GUIDANCE ON TREATED AND UNTREATED PRODUCED WATER SAMPLING PROCEDURE

NEW MEXICO PRODUCED WATER RESEARCH CONSORTIUM

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PREFACE

This guidance report was prepared by the New Mexico Produced Water Research Consortium (NMPWRC or the Consortium) in support of the New Mexico Environment Department and the United States Environmental Protection Agency's National Water Reuse Action Plan.

The report presents a general water sampling protocol for produced water quality analysis, pilot demonstration of produced water treatment, and use for fit-for-purpose applications. The guidance is based on the standard methods SW-846 by the United States Environmental Protection Agency, and methods used by commercial laboratories for produced water analysis[1]. The sampling protocol provides the standard operating protocol for collecting untreated and treated produced water samples during field measurements and for laboratory analyses of inorganic, wet chemistry, metals, organics, radioactive materials, microbes, and Whole Effluent Toxicity tests. For sampling of soil, plants, and groundwater during treatment and fit-for-purpose uses, the case-specific protocols should be followed and approved by the Technical Steering Committee of the Consortium.

The protocol provides step-by-step guidance and information on sample collection and preservation of produced water samples in the oil and gas field. It aims to serve as a guide to the field sampling crew. This document is general guidance, from which study-specific or laboratory-specific standard operating procedures are developed for strict adherence. The technology and use developer will provide more specific sampling plans, and the Consortium will approve on a case-by-case basis.

[1] https://www.eurofinsus.com/media/447768/appendix-d-section-5-attachment-holdtime-container-list_2016-july.pdf

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Acronyms

bbl	Barrels (42 gallons)
BOD_5	Biochemical Oxygen Demand, 5-day
COD	Chemical Oxygen Demand
EPA	Environmental Protection Agency
HASP	Health and Safety Plan
HEM/SGT-HEM	n-Hexane Extractable Material/ Silica Gel Treated n-Hexane Extractable Material
HPLC	High Performance Liquid Chromatography
GC	Gas Chromatography
ITTD	Innovative Technology Treatment Demonstration
NMED	New Mexico Environment Department
NMPWRC	New Mexico Produced Water Research Consortium
ORP	Oxidation-Reduction Potential
OSHA	Occupational Safety and Health Administration
PFAS	Perfluoroalkyl and Polyfluoroalkyl Substances
PPE	Personal Protection Equipment
QA/QC	Quality Assurance and Quality Control
SOP	Standard Operating Procedure
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TSC	Technical Steering Committee
VOA	Volatile Organic Analysis

SAMPLING PROCEDURE

OBJECTIVE: provide general information and guidance regarding sample collection and preservation through the life cycle of produced water from production (well head), preliminary treatment, storage (tanks), to pretreatment, treatment and desalination, post-treatment, applications, and residual management in the oil and gas field. This document serves as a guide from which a standard operating procedure (SOP) should be developed to be adhered to by the field sampling crew. A specific field sampling and analysis plan will be prepared for each site and pilot test based on this general guidance and other relevant information.

SAFETY: Samplers must wear personal protection equipment, such as safety goggles, gloves, and other personal protection equipment (PPE) required by the facility. Always work in a team of two or more. If no facility requirements exist, then follow PPE includes safety glasses or goggles, appropriate gloves for the process at hand (e.g., nitrile gloves for sample handling), coveralls or a protective apron, and face shields if necessary, for handling materials that can splash and are hazardous. Gloves should be chosen to match the properties of liquids or solids handled. Training should be provided for sampling personnel so that they can choose the correct PPE while following the sampling procedures. Figure 1 shows proper PPE based on Occupational Safety and Health Administration (OSAH) requirements. Table 1 provides PPE instructions for samplers to follow. For detailed information, check 29 CRF 1910 subpart I.

Figure 1. Proper personal protective equipment. (Source: www.futuremanagers.com)

Table 1. Examples of personal protection equipment.

	Examples of equipment		Examples of equipment
Head Protection	Helmets have a full brim; helmets are brimless with a peak extending forward from the crown.	Hand Protection	Disposable safety gloves.
Foot Protection	Metatarsal guards; toe guards; safety shoes or boots; combination foot and shin guards.	Respiratory Protection	Filtering face pieces (dust masks) and other air-purifying respirators; atmosphere-supplying respirators.
Eye and Face Protection	Safety spectacles or glasses; goggles; face shields; welding shields.	Body Protection	Coveralls; fire retardant clothing; reflective clothing.
Hearing Protection	Single use earplugs; earmuffs; pre-formed or molded earplugs.		

General Guidelines

Samplers and analytical laboratories must maintain close coordination to ensure that adequate sampling procedures and sampling quality control objectives are met.

To ensure sample representability, comparability, and reproducibility of the performance of the treatment facility, sampling personnel must verify with the facility operators that the facility had not shown any upset, alteration, or disruption of their normal operations; this can be done based on the overall data repository and routine measurements of the facility. If the facility has shown any alteration of their normal operation during the days of sampling procedures or five (5) days before, the sampling procedures must be re-scheduled when the facility retrieves normal operations.

In the event that sampling personnel considers that any of the procedures described in this manual are inappropriate, inadequate, or impractical and that another procedure must be used to obtain the sample, the variant procedure must be documented and provided to the analytical laboratory with the field notes.

1. SAMPLING POINTS

Sampling points and locations have to be chosen to be representative of the water samples in the treatment facility. Typical sampling points include well head, surge tanks, oil-water separator tanks, storage tanks, points before and after treatment units, and locations identified during

applications (Figure 2). Sampling locations will vary depending on the purpose of the proposed study. Sampling points should be chosen so that sampling events will be consistent over the timeframe of the test plan, to assure sample representability, comparability, and reproducibility.

Samplers need to work in teams of two or more to ensure each team member's safety, that proper sampling techniques are followed, and that adequate notes are taken at each sampling location. Take pictures of each sample location and record any observations specific to the sample location in the field notes. To prevent sample cross-contamination, samplers should wear a new pair of nitrile disposable gloves at each sampling point and use new disposable equipment or properly cleaned reusable equipment for sampling.

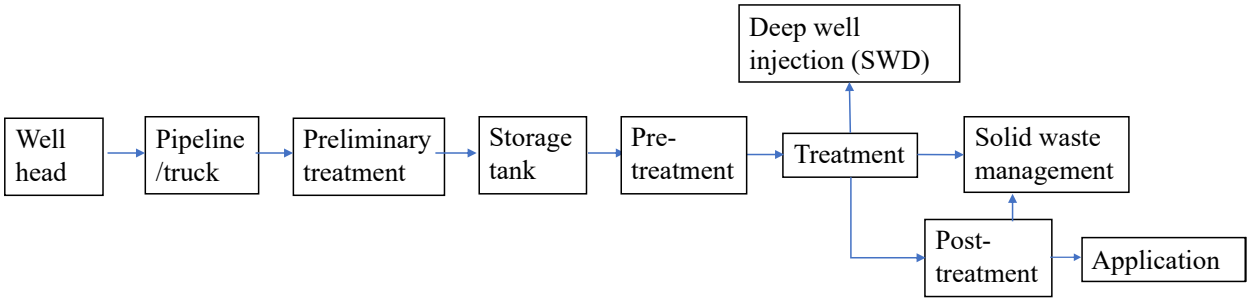

Figure 2. Common sampling points for produced water analysis.

2. ANALYTE SELECTION, CONTAINERS, AND LABELS

Sampling personnel must only use the container indicated by the analytical laboratory. Laboratory members should carefully choose the appropriate container for the target analyte(s) and coordinate with sampling personnel on the type and volume of the container to use. Table 2 lists the containers for different analytes. Container size can be different, but sample volume and characteristics for analysis should be collected strictly following the requirements of the analytical laboratory, e.g. samples collected in zero-headspace containers for volatile organic analysis (VOA). Certified clean containers, available from many scientific product vendors, are recommended for all samples.

It must be ensured that the sample container material is compatible with the analysis and "strictly follows" lab and/or Standard Methods requirements (Table 2). The most conservative container type should be selected based on the proposed analytical/testing request (e.g. if a tests program recommends two different containers, glass, and plastic, the primary sample should be taken in glass, and at no time should the sample touch a plastic container until separated for analyses that allow for plastic sampling containers). The same is true for analysis. If the sample received is in a plastic container, but the analysis requires a sample from a glass container, the desired analytical test may not be conducted if a sample is taken or received in the incorrect container.

Sampling personnel should code each sample with a unique sample ID and label it prior to sample collection to maintain identity and integrity. A sample identification protocol should be

established, which assigns completely unique sample numbers that cannot be mistaken for other containers. Sample numbers should also be unique to the date and time of sampling. It is recommended to prepare the sample labels and label the sample containers prior to sampling, and to log each sample number into a log sheet or spreadsheet prior to field collection. The log sheet can be printed for field use, or samples can be logged electronically in the field.

Sample labels should be made of material that is waterproof and will adhere to the sample containers even if wet. Label printing should also be waterproof. If there is a change in sample collection procedures that are made at the site that necessitates a label change, samplers should complete labels as they collect each sample and add them to the spreadsheet. Each self-adhesive label should be completed in indelible ink and contains the following information: sampling episode, sample ID, additives, sampling point, sample analysis, date and time of sample collection, bottle type, preservation, and samplers' initials. It is a good practice to prepare a bottle sample summary sheet that lists bottle type, size, preservative and intended analysis. This can serve as a checklist for both the sampler and the laboratory to ensure all containers are properly accounted for. If there is not enough space on the label, the sample ID and generic description should be recorded on the container and the remaining information should be recorded on the log sheet.

If any of the pre-printed information is incorrect, samplers should revise it using indelible ink. In particular, if a required preservation is not used, samplers should mark it out and document the deviation in the sample log sheet (Refer to an example in Appendix B).

Samplers will follow the following general protocols to maintain proper sample custody and to ensure that bottles do not get mixed up:

- Once the bottle label is applied to the sample container, cover labels with clear tape to prevent tampering, abrasion, smearing, peeling off, or loss during transit, sample preservation, or handling.
- Assemble the required sample containers for each sampling location and store them in boxes or ice chests labeled for each sampling location;
- Sample bottles have to be numbered on the lids using a permanent marker to ensure that none are missing;
- Sample bottles have to be filled in numerical order and double checked to ensure that none are skipped; and
- Samplers must keep samples in visual sight or in locked areas at all times. A chain of custody (Refer to an example in Appendix C) has to be filled to trace each sample container from the sampling point through shipping, analysis, and subsequent disposal.

3. SAMPLING AND PRESERVATION

3.1 Field measurement

During the sampling process, several parameters should be measured onsite when each sample is collected to estimate the sample variation, verify normal operations of the facility, and guide sample preservation methods. Samplers first need to perform the purge process as in Section 3.2 when sampling from a sample tap. Then samplers need to fill a 1-L glass jar during the collection of each sample or use a flow cell for some sampling points for field measurements.

- Temperature (SM 2550, a thermometer)
- pH [a pH meter or SM 4500-H B (Four color indicator strip)]
- Total sulfides (to include H_2S, EPA method 9030B)
- Conductivity (2520 B, a conductivity meter)
- Oxidation-Reduction Potential (ORP) (e.g., SESDPROC-113-R2, an ORP probe, or HQ11D Portable ORP/RedOx Meter)
- CO_2 (ASTM D 513-88, a gas sensing electrode or a titrator)
- Alkalinity (SM 2320 B-1997, a pH meter and a titrator)
- Ammonia
- If chlorine is used in the operation process, free residual chlorine in chlorinated water should be measured (SM 4500-Cl G). If a suitable disposal method/location is not available in the field for method SM 4500-Cl G, the EPA DPD method can be used by using a Hach test kit.

Temperature, pH, and total sulfides should be measured immediately after sample collection. All the meters should be calibrated before measurement based on procedures specified by the manufacturer. If a pH paper is used to measure the pH, measure the pH of the sample by transferring a drop of a sample using a disposable lab-certified-clean plastic pipette onto a pH paper. **The pH paper should not be inserted into the sample bottle**. Free chlorine measurements will be used to guide the sample preservation. Gross density and conductivity do not require immediate analysis and may be analyzed at the sampling point or later at the sampling staging area. If more field tests are required, such as chemical oxygen demand (COD), cyanide, and dissolved oxygen, a Hach DR900 Portable colorimeter with test kits could be a good candidate for these tests. Field measurement data should be included alongside samples for the duration of their life. If samples are taken and shipped to another facility, field measurement data should accompany all samples.

3.2 Sampling

Samplers will collect all samples as one-time grab samples unless other instructions are given by the analytical laboratory. Depending on the sampling points, an appropriate sample collection methodology should be chosen.

Sampling from a sample tap: the first step is to sufficiently purge the sample line by opening the tap and flushing the sample line, allowing water to flow into a slop bucket. The slop bucket should have a volume large enough to ensure that all non-sampled water can be accommodated in the bucket without any overflow. The sample tap should be allowed to flush for a minimum of 30 seconds, or 2 to 3 gallons (whichever results in a smaller flush volume) prior to collecting samples. After finishing this step, the water should be allowed to flow slowly and continuously into the slop bucket (that is, do not close the sample tap). The sampler will start filling sample bottles as follows:

- Retrieve a sample bottle, confirm that the label already affixed to the bottle matches the location being sampled, and remove the cap. Do not touch the inside of the sample bottle or the underside of the cap.
- Introduce the sample bottle into the water stream and fill to the required level. Then replace the cap. Samplers should be careful to prevent contact with the sample tap with the inside of the sample bottle. Sample bottles should be filled carefully, with minimal agitation or aeration allowed.
- Retrieve the next sample bottle and repeat the above steps until all bottles have been filled.
- Once all bottles have been filled, close the tap and dispose of the contents of the slop bucket via the facility's drain system, or bring to the lab for safe disposal.

Sampling from a water tank: Samplers will use a pole dipper to sample. Sample containers will be filled directly and sequentially by attaching them to the pole dipper using a zip tie. For 40-ml volatile organic analysis (VOA) vials and any other sample bottles that cannot be attached to the pole dipper, a 1-L glass transfer jar will be filled directly by attaching it to the pole dipper using zip-ties and lowering it directly into the open tank. The 1-L sample jar will also be used for field measurements as described above, taking care not to use the field sample "dip" for the analytical samples but rather discarding into the slop bucket for disposal in the sewer. Samplers will fill sample containers by pouring the contents slowly, avoiding aeration that may oxidize sensitive metals, from the sample transfer jar directly by tipping the pole dipper. Samplers have to minimize direct contact with the sample transfer jar and any part of the pole dipper that is lowered into the open tank. One approach may be to have one sampler manage the pole and outside of the jar while one or more others are careful to avoid all contact with it while taking samples and field measurements and recording information. It might be worthwhile to consider three-person sample teams if sample access will be via dipping or other approaches than sample taps.

When sampling from any tank, samplers must observe the presence/absence of an oil sheen. If the water tank is stratified, using a dipper will not produce a representative sample. Sludge judge can determine the presence/absence of multiphasic layers and provide information on the relative abundance of each layer. Tanks have guided wave radar level sensors that can also provide

information on phase presence. Representative samples must be collected based on the target analytes of the study and the instructions of the analytical laboratory.

Sampling from solid residual: The sampler can collect the sample by scooping a sample directly into the sample bottle and/or using a clean spatula to move solids into the sample container. The scoop and spatula must be cleaned between samples using reagent grade (or better quality) water. Samplers will be careful to keep the outside of the bottle clean by using gloves and minimizing contact of the outside of the bottle and the trough contents. It is important to ensure that the solid sample is representative of the residual being analyzed. The lab handling the solid sample should homogenize the solid sample and perform disaggregation if necessary.

Sample collection in VOA vials: For samples collected in 40-mL VOA vials, the VOA vials will be pre-preserved with HCl if needed. If free chlorine exists in a sample (Section 3.1), sodium thiosulfate will need to be added to the VOC method 624 VOA vials (Table 1). If sodium thiosulfate is needed a few crystals (10 mg/40 mL is sufficient for up to 5 part-per-million (ppm) Cl_2) must be added immediately after sample collection and prior to capping the vial.
For all VOA vials, samplers should eliminate any headspace in the vials by first reducing water flow and collecting the sample at an angle so that the water flows gently into the vial along the inner sidewall to reduce agitation and avoid introducing air bubbles, then filling the vial to form a convex meniscus of water (forms a "dome" just above the vial top) at the mouth of the vial. Cap the vial to ensure no bubbles are present once the lid has been placed. Check to make sure that the vial does not contain bubbles by inverting the bottle several times.

After the sample is collected, check vial threads to ensure they are clean and free of debris that would inhibit complete closure. Tighten the lid on each filled sample bottle, being careful not to over-tighten. If bottle threads are dirty such that the lid is impeded from closing, clear the threads on the bottle, being careful not to introduce contamination into the sample. Clean the sample bottle with a clean, dry cloth or paper towel. Samples should be stored properly as practically possible, as discussed below. Samplers need to put sampling point description, sample information, and sample representativeness and concerns in the field sampling log sheets (Refer to an example in Appendix A) at each sampling point. Take sampling point pictures with any observations.

Sampling for Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS): Sampling equipment used for PFAS sampling must be made from acceptable materials, which include high-density polyethylene (HDPE), polypropylene, silicone, stainless steel, nylon, polyvinyl chloride (PVC), acetate, and cotton. Sampling equipment that contain PFAS-based (fluoropolymers) parts that would be in direct contact with the sample or sampling environment are prohibited. These fluoropolymers include, but are not limited to polytetrafluoroethylene (PTFE, including the trademark Teflon® and Hostaflon®), polyvinylidene fluoride (PVDF, including the trademark

Kynar®), polychlorotrifluoroethylene (PCTFE, including the trademark Neoflon®), ethylene-tetrafluoro-ethylene (ETFE, including the trademark Tefzel®), fluorinated ethylene propylene (FEP, including the trademarks Teflon® FEP, Hostaflon® FEP, and Neoflon®).

All sample containers used for PFAS sampling should come from the laboratory that is performing the PFAS analysis. High-density polyethylene (HDPE) or polypropylene sample bottles with Teflon®-free caps are the preferred sampling containers for PFAS sampling. PFAS may adsorb to glass containers and therefore should not be used for water, leachate, or other aqueous samples.

3.3 Quality assurance of samples

For quality assurance, samplers need to collect duplicate samples. The number of duplicate samples with sampling locations should be given before sampling; duplicate sample jars should be numbered and identified prior to field sampling, in the same manner as the regular samples. Samplers should collect duplicate samples as sequential grab samples. To minimize duplicate sample variability resulting from temporal variability in wastewater characteristics, the duplicate sample bottle for each analyte will be filled immediately after the original sample bottle for that analyte is filled (as opposed to filling all sample bottles for the original sample and then filling all the samples bottles for the duplicate sample). Duplicate sampling should follow the same procedure as the original samples. It may be advisable to label all samples with an alphanumeric code instead of an identification that describes the location to minimize the 'bias' when laboratory testing the samples.

Field blanks must be collected to evaluate potential sample contamination from exposure to the sampling site conditions, field handling, storage, and preservation procedures. Field blanks will be collected in the same type of bottles for each analytical type and be analyzed for the same list of analytes. To collect field blanks, samplers will pour the laboratory prepared water (deionized water has been analyzed for the parameters of interest) into sampling bottles and follow the sample procedures for other samples. Equipment blanks are collected to determine if the sampling equipment is a source of sample contamination. They are collected by rinsing sampling equipment with an analyte-free matrix (typically HPLC grade water), and in the case of tubing and similar disposable (single use) collection equipment, one equipment blank will be prepared for each lot of equipment purchased. Equipment blanks will be analyzed for the same parameters as those analyzed on the samples collected using the sampling equipment.

3.4 Sample Preservation

Table 2 provides the sample container and preservation information for various target analytes. The type and amount of preservative used have to be recorded on sample preservation log sheets (Appendix B). The preservatives must be analyzed for the parameters of interest in the research lab to certify that the concentrations are below the reporting limit of concentration of concern. During the sampling process, the sampling team has to confirm that the pH of the samples meets

the preservation requirement. If not, then the sampling team will add additional preservatives to each sample to adjust the pH to meet the requirement.

Preservatives can be added in the lab before field sampling to minimize the field work. For example, 1 mL of concentrated nitric acid can be added into 1-L glass bottle for total metal sampling before the field sampling trip. However, the preservative should never exceed 10 percent of the total volume.

pH adjustment for plastic bottles:

1. For samples collected in plastic bottles that require pH adjustment, samplers will measure the pH of the sample by transferring a drop of the sample using a disposable lab-certified-clean plastic pipette onto a pH paper. Record value as initial pH on sample preservation log sheet (Appendix B). If the sample does not meet the pH preservation requirement, complete step 2.
2. Add 20 drops (1 mL) of the specified preservation chemical to every 1-liter sample using a plastic pipette (e.g., graduated disposable pipettes, 3 mL) dedicated to that preservation chemical. Close and tighten the sample container lid and then mix the sample. Record the quantity of preservative addition on the sample preservation log sheet.
3. Repeat steps 1 and 2 as needed until the target preservation is reached without exceeding 10% of the sample volume.

pH adjustment for glass bottles:

Some analytical methods may require glass containers (e.g., non-borosilicate glass that does not leach Na, clear or amber borosilicate glass VOA vials) and chemical preservation. For example, the measurement of n-Hexane extractable material/silica gel treated n-Hexane extractable material (HEM/SGT-HEM) requires the samples collected in VOA vials (Table 2). VOA vials will be pre-preserved with acid and then screened for the presence of free chlorine.

HEM/SGT-HEM samples will be preserved as follows:

1. An additional 1-L glass field jar will be used to collect an extra sample that will be used to determine the amount of chemical preservation needed for a 1-L sample. This extra sample will be used only for the purpose of determining HEM/SGT-HEM preservation, and then the contents will be disposed of.
2. Samplers will measure the pH of the extra sample by transferring a drop of sample using a disposable lab-certified-clean plastic pipette onto a pH paper. Record value as initial pH on sample preservation log sheet. If the sample does not meet the pH preservation requirement, continue to step 3.
3. Add 20 drops (1 mL) of preservation chemical to every 1-liter sample using a plastic pipette (e.g., graduated disposable pipettes, 3 mL) dedicated to the preservation chemical. Close and tighten the extra sample container lid and then mix the sample. Record quantity of preservation addition on the sample preservation log sheet.

4. Repeat step 2 and 3 as needed until the target preservation is reached without exceeding 10% of the sample volume.
5. Once the target preservation pH is met and the total volume of required preservative is known, samplers will add the same volume of acid to the HEM/SGT-HEM samples that will be sent to the lab for that sampling point. These sample jars will not be pH tested using pipettes to minimize loss of oil and grease onto the pipette.

After sampling, field sampling log sheets will be filled to record the sampling method, sampling equipment, names of the samplers, sample collection times, field measurements, and any notes and observations.

4. SAMPLE PACKING, SHIPPING, AND TRAFFIC REPORT

If the collected samples need to be stored in cool conditions (Table 2), the samples will be quickly chilled by immersion in ice water, packed in ice chests with sufficient wet ice to maintain a temperature below 6 °C, and then sent to analytical laboratories as soon as possible. For samples with a holding time of less than 48 hours, it is more practical to perform onsite analysis if possible, or the sample should be sent out on the sampling day or the next day after collection. Each shipment to the laboratory will contain a temperature blank, and the temperature will be taken and noted on the traffic report at the time of shipping. The temperature of the temperature blank will also be recorded by the laboratory upon receipt of samples. Exceptions include metals samples and radiological solids samples which have no temperature preservation requirements. The details about sample holding time are summarized in Table 2.

To maintain a record of sample collection, transfer between personnel, shipment carrier, and the laboratory, samplers will complete Chain of Custody reports for all samples sent to all laboratories. These forms are used to document sample custody transfer and preservation maintenance from the field to the laboratory.

Table 2. Analytes, containers, preservations, and holding times

Analyte	Method (Technique)	Sample Container[1]	On-Site Preservation	Holding Time
Inorganic and Wet Chemistry				
Alkalinity, Carbonate, Bicarbonate	SM 2320 B-1997 (Titration)	250 mL - Plastic	Cool to ≤ 6°C	14 Days[2]
Ammonia	EPA 350.1 (Colorimetric)	250 mL - Plastic	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Asbestos	EPA 100.1/100.2	1 L- Plastic	None. Contact with acid should be avoided	Not specified
Biochemical Oxygen Demand (BOD_5)	SM 5210 B-2001 (Titrimetric)	1000 mL - Plastic	Cool to ≤ 6°C	48 Hours
Chemical Oxygen Demand (COD)	EPA 410.4 (Spectrophotometric)	500 mL - Plastic	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Chlorine, Total Residual	SM 4500 Cl- G	250 mL - Plastic	Not required	15 Minutes
Dissolved Oxygen	SM 4500–O G–2011 (Probe method)	500 mL - Glass	Not required	15 Minutes
Dissolved Organic Carbon	EPA 415.1 SM 5310 B-2000 (Combustion)	250 mL – Amber Glass	H_2SO_4 or H_3PO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Fluoride, Chloride, Nitrite, Ortho-Phosphate-p, Bromide, Nitrate, Sulfate, Bromate, Chlorite, Chlorate	EPA 300.0 (Ion Chromatography)	500 mL - Plastic	Cool to ≤ 6°C	28 Days except NO_2, NO_3, Ortho-P 48 Hours
Fluoride, Chloride, Nitrite, Ortho-Phosphate, Bromide, Nitrate, Sulfate	ASTM D4327 (Suppressed Ion Chromatography)	500 mL - Plastic	Cool to ≤ 6°C	28 Days except NO_2, NO_3, Ortho-P 48 Hours
Hardness	SM 2340B	250 mL - Plastic	HNO3 until pH is < 2, Cool to ≤ 6°C	6 Months
Iodide	EPA 345.1	250 mL - Plastic	Cool to ≤ 6°C	24 Hours
Methylene Blue Active Substances (Surfactants, anionic)	EPA 425.1 or SM 5540 C	250 mL - Plastic	Cool to ≤ 6°C	48 Hours

N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM)	EPA 1664A (Gravimetric)	1 L - Wide-Mouth Glass	HCl or H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Nitrogen, Ammonia	SM 4500 NH3-B,C	500 mL - Plastic	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Nitrogen, Total Kjeldahl	SM 4500Norg B,C SM 4500 NH3-C	500 mL - Plastic	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Oxidation Reduction Potential (ORP)	SM 2580 B-1997	100 mL - Plastic	Not specified	15 minutes
Perchlorate	SW-846 6860	125 mL - Plastic	0.2 µm filtration through PTFE membrane within 15 mintes	28 Days
pH	SM 4500–H+ B–2011	100 mL – Plastic	Not required	15 mintues
Phenolics	EPA 420.4	1 L - Glass	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Phosphorous, Total	ASTM D515	500 mL - Plastic	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Salinity	SM 2520	250 mL - Plastic	Cool to ≤ 6°C	28 Days
Silica	EPA 200.7/6010 D	250 mL - Plastic	Cool to ≤ 6°C	28 Days
Specific Conductance	2510 B–2011 (Conductivity Meter)	100 mL – Plastic	Cool to ≤ 6°C	28 Days
Sulfate	300.0/375.4	500 mL - Plastic	Cool to ≤ 6°C	28 Days
Sulfide	SM 4500-S^{2-} D-2011	500 mL - Plastic	Cool to ≤ 6°C Zn Acetate & NaOH to pH > 9	7 Days
Sulfite	SM 4500 SO3-B	100 mL - Plastic	Not required	15 Minutes
Temperature	SM 2550 B–2010	100 mL – Plastic	Not required	15 Minutes

Total Dissolved Solids (TDS)	SM 2540 C-1997 (Gravimetric)	250 mL - Plastic	Cool to ≤ 6°C	7 Days
Total Hardness	SM 2340 C-1997 (Titrimetric)	250 mL - Plastic	HNO_3 or H_2SO_4 until pH is < 2, Cool to ≤ 6°C	6 Months
Total Organic Carbon (TOC)	EPA 415.1 SM 5310 B-2000 (Combustion)	250 mL – Amber Glass	H_2SO_4 or H_3PO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Total Suspended Solids (TSS)	SM 2540 D-1997 (Gravimetric)	1000 mL - Plastic	Cool to ≤ 6°C	7 Days
Turbidity	EPA 180.1	100 mL - Plastic	Cool to ≤ 6°C	48 Hours
Metals				
Trace elements [Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Au, Fe, Pb, Li, Mg, Mn, Mo, Ni,P, K, Se, Ag, Na, Sr, Tl, Sn, Ti, U, V, Zn] (Total)	EPA 200.7 (ICP), EPA 200.8/EPA 6020B(ICPMS)	500 mL - Plastic	HNO_3 until pH is < 2	6 Months
Trace elements [Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Au, Fe, Pb, Li, Mg, Mn, Mo, Ni,P, K, Se, Ag, Na, Sr, Tl, Sn, Ti, U, V, Zn] (Dissolved)	EPA 200.7 (ICP), EPA 200.8/EPA 6020B(ICPMS)	500 mL - Plastic	0.45 µm filtration in 15 minutes, HNO_3 until pH is < 2	6 Months
Mercury	EPA 245.1 or 245.2 (Cold Vapor Atomic Absorption)	500 mL - Plastic	HNO_3 until pH is < 2	28 Days
Silica	EPA 200.7/6010 D	250 mL - Plastic	Cool to ≤ 6°C	28 Days
Hexavalent Chromium	SM 3500 -Cr B-2009 (Colorimetric)/ EPA 7199	250 mL - Plastic	Cool to ≤ 6°C	24 Hours
Organics				
2,4-dichlorophenoxyacetic acid	EPA 615	1-L - Glass	Cool to ≤ 6°C	7 Days

Agent Breakdown Products	EPA Method 538	40-mL VOA vials (Amber)	1.5 g/L Ammonium acetate and 64 mg/L Sodium Omadine, Cool to ≤ 6°C	14 Days
Alcohols	EPA 8260C, 8270D, and 8015C (GC/MS)	40-mL VOA vials	HCl until pH < 2, Cool to ≤ 6°C	14 Days
Aldehydes	EPA 8315(HPLC)	250 mL - Amber Glass	Cool to ≤ 6°C	3 Days
Carbaryl	EPA 632	1-L - Glass	Cool to ≤ 6°C	7 Days
Chlorpyrifos	EPA 622	1 L - Glass	Cool to ≤ 6°C	7 Days
Diazinon	EPA 614	1 L - Glass	Cool to ≤ 6°C	7 Days
Demeton	EPA 614	1 L - Glass	Cool to ≤ 6°C	7 Days
Dioxins	EPA 1613B; SW846 (2,3,7,8 TCDD)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Diesel Range [C10 - C28]	EPA 3520C (sample preparation) EPA 8015D (analysis) (GC)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Explosives	SW 846 – 8330B (HPLC)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Gasoline Range [C6 - C10]	EPA 5030B (sample preparation) EPA 8015D (analysis) (GC)	40-mL VOA vials (Amber)	Cool to ≤ 6°C	7 Days
GCMS Purgeables	EPA 524.2	40-mL VOA vials (Amber)	Ascorbic acid and HCl until pH < 2, Cool to ≤ 6°C	14 Days
GCMS Purgeables	EPA 624/8260C	40-mL VOA vials (Amber)	HCl until pH < 2, Cool to ≤ 6°C	14 Days
Guthion (Azinphos-methyl)	EPA 614	1 L - Glass	Cool to ≤ 6°C	7 Days
Haloacetic Acids	EPA 552.2	250 mL - Amber Glass	Cool to ≤ 6°C, NH4Cl	14 Days
Herbicides	EPA 8151A (GC)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days

Malathion	EPA 614	1 L - Glass	Cool to ≤ 6°C	7 Days
Mirex	EPA 617	1 L - Glass	Cool to ≤ 6°C, pH adjusted to 6-8 with NaOH or H_2SO_4	7 Days
Oil & Grease	EPA 1664B (Extraction and Gravimetry)	1-L Amber Glass	HCl or H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Oil Range [C28-40]	EPA 5030B (sample preparation) EPA 8015D (analysis) (GC)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Organic Acids	SM 5560 C	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)	SW-846 Method 8327	1-L HDPE, no contact with Teflon	5 ml HNO_3	28 Days
Pesticides	EPA 608/8081B /8115 (GC)	1-L Amber Glass	Cool to ≤ 6°C	7 Days
Polyaromatic hydrocarbons (PAHs)	SW 8270 C	1-L Amber Glass	Cool to ≤ 6°C	7 Days
Polychlorinated biphenyls (PCBs)	SW 8082 A	1-L Amber Glass	Cool to ≤ 6°C	Not specified
Semivolatile Organic Compounds + Tentative Identified compounds	EPA 3520C/8270C (GC /MS)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Semivolatile Organic Compounds + Tentative Identified compounds	EPA 625/8270D (GC)	1-L - Glass	Cool to ≤ 6°C, Add $Na_2S_2O_3$in the presence of residual chlorine	7 Days
Total Organic Halides (TOX)	SW 846 9020	250 mL Amber Glass	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Total Petroleum Hydrocarbons	EPA 1664B (Extraction and Gravimetry) EPA 8015D (GC)	1-L Amber Glass	HCl or H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Tributyltin	EPA 6020: Metals-Total Subbed	1 L - Glass	Cool to ≤ 6°C	Not specified

Tributyltin (Tributyltin chloride)	EPA 8323	1 L - Glass	Cool to ≤ 6°C	24 Hours
Volatile Organic Compounds + Tentative Identified compounds	EPA 5030 or EPA 5035/8260B (GC/MS)	40-mL VOA vials (Amber)	HCl until pH < 2, Cool to ≤ 6°C	14 Days
Volatile Organic Compounds + Tentative Identified compounds	EPA 624.1 (GC /MS)	40-mL VOA vials (Amber)	HCl until pH < 2, Cool to ≤ 6°C, Add $Na_2S_2O_3$ (a few crystals) in the presence of residual chlorine	14 Days
Radioactive				
Total Radium 226 (Liquid Samples)	EPA 903.1 (Radon Emanation)	1-L - Plastic	HNO_3 until pH is < 2	6 Months
Total Radium 228 (Liquid Samples)	EPA 904.0 (Radiochemical/Precipitation)	1-L - Plastic	HNO_3 until pH is < 2	6 Months
Total Radium 226 and 228 (Solid Samples)	EPA 901.1 (Gamma Spectroscopy)	215 grams - Wide-Mouth Plastic	None	6 Months
Gross Alpha/Beta (Liquid Samples)	EPA 900.0 (Evaporation)	500 mL –Wide-Mouth Plastic	HNO_3 until pH is < 2	6 Months
Gross Alpha/Beta (Solid Samples)	EPA 900.0 (Evaporation)	30 grams - Wide-Mouth Plastic	None	6 Months
Strontium 90	EPA 905.0	1-L - Plastic	HNO_3 until pH is < 2	6 Months
Microbiological				
Coliform, Fecal	SM 9222D	250 mL - Sterile Plastic	Cool to ≤ 6°C	8 Hours
Coliform, Fecal Strep	SM 9230A/B	250 mL - Sterile Plastic	Cool to ≤ 6°C	6 Hours
Coliform, Total	EPA 1603	250 mL - Sterile Plastic	Cool to ≤ 6°C	8 Hours
Coliform, E.Coli	EPA 1603	250 mL - Sterile Plastic	Cool to ≤ 6°C	8 Hours
Enterococci	EPA 1600	250 mL - Sterile Plastic	Cool to ≤ 6°C	8 Hours
Heterotrophic Plate Count	SM 9215B	250 mL - Sterile Plastic	Cool to ≤ 6°C	8 Hours

Whole Effluent Toxicity (WET)				
Acute Nonvertebrate	*Ceriodaphnia dubia* EPA 2002.0	4-L –Plastic Cubitainer	Cool to ≤ 6°C	36 Hours
Acute Vertebrate	*Pimephales promelas* EPA 2000.0	4-L –Plastic Cubitainer	Cool to ≤ 6°C	36 Hours
Chronic algae	*Selenastrum capricornutum* EPA 1003.0	4-L –Plastic Cubitainer	Cool to ≤ 6°C	36 Hours
Chronic Nonvertebrate	*Ceriodaphnia dubia* EPA 1002.0	4-L –Plastic Cubitainer	Cool to ≤ 6°C	36 Hours
Chronic Vertebrate	*Pimephales promelas* EPA 1000.0	4-L - Plastic Cubitainer	Cool to ≤ 6°C	36 Hours

1. The sample container material must be chemically inert and compatible with the analytes and "strictly follows" lab and/or Standard Methods requirements
2. Alkalinity: 14 days holding time for treated samples, and should be analyzed as soon as possible for untreated samples.

Appendix A. Field Sampling Log Sheet

Samplers' Names: _____

Sampling Episode: _____

Sampling Method and Sampling Equipment Used:

_____

_____

_____

Sample ID	Date and Time	Temp (ºC)	pH	Conductivity	Weight of 100 mL of Sample	Free Chlorine

Notes: (include observations of odor and color of each aliquot, take photographs, and note any deviations from the plan):

_____

_____

_____

_____

Appendix B. Sample Preservation Log Sheet

Preservation Chemicals - List Strength of Solution from Bottle								
HCl _____ HNO_3 _____ H_2SO_4 _____ $Na_2S_2O_3$ _____NaOH _____ Other_____								
Sample Number	Analysis	Bottle type	Date	Name of Sampler	Chemical	Initial pH	Final pH	Number of Drops

Appendix C. Sample Chain of Custody

CHAIN OF CUSTODY

Address:

WEATHER		Fog	Rain	Snow	Wind	Clear
LEVEL	None					
	Light					
	Moderate					
	Heavy					

REQUESTED SERVICES

CONTACT INFORMATION			
Company:		Address:	
Contact:		Special instructions:	
Phone:			

PROJECT INFORMATION				TRUN AROUND TIME CODES - (TAT)	
Project ID:				STD - Standard (Defualt)	Rushes received after 2pm or on weekends, will be considered received the next business day. Please alert us in advance of weekend analysis needs.
Project Description:				ND - Next Business Day	
Project Zip Code		Sampling Date/Time:		SD - Same Business Day	
PO number		Sampled By:		WH - Weekend/Holiday/ASAP	

SAMPLE ID	DESCRIPTION	Sample Type (Below)	TAT (Above)	Total Volume/Area (as applicable)		NOTES (Time of the day, Temp, RH, etc.)		

SAMPLE TYPE CODES				RELINQUISHED BY	DATA & TIME

RECEIVED BY	DATA & TIME