New Mexico Produced Water Research Consortium

# Guidance on Produced Water Sampling Procedure


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# PREFACE

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

The report presents a water sampling protocol for pilot demonstration of produced water treatment and use in for fit-for-purpose applications. The guidance is based on the standard methods SW-846 by Environmental Protection Agency, and methods used by commercial laboratories (e.g., Eurofins[1]) for produced water analysis.

The protocol provides step-by-step guidance and information on sample collection and preservation of produced water samples in oil and gas field. It aims to serve as a guide to the field sampling crew.

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

# ACRONYMS

| | |
|---|---|
| bbl | Barrels (42 gallons) |
| $BOD_5$ | Biochemical Oxygen Demand |
| COD | Chemical Oxygen Demand |
| EPA | Environmental Protection Agency |
| HEM/SGT-HEM | n-Hexane Extractable Material/ Silica Gel Treated n-Hexane Extractable Material |
| HPLC | High Performance Liquid Chromatography |
| GC | Gas chromatography |
| ITRD | Innovative Technology Treatment Demonstration |
| NMED | New Mexico Environment Department |
| NMPWRC | New Mexico Produced Water Research Consortium |
| PPE | Personal Protection Equipment |
| QA/QC | Quality Assurance and Quality Control |
| SOP | Standard Operating Procedure |
| TDS | Total Dissolved Solids |
| TICs | Tentative Identified Compounds |
| TOC | Total Organic Carbon |
| TSS | Total Suspended Solids |
| TSC | Technical Steering Committee |
| VOA | Volatile Organic Analysis |

## SAMPLING PROCEDURE

**Objective**: provide information and guidance regarding sample collection and preservation for produced water samples in oil and gas field. Serve as a guide to the field sampling crew.

**Safety:** Samplers have to wear personal protection equipment, such as googles, gloves, and other personal protection equipment (PPE) required by the facility. Always work in team of two or more. Follow the safety instructions of the facility.

## 1. Sampling points

Sampling points and locations have to be chosen to be representative of the water samples in the facility, common sampling points include well head, surge tank, oil water separator, storage tank, points before and after treatment unit, and during applications (Figure 1). Also, the sampling points have to be consistent to assure the results from different period of measurements comparable.

Samplers need to work in teams of two or more to ensure that proper sampling techniques are followed, and adequate notes are taken at each sampling location. To prevent sample cross-contamination, samplers have to wear a new pair of disposable gloves at each sampling points and use new disposable equipment for sampling.

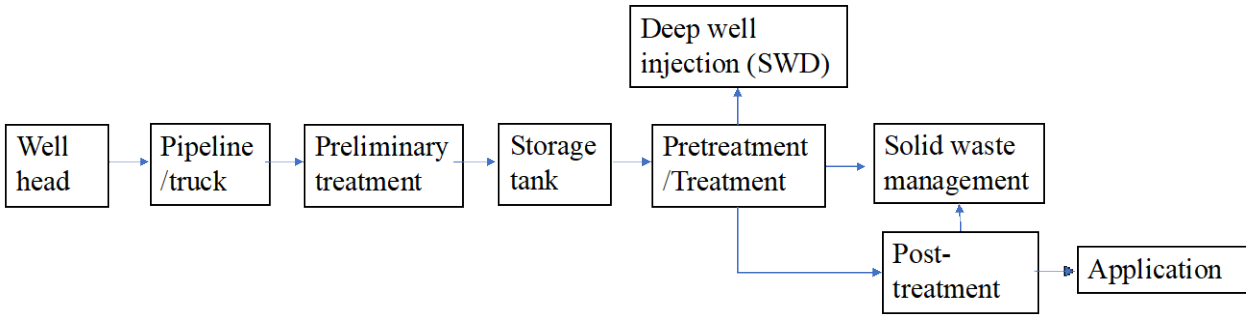


Figure 1. Common sampling points for produced water analysis.

## 2. Analyte selection, containers, and labels

Samplers have to carefully choose appropriate container for the target analyte. Table 1 lists the containers for different analytes. Container size can be different, but enough sample volume for analysis should be collected.
The samplers have to code each grab sample with a unique sample number and label it prior to sample collection to maintain identity and integrity. It is recommended to prepare the sample labels prior to sampling. If there is a change in sample collection procedures that are made at the site that necessitates a label change, samplers may complete labels as they collect each sample. Each self-adhesive label is completed in indelible ink and contains the following information: sampling episode, sample ID, sampling point number, sample analysis, date and time of sample collection, bottle type, analysis, and preservation.

If any of the pre-printed information is incorrect, samplers need to revise it using indelible ink. In particular, if a required preservation is not used, samplers have to mark it out and document the deviation in the sample preservation 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 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 have to keep samples in visual sight or in locked areas at all times.

## 3. Sampling and preservation

### *3.1 Field measurement*

During sampling process, several parameters should be measured onsite when each sample is collected to estimate the sample variation and to guide sample

preservation methods. Samplers need to fill a 1-L glass jar during collection of each sample for field measurements.

- Temperature (SM 2550, thermometer)
- pH [pH meter or SM 4500-H B (Four color indicator strip)]
- Free residual chlorine (SM 4500-Cl G) should be measured immediately after sample collection.
- Gross density (Mass of 100 ml of sample using a scale
- Conductivity (2520 B conductivity meter)

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 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.

### *3.2 Sampling*

Samplers will collect all samples as one-time grab samples, unless other instructions are given. Depending on the sampling points, different 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 allow water to flow into a slop bucket for a minimum of 30 seconds, or 2 to 3 gallons prior to collecting samples. After finishing this step, the water should be continuing flow into the slop bucket. Sampler will start filling sample bottles as follows:

- Retrieve a sample bottle, confirm that the bottle 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 of the sample tap with the inside of the sample bottle.
- Retrieve the next sample bottle and repeat the above steps until all bottles have been filled.
- Once all bottles have been filled, the contents of the slop bucket will be disposed of via the facility's drain system.

**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. Samplers will fill sample containers by pouring the contents of the sample transfer jar directly by tipping the pole dipper. Samplers have to minimize direct contact with the sample transfer jar and parts of the pole dipper that is lowered into the open tank.

**Sampling from solid residual**, sampler can collect the sample by scooping a sample directly into the sample bottles. 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.

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) $Cl_2$) will be added immediately after sample collection and prior to capping the vial.

For all VOA vials, samplers have to 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 meniscus of water at the mouth of the vial. Cap the vial to ensure that 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 sample is collected, 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 to not 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. Sampling point pictures are also recommended if applicable.

### *3.3 Quality assessment samples*

For quality assessment, samplers need to collect duplicate samples. The number of duplicate samples with sampling locations should be given before sampling. 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). Sampling duplicate samples should follow the same procedure for original samples.

Field blanks have to be collected to evaluate potential contamination of the sample from exposure to the sampling site conditions, field handling, storage, preservation, and all analytical 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 HPLC grade water into sampling bottles and follow the sample procedures for other samples. Equipment blanks are collected to document non-contaminated condition of sampling equipment. 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 Preservation*

Table 1 provides the sample container and preservation information for target analyte. The type and amount of preservation used have to be recorded on sample preservation log sheets (Appendix B). During sampling process, the sampling team has to confirm that the pH of samples meets the preservation requirement. If not, then the sampling team will add additional preservative to each sample to adjust the pH to meet the requirement. However, the preservation should never exceed 10 percent of the total volume.

**pH adjustment for plastic bottles**:

1. For samples collected in plastic bottles and that require pH preservation, samplers will measure the pH of the 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

(Appendix B). If the sample does not meet the pH preservation requirement, complete step 2.
2. Add 20 drops (1 mL) of preservation chemical to every 1-liter sample using a plastic pipette dedicated to the preservation chemical. Close and tighten the sample container lid and then mix the sample. Record quantity of preservation addition on the sample preservation log sheet.
3. Repeat step 1 and 2 as needed until the target preservation is reached without exceeding 10% of the sample volume.

**pH adjustment for glass bottles:**

Analytical methods that require glass containers and chemical preservation include n-hexane extractable material/ Silica gel treated n-Hexane extractable materia (HEM/SGT-HEM) and samples collected in VOA vials. VOA vials will be pre-preserved with acid and then preserved 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 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 has to 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 condition (Table 1), the samples will be packed in ice chests with sufficient wet ice to maintain a temperature below 6 °C and be sent to analytical laboratories as soon as possible. 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.

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

Table 1. Analytes containers, preservations, and holding time

| Analyte | Method (Technique) | Sample Container | On-Site Preservation | Holding Time |
|---|---|---|---|---|
| **Wet Chemistry** | | | | |
| Total Dissolved Solids (TDS) | SM 2540 C-1997 (Gravimetric) | 250 mL - Plastic | Cool to ≤ 6˚C | 7 Days |
| Total Suspended Solids (TSS) | SM 2540 D-1997 (Gravimetric) | 1000 mL - Plastic | Cool to ≤6˚C | 7 Days |
| Specific Conductance | SM 2510 B-1997 (Conductivity Meter) | 100 mL - Plastic | Cool to ≤6˚C | 28 Days |
| Alkalinity | SM 2320 B-1997 (Titration) | 250 mL - Plastic | Cool to ≤6˚C | 14 Days |
| Chemical Oxygen Demand (COD) | EPA 410.4 (Spectrophotometric) | 500 mL - Plastic | $H_2SO_4$ until pH < 2, Cool to ≤ 6˚C | 28 Days |
| Total Organic Carbon (TOC) | 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 |
| Ammonia | EPA 350.1 (Colorimetric) | 250 mL - Plastic | $H_2SO_4$ until pH < 2, Cool to ≤ 6˚C | 28 Days |
| 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 |
| Biochemical Oxygen Demand (BOD5) | SM 5210 B-2001 (Titrimetric) | 1000 mL - Plastic | Cool to ≤6˚C | 48 Hours |
| Total Hardness | SM 2340 C-1997 (Titrimetric) | 250 mL - Plastic | HNO3 or $H_2SO_4$ until pH is < 2, Cool to ≤ 6˚C | 6 Months |
| **Anions** | | | | |

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|---|---|---|---|---|
| Fluoride, Chloride, Nitrite, Ortho-Phosphate, Bromide, Nitrate, Sulfate | ASTM D4327 (Suppressed Ion Chromatography) | 500 mL - Plastic | Cool to ≤ 6˚C | 28 Days except NO2, NO3, Ortho-Phosphate 48 Hours |
| 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 NO2, NO3, Ortho-Phosphate 48 Hours |
| **Total Metals** | | | | |
| Trace elements | EPA 200.8 | 500 mL - Plastic | $HNO_3$ 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 |
| Hexavalent Chromium | SM 3500-Cr B-2009 (Colorimetric) | 250 mL - Plastic | Cool to ≤ 6˚C | 24 Hours |
| **Organics** | | | | |
| Diesel Range | EPA 3520C (sample preparation) EPA 8015C (analysis) (GC) | 1-L - Amber Glass | Cool to ≤ 6˚C | 7 Days |
| Gasoline Range | EPA 5030B (sample preparation) EPA 8015C (analysis) (GC) | 40-mL VOA vials | Cool to ≤ 6˚C | 7 Days |
| Volatile Organic Compounds + Tentative Identified compounds (TICs) | EPA 5030 or EPA 5035/8260C (GC /MS) | 40-mL VOA vials | HCl until pH < 2, Cool to ≤ 6˚C | 14 Days |
| Volatile Organic Compounds + TICs | EPA 624 (GC /MS) | 40-mL VOA vials | HCl until pH < 2, Cool to ≤ 6˚C, Add $Na_2S_2O_3$ (a few crystals) in the presence of residual chlorine | 14 Days |

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|---|---|---|---|---|
| Semivolatile Organic Compounds + TICs | EPA 3520C/8270D (GC /MS) | 1-L - Amber Glass | Cool to ≤ 6˚C | 7 Days |
| Semivolatile Organic Compounds + TICs | EPA 625 (GC) | 1-L - Glass | Cool to ≤ 6˚C, Add $Na_2S_2O_3$in the presence of residual chlorine | 7 Days |
| Alcohols | EPA 8260C, 8270D, and 8015C (GC/MS) | 40-mL VOA vials | HCl until pH < 2, Cool to ≤ 6˚C | 14 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 |
| Total Petroleum Hydrocarbons | EPA 1664B (Extraction and Gravimetry) | 1-L Amber Glass | HCl or $H_2SO_4$ until pH < 2, Cool to ≤ 6˚C | 28 Days |
| Total Petroleum Hydrocarbons by GC | Modified EPA 8100 (GC) | 1-L Amber Glass | HCl until pH < 2, Cool to ≤ 6˚C | 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 |
| **Whole Effluent Toxicity (WET)** | | | | |

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|---|---|---|---|---|
| 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 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 |

## Appendix A. Field Sampling Log Sheet

Samplers' Names: _____

Sampling Episode: _____

Sampling Method and Sampling Equipment Used:

_____

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| Sample ID | Date and Time | Temp (ºC) | pH | Conductivity | Weight of 100 mL of Sample | Free Chlorine |
|---|---|---|---|---|---|---|
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Notes: (include observations of odor and color of each aliquot, take photographs, and note any deviations from the plan):

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## 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 | Date | Name of Sampler | Chemical | Initial pH | Final pH | Number of Drops |
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