

ATTACHMENT 5

GROUND WATER SAMPLING AND ANALYSIS PLAN



**Groundwater
Sampling and Analysis Plan**

**Site A
Bruneau, Idaho
U.S. EPA I.D. # IDD000773952**

Revised September 2017

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SITE A

GROUNDWATER SAMPLING AND ANALYSIS PLAN

This Groundwater Sampling and Analysis Plan (SAP) outlines the sampling procedures designed to collect representative samples from the groundwater aquifer beneath the Site A facility, and the analytical procedures and QA/QC controls needed to produce reliable data. This SAP includes the following elements:

- Monitoring Well Instrumentation
- Sample collection
- Sample preservation and handling
- Chain-of-custody control
- Analytical procedures
- Field and laboratory quality assurance/quality control
- Quality Assurance Project Plan (attached)

SAMPLE PARAMETERS

All Site A wells are sampled bi-annually for the custom list of 27 VOC's listed in Table 1, pH, and conductivity. Conductivity and pH are measured in the field and recorded in the sampling logbook, as well as being analyzed by the laboratory. Any wells in the Compliance Monitoring Program are analyzed for 40 CFR 264 Appendix IX elements and constituents once every three years.

MONITORING WELL INSTRUMENTATION

All monitoring wells will be equipped with dedicated electric submersible sampling pumps. The pumps will be suspended on stainless steel discharge pipe. Single piece electrical cable will be used below water to avoid potential leaching of organic contaminants from the cable splice and insulating materials. The pumps will be equipped with a check valve to prevent uncontrolled backflow into the well when the pump is shut off. To prevent standing water in the discharge pipe from freezing between sampling events, the check valve will have a small diameter bleeder hole drilled through it.

If, during any sampling event, a pump fails it will be removed and inspected as soon as a pump contractor can be mobilized. As appropriate, a new pump, new motor, or complete pump and motor will be ordered. The replacement pump will be installed as soon possible and the well will be sampled immediately following pump replacement

Water levels in each monitoring well and piezometer will be measured using portable probes. Each monitoring well is equipped with a dedicated 1-inch diameter stainless steel water level monitoring tube. Piezometers are not equipped with monitoring tubes.

Any sampling equipment or procedural changes will be documented in the operating records for Site A groundwater monitoring wells.

SAMPLE COLLECTION

Inspecting Wellheads and Screening for Organic Vapors

On arrival at each wellhead, the sampling team checks for organic vapors. Background levels in the breathing zone, at the wellhead, and inside the well casing are measured with a Photoionization-type organic vapor detection device.

The wellhead is visually inspected for signs of tampering and needed maintenance. Background and wellhead organic vapor readings, along with the observations of wellhead conditions, are entered into the field sampling logbook. The organic vapor detection device is calibrated to known standards at the frequency recommended by the manufacturer. Potential interferences, notably wind and humidity, are taken into account, and field operational checks are made when using the organic vapor detector.

Measuring Static Water Level

To minimize the potential for errors caused by variations in barometric pressure, all static water level measurements are obtained on a single day, or within consecutive days during which the barometric pressure changed by no more than 0.5 inches of Mercury. Portable water-level probes are used to determine the depth to groundwater. Previous water level measurements are reviewed to assure that an erroneous reading is not incorporated into the data base. Groundwater elevations are measured to the nearest 0.10 foot. Water levels at Site A are at depth of about 950 feet. The fully

extended water level probe is heavy and care must be taken to avoid dragging it over the lip of the water level tube which will destroy the probe wire. Retrieving the probe and simultaneously winding the tape back onto a reel is a two person job.

Before using the electronic water level measuring device for the first time each day, the probe and the first 50 feet of cable will be washed with phosphate free laboratory grade detergent and rinsed with distilled water to remove any contamination. Prior to use after cleaning, the probe may be wiped dry or allowed to drip dry.

Once the depth to groundwater has been determined, at least three measurements will be taken and recorded in the field logbook. Depth to groundwater is measured to the nearest 0.10-foot from the top of the casing or the access port (a permanent reference point). The same measure point will be used each time a water level is measured.

When the probe is removed from the well, the end of the probe and the bottom 10-feet of cable are to be washed with laboratory grade detergent and rinsed with distilled water to minimize the potential for cross-contamination to the next well.

The well elevation datum and water-level measurement point relative to USGS Datum are surveyed by a registered surveyor. These points are related to a fixed reference point on the well casing. The water-level measuring point will be marked on the well and described in the field notebook.

Pre-Sample Purging

The wells are purged prior to sample collection to ensure that samples collected from the well are representative of the water in the formation. This is done by purging the well until field parameters - namely, pH, specific conductivity, and temperature have stabilized. Stabilization of field parameters has been used by numerous investigators to determine when actual aquifer water is being removed, rather than the stagnant water. Stabilization of conductivity values to within 10 $\mu\text{mhos/cm}$ for cased wells with conductivities less than 1,000 $\mu\text{mhos/cm}$ over successive measurements represents reasonable field criteria for judging purging effectiveness (Barcelona, et. al., 1994). Values of pH, conductivity, and temperature will stabilize after the standing water in the well column is replaced by water from the aquifer under low flow rate conditions. Therefore, stabilization of these field parameters would indicate when actual "fresh" aquifer water is being drawn into the well.

A common sample tee is attached to the dedicated pump discharge valve at each well. The discharge valve is used to control the pumping rate. The wells will be generally purged at low flow rates (<3 gpm). Initial discharge rates exceeding 3 gpm may be used to clear sediment and volcanic cinders that tend to accumulate in the wells between sampling events. The cinders and sediment tend to plug off the discharge valve requiring frequent opening and closing the valve to regain flow. Once most of the cinders have been cleared constant discharge rates can be achieved. The discharge tee consists of two separately valved discharged points. The end of the tee is routed to the purge water containment drums and the sample hose is attached to the second valve.

Under low flow rate conditions, the field parameters will stabilize generally within one purge volume. Purge volumes will be dependent upon the stabilization of the field parameters measured during purging. Field parameters will be measured initially and every time thereafter whenever 10 to 20 gallons are removed from the borehole. Field parameter values will be considered stabilized when three successive measurements of pH and specific conductivity vary by no more than 10 percent. The purge data will be included in the field notes for the sampling event. A minimum of one casing volume will be removed prior to sampling.

All monitoring wells will be sampled using the dedicated sampling pumps installed in each well. The pump is not to be turned off until all required samples have been collected. A dedicated sampling tube will be used at each well. This tube will be rinsed with distilled water and is attached to the discharge tee. The two valves on the discharge tee will be adjusted to direct a controlled, non agitated, non-aerated stream of water out the sample hose to allow filling the sample bottles. All samples will be collected to minimize agitation or aeration to prevent loss of the constituent.

Measuring Field Parameters

Three field parameters - temperature, pH, and specific conductivity - will be measured. Sample water will be poured into four separate 500-ml containers. Temperature will be measured and recorded on only the first aliquot. Conductivity and pH will be measured and recorded for each separate aliquot. Field parameter sample water will be stored with the purge water. Normal laboratory procedures will be followed in measuring field parameters. The temperature of the sample will be measured as soon as it is collected. The pH meter will be corrected for temperature and will be standardized with pH 7 and 10 buffers until the reading is within 0.1 pH units of the

standard buffers. The conductivity meter will be calibrated with commercially available standard solution of approximately 1413 μ S before use.

Monitoring for Immiscible Layers

Each monitoring well is checked for light or dense immiscibles during each sampling event. When the well is purged, the initial water to be discharged will be collected in a large glass jar. The liquid will be allowed to settle for at least 15 minutes to determine if a phase-separation occurs. If an immiscible layer is visible the water will be decanted off and the immiscible layer will be collected in extra VOC sample vials included with the Site A sample containers. The sample of immiscible fluids will be submitted for preliminary identification of its component constituents. If immiscible compounds are detected additional subsequent sampling of the impacted well will be required when the appropriate sample containers can be obtained from the laboratory.

SAMPLE PRESERVATION AND HANDLING

A contract laboratory provides the sample containers and preservatives required for the sampling event. All sample bottle preconditioning, such as baking or acid-washing, is performed by the contract laboratory. All samples are collected, preserved, and handled in accordance with the current edition of EPA's SW-846. In addition to the well samples, the sampling includes field blanks and trip blanks, as discussed in the QA/QC section.

CHAIN-OF-CUSTODY CONTROL

Sample Packing and Shipment

Once all of the samples are collected and prepared and the chain-of-custody forms are filled out, the samples are prepared for shipment. The sample containers are packed with insulation inside the shipping containers along with the chain-of-custody forms. Ice, or similar coolant, is placed in the shuttle in order to keep the samples cold. Because the groundwater at Site A is at approximately 50° C the samples are allowed to cool before being iced in the field (to avoid bottle breakage) and are kept on temporary ice prior to being repacked prior to shipping. The shuttle lids are secured and sealed with a chain-of-custody tag. The shuttles are shipped by express service to the contract laboratory for analysis. The sample analysis request form is provided directly to the contract laboratory by USEI or its sampling contractor.

Chain-of-custody control, as more fully discussed in the attached project plan, will be followed.

ANALYTICAL PROCEDURES

All analytical procedures will comply with EPA SW-846. Changes in detection limits due to matrix problems or interferences that may affect detection limits for individual samples will be noted in the final analytical report.

WASTEWATER MANAGEMENT

Water collected when purging wells, testing for indicator parameters, collecting samples for lab analysis, or other purposes will be stored temporarily on-site in 55-gallon drums in the vicinity of each monitoring well. Each drum is labeled with well number, date, gallons and the descriptor “purge water”.

Table 1: Analytes, PQLs and 1E-04 Risk Values

| Analyte (by Method 8260b) | CAS Number | PQL (ug/L) | 1E-04 residential risk* (ug/l) |
|---|------------|------------|-----------------------------------|
| 1,1,2,2-Tetrachloroethane | 79-34-5 | 1 | 7.6E+00 |
| 1,1,1-Trichloroethane | 71-55-6 | 1 | 8E+05 |
| 1,1,2-Trichloro-1,2,2- Trifluoroethane (CFC 113) | 76-13-1 | 1 | 5.5E+06 |
| 1,1,2-Trichloroethane | 79-00-5 | 1 | 2.8E+01 |
| 1,1-Dichloroethane | 75-34-3 | 1 | 2.8E+02 |
| 1,1-Dichloroethylene | 75-35-4 | 1 | 2.8E+04 |
| 1,2-Dichloroethane | 107-06-2 | 1 | 1.7E+01 |
| 1,2-Dichloropropane | 78-87-5 | 1 | 4.4E+01 |
| Benzene | 71-42-2 | 1 | 4.6E+01 |
| Bromodichloromethane | 75-27-4 | 1 | 1.3E+01 |
| Bromoform | 75-25-2 | 1 | 3.3E+02 |
| Bromomethane | 74-83-9 | 1 | 7.5E+02 |
| Carbon Tetrachloride | 56-23-5 | 1 | 4.6E+01 |
| Chlorobenzene | 108-90-7 | 1 | 7.8E+03 |
| Chlorodibromomethane | 124-48-1 | 1 | 8.7E+01 |
| Chloroethane | 75-00-3 | 1 | 2.1E+06 |
| Chloroform | 67-66-3 | 2 | 2.2E+01 |
| Chloromethane | 74-87-3 | 1 | 1.9E+04 |
| Cis-1,2-Dichloroethylene | 156-59-2 | 1 | 3.6E+03 |
| 1,3-Dichloropropene | 542-75-6 | 1 | 4.7E+01 |
| Ethyl benzene | 100-41-4 | 1 | 1.5E+02 |
| Methylene Chloride | 75-09-2 | 1 | 1.1E+03 |
| Tetrachloroethylene (PCE) | 127-18-4 | 1 | 1.1E+03 |
| Toluene | 108-88-3 | 1 | 1.1E+05 |
| Trans-1,2-Dichloroethylene | 156-60-5 | 1 | 3.6E+04 |
| Trichloroethylene (TCE) | 79-01-6 | 1 | 4.9E+01 |
| Vinyl Chloride | 75-01-4 | 1 | 1.9E+00 |

* Source: US EPA Regional
Screening Levels May 2016,
<https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-may-2016>
Risk=1E-04



**Groundwater Sampling
Quality Assurance Project Plan**

**Site A
Bruneau, Idaho
U.S. EPA I.D. # IDD000773952**

Revised September 2016

INTRODUCTION

In the late 1950's, the United States Air Force constructed three Titan Intercontinental Ballistic Missile (ICBM) complexes in southern Idaho. US Ecology Idaho now owns two of the three former Titan ICBM complexes. One of these facilities, Site A is an inactive, closed facility located 18 miles south of Bruneau, Idaho.

This Quality Assurance Project Plan (QAPP) describes the quality assurance/quality control procedures related to environmental sampling events during the post-closure care period at the Site A facility.

QUALITY ASSURANCE OBJECTIVES

The QAPP ensures the accuracy and reliability of the analytical results used to monitor environmental performance of Site A during the post-closure care period. The following objectives are met by this plan:

- Establishes personnel responsibilities and organizational authority;
- Trains personnel according to functions;
- Assigns experienced technical personnel for QAPP implementation;
- Maintains field sampling equipment;
- Properly executes each aspect of sample collection and handling;
- Documents field measurements and maintenance of field records; and,
- Documents analytical results and maintenance of laboratory records.

This QAPP will be updated, as needed, to reflect changes in sampling requirements and/or field conditions as determined by review by the Environmental Compliance Manager, or designee, and as approved by the Idaho DEQ per the procedures of 40 CFR §270.42.

PROJECT DESCRIPTION

Groundwater sampling at Site A has been conducted since 1981. A Closure/Post-Closure Plan/CAMU permit updated in August 2002 and again in March 2007 establishes a groundwater monitoring program for the site. This QAPP accompanies an application for renewal of that permit, and may be amended, as noted above, once the permit is re-issued or modified.

PROJECT ORGANIZATION AND RESPONSIBILITY

The Environmental Compliance Manager, or designee is responsible for:

- Approving all changes and arranging for periodic audits of program objectives
- Implementing, evaluating, and documenting the QAPP program
- Assigning tasks to field sampling personnel
- Ensuring that all sample collection is performed in accordance with this QAPP
- Reviewing and maintaining chain-of-custody documentation
- Coordinating performance auditing, including the insertion of blind QA spikes and blanks
- Reviewing analytical results (including raw data)

- Monitoring documentation and maintenance of records
- Identifying and implementing training for field sampling personnel, including safety and emergency response procedures, and
- Ensuring field equipment is routinely maintained and calibrated.

Sampling Team members must:

- Be familiar with this plan
- Observe and record field conditions in the field logbook
- Collect the groundwater samples using appropriate procedures and equipment
- Follow applicable chain-of-custody protocols
- Report irregularities to the Environmental Compliance Manager, or designee, and
- Be trained in safety practices and emergency response procedures.

SAMPLING PROCEDURES

Samples must be collected so that no foreign material is introduced into the sample and no material of interest escapes from the sample prior to analysis. Groundwater sampling and analysis conforms to the protocols of EPA SW-846, most recent edition, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. The Groundwater Sampling and Analysis Plan further details sampling procedures. Table 1 outlines the analytical parameters and SW-846 methodology used at Site A.

SAMPLE AND DOCUMENT CUSTODY CONTROL

Sample and Chain-of-custody is controlled as follows:

The sample bottles are prepared and shipped by the contract laboratory. The sample bottles are not shipped under Chain of Custody but the laboratory shall include signed documentation of what was shipped. When the bottles are received by US Ecology, US Ecology's representative will open the shipping container(s) and verify the contents and conditions of the bottles. The sample bottles shall be stored under clean and secure conditions within the Environmental Compliance Department. Prior to mobilizing to Site A the sampling team shall assemble the bottles into the appropriate sample coolers. From that point on, every time the shipping containers that contain the sample bottles (whether the sample bottles are empty or full) change hands (with the exception of the shippers), both parties sign and date the transfer.

After the shipping containers that contain the sample bottles are delivered to the laboratory, a copy of the chain-of-custody form is returned to the Environmental Department for inclusion in the facility records.

The chain-of-custody form includes the following information:

- Sample number;
- Signature of sampler:

- Date of collection (time logged in field logbook);
- Place and address of collection;
- Type of sample;
- Sample analysis request;
- Number and type of containers;
- Inclusive dates of possession; and,
- Signature of receiver.

Other components of the chain-of-custody include sample labels, sample seals, field logbook, the laboratory logbook, sample packing and shipment, and sample receipt.

Sample Labels

A sample label is affixed to each sample bottle to provide the sample number. To minimize sample bias on behalf of the analytical laboratory, sample numbers other than the well number are used to label each sample bottle.

Sample Seals

A seal is affixed to each sample shipping container (not each bottle). The seal is secured to the shipping container, after it has been packed, and is broken at the laboratory under chain-of-custody procedures. The laboratory notes the status of the custody seal on their sample receipt checklist

Field Logbook

A field logbook will be used to document each sampling event. A new field book will be prepared prior to each sampling event. The field logbook will contain all field data and miscellaneous information, observations, and occurrences. Field data includes the names of all sampling personnel, daily weather observations, water levels, and the sampling data, including the purge volumes and sample identification number(s) for each well to be sampled. The completed field book will be bound in the final sampling report prepared after each sampling event.

Laboratory Logbook

A scanned copy of the laboratory log-in records is initially provided in an email with a scan of the original chain-of-custody form. The original documents are kept at the contract laboratory facility, per the contract laboratory protocols and procedures. Copies of the documents are also provided with the final laboratory report provided to the facility.

Sample Packaging and Shipment

Once all of the samples are collected and prepared and the chain-of-custody forms are filled out, the samples are prepared for shipment. The shipping containers are packed with sealed frozen coolant. The shipping container lids are then secured and sealed with a sample seal.

The groundwater samples are shipped in the shipping containers via express shipment to the contract laboratory for analysis. The chain-of-custody form is provided to the contract laboratory by the field sampling personnel.

Sample Receipt

Upon receipt of the samples at the contract laboratory, the security of the shipping containers is checked. Outer seals that are broken or missing are noted and reported to the Environmental Compliance Manager, or designee.

The following procedures are then followed at the lab:

- The chain-of-custody form is obtained from inside the shipping container, signed, and compared against the contents of the shipping container;
- The chain-of-custody record is checked for a signature;
- The request for analysis is checked to determine the analyses requested;
- A laboratory sample number is assigned; and,
- The sample is stored per the laboratory protocols and procedures to await analysis.

CALIBRATION PROCEDURES AND FREQUENCY

Field Procedures

Normal laboratory procedures are followed in measuring field parameters; that is, all meters are warmed up and calibrated before being used. The pH meter is calibrated with pH 7.0 and pH 10.0 buffer solutions. The pH meter is corrected for temperature before the pH is read. The pH standardization procedure is repeated until the reading agrees within 0.1 pH unit with the calibration buffers. The conductivity meter is calibrated with commercially available conductivity standards of not more than 1413 μS before use. The temperature of the sample is measured as soon as it is collected. The organic vapor photo-ionization type detector is calibrated according to the manufacturer's specifications. All meter calibrations are recorded in the field logbook. Table 2 summarizes field meter calibrations and standard checks, and lists the corrective actions to be taken.

Laboratory Procedures

USEI uses a certified contract laboratory to perform all groundwater analyses. The lab provides documentation, as part of the final report, outlining calibration, QA/QC, spike, and blank results.

Table 2: Field Meter Calibration

| Meter | Calibration Method | Calibration Frequency | Standard Check | Corrective Action |
|------------------------------|---|------------------------------------|---|---|
| pH | Calibrate to 7.0 and 10.0 standard buffer solutions. | Daily when in use | Check against pH 7.0 standard prior to use at each well. | If 7.0 standard not within +/- 0.2 S.U., recalibrate |
| Specific Conductivity | Calibrate with an approximate 1,000 micro Siemens standard. | Daily when in use | Check with calibration standard prior to use at each well | If SC not within 20% of true value, replace standard. If still outside 20%, return meter for repairs. |
| PID | Calibrate to 100 ppm Isobutylene or equivalent | Per manufacturers' recommendations | Meter is calibrated by USEI prior to being used in the field. Field calibration is not performed. An operational check using a "Sharpie" or similar marker will be made before use. | If reading is not within +/- 20% of true value, then recalibrate. |

SAMPLE PREPARATION METHODS AND ANALYTICAL PROCEDURES

In the field, samples are placed directly into the appropriate containers and preserved as specified in accordance with SW-846 protocols (see Table 3). Also listed in Table 3 are the maximum holding times for each parameter per the SW-846 requirements. Laboratory sample preparations and analyses are performed in accordance with the methodologies outlined in EPA's Third Edition (or more recent) of *SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* and in accordance with permit conditions.

Table 3: Analytical Methodology, Sample Volume Requirements, and Holding Times

| Parameter | EPA Method | Container Type | Preservative | Holding Time |
|-------------------|-------------------------------|-----------------------|---------------------|---------------------|
| Volatile Organics | 8260b per permit requirements | 3-40 ml VOA's | HCL, Cooled to 4°C | 14 days |

DATA REDUCTION, VALIDATION, AND REPORTING

Data Reduction and Validation

All analytical data generated within the contract laboratory is reviewed by contract laboratory personnel prior to report generation to assure the accuracy of the reported data. The data reporting process consists of data generation, reduction, and review. In accordance with laboratory protocols, review of the data is performed by the person generating the data, and an independent technical reviewer to ensure that the work is error-free and that errors missed in the first review are corrected. The laboratory project manager reviews the data to ensure that the data meets the needed requirements of the project. In each stage of the review, in accordance with laboratory protocols, the review is documented by the signature of the reviewer and the date reviewed.

The objective of the data validation is to identify any unreliable or invalid laboratory measurements (Figure 1). Upon receipt of the laboratory data, the following contract compliance screening validation, reduction, and reporting scheme will be executed:

1. Contract compliance screening represents the first level of data validation and reduction. Its purpose is twofold:
 - To evaluate whether the laboratory met contract performance requirements in analyzing the submitted samples as listed in Table 4 for Field Quality Control samples and Table 5 for Laboratory Quality Control samples.

To determine if specific samples were associated with certain out-of-control analytical Data reviewers evaluate each data package as received from the laboratory to check sample holding time, instrumentation calibration, review of calibration and preparation blanks, laboratory control samples, specific sample results, and field and other QC sample results. Results of the contract compliance screenings with a narrative of findings will be incorporated in each sampling report.

2. Measurement data will then be reduced and evaluated in accordance with the procedures described in Appendix A of the QAPP document.
 - Representativeness
 - Accuracy
 - Precision
 - Completeness
 - Comparability

Laboratory Data Reporting

All laboratory analytical reports will contain, at a minimum, the following information:

- General Discussion - Description of sample types, tests performed, any problems encountered, and general comments.
- Analytical Data - Data are reported by sample or by test with the appropriate significant figures and reporting limits, adjusted for dilution. Pertinent information including dates sampled, received, prepared, and extracted are provided.

- Laboratory Performance QC Information - The results of the laboratory control samples analyzed with the project are listed, together with the control limits. Also, the analytical results for method blanks generated during analysis of organics, and pertinent wet chemistry parameters are given.
- Matrix-Specific QC Information - Results of any sample duplicates, matrix spikes, matrix spike duplicates or other project specific QC requested are also reported. The results include supporting information such as amount spiked, percent recovery or percent difference.
- Methodology - Reference for analytical methodology used is cited
- situations, and to identify these specific samples.

Figure 1 – Contract Compliance, Data Validation and Reduction Flow Chart

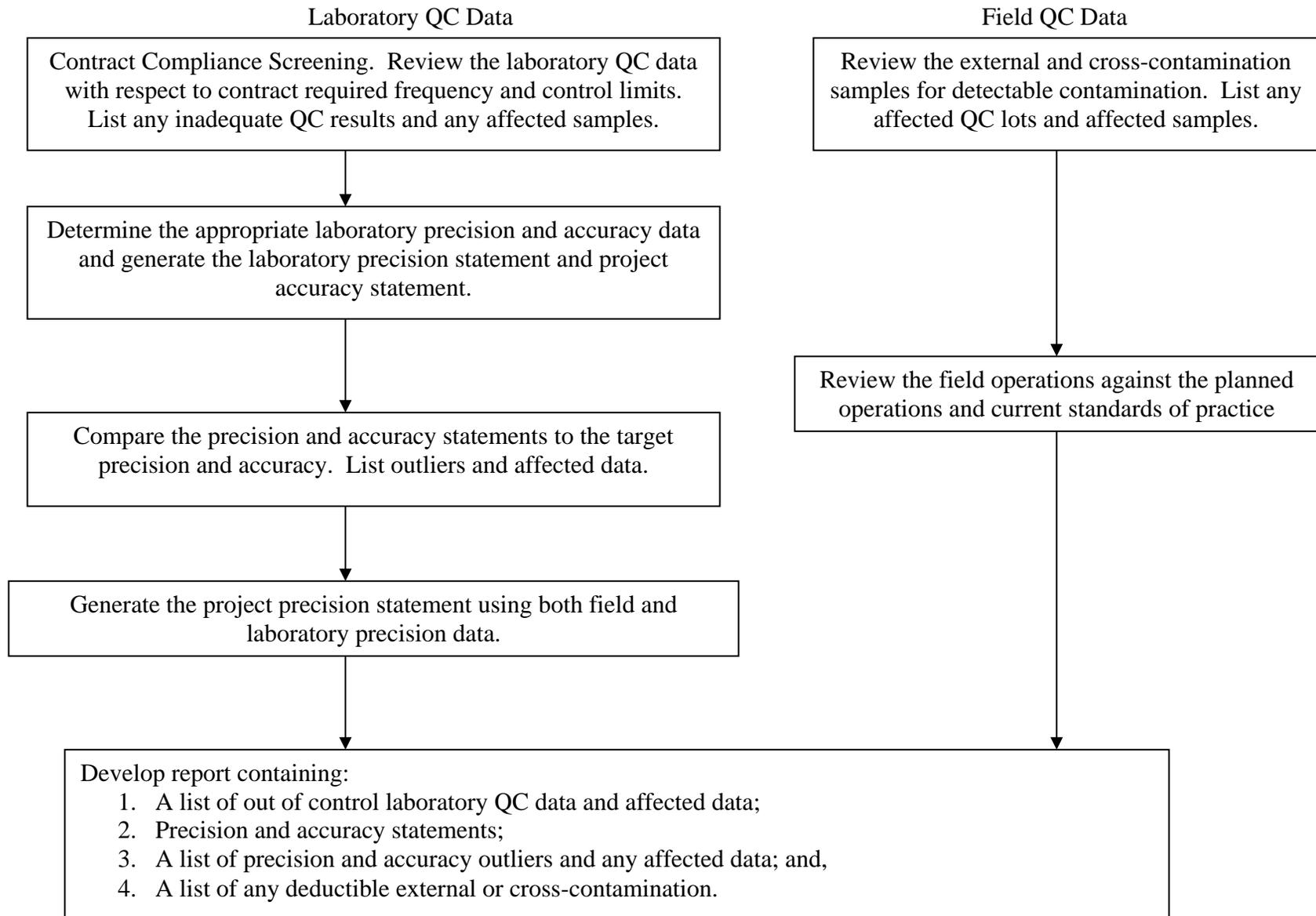


Table 4: Quality Control Target Limits for Field Quality Control Samples

| Field QC Sample | QC Target Limit | Corrective Action |
|------------------------|---|--|
| Field Replicates | Organic replicate analysis will have RPD's as specified in the method. | <ol style="list-style-type: none">1. Reanalyze sample2. If still outside +/- 20%, all associated data will be flagged. |
| Field Container Blank | Value should be less than the contract required detection limit (CRDL). | <ol style="list-style-type: none">1. Reanalyze sample2. If value is above CRDL, samples with concentrations ≤ 10 times the blank, then no action. Samples with concentrations ≥ 10 times the blank will be flagged. |
| VOA Trip Blank | Value shall be less than the contract required detection limit. | <ol style="list-style-type: none">1. Reanalyze sample2. If value is above CRDL, samples with concentrations ≤ 10 times the blank, then no action. Samples with concentrations ≥ 10 times the blank will be flagged. |

Table 5: Laboratory Quality Control

| Quality Control Item | Minimum Frequency | Control Limits | Correction Action |
|--|---|--|--|
| 1. Initial Calibration Verification | At the start of analysis batch, analyze a calibration control standard (CCS). | Organics – As specified in the EPA method. | <ol style="list-style-type: none"> 1. Recalibrate and re-standardize the instrument including fresh stock and working standards, as necessary. 2. Analyze a second CCS; if within control limits, proceed. 3. Repeat 1 and 2 until instrument calibration has been verified. |
| 2. Initial Calibration Blank | At the start of analysis of each batch, analyze a calibration blank | Results for the calibration blank must be below required detection limits. | <ol style="list-style-type: none"> 1. Same as QC Item 1 using the calibration blank instead of the CCS. |
| 3. Continuing Calibration Verification and Continuing Calibration Blank. | During the analysis, a CCS and calibration blank shall be run at a frequency of one per ten analytical samples. | CCS Organics – as specified in the method. Calibration blank must be below required detection limit. | <ol style="list-style-type: none"> 1. Recalibrate and re-standardize the instrument using the same standards from the initial calibration. 2. Reanalyze samples from point where instrument was last “in control”. |
| 4. Preparation or Reagent Blank Analysis. | One per batch or one per every 20 samples digested, whichever is more frequent. Preparation blanks should be analyzed before analysis of samples. | Preparation blank results must be below the required detection limits. | <ol style="list-style-type: none"> 1. Check for reagent and glassware contamination. Correct any contamination. 2. Samples with concentrations ≥ 10 times the blank, then no action. Concentrations ≤ 10 times, redigest and reanalyze. |
| 5. Natural, Matrix Spike Analysis (Pre-Spike) | One natural matrix spike shall be prepared for each batch or for every 20 samples in the sample set, whichever is more frequent. Natural matrix spikes shall not be performed on the field bottle blank or standard reference material. | The spike recovery must be within limits specified in the method. | <ol style="list-style-type: none"> 1. Check the analytical procedure. 2. Repeat spike sample analysis on an additional sample. If the second spike is with control, proceed with the analysis. If the second spike is out of control, analyze the spike samples and their sister samples by full method of standard additions. If the spike recoveries are out of control following analysis by MSA, the problems must be identified and corrected and the samples associated with the out of control spike redigested and reanalyzed. If analysis by MSA corrects the spike recoveries, all samples shall be analyzed by MSA. |

Table 5: Laboratory Quality Control (continued)

| | | | |
|--|---|---|--|
| <p>6. Duplicate Sample Analysis</p> | <p>Duplicate samples shall be prepared at a frequency of one per 20 samples received for each analyte.</p> | <p>Duplicate samples shall have a RPD less than 20% for all analytes, if analyte $\geq 5 \times$ CRDL.</p> | <ol style="list-style-type: none"> 1. Check instrument calibration. 2. Check analytical calibration 3. If the duplicate sample results are outside the control limits, flag all associated data with a “*”. |
| <p>7. Laboratory Control Sample Analysis (the appropriate LCS for each sample is presented in the text).</p> | <p>The appropriate LCS’s shall be prepared and analyzed at a frequency of one in 20 natural samples received.</p> | <p>LCS results must be within the range stated by the certifying agency (EPA, NBS).</p> | <ol style="list-style-type: none"> 1. Check analytical procedure. 2. Check instrument calibration. Reanalyze LCS’s. If LCS’s are still out of control. Identify the problem and correct before proceeding with analysis. |

INTERNAL QC CHECKS

The laboratory QA/QC program controls, monitors, and assesses data quality with internal QC checks. Three types of internal QC checks are used:

- To ensure that laboratory operations are "in control" during data generation,
- To determine the effect the sample matrix has on the data being generated, and
- To determine the effect field conditions have on the analytical results.

Laboratory performance QC is based on the use of a standard control matrix to generate precision and accuracy data that are compared, on a daily basis, to control limits. This information, in conjunction with method blank data, is used to assess daily laboratory performance.

Matrix specific QC is based on the use of an actual environmental sample for precision and accuracy determinations and commonly relies on the analysis of matrix spikes, matrix duplicates, and matrix spike duplicates. This information is used to assess the affect of the matrix on analytical data.

Field QC samples that include field container blanks, trip blanks and field duplicates are used to monitor the collection, transport, and storage of environmental samples. Table 6 defines the different field QC samples that will be used during the groundwater sampling, and the frequency of collection of the QC samples.

Table 6: Definitions of Field QC Samples

| | |
|-----------------------|--|
| Field Container Blank | Is an analysis of contamination in an empty sample container. A sample container is filled with deionized water provided by the contract laboratory, and then the water is analyzed for parameters of interest. Frequency is a minimum of one per day. |
| Field Replicate | Two samples are taken from the same media at the same time. The field replicates are submitted blind to the laboratory for analysis. Frequency is a minimum of one per day. |
| VOA Trip Blank | Is ultra pure, distilled, deionized water sealed in a sample container at the laboratory, then shipped out to the sampling crew. The sampling crew retains the VOA trip blank until sampling is completed. The VOA trip blank is then shipped back to the laboratory along with natural samples for analysis for volatile organic compounds. One VOA trip blank is used for each shipping container that contains samples that will be analyzed for volatile organics. |

PERFORMANCE AND SYSTEM AUDITS

Performance and system audits identify laboratories capable of generating scientifically sound data. The system audit reviews laboratory operations to verify necessary facilities, equipment, staff and

procedures are in place to generate acceptable data. Performance audits verify the laboratory's ability to correctly identify and quantify compounds in blind check samples submitted by the auditing agency.

PREVENTATIVE MAINTENANCE

To minimize downtime and interruption of analytical work, preventative maintenance is performed on each analytical instrument. Laboratory personnel are trained in routine maintenance. Repairs are performed by trained staff or trained service engineers employed by the instrument manufacturer. The laboratory maintains detailed logbooks documenting maintenance and repairs for each analytical instrument.

Field equipment is maintained as specified by the instrument manufacturer or when calibration cannot be achieved. Replacement equipment is available.

DATA MEASUREMENT ASSESSMENT PROCEDURES

The effectiveness of a QA program is measured by the quality of data generated by the laboratory. Data quality is judged in terms of its precision, accuracy, representativeness, completeness, and comparability. These terms are described as follows:

Precision

Precision is a measure of mutual agreement among individual measurements of identical samples. The laboratory precision statement will be developed from the field replicate and laboratory replicate analysis (split samples, split digestants, duplicate analysis, etc.). Because several types of replicates can be performed by the laboratory and it is inappropriate to combine them, the following priority will be followed to determine which type of laboratory replicate is used for the laboratory precision statement.

1. Laboratory Split Samples - These are samples split by the laboratory prior to any digestions or extractions.
2. Laboratory Split Digestant/Extractants - These are samples that have been digested/extracted, then split by the laboratory. For homogeneous samples, like filtered, acidified waters, there is no difference between a laboratory split sample and a split digestant. Presumably, the digestants are split and labeled in such a manner that they are submitted blind to the analyst.
3. Laboratory Duplicate Analyses - These are single sample digestants/extractants that are analyzed twice. Laboratory duplicate analyses normally are not be used for developing a laboratory precision statement unless no other duplicate analyses are available.

An overall precision statement is developed using the field replicates and the laboratory replicates. These replicates are given equal weight when developing the overall precision statement. In cases where the laboratory replicates and field replicates have been performed at the same frequency, no data normalization is necessary to achieve equal weight. In cases where the frequencies for the laboratory and field replicates are different and, therefore, the total number of each type of replicate is different, the replicate data is normalized to achieve equal weight.

Accuracy

Accuracy determines how close the measurement is to the true value. Accuracy is defined as laboratory accuracy.

Two types of QC samples are used to assess laboratory accuracy. The following priority of sample results is used to determine accuracy statements:

1. Blind field standards (BFS) - These are certified materials produced by agencies such as EPA, and the National Bureau of Standards (NBS). These samples are submitted blind to the laboratory, along with the natural samples. Although the laboratory can most likely recognize the BFS, they do not know which certified material it is. Blind field standards will be used to evaluate the accuracy of the analyses. One blind field standard will be utilized for each sampling event.
2. Laboratory natural matrix spikes (Pre-spikes) - These are spiked samples prepared in the laboratory by splitting a sample and spiking one portion with a known amount of the analyte(s) of interest. The spiked sample result and the natural sample result are compared, and the spike recovery is calculated. The spike recovery is the measure of accuracy and of matrix effect. Matrix spikes will be analyzed at a minimum frequency of one in 20 or one per batch, whichever is more frequent. Recovery of natural matrix spikes will be used to assess accuracy when the BFS are not available for a particular analyte.

Accuracy statements will be generated based on the recovery of BFS and spike recoveries.

Representativeness

Representativeness is the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is accomplished by choosing the number of samples, sampling locations, and the sampling procedures that will produce results that depict, as accurately and precisely as possible, the matrix and conditions being measured; by developing protocols for storage, preservation, and transportation that preserve the representativeness of the collected samples; and by following the sampling and analysis plan requirements to document that protocols have been followed and that samples are properly identified so that their integrity is maintained.

Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared with the amount that was expected to be obtained under normal conditions. To be considered complete, the data set must contain all analytical results and data specified for the project. In addition, data must be compared to project requirements to ensure that specifications have been met.

Comparability

Comparability expresses the confidence with which one data set can be compared to another data set measuring the same property. Comparability is ensured through the use of established and approved analytical methods, consistency in the basis of analysis, consistency in reporting units, and analysis of standard reference materials.

Precision, accuracy, and completeness requirements are specified per the methodology. Precision, accuracy, and completeness limits will be either the CLP limits or historically derived laboratory data, whichever is tightest.

The detection limits also affect the quality or usefulness of the data to the project. The detection limits required for Site A analytical work are listed in Table 1. These detection limits can be met using SW-846 methodologies.

CORRECTIVE ACTION

When errors, deficiencies, or out-of-control situations exist, the laboratory QA program or field sampling program must provide systematic procedures to resolve problems and restore proper functioning to the system.

Laboratory personnel are alerted that corrective actions may be necessary if:

- QC data are outside the acceptable limits for precision and accuracy;
- Blanks contain contaminants above acceptable levels;
- Undesirable trends are detected in control sample recoveries;
- There are unusual changes in detection limits;
- Deficiencies are detected during internal or external audits or from the results of performance evaluation samples; or,
- Inquiries concerning data quality are received from clients.

Corrective action procedures should be handled at the bench level by the analyst. If the problem cannot be identified, the matter should be referred to the laboratory manager and/or QA department for further investigation. Every effort must be made to determine the cause of the problem so that a permanent solution can be implemented. Once resolved, full documentation of the corrective action procedure must be filed with the project records.

APPENDIX A

**PROCEDURES
FOR CALCULATING
PRECISION, COMPLETENESS, AND ACCURACY**

Precision

The primary measurement of data precision is the Relative Percent Difference (RPD) between a duplicate pair of data points:

$$RPD = [(X_2 - X_1) / \{ (X_1 + X_2)/2 \}] \times 100$$

where: X_1 = First duplicate point value

X_2 = Second duplicate point value

Completeness

Completeness is the ratio of acceptable measurements obtained compared to the total number of planned measurements for an activity. Completeness (C) can be defined as:

$$C = \frac{\text{(Number of acceptable data per target quality control limits)}}{\text{(Total number of data points)}} \times 100$$

Accuracy

1. The percent recovery of the blind field standard and the recovery of each spiked pair are calculated separately as:

$$\% \text{ Recovery of BFS} = (VA/VK) \times 100 \quad \text{OR} \quad \% \text{ Recovery of Spike} = [(SSR - SR) / SA] \times 100$$

where: VA = Analytical value of BFS

VK = Known (or certified) value of BFS

SSR = Spiked sample results

SR = Sample results

SA = Spike added

Perfect accuracy would be 100-percent recovery.

2. Calculate the standard deviation (SD) of all pairs as:

$$SD = [(\text{Recovery}_i - \text{Recovery}_{\text{avg}})^2 / (n-1)]^{1/2}$$

where: Recovery_i = Individual recoveries

$\text{Recovery}_{\text{avg}}$ = Average recovery

n = Number of values

3. The range of uncertainty (R) in the recovery is then calculated as:

$$\pm R = \pm tSD/(n)^{1/2}$$

where: R = Range of uncertainty expressed as a percent

t = Value of the t distribution for the selected confidence level (90%) and n-1 degree of freedom

n = Number of samples

SD = Standard deviation

The range of uncertainty is used in conjunction with the average recovery to determine if bias adjustments are required.

4. Together, the final average recovery value and the corresponding range of uncertainty constituted the statement of accuracy for a particular sampling program.

Table A-1: Chauvenet’s Criterion for Rejecting a Suspected Value^a

| <u>Number of Samples (n)</u> | <u>Maximum Allowable Values for $(\text{Recovery}_i - \text{Recovery}_{\text{avg}})/\text{SD}^b$</u> |
|------------------------------|---|
| 3 | 1.901 |
| 4 | 1.983 |
| 5 | 2.015 |
| 6 | 2.111 |
| 7 | 2.164 |
| 8 | 2.195 |
| 9 | 2.214 |
| 10 | 2.228 |
| 11 | 2.279 |
| 12 | 2.318 |
| 13 | 2.348 |
| 14 | 2.373 |
| 15 | 2.393 |
| 16 | 2.409 |
| 17 | 2.424 |
| 18 | 2.435 |
| 19 | 2.445 |
| 20 | 2.454 |
| 21 | 2.462 |
| 22 | 2.469 |
| 23 | 2.475 |
| 24 | 2.480 |
| 25 | 2.485 |
| 26 | 2.502 |
| 27 | 2.517 |
| 28 | 2.530 |
| 29 | 2.543 |
| 30 | 2.555 |
| 31 | 2.634 |

^a Based on “t” distribution rather than the traditional “normal” distribution

^b Recovery_i = Individual recoveries

$\text{Recovery}_{\text{avg}}$ = Average Recovery

SD = Standard deviation