New Mexico Environment Department (NMED) Surface Water Quality Bureau (SWQB)

Standard Operating Procedure (SOP) for

CHEMICAL SAMPLING IN LOTIC ENVIRONMENTS

Approval Signatures

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1.0 Purpose and Scope

The purpose of this SOP is to describe the sample collection techniques, preservation and acidification requirements, equipment, and quality control activities associated with the chemical sampling of surface water in lotic environments. This SOP also applies to chemical sampling in lakes (Lentic environments). However, it does not include sample collection procedures for conducting lake sampling, refer to the SWQB SOP 12.1 for *Lake Sampling* protocols (NMED/SWQB 2020a).

2.0 Personnel Responsibilities

The Monitoring, Assessment and Standards Section (MASS) Program Manager coordinates with Monitoring Team Supervisor, and the Quality Assurance Officer (QAO) as applicable to ensure quality data is collected, verified, and validated to support program commitments. The Program Manager will provide input on the scope and intent of the Standard Operating Procedure (SOP) as it pertains to the program's goals and objectives. The Program Manager will review this SOP every two (2) years after revision by Subject Matter Expert (SME) and/or QAO.

The QAO is involved in the development and revision of this SOP to ensure the SOP meets the requirements of the SWQB's *Quality Assurance Project Plan for Water Quality Monitoring Programs* (QAPP) (NMED/SWQB 2021a). The QAO, along with the SME and Program Manager will determine if any revisions to this SOP are needed at a minimum of every two (2) years in accordance with SOP 1.1 for the *Creation and Maintenance of SOPs* (NMED/SWQB 2020b). Pending the review and approval of the document, the QAO will ensure the SOP is accessible through the SWQB's website.

The SME reviews SOP every two (2) years and updates the SOP as the procedure or equipment changes in coordination with the QAO and Program Manager. The Monitoring Team Supervisor is considered the SME for this SOP and is responsible for fulfilling the chemical sampling requirements for a particular survey according to Field Sampling Plan (FSP), which includes sampling, management of monitoring personnel who conduct sampling and ensuring Project Managers adhere to sample frequency and sampling locations in current FSP. Other responsibilities include assigning Project Managers, assigning individual(s) responsible for delivering samples to the State Laboratory Division (SLD) and ordering and/or assigning ordering of chemical sampling supplies (e.g., preservatives, pipettes, sample containers, etc.)

All SWQB personnel who collect chemical samples in lotic environments or process samples for chemical sampling in lotic environments are responsible for implementing procedures detailed in this SOP. SWQB staff who conduct procedures described under this SOP are required to sign the SOP acknowledgment statement for Chemical Sampling in Lotic Environments, prior to conducting procedures described in this SOP.

3.0 Background and Precautions

3.1 Background

All chemical water sampling activities in lotic and lentic waters shall comply with this SOP. Methods of sample collection, preservation, and handling used in this SOP shall comply with methods described in the following references or that are approved by EPA:

- "Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act," 40 CFR Part 136 or any test procedure approved or accepted by EPA using procedures provided in 40 CFR Parts 136.3(d), 136.4 and 136.5;
- Standard Methods for the Examination of Water and Wastewater, latest edition, American Public Health Association;
- Methods for Chemical Analysis of Water and Waste, and other methods published by EPA Office of Research and Development or Office of Water;
- Techniques of Water Resource Investigations of the USGS;
- Annual Book of American Society for Testing and Materials (ASTM) Standards. Volumes 11.01 and 11.02, Water (I) and (II), latest edition, ASTM International;
- Federal Register, latest methods published for monitoring pursuant to Resource Conservation and Recovery Act regulations;
- National Handbook of Recommended Methods for Water-Data Acquisition, latest edition, prepared cooperatively by agencies of the U.S. Government under the sponsorship of the USGS; or
- Federal Register, latest methods published for monitoring pursuant to the Safe Drinking Water Act regulations.
- State of New Mexico Standards for Interstate and Intrastate Surface Waters (20.6.4 NMAC). Most current amendments.

3.2 Procedural Precautions

If other stream sampling work (e.g., collection of stream flow, physical habitat measurements) is to be done simultaneously, or prior to the collection of chemical water samples, then collect chemical water samples upstream of any other work/disturbances to prevent contamination with the water chemistry or wait for disturbed water to flow past the collection site.

It is recommended to contact a staff member from the laboratory(s) and/or section lead prior to sampling to ensure analyses can be carried out within holding times. Analyses and holding times are impacted by holidays. If samples need to be rushed, due to an emergency or spill, contact the Chemistry Bureau Chief and the Surface Water Quality Bureau Chief to obtain approvals, ensure the proper coding is used for sample submission, and to ensure staff are available after normal work hours/days to receive samples.

Organics sample containers, trip blanks, and hydrochloric acid (HCL) should be obtained from the SLD Organics Section. The Organics Section should be contacted at least one week prior to sample collection to ensure extractions and analyses can be carried out within holding times. Use self-adhering labels for organic sample bottles. Fill out labels on organics bottles and label containers before sampling to avoid having to write on wet surfaces. Only use pencils to fill out labels for organics to avoid sample contamination.

Site conditions or project-specific data collection objectives may necessitate the use of field procedures not included in this SOP. The use of field methods other than those presented in this SOP must be

approved by the Program Manager or QAO for the project prior to use of modified field procedure or equipment. The change will need to be documented in the current surveys FSP.

3.3 Safety Precautions

Do not attempt to wade into a stream if the depth (in ft) multiplied by the velocity (in ft/s) equals or exceeds the "rule of ten" or 10 square feet per second (ft2/s). For example, a stream that is 2 ft deep, and has velocities of 5 ft/s or more, should be considered too dangerous to wade. Do not attempt to wade a stream if you feel it is unsafe, regardless of the outcome of the "rule of ten." **S**ome channels have quicksand-like areas, deep holes, sharp rocks, excessive fallen logs, etc., that can lead to foot entrapment, injury, or falls. Staff should use best professional judgment to assess risks involved with data collection. Use gloves when working in waters suspected of having high bacterial contamination. Refer to SWQB's JHA for further safety precautions when conducting field work.

Consult the SWQB Chemical Hygiene Plan (CHP) or the SWQB Lab Safety Officer regarding acceptable practices for transferring concentrated acid in the Runnels Building Laboratory. Concentrated acid must always be transported in secondary containment in vehicles and boats with a short-term exception allowed for pre-acidified sampling containers enroute from vehicles to stream or lake.

4.0 Definitions and Acronyms

Analyte-Free Water – Water free of, or with the lowest attainable concentrations, of the analytes tested for in the requested analyses for a blank. Usually deionized (di), polished water obtained from the SLD Organics Section. Purer water may be necessary for some organic's analyses.

Field Sampling Plan (FSP) – A document that provides guidance for all fieldwork by defining in detail the sampling and field data-gathering methods as well as resource requirements for the project.

Lentic – Inhabiting or situated in still, fresh water (as lakes or ponds).

Lotic – Inhabiting or situated in rapidly moving fresh water (as rivers or streams).

Program Manager – An individual within the SWQB that manages a program such as the Watershed Protection Section (WPS), the Point Source Regulation Section (PSRS) or the Monitoring, Assessment and Standards Section (MASS). The Program Manager and Project Manager are not synonymous.

Quality Assurance Officer (QAO) – An individual within the MASS that is responsible for overseeing the development and implementation of all quality assurance procedures and processes within the SWQB including those projects that receive support or funding from the SWQB.

RID – is a unique reference ID number for samples submission.

Standard Operating Procedure (SOP) – A document that lists the steps that should be completed when doing a task.

Subject Matter Expert (SME) – A person who is familiar with the purpose and procedure for accomplishing a task. The SME may be the same individual as the Project Manager.

Sample – The medium, and any reagents or acids dissolved in the medium. The sample includes those materials that cannot be readily separated from the medium that is sampled.

Sampling Run –used to define the most common collecting period or grouping of sampling activities that are indicative of a SWQB MASS sampling operation. Typically, most samples are collected during multi-day collection events that depart and return to the office in a week (M-F). Blanks associated with a sampling run are assumed to represent a group of samples collected by the same staff, and using the same equipment, vehicle, reagents, and acids. When multiple, single day sampling runs are conducted within a given week that maintain constant variables as described above, the single day sampling runs are considered collectively as a single sampling run, provided the number of blanks collected is at least 10% of the environmental samples collected, preferably at a one blank sample per ten ambient sample frequency to allow for QC blank distribution.

Surface Water Quality Information Database (SQUID) – is the SWQB database for storing, retrieving and reporting laboratory results, field observations, biologic assemblage data, long-term deployment data, and stream habitat/geomorphic data.

Quality Control (QC) Sample Definitions

Field blank – A sample of analyte-free water and acid, if required, that is exposed to ambient environmental conditions at the sampling site and to transportation and storage conditions. Field blanks check for contamination from the sampling equipment, added reagents or acids, and from the environment. Field blanks are currently collected for E. *coli*, nutrient samples, and organic samples other than volatile organics samples (VOCs).

Trip blank – A blank prepared with analyte-free water and acid that is made at the analytical facility, sealed, transported and analyzed with environmental samples. Trip blanks are not exposed directly to ambient environmental conditions at the sampling site. Trip blanks are transported to the lab in the same manner as environmental samples. The purpose of a trip blanks is to assess the potential for in-transit contamination of samples. Trip blanks are currently run only for VOCs.

Reagent blank – A blank prepared in the lab using analyte-free water and reagent that is not exposed to ambient sampling conditions. Reagent blanks check for contamination from sample containers, analyte-free water and reagent. Reagent blanks are currently collected only for SLD nutrient samples.

Equipment blank – A sample prepared in the field, using analyte-free water and acid that has contacted all sampling equipment. Equipment blanks assess contamination from the sampling equipment and the acid, as well as from the ambient environment at the sampling site. Equipment blanks are currently collected for only for dissolved metals.

Duplicate – A sample that is split from a common container after sample collection and analyzed as two samples. Duplicates are used to assess the precision of sample collection and analysis.

Replicate – A second sample that is collected within 15 minutes and within 1 meter of an initial sample.

5.0 Equipment and Tools

The following list (Table 1) includes equipment that may necessary for surface water chemical sampling in lotic waters:

Table 1. Sampling equipment for lotic waters.

SAMPLING SUPPLIES	GENERAL
Tablet or Laptop	Access authorization documents
Field sheets	Defensive driving certificate
Submittal forms	Cell phone
RID stickers	Coolers
Cartridge filters (0.45 □m and 10 □m)	First aid kit
Acid washed silicon tubing	Flashlight
Cubitainers (quarts, gallons)	Maps
Geo pump, with appropriate power cord(s)	NMED ID
Kimwipes	Business cards
Acid kit with concentrated sulfuric, nitric acid, HCL,	Shovel
Pipets	Toolbox or multitool
Nitric Acid	Vehicle Kit
Sulfuric Acid	Hat
Phosphoric Acid	Sunscreen
Nitrile gloves	Nitrile power free gloves
Organics sample bottles (vials/bottles)	Rain gear
8oz glass amber bottle (DOC)	Sunglasses/polarized glasses
Pencils	Clipboard
Sharpies (fat and fine point)	Boots/waders/sandals
Gallon Cubie with tap water for cleaning equipment	Garbage bags
Analyte-free water for preparing blanks	Apron
Hammer	
Measuring tape (in feet and/or meters)	
Wading rod	
Flow meter and cable	
Potassium iodide (KI) starch Test Paper (cyanide samples)	
Nylon rope	
Metal bucket	
Plastic bucket	
Ice	

Coolers 10% HCl for acidifying VOC samples Whirl-Packs Reference ID stickers Ascorbic acid (cyanide samples) VOC trip blanks Safety glasses HACH Chlorine Pocket Colorimeter kit Pole sampler	

6.0 Collection of Water Samples for Chemistry Analyses (PROCESS DESCRIPTION)

For planning and scheduling purposes, review the current survey's FSP to confirm planned chemical sampling stations, requested analytical suite and other data needs before conducting field work. A chemical sampling event will need to be created in SQUID for each sampling station that will be sampled, when conducted for a MASS survey. Reference ID (RID) stickers will need to be obtained from SLD before field work commence for chemical sampling.

Label all sample containers with the sample site location and sample type (e.g. dissolved metals) and place the pre-printed RID stickers on the lid of one liter and one-gallon flexible plastic containers or they can be placed on the sides of rigid plastic or glass containers. When labeling sample containers, sample type is typically abbreviated. Write the RID number on the container with a Sharpie®. A summary of the required containers, preservatives, and holding times for various analyses is given below (Table 3). The RID numbers of each sample container (e.g. dissolved metals) is recorded in the Activity ID's/RIDs section of the Stream and River Field Form. Before sampling ensure RIDs on containers, and sample type match the RIDs for each analytical suite identified in the Stream and River Field Form.

Use self-adhering labels for organic bottle. Fill out labels on organics bottles and label containers before sampling to avoid having to write on wet surfaces. Only use pencils to fill out labels for organics.

Instantaneous sonde measurements (i.e., temperature, specific conductance, salinity, dissolved oxygen, saturated dissolved oxygen, pH and turbidity) and stream flow are required to be collected at each chemical sample station. Stream flow can be obtained from USGS stream flow gage, if working gage exist is in close proximity to sample station. Data is recorded on the Stream and River Field Data Form. Instantaneous sonde measurements can be taken simultaneously with chemical samples, if taken so that the sediment is not disturbed at the chemical sampling point. Refer to SOP 6.1 *Sonde Calibration and Maintenance* (NMED/SWQB 2021b) and SOP 6.2 *Sonde Deployment* (NMED/SWQB 2018) for information regarding required calibration and collection of sonde measurements. Refer to SOP 7.0 *Stream Flow Measurements* (NMED/SWQB 2022) for information regarding flow measurements. If no flow is observed during sample run, ensure it is recoded on Stream and River Field Data Form.

Collect water samples by immersing the sample container below the surface of the water with the container mouth facing upstream and all exposed flesh downstream from the opening of the container.

Attempt to sample where the stream is flowing, well mixed and preferably more than 6 inches deep. Sample at mid-channel or as far away from the bank as possible. Avoid getting streambed sediment or water surface materials in the sample. For Equal-Width-Increment and Depth-Integrated Sample Collection Methods refer to the procedure under related field forms for this SOP.

It is not necessary to rinse new sampling containers, except for organic carbon samples (see organic carbon sampling below), with analyte-free or sample water before collecting the sample. If re-using sampling containers such as buckets or one-gallon cubitainers to collect water for multiple samples, rinse the container twice with ambient water before collecting the sample. When adding acid to cubitainers, never insert the pipettor below the top of the neck of the cubitainer and keep the pipettor at an angle above the cubitainer to reduce the chance of debris falling off the pipettor or your hand into the sample. Pipettes need to be stored separately, in a dry secure container, where pipettes are not exposed to elements during transportation. Typically, container used for storage of pipettes would be similar to a Tupperware® container. Sample containers can be pre-acidified up to one week before use. Pre-acidified containers should be labeled and stored in secondary containment, such as coolers, with the lid propped open to minimize vapor buildup. Pre-acidified containers should not be opened in a closed area or near the face. Pre-acidified nutrient containers must be stored separately from pre-acidified total metals and dissolved metal containers so that cross contamination does not occur.

Use a bucket with a nylon rope, disposable bailer, or a pole sampler to collect water if sampling containers cannot be dipped directly in the water. Avoid contaminating the sample with debris from the rope and bridge, or other sampling platform. Use the first and second bucketful/container of water to rinse the bucket/container. Use the third bucket/container of water to collect the sample. Use a metal bucket when collecting organic samples and a plastic bucket when collecting metals samples. Do not let the metallic sonde components touch the sample water prior to collecting the sample from a bucket if sampling for metals.

6.1 Sample Collection and Processing for Specific Parameters

Refer to the SLD Submittal Form, an interactive submission form for analytical suite compositions, submission form can be accessed at https://www.env.nm.gov/surface-water-quality/sop/ under related field forms for SOP 8.2.

The 1-quart and 1-gallon cubitainer used for chemical sampling in lotic environments are required to have a polyethylene liner and a polyethylene (or a fluoropolymer sampling vessel) cap to meet requirements described in the Background and Precaution section of this SOP.

6.1.1 Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Chloride (Cl), and Sulfate (SO4)

Fill a 1-quart cubitainer. Keep sample on ice, at 6°C or less. Prepare a field blank by filling a 1-quart cubitainer with di water from SLD. Keep field blanks on ice, at 6°C or less.

6.1.2 Nutrients

Fill a 1-quart cubitainer and acidify with approximately 1 ml concentrated sulfuric acid. If the conductivity is above 1000 uS/cm, check the pH with pH paper, a pH pen or other method, and add concentrated sulfuric acid iteratively in 1 ml aliquots until the pH is <2. If using a pre-acidified container, do not overfill.

Prepare a field blank by filling a 1-quart cubitainer with DI water from SLD on site and acidifying with 1 ml of concentrated sulfuric acid. Keep field blanks on ice, at 6°C or less. It may be desirable to prepare a reagent blank using a cubitainer filled with analyte-free water (di water) by the SLD water chemistry section that is kept 20°C or less, and in the dark to the extent possible, and acidified in the lab.

6.1.3 Total Metals

Fill a 1-quart cubitainer and acidify with 2 ml of concentrated nitric acid. If using a pre-acidified container, do not overfill. Keep sample at ambient temperature. There are no blanks collected for total metals samples.

6.1.4 Total Recoverable Aluminum

If stream turbidity is 30 NTUs or below, follow the instructions for total metals samples. If stream turbidity is greater than 30 NTUs, follow the instructions for dissolved metals samples but use a 10 µm filter instead of a 0.45 µm filter. There are no blanks collected for total recoverable aluminum samples. During lake sampling an additional aluminum sample should be taken if the average of the turbidity at the depths the composite sample is taken from is greater than 30 NTUs.

6.1.5 Hardness and Dissolved Metals

To prepare an environmental sample for hardness and dissolved metals follow the steps below:

- Fill a cubitainer with at least 1 quart of stream, river, or lake water.
- Attach a 0.45 µm filter to one end of acid washed, 0.19-inch internal diameter silicone tubing. Do this by pulling the plastic bag containing the filter over the upstream barbed fitting on the filter until it perforates the bag. Open the tubing bag, expose about 5 inches of tubing, and push the tubing onto the exposed barbed fitting. Leave the plastic bag on the filter.
- Expose more of the tubing from the bag and insert the tubing into the Geo Pump and clamp.
- Remove the rest of the tubing from the bag and place the other end into the sample.
- Then remove the bag on the filter or push the downstream barb of the filter through the bag.
- Turn the pump on and pump at least 75 ml of sample through the filter, discard, and collect the remainder in a 1-quart cubitainer. Keep the filter to the side of the neck of the receiving cubitainer to prevent dirt and dust from falling into the sample.
- Acidify the sample with 2 ml of concentrated nitric acid.
- Keep the sample at ambient temperature.
- Place the used tubing in a separate bag from clean tubing and save for cleaning in the lab.
- Discard the 0.45 µm filter.

To prepare a blank, fill a new cubitainer with at least a quart of DI water from SLD and follow the filtering instructions above starting at step 2. **Do not reuse** tubing and filters from blanks in environmental samples.

6.1.6 RADIONUCLIDES

Fill two, 1-gallon cubitainers. Keep sample at ambient temperature. No blanks are collected for Radionuclide. SLD completes the preservative requirements.

6.1.7 CYANIDE

If chlorine is suspected, evaluate the sample water for the presence of chlorine. Samples from streams that are not immediately downstream from outfalls are unlikely to contain chlorine. If the chlorine is suspected to be present, samples can be checked using potassium iodide (KI)-starch test paper. A blue color indicates the presence of chlorine. A HACH Chlorine Pocket Colorimeter kit can also be used (see below).

Fill a 1-quart cubitainer with sample. If chlorine is present, remove it by adding ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the starch test paper, then add one additional crystal.

After adding ascorbic acid (if necessary), preserve samples for cyanide analysis with sodium hydroxide. Determine the pH of the sample on an aliquot (after adding ascorbic acid) using pH test paper. Preserve the sample with sufficient NaOH to produce a pH of 12 or greater. Most samples will require about 0.5 g solid NaOH per liter, approximately five pellets. Handle the pellets with wooden or plastic utensil or pour directly from the container. Keep samples on ice, at 6°C or less.

6.1.8 ORGANIC CHEMICALS

When collecting samples for organic compounds, wear clean nitrile gloves. Gloves are worn to prevent organic compounds that may be present on skin from contaminating samples. Avoid the false sense of security gloves may give; a gloved hand can still spread contamination. Put gloves on as close to the time of sample collection as possible. Avoid situations where a collector may come in contact with gasoline, such as, fueling vehicles or boats for field work. Use sampling equipment with fluorocarbon polymer, glass, or metal components if components will directly contact samples to be analyzed for organic compounds. Do not use plastics other than fluorocarbon polymers. Follow any special procedures that may be provided by the laboratory.

6.1.9 VOLATILE ORGANIC COMPOUNDS (VOCS)

For each sample planned, obtain 2-40 ml vials in a Whirl-Pack from the SLD Organics Section. Fill the vials by submersion. If the sample is suspected of having residual chlorine (e.g. chlorinated wastewater plant effluent), add 25 mg of ascorbic acid and let stand for 1 minute. Add 2 drops of 10% HCl (also obtained from the SLD Organics Section and less than 3 months old) to each vial. Fill the caps with sample water and cap the vials without leaving a headspace. Keep the vials together in a closed Whirl-Pack, on ice, at 6°C or less.

Obtain a VOC Trip blank from the SLD Organics Section for each sample run that includes collecting VOC samples. Carry the trip blank into the field in a cooler, on ice, and remove the two vials from the Whirl-Pack at a sampling station. Do not open the vials or acidify. Replace the vials in the Whirl-Pack and keep them in a cooler, on ice with the environmental samples until delivered to the lab.

Trip blanks and HCL that have be obtained prior to sampling should be stored in the walk-in cooler until taken to the field.

6.1.10 Semi-volatile Organic Compounds (SVOCs), Herbicides, Pesticides

For each sample planned, obtain two 1L glass, amber colored bottles with Teflon lined caps and a bubble wrap sleeve for each from the SLD Organics Section. Fill both bottles by submersion and replace the lids underwater if possible. If the stream is not deep enough to submerse the sample container, use a third, new, 1-L glass amber bottle to fill the two sample bottles. A headspace is acceptable with SVOC samples. Keep jars in bubble-wrap sleeves, obtained from the SLD organics section, before and after filling to avoid breakage. Store samples out of direct sunlight, on ice, at 6°C or less.

6.1.11 Total Residual Chlorine (TRC)

Collect samples for residual chlorine measurements directly below wastewater treatment plant outfalls when sampling for total residual chlorine for discharge monitoring from point sources. Fill the 10 ml sample cells provided in the HACH Chlorine Pocket Colorimeter kit to the line either directly from stream or from an aliquot of sample water. Wipe off excess water from the outside of sample bottles with lens paper or a KimWipe® and ensure that the glass is dry and clean (no fingerprints or smudges). Add the content of one DPD Total Chlorine Powder Pillow to one 10-ml sample cell and gently shake for 20 seconds. Let it stand for 3 to 6 minutes before reading. During this period, place the other 10 ml cell bottle (the blank) into the colorimeter cell holder, with the diamond mark facing you. Tightly cover the cell with the instrument cap and press zero. Remove the blank sample cell bottle from colorimeter cell holder. Place the cell with dissolved reagent into the colorimeter cell holder and cover tightly with instrument cap. Between 3 and 6 minutes after adding the reagent to the sample press READ and record the total residual chlorine value in the comment section of field sheet.

6.1.12 Dissolved Organic Carbon

For each sample planned, obtain an 8oz amber glass bottle from the SLD Water Chemistry Section. To prepare an environmental sample for dissolved organic carbon follow the steps below:

- Fill a cubitainer with at least 1 quart of stream, river, or lake water.
- Attach a 0.45 µm filter to one end of acid washed, 0.19-inch internal diameter silicone tubing. Do this by pulling the plastic bag containing the filter over the upstream barbed fitting on the filter until it perforates the bag. Open the tubing bag, expose about 5 inches of tubing, and push the tubing onto the exposed barbed fitting. Leave the plastic bag on the filter.
- Expose more of the tubing from the bag and insert the tubing into the Geo Pump and clamp.
- Remove the rest of the tubing from the bag and place the other end into the sample.
- Then remove the bag on the filter or push the downstream barb of the filter through the bag.
- Turn the pump on and pump at least 75 ml of sample through the filter.
- When filling sample bottle keep the filter to the side of the neck of the receiving sample bottle to prevent dirt and dust from falling into the sample.

- Fill the 8oz glass amber bottle halfway (4oz) with filtered water as a rinse, cap and shake, and discard. Repeat this process 3 times total.
- Fill the 8 oz glass amber bottle and allow adequate volume for addition of preservative. provided by SLD.
- Acidify the sample with concentrated phosphoric acid (H_3PO_4) to a pH ≤ 2, approximately 3 drops for an 8 oz amber glass bottle.
- Keep samples on ice, at 6°C or less.
- Place the used tubing in a separate bag from clean tubing and save for cleaning in the lab.
- Discard the 0.45 µm filter.

*After filtering the DOC sample, the same tubing and filter can be used to filter dissolved metals sample.

6.2 Ambient Water Toxicity Testing

The USEPA Region 6 Laboratory conducts aquatic toxicity tests of water as part of the EPA Region 6 Ambient Toxicity Monitoring Program. An application process is required by EPA before selecting and scheduling ambient water toxicity testing. Contact the lab at 214-665-6722 for further information.

6.3 Quality Control Sampling

Prepare and submit blanks at a frequency of one per sampling run, unless otherwise indicated by the FSP. See Section 4.0 for definitions of quality control samples.

Table 2. Blank types and frequencies. Analytes not listed do not require blanks.

Analytical Suite	21* Field Blank	26* Trip Blank	27* Reagent Blank	28* Equipment Blank	Submittal Frequency (per run**)
TSS/TDS/ Cl/SO_4	X				1
SWQB Nutrients	X				1
DOC				X	1
Total Metals	X				project-specific

Analytical Suite	21* Field Blank	26* Trip Blank	27* Reagent Blank	28* Equipment Blank	Submittal Frequency (per run**)
Dissolved Metals				X	1
VOCs		X			1

* Numbers refer to Water Quality Exchange (WQX) activity type.
** Run is usually equivalent to a sampling trip. Some runs are composed of multiple day trips in which case blanks should be collected at a rate of 10% of the total number of samples for each parameter.

6.4 Handling, Packaging, and Transporting Samples

After collection, place samples with temperature storage requirements in coolers. Ensure that all samples required to be kept cool are surrounded and in contact with enough ice to cool to approximately 6°C or less. It is important that containers are in an ice bath; i.e. in contact with water that is in contact with ice, especially in warm weather, to ensure adequate cooling. Make sure that all glass sampling containers are placed in bubble-wrap sleeves to protect from breaking. Bubble-wrap may insulate samples and prevent adequate cooling. It may be necessary to place additional ice in coolers. Check to see that samples are adequately labeled and that container lids are secure. Handling procedures and holding times are summarized below (Table 3).

6.4.1 SAMPLE CUSTODY

Samples taken for ambient water quality monitoring, do not require formal chain of custody procedures, the SWQB QAPP (NMED/SWQB 2021a) provides more information on chain of custody procedures for specific data acquisition type conducted by the SWQB.

Table 3. SWQB chemical sample handling procedures and holding times.

Sample Type	Sample Container	Preservation and Storage	Maximum Holding Time
TSS/TDS/Cl/SO_4	1-quart polyethylene cubitainer	On ice, approximately 6°C	7 days TSS – TDS 14 days Cl– SO_4
Total Nutrients	1-quart polyethylene cubitainer	1.0 ml concentrated sulfuric acid, on ice, approximately 6°C	28 days

Sample Type	Sample Container	Preservation and Storage	Maximum Holding Time
DOC	8 oz amber glass bottle	2-3 ml concentrated phosphoric acid, on ice, approximately 6°C	28 days
Cyanide	1-quart polyethylene cubitainer	5-7 pellets NaOH, 0.6g ascorbic acid if chlorine present, on ice, approximately 6°C	14 days
Total Metals	1-quart polyethylene cubitainer	2.0 ml concentrated nitric acid	28 days mercury – 6 months other*
Total Recoverable Aluminum	1-quart polyethylene cubitainer	Filter (10 μm) within 15 min of sample collection; 2.0 ml concentrated nitric acid.	6 months
Dissolved Metals / Hardness	1-quart polyethylene cubitainer	Filter (0.45 μm) within 15 min; 2.0 ml concentrated nitric acid	28 days mercury – 6 months other*
Semivolatile Organic Compounds, Herbicides, Pesticides	Two 1-liter glass amber bottles (lab)	On ice, approximately 6°C	7 days
Volatile Organic Compounds	Two 40-ml glass vials (lab) in a Whirl-Pack	5 drops 10% HCl per vial (HCl provided by lab and prepared within 30 days of use), on ice, approximately 6°C	14 days
Radionuclides	Two 1-gallon polyethylene cubitainers	No preservative, store at room temperature	6 months

* Metals, except boron, chromium VI, and mercury

6.5 Stream and River Field Data Form Completion

Either the paper or electronic versions of the Stream/River Field Data Form may be used to document sample collection. The forms are identical; however, the electronic form has built in data entry quality checks and automated functions. Use of the electronic form also allows batch laboratory submittal sheet generation and SQUID sample event upload. Station and RID information on either form may be entered in preparation of the sampling event.

6.5.1 Paper Form

- Type or enter the Project Name
- Enter site information, site ID, latitude, longitude, elevation, ecoregion, and driving directions
- Enter sampling event information: date and time, field staff, sonde and handset used, sampling equipment, sampling media, and indicate DO recalibration and pressure.
- Enter field measurements. Indicate missing values with “MDP.”
- Enter flow condition rating
- Enter RID numbers, Analytical Suites, and sample processing and preservation information.
- Enter observed probable sources in the Sampling Notes section
- Enter streamflow measurement method and result. Add any streamflow comments to the Flow Comments section
- Add any other relevant sampling event comments to the Sampling Notes section

6.5.2 Electronic Form

- Type in the Project Name
- Select the Station Name from the drop-down list
- Enter sampling event information: date and time (use the “Now” button as a shortcut). Select from the drop-down lists: field staff, sonde and handset used, sampling equipment, sampling media, and indicate DO recalibration and enter pressure.
- Select flow condition rating
- Enter RID numbers (the grey button on the right side of the RDI field adds the next number in sequence) and select Analytical Suites and sample processing/preservation information
- Press the Probable Source Observations drop-down list button. Click on an observed probable source then press the “Select Probable Source” button. Repeat for all observed sources then press the “Add to Comments” button.
- Select the Streamflow Measurement method and enter the flow result. Add any streamflow comments to the Flow Comments Section.
- Import site photos taken with the device using the directional import buttons.
- If the form is complete, press the “Publish Field Sheet” button. Resolve any error messages. If the form is not complete, press the “Save Draft” button to save the file and complete at a later time.
- Published and draft files are saved in the C:\FIELD_SHEETS folder on the local hard drive.

7.0 Data and Records Management

When entering data into the SQUID, it is important to select the correct blank type from the list appearing in the drop-down menu.

A Stream and River Field Data Form is filled out at every chemical sample station. All data obtained during chemical sampling is recorded on the Stream and River Field Data Form. The Stream and River Field Data Form is then published and filed in project folder after data collection is complete and Project Manager has verified data is accurate on form. Information collected at sampling station and recorded on Stream and River Field Data Form are then upload into SQUID. Refer to section below regarding SQUID upload instructions.

7.1 Uploading Chemical Sampling Event into Squid

To upload chemical sampling event data for a chemical sample station either upload the data manually or use the macro-enabled Excel spreadsheet.

7.1.2 Upload Chemical Sampling Event Into SQUID Using Macro-enabled SLD Submittal Form

- Locate the most recent version of the macro-enabled SLD Submittal Form (available on the SWQB SOP website).
- Insert the correct survey name and year, user code for the survey (listed in the “lists” tab) and the collectors contact information as well as the date and approximate time of laboratory submittal.
- Make sure that all chemical sampling event data sheets for the sampling run are complete and published.
- In the SLD Submittal form instructions tab select “Select Files” and navigate to the project folder containing the published final drafts of the chemical sampling (Stream/River Field Data Form). Select all applicable chemical sampling events and flow events for upload.
- In the SLD Submittal form instructions tab select “create submittals.” The resulting submittals in the chemical suite tabs are the forms that are submitted to SLD when chemical samples are delivered for analysis. Each chemical suite sheet should contain the sample RID and a corresponding barcode (requires special computer software listed on the instructions tab), the collection date and time, the conductivity, and all appropriate header information.
- After sample RIDs are confirmed and successfully submitted to the laboratory for analysis, proceed with the chemical sampling event data upload in SQUID.
- Ensure that all data is complete and create a .csv file from the combined data tab in the SLD Submittal form.
- In SQUID, select the “data management” tab at the upper left corner of the database, and select “imports” from the drop-down menu. In the “imports” sub-menu select “sampling event data.”
- The Import Sampling Event Data page should open. Select the applicable project from the project field menu, and then select “choose file.” Navigate to the .csv version of the sampling event data and then select “open.” In SQUID, select “upload file.”
- Ensure that there are no invalid records found with error messages. Error messages will appear as a red exclamation point in the “valid” column along with the message “X

invalid records found." Correct errors if invalid records are found. Once there are no invalid records, select "import all valid records." A notification that upload was successful should appear.

- Navigate to the project folder and select a station to ensure that the sampling events were successfully uploaded.

7.1.2. UPLOAD CHEMICAL SAMPLING EVENT DATA MANUALLY TO SQUID

- Navigate to the applicable project folder in SQUID by selecting the "project" tab on the navigation bar, then selecting the appropriate folder icon with a green arrow under the "View/Add Monitoring Locations" column.
- All stations that have been added to the selected project folder should appear. To upload a chemical sampling event to a particular station, select the folder icon with a green arrow under the "sampling events" column for that particular sampling station.
- In the Sampling Events page, select "add a new sampling event" in the top navigational bar. Select a sampling event type from the drop-down menu. For River/Stream chemical sampling event data select "RIVER/STREAM-CHEMICAL." Select the "add new sampling event."
- A sampling event details box will appear. Populate the fields in the general tab with the appropriate data.
- In the RIDS tab, enter the number of RIDs associated with that station. Enter the RID and select each corresponding Analyte Suite from the drop-down menu.
- In the Field Measurements tab enter all sonde data that was collected at the time of sampling. Indicate a flow condition rating associated with the event. This rating should correspond to the rating from the flow section of the Stream/River Field Data Form. **Note: that a flow event will not be created when chemical sampling events are manually uploaded and will have to be created for the station separately
- Select "save." The chemical sampling event and associated RIDs should appear under the sampling events.
- Navigate to the project folder and select a station to ensure that the sampling events were successfully uploaded.

7.2 Upload of Chemical Analytical Results

The QAO uploads all chemical results completed by the State Laboratory Division and any other contracted laboratory. See QAO for additional details regarding result upload procedure.

8.0 Quality Control and Quality Assurance

The SWQB controls the quality of chemical sampling in lotic environments by using standardized methods that are documented in this SOP. All personnel who collect conduct chemical sampling in lotic environments or process samples for lotic environments must be familiar with these protocols, sign acknowledgment form associated with this specific SOP and collect data in accordance with the procedures as they are defined in this SOP and all other applicable SOPs. In addition to standardized methods, proper training of field personnel represents a critical aspect of meeting the data quality objectives in order to fulfill the goals of the SWQB's QAPP (NMED/SWQB. 2021a). Different types of quality control samples are collected to check for contamination and background levels of analytes that

may be introduced through exposure to the environment, sampling containers, reagents and acids, and laboratory equipment used to collect and analyze the various types of samples.

Assurance of field data collection for chemical sampling are done through adherence to the procedure detailed in this and other applicable SOPs and oversight of the process by the QAO. If at any time the QAO determines this process is not being adhered to, the QAO has the authority to cease activities specific to this SOP with prior support and approval by the SWQB Bureau Chief and MASS Program Manager, until such a time that the issue can be resolved.

9.0 Related Forms

Stream/River Field Data Form
Chemical Sampling Equipment Checklist
Total Residual Chlorine Data Upload Form
SLD submittal forms

10.0 Revision History

Original. March 12, 2011.

Revision 1. January 23, 2012. Minor edits throughout SOP.

Revision 2. December 20, 2012. Updated Table 3 and additional language regarding total recoverable aluminum.

Revision 3. April 2, 2013. Minor edits to language and some clarification regarding preservation.

Revision 4. April 15, 2015. Changes to blank definitions and types. Added TSS/TDS/Cl/SO_4 blanks. Vacant, QAO; Douglas Eib, SME; Shelly Lemon, MASS Program Manager

Revision 5. March 14, 2022. Removed blank for SVOCs to follow QAPP; changed formatting to be consistent with SOP 1.1; added SLD submittal forms for organics and radionuclides; Removed discussion on compliance sampling because it is covered in SOP 8.3. Added details regarding the addition of chemical sampling data event in SQUID. Clarity and details added to the step-by step procedure. Added steps for field sheet completion. Added DOC sampling methods.
Miguel Montoya, QAO; Chuck Dentino, SME; Kristopher Barrios, MASS Program Manager

Revision 6. May 2, 2022. Addressed minor grammatical mistakes, inconsistencies with SOP format numbering, and updated the next revision date to be consistent with details in SOP 1.1 Creation and Maintenance of SOPs. Staff who have signed the acknowledgment statement for the SOP for Chemical Sampling in Lotic Environments, Revision 5, are not required to sign the acknowledgment statement for SOP for Chemical Sampling in Lotic Environments, Revision 6 due to no substantive changes to objectives, procedures, or equipment detailed in SOP.

11.0 References

New Mexico Environment Department/Surface Water Quality Bureau (NMED/SWQB). 2018. Standard Operating Procedure 6.2 for Sonde Deployment. Available at: https://www.env.nm.gov/surface-water-quality/sop/

New Mexico Environment Department/Surface Water Quality Bureau (NMED/SWQB). 2020a. Standard Operating Procedure 12.1 Lake Sampling. Available at: https://www.env.nm.gov/surface-water-quality/sop/

New Mexico Environment Department/Surface Water Quality Bureau (NMED/SWQB). 2020b. Standard Operating Procedure 1.1 for the Creation and Maintenance of Standard Operating Procedures. Available at: https://www.env.nm.gov/surface-water-quality/sop/

New Mexico Environment Department/Surface Water Quality Bureau (NMED/SWQB). 2021a. Quality Assurance Project Plan for Water Quality Management Programs. Available at: https://www.env.nm.gov/surface-water-quality/protocols-and-planning/

New Mexico Environment Department/Surface Water Quality Bureau (NMED/SWQB). 2021b. Standard Operating Procedure 6.1 for Sonde Calibration and Maintenance. Available at: https://www.env.nm.gov/surface-water-quality/sop/

New Mexico Environment Department/Surface Water Quality Bureau (NMED/SWQB). 2022. Standard Operating Procedure 7.0 for Stream Flow Measurements. Available at: https://www.env.nm.gov/surface-water-quality/sop/