

Washington State Department of Ecology

Environmental Assessment Program

Standard Operating Procedures for Collecting Groundwater Samples for Metals Analysis from  
Monitoring Wells

Version 1.0

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*Please note that the Washington State Department of Ecology's Standard Operating Procedures (SOPs) are adapted from published methods, or developed by in-house technical and administrative experts. Their primary purpose is for internal Ecology use, although sampling and administrative SOPs may have a wider utility. Our SOPs do not supplant official published methods. Distribution of these SOPs does not constitute an endorsement of a particular procedure or method.*

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*Although Ecology follows the SOP in most instances, there may be instances in which the Ecology uses an alternative methodology, procedure, or process.*

SOP Revision History

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## Environmental Assessment Program

### Standard Operating Procedure for Collecting Groundwater Samples for Metals Analysis from Monitoring Wells

#### **1.0 Purpose and Scope**

- 1.1 This document is the Environmental Assessment Program (EAP) Standard Operating Procedure (SOP) for Collecting Groundwater Samples for Metals Analysis from Monitoring Wells.
- 1.2 Heavy metals, metalloids, and inorganic trace elements (e.g. aluminum, antimony, arsenic, cadmium, copper, iron, lead, manganese, nickel, selenium, and zinc) are collectively referred to here as metals.
- 1.3 There are various purposes for collecting groundwater samples from monitoring wells. Typical purposes involve characterization of ambient conditions, definition of the nature and extent of groundwater pollutants, identification of trends in contaminant concentrations, and determination of compliance with regulatory standards.
- 1.4 In order to avoid bias in sampling results, groundwater measurements and samples must be as representative of in situ conditions as possible. The in situ geochemical condition of the groundwater at the time of sampling, as well as turbidity and atmospheric exposure of the sample are some of the critical factors to consider when sampling for metals. This SOP summarizes the general procedures and practices that EAP staff use to collect representative groundwater samples for metals analysis from monitoring wells, piezometers, or other wells (e.g. irrigation wells) that do not have dedicated or in-place pumps.

#### **2.0 Applicability**

- 2.1 This SOP applies to EAP staff collecting groundwater metals samples from monitoring wells. Variations from the procedures outlined in this SOP may be justified based on a project's technical objectives and field conditions, and should be documented in both the project work plan and final project report. Projects that include analysis of metals at ultra-low concentrations (e.g. below standard Manchester Environmental Laboratory reporting limits) may require specialized field techniques and ultra-clean equipment; these methods are not discussed here.

### **3.0 Definitions**

- 3.1 Aquifer – An underground layer of saturated permeable/porous rock or sediments (e.g. gravel, sand or silt) that is capable of storing and releasing water to wells and springs.
- 3.2 Dissolved Oxygen – The relative amount of oxygen that is dissolved or carried in water.
- 3.3 Depth-to-Water – The measured depth to the top of the groundwater surface in a well. Also referred to in this SOP as water level measurement.
- 3.4 EAP – Environmental Assessment Program
- 3.5 Ecology – Washington State Department of Ecology
- 3.6 Field Data Sheets – Weather resistant sheets (“Rite in the Rain” ® writing paper) used to document all field activities, sample data, methods, and observations for each collection site.
- 3.7 GPS - Global Positioning System
- 3.8 Measuring Point – A fixed and clearly marked point on a well casing from which depth-to-water/water level measurements are made. Fixed water level measuring points are established to ensure data comparability over time and among field samplers.
- 3.9 ORP – Oxidation-Reduction Potential. The electric potential required to transfer electrons from one compound or element (the oxidant) to another compound (the reductant). Used as a qualitative measure of the state of oxidation in water.
- 3.10 pH – A measure of the acidity or alkalinity of water. A pH value of 0 to 7 indicates that an acidic condition is present, while a pH value of 7 to 14 indicates a basic or alkaline condition. A pH of 7 is considered to be neutral. Since the pH scale is logarithmic, a water sample with a pH of 8 is ten times more basic than one with a pH of 7.
- 3.11 Quality assurance project plan (QAPP) – A written plan that describes how a study will be conducted and its results assessed.
- 3.12 Specific Conductance (SC) – A measure of the water’s ability to conduct an electrical current. Specific conductance is related to the concentration and charge of dissolved ions in water.
- 3.13 Static Water Level – The level of water in a well that is not being affected by the withdrawal or injection of water.

## **4.0 Personnel Qualifications/Responsibilities**

- 4.1 EAP staff who conduct groundwater sampling are responsible for complying with this SOP, and with EAP078, the Standard Operating Procedure for Purging and Sampling Monitoring Wells. Additionally, EAP staff must comply with the requirements of the EAP safety manual - particularly Chapter 1 'General Field Work' and the following section of Chapter 2: 'Groundwater Sampling and Water-Level Measurements' (Ecology, 2015).
- 4.2 Documents such as the USGS National Field Manual for the Collection of Water-Quality Data (USGS, 1997) or the Essential Handbook of Groundwater Sampling (Nielsen and Nielsen, 2007) have additional detailed explanations of what factors to consider when sampling monitoring wells.
- 4.3 Users seeking additional technical information specific to groundwater metals sampling procedures are encouraged to review the benchmark publications on these topics, including: Puls and Barcelona, 1989; Puls et al., 1990; Puls et al., 1991; Puls et al., 1992; Puls and Powell, 1992; Gibbons and Sara, 1993; McLean and Bledsoe, 1992; Pohlmann et al., 1994; and Puls and Barcelona, 1995. In addition, EAP staff must read and be familiar with the considerations explained in Appendix A of this SOP prior to initiating sampling.
- 4.4 Field staff should have a detailed working knowledge of the project QAPP to ensure that credible and useable data are collected, and should be briefed by the field lead on the sampling goals and objectives prior to arriving at the site.
- 4.5 This document supplements but does not replace the need for on-the-job training. All field staff should be familiar with the sampling equipment and instruments being used. The field lead is responsible for ensuring that all field staff adhere to prescribed sampling methods when conducting field work.

## **5.0 General List of Equipment and Supplies**

- 5.1 Sample Measuring and Collecting Equipment
- 5.1.1 Field data sheets
- 5.1.2 Water level measuring equipment (calibrated electric water level meter, graduated steel tape)
- 5.1.3 Water quality meters and probes (pH, SC, DO, temperature, ORP, turbidity)
- 5.1.4 Probe calibration standards/reagents
- 5.1.5 Flow cell
- 5.1.6 Pump (submersible, peristaltic, bladder)
- 5.1.7 Power supply (generator, battery)
- 5.1.8 Extension cord
- 5.1.9 Tubing and connectors
- 5.1.10 Sample containers/bottles; pre-preserved, as needed.
- 5.1.11 Sample preservatives

- 5.1.12 Filters (analyte specific)
- 5.1.13 Coolers with ice or ice packs
- 5.1.14 55-gallon barrels (to store and properly dispose of contaminated purge water)
  
- 5.2 Cleaning and Disinfecting Supplies
- 5.2.1 Deionized water
- 5.2.2 Laboratory grade soap (Liquinox®)
- 5.2.3 Dilute chlorine bleach solution
- 5.2.4 Cleaning solvents, if applicable
  
- 5.3 Safety Equipment
- 5.3.1 Nitrile gloves
- 5.3.2 Hearing protection
- 5.3.3 Safety goggles
- 5.3.4 Hard hat
- 5.3.5 First aid kit
- 5.3.6 Orange vest, Ecology issued
- 5.3.7 Traffic cones
- 5.3.8 Traffic signs, if applicable
  
- 5.4 Miscellaneous Equipment
- 5.4.1 Well location map
- 5.4.2 All applicable SOPs
- 5.4.3 Field paper work: property owner contact information, field data sheets, sample bottle labels and tags, chain-of-custody sheets.
- 5.4.4 Pencils, pens, etc.
- 5.4.5 Permanent marking pen or paint stick (for marking measuring point)
- 5.4.6 Calculator
- 5.4.7 Well keys, if applicable
- 5.4.8 Compass
- 5.4.9 GPS unit
- 5.4.10 Digital camera
- 5.4.11 Paper towels or clean rags
- 5.4.12 Plastic garbage bags
- 5.4.13 Plastic sheeting for ground cover
- 5.4.14 Buckets, plastic 5-gallon
- 5.4.15 1-liter container (to calibrate purge volume/rate)
- 5.4.16 Stop watch
- 5.4.17 Field bag (containing rain gear, rubber boots, work gloves, etc.)
- 5.4.18 Hand cleaner
- 5.4.19 Product/Water interface probe, if applicable
  
- 5.5 Tools
- 5.5.1 Steel hand measuring tape (engineer scale)
- 5.5.2 Socket wrench set
- 5.5.3 Allen wrench set

- 5.5.4 Pipe wrenches
- 5.5.5 Crescent wrenches
- 5.5.6 Set of screwdrivers
- 5.5.7 File
- 5.5.8 Knife
- 5.5.9 Hammer
- 5.5.10 Pliers
- 5.5.11 Hack saw
- 5.5.12 Crow bar/manhole hook
- 5.5.13 Shovel
- 5.5.14 Machete
- 5.5.15 Whiskbroom
- 5.5.16 Spare well cover bolts/nuts
- 5.5.17 Spare well caps/plugs
- 5.5.18 Spare pad locks/keys
- 5.5.19 Wire brush
- 5.5.20 WD-40 (to be used away from the well head)
- 5.5.21 Bailing device (e.g. cooking baster, peristaltic pump with battery)
- 5.5.22 Flashlight
- 5.5.23 Spare batteries (e.g. electric-tape, GPS, flashlight)
- 5.5.24 Tape (duct tape/electrical tape)
- 5.5.25 Well tagging equipment

## **6.0 Summary of Procedure**

### **6.1 Project Planning**

- 6.1.1 A Quality Assurance Project Plan (QAPP) must be completed and approved before collecting water quality samples for analysis. The QAPP details project goals, data quality objectives, quality assurance program procedures, sample handling requirements (container requirements, preservation, holding times), and field and laboratory procedures. [Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies](#) (Lombard, 2004) provides detailed guidance on developing EAP project plans. A QAPP can reference SOPs for standard field monitoring or measurement procedures; however, non-standard procedures or deviations should be described in detail in the QAPP.
- 6.1.2 Detailed information should be collected for each well location whenever practical, including well construction logs, water level data, site access agreements, and any other relevant information about the wells to be sampled. An example of a well reconnaissance field form is included in Appendix B.
- 6.1.3 Well location and construction information for wells that are sampled should be entered into Ecology's Environmental Information Management (EIM) system database.

- 6.1.3.1 If the well hasn't been previously inventoried, use a GPS receiver when visiting the well to define a preliminary latitude and longitude coordinates as described in SOP EAP013, *Determining Coordinates via Hand-Held GPS Receivers* (Janisch, 2006). The field-collected coordinates can be refined using mapping tools when entering the well into the EIM system.
- 6.1.3.2 If the well hasn't been assigned a Department of Ecology unique well ID tag, then it should be tagged as described in SOP EAP081, *Procedures for Tagging Wells* (Pitz, 2011). Well tags are available from Ecology's Water Resources Program. Securely attach the tag to the well casing or any other permanent, easily seen fixture of the well. Once a well is tagged, complete the well tag form and submit to Ecology's Water Resource Program along with a copy of the well log.
- 6.1.4 Selecting equipment for purging and sampling a well requires site- and project-specific considerations. Equipment, materials, and manner of operation must be compatible with characteristics of the well and the analytes being sampled to obtain data that will meet the project objectives and data quality requirements. Considerations for well construction and equipment selection and installation that are specific to sampling for metals are discussed in Appendix A.
- 6.2 Field Work Preparation
- 6.2.1 Prior to sampling, inventory consumable field supplies such as disposable gloves, calibration standards, tubing, filters, etc. Order necessary supplies. Allow ample time for delivery.
- 6.2.2 Arrangements must be made with Ecology's Manchester Environmental Laboratory before sampling. The Manchester Environmental Laboratory (MEL) Laboratory User's Manual (Ecology, 2008) contains detailed guidance on the planning steps necessary to request, track, ship, and analyze water quality samples collected in the field.
- 6.2.2.1 To notify the lab submit a Pre-sampling Notification Form and a Sample Container Request Form a minimum of 2 weeks prior to sampling. For large projects the lab should be informed 4-6 weeks prior to sampling.
- 6.2.2.2 Coordinate with the lab regarding any special arrangements such as contract lab analysis, special courier or delivery of samples.
- 6.2.2.3 Inventory sample bottles when they arrive to ensure the lab provided the correct type and number.
- 6.2.3 Establish the order the wells will be sampled. Sample order is either based on logistics or the known or suspected water quality of a sample location. For contaminated wells, the order of sampling should be from least potentially contaminated well to most potentially contaminate well. This minimizes the possibility for cross-contamination of the sample equipment.

- 6.2.3.1 Obtain permission for site access if needed. Contact the property owner, property operator or resident to confirm the sampling date and time and to discuss any site access issues.
- 6.2.3.2 Before going in the field prepare field data sheets for each well location. It can be helpful to bring previous sample data for each well such as water level, pump intake placement, pump rate, total purge time, stabilized field parameter values, etc. Other sample paperwork should also be filled out as much as possible. Sample paperwork typically includes: bottle labels and tags, as well as Manchester Labs Chain-of-Custody/Lab Analysis Required Form (LAR) for the project sample event. Examples of field data sheets are provided in Appendix B.
- 6.2.4 Inspect all equipment and verify that water quality field meters are in good working order, calibrate properly, and are fully charged. Calibration procedures are normally outlined in the meter user's manual. When using a Hydrolab multimeter, follow SOP EAP033 for field preparation and calibration (Swanson, 2007).
- 6.2.5 Field equipment, especially equipment being placed in a well, that is going to be reused must be properly cleaned, disinfected, or decontaminated prior to and after use in each well. Cleaning procedure depends on the equipment being used (water level equipment, field parameter probes, down well sample equipment) and the type of well being sampled (e.g. observation well, piezometer, or regulated facility monitoring well).
  - 6.2.5.1 It is recommended that gloves (Nitrile) be worn when cleaning sample equipment. This will help maintain sanitary conditions of the cleaned equipment and will protect the sampler from the cleaning products being used. When not in use, equipment should be placed on a clean surface, such as a clean plastic sheet. If the equipment is not re-used immediately it should be wrapped in plastic sheeting or aluminum foil. Equipment should never be placed on bare soil prior to using it in a well.
  - 6.2.5.2 Water level measuring equipment: rinse the probe and any submerged tape with deionized water before and after use in a well. Wipe or air dry. If the well is suspected or known to be contaminated, the probe and any submerged tape should be wiped with a disinfectant-soaked towel or washed in a laboratory grade soap (e.g. Liquinox) solution, followed by a tap water and deionized water rinse.
  - 6.2.5.3 Water quality field probes should be rinsed with deionized water between sample locations. If the probes are slow to respond and additional cleaning is needed, then the probes should be cleaned and maintained according to the manufacturer's instructions.
  - 6.2.5.4 Down well equipment, such as a submersible pump, should be washed in a laboratory grade soap (e.g. Liquinox) solution. Use a brush to scrub the exterior of the sample equipment. Rinse the equipment with tap water, followed by a deionized water rinse. Parts of the sample equipment that are difficult to

submerge while cleaning, like a pumps electrical cable, can be wiped down with a disinfectant-soaked towel.

6.2.5.5 If the equipment is used in a contaminated well, additional cleaning may be required. The equipment may need a chemical rinse (e.g. acetone, nitric acid, methanol, isopropyl alcohol) depending on what analytes are being sampled. Rinse the equipment with deionized water. Place the equipment on a clean surface to air dry.

6.2.5.6 Equipment that is difficult to clean, such as pump tubing, should be replaced between sample locations. As mentioned previously pump tubing has the potential to provide a source of error because of the amount of contact with the sampled water. Therefore to help prevent possible cross-contamination do not reuse sample tubing between sample locations. For long-term projects tubing may be dedicated to a well, but should not be used at other locations.

### 6.3 Sampling Procedure

6.3.1 These sampling procedures assume sampling is being conducted using a dedicated pump that is already installed in the monitoring well of interest, or a non-dedicated pump that has been installed and allowed to equilibrate in the water column for 24 hours prior to sampling (see Appendix A for instructions on pump installation for metals sampling). If for any reason you skip the pump equilibration step, additional time may be required during the well purge to reach the desired turbidity limit of < 10 NTU.

6.3.2 After measurement of the static water level (see SOP EAP052), connect a closed-atmosphere flow-cell to the discharge end of the pump tubing. If using separate flow cells for the measurement of turbidity and standard field parameters, make sure to place the turbidity cell upstream of the remaining equipment.

6.3.3 Start the sampling pump and adjust the discharge rate to  $\leq 0.3$  L/min. Once the well purge and sampling process has begun, a steady pumping rate should be maintained until sampling is complete. Do your best to avoid stopping and starting the pump during the purge and sample process (doing so may cause problems with excess turbidity).

6.3.4 Purge the well until standard metals-sample field parameters (pH, specific conductance, dissolved oxygen, temperature, and ORP) equilibrate (stabilize).

Field parameters are considered stable when 3 consecutive readings fall within the following stabilization criteria:

pH	$\pm 0.1$ standard units
Specific Conductance	$\pm 10.0$ $\mu\text{mhos/cm}$ for values < 1000 $\mu\text{mhos/cm}$ $\pm 20.0$ $\mu\text{mhos/cm}$ for values > 1000 $\mu\text{mhos/cm}$
Dissolved Oxygen	$\pm 0.05$ mg/L for values < 1 mg/L $\pm 0.2$ mg/L for values > 1 mg/L

Temperature            $\pm 0.1^\circ$  Celsius  
ORP                      $\pm 10$  millivolts

- 6.3.5           After the field parameters listed above have equilibrated, collect a turbidity measurement per Figure 1 instructions. Follow the manufacturer's instructions for turbidity meter/probe calibration and measurement procedures.
- 6.3.6           If measuring turbidity in a closed-atmosphere flow cell, watch for sediment build up in the flow cell chamber that could bias the measurement. If using separate flow cells for the measurement of turbidity and standard field parameters, make sure to place the turbidity cell upstream of the remaining equipment.
- 6.3.7           If using a standalone, cuvette-based turbidimeter, measurements should be made on a sample collected directly from the discharge end of the sample tubing (disconnect the flow-cell chamber used for the measurement of other parameters). Conduct the turbidity measurement as soon as possible after filling the cuvette.

- 6.3.8 Record the turbidity value to the closest 0.1 NTU. If the turbidity measurement at this point is  $\geq 10$  NTU, refer to Figure 1 for further guidance. If the turbidity measurement is  $< 10$  NTU, proceed to the next step of the sampling process.
- 6.3.9 Following measurement of turbidity, collect and analyze samples for field-sensitive parameters using spectrophotometry, as necessary (confirmation of DO concentration when the equilibrated value is  $\leq 1.0$  mg/L, ferrous iron, manganese; see Appendix A for detailed instructions for conducting these analyses. Maintaining the flow rate at  $\leq 0.3$  L/min, attach a sampling cone to the pump discharge line. Keeping the sample cone in an upright position, submerge the vacuum vial in the flowing discharge. Allow the temperature of the vial to equilibrate briefly with the water discharge.
- 6.3.10 Snap the vial and proceed with spectrophotometric measurement (Figure 2; see further instructions in spectrophotometer operating manual).



Figure 2. Using a sampling cone to fill a vacuum vial for spectrophotometric analysis

- 6.3.11 Once all field analyses are complete, collect samples destined for laboratory analysis<sup>1</sup>. Refer to Figure 3 to determine the need for filtration.
- 6.3.12 For unfiltered metals samples, maintain the pump discharge rate at  $\leq 0.3$  L/min, and collect water directly from the discharge end of the sample tubing into a pre-

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<sup>1</sup> See Section 6.4.21 of SOP EAP078 for further guidance on sampling order if sampling for additional analytes groups.

preserved sample container. Immediately place the sample on ice for transport to the laboratory.

6.3.13 For filtered metals samples, use the decision-tree shown on Figure 3 as guidance for appropriate filtering procedures and filter sizes.

6.3.13.1 Attach the appropriate high-capacity filter to the discharge end of the tubing.

6.3.13.2 Maintaining the pump discharge rate at  $\leq 0.3$  L/min, hold the filter upright, with the outlet facing upward (to purge air from the filter). Discard the first 500-1000 mL of the filtrate before collecting the sample (Yeskis and Zavala, 2002).

6.3.13.3 Collect the filtered sample directly into a pre-preserved container. Be careful not to allow water on the outside surface of the filter to enter the container (this is best accomplished by pointing the filter outlet upward at an angle and arcing the filter discharge into the container; Figure 4).

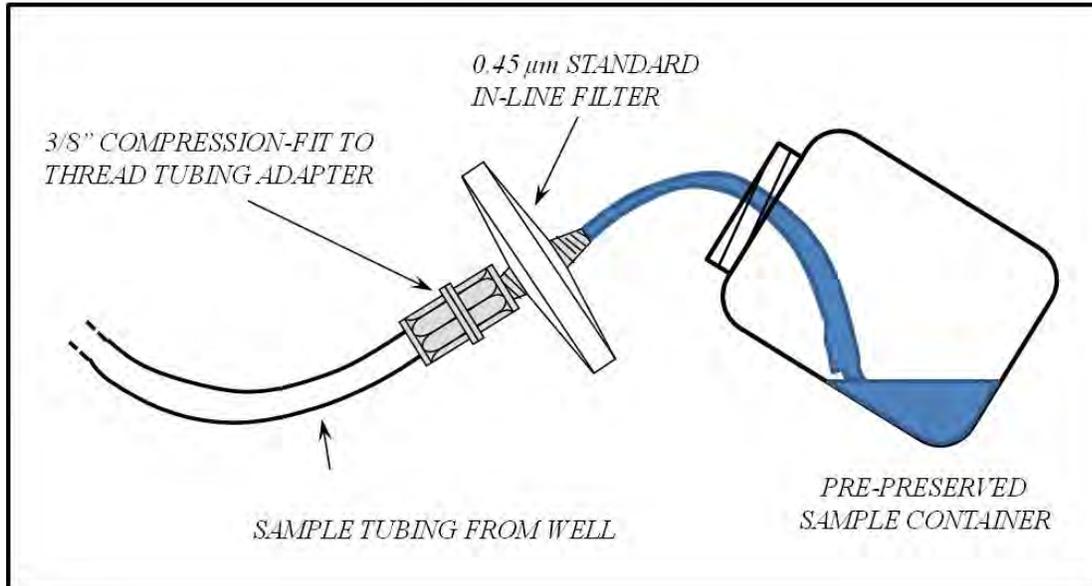


Figure 4 Angling the filter discharge into a sample container

6.3.14 Immediately place the sample on ice for transport to the laboratory.

6.3.15 See Figures 1 and 3 for decision tree summaries related to turbidity measurement and sample filtration, respectively.

## 7.0 Records Management

7.1 Monitoring wells that EAP samples must be documented to enable information about their location, construction, and subsequent monitoring data to be archived in Ecology's Environmental Information Management (EIM) system and well log

imaging databases. Consult the EIM help documents for a list of the well specific metadata required by EIM.

- 7.2 Station information and monitoring notes should be documented, during each site visit on site specific field data sheets. Examples are presented in Appendix B. All field entries should be neat and concise. The field lead is responsible for reviewing the form(s) for completeness before leaving a field site.
- 7.3 EAP staff have developed a number of data analysis spreadsheets, field forms, and other tools to standardize data collection and processing for groundwater monitoring projects. See the EAP Groundwater Assessment SharePoint site for the most up-to-date version of these tools. Examples of some of the field forms are provided in Appendix B.
- 7.4 All hardcopy documentation, such as well reports and field data sheets, are kept and maintained by the project lead and are subject to agency records retention schedules. At the completion of a project, hardcopies are boxed and moved to EAP archives.

## **8.0 Quality Control and Quality Assurance**

- 8.1 To ensure that good quality data are obtained throughout a project, a Quality Assurance Project Plan (QAPP) must be completed and approved before performing any field work. The QAPP details project goals, data quality objectives, quality assurance program procedures, sample handling requirements, and field and laboratory procedures.
- 8.2 Both the equipment and procedures used in collecting and handling groundwater samples have limitations that introduce a certain level of error, variability and bias into the final analytical results. To minimize the level of error, all field staff should follow these general QA/QC procedures when collecting samples:
  - 8.2.1 Follow the project QAPP and any applicable standard operating procedures (SOP) when collecting and handling samples.
  - 8.2.2 Calibrate field water quality meters according to the manufacturer instructions.
  - 8.2.3 Use equipment to purge and sample that is compatible with the characteristics of the well and analytes being sampled. Operate equipment in accordance with the manufacturer instructions, unless otherwise specified in the project QAPP.
  - 8.2.4 Properly collect, handle and store samples.
  - 8.2.5 Collect the appropriate quality control samples. These may include a field replicate, and field blanks (e.g. filter, equipment, transport). The types and number of quality control samples should be specified in the project QAPP.

- 8.2.6 Follow the procedures in the project QAPP or Manchester Lab Manual for sample handling and management (e.g. chain of custody).
- 8.2.7 Document all data, observations, notes, deviations from project QAPP, etc. on the field data sheets and other project paperwork.
- 8.2.8 Properly clean, maintain, and store all field equipment after use.
- 8.2.9 Use consistent procedures from well to well.

## **9.0 Safety**

- 9.1 Proper safety precautions must be observed when collecting groundwater samples. Field work should follow protocols described in the Environmental Assessment Program Safety Manual (Ecology 2015). A working knowledge of sections ‘Groundwater Sampling and Water-Level Measurements’ and ‘Hazardous Waste Sites’ in Chapter 2 is expected. Protocols in the EAP Safety Manual should be used to complement the judgment of an experienced field professional.
- 9.2 A Field Work Plan Form must be completed to document field personnel, sampling locations, overnight lodging, planned itinerary, contact person(s), and emergency contacts. If using a boat to access a site an Ecology Float Plan must be completed.
- 9.3 Always consider the safety situations when sampling a monitoring well. In addition to the possible chemical hazards if the water to be sampled is contaminated, there are many physical hazards associated with sampling monitoring wells. Monitoring wells are frequently located on or near active business or industrial sites, so field staff must remain aware of the typical hazards associated with these sites such as traffic. Many wells are located in parking lots, alleyways, or along roadways. Consult the EAP Safety Manual for further guidance regarding working near traffic. Other physical hazards can include heavy lifting, noise, electricity, steep, slippery, or uneven terrain, animals or insects, and the weather.
- 9.4 All EA Program field staff who work on hazardous waste sites are required to complete and maintain certification in FIRST AID/CPR and the 40-hour Hazardous Materials Safety & Health Training.

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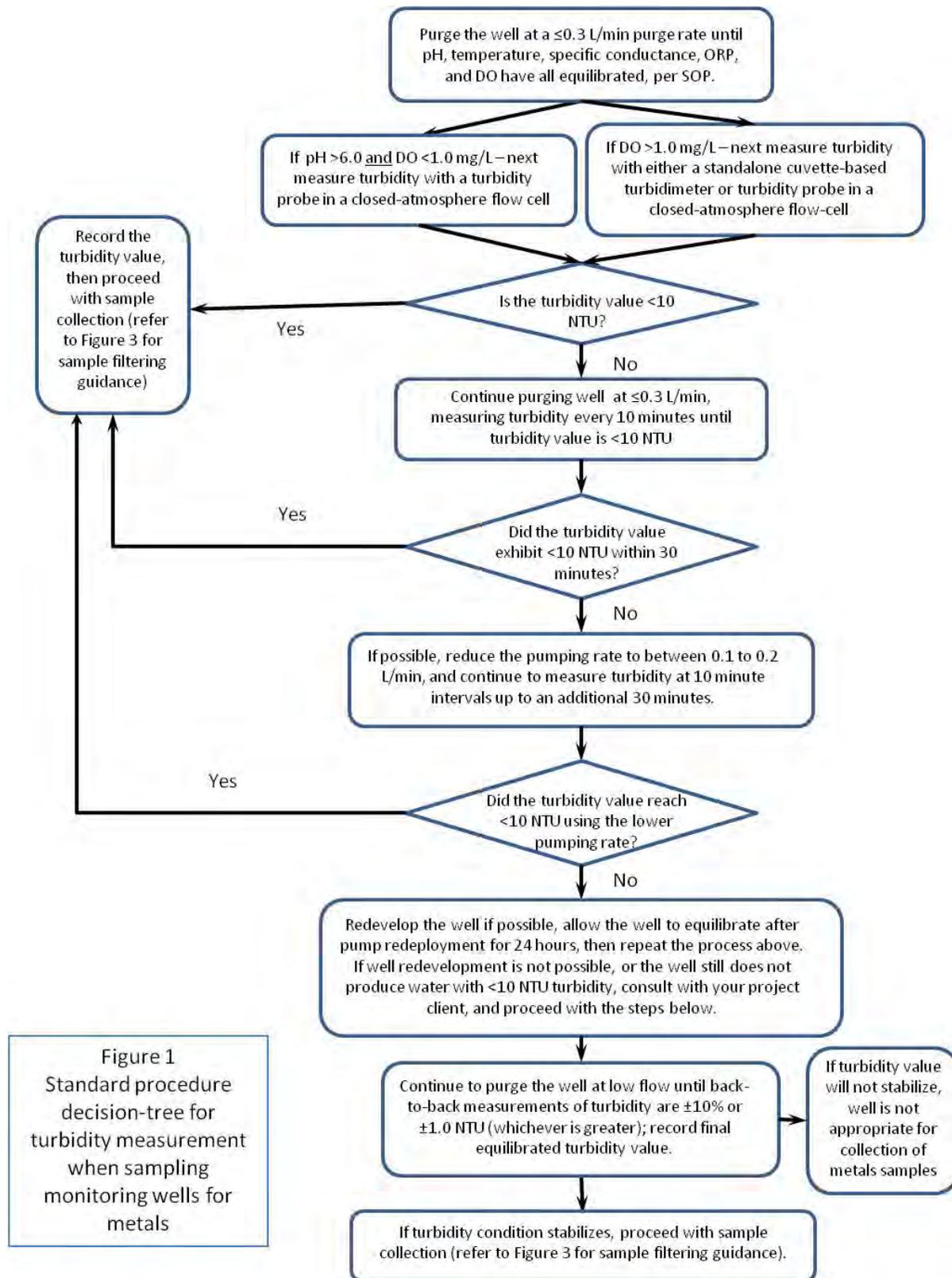
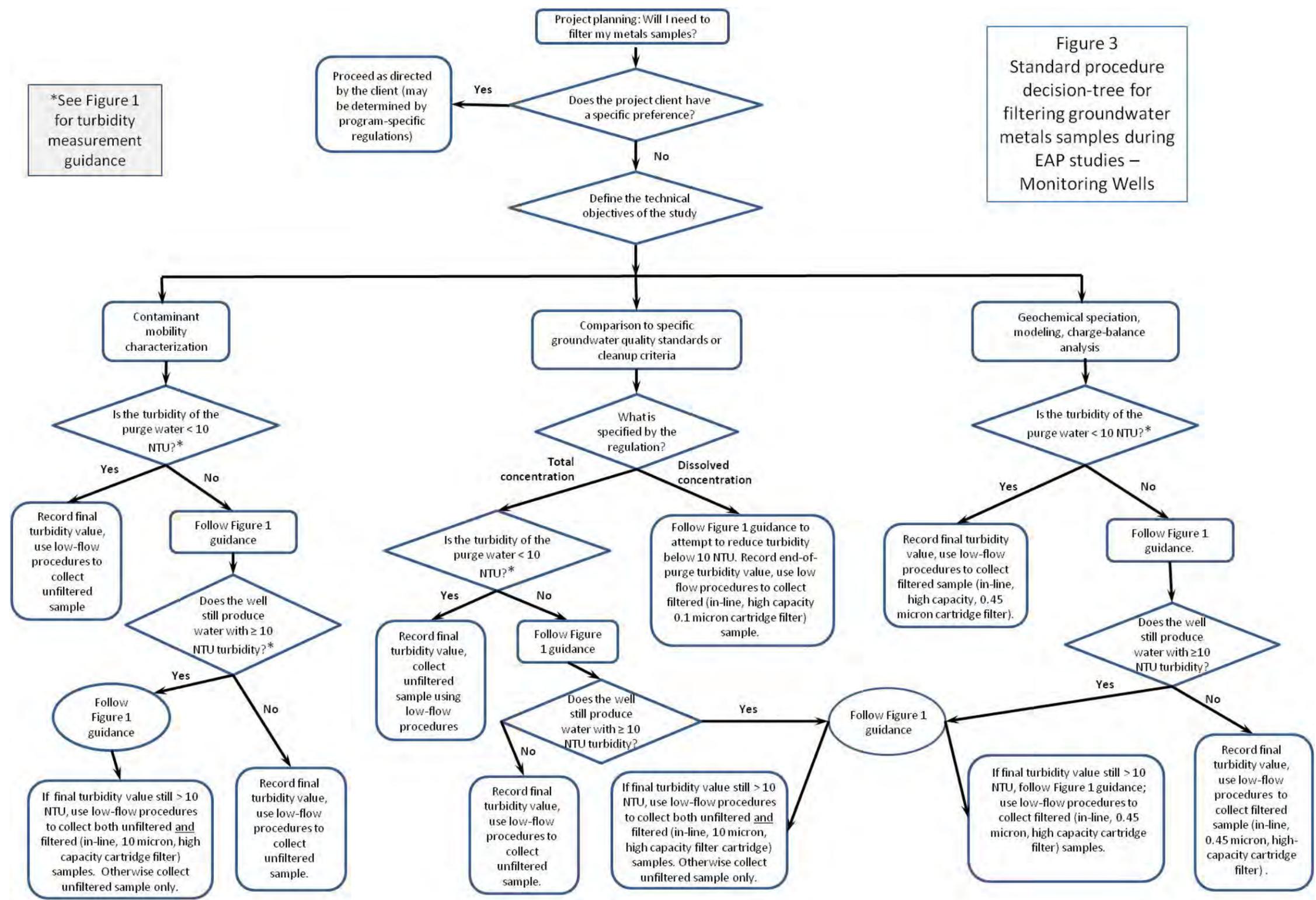


Figure 1  
Standard procedure  
decision-tree for  
turbidity measurement  
when sampling  
monitoring wells for  
metals

Note: Turbidity calibration and measurement procedures are specific to the measurement device. Follow instrument manufacturer instructions.

Figure 3  
Standard procedure  
decision-tree for  
filtering groundwater  
metals samples during  
EAP studies –  
Monitoring Wells



\*See Figure 1 for turbidity measurement guidance

Note: If your project has multiple technical objectives, follow the procedures outlined in Figure 1, and then collect all sample types that apply (unfiltered, 0.1 micron, 0.45 micron, 10 micron)

## **Appendix A: Considerations for sampling metals in groundwater**

Procedures for collecting representative groundwater samples for metals have been a subject of scientific research and debate for many years. There are a variety of important and interrelated procedural considerations to keep in mind when sampling for metals in groundwater, including controlling turbidity in the sample stream, minimizing atmospheric exposure of the sample, decisions about filtration, and material bias concerns. Failure to consider these aspects of metals sample collection can result in significant bias in the analytical results ultimately reported by the laboratory.

In addition to careful attention to sampling procedures, accurate characterization of the in-situ geochemical condition of the water at the time of sampling (e.g. pH, dissolved oxygen, redox potential) is also a key component of the metals sample collection process. The geochemical condition of the water can significantly influence the speciation, mobility, bioavailability, and toxicity of metals of environmental interest. The geochemical measurements you collect in the field along with your metals samples often guide the interpretation of the analytical results received from the lab and can be essential parameters for geochemical modeling.

### **Sampling Monitoring Wells for Groundwater Metals Concentrations – Considerations**

There are a variety of special considerations related to the collection of groundwater metals samples from monitoring wells. These considerations should be evaluated during the project planning and well selection process, prior to starting your field work.

#### ***Clean Hands/Dirty Hands Sampling Protocol***

Whenever collecting samples for metals analysis from monitoring wells, sampling teams should use industry standard “clean hands/dirty hands” field protocols (see, for example USGS, 1997). The “dirty hands” member of the sampling team is responsible for aspects of the sample collection process that do not involve direct contact with the sample or sample containers (e.g. pump operation). The “clean hands” team member is responsible for all aspects of work involving contact with containers and collection of water for analysis.

#### ***Control of sample turbidity***

Controlling the turbidity of the sample stream is the primary data-bias consideration when sampling groundwater monitoring wells for metals, and the turbidity condition of the pump discharge from the well can directly influence sampling procedures and filtration decisions.

Many metals tend to 1) strongly adsorb to solid mineral or organic particulate surfaces by ion exchange or 2) be directly incorporated into the chemical structure of particulates by precipitation/complexation reactions. These sorption reactions can significantly limit metals occurrence and mobility in the aqueous phase by binding metals to aquifer matrix solids that are physically immobile under normal groundwater pore-velocity conditions (McLean and Bledsoe, 1992; NGWA, 2011; Puls and Powell, 1992).

Due to their large surface areas and negative electrostatic surface charge (pH dependent), sorption of metals often occurs in association with fine-particles (e.g. colloids, clay, and organic material) or with

amorphous oxide and (oxy)hydroxide particle coatings of iron and manganese. These types of materials are ubiquitous in groundwater aquifers (Langmuir et al., 2004; NGWA, 2011).

Sampling procedures that mobilize and then capture metal-bearing particles that would normally remain immobile in groundwater can introduce significant positive bias into reported sample concentrations (Puls and Powell, 1992; Puls et al., 1992). If such particles are entrained in the sample sent to the laboratory, and then digested during analysis, the reported metals concentration will be higher than the in situ groundwater condition.

Research has shown that colloidal-scale particles (up to 10 microns in diameter) can be mobile in the groundwater environment under normal fluid velocities (Puls et al., 1991; Puls and Powell, 1992). It is important to use sampling procedures that account for colloidal transport of metals, particularly if attempting to characterize contaminant mobility at a project site. Filtering such particles out prior to analysis can introduce a significant negative bias into the reported concentrations (i.e. the lab will report metal concentrations that are lower than the in situ groundwater condition). As a result, standard industry practice is to leave most groundwater metals samples unfiltered, and focus on controlling artificial or 'induced' turbidity effects caused by poor well design or excessive pumping rates.

Proper well selection, minimization of well disturbance due to equipment deployment, and use of low-flow purge and sample procedures are the primary methods for controlling artificial turbidity when sampling a monitoring well. For metals sampling, the purge and sample discharge rate of the pump should always be maintained at a steady value of  $\leq 0.3$  L/min (Puls, et al., 1992). If a monitoring well still produces overly turbid water ( $\geq 10$  NTU; Yeskis and Zavala, 2002) under a low pumping rate, re-development of the well may be required prior to sampling, if allowed by the well owner.

Filtration should never be used to control the turbidity of a sample, or be an easy substitute for careful well selection and proper sampling techniques. In some cases, filtration may be the only available response when sampling monitoring wells exhibiting an elevated natural turbidity condition, but this should be a measure of last resort. If you must filter samples due to problems with the turbidity condition of the water, you should always collect an additional, unfiltered sample for comparison.

A decision tree outlining conditions, decision points, and methods for monitoring turbidity conditions is presented in Figure 1 and discussed in more detail below. Figure 3 provides related guidance on how the turbidity condition of the water influences the decision to filter or not, in light of the project objectives.

### ***Control of pressure changes and atmospheric exposure of a groundwater metals sample***

The concentration, phase, and mobility of metals can be highly sensitive to changes in the pressure condition or oxidation state of groundwater that can occur during the sampling process. Bringing a groundwater sample to the surface and exposing it to the atmosphere can alter both the pH (due to a change in the partial pressure of CO<sub>2</sub>) and the redox potential (Eh) of the water. This is particularly true if the sample is agitated or aerated in any way during collection.

Changes in pH and Eh condition can result in a change in solubility for many metals (e.g. As, Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn), and can lead to unwanted precipitation or sorption reactions that can alter dissolved phase concentrations and misrepresent (often negatively bias) the in-situ condition of the water. For example, exposing a groundwater sample to the atmosphere can result in a change from a reduced state to

an oxidized state, causing many metals to precipitate out of solution and rapidly sorb onto solid particle surfaces. The precipitation of iron is of particular concern since ferric (oxy)hydroxide, acts as an important sorption site for many other metals (NGWA, 2011; McLean and Bledsoe, 1992; Puls and Powell, 1992). These reactions can rapidly scavenge metals out of solution. If the particles bearing sorbed metals are filtered from the sample before analysis, the resulting groundwater concentrations reported by the lab could be biased low.

It is important to recognize that the reactions that influence metals phase distribution in the water/solid environment can potentially occur over very short time frames (Langmuir, 1997; NGWA, 2011; Puls et al., 1990; Puls and Powell, 1992); as a result it is critical to recognize the importance of closely following the sequence of the steps outlined in this SOP.

Although some degree of change in pressure or exposure of the sample to the atmosphere is unavoidable, it is important to always take steps to minimize the impact of these changes on a sample. When sampling monitoring wells, the primary techniques for controlling these concerns include:

Always purge monitoring wells prior to sample collection using a flow rate of  $\leq 0.3$  L/min.

Always use a closed-atmosphere flow cell to measure the standard field parameters used to judge purge equilibration [temperature, pH, specific conductance (SC), dissolved oxygen (DO), and oxidation/reduction potential (ORP)].

Depending on the redox and pH condition of the in-situ groundwater, turbidity measurements may also have to be taken in a closed-atmosphere environment (since transitioning a sample from a reduced condition to an oxidized condition can change the turbidity of the sample due to precipitation reactions or colloidal flocculation). See Figure 1 (and guidance later in this appendix) for more detail regarding field measurement of turbidity.

Always collect samples into containers using a flow rate of  $\leq 0.3$  L/min to minimize aeration of the sample as it enters the container.

If a metals sample needs to be filtered, always filter the water prior to contact with the atmosphere. See Figure 3 (and guidance later in this appendix) for more detail regarding sample filtration procedures.

Preserve samples immediately upon collection to prevent ongoing sorption and precipitation reactions.

### ***Control of sample temperature changes***

In some cases, the redox-driven precipitation reactions that can change dissolved metals concentrations are kinetically favored at higher temperatures. Therefore it is important to try to always keep groundwater samples at a temperature that is at or below the in situ condition.

While in the field try to keep unfilled sample bottles in a cool place (e.g. shade, ice-filled cooler).

Samples should be placed in an ice-filled cooler immediately upon collection.

Avoid using pumps that can heat groundwater samples during collection. Friction at the pump head of a peristaltic pump can be a significant source of heat.

### ***Well Selection Considerations***

The design, construction, and development of a monitoring well can all exert a significant influence on the ability to obtain a groundwater sample that is representative of in situ metals conditions in an aquifer.

EAP hydrogeologists do not always have control over how wells (and their associated filter packs and screens) are designed and installed, and it may not be possible to obtain permission to redevelop a monitoring well that exhibits excess turbidity during pumping. The primary aspects of a project EAP staff will normally have control over include careful well selection and the use of proper sampling techniques.

The key criteria when evaluating and selecting monitoring wells for metals sampling include identifying wells that are:

- most likely to have the ability to produce and maintain a low turbidity condition in the pump discharge, and

- least likely to introduce a chemical bias into your samples or result in a significant change in the geochemical condition of the groundwater during pumping.

Considerations when selecting wells for metals sampling include:

#### Time elapsed since well construction and development

Studies have indicated that the process of well construction can significantly alter the geochemical condition of groundwater in the near vicinity of the well borehole (including trace elements and major ions). In addition, overly aggressive development procedures, or development approaches that rely on the forced injection of air or water into the aquifer formation, can cause large changes in water chemistry that can require long time frames to re-equilibrate.

The literature on this topic suggests waiting periods between initial well installation and development and sampling between 48 hours, and potentially many months, dependent on site- and installation-specific factors (Puls and Barcelona, 1989; Puls and Powell, 1992).

Metals samples collected from wells and filter packs that have been able to chemically equilibrate with the formation sediments after construction and development are preferred over samples from newly constructed wells.

#### Well screen and filter pack design

Monitoring wells that have been designed and constructed with a filter pack and screen slots that are sized appropriately for the aquifer matrix of interest are most likely to produce water with low turbidity.

#### Casing material of the well

Monitoring wells constructed of PVC casing are best for sampling metals (Llopis, 1991). Due to the potential for chemical bias from corrosion, monitoring wells constructed of metal-based casing (e.g. steel or stainless steel) should be avoided. Monitoring wells constructed of PTFE (Teflon) are also acceptable for metals sampling, but are rarely encountered during EAP groundwater studies.

#### Design and integrity of the well annular seal

Monitoring wells that have leaky or improperly constructed grout seals may allow cross contamination of samples by surface leakage, and may produce water with a higher than normal level of turbidity.

#### Character of the aquifer matrix adjacent to the open interval

Monitoring wells screened in sediments that have a significant percentage of silt/clay may continue to produce groundwater with an elevated turbidity level, even after redevelopment.

Purging monitoring wells screened in low permeability sediments may result in a large amount of water level drawdown, or even pumping the well dry. This can lead to exposure of some, or all, of the well screen to the atmosphere, allowing groundwater entering the casing from the formation to be oxidized. This process can significantly bias the dissolved concentration of metals in the sample retrieved from the well.

Low-yield wells that experience significant drawdown or pump dry during purging, should be avoided for metals sampling if possible. Nielsen and Nielsen (2007) provide guidance for minimal purging procedures when the use of such wells is unavoidable.

#### Time elapsed since previous sampling

Monitoring wells that have not been sampled for an extended period of time are more likely to exhibit excess turbidity and require redevelopment.

#### Length of the well open interval

The objectives of your project, and the site hydrogeology, dictate the ideal length of the screened interval open to the adjacent aquifer, but shorter screen lengths ( $\leq 10$  feet) are widely preferred for the most accurate measurement of in situ groundwater chemistry (and hydraulic head). Although longer well screens have been used for the purpose of contaminant detection across long vertical sections or multiple water-bearing zones, research has shown that longer screens can provide misleading water quality and water level results (McIlvride and Rector, 1988; Cleary and Miller, 1993; Ohio EPA, 2008).

If your project goal requires characterization of groundwater metals concentrations across multiple water bearing zones or in an aquifer with significant potential for vertical chemical stratification, consider adopting alternative monitoring approaches (e.g. sampling multiple short-screened wells constructed at different positions in the aquifer;

use of multi-level samplers; use of packers to isolate particular portions of a longer screen).

#### Water table position

If the top of the well screen lies above the water table (under either static or pumping conditions), groundwater may experience atmospheric exposure and gas diffusion during sampling, potentially altering the geochemistry condition of the sample. The dissolved concentration of many metals can be highly sensitive to these changes, resulting in a bias in the reported sample concentration. Monitoring wells constructed in a manner that keeps the full length of the screened interval saturated under the full range of site water level conditions are preferred for metals sampling.

Monitoring wells screened in fine material, or that have not been sampled in some time, may require preliminary field testing to determine if the well can produce a representative sample free of excess turbidity. This initial testing also provides an opportunity to identify the need for well redevelopment.

Wells that exhibit excess turbidity but cannot be redeveloped should be avoided as sampling locations if possible. Filtering procedures should never be used as an easy substitute for proper well selection and turbidity control techniques.

If an existing well does require redevelopment (and permission is granted), conduct the redevelopment process a minimum of 48 hours prior to sample collection. Suggested practices for well redevelopment can be found in ASTM, 2005 and OEPA, 2009.

#### ***Sampling Pump and Tubing Selection***

The pump type selected for purging and sampling groundwater for metals analysis can also play an important role in the representativeness of samples. The key goal is to select a device that:

operates at a low enough flow rate to minimize the suspension of normally immobile particles into the sample stream,

is assembled of inert sample contact materials that will not leach or sorb metals of interest, and

does not cause aeration, degassing, or heating of the sample prior to collection.

For EAP groundwater studies, dedicated, down-hole positive-displacement bladder pumps, equipped with polyethylene or PTFE (Teflon™) bladders and capable of maintaining a low flow rate, are the preferred pump type for metals sampling. Dedicated pumps are preferred for the collection of metals samples due to the fact that the act of deploying a pump into a monitoring well can significantly increase the turbidity of the water column in the well casing for a period of as long as 24 hours (Kearl et al., 1992; Puls et al., 1992).

If dedicated pumps are not practical for a project requiring the collection of metals samples, consider placing your non-dedicated sampling pump into the well a day prior to the actual monitoring event to allow the turbidity condition to equilibrate (particularly in fine-grained settings). When deploying the

pump and sampling line into position in the water column, lower the equipment as carefully as possible to minimize the amount of disturbance you cause to the turbidity condition.

Stainless steel submersible pumps should be avoided if sampling for Cr, Ni, Fe, Mn, or Mo, particularly if the pump shows any signs of corrosion. Submersible pumps can also alter metal concentrations through agitation and heating of the sample. Justification for the use of a submersible pump for metals sampling should be documented on a case-by-case basis. As with bladder pumps, submersible pumps should be installed a day before sampling if possible, and should be deployed downhole with the utmost care.

Suction-lift (peristaltic and surface-centrifugal) pumps, and inertial lift (tubing check valve) pumps can introduce significant turbidity-, pressure- or temperature-related bias into metals samples, and should be avoided whenever possible (Nielsen and Nielsen, 2007; Puls and Barcelona, 1989).

Bailers should never be used to sample metals concentrations in monitoring wells (Yeskis and Zavala, 2002; Puls and Powell, 1992). Research has shown that bailers can lead to highly inconsistent results between filtered and unfiltered samples.

Sample delivery lines attached to the pump should also be made from a material that is inert with respect to metals sorption or leaching. High density polyethylene or PTFE tubing are the preferred tubing types for EAP studies focused on metals.

As part of the project QA program, equipment blank samples (using trace-metal-free DI water) should always be collected through any non-dedicated pump and tubing used for sample collection.

### ***Equipment Decontamination Procedures***

Factory-new sample-contact equipment used on a one-time basis to collect or process groundwater for metals analysis (such as sample tubing or filters) does not require decontamination prior to use. An equipment blank sample (using trace-metal-free DI water) should, however, be collected through the new equipment at the beginning of your project in order to quantify any positive material bias on the sample results.

Sampling equipment dedicated to, and remaining in, a particular well between sampling rounds (such as sample tubing or a dedicated sample pump) does not normally require decontamination. Equipment that is dedicated to a particular well, but does not remain in that well between sampling events (such as tubing), may be DI-water-rinsed and bagged between sampling rounds.

The sample-contact portion of any pumps that are moved from well-to-well should always be field decontaminated between sampling locations. Because it cannot be effectively deconned between wells, sampling tubing should always be either a) dedicated to a specific well, or b) replaced with new tubing between different wells.

Standard procedures for decontamination of sample-contact equipment for metals analysis includes the following steps:

Tap/phosphate-free detergent brush wash (pumping wash in the case of pumps),

Tap rinse,

Triple rinse with metals-free DI water (pumping rinse in the case of pumps),

Foil wrap until use.

If site-specific conditions indicate a high potential for cross contamination between sampling locations, a 10% nitric acid rinse should be inserted between steps 2 and 3 above.

Equipment rinse blanks (using laboratory supplied, trace-metal free DI water) should be collected after cleaning to determine the adequacy of the decon procedures for preventing cross-contamination between sampling locations. Do not use DI water from the EAP Operations Center to prepare blank samples.

See additional details regarding equipment decon procedures in Section 6.3.5.

### ***Sampling Pump Placement***

Care should always be taken when first positioning a sampling pump in a monitoring well (dedicated or non-dedicated) for the purpose of collecting groundwater metals samples. The pump should be lowered slowly and smoothly into position to minimize disturbance of the water column. Doing so will limit mobilization of fine-grained material present in the formation adjacent to the open interval or at the bottom of the well casing. Pumps and pump lines should never be dropped or rapidly submerged in the water column.

As indicated above, pumps that are not permanently dedicated to a well should ideally be allowed to sit still in the water column of the well casing for a minimum of 24 hours prior to the start of sampling (to ensure any turbidity disturbance that has occurred has the opportunity to re-equilibrate). If this time frame is not practical for your project, pay particular attention to maintaining a very slow pumping rate ( $\leq 0.3$  L/min) during the well purge process. Without a pump equilibration period prior to sampling, the total time to purge the well and reach a turbidity condition that is below 10 NTU may be extended.

The sampling pump intake should always be positioned adjacent to the open interval of the well, but should not be placed in a position too close to the bottom of the well casing. Pumps placed near the base of the well may mobilize and capture sediments accumulated in the casing.

In cases where the water table is located below the top of the screen, the pump should be positioned as far below the water level in the well as possible, but not so low as to mobilize sediment accumulated at the base of the well casing.

## **Field Measurements Associated with Groundwater Metals Samples**

### ***Measurement of Turbidity***

Careful monitoring of the groundwater turbidity condition is critical for obtaining representative metals samples from an aquifer). A decision tree outlining conditions, decision points, and methods for monitoring the groundwater turbidity condition is presented in Figure 1.

Field staff should recognize that turbidity is usually the final field parameter to equilibrate during monitoring well purging, followed by DO and ORP (Puls et al., 1990; Puls et al., 1991; Puls et al., 1992).

For the purpose of metals characterization, reaching a turbidity value of less than 10 NTU is the key decision point to proceed to sampling (assuming all other parameters have stabilized).

Turbidity can be measured once all other purge parameters have equilibrated. Always maintain a steady pumping rate at a level  $\leq 0.3$  L/min during measurement of turbidity to minimize artificial mobilization of particles that can bias the accuracy of the measurement.

If the equilibrated DO of the purge water from the well indicates a potentially anoxic groundwater condition ( $<1$  mg/L), and the pH is  $>6$  S.U., turbidity should be measured within a closed atmosphere to prevent bias introduced by precipitation reactions that may occur on contact of the water with air. If using separate flow cells for measurement of turbidity and other standard field parameters, place the turbidity flow cell upstream of other instruments (see for example Puls et al., 1991).

### ***Measurement of dissolved oxygen (DO)***

In addition to serving as a standard field parameter for determining the adequacy of well purging prior to sample collection, dissolved oxygen measurements are used to support the geochemical interpretation of groundwater metals data. Accurate field measurements of DO condition should always be part of metals sample collection.

Whenever end-of-purge measurements collected using a standard calibrated DO probe (e.g. the EAP groundwater team Hach Hydrolab Surveyor LDO probe) indicate an equilibrated DO concentration of  $\leq 1.0$  mg/L, standard EAP procedure is to collect a field spectrophotometer confirmation measurement using a Rhodazine D-based test kit prior to sample collection (CHEMtrics Kit K-7553; ASTM, 2014; Rounds et al., 2013). The sample should be collected from a flowing sample stream prior to contact with the atmosphere using a sample cone and self-filling vacuum sample vial, per manufacturer's instructions (Figure 2).

### ***Measurement of Redox Potential***

The redox potential of the sample should also always be measured when collecting samples for metals analysis (this provides information useful for evaluating the expected oxidation state of dissolved metals, particularly if collected in tandem with pH condition).

Due to its sensitivity to rapid change upon exposure of the sample to the atmosphere, redox potential must be measured in the field at the time of sample collection, prior to contact of the sample with air. Standard procedure for quantifying groundwater redox potential during EAP groundwater studies relies on the measurement of the oxidation/reduction potential (ORP) in a closed-atmosphere flow cell, using a calibrated ORP probe.

Geochemical interpretation of groundwater metals data normally requires an estimate of the Eh (or pe) condition. ORP field measurements can be converted to Eh using:

$$Eh = ORP + E' \qquad \text{Eq. 1}$$

where:

$Eh$  = the oxidation-reduction potential of a solution relative to a standard hydrogen electrode (SHE)(mV)

$ORP$  = Oxidation-reduction potential relative to a reference electrode (mV)

$E'$  is the half cell potential of the specific metal electrode and reference solution your ORP probe is comprised of (mV):

- $E'$  for ORP probes using a calomel (mercury chloride) reference electrode = 244 mV (at 25°C)
- $E'$  for ORP probes using an Ag/AgCl reference electrode = 199 mV (at 25°C)

$Eh$  can alternatively be reported as  $pe$ . At 25°C:

$$Eh (mV) = 59 pe \qquad \text{Eq. 2}$$

where:

$pe$  = measure of the electron activity of a solution ( $-\log\{e^-\}$ ).

### **Field analysis of Rapidly Oxidized Metals**

Due to their tendency to rapidly oxidize upon exposure to the atmosphere, analysis for ferrous iron ( $Fe^{2+}$ ) and manganese should be conducted in the field, particularly in cases when the equilibrated pH of the groundwater sample stream is  $> 6.0$  and the DO is  $< 1.0$  mg/L.

Field spectrophotometer analysis is the standard EAP procedure for measuring groundwater ferrous iron (phenanthroline method; CHEMetrics Kit K-6203; APHA, 2005) and manganese (periodate method; CHEMetrics Kit K-6503; APHA, 1975) concentrations. These measurements should be conducted on a sample captured prior to contact with the atmosphere (the process of filtration may introduce oxygen into the sample, causing a conversion to ferric hydroxide precipitate).

Samples for analysis with a spectrophotometer should be collected directly from a flowing sample stream using a sampling cone and self-filling vacuum vial, per manufacturer's instructions (Figure 2). When conducting field analysis for  $Fe^{2+}$  or Mn, do not filter the water prior to analysis. The process of filtration can introduce oxygen into the sample, potentially leading to unwanted precipitation reactions.

### **Sample filtration**

The technical objective of the project and the turbidity condition of the sample stream both play an important role in a) determining if metals samples require field filtration prior to laboratory analysis, and b) determining what filter size is appropriate if filtration is necessary. Figure 3 presents a decision tree outlining standard EAP guidance for groundwater metals-sample filtration procedures for monitoring wells.

The process of sample filtration has a variety of potential disadvantages (e.g. aeration of the sample leading to precipitation reactions, filter clogging, filter media bias), so samples should only be filtered if your project objectives require it, and/or all other efforts to control excess ( $\geq 10$  NTU) water turbidity have been exhausted. For some projects, it may be best to collect both unfiltered and filtered samples, or

to collect samples using different filter pore sizes, to determine the impact of filtration on the reported metals concentrations.

To minimize bias introduced by redox-driven precipitation reactions that can occur after contact of the sample with the atmosphere, groundwater samples collected for metals analysis should never be filtered in the laboratory. This process must be conducted at the time of sample collection, prior to contact of the sample with the atmosphere, and prior to contact of the sample with an acid preservative.

In some cases (e.g. silty/clayey aquifer matrix, low ionic strength waters), the natural turbidity of the groundwater produced by the well may necessitate filtration (see Figure 1). In such cases you should always collect both a filtered and unfiltered sample to allow evaluation of the impact of the filtration process on the reported concentration.

Studies focused on assessing metals (and other inorganic species) concentrations in groundwater for geochemical speciation modeling or charge balance analysis purposes normally require the collection of filtered samples. EAP standard procedure of using a 0.45 micron high capacity in-line filter for this purpose is based on recommendations provided by the National Ground Water Association (NGWA, 2011).

Samples intended to characterize truly dissolved concentrations of metals should be filtered with a 0.1 micron high capacity in-line filter (Puls et al., 1991; Puls and Powell, 1992).

Unfiltered samples are strongly preferred for studies focused on assessing metal contaminant mobility in an aquifer. However, in cases where the turbidity cannot be brought below 10 NTU during purging, filtration of the sample may be required as a method of last resort (see Figure 1). EAP standard procedure under this scenario is to filter the sample using a 10 micron filter (as well as collecting an unfiltered sample for comparison purposes). The use of a larger filter size in this case is intended to allow the collection of metals associated with colloidal-sized particles that may be mobile under ambient groundwater velocities and gradients (i.e. particulates suspended and transported in solution)(Puls and Powell, 1992; Yeskis and Zavala, 2002).

EAP staff are encouraged to consider the ultimate use of the data, and the characteristics of the aquifer of interest, to determine the need for a non-standard filter size. This may include initial testing using sequential filter sizes to determine the influence of filter size on the reported concentration.

Whenever filtering samples for metals analysis always collect a filter blank to determine if any positive bias is introduced into the sample results by the sample-contact filter media. Blanks should be collected through a new filter using trace-metal-grade deionized (DI) water supplied by the Manchester Environmental Laboratory (do not use the EAP Operations Center DI water).

Filtration of anoxic samples can result in oxidation and colloidal formation within the filter media, resulting in clogging. Standard EAP procedure to minimize this problem is to use high capacity filter cartridges whenever filtering metals samples.

Preferred filter media types for metals include polyethersulfone or polypropylene.

Never use vacuum filtration for metals samples.

### ***Sample preservation***

Groundwater metals samples should always be preserved immediately upon collection into the sample container. (Please note, this requirement is contrary to, and takes precedence over, instructions provided in the current version of the Manchester Environmental Laboratory Lab Users' Manual (9th Edition; September 2008)). Standard procedure is to collect all groundwater metals samples directly into pre-preserved containers supplied by MEL.

## **Appendix B: Example Field Forms**

EAP has developed several spreadsheet templates and field form to speed and where possible automate the tasks required to evaluate, install, and process groundwater sampling data. Examples of commonly used forms are included here. See EAP's Groundwater Assessment SharePoint site for up-to-date versions. These tools and forms can easily be modified to accommodate the needs of particular instruments or projects.

# Well Reconnaissance Field Sheet

Date: \_\_\_\_\_ Time: \_\_\_\_\_

Field Crew: \_\_\_\_\_

Well ID: \_\_\_\_\_

Well Tag ID: \_\_\_\_\_

Well Owner Name: \_\_\_\_\_

Facility Name: \_\_\_\_\_

Current Phone Number: \_\_\_\_\_

Current Mailing Address: \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Renter?  Name: \_\_\_\_\_

Permission granted to locate well?

Permission granted to collect Water Level?

Permission granted to sample well for Water Quality?

Permission granted to tag well?  Tagged?

Call ahead required before site visit?

Recon GPS Well Coordinates:

Recording Datum: NAD83HARN  NAD83  NAD27

DDLAT: \_\_\_\_\_ DDLONG \_\_\_\_\_

Wellhead Photo #: \_\_\_\_\_

Comments: \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

Add sketch map of well location on back.

# Field Meter Calibration Record

Project Name:

Recorder:

Calibration date and time \_\_\_\_\_

Post-sampling check date and time \_\_\_\_\_

Meter Number: Hydrolab, GW

Pre-use calibration				Post-use calibration check			
Reference standard	Meter reading	Difference	Accept/Reject	Reference standard	Meter reading	Difference	Accept/Reject
<b>pH</b>							
<b>Specific conductance</b>							
<b>Dissolved Oxygen</b>							
	DO reading			DO reading			
	% Saturation			% Saturation			

## Pre and Post Use Calibration Acceptance Criteria by Parameter

<b>pH slope and asymmetry acceptance criteria</b>		<b>pH post Calibration Standard Checks</b>	
Slope	Acceptable: -50 to -62 mV/pH Ideal: -58 to -60.5 mV/pH	less than or equal to $\pm 0.15$ = pass greater than $\pm 0.15$ and less than or equal to $\pm 0.5$ = "J" qualify greater than $\pm 0.5$ = reject	
Asymmetry	Acceptable: $< \pm 30$ mV Ideal: $< \pm 15$ mv	<b>Conductivity post Calibration Standard Checks</b>	
		less than or equal to $\pm 5\%$ = pass greater than $\pm 5\%$ and less than or equal to $\pm 10\%$ = "J" qualify greater than $\pm 10\%$ = reject	
<b>DO relative slope acceptance criteria</b>		<b>DO% Saturation post Calibration Evaluation Criteria</b>	
Relative slope	Acceptable: 0.6 to 1.25 Ideal: 0.8 to 1.25	less than or equal to $\pm 5\%$ = pass greater than $\pm 5\%$ and less than or equal to $\pm 10\%$ = "J" qualify greater than $\pm 10\%$ = reject	

Append calibration remarks or comments below:





**Groundwater Quality Sampling Field Sheet (cont.)**

**Well Tag ID:** \_\_\_\_\_ **Well Name:** \_\_\_\_\_

**Purge Parameters (cont.):**

Time	pH	Temp (°C)	Cond (µS/cm)	DO (mg/L)

**Photometric O<sub>2</sub> :** \_\_\_\_\_ **Kit:** \_\_\_\_\_ **Conc.** \_\_\_\_\_

**Photometric O<sub>2</sub> :** \_\_\_\_\_ **Kit:** \_\_\_\_\_ **Conc.** \_\_\_\_\_

**Colormetric O<sub>2</sub> :** \_\_\_\_\_

**Field Alkalinity :** \_\_\_\_\_ **Kit:** \_\_\_\_\_ **Conc.** \_\_\_\_\_

**ORP:** \_\_\_\_\_

**Other:** \_\_\_\_\_

**Comments :**



# Sample Container Request Form

Please FAX to Leon Weiks: (360) 871-8850  
 (Phone for Leon Weiks: (360) 871-8825)

Requestor: \_\_\_\_\_

Project Name: \_\_\_\_\_

Phone: \_\_\_\_\_

Today's Date: \_\_\_\_\_

Location for Delivery: \_\_\_\_\_

Date Needed by: \_\_\_\_\_

Index #	Description	Qty.
1	1 gallon jar *	
2	1/2 gallon jar *	
3	1 liter jar * (wide mouth) (special request only)	
4	1 liter jar ( narrow mouth) (oil & grease) **	
5	8 oz short jar *	
6	8 oz short jar **	
8	4 oz short jar *	
9	4 oz short jar **	
11	40 mL vial w/septum *	
13	2 oz short jar w/septum * (Volatiles: solids only)	
14	125 mL amber glass bottle * (carbamate)	
15	1 liter amber bottle * (narrow mouth)	
16	500 mL HDPE bottle (metals)	
17	1 gallon cubitainer	
19	125 mL clear Nalgene (nutrients or COD; bottle contains 1:1 sulfuric acid)	
20	125 mL amber Nalgene (filters and syringe also required for orthophosphate)	
21	125 mL polypropylene bottle (hardness - bottle contains acid) <b>For Hexachrome, request bottle without acid</b>	

Index #	Description	Qty.
22	500 mL poly bottle	
23	1000 mL poly bottle	
24	1000 mL amber poly	
25	250 mL amber poly bottle (Cyanide) (contains Sodium Hydroxide)	
26	60 mL poly bottle (TOC/DOC or TP; bottle contains 1:1 hydrochloric acid)	
27	250 mL glass or poly bottle (fecal coli)	
28	500 mL glass bottle or poly (multiple micro tests)	
29	250 mL glass or poly bottle <b>with thiosulfate</b> (fecal coliform - chlorinated)	
30	500 mL glass or poly bottle <b>with thiosulfate</b> (multiple micro tests - chlorinated)	
31	8 oz plastic jar (grain size only)	
32	1 liter jar ** with <b>sulfuric acid</b> (wide mouth, clear; for phenolics)	
33	sterile specimen cup (micro)	
34	2 oz short jar (TOC - NO septum)**	
35	Soil VOA/BTEX Airtight Sampling Capsules (3 per sample)	
36	Soil VOA/BTEX Sampling Handle (1 per sampling event)	
	<b>Other Supplies</b>	

\*organic free with Teflon lined lids, with Certificate of Analysis. \*\*same as "\*" but does not include Certificate of Analysis.



# PRE-Sampling Notification

Fax to Manchester Laboratory: (360) 871-8850

Requested by: \_\_\_\_\_ Sampling Date(s): \_\_\_\_\_  Enforcement  
 Program: \_\_\_\_\_ Date to Lab: \_\_\_\_\_  Monitoring  
 Phone No.: \_\_\_\_\_ Sample Pickup Location: \_\_\_\_\_  Emergency  
 QAPP:  Yes  No Date results needed by: \_\_\_\_\_  Class II  
 Preliminary Invest.  Special turnaround

General Chemistry	W	S	O	Microbiology	W	S	O	Organic Chemistry	W	S	O
Alkalinity				Fecal Coliforms <input type="checkbox"/> MF <input type="checkbox"/> MPN				Base/Neutral/Acids (BNA)			
Conductivity				E. Coli MF <input type="checkbox"/> "MUG" <input type="checkbox"/> mTEC2				Polynuclear Aromatics (PAH)			
Hardness				E. Coli MPN							
pH				% Klebsiella				Volatile Organic Analysis (VOA)			
Turbidity								BTEX			
<input type="checkbox"/> Fluoride <input type="checkbox"/> Chloride <input type="checkbox"/> Sulfate								Pest/PCB's (Organochlorine)			
Cyanide <input type="checkbox"/> Total <input type="checkbox"/> Dissociable				<b>Metals</b>	<b>W<sub>T</sub></b>	<b>W<sub>D</sub></b>	<b>S</b>	<b>O</b>	Pesticides only (Organochlorine)		
Total Solids				Priority Pollutant Metals (13 elements)					PCB's only		
Total Nonvolatile Solids				TCLP metals					OP - Pests (Organophosphorous)		
Total Suspended Solids				Hardness					Herbicides (Chlorophenoxy)		
Total Nonvolatile Suspended									Nitrogen Pesticides		
Total Dissolved Solids				Mercury (Hg) <input type="checkbox"/> Low Level <input type="checkbox"/> Regular					PCL Pesticides (8085)		
Chlorophyll <input type="checkbox"/> Filtered in field <input type="checkbox"/> Filtered at lab				Other: List individual elements:					PBDEs		
% Solids									Hydrocarbon ID (match to source)		
% Volatile Solids (TVS)									TPH-ID (gas/diesel/oil)		
Total Organic Carbon									TPH-G <sub>x</sub>		
Dissolved Organic Carbon									TPH-D <sub>x</sub>		
Biochemical Oxygen Demand (BOD) 5 day											
BOD - Inhibited									TCLP-VOA		
BOD - Ultimate									TCLP-BNA		
Ammonia									TCLP-Herbicides		
Nitrate-Nitrite									TCLP-Pesticides		
Orthophosphate											
Total Phosphorous											
<input type="checkbox"/> TPN <input type="checkbox"/> TKN				Asbestos							

Comments: Enter the number of samples in the appropriate box(es) above.  
 W = water S = soil/sediment O = other (please specify) W<sub>TR</sub> = water total W<sub>D</sub> = water dissolved



<b>Matrix Codes</b>	<b>Source Codes</b>	<b>Code Description</b>
<p><b>Code Description</b>            10 Water            11 Field Filtered Water            12 Filter from Water            13 Water to be filtered upon receipt at lab            40 Soil/Sediment            41 Frozen Soil/Sediment (PSEP)            45 Semi-Solid/Sludge            70 Tissue            80 Oil/Solvent            90 Waste            00 Other (Use only if no other apply)</p>	<p><b>Code Description</b>            00 Unspecified Source            01 Unknown Liquid Media (Drum/Tank)            02 Unknown Liquid Media (Spill Area)            03 Unknown Liquid Media (Waste Pond)  <b>10 Water (General)</b>            12 Ambient Stream/River            13 Lake Reservoir            14 Estuary/Ocean            15 Spring/Seepage            16 Rain            17 Surface Runoff/Pond (general)            18 Irrigation Canal/Return Flow  <b>20 Well (General)</b>            21 Well (Industrial/Agricultural)            22 Well (Drinking Water Supply)            23 Well (Test/Observation)            24 Drinking Water Intake            25 Drinking Water (At Tap)  <b>30 Effluent Wastewater (General)</b>            31 Municipal Effluent            32 Municipal Inplant Waters            33 Industrial Surface Runoff/Leachate            34 Industrial Effluent            35 Industrial Inplant Waters            36 Industrial Surface Runoff/Pond            37 Industrial Waste Pond            38 Landfill Runoff/Pond/Leachate  <b>40 Sediment (General)</b>            42 Bottom Sediment or Deposit            44 Sludge (General)            45 Sludge (WastePond)            46 Sludge (Drum/Tank)            48 Soil (General)            49 Soil (Spill/Contaminated Area)</p>	<p>50 Bore Hole Material  <b>60 Air (General)</b>            61 Ambient Air            62 Source or Effluent Air            63 Industrial or Workroom Air  <b>70 Tissue (General)</b>            71 Fish Tissue            72 Shellfish Tissue            73 Bird Tissue            74 Mammal Tissue            75 Macroinvertebrate            76 Algae            77 Periphyton            78 Plant/Vegetation  <b>80 Oil/Solvent (General)</b>            81 Oil (Transformer/Capacitor)            82 Oil/Solvent (Drum Tank)            83 Oil/Solvent (Spill Area)            84 Oil/Solvent (Waste/Pond)  <b>90 Commercial Product Formulation</b>            95 Well Drill Water            96 Well Drill Mud            97 Well Sealing Material            98 Gravel Pack Material</p>