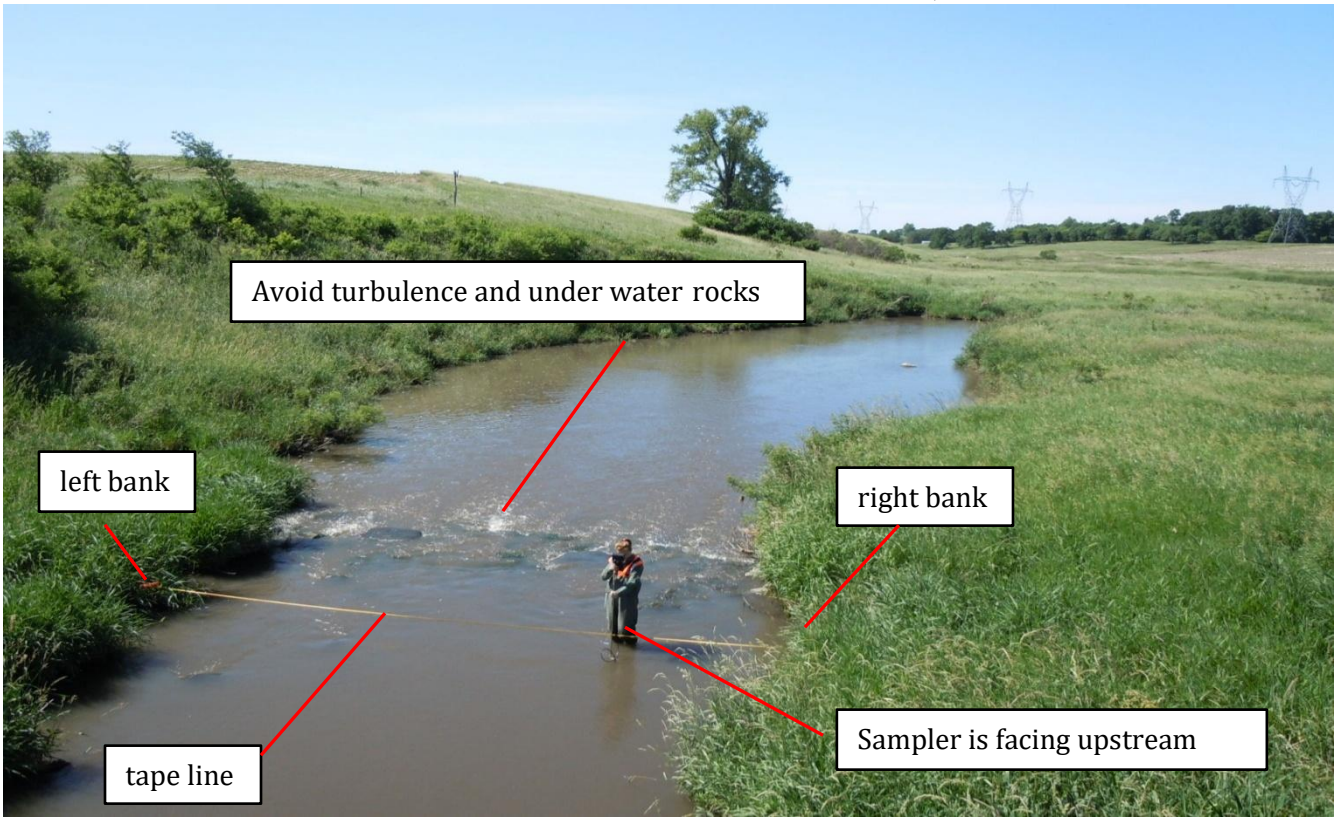



Figure 1. Taking a flow measurement with SonTek FlowTracker.

## LABORATORY SHEETS AND CHAIN-OF-CUSTODY

Most samples collected for ambient monitoring, fish kills, complaints, and other sampling projects do not need complete custody documentation. However, under certain conditions, such as compliance investigations, DANR must be able to prove that any analytical data offered into evidence accurately represent environmental conditions existing at the time of sample collection. Due to the evidentiary nature of such samples, possession must be traceable from the time the samples are collected until they are introduced as evidence in legal proceedings. It must be clearly demonstrated that the involved samples were not tampered with during collection, transfer, storage, or analysis. DANR chain-of-custody protocols and procedures are described below.

### Documentation

To maintain and document sample possession, follow these chain-of-custody procedures.

1. Sample Custody - A sample is considered in custody under one of the following conditions:
    a. It is in your direct possession (you are holding it).
    b. It is in your direct line-of-sight after being in your possession (you can see it).
    c. It was in your possession; you locked it up or placed it in a sealed container to prevent tampering (no one can access the sample without leaving evidence of access, e.g. seal broken, tape removed, etc.).
    d. It is in a designated, secure area (typical evidence holding area).
2. Field Custody
    a. The project officer will advise lab personnel that a sample requiring chain-of-custody will be collected and will specify the approximate date and time that it will arrive at the lab. In

instances where date and time are not known in advance of a field trip, the lab should be notified as soon as possible about the arrival of such samples.

b. The samples must be collected in accordance with required and established methods set forth in this SOP, the Quality Assurance Project Plan (SWQ QAPP), and 40 CFR Part 136 (or other applicable section).

### Transfer of Custody

1. To establish the documentation necessary to trace sample possession, chain-of-custody record (refer to DANR WQP QAPP) must be filled out on the SD DANR Water Quality Data Sheet and accompany each set of samples. The record should accompany the water quality data form and the samples to the laboratory. This record tracks sample custody transfers between the sampler and laboratory analysts. At a minimum, the record should contain:
   a. The StationID or sample identification.
   b. The signature of the collector and witnesses when present.
   c. The date and time of collection; place and address of collection.
   d. Substances sampled.
   e. Signatures and dates involved in the chain of possession (can also include time).

All chemical water samples collected using this SOP utilize the DANR Water Quality Data Sheet (commonly referred to as the lab sheet) or Fish Flesh Chain of Custody (refer to SD DANR WQP QAPP for these forms) as the laboratory data sheet and chain-of-custody document. When properly signed by all affected personnel, the SDDANR Water Quality Data Sheet and Fish Flesh forms comply with chain of custody requirements.

1. Samples will be packaged properly for shipment and dispatched to the appropriate laboratory for analysis. The samples for each shipping container shall be placed in the large plastic bags provided by the laboratory.
2. If samples are split with a source or government agency, it will be noted in the remarks section of the Chain-of-Custody Record. The note should indicate with whom the samples are being split and be signed by both the sampler and recipient.
3. Each transfer of sample custody must be documented on the Chain-of-Custody Record.
4. The Chain-of-Custody Record identifying its contents will accompany all shipments. The original record will accompany the shipment, and the project officer will retain a copy and place it in the project file.
5. The laboratory should have assigned laboratory receiving personnel who are responsible for overseeing the reception of all controlled custody samples.
6. When the samples are not in the immediate possession of the individual having official custody, they must be kept in a locked enclosure.
7. After the laboratory has completed the sample analysis, the Water Quality Data form and the Chain-of-Custody record will be returned to the appropriate program. These items will be kept on file for at least five years. Access to the Chain-of-Custody file is limited to program personnel.

### Delivery or Shipment of Samples

Samples must be packed in coolers on loose ice for shipment or delivery to the laboratory. You must include appropriate paperwork. Make sure the container does not leak, and all shipping or delivery labels are legible. Generally, samples need to be chilled to less than 6° Celsius. Make sure there is adequate ice in the cooler to keep samples chilled during transit.

1. Completely fill out a DANR Water Quality Data Sheet (see WQP QAPP) for each site.

2. If the samples are being shipped or sent with the courier, place all sample containers in a large plastic bag. Add loose ice to the bag and tie closed inside the shipping cooler.
3. Make sure that all DANR Water Quality Data Sheets are filled out completely. Seal datasheets in a Ziploc before putting them on top of the samples in the shipping cooler.
4. Securely seal the cooler with packing tape.
5. Shipping coolers are shipped via mail (USPS, FedEx, etc.), delivered by the courier, or delivered by the sampler to the appropriate laboratory.

## QUALITY ASSURANCE

### General Information and Handling Procedures

This section is supplemental to quality activities and requirements outlined in the WQP QAPP. Refer to WQP QAPP for specific info on data objectives, quality activities, and corrective actions.

1. If sampling multiple sites in a day, try to begin with the cleanest sites and progress to more polluted ones to minimize the risk of cross-contamination from equipment (waders or meters).
2. Sampling equipment (meters, graduated cylinders, field bottles, etc.) should be triple rinsed with water from the waterbody being sampled prior to collecting the water sample.
3. The sample container and preservation must be appropriate to the sampled parameter. See figures 3, 5, and 6.
4. Field instrumentation must be calibrated before use. Calibration frequency is outlined in the WQP QAPP. Calibration ensures proper function and compliance with manufacturer specifications. All calibrations must be recorded in Survey123 app or a calibration logbook.
5. If field equipment cannot be calibrated or is malfunctioning, the sampler should attempt on-site repairs. For individually assigned meters, such as regional staff, that person is responsible for the maintenance. In Pierre, the designated sampler, identified in the WQP QAPP is responsible for maintenance, repairs, ordering parts or service for field equipment.
6. All WQP field equipment will be examined for proper operation, maintenance, and repair; this information is recorded in the Survey 123 app. Repair and/or maintenance are done prior to instruments next use.

## LABORATORY ANALYTICAL METHODS

Water Quality Program, analytical procedures to determine conformity with water quality standards are made in accordance with methods approved in 40 CFR Part 136. The project officer ensures the lab uses approved analytical methods listed in 40 CFR Part 136 for all WQP water samples.

## SAMPLE CONTAINERS, PRESERVATION AND HOLDING TIMES

Appropriate sample containers, preservation techniques, and holding times for water quality samples are listed in 40 CFR Part 136. The project officer ensures appropriate sample containers and preservation techniques are used during sample collection. The laboratory manager must ensure the water sample is analyzed within appropriate holding time. However, the project officer should verify that the holding time was met as a part of standard quality control practices (see WQP QAPP).

In addition to sample container, preservation, and holding time information, 40 CFR Part 136 places additional requirements on some tests in the form of footnotes. These footnotes are important and are a required step in achieving meaningful results.

Figure 2 displays common test parameter suites used by the WQP, and the appropriate container type, preservation requirement, and maximum holding time for the parameter with the shortest holding time in that bottle. For individual parameter holding times, refer to 40 CFR 136. As appropriate, footnotes are included and their action described at the bottom of the table.

**Figure 2. Sample Parameter Suites and Information**

| Bottle | Size & Material | | Preservative | Parameters | Holding Time[4] |
|---|---|---|---|---|---|
| A | DOH | 1000 mL HDPE | Cool to 6°C | Alkalinity, total solids, TSS, volatile solids, TDS, BOD, CBOD, $CO_3$, Hardness, K, lab pH, lab conductivity, nitrate, chloride, fluoride, $HCO_3$, $SO_4$ | 48 hours |
| | Midco | 500 mL polypropylene | | | |
| B | DOH | 1000 mL HDPE | 2 mL $H_2SO_4$ pH <2 Cool to 6°C | Ammonia, Nitrite+Nitrate, TKN, Total P, COD | 28 days |
| | Midco | 500 mL polypropylene | | | |
| C | DOH | 100 mL sterilized polystyrene | $Na_2SO_3$ if chlorinated Cool to 6°C | Fecal coliform, *E coli*, total coliform, enterococci, fecal PFG | 6 hours[1] |
| | Midco | 100 mL sterilized polystyrene | | | |
| D | DOH | 100 mL polystyrene | Field filter 0.25 mL $H_2SO_4$ pH <2 Cool to 6°C | Dissolved P, dissolved inorganic nitrogen | 28 days |
| | Midco | 250 mL polypropylene | | | |
| Metals – Dissolved | DOH | 250 mL polypropylene | Field filter Cool to 6°C | Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Cu, Hg, Pb, Mg, Mn, Ni, Se, Ag, Na, Ti, U, Vn, Zn, Fe, Mo, fluoride, K, Cl, silica. Acid preserved by the lab before 14 days. | 28 days |
| | Midco | 250 mL polypropylene | | | |
| Metals – Total Recov | DOH | 250 mL polypropylene | Cool to 6°C | Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Cu, Hg, Pb, Mg, Mn, Ni, Se, Ag, Na, Ti, U, Vn, Zn, Fe, Mo. Acid preserved by the lab before 14 days. | 28 days |
| | Midco | 250 mL polypropylene | | | |
| Oil & Grease | all | 1000 mL amber glass | 2 mL HCl pH <2 Cool to 6°C | Oil & Grease | 28 days |
| R | all | 1 gal cubitainer polypropylene | Cool to 6°C | Radium-226, radium-228 | 6 months |
| CN | DOH | 125 mL brown polypropylene | NaOH pH>10 Cool to 6°C | Total cyanide, Free cyanide, WAD cyanide *Mitigate interferences as described in 40 CFR136 | 48 hours[2] |
| | Midco | 125 mL brown polypropylene | | | |
| H | all | 1000 mL amber glass | Cool to 6°C | TPH – diesel, caffeine | 14 days[3] |
| V | DOH | 40 mL amber glass vial | Cool to 6°C | VOC, TOC, DOC (125 or 250 mL amber glass and lab filtered & preserved within 48 hours), TPH -gasoline | 14 days[3] |
| | Midco | 40 mL amber glass vial | | | |

**To sample for an analyte that is not on this list – contact the lab for bottle, preservation, and holding time information.**

[1]The holding time for bottle C parameters is 6 hours for compliance samples. Noncompliance samples must be analyzed within 24 hours of collection. [2]The maximum holding time for total and WAD cyanide is 14 days as long as all interferences have been mitigated as described in 40 CFR 136. If interferences are unknown the maximum holding time is 6 hours. 40 CFR 136 may be viewed at http://www.ecfr.gov. [3]The holding time for bottles H and V is 14 days from the time of collection to laboratory extraction. [4]Maximum holding time is based on the analyte with the shortest hold time.

## DECONTAMINATION OF SAMPLE CONTAINERS AND SAMPLING EQUIPMENT

The laboratory provides new containers or decontaminates previously used sample containers. Sample container decontamination by the laboratory involves detergent washing, rinsing with dilute chromic acid and final rinsing with laboratory-grade distilled water. Decontamination of sampling equipment (probes and instruments) will be accomplished by triple rinsing with the calibration solution, distilled, tap, or blank water as appropriate by field personnel.

Field personnel do not need to triple rinse clean, sterile, or pre-preserved bottles supplied by the laboratory. However, when using a field bottle to collect a sample then transports it to another container, the field bottle must be triple rinsed with the water being sampled prior to filling.

## PROCEDURES FOR SURFACE WATER SAMPLING

### A. Field Observations

Record all field observations of conditions at the sampling sites that could influence the water quality of the collected sample. These observations are recorded on pre-printed project sheets, field logbook, or Survey 123 app. Examples of observations recorded under COMMENTS could include: “cloudy, recent rainfall, windy, cattle in stream, dense cattails present at sampling site, etc.”

In addition to comments, specific observations should be recorded as follows:

| | |
|---|---|
| Flow- | Record in cubic feet per second (cfs) |
| Specific Conductance- | Record in micromhos per centimeter (umhos/cm) |
| Dissolved Oxygen- | Record in milligrams per Liter (mg/L) |
| Field pH- | Record in standard units (su) |
| Water Temperature- | Record in degrees Celsius (C) |
| Secchi- | Record in meters (m) |
| ORP- | Record in millivolts (mV) |

### B. Field Analyses

Calibrate all instruments prior to field use as described in Section 4.0. Record all field data on pre-printed project sheets, field logbook, or Survey 123 App.

1. DO, pH, ORP, specific conductance, and temperature
    a. If water is static, provide stirring by gently swishing the probe back and forth. This is especially important for DO.
    b. Allow sufficient time for the probe to stabilize.
    c. Record data in Survey123 App or field logbook and pre-printed lab sheet.
2. Secchi Depth
    a. Lower the Secchi on a calibrated rope into the water on shaded side of the boat.
    b. Drop the Secchi down until it is no longer visible.
    c. Bring the Secchi up until you can just barely make out the cross pattern.
    d. Record the depth of the Secchi Disk in meters. Repeat the above procedure and average the two readings for the final Secchi depth reading.
3. Flow (SonTek)
    a. Calibrate and operate the meter. Instructions found in Section 4.0 of this SOP.
    b. Record the stream discharge in cubic feet per second.

### C. Sample Collection

The types of samples collected during sampling activities depend on the parameters that are necessary for the project. Sample parameters must be determined prior to conducting sampling activities. This will ensure that samples are adequately collected, handled, preserved, and that the

sampling will address the project objectives. Figure 2 displays the parameter groupings, preservation requirements, and bottle type and size information used by the WQP. Figures 4 and 5 are depictions of bottle information and preservation requirements. Figure 3 is a depiction of the disposable filters used to field filter water samples.

In the event a sample needs to be collected, and the necessary information is not contained in Figure 2, refer to 40 CFR 136 or other appropriate chapter for approved methods and information.

When collecting a water sample from a river, stream, lake, or wetland, follow these basic principles:

1. Use the appropriate sample bottle as directed in Figure 2. Affix a waterproof label that contains the station identification, sample date/time, and bottle identification.
2. If sampling a wadable waterbody, wade into the waterbody to collect the sample. Wade into the thalweg or deepest part of the channel to collect the sample. However, it is acceptable to use a dip rid from the bank, bridge it or bucket from a bridge to collect a sample if it is unsafe to wade into the waterbody or for other safety reasons. Do not endanger yourself by wading into unsafe conditions (ice jams, high flows, etc.).
3. If sampling a non-wadable waterbody, access by boat, boat dock, or other method.
4. Face upstream or into the flow when collecting a sample. Remove the bottle lid and submerge the bottle beneath the surface of the water taking care not to disturb the bottom sediment. It is imperative that surface debris or bottom sediment do not enter the bottle. After filling the bottle, secure the bottle lid. Preserve according to Figure 2 and place in a cooler of loose ice (even during winter months).
5. If the bottle is pre-preserved, do not overfill the bottle or rinse the bottle prior to filling. It is ok to use the “A bottle” or a field bottle to fill the pre-preserved bottles.
6. If using a field bottle to collect a sample that will be field filtered, like dissolved metals, make sure you triple rinse with water from the waterbody being sampled before filling.
7. For samples that require field filtering, use 45-micron non-cellulosic disposable filters. See Figure 3 below. Attach the tube from the vacuum pump to the vacuum port on the disposable filter. Remove the filter lid to the filter apparatus and pour an appropriate amount of water into the top of the filter apparatus. The vacuum pump creates negative pressure in the filter apparatus. This will vacuum water through the 45-micron filter into the receiving bottle. Field filtering must be done on site within 15 minutes of sample collection. If the filtering time cannot be met, note it on the lab sheet.
8. Preserve the sample as directed in Figure 2 immediately after sample collection and chemical preservation. If you are unfamiliar with the buffer capacity of the water being sampled (feedlot waste, point source discharges, mining wastewater, etc., may be highly buffered), make sure you verify the pH with pH paper to make sure enough preservative has been added. Place all samples in a cooler with loose ice immediately.

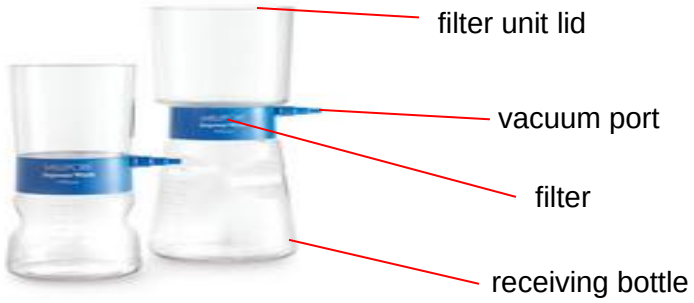



**Figure 3. Disposable Filter Apparatus (Millipore Stericup)**

**Figure 4. Sample Bottles for DOH Laboratory**

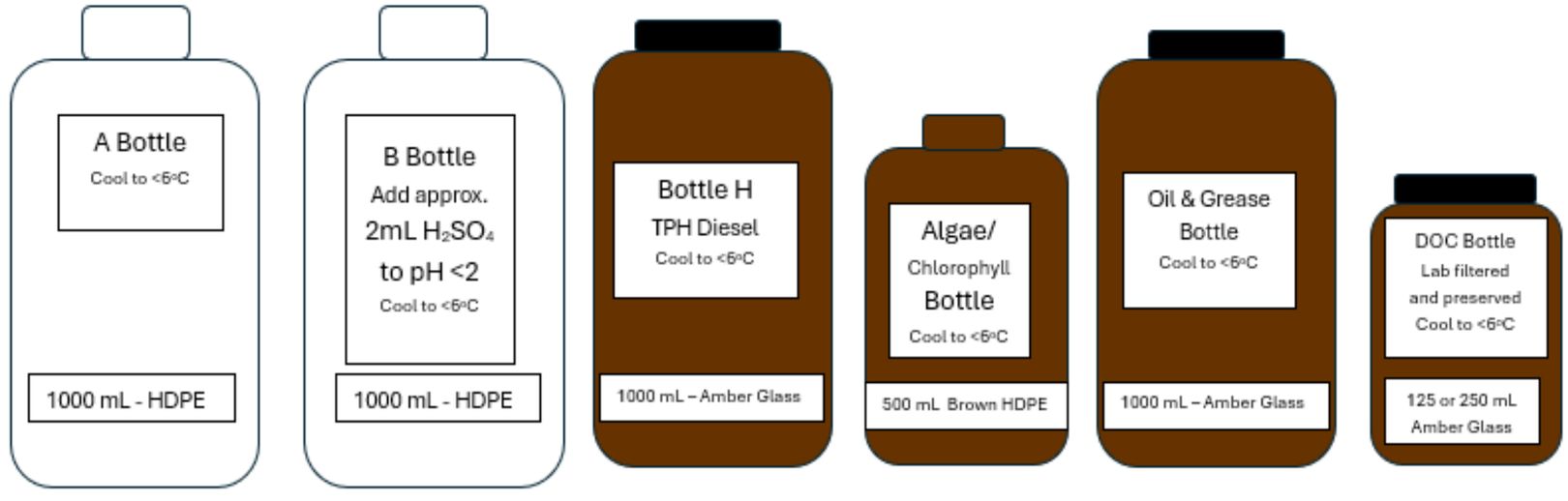
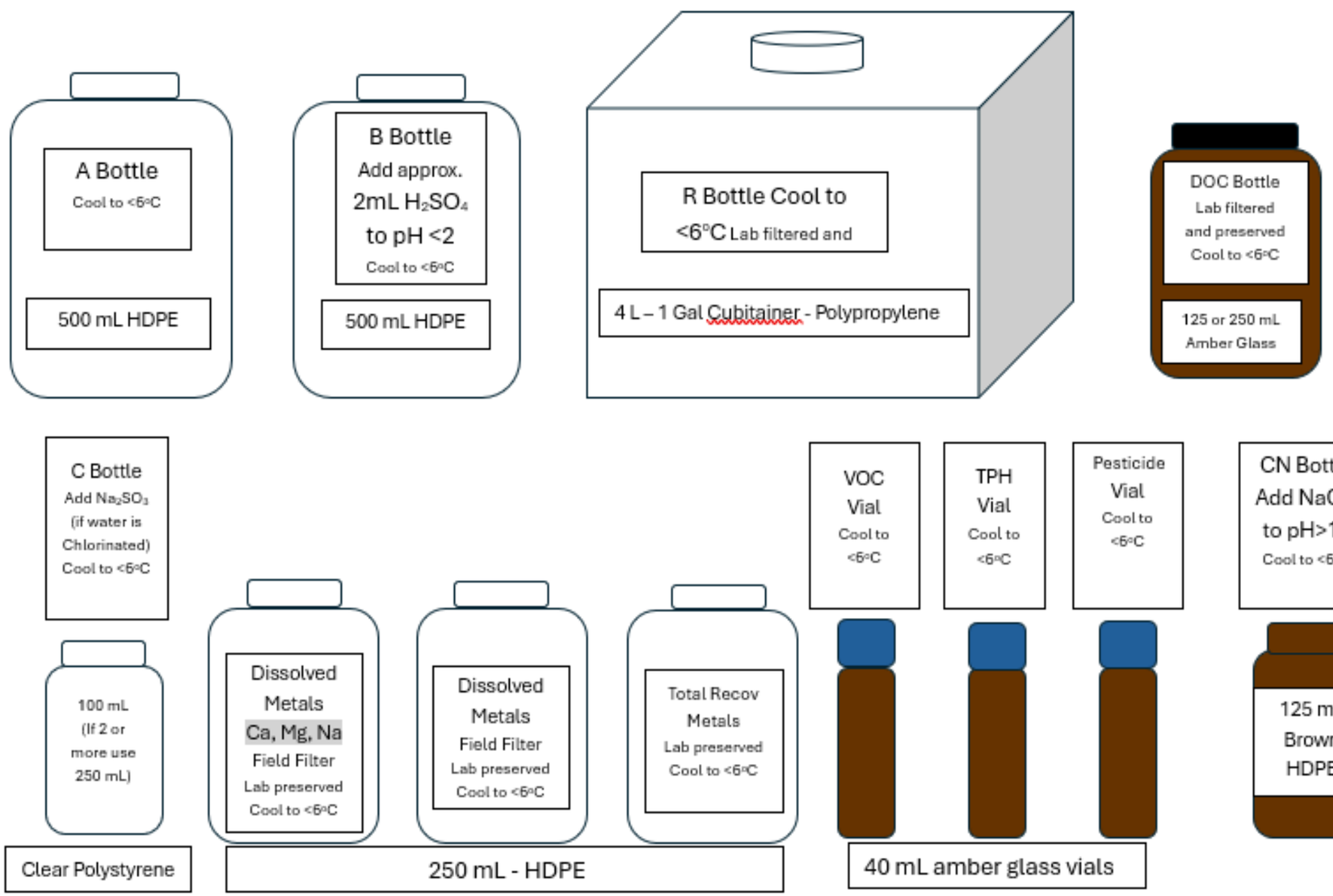
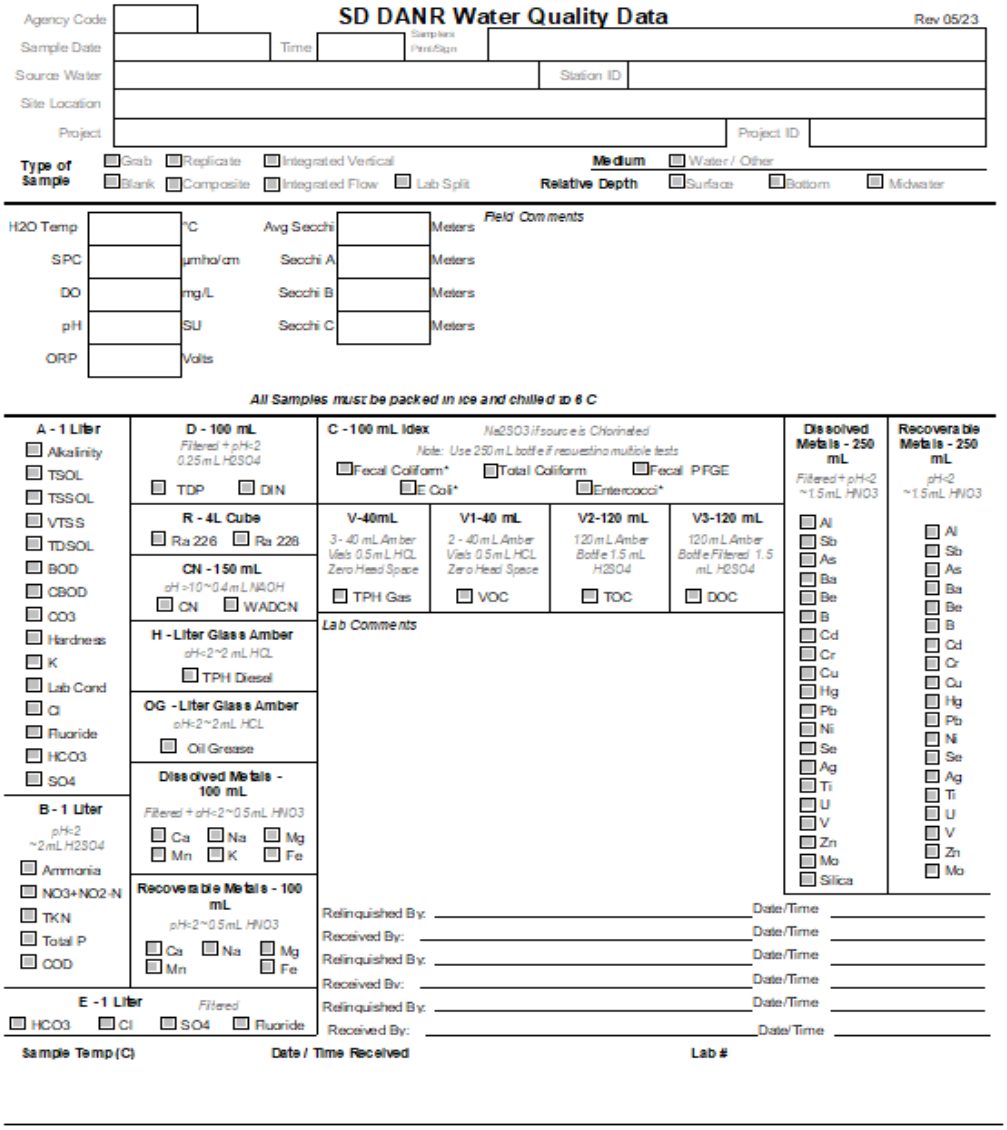


**Figure 5. Sample Bottles for Midcontinent**



## Figure 6. Lab Data Sheet



SD DANR Water Quality Data

Rev 05/23

Agency Code | Sample Date | Time | Sampler's Print/Sign | Source Water | Station ID | Site Location | Project | Project ID

Type of Sample: Grab, Replicate, Integrated Vertical, Blank, Composite, Integrated Flow, Lab Split

Medium: Water / Other

Relative Depth: Surface, Bottom, Midwater

| | | | | | |
|---|---|---|---|---|---|
| H2O Temp | °C | Avg Secchi | Meters | Field Comments | |
| SPC | µmho/cm | Secchi A | Meters | | |
| DO | mg/L | Secchi B | Meters | | |
| pH | SU | Secchi C | Meters | | |
| ORP | Volts | | | | |

All Samples must be packed in ice and chilled to 6 C

**A - 1 Liter**
- Alkalinity
- TSOL
- TSSOL
- VTSS
- TDSOL
- BOD
- CBOD
- CO3
- Hardness
- K
- Lab Cond
- Cl
- Fluoride
- HCO3
- SO4

**B - 1 Liter** pH<2 ~2mL H2SO4
- Ammonia
- NO3+NO2-N
- TKN
- Total P
- COD

**D - 100 mL** Filtered + pH<2 0.25mL H2SO4
- TDP
- DIN

**R - 4L Cube**
- Ra 226
- Ra 228

**CN - 150 mL** pH >10~0.4mL NAOH
- CN
- WADCN

**H - Liter Glass Amber** pH<2~2 mL HCL
- TPH Diesel

**OG - Liter Glass Amber** pH<2~2mL HCL
- Oil Grease

**Dissolved Metals - 100 mL** Filtered + pH<2~0.5mL HNO3
- Ca, Na, Mg, Mn, K, Fe

**Recoverable Metals - 100 mL** pH<2~0.5mL HNO3
- Ca, Na, Mg, Mn, Fe

**E - 1 Liter** Filtered
- HCO3, Cl, SO4, Fluoride

**C - 100 mL Idex** Na2SO3 if source is Chlorinated
Note: Use 250 mL bottle if requesting multiple tests
- Fecal Coliform*
- Total Coliform
- Fecal PFGE
- E Coli*
- Enterococci*

| V-40mL | V1-40 mL | V2-120 mL | V3-120 mL |
|---|---|---|---|
| 3 - 40 mL Amber Vials 0.5mL HCL Zero Head Space | 2 - 40 mL Amber Vials 0.5mL HCL Zero Head Space | 120 mL Amber Bottle 1.5 mL H2SO4 | 120 mL Amber Bottle Filtered 1.5 mL H2SO4 |
| TPH Gas | VOC | TOC | DOC |

Lab Comments

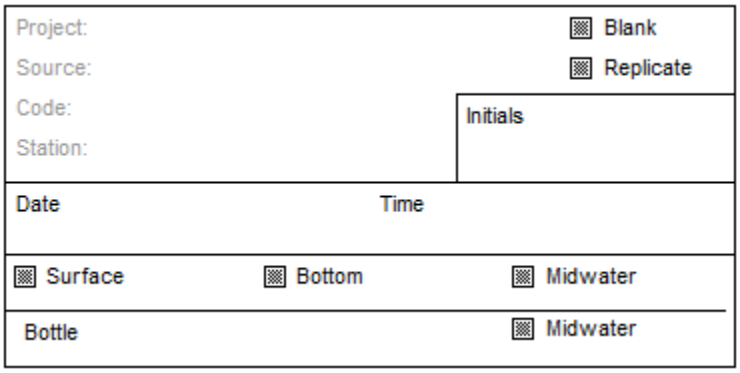
**Dissolved Metals - 250 mL** Filtered + pH<2 ~1.5mL HNO3
- Al, Sb, As, Ba, Be, B, Cd, Cr, Cu, Hg, Pb, Ni, Se, Ag, Ti, U, V, Zn, Mo, Silica

**Recoverable Metals - 250 mL** pH<2 ~1.5mL HNO3
- Al, Sb, As, Ba, Be, B, Cd, Cr, Cu, Hg, Pb, Ni, Se, Ag, Ti, U, V, Zn, Mo

Relinquished By: _____ Date/Time _____
Received By: _____ Date/Time _____
Relinquished By: _____ Date/Time _____
Received By: _____ Date/Time _____
Relinquished By: _____ Date/Time _____
Received By: _____ Date/Time _____

Sample Temp (C) | Date / Time Received | Lab #

## Figure 7. Bottle Labels



Project: ☐ Blank
Source: ☐ Replicate
Code:
Station:
Initials
Date Time
☐ Surface ☐ Bottom ☐ Midwater
Bottle ☐ Midwater

## 1. Grab Sampling

### Collecting a Sample

Avoid introducing contaminates to the sample. Don't touch bottle opening or inside of bottle cap. For Delivery and Shipment of samples for analysis refer to Pages 8 & 9 of this document.

a. **The "A" bottle –one liter or 500 mL HDPE bottle**
   i. Hold the bottle at the base and remove the cap. Submerge the bottle upstream, into flow, below the surface to avoid collecting surface film and scum.
   ii. Sample at a depth of 6-12 inches below the water surface, if possible. In shallow water be careful not to collect stirred up bottom sediments into sample.
   iii. Bottle should be tipped slightly upward to allow air to escape as it fills.
   iv. The "A" sample bottle should be filled to the neck of the bottle and then capped.
   v. Place sample in cooler on loose ice (<6°C), no other preservation is required.

b. **The "B" bottle –one liter or 500 mL HDPE bottle**

   Follow collection procedures for filling bottle "A" to fill bottle "B." Preserve the sample using the following procedure.
   i. **Add approx. 2 mL of concentrated sulfuric acid ($H_2SO_4$)** to the sample to lower the pH below 2. Use pH paper to confirm if needed.
   ii. Inverted the bottle several times to ensure mixing throughout the sample.
   iii. Place sample in a cooler on loose ice (<6°C) for transport to the lab.

c. **The "C" bottle (bacteriological sample)-250 mL polypropylene or 100 mL clear polystyrene**

   Use the 250 mL bottle when the sample requires more than one bacteriological analysis. If the sample only requires one bacteriological analysis, the 100 mL bottle may be used. Follow collection procedures for filling bottle "A" to fill bottle "C."
   i. The "C" bottle **should not be rinsed** with sampling site water.
   ii. On the initial plunge, the "C" sample bottle should be filled completely. Immediately after obtaining the sample, pour off any excess sample water from the container until the sample volume is 250 mL or 100 mL and cap.
   iii. If the sample bottle is not filled at least to the designated mark on the sampling bottle, discard the sample and sample bottle and repeat the process with a new "C" bottle. **DO NOT re-immerse the original bottle to add more sample volume**.
   iv. Place sample bottle in a cooler on ice (<6° C), no other preservation is required.
   v. For compliance samples, bacteriological samples need to arrive at the laboratory within 6 hours after collection and processed within 2 hours. For all other types of samples, the holding time is increased to 24 hours.

d. **The "CN" bottle – 125 mL brown HDPE**
   i. Fill the bottle as directed for the "A" bottle.
   ii. Add 1 pellet of sodium hydroxide (NaOH) or use an ampule of liquid NaOH from the lab. Swirl the bottle to dissolve the pellet or mix liquid NaOH.
   iii. Use pH paper to confirm the sample pH is >12. If pH is <12, add more NaOH.
   iv. Cap the bottle and place in a cooler with loose ice.

e. **The "H" bottle – amber glass liter**
   i. Fill the bottle as directed for the "A" bottle.
   ii. Place sample in a cooler on loose ice (<6°C) no other preservation is required.

f. **The "Oil and Grease" bottle – amber glass liter**
   i. Fill the bottle as directed for the "A" bottle.

ii. Preserve the bottle by adding 2 mL of hydrochloric acid (HCl). Use a disposable pipette to put a drop of sample onto pH paper, verify the resulting pH is < 2. If not <2 pH repeat process with a new pipette, each time, until it is.
iii. Place the acidified "Oil and Grease" bottle into a cooler on loose ice.

**g. The "V" or "pesticide" is 40 mL amber glass vial or DOC 125, 250 mL amber glass**

The 'V" bottle is a 40 mL amber glass vial pre-preserved with ascorbic acid and hydrochloric acid. Do not rinse the vial. Do not use a marker to write on the vial – use a pencil or preprinted labels and allow the ink to fully cure before opening the vial (due to risk of VOC contamination from marker). Do not allow contamination (even airborne) from organic compounds such as vehicle exhaust or cleaning compounds. Do not allow the bottle cap, bottle threads, or inside of bottle to be touched or contaminated. For VOC analysis, the laboratory will also send 2 trip blanks-Do not open and they must accompany the vials the whole trip and back to the lab.
No trip blanks for DOC and pesticide samples. Pesticide samples are not preserved.
***For DOC - samples are lab filtered & preserved within 48 hours.

i. Open the vial and completely submerge to fill. Underwater, tip the vial vertically so that it will completely fill and create a convex meniscus.
ii. Gently tap the vial to dislodge any air bubbles. Cap the vial and invert to mix preservative, if necessary, and visually verify there are no air bubbles.
iii. Glass vials can easily break. Put vials in bubble wrap pouch if supplied by the lab or wrap in bubble wrap. Securely place the vials in a cooler of loose ice.

**h. The "R" bottle – 1 gal/4L polypropylene cubitainer**

The cubitainer must be expanded before filling. Do not blow into or place fingers inside the cubitainer. To expand, partially unscrew the lid to allow air to enter the cubitainer and pull at the seams or have lab blow open with air.

i. Fill the cubitainer as directed for the "A" bottle.
ii. If unable to submerge the cubitainer without disturbing bottom sediment, use the "field" bottle to collect the sample and pour the water into the cubitainer.
iii. The "R" bottle is filtered and preserved by the lab due to the large volume of filtered water required and the difficulty in filtering water from "R" bottle sites.
iv. Place sample in a cooler on loose ice. No other preservation is required.

**i. The "Metals-Tot Recov bottle" – 100 mL polystyrene, 250 mL HDPE or polypropylene**

i. Fill the bottle as directed for the "A" bottle.
ii. Sample can be lab preserved within 14 days of collection or field preserve the bottle by adding 0.25 to 1 mL of concentrated Nitric Acid ($HNO_3$) based on bottle size. As needed, use pH paper to verify the resulting pH is less than 2.
iii. Place the "Metals-Tot Recov" bottle into a cooler on loose ice.

**j. Collection of the "field bottle" - one liter bottle**

Triple rinse the field bottle with water from the waterbody being sampled.

i. Fill the bottle as directed for the "A" bottle.
ii. This water can then be poured into a Millipore filter unit and filtered for dissolved phosphorus and/or dissolved metals.

**k. The "D" bottle -100 mL polystyrene bottle**

Water to be filtered for this sample comes from the field bottle. The procedure to field filter and preserve is described below.

i. Open Millipore filter and check that the bottle and filter connection is tight. Attach vacuum pump hose to the vacuum port on the filter.
ii. Pour water from the field bottle into the filter unit and cap with the filter lid.

iii. Use an electric vac pump or hand vac pump to create a vacuum (Do not exceed 22 psi). Water filters through the 45-micron filter and accumulates in the receiving bottle. Dirty water that won't filter or requires more than 2-3 disposable filter units to get required volume of water for samples will have to be filtered and preserved by lab. Notify lab by writing a note on bottle and lab sheet.

iv. After water is filtered, unscrew the receiving bottle. Pour in the 100 mL "D" bottle.

v. Add 0.25 mL of concentrated $H_2SO_4$. As needed, verify the pH with pH paper to ensure the pH is <2.

vi. Place the acidified bottle into a cooler on loose ice.

l. **The "Metals- Dissolved" bottle -100 mL polystyrene, 250 mL HDPE or polypropylene**

Follow collection procedures for "field bottle" and "D" bottle steps i. through v. Preserve the sample using the "Metals-Tot Recov bottle" procedure.

m. **"Caffeine" bottle – 1000 mL amber glass with Teflon lid**

Caffeine sampling is conducted to provide information which may correlate contamination with human waste from septic leachate.

i. Fill the bottle as directed for the "A" bottle.

ii. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of water.

iii. Place sample in a cooler on loose ice.

iv. If the sample cannot be analyzed by the laboratory within 48 hours, contact lab about freezing the sample to increase holding time to 7 days.

n. "**Algae/Chlorophyll *a*" bottle – 500 mL brown HDPE**

Algae or chlorophyll *a* are samples that may be collected during a complaint or fish kill to provide information on the water quality. These samples may be analyzed internally or contracted with an outside laboratory.

i. Fill the bottle as directed for the "A" bottle.

ii. Place sample in a cooler on loose ice. No other preservation is required.

## 2. Composite Sampling

### Collecting a Sample

The sampling plan or project manager will determine which samples are to be composite samples. Unless specified, most samples will be "grab" samples.

a. Triple rinse a plastic graduated cylinder with sample site water.

b. Collect a sample in a rinsed Van Dorn sampler or other sampling device.

c. Calculate the amount of water needed from each sub-sample. Divide the size of your container (milliliters), by the number of sampling sites to be composited.

Example: Compositing three sites and placing them in the "A" bottle (1,000 mL).

**1000 mL/ 3 = 333 mL**

d. Pour the previously calculated amount (i.e. 333 mL) from one sub-sample into the graduated cylinder.

e. Pour the water from the graduated cylinder into each sample bottle.

f. Repeat procedures "a" through "e" on the remaining sub-sample sites.

g. Preserve each bottle following the procedures in Grab Sampling section (pages 15-17).

**Other sampling documents that provide more information can be found at:**
M:\DANR\Office_of_Water\Water_Quality\02_STANDARDS TEAM\AARON\Quality Assurance\SOP
Under titles Calibration and Preservation Items Guidelines and WQM SOP for the WQP.

## REFERENCES

American Public Health Association, American Waterworks Association, and Water Environment Federation. 1998. Standard Methods for the Examination of Water and Wastewater, 20th edition. APHA, Washington, D.C.

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Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 136.

South Dakota Department of Agriculture and Natural Resources. 2024. Water Quality Program and Quality Assurance Project Plan.

## Revision History

Revision V-- November 2025 Changes in field/lab techniques, data collection, and instructions.
Revision IV- May 2024 DENR and Ag merger and separation from feedlots/livestock services.
Revision III--January 2016
Revision II---NA
Revision I----NA