DEPARTMENT OF ECOLOGY
State of Washington

# Quality Assurance Project Plan

# Assessing Dioxin in Groundwater Lower Yakima Valley

March 2020
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# Publication Information

Each study conducted by the Washington State Department of Ecology must have an approved Quality Assurance Project Plan (QAPP). The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completing the study, Ecology will post the final report of the study to the Internet.

This QAPP is available on Ecology's website at
https://fortress.wa.gov/ecy/publications/SummaryPages/2003105.html

Data for this project are available in Ecology's EIM Database. Study ID: MRED0003.

The study area for this project is in Water Resource Inventory Area (WRIA) 37.

The Activity Tracker Code for this study is 20-021.

This plan was prepared by a licensed hydrogeologist. A signed and stamped copy of the report is available upon request.

# Contact Information

Publications Coordinator
Environmental Assessment Program
P.O. Box 47600, Olympia, WA 98504-7600
Phone: 360-407-6764

Washington State Department of Ecology–Washington State Department of Ecology

- Headquarters, Olympia 360-407-6000
- Northwest Regional Office, Bellevue 425-649-7000
- Southwest Regional Office, Olympia 360-407-6300
- Central Regional Office, Union Gap 509-575-2490
- Eastern Regional Office, Spokane 509-329-3400

# Quality Assurance Project Plan

# Assessing Dioxin in Groundwater Lower Yakima Valley

March 2020

**Approved by:**

| | |
|---|---|
| Signature: | Date: |
| Sage Park, Client, Regional Director, Central Regional Office<br><br>Signature: | Date: |
| Melanie Redding, Author / Co-Project Manager, Co-Principal Investigator, EAP<br><br>Signature: | Date: |
| Pam Marti, Author / Co-Project Manager, EAP<br><br>Signature: | Date: |
| Keith Seiders, Author / Co-Principal Investigator, EAP<br><br>Signature: | Date: |
| George Onwumere, Eastern Operations Section Manager, EAP<br><br>Signature: | Date: |
| Jessica Archer, Section Manager for Project Study Area, EAP<br><br>Signature: | Date: |
| John Weakland (for Alan Rue), Director, Manchester Environmental Laboratory<br><br>Signature: | Date: |
| Arati Kaza, Ecology Quality Assurance Officer | |

Signatures are not available on the Internet version.
EAP: Environmental Assessment Program

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# 2.0 Abstract

This study is designed to determine the presence of dioxins/furans, nitrate, lead, and arsenic in drinking water from private domestic wells in the Lower Yakima Valley. This study will sample 15 groundwater wells over two or three seasons to determine seasonal variations. This will include three private domestic wells where dioxins/furans were detected in a privately conducted study.

Data collection methods will follow the requirements established in the Water Quality Data Act (RCW 90.48.570 through 90.48.590). The dioxins/furans results from this study will be validated by an independent third party and also reviewed internally.

# 3.0 Background

## 3.1 Introduction and problem statement

A private study reported elevated levels of dioxins/furans, nitrate, lead, and arsenic in three private domestic wells in the Lower Yakima Valley. In response to these reported findings, the Washington State Department of Ecology (Ecology) will investigate the presence of the detected chemicals in private domestic drinking water wells in the Lower Yakima Valley. This work includes sampling 15 wells over two to three seasons to account for seasonal variation.

## 3.2 Study area and surroundings

The Lower Yakima Valley is the subject of a Groundwater Management Area (GWMA), with the goal to reduce nitrate concentrations in groundwater in order to meet Washington State drinking water standards. This area has been the focus of numerous studies and has been physically characterized with descriptions of topography, geology, surficial hydrogeologic units, groundwater flow direction, land use, soil types, and climate. A compilation of this work is available on Ecology's website[1].

The Lower Yakima Valley is located south of Union Gap and west of the Yakima-Benton County line (Figure 1). The northern boundary generally lies on the southern slopes of the Ahtanum Ridge. Incorporated communities in the valley include Zillah, Sunnyside, Granger, Grandview, Mabton, Buena and Outlook. The lands of the Yakama Nation are located to the southeast of the valley and include the towns of Wapato, Harrah, and Toppenish.

[1] Ecology Lower Yakima Valley Groundwater Management Area

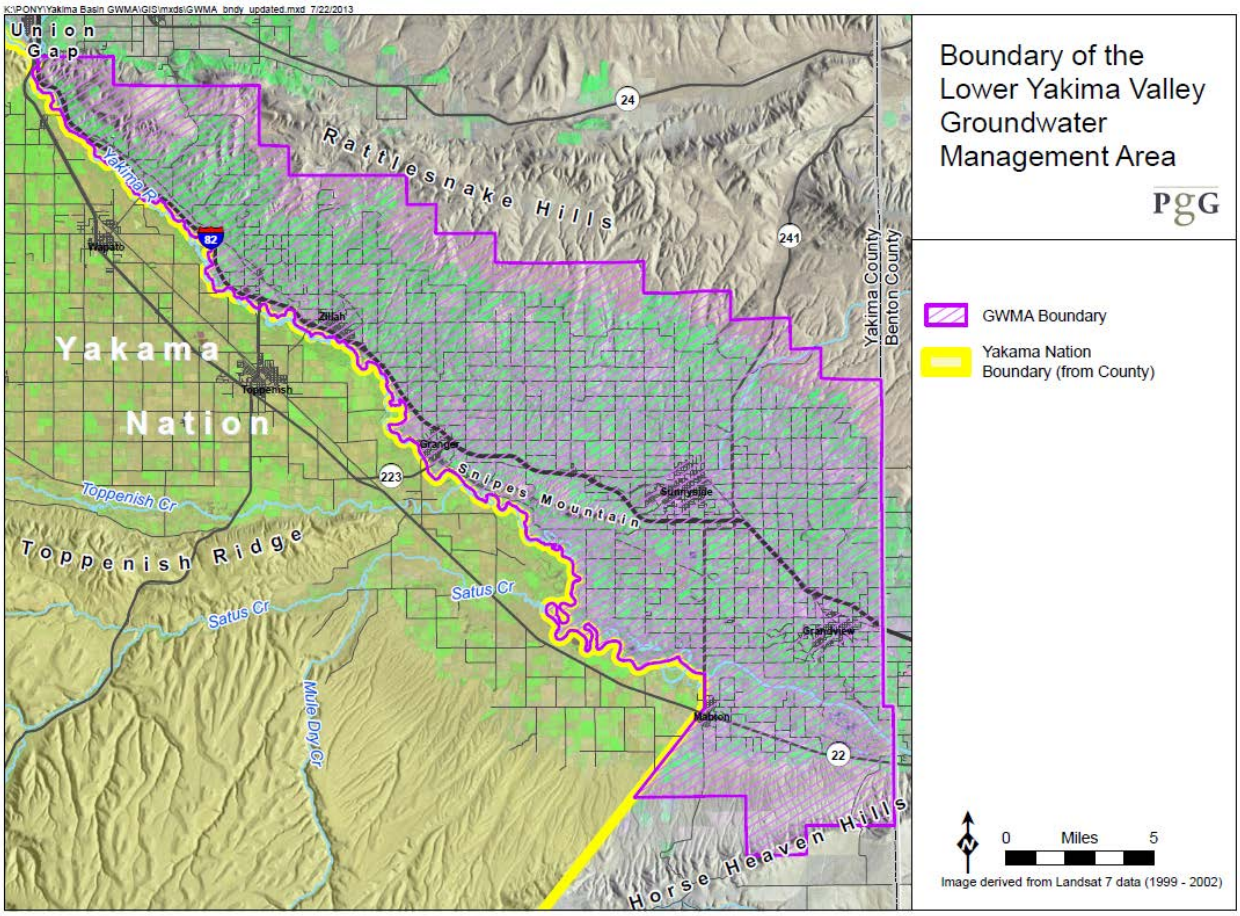


**Figure 1. Map of the Lower Yakima Valley Groundwater Management Area.**
*(Pacific Groundwater Group, 2014)*

### 3.2.1 History of study area

Groundwater in this area originates from precipitation infiltrating into the ground, as well as infiltration of other types of water including streams, irrigation, stock water, canals, agricultural fields and sprayfields. Infiltration of on-site sewage systems also recharges groundwater. Recharge water can transport chemicals as it infiltrates into the soils and migrates to groundwater.

Groundwater in the Lower Yakima Valley is contaminated with elevated concentrations of nitrate. The Lower Yakima Valley aquifer is the principal drinking water source for over 56,000 residents in the area. Recent groundwater monitoring indicated that 45% of 30 randomly placed monitoring wells and over 20% of 159 private drinking water wells sampled exceeded (did not meet) the safe drinking water standard for nitrate (Pacifica Groundwater Group, 2019; USGS, 2018). These results indicate that elevated nitrate levels in the area's groundwater is a pervasive problem and that residents in the Lower Yakima Valley are drinking water that may pose health risks.

Nitrate sources include commercial fertilizers, manure, compost, lagoons, on-site sewage systems, hobby farms, and abandoned wells, among others. Agriculture is the primary economic and land-use activity in the Lower Yakima Valley, and most of the cropland is irrigated. The

elevated nitrate concentrations detected in groundwater indicate impacts by these activities. These impacts can be significant to human health. Drinking water high in nitrates is a potential health risk for infants, pregnant women, and people with compromised immune systems. The Washington State Department of Health (DOH) has warned that drinking water high in nitrate concentrations can lead to a serious condition that reduces oxygen to red blood cells.

A groundwater management area (GWMA) was established to assess and manage the nitrate issues in the Lower Yakima Valley. This GWMA program addresses only nitrate and no other contaminants.

A recent privately conducted study detected dioxins/furans levels in area private domestic wells. Lead, arsenic, and nitrate were also detected in some wells. The private study was the catalyst for this investigation.

### 3.2.2 Summary of previous studies and existing data

A private study was conducted in the Yakima Basin in 2017 and 2018, sampling private domestic drinking water wells, municipal drinking water wells, surface water, commercially available bottled water, and sewage sludge that might be applied to upland areas. Results were reported for the 17 toxic dioxins/furans (aka PCDD/Fs), nitrate, lead, arsenic, and several pesticides. Dioxins and furans are described in Section 3.2.3 below.

Results from the private study for PCDD/Fs, expressed as TCDD-TEQs, are summarized in Figure 2. Figure 2 also shows various thresholds for the protection of human health from PCDD/Fs. While most thresholds are based on 2,3,7,8-TCDD, the use of the TCDD-TEQ value is widely accepted because it incorporates the cumulative toxicity of all 17 toxic congeners. The derivation of TCDD-TEQ is discussed in Section 3.2.3 of this document. The water quality standards which incorporate these thresholds are described in Section 3.2.4. The reported values which exceeded these thresholds are a concern and are the reason this study is being conducted.

Figure 2 was compiled from the data collected from the private study. These data indicate that two domestic wells exceeded (did not meet) the drinking water standard of 30 pg/L and that seven domestic wells had PCDD/F concentrations above the 0.6 pg/L groundwater criterion for Washington's Ground Water Quality Standards (Chapter 173-200-040 WAC). One of these wells (Source Code DW-7) exceeded the groundwater criterion in both the spring and fall sampling events of 2018. All of the bottled water tested had levels below (meeting) the drinking water standard for PCDD/Fs. None of the surface water samples met the federal Clean Water Act Human Health criterion for PCDD/Fs (0.013 pg/L). All samples reported for municipal water supply wells met the drinking water standard and Washington's groundwater quality standard.

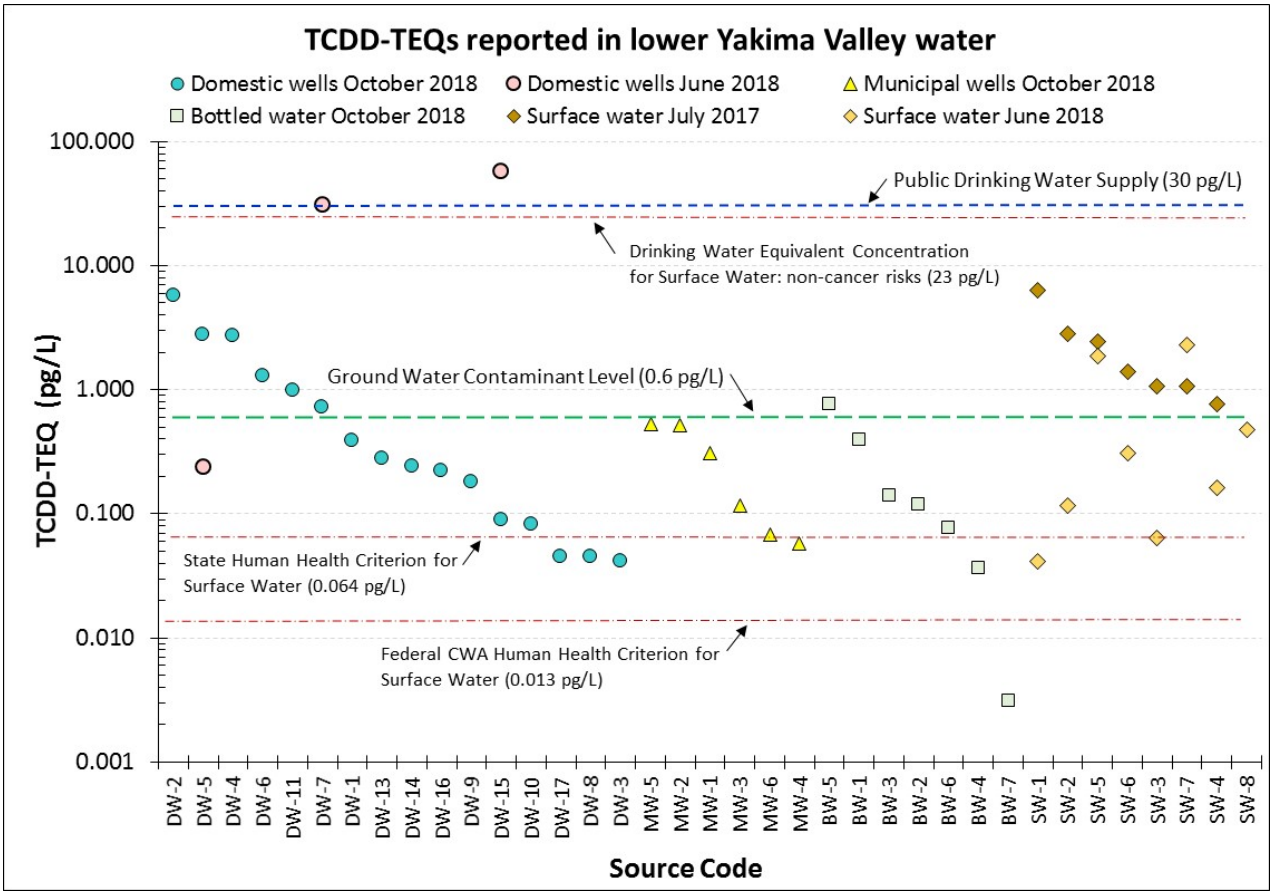


**Figure 2. TCDD-TEQs reported from the private study.**

Toxicity Equivalent Factor (TEF)
Tetrachlorodibenzodioxin (TCDD) also known as Dioxin
Toxic Equivalence (TEQ)

## 3.2.3 Parameters of interest and potential sources

The parameters monitored in this Ecology study were detected above standards in the private study. These include dioxins/furans, nitrate, lead, and arsenic.

### *Dioxins/furans*

Dioxins/furans is a term used for a group of chlorinated chemicals called polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). This group shares chemical characteristics and some have a similar mode of toxicity. Dioxins and furans, also abbreviated as PCDD/Fs, are byproducts of combustion processes (e.g. waste incineration, forest fires) and chemical processes, such as chlorine bleaching in paper production, and manufacturing of some chlorinated pesticides (ATSDR, 1998). They are highly persistent and widely distributed in the environment. There are 17 PCDD/F toxic congeners (individual molecules) and they have different levels of toxicity compared to 2,3,7,8-TCDD, the most toxic form.

Adverse health effects have been associated with the digestive, endocrine, immune, nervous, and reproductive systems. The single dioxin compound, or congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) is the most potent animal carcinogen EPA has evaluated and is a probable human carcinogen (ATSDR, 1998).

In order to assess the cumulative risks of the 17 toxic congeners to human and environmental health, PCDD/F concentrations are commonly expressed as a toxic equivalent (TEQ) to the most toxic congener which is 2,3,7,8-Tetrachlorobibenzodioxin (TCDD). This TEQ is often expressed as "TCDD-TEQ". The TCDD-TEQ is calculated by multiplying each congener result by its congener-specific Toxicity Equivalent Factor (TEF) and then summing these products to obtain TCDD-TEQ. Various TEFs have been developed over time as a result of research into the toxicity of individual congeners. The 2005 World Health Organization mammalian TEFs described by Van den Berg et al. (2006) are commonly used in summarizing PCDD/F results because they are based on more recent research and have broad international support.

***Nitrate, lead, arsenic, and other chemicals***

Other chemicals detected above drinking water standards will be monitored in this study: nitrate, total lead, and total arsenic.

Additional parameters will be measured to help characterize the groundwater and interpret results for PCDD/Fs and metals. These ancillary parameters are total organic carbon (TOC), dissolved organic carbon (DOC), alkalinity, and turbidity. Organic carbon may be a factor affecting the transport of PCDD/Fs and metals in water. Alkalinity, as one indicator of the amount of dissolved material in the water, may also be helpful when interpreting results. Turbidity may be measured at sites where water appears turbid which may affect the transport of PCDD/Fs and metals. Turbid groundwater may be present from poorly constructed wells or wells with very shallow groundwater levels.

### 3.2.4 Regulatory criteria or standards

Various contaminant concentration thresholds for the protection of human health and the environment exist. These thresholds are often based on various assumptions used in determining risk, such as daily consumption rates, toxicological data used in calculations, and risk levels. Thresholds relevant for drinking water from groundwater and surface water in the state are:

- Washington's drinking water standards for public systems (Chapter 246-290 WAC).
- Washington's groundwater quality standards (Chapter 173-200 WAC).
- Washington's surface water standards for protecting human health (provided for context).

***Washington State Drinking Water Standards***

Drinking water standards are established to protect public health and to ensure the quality of drinking water. EPA establishes regulatory limits in the Safe Drinking Water Act that apply to public water supply systems. These standards do not apply to private individual wells. EPA works with Washington State Department of Health to implement the standards in Chapter 246-290 WAC. The purpose of Washington's regulation is to define the basic regulatory requirements and to protect the health of consumers using public drinking water supplies.

***Washington State Groundwater Quality Standards***

The state Ground Water Quality Standards (GWQS) (Chapter 173-200 WAC) apply to all groundwaters of the state. Other parameters of interest for this study are nitrate, lead, and arsenic. Groundwater quality criteria for these parameters are 10 mg/L (nitrate-N), 0.05 mg/L (total lead), and 0.05 ug/L (total arsenic). The groundwater quality criterion for nitrate

corresponds with the federal maximum contaminant level for nitrate-N in drinking water (40 CFR Part 41). The criterion is based on one in a million cancer risk.

### *Washington's surface water quality standards*

These standards protect the health of people, fish, shellfish, and wildlife and were revised in October 2017 (Ecology, 2017). These standards are codified in Washington Administration Code (WAC) Chapter 173-201A.

The water quality standards "consist of water quality criteria, designated uses, and antidegradation components. The water quality standards represent the chemical, physical, and biological conditions necessary to support the state designated uses of a waterbody." (Ecology, 2018). Ecology's Water Quality Program Policy 1-11 describes the methodologies for using environmental data to assess the health of surface waters by determining whether water quality standards are met (Ecology, 2018). For toxic substances, Washington's water quality standards employ both numeric and narrative criteria for both marine water and freshwater.

Numeric criteria are based on data and scientific assessment of adverse effects from specific chemicals or conditions. A typical numeric criterion for protecting aquatic life usually contains a concentration and averaging period. For example, the aquatic life chronic criterion for cyanide is 5.2 ug/L as a 4-day average concentration. The numeric criteria found in WAC 173-201A-240 (Ecology, 2017) were developed to protect both aquatic life and human health from toxic chemicals.

Narrative criteria are statements that describe the desired water quality goal, such as waters being "free from" pollutants such as oil and other substances or conditions that can harm people or aquatic life. These criteria protect water bodies from pollutants for which numeric criteria are difficult to specify. Narrative criteria for toxic substances are rooted in WAC 173-201A-260(2)(a) which protects existing and designated uses for freshwater and marine water (Ecology, 2017):

> (2) Toxics and aesthetics criteria. The following narrative criteria apply to all existing and designated uses for fresh and marine water:
>
> > (a) Toxic, radioactive, or deleterious material concentrations must be below those which have the potential, either singularly or cumulatively, to adversely affect characteristic water uses, cause acute or chronic conditions to the most sensitive biota dependent upon those waters, or adversely affect public health (see WAC 173-201A-240, toxic substances, and 173-201A-250, radioactive substances).

The narrative criteria for toxic pollutants are also described in Ecology's WQP Policy 1-11, Section 1E, which states that "Ecology will consider the assessment of narrative criteria that demonstrates the impairment of a designated use":

> Assessment of Studies to Determine Impairment based on Narrative Standards
>
> > Parts 2 and 3 of this policy describe the methodology for assessing specific water and sediment quality parameters. Most of the parameter sections focus on evaluations based on numeric criteria. However, Ecology also evaluates the attainment of designated uses based on narrative criteria. For example, narrative criteria are applied for the bioassessment parameter (to protect aquatic life uses), and for human health toxics parameters (to protect fish and shellfish harvesting and domestic water supply uses). Ecology may use narrative criteria in conjunction with numeric criteria as described in the parameter sections.

The narrative criteria incorporate factors, such as a chemical-specific drinking water exposure concentration (DWEC) and environmental data requirements (e.g. sample size, frequency, and sample results), to help determine whether the designated use domestic water supply is supported in a waterbody.

**Table 1. Thresholds for protecting human health from 2,3,7,8-TCDD.**

| Threshold Concentration (pg/L) | Description | Source of Regulation |
|---|---|---|
| 30 | Public Drinking Water Supply | WAC 246-290-310 (7)(c)(i): by reference to 40 CFR 141.61c |
| 0.6 | Groundwater Criterion | Chapter 173-200-040 WAC, Table 1 (also Implementation Guidance for the Ground Water Quality Standards, Table 9.1 in Appendix A) |
| 23 | Drinking Water Equivalent Concentration for protection from non-cancer risks (DWECn): surface water narrative standard | Ecology Water Quality Program Policy 1-11 for implementing WAC 173-201A |
| 0.013 | Human Health Criterion for Fresh Water: surface water numeric standard | Ecology Water Quality Program Policy 1-11 for implementing WAC 173-201A: for Clean Water Act situations |
| 0.064 | Human Health Criterion for Fresh Water: surface water numeric standard | WAC 173-201A-040: for non-Clean Water Act situations |

**Table 2. Thresholds for protecting human health from Hexachlorodibenzo-p-dioxin mix.**

| Threshold Concentration (pg/L) | Description | Source of Regulation |
|---|---|---|
| 10 | Groundwater Criterion | Chapter 173-200-040 WAC, Table 1 (also Table 9.1 in Appendix A of Implementation Guidance for the Ground Water Quality Standards) |

The regulatory description for Hexachlorodibenzo-p-dioxin is ambiguous in that the CAS given in Table 2 of the WAC is for a single congener (1,2,3,7,8,9-HxCD; CAS 19408-74-3) while the name implies a "mix" of congeners. The intent of the language in the WAC is not yet clear: the mix of congeners could possibly be the sum of the three HxCDDs or the TCDD-TEQ. This project will analyze all 17 toxic PCDD/F congeners which will allow results to be compared to the various possible interpretations related to the criterion for 1,2,3,7,8,9-HxCD.

Two important points about the thresholds above as related to WAC 173-201A and Ecology's Water Quality Assessment and Clean Water Act (CWA) 303(d) listings:

- The criteria apply only to the single congener 2,3,7,8-TCDD. However, for Category 2 classification, the criteria for 2,3,7,8-TCDD is used for the toxic equivalent (TEQ) value which is generated from results for all 17 toxic congeners. Category 2 (Waters of Concern) is not part of the CWA 303(d) list so no regulatory action is taken.
- Results that are reported as non-detect (U or UJ) or tentatively identified (N or NJ) are not considered in the WQ Assessment process, either for the single congener 2,3,7,8,-TCDD or in the calculation of TEQs. Such results are essentially set to zero because of uncertainty that the analyte was present in the sample.

### *MTCA Cleanup Standards*

The Model Toxics Control Act (MTCA) has numerical thresholds for dioxins/furans which may need to be considered after results are received. We expect that results for PCDD/Fs will be well below the MTCA thresholds, which are described in Table 3. However, if PCDD/F levels approach MTCA thresholds, the report would likely recommend additional work to identify potential sources and address options to address sources of dioxin.

**Table 3. MTCA Cleanup Levels for dioxin/furans.**
(as 2,3,7,8-TCDD)

| Groundwater | | | | Surface Water | | | |
|---|---|---|---|---|---|---|---|
| Method B Non cancer (µg/L) | Method B Cancer (µg/L) | Method C Non cancer (µg/L) | Method C Cancer (µg/L) | Method B Non cancer (µg/L) | Method B Cancer (µg/L) | Method C Non cancer (µg/L) | Method C Cancer (µg/L) |
| 1.10E-05 | 6.70E-07 | 2.50E-05 | 6.70E-06 | 3.60E-07 | 1.00E-08 | 9.10E-07 | 2.50E-07 |

## 3.3 Water quality impairment studies

N/A

## 3.4 Effectiveness monitoring studies

N/A

# 4.0 Project Description

Groundwater in the Lower Yakima Valley contains elevated nitrate concentrations indicating that the water has been impacted by human activities. A private study recently detected dioxins/furans above the public drinking water standard in two private domestic wells and above the groundwater quality criterion in seven wells.

This project will focus on sampling private domestic wells that produce water representative of a resident's drinking water. Fifteen wells will be sampled, including some wells sampled previously in the private study where the groundwater quality criterion and the drinking water standard were exceeded for dioxins/furans. Selected wells will be screened to ensure they are properly constructed and will produce groundwater samples that are representative of the conditions in the aquifer.

Wells will be sampled over a minimum of two seasons (fall and spring) to address seasonal variation and associated differences in the groundwater elevation. A third round of sampling could be done if the results of the first two rounds warrant further sampling. Samples will be collected for dioxins/furans, the primary parameters of concern. We will also test for nitrate, total lead, and total arsenic.

Quality assurance measures are important to assure credible data. We will determine the quality of our sampling methods using travel blanks, transfer blanks, equipment blanks, and replicate samples. Additionally, the laboratory will conduct internal quality control (QC) measures using replicates, matrix spikes, blanks, and surrogates.

Data validation of the dioxins and furans data package is needed for this proposal in order to meet standard practices with these types of data. Since this is an urgent project in a sensitive area, we will use an external independent third-party validator, with internal review of the validation package.

Based on the contract and quality assurance timeframes, it is anticipated that the first round of sampling will occur the week of November 4, 2019. Ecology's team includes: Pam Marti, Keith Seiders, Arati Kaza, Alan Rue, Ginna Grepo-Grove, Brian Gallagher, Will Hobbs, and Melanie Redding (Table 4).

## 4.1 Project goals

The goal of this study is to investigate the presence of dioxins/furans, nitrate, total lead, and total arsenic in private domestic drinking water wells in the Lower Yakima Valley.

## 4.2 Project objectives

The following activities will be accomplished as part of this study:

- Collect water samples from 15 private domestic drinking water wells. Wells where dioxins/furans were reported to be present in the private study will be sampled along with additional wells in the area.
- Analyze water samples for dioxins/furans, nitrate, lead, arsenic, and ancillary parameters such as total organic carbon, dissolved organic carbon, alkalinity, pH, conductivity, dissolved oxygen, and oxidation-reduction potential (ORP). Turbidity may also be analyzed if turbid water is encountered.

- Sample wells once in the fall and once in the spring to account for seasonal variability. If needed for verification, a third round of dioxin/furan samples may be collected.
- Communicate results of the study to local residents.
- Write a report to describe the investigation and the results.

## 4.3 Information needed and sources

Groundwater quality data will be collected from private domestic drinking water wells to assess the presence of chemicals and determine if there are possible health risks. Before collecting a sample, each well will be assessed for integrity, field measurements will be taken, and the well will be adequately purged. Samples will be collected from the well when the stabilization criteria have been met (described in Section 8.2).

## 4.4 Tasks required

The main tasks for this study include:

- Develop a communication plan for community outreach.
- Develop a flyer (English and Spanish) that will be distributed to residents when seeking permission to sample their well.
- Wells for sampling will be selected based on criteria established in this document.
- Obtain permission from well owners to sample their wells.
- Measure field parameters in well water including temperature, dissolved oxygen, conductivity, pH, and ORP. These measurements will be taken as the well borehole is purged.
- Sample all wells for analysis of: PCDD/Fs, nitrate, lead, arsenic, TOC, DOC, alkalinity, and turbidity; sampling will be done a minimum of two times, once in the fall of 2019 and once in the spring of 2020.
- Evaluate results for quality using Ecology's Environmental Assessment Program (EAP) procedures.
- Compare analytical results to Washington State drinking water standards and groundwater quality standards.
- Notify homeowners and residents of results and provide context and other information to help the public understand the results.
- Enter project data into Ecology's Environmental Information Management database (EIM).
- Prepare a final study report at the completion of sampling.

## 4.5 Systematic planning process

This Quality Assurance Project Plan serves as the planning document for the project.

# 5.0 Organization and Schedule

## 5.1 Key individuals and their responsibilities

**Table 4. Organization of project staff and responsibilities.**

| Staff [1] | Title | Responsibilities |
|---|---|---|
| **Sage Park**<br>Regional Director<br>Central Regional Office<br>Phone: 509-457-7120 | EAP Client | Clarifies scope of the project. Provides internal review of the QAPP and draft report. Leads the public outreach effort. Secures funding for the project. |
| **Melanie Redding**<br>Hydrogeologist<br>Eastern Operations Section/HQ<br>Phone: 360-407-6524 | Primary Project Manager, Co-Principal Investigator, Licensed Hydrogeologist | Coordinates all aspects of the study internally and with external partners. Co-authors QAPP. Oversees site reconnaissance, field sampling and transportation of samples to the laboratories. Conducts QA review of data, analyzes and interprets data. Co-authors the draft report and final report. |
| **Pam Marti**<br>Hydrogeologist<br>Groundwater/Forests & Fish Unit, SCS<br>Phone: 360-407-6768 | Co-Project Manager, Licensed Hydrogeologist | Co-authors QAPP, Conducts QA review of data, analyzes and interprets data. Co-authors the draft report and final report. |
| **Keith Seiders**<br>Toxics Studies Unit<br>SCS<br>Phone: 360-407-6689 | Co-Principal Investigator | Co-authors QAPP, primary lead for dioxins/furans, works with MEL to arrange, contract lab and independent data validator for dioxins/furans analyses. Conducts QA review of data, analyzes and interprets data. Co-authors draft and final report. |
| **Brian Gallagher**<br>Eastern Operations Section<br>Phone: 509-329-3437 | Field Assistant | Develops maps, consolidates existing information. Helps with site reconnaissance, sample collection and records field information. Enters data into EIM. |
| **George Onwumere**<br>Eastern Operations Section<br>Phone: 509-454-4244 | Section Manager for the Project Manager | Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP. Reviews the draft report and approves the final report |
| **Jess Archer**<br>SCS<br>Phone: 360-407-6698 | Section Manager for the Study Area | Reviews the project scope, reviews the draft QAPP, and reviews the draft report. |
| **Alan Rue**<br>Manchester Environmental Laboratory<br>Phone: 360-871-8801 | Manchester Lab Director | Assists with securing contract lab services and data validation. Reviews and approves the final QAPP. |
| **Contract Laboratories** | Project Manager | Provides analytical services as requested. Coordinates with MEL Lab Director on scope of work for analyses and reporting of results, sample container supplies, and sample shipping. |
| **Arati Kaza**<br>Phone: 360-407-6964 | Ecology Quality Assurance Officer | Reviews the draft QAPP and approves the final QAPP. Approval to begin sampling. Reviews the draft report. |

[1]All staff are from EAP.
EAP: Environmental Assessment Program
EIM: Environmental Information Management database
QAPP: Quality Assurance Project Plan
SCS: Statewide Coordination Section

## 5.2 Special training and certifications

A hydrogeologist license is required for the person overseeing hydrogeologic studies (Chapter 18.220.020 RCW).

All field staff should have a detailed working knowledge of the QAPP and any applicable SOPs to ensure credible and useable data are collected. This includes being familiar with the sampling equipment and instruments being used. See Section 8.0.

## 5.3 Organization chart

We will work cooperatively with the Yakima Health District on all health related issues. Yakima Health District will be involved with outreach to the community and residents whose wells will be sampled. They will also provide translation and interpreter services.

We will also coordinate with the Washington State Department of Health and the Yakama Nation.

## 5.4 Proposed project schedule

Field work will be conducted in fall 2019 and spring 2020. A third round of dioxin sampling is reserved for fall 2020 if necessary.

**Table 5. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.**

| **Field and laboratory work** | **Due date** | **Lead staff** |
|---|---|---|
| Field work completed | November 2019 | Melanie Redding, Brian Gallagher |
| Field work completed | April 2020 (and possibly October 2020) | Melanie Redding, Brian Gallagher |
| Laboratory analyses completed | 6 weeks after sample collection | |
| Data Validation completed | 3 months after lab analyses completed | |
| **Environmental Information System (EIM) database** | | |
| EIM Study ID | ID number: MRED0003 | |
| Product | Due date | Lead staff |
| EIM data loaded [1] | 3 months after all data is received | Brian Gallagher |
| EIM data entry review [2] | 2 months after data is entered | Siana Wong |
| EIM complete [3] | 1 month after EIM data entry review is complete | Brian Gallagher |
| **Final report** | | |
| Author lead / Support staff | Melanie Redding, Pam Marti, Keith Seiders, | |
| Schedule | | |
| Draft due to supervisor | 3 months after all data validation is received | |
| Draft due to client/peer reviewer | 3 weeks after comments from supervisory review received | |
| Draft due to external reviewer(s) | 3 weeks after comments from client/peer review received | |
| Final (all reviews done) due to publications coordinator | 4 weeks after external review comments received. | |
| Final report due on web | 4 weeks after final submitted to publications | |

## 5.5 Budget and funding

This project requires $80,000 to complete work requested by the Regional Director at Ecology's Central Regional Office. The budget for analytical work is contained in Table 6. The budget for staff work, $45,076, is estimated at 0.47 FTE (and 0.57 FTE if a 3rd round of sampling is required).

The proposal includes sampling three rounds with the first two rounds including all parameters, but the 3rd round sampled PCDD/Fs only if necessary.

Dioxin/furan data will be validated by an independent third party. MEL staff will provide an in-house review of the finished product from the validators. The prices in Table 6 include analytical costs, MEL's contracting fees, and data validation costs.

**Table 6. Project budget and funding.**

| Parameter | Number of Samples | Number of QA samples | Cost per sample | Analytical Costs | Data Validation fees | Contracting fees | Total |
|---|---|---|---|---|---|---|---|
| Arsenic and Lead | 30 | 8 | $45 | $1,710 | | $513 | $2,223 |
| Nitrate | 30 | 8 | $30 | $1,140 | | $342 | $1,482 |
| TOC | 45 | 4 | $35 | $1,715 | N/A | N/A | $1,715 |
| DOC | 45 | 4 | $45 | $2,205 | N/A | N/A | $2,205 |
| Alkalinity | 45 | 4 | $20 | $980 | N/A | N/A | $980 |
| Turbidity | 15 | 2 | $15 | $255 | N/A | N/A | $255 |
| Dioxin/Furans | 45 | 15 | $329 | $19,740 | $4,095 | $1,229 | $25,064 |
| | | | | | | Lab Total | $33,924 |
| | | | | | | | |
| | | | | | | Equipment | $1,000 |
| | | | | | | **Project Total** | **$34,924** |

# 6.0 Quality Objectives

## 6.1 Data quality objectives[2]

The data quality objective for this project is to obtain data of sufficient quantity and quality for use in comparison to thresholds for the protection of human health. This objective will be achieved through attention to sample design, sample collection and processing, laboratory measurement of target analytes, collection and review of historical data, data management, and quality control (QC) procedures described or referenced in this plan.

## 6.2 Measurement quality objectives

Measurement quality objectives (MQOs) for all parameters are shown in Table 7. The MQOs for calibration verification, ongoing precision and recovery, and labeled compound recovery correspond to the QC acceptance limits of the analytical methods.

Most of these MQOs correspond to the acceptance limits specified in the analytical method. The lowest concentrations of interest shown in the tables should be attainable and are expected to be met by contract labs. Results not meeting these MQOs will be evaluated for possible corrective action or use with qualification.

For most analytes, the designated method's achievable limit of quantitation (LOQ) will be adequate for this project. For PCDD/Fs, contract labs will be required to report down to the estimated detection limit (EDL) for all congeners and also qualify results between the EDL and LOQ as estimates (Table 9). These reporting practices improve the ability to compare results to thresholds for the protection of human health.

### 6.2.1 Targets for precision, bias, and sensitivity

The MQOs for laboratory analyses are expressed in terms of acceptable precision, bias, and sensitivity. These MQOs are summarized in Table 7 for each analytical method. These MQOs are then briefly discussed. Laboratory case narratives will discuss the outcomes of QC practices and address these MQOs for each batch of sample analyses.

The MQOs for field parameters are listed in Table 8.

[2] DQO can also refer to ***Decision*** Quality Objectives. The need to identify Decision Quality Objectives during the planning phase of a project is less common. For projects that lead to important decisions, data quality objectives (DQOs) are often expressed as tolerable limits on the probability or chance (risk) of the collected data leading to an erroneous decision. And for projects that intend to estimate present or future conditions, DQOs are often expressed in terms of acceptable uncertainty (e.g., width of an uncertainty band or interval) associated with a point estimate at a desired level of statistical confidence.

**Table 7. Measurement quality objectives.**

| MQO → | Precision | | Bias | | | Sensitivity |
|---|---|---|---|---|---|---|
| Parameter | Duplicate Samples | Matrix Spike-Duplicates | Verification Standards (LCS,CRM, CCV) | Matrix Spikes | Surrogate Standards* | MDL or Lowest Concentration of Interest |
| | Relative Percent Difference (% RPD) | | Recovery Limits (%) | | | Concentration Units |
| Water level | +/-0.03' | N/A | N/A | N/A | N/A | 0.01 ft |
| Temperature | 10% | N/A | N/A | N/A | N/A | 0.1°C |
| pH | 10% | N/A | See Table 8 | N/A | N/A | 0.1 standard units |
| Specific conductivity | 10% | N/A | See Table 8 | N/A | N/A | 10 uS/cm |
| Dissolved oxygen (DO) | 10% | N/A | See Table 8 | N/A | N/A | 0.1 mg/L |
| Oxidation reduction potential (ORP) | 10% | N/A | See Table 8 | N/A | N/A | 0.1 millivolts |
| PCDD/Fs (high resolution) | ≤ 40% | N/A | a | N/A | a | LOQ 0.017-0.5 pg/L [b] |
| Nitrate-N | ≤ 20% | ≤ 20% | +/-20% | +/-25% | N/A | 0.10 mg/L (RL) |
| Lead | ≤ 20% | ≤ 20% | +/-20% | +/-25% | N/A | 0.1 ug/L (RL) |
| Arsenic | ≤ 20% | ≤ 20% | +/- 20% | +/-25% | N/A | 0.5 ug/L (RL) |
| Total organic carbon (TOC) | ≤ 20% | NA | +/- 20% | +/-25% | NA | 0.1 mg/L (RL) |
| Dissolved organic carbon (DOC) | ≤ 20% | NA | +/- 20% | +/-25% | NA | 0.1 mg/L (RL) |
| Alkalinity | ≤ 20% | NA | +/- 20% | NA | NA | 1 mg/L RL) |
| Turbidity | ≤ 20% | NA | +/- 20% | NA | NA | 1 NTU (RL) |

*Surrogate recoveries are compound-specific.
a - Per method for Ongoing Precision and Recovery (OPR), Internal Standards, and Labelled Compounds.
b - See Table 13 for analyte-specific reporting limits (RLs) for dioxins/furans.
NA - Not applicable.

**Table 8. Measurement quality objectives for field parameters expressed as acceptance criteria for field instrument pre-calibration and post-calibration. (Anderson, 2016)**

| Parameter | Units | Accept | Qualify | Reject |
|---|---|---|---|---|
| pH | standard units (su) | < or = ± 0.3 | > ± 0.3 and < or = ± 1.0 | > ± 1.0 |
| Conductivity | uS/cm | < or = ± 10% | > ± 10% and < or = ± 20% | > ± 20% |
| Temperature | ˚C | < or = ± 0.2 | > ± 0.2 and < or = ± 1.0 | > ± 1.0 |
| Dissolved Oxygen | mg/L | < or = ± 0.3 | > ± 0.3 and < or = ± 1.0 | > ± 1.0 |
| ORP | mV | < or = ± 5% | > ± 5% and < or = ± 10% | > ± 10% |

ORP=Oxygen Reduction Potential

**Table 9. Quantitation and detection limits, and TEFs, for PCDD/F congeners.**

| Dioxin/Furan Congener | CAS Number | TEFs: WHO 2005 | EDL (pg/L) | LOQs (pg/L) |
|---|---|---|---|---|
| 2,3,7,8-TCDD | 1746-01-6 | 1 | 10 | 20 |
| 1,2,3,7,8-PeCDD | 40321-76-4 | 1 | 15 | 25 |
| 1,2,3,4,7,8-HxCDD | 39227-28-6 | 0.1 | 15 | 25 |
| 1,2,3,6,7,8-HxCDD | 57653-85-7 | 0.1 | 15 | 25 |
| 1,2,3,7,8,9-HxCDD | 19408-74-3 | 0.1 | 15 | 25 |
| 1,2,3,4,6,7,8-HpCDD | 35822-46-9 | 0.01 | 15 | 25 |
| OCDD | 3268-87-9 | 0.0003 | 20 | 40 |
| 2,3,7,8-TCDF | 51207-31-9 | 0.1 | 10 | 20 |
| 1,2,3,7,8-PeCDF | 57117-41-6 | 0.03 | 15 | 25 |
| 2,3,4,7,8-PeCDF | 57117-31-4 | 0.3 | 15 | 25 |
| 1,2,3,4,7,8-HxCDF | 70648-26-9 | 0.1 | 15 | 25 |
| 1,2,3,6,7,8-HxCDF | 57117-44-9 | 0.1 | 15 | 25 |
| 1,2,3,7,8,9-HxCDF | 72918-21-9 | 0.1 | 15 | 25 |
| 2,3,4,6,7,8-HxCDF | 60851-34-5 | 0.1 | 15 | 25 |
| 1,2,3,4,6,7,8-HpCDF | 67562-39-4 | 0.01 | 15 | 25 |
| 1,2,3,4,7,8,9-HpCDF | 55673-89-7 | 0.01 | 15 | 25 |
| OCDF | 39001-02-0 | 0.0003 | 20 | 40 |

**CDDs/CDFs:**
TCDD=Tetrachlorinated dibenzo-p-dioxin
TCDF =Tetrachlorinated dibenzofurans
PeCDD=Pentachlorinated dibenzo-p-dioxin
PeCDF=Pentachlorinated dibenzofurans
HxCDD=Hexachlorinated dibenzo-p-dioxin
HxCDF=Hexachlorinated dibenzofurans
HpCDD=Heptachlorinated dibenzo-p-dioxin
HpCDF=Heptachlorinated dibenzofurans
OCDD=Octachlorinated dibenzo-p-dioxin
OCDF=Octachlorinated dibenzofurans

#### *6.2.1.1 Precision*

Precision is a measure of variability between results of replicate measurements that are due to random error. Laboratory precision will be estimated by the labs most often using results from duplicate analyses and expressed as Relative Percent Difference (RPD). Table 7 includes acceptance limits which are typically set by the lab.

Sampling precision will be estimated using results from true field replicates and expressed as the Relative Standard Deviation (RSD). This project has no acceptance limits for estimates of sampling precision. The information helps to characterize the variability of the sampled population and inform evaluation and analyses of results.

#### *6.2.1.2 Bias*

Bias is the difference between the sample result and the true value. Bias will be evaluated and compared to method-specific limits by using various control standards and surrogate compounds that are analyzed along with study samples. Laboratory control samples contain known amounts of analyte and indicate bias due to sample preparation and/or calibration. Matrix spikes are used to indicate bias due to matrix effects. Matrix spike duplicates provide an estimate of the precision of this bias.

Where isotopic dilution methods are used (e.g. PCDD/F congeners), each sample is spiked with labeled congeners. The concentration of target compounds is corrected for recovery of labeled congeners or other techniques allowed by the analytical method. Table 7 shows targets for acceptable bias.

#### *6.2.1.3 Sensitivity*

Sensitivity is a measure of the capability of a method to detect a substance. It is commonly described as a detection limit. In a regulatory setting, the method detection limit (MDL)[3] is often used to describe sensitivity. Targets for acceptable sensitivity for lab measurements are given in Table 7.

### 6.2.2 Targets for comparability, representativeness, and completeness

#### *6.2.2.1 Comparability*

The comparability of study results to findings from historical work and thresholds for the protection of human health will be maximized as best as possible through sample design, sample collection, laboratory analyses, and data evaluation.

The collection and processing of drinking water samples will follow EAP standard operating procedures (SOPs):

- EAP096 for sampling water supply wells for general chemistry (Marti, 2019)
- EAP077 for purging and sampling water supply wells (Marti, 2016)
- EAP098 for sampling water supply wells for metals analysis (Pitz, 2019)

[3] The lowest quantity of a physical or chemical parameter that is detectable (above background noise) by each field instrument or laboratory method.

Sample preparation and laboratory analyses for each suite of analytes will follow the methods described in Section 9.1. Laboratory-specific SOPs for the preparation and analysis of samples, data reduction, and data review for each analysis are expected to be followed. These are not listed here but should be available at each laboratory conducting the analyses.

Where analytical methods or laboratories conducting the analyses differ among data sets from different times, the comparability of the methods and results will need to be evaluated. Specifically, the EPA 8290 method was used in the previous private study while EPA 1613B is being used for this study. The EPA 1613B method is also the only method approved for PCDD/Fs in drinking water.

Differences in data reduction practices among studies over time may affect the comparability of results. For example, different treatment of non-detect values in determining the TCDD-TEQ can lead to different values. Some studies may exclude non-detects whereas others may include them and use the value of the detection limit in calculations. Where data reduction practices for historical results are not documented or comparability is otherwise uncertain, sums or TEQs may be recalculated using original laboratory data, following guidance developed by Ecology's Toxics Studies Unit (TTCT, 2008).

#### *6.2.2.2 Representativeness*

The water samples collected for this project are considered to be representative of existing exposures to humans at the time they were collected. Groundwater samples will be collected in the fall and spring to account for seasonal variability. Groundwater samples will be collected using industry standard sampling methods, which will help ensure that representative samples are collected.

#### *6.2.2.3 Completeness*

The goal of completeness for laboratory analytical data and for field measurements is 90%. The loss of any analytical or field data may decrease the ability of this project to achieve its objectives. If needed, additional efforts will be taken to achieve 90% completeness of field and laboratory data. For example, additional sampling or analyses, or iterative reviews and corrections of laboratory data, may be requested until a data set is complete and accurate.

## 6.3 Acceptance criteria for quality of existing data

This project was prompted by results reported from a private study. While the quality of the private study results was not formally evaluated, the potential risks from PCDD/Fs in drinking water were deemed adequate to pursue further investigation. Ecology chose to conduct this study to assess the potential human health risks.

The documentation of the private study may be more closely reviewed to determine the quality of its results if any comparisons to results from this study will be conducted.

## 6.4 Model quality objectives

N/A

# 7.0 Study Design

## 7.1 Study boundaries

This study is being conducted in the Lower Yakima Valley (Figure 3).


**Figure 3. Map showing project study area.**

## 7.2 Field data collection

### 7.2.1 Sampling locations and frequency

The goal is to collect groundwater samples from 15 private domestic drinking water wells, and attempt to include the wells where TCDD-TEQ was reported to be above the groundwater quality criterion of 0.6 pg/L in the private study. Well locations and construction details will be included in the study report. The wells will be sampled for all parameters once in the fall and once in the spring to account for seasonal variability. If needed for verification, a third round of dioxin/furan samples may be collected.

The well locations in this study (shown in Figure 4) were selected using the following criteria:

- The well must be completed exclusively in the uppermost surficial aquifer.
- The property owner must give permission to participate in the study.
- Well construction must meet well construction standards specified in Chapter 173-160 WAC.
- The well log should be available and the completed well depth known.
- The well must be accessible to sample using a faucet.
- The water must be untreated prior to discharging from the faucet/sample point.

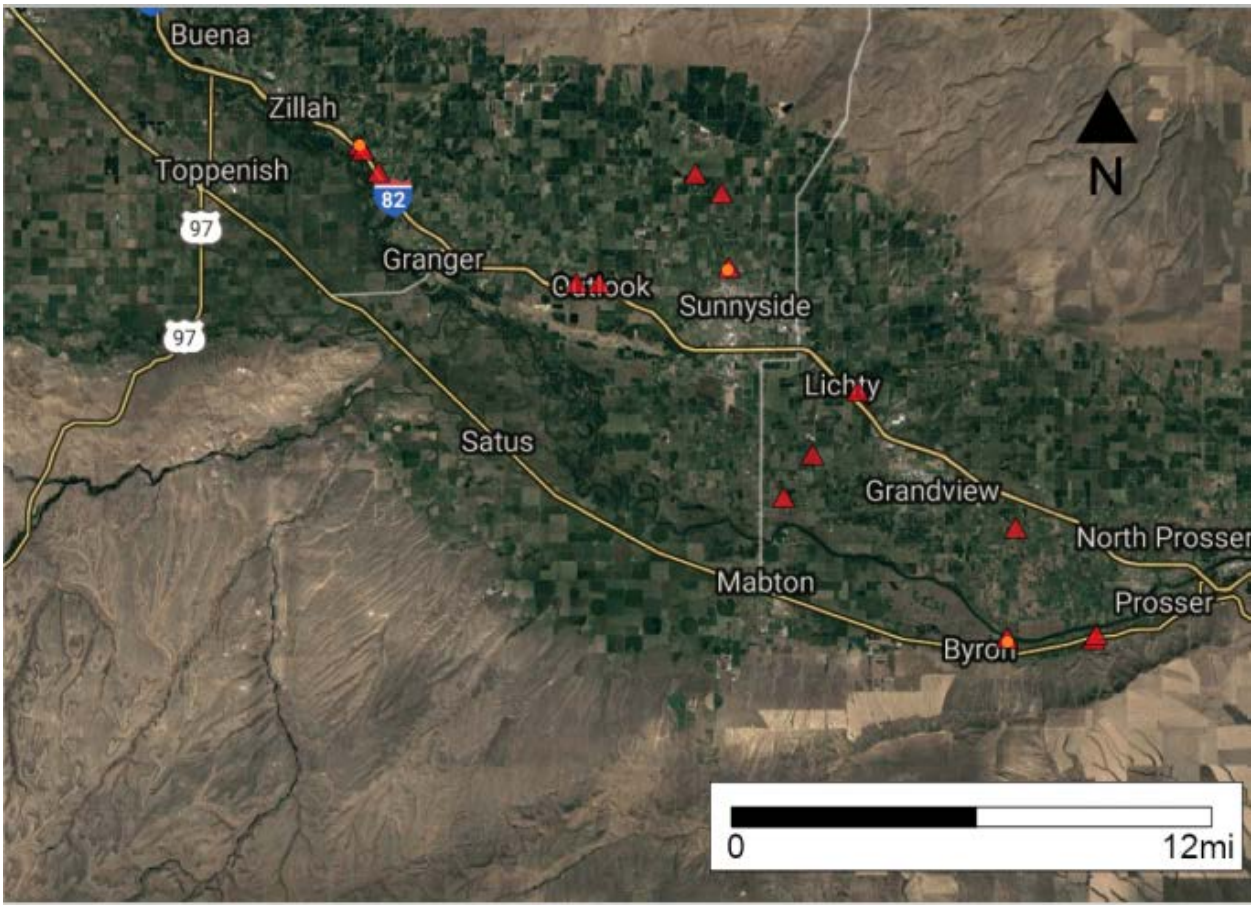


**Figure 4. Location of private domestic wells that will be sampled.**

### 7.2.2 Field parameters and laboratory analytes to be measured

The parameters to be measured and sampled include:

- Temperature (Field)
- pH (Field)
- Specific Conductivity (Field)
- Dissolved Oxygen (DO) (Field)
- Oxidation/Reduction Potential (ORP) (Field)
- Total Arsenic and Lead (Laboratory)
- Nitrate-N (Laboratory)
- TOC and DOC (Laboratory)
- Dioxin/Furans (Laboratory)
- Alkalinity (Laboratory)
- Turbidity (Laboratory)

## 7.3 Modeling and analysis design

N/A

### 7.3.1 Analytical framework

N/A

### 7.3.2 Model setup and data needs

N/A

## 7.4 Assumptions underlying design

The study design is based on the following assumptions:

- Sampling of private domestic wells will provide information representative of drinking water obtained from the same aquifer commonly used by the community.
- Sampling at the same time of year as the previous study, fall and spring, will minimize the influence of seasonal variation when comparing results. This assumes that seasonal climate factors (e.g., precipitation, temperature) that affect sample results are consistent each year.

## 7.5 Possible challenges and contingencies

The primary challenge of this study relates to accessing private property to sample domestic water supply wells over the course of this project.

Any circumstance that interferes with data collection and quality will be noted and discussed in the study report.

### 7.5.1 Logistical problems

Miscommunication with property owners is the main potential logistical problem. We will make sure that property owners have given verbal or written permission to sample their wells and that they have agreed to the date and time that we will be there to sample. If our schedule changes during the sampling event, we will notify the affected property owners.

### 7.5.2 Practical constraints

Sampling 15 wells within a one-week period will require efficient and logistical planning. We plan to have one team of at least two people working for approximately one week.

There are short holding times for many of the parameters that will be analyzed. Samples will be shipped overnight. This requires planning and advance arrangement with the analytical laboratory and shipping vendors (e.g., FedEx).

### 7.5.3 Schedule limitations

Changes in project prioritization and workload for EAP staff could affect the project schedule. Factors that can cause delays to the proposed project schedule include:

- Time required for QAPP review and approval.
- Unforeseen field or laboratory complications (e.g., inability to collect samples from selected wells, problems with laboratory analytical equipment).

# 8.0 Field Procedures

## 8.1 Invasive species evaluation

N/A

## 8.2 Measurement and sampling procedures

Groundwater sampling procedures for the study will follow Ecology SOPs:

- EAP033 for measurements using a Hydrolab (Anderson, 2016)
- EAP077 for purging and sampling water supply wells (Marti, 2016)
- EAP096 for sampling water supply wells for general chemistry (Marti, 2019)
- EAP098 for sampling water supply wells for metals analysis (Pitz, 2019)

Water samples should be collected as close to the wellhead as possible. It is preferable that the faucet used to collect samples is located before the water passes through any storage tanks, pressure tanks, or physical/chemical treatment system that may alter the quality of the groundwater sample.

Water supply wells will be purged using a Y-fitting on a faucet as close to the well head as possible (Figure 5). One discharge from the Y-fitting will be connected to a garden hose and set at a high discharge rate. The other outlet from the Y-fitting will be connected to an airtight flow-cell set at a low flow rate (~ 300 ml/minute).

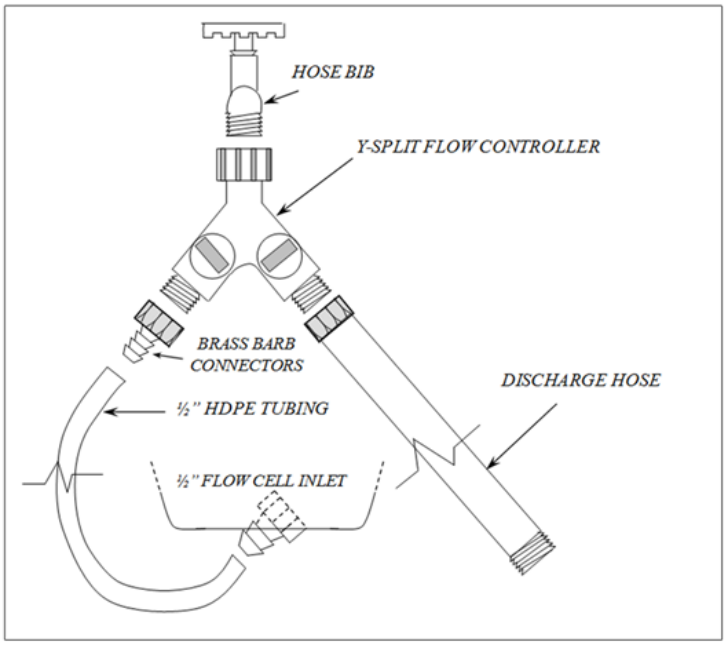


**Figure 5. Y-fitting for purging and sampling water supply wells.**

*Purge water from the well and storage tank discharge from the right side of the Y. The sample tubing is attached to the left side of the Y.*

Field measurements will be made at all sampling sites and recorded on waterproof field datasheets. Measurements for temperature, pH, specific conductivity, oxidation/reduction potential (ORP), and dissolved oxygen (DO) will be collected using a calibrated Hydrolab MiniSonde® following Ecology's SOP EAP033 (Anderson, 2016) and manufacturer's recommendations. Field measurement methods are listed in Table 10.

**Table 10. Field measurement methods**

| Analyte | Sample Matrix | Expected Range of Results | Detection or Reporting Limit | Instrumental Method |
|---|---|---|---|---|
| Temperature | Water | 8-12°C | 0.2°C | Hydrolab MS-5 |
| pH | Water | 4-8 S.U. | NA | Hydrolab MS-5 |
| Specific conductivity | Water | 50-1000 uS/cm | 5 uS/cm | Hydrolab MS-5 |
| Dissolved oxygen | Water | 0.0-10 mg/L | 0.1 mg/L | Hydrolab MS-5 |
| Oxidation/reduction potential | Water | -300 to 350 mv | NA | Hydrolab MS-5 |

Purging will continue until the field parameters (temperature, pH, specific conductance, dissolved oxygen and oxidation/reduction potential) are stable, as specified in Table 11.

**Table 11. Stability criteria for sampling groundwater**

| Field Parameter | Criteria | Typical Change |
|---|---|---|
| Temperature | 0.2ºC | 2% |
| pH | 0.2 SU | 3% |
| Electrical conductivity | 10 µmhos/cm | 7% |
| Dissolved oxygen | 0.3 mg/l | 10% |
| Oxidation-reduction potential | 20 mV | 20% |

Once field parameters have stabilized, the flow cell will be disconnected from the Y-fitting. Samples for dioxins/furans, nitrate, total arsenic and lead, TOC, turbidity, and alkalinity will be collected directly from the faucet. DOC samples will be field filtered using a disposable syringe (0.45 µm) filter.

Field personnel will wear clean nitrile gloves while handling the samples throughout the sample collection process. Field personnel will follow EPA's "clean hands/dirty hands" protocol for all sampling, where one person (clean hands) is responsible for handling the sample bottles while the other (dirty hands) is responsible for setting up and handling the sampling apparatus (e.g., USEPA, 1996). Care will be taken not to contaminate the samples with extraneous material.

Field quality control (QC) samples for PCDD/Fs will include field replicates, equipment blanks, travel blanks, and transfer blanks. Detailed plans regarding where QC samples will be collected, will be made after site reconnaissance has been conducted. Blank water for the PCDD/F samples will be provided by the contract lab and will be ultra-pure grade suitable for high-resolution analysis.

Once collected, samples will be properly labeled and stored in ice-filled coolers. All samples will be shipped directly from the field to the laboratories in order to meet short holding times. Chain-

of-custody procedures will be followed according to Manchester Environmental Laboratory protocol (MEL, 2016).

## 8.3 Containers, preservation methods, holding times

Table 12 shows the parameters, sample containers, preservation, and holding times required to meet project goals and objectives. Containers should be suitable for the specific analyses to be performed on the sample. Containers should also be free of contaminants according to EPA (1992) and meet quality assurance certification from the supplier.

**Table 12. Sample containers, preservation, and holding times.**

| Parameter | Matrix | Minimum Quantity Required | Container | Preservative | Holding Time |
|---|---|---|---|---|---|
| PCDD/Fs | Water | 2 liters | Two (2) pre-cleaned 1-liter amber narrow mouth glass jar w/Teflon cap | Cool to ≤6°C. | 7 days to extraction, then 40 days to analysis* |
| Nitrate-N | Drinking Water | 125 mL | 125mL Nalgene HDPE WM, CLR, | Cool to ≤6°C | 48 hours |
| Total As and Pb | Drinking Water | 350 mL | 500mL HDPE bottle w/5mL 1:1 nitric acid | Pre-acidified with $HNO_3$ Cool to ≤6°C | 6 months |
| TOC | Water | 125 mL | 125mL Nalgene HDPE WM, CLR, w/w/ 1:1 hydrochloric acid | 1:1 HCl to pH<2; Cool to ≤6°C | 28 days |
| DOC | Filtered Water | 125 mL | 125mL Nalgene HDPE WM, CLR, w/w/ 1:1 hydrochloric acid | 1:1 HCl to pH<2; Cool to ≤6°C | 28 days |
| Alkalinity | Water | 500 mL | 500mL Nalgene HDPE WM, CLR | Cool to ≤6°C; No Headspace | 14 days |
| Turbidity | Water | 500 mL | 500mL Nalgene HDPE WM, CLR | Cool to ≤6°C | 48 hours |

* We will try to meet the CWA holding time for water and wastewater (40 CFR 136) which is for samples that may have two or more chemical categories present. We wish to apply the most conservative holding times for this project. The SDWA (40 CFR 141) holding time for properly preserved dioxin samples is one year.

WM=Wide Mouth; NM=Narrow Mouth; CLR=Clear

## 8.4 Equipment decontamination

The need for decontamination when sampling PCDD/Fs will be evaluated for each site. Generally, decontamination will not be needed if sampling direct from a faucet. If tubing or other equipment is used to direct water from the faucet to the sample bottle, such equipment will be decontaminated by washing with soap/water, then rinsing with deionized (DI)water followed by solvent rinses of acetone and methanol (Friese, 2014). Sections of decontaminated tubing will be prepared in advance for use in the field, if necessary. If tubing is needed to collect a sample, an equipment blank will also be collected.

A new pre-packaged syringe filter will be used for collecting each DOC sample. The syringe will be triple rinsed and then 5 to 10 mls of sample water will be pushed through the filter before collecting a sample.

## 8.5 Sample ID

Well IDs will use a combination of the well location and sample number. Also the unique well tag number will be noted.

MEL will provide the field lead with work order numbers for all scheduled sampling dates. The work order number will be combined with a field ID number that is given by the field lead. This combination of work order number and field ID number constitute the sample ID. All sample IDs will be recorded in field logs and in an electronic spreadsheet for tracking purposes.

## 8.6 Chain of custody

Chain-of-custody procedures will be followed according to MEL protocol (MEL, 2016). Once collected, samples will be properly labeled and stored in ice-filled coolers inside the sampling vehicle. If the sample vehicle is left unattended, it will be locked to maintain chain-of-custody.

For samples shipped from the field, a separate Laboratory Analysis Required (LAR) sheet will serve as the *Chain of Custody* form. Shipment information from the shipping vendor will also be recorded in field logs. The analytical laboratory will receive the samples from the shipper and contact the project officer when they receive the samples.

Other samples will be driven to Ecology's Operations Center (OC), where the chain-of-custody portion of the LAR sheet will be filled out and the coolers will be placed in the walk-in cooler within a locked chain-of-custody room.

Sample coolers will be secured with either metal clips or seal. ID numbers for the metal clips or seals will be recorded on the LAR form that will be placed in a plastic bag inside one of the coolers.

If the sample team returns to the OC on Friday, samples will be placed in new coolers with blue ice to maintain temperatures in the coolers stored in the OC walk-in cooler for transport to MEL on Monday morning. Samples brought to the OC on Thursday do not require transfer to new coolers and will be transported to MEL on Friday morning (Marti, 2019).

## 8.7 Field log requirements

A field log will be maintained by the field lead and used during each sampling event. The following information will be recorded:

- Name of sampling location.
- Field staff.
- Environmental conditions.
- Field measurement results.
- Date, Time, Sample ID, description of samples collected.
- Identity of QC samples (if appropriate).
- Pertinent observations and/or any problems with sampling, including deviations from the QAPP.
- Unusual circumstances that might affect interpretation of results.

Field logs will consist of waterproof 8.5 x 11-inch field sheets pre-printed for ease of recording and kept in an enclosed metal clipboard. Permanent, waterproof ink or pencil will be used for all entries. Corrections will be made with single-line strikethroughs, initialed, and dated.

## 8.8 Other activities

Additional activities include:

- Any field staff new to the type of sampling conducted for this study will be trained by senior field staff or the project manager, following relevant Ecology SOPs.
- The Hydrolab MS-5 MiniSonde® will be calibrated at the beginning of the week and checked at the beginning of each day for stability of calibration. If needed, MiniSondes® will be re-calibrated to meet MQOs (Table 8).
- The project lead will notify the lab of any changes in scheduling.
- The project lead will work with MEL's courier to develop a schedule for delivery of sampling containers in order to ensure that the appropriate number and type of required samples containers are available.
- Project staff will work with the contract laboratories to develop a schedule for the delivery of sampling containers, preservatives, and blank water to the sampling team.

# 9.0 Laboratory Procedures

## 9.1 Lab procedures table

Analytes for this project, along with the expected number of samples and an expected range of results, are listed in Table 13. Drinking water methods will be used for the parameters of interest.

**Table 13. Measurement methods (laboratory).**

| Analyte | Sample Matrix [1] | Samples (Number/ Arrival Date) | Expected Range of Results | Detection Limit (DL) or Reporting Limit (RL) | Sample Prep Method | Analytical (Instrumental) Method |
|---|---|---|---|---|---|---|
| PCDD/Fs | water | 20 samples Nov 5-7 2019; Apr 2020; Oct 2020. Arrival dates | 0.03-7.0 pg/L, depending on congener | 10-20 pg/L [d] | EPA 1613B, lab SOPs | EPA 1613B (HR GC/MS) |
| Nitrate-N | water | 20 samples Nov 5-7 2019; Apr 2020 | 0.1-60.0 mg/L | RL=0.10 mg/L, DL=0.1 mg/L | N/A | EPA 300.0 |
| Total Lead | water | 20 samples Nov 5-7 2019; Apr 2020 | <0.1-1 ug/L | RL=0.1 ug/L, DL=0.068 | per method | EPA 200.8 |
| Total Arsenic | water | 20 samples Nov 5-7 2019; Apr 2020 | <0.1-1 ug/L | RL=0.5 ug/L, DL=0.06 | per method | EPA 200.8 |
| | | | | | | |
| TOC | water | 20 samples Nov 5-7 2019; Apr 2020 | 0.1-5 mg/L | RL=0.5 mg/L, DL=0.122 mg/L | per method | SM 5310B |
| DOC | water | 20 samples Nov 5-7 2019; Apr 2020 | 0.1-5 mg/L | RL=0.1 mg/L, DL=0.122 mg/L | per method | SM 5310B |
| Alkalinity | water | 20 samples Nov 5-7 2019; Apr 2020 | 10-400 mg/L | RL=5 mg/L, DL=0.5 mg/L | per method | SM 2320B |
| Turbidity | water | 20 samples Nov 5-7 2019; Apr 2020 | 0.1-5 NTU | RL=0.5 NTU, DL=0.1 NTU | per method | SM 2130B |

d - See Table 9 for analyte-specific RLs for dioxins/furans.
[1] Filtered water
[2] *Standard Methods for the Examination of Water and Wastewater, 23rd Edition*, 2017. American Public Health Association

## 9.2 Sample preparation method(s)

The laboratory will follow standard sample preparation procedures for the measurement methods listed in Table 13.

## 9.3 Special method requirements

There are no special method requirements for this project.

## 9.4 Laboratories accredited for methods

This project will use accredited labs for all analyses (e.g., PCDD/Fs, nitrate, arsenic, lead) where results will be compared to criteria for drinking water. Ancillary parameters will also be analyzed by an accredited lab.

# 10.0 Quality Control Procedures

Quality control (QC) procedures provide the information needed to assess the quality of the data that are collected. They can also help identify problems or issues associated with data collection and analysis while the project is underway.

## Field

QC procedures for field work will follow Ecology's EA Program (EAP) SOPs related to groundwater sampling.

Field measurements made when collecting samples (temperature, pH, specific conductance, dissolved oxygen, and oxidation/reduction potential) will follow groundwater sampling SOPs (Section 8.2).

Field replicates will consist of duplicate samples from the same well.

Field QC samples for PCDD/Fs will include field replicates, equipment blanks, travel blanks, and transfer blanks. Detailed plans regarding where QC samples will be collected will be made after site reconnaissance has been conducted. Blank water for the PCDD/F samples will be provided by the contract lab and will be ultra-pure grade suitable for high-resolution analysis.

Various field blanks will be used to help characterize potential contamination from different steps of the sampling process. Equipment blanks will consist of rinsing any equipment used for sampling with blank water and directing the rinsate into a sample container. Travel blanks consist of a container filled with blank water by the lab and is never opened; this container travels with other sample bottles from the lab to the field and back to the lab. Field transfer blanks consist of the transfer of water that is free of target analytes supplied by the lab from one sample container to an empty sample container. This transfer will take place in the same space and close to the well faucet where field samples are taken.

## Laboratory

Laboratory QC procedures will include the use of calibration standards, lab control samples, blanks, and replicates to evaluate the quality of data that is generated. Precision will be estimated using results from duplicate analyses and be expressed as the Relative Percent Difference (RPD). The project manager may indicate which samples should be used for laboratory replicates.

## 10.1 Table of field and laboratory quality control

**Table 14. Quality control samples, types, and frequency.**

| Parameter | Field | | Laboratory[a] | | | |
|---|---|---|---|---|---|---|
| | Blanks[1] | Replicates | Check Standards | Method Blanks | Analytical Duplicates | Matrix Spikes |
| PCDD/Fs | 4-5 per event | 2-3 per event | 1/batch (LCS and OPR[b]) | 1/batch | 1/batch | NA |
| Nitrate | 1/batch | 10% | 1/batch | 1/batch | 1/batch | 1/batch |
| Lead | 1/batch | 10% | 1/batch | 1/batch | 1/batch | 1/batch |
| Arsenic | 1/batch | 10% | 1/batch | 1/batch | 1/batch | 1/batch |
| TOC | None | 10% | 1/batch | 1/batch | 1/batch | 1/batch |
| DOC | 1/batch | 10% | 1/batch | 1/batch | 1/batch | 1/batch |
| Alkalinity | None | 10% | 1/batch | 1/batch | 1/batch | NA |
| Turbidity | None | 10% | 1/batch | 1/batch | 1/batch | NA |

[1] Field blanks for PCDD/Fs include one each of travel, transfer, and equipment blank per event.
[a] *Batch* is defined as up to 20 samples analyzed together.
[b] Labeled compounds in each sample and Ongoing Precision and Recovery (OPR) standards in each batch.

Each type of QC sample listed in Table 14 will have MQOs associated with it (Section 6.2) that will be used to evaluate the quality and usability of the results.

## 10.2 Corrective action processes

Corrective actions will be taken if activities are found to be inconsistent with the QAPP, field procedures, laboratory analyses, data review processes, MQOs, or performance expectations, or if some other unforeseen problem arises. Such actions may include:

- Re-calibrating the measurement system.
- Collecting new samples using the method described in the approved QAPP.
- Accepting and qualifying lab results that do not meet all QC criteria.
- Reanalyzing lab samples that do not meet QC criteria.
- Convening project personnel and technical experts to decide on the next steps that need to be taken to improve performance of project components.

# 11.0 Data Management Procedures

As field and lab data are completed, data will be organized using various tabular and graphical formats for additional review, calculations, characterization, and reporting.

Data from historical studies will be obtained from various sources. The primary source will be Ecology's EIM databases and other Ecology repositories. Data from other agencies may also be used (e.g., EPA, USGS). The quality of such data will be reviewed for its usability on a case-by-case basis, and factors leading to use of the data will be documented in quality assurance (QA) reviews for each sampling effort.

## 11.1 Data recording and reporting requirements

### Field

Data management for this project will include written and electronic media generated from field activities. The EA Program (EAP) SOPs, described previously for the collection of samples from water supply wells, describe formats to be used for all phases of recordkeeping.

Field notes and observations will be recorded by hand into prepared field forms, notebooks, and/or maps/sketches. Pertinent data collected in field books will be transferred to electronic media using Microsoft Office products (Word, Excel, Access) and ArcView GIS.

After entry into electronic media, about 10% of the electronic data will be reviewed and compared to handwritten data to check and correct data entry errors.

After these reviews, pertinent field data will be reduced and entered into Ecology's electronic EIM database. Printed and electronic data not entered into EIM will be retained in a file system maintained by the project manager.

### Laboratory

Laboratory analyses of samples generate data recorded in handwritten and electronic formats. These data will be verified as described in Section 13 below. Laboratory data generated by MEL will be entered into the Laboratory Information System (LIMS) by MEL staff. When notified of the availability of data, project staff can then access LIMS data and load appropriate data into EIM via the EIM template. Laboratory data generated by contract labs will be verified and validated as described in Section 13 below. After errors and concerns are addressed, these data will be loaded into EIM via the EIM template.

For dioxins and furans (PCDD/Fs), the cumulative toxicity of the 17 most toxic congeners will be calculated using the international convention (Van den Berg et al., 2006) of expressing the cumulative toxicity of mixtures of congeners as a toxic equivalent (TEQ) to 2,3,7,8-TCDD, the index congener. This TCDD-TEQ is calculated by multiplying the result for each congener by its congener-specific Toxicity Equivalent Factor (TEF) and then summing the products (which are congener-specific TEQs) to obtain the TCDD TEQ. The treatment of non-detect values is described below in Section 14.2.

## 11.2 Laboratory data package requirements

Laboratory results from MEL analyses will be sent to the project manager in electronic format (from LIMs) and be accompanied by a case narrative. The case narrative will address various data verification checks described in Section 13 below.

Results from contract laboratories will be delivered to MEL and contain information specified in the Request for Qualifications (RFQ) document. The RFQ is developed by designated MEL staff and the Project Co-Investigator. The RFQ specifies the requirements of the analytical work and is used as a solicitation for bids from analytical laboratories for the work to be done.

The contract lab conducting the analyses of PCDD/Fs will deliver analytical results in a Level 4 data package and summarize findings in a case narrative. The Level 4 data package, in addition to the electronic data deliverable (EDD) described below, provide everything needed for a Stage 4 data validation. MEL will send the data package to an independent third-party commercial vendor who is experienced in data validation. The vendor will then send their Validation Report to MEL and the Project Co-investigator.

Inorganic parameters (nitrate-N, arsenic, lead) will be analyzed by a contract lab, which will send Level 4 deliverables to MEL. The information delivered to Ecology will include a case narrative, copies of all raw data necessary to perform an independent evaluation of the results, calibration and verification standards, EIM EDD, sample and QC bench sheets.

## 11.3 Electronic transfer requirements

Laboratory data generated by MEL will be entered into the Laboratory Information System (LIMS) by MEL staff. When notified of the availability of data, project staff can then access LIMS data and receive the data in an Excel file formatted similar to the EIM loading template.

Results for nitrate and metals analyses will be delivered to MEL. This data will also be transmitted via LIMS to Ecology staff.

Results for PCDD/F analyses will be provided by contract lab in an Excel-compatible (e.g.,.csv) format for ease of review, editing, and transfer into EIM. The typical electronic data deliverable (EDD) format is shown in Table 15. Other items may be included as needed to help us understand the data package. Other information about the PCDD/F analyses will be provided in pdf or other formats for use during data validation.

**Table 15. Required fields for electronic data deliverables (EDDs) from contract labs.**

| Ref # | Field Name | *Example* Value |
|---|---|---|
| 1 | Study ID (Project Name provided to contract lab) | XXXX 2018 |
| 2 | Field Station Identification (Ecology Field ID provided to contract lab) | STA5-CCC |
| 3 | Contract Lab Sample ID | L180327-5 |
| 4 | MEL Work Order Sample ID (Ecology Sample ID provided to contract lab) | 1803015-01 |
| 5 | Field Collection Date (listed in COC) | 10/25/2018 |
| 6 | Date of Receipt at Contract Lab | 3/15/2019 |
| 7 | Sample Matrix (provided to contract lab) | Tissue |
| 8 | Sample Preparation Method | 1668C |

| Ref # | Field Name | *Example* Value |
|---|---|---|
| 9 | Analysis Method | 1668C |
| 10 | Parameter Name (the 7-character format for PCBs is required) | PCB-001 |
| 11 | CAS Number | 2051-60-7 |
| 12 | Sample Extraction Date | 3/30/2018 |
| 13 | Analysis Date | 4/10/2018 |
| 14 | Analysis Time | 12:22 |
| 15 | Lab Batch ID (to associate results with QC samples) | L80882 |
| 16 | Contract Lab Name | MegaMSLab |
| 17 | Result Value | 0.743 |
| 18 | Result Value Units | ng/g |
| 19 | Result Reporting Limit | 4.33 |
| 20 | Result Reporting Limit Type (e.g. LOQ/MRL) | LOQ |
| 21 | Result Detection Limit | 0.743 |
| 22 | Result Detection Limit Type (e.g. EDL/CRDL/MDL) | EDL |
| 23 | Result Value Qualifier | UJ |
| 24 | Result Basis (Wet/Dry) | Wet |
| 25 | Lab Duplicate (Y/N) | N |
| 26 | Lab Reanalysis (Y/N) | N |
| 27 | Amended Result Value (entered by data reviewer/validator) | 0.743 |
| 28 | Amended Result Value Qualifier (entered by data reviewer/validator) | U |
| 29 | Reason for Amendment(s) (entered by data reviewer/validator) | Blank contamination |

Where the verification/validation process for contract lab data results in changes to laboratory flags or qualifiers and reported values, the person conducting the verification/validation will create three new fields in the EDD and enter the amended values along with the reason for the change (as in items #27-29 in Table 15 above).

## 11.4 EIM/STORET data upload procedures

Data will be loaded into Ecology's EIM database following EIM guidance. Data from the field, MEL, and contract labs will be entered into an EIM upload template.

After laboratory data are entered into EIM, the EIM Data Review Procedure requires checks for approximately 10% of the data to ensure that the data were entered correctly.

## 11.5 Model information management

N/A

# 12.0 Audits and Reports

## 12.1 Field, laboratory, and other audits

Field audits are always appropriate for a project involving either field measurements or sampling. It is likely that insufficient QA resources are currently available for auditing activities; however, there could be a field consistency review of the project by another experienced EAP hydrogeologist. The aim of such reviews is to improve field-work consistency, improve adherence to SOPs, provide a forum for sharing innovations, and strengthen our data QA program.

## 12.2 Responsible personnel

See Section 12.1.

## 12.3 Frequency and distribution of reports

A final technical report will be published according to the project schedule shown in Section 5.4.

Results will be communicated to homeowners as the results become available and in accordance with the project communications plan.

## 12.4 Responsibility for reports

The primary EAP Project Manager will be the lead on the final report.

# 13.0 Data Verification

This section describes data verification and validation which are typically sequential steps. EPA (2002) defines data verification as "The process of evaluating the completeness, correctness, and conformance/compliance of a specific data set against the method, procedural, or contractual requirements." Data validation is defined as "The analyte-specific and sample-specific process that extends the evaluation of data beyond method, procedural, or contractual requirements (i.e., data verification) to determine the analytical quality of a specific data set."

For this project, data verification and validation may be performed by various parties. For results generated by MEL, the data are verified and validated using MEL SOPs for data review. The validation steps in this case are considered "same-party" validation. For PCDD/F, arsenic, lead, and nitrate results generated by a contract laboratory, data verification and validation will be performed by an independent party and is considered "third-party" validation. The contract lab data for PCDD/F will be validated by a commercial business. Arsenic, lead, and nitrate contract lab data will be validated by MEL. For data generated by EAP field staff, data are verified by the field leader or project manager, usually before leaving the sampling site.

## 13.1 Field data verification, requirements, and responsibilities

Field-collected data will be verified by examining field notes, sketches or diagrams of the sampling point, maps, and other notes for legibility, completeness, and errors. Where omissions or errors in the data are found, the generator of the data (e.g., field crew) will be consulted to determine the correct value or form of the data in question. Corrections or qualifications will be made where possible. Where corrections cannot be made, additional information will be noted to explain the error. The data in question may also be qualified or rejected for further use.

Field data will be verified by the field lead before leaving the locations where field data are collected.

After field data are entered into EIM, the EIM Data Review Procedure checks about 10% of the data to ensure that the data were entered correctly.

## 13.2 Laboratory data verification

All data will undergo a verification and validation analysis, which will be conducted by an independent qualified professional (who did not conduct the laboratory analysis).

Data from the PCDD/F analyses will be verified and validated to the Stage 4 standard described in EPA's Guidance for Labeling Externally Validated Lab Data for Superfund Use (EPA, 2009). Additional verification/validation will be performed as recommended by the data reviewer and/or the project manager.

For results generated by a contract lab, the verification will include checks to see whether specific requirements described in the contracts' Request for Qualifications (RFQ) were followed, such as using the proper EDD format and analyzing QC samples as specified. Data validation for PCDD/Fs will be performed independently by an outside vendor followed by a peer review of the data validation package by MEL staff. Arsenic, lead, and nitrate contract lab data will be validated by MEL, following MEL SOP 770005.

For validation of PCDD/F data, the amount of recalculation done during Stage 3 (which is part of the Stage 4 effort) will be in line with industry standards, which is recalculation of about 10% of sample results in a batch, all initial calibrations, and many other QC samples. This amount of sample recalculation depends in part on the number of detections because it is not useful to recalculate non-detected results. Data validators may preferentially choose to recalculate results that have dilutions and detections, and then if there are no detections, they may recalculate QC samples with positive results.

The outcome of the verification and validation process will be documented in case narratives and related documents provided by the analytical laboratories and data verifiers/validators. These documents identify the person(s) who conducted the review on each particular data set. The project manager reviews the case narratives and works with the data reviewers to resolve any concerns. The case narratives typically summarize:

- The nature of the verification and validation effort.
- The location where results and related details are stored (e.g., analytical method used, sample ID scheme, QC results, and batch IDs).
- Compliance with analytical method, lab QA/QC limits, and the MQOs described in this QAPP or subsequent QAPP addendums.
- Explanations and discussion about challenges or circumstances that affect the quality of the data.
- The assignment, and definitions, of data qualifiers.

Data qualifiers are typically assigned to results as part of the analysis and data review process. Qualifiers may also be assigned or changed during the data validation process or by the project manager during the broader data quality assessment. Table 16 shows the most common data qualifiers used with results for this project's target analytes.

**Table 16. Data qualifiers and definitions.**

| Qualifier | Definition |
|---|---|
| U | The analyte was analyzed for but was not detected at the reported quantitation limit. |
| J | The analyte was positively identified and the associated numerical value is the approximate concentration of the analyte in the sample. |
| UJ | The analyte was not detected at or above the reported quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample. |
| REJ | The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet the quality control criteria. The presence or absence of the analyte cannot be verified. |
| E | Reported result is an estimate because it exceeds the calibration range. |
| NAF | Not analyzed for. |
| NC | Not calculated. |

## 13.3 Validation requirements, if necessary

See previous section regarding verification and validation. Some elements of validation will be conducted as described in the previous section. How the validation is conducted depends on which laboratory analyzes the samples.

## 13.4 Model quality assessment

N/A

### 13.4.1 Calibration and validation

N/A

#### *13.4.1.1 Precision*

N/A

#### *13.4.1.2 Bias*

N/A

#### *13.4.1.3 Representativeness*

N/A

#### *13.4.1.4 Qualitative assessment*

N/A

### 13.4.2 Analysis of sensitivity and uncertainty

N/A

# 14.0 Data Quality (Usability) Assessment

## 14.1 Process for determining project objectives were met

After all laboratory and field data are verified, a detailed examination of the data package using statistics and professional judgment will be performed. The project manager will examine the entire data package to determine if all the criteria for MQOs, completeness, representativeness, and comparability have been met. If the criteria have not been met, the project manager will decide if affected data should be qualified or rejected based upon the decision criteria from the QAPP. The project manager and client will decide how any qualified data will be used in the technical analysis.

## 14.2 Treatment of non-detects

Non-detect values will usually be handled using one to three of the following substitution methods, depending on the purpose of the analysis:

- Substitute the reporting limit. Typically used for general characterization of the data to provide a high-level view of the results and where substituting the reporting limit does not compromise decisions related to regulatory actions. This substitution method assumes that all target analytes were detected and yields the highest contaminant concentration values. This method can provide a worst-case scenario for risk assessment.
- Substitute one-half of the reporting limit. Also used for general characterization of the data. This assumes that all target analytes were detected, but at a level between the detection limit and zero. This method provides another scenario for risk assessment.
- Substitute the value of zero. Typically used when results are used for comparison to Washington's surface water quality standards. The surface water quality standards require that the summing of certain results to obtain a "total" value, such as for TCDD-TEQ, use only detected values for the addends that are being summed. Addends that are non-detects have their values set to zero for the summing process.

### Data reduction

Data from various sources will be compiled using Microsoft products such as Excel and Word. All acceptable and appropriate lab and field results will be compiled in Excel tables from which further data reduction will occur. Individual tables are used for compiling data that originate from different sources. These source tables are then used for data reduction tasks performed in different spreadsheets. The most common data sets will be:

- Field measurements.
- Laboratory results from MEL: sample and some QC results.
- Laboratory results from Contract Labs: sample and some QC results.

A final data set is compiled from, and includes results from, other data reduction efforts. The final data set for further analysis and reporting purposes will be a single Excel table that includes:

- Sample ID, location, collection date.
- Results and related parameter, method, and lab results for all target analytes.

### Calculation of "total" values

As field and lab data are completed, data will be organized using various tabular and graphical formats for additional review, calculations, characterization, and reporting. Procedures for summing and handling qualified values such as non-detects will follow in-house guidance or be explained in reports. The TCDD-TEQ will be calculated from PCDD/F results as described above.

### Data analyses

Further analysis and reporting will proceed using Excel for data management and statistics, statistical software such as SYSTAT or R for data analyses, and Arc GIS for mapping. Common analyses are expected to include:

- Summary statistics.
- Plots and tables to identify exceedances of thresholds for protection of human health.
- Plots to compare contaminant concentrations among sampling sites.

## 14.4 Sampling design evaluation

The sampling design for this project is expected to be adequate to meet objectives most of the time. However, smaller sample numbers and higher variability than expected may render the sampling design to be less effective than desired in some cases. In most cases, the project team will use the quality and quantity of results available and will note in the final report any impacts on attaining objectives.

## 14.5 Documentation of assessment

Documents used for the data usability assessment will include a variety of notes and reports described above, such as:

- Field notes and laboratory case narratives.
- Verification and validation reports from vendors, laboratories, and project staff.
- Worksheets and tables comparing results from field and QC samples to MQOs and other data quality indicators.

A Data Quality Review worksheet may be created to record the overall decision about how to use laboratory results for each group of analytes for each sampling event. Further documentation of the data usability assessment will occur in the final report *Methods* section.

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# 16.0 Appendix. Glossaries, Acronyms, and Abbreviations

## *Glossary of General Terms*

**Clean Water Act (CWA):** A federal act passed in 1972 that contains provisions to restore and maintain the quality of the nation's waters. Section 303(d) of the Clean Water Act establishes the TMDL program.

**Congener:** molecules that are related to each other by origin, structure, or function. Dioxins, for example, share the same core molecular structure (two benzene rings joined by two oxygen atoms) while different congeners differ by the number and position of chlorine atoms that are attached to the core structure.

**Dissolved oxygen (DO):** A measure of the amount of oxygen dissolved in water.

**Geometric mean:** A mathematical expression of the central tendency (an average) of multiple sample values. A geometric mean, unlike an arithmetic mean, tends to dampen the effect of very high or low values, which might bias the mean if a straight average (arithmetic mean) were calculated. This is helpful when analyzing bacteria concentrations, because levels may vary anywhere from 10 to 10,000 fold over a given period. The calculation is performed by either: (1) taking the nth root of a product of n factors, or (2) taking the antilogarithm of the arithmetic mean of the logarithms of the individual values.

**Nutrient:** Substance such as carbon, nitrogen, and phosphorus used by organisms to live and grow. Too many nutrients in the water can promote algal blooms and rob the water of oxygen vital to aquatic organisms.

**pH:** A measure of the acidity or alkalinity of water. A low pH value (0 to 7) indicates that an acidic condition is present, while a high pH (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.

**Sediment:** Soil and organic matter that is covered with water (for example, river or lake bottom).

**Surface waters of the state:** Lakes, rivers, ponds, streams, inland waters, salt waters, wetlands, and all other surface waters and water courses within the jurisdiction of Washington State.

**Turbidity:** A measure of water clarity. High levels of turbidity can have a negative impact on

## *Acronyms and Abbreviations*

| | |
|---|---|
| CWA | Federal Clean Water Act |
| DO | (see Glossary above) |
| DOC | Dissolved organic carbon |
| DOH | Washington State Department of Health |
| e.g. | For example |
| EAP | Ecology's Environmental Assessment Program |
| Ecology | Washington State Department of Ecology |
| EDD | Electronic Data Deliverable (e.g. a spreadsheet of results) |
| EDL | Estimated Detection Limit |

| | |
|---|---|
| EIM | Environmental Information Management database |
| EPA | U.S. Environmental Protection Agency |
| et al. | And others |
| GIS | Geographic Information System software |
| GWMA | Groundwater Management Area |
| i.e. | In other words |
| MEL | Manchester Environmental Laboratory |
| MQO | Measurement quality objective |
| MTCA | Model Toxics Control Act |
| OPR | Ongoing Precision and Recovery |
| ORP | Oxidation or Oxidative reduction potential |
| PCDD | Polychlorinated dibenzo-p-dioxins |
| PCDD/F | PCDDs and PCDFs |
| PCDF | Polychlorinated dibenzofurans |
| QA | Quality assurance |
| QAPP | Quality Assurance Project Plan |
| QC | Quality control |
| RPD | Relative percent difference |
| RSD | Relative standard deviation |
| SDWA | Federal Safe Drinking Water Act |
| SOP | Standard operating procedures |
| TCDD | 2,3,7,8-tetrachlorodibenzo-p-dioxin |
| TCDD-TEQ | Toxic Equivalent to TCDD |
| TEF | Toxicity Equivalent Factor |
| TEQ | Toxic Equivalent |
| TOC | Total organic carbon |
| USGS | United States Geological Survey |
| WAC | Washington Administrative Code |

***Units of Measurement***

| | |
|---|---|
| °C | degrees centigrade |
| ft | feet |
| g | gram, a unit of mass |
| kg | kilograms, a unit of mass equal to 1,000 grams |
| kg/d | kilograms per day |
| L | liter |
| m | meter |
| mm | millimeter |
| mg | milligram |
| mg/kg | milligrams per kilogram (parts per million) |
| mg/L | milligrams per liter (parts per million) |
| mL | milliliter |
| ng/g | nanograms per gram (parts per billion) |
| ng/kg | nanograms per kilogram (parts per trillion) |
| ng/L | nanograms per liter (parts per trillion) |
| NTU | nephelometric turbidity units |
| pg/g | picograms per gram (parts per trillion) |

| | |
|---|---|
| pg/L | picograms per liter (parts per quadrillion) |
| s.u. | standard units |
| µg/g | micrograms per gram (parts per million) |
| µg/kg | micrograms per kilogram (parts per billion) |
| µg/L | micrograms per liter (parts per billion) |
| µmhos/cm | micromhos per centimeter |
| µS/cm | microsiemens per centimeter, a unit of conductivity |

## *Quality Assurance Glossary*

**Accreditation:** A certification process for laboratories, designed to evaluate and document a lab's ability to perform analytical methods and produce acceptable data. For Ecology, it is "Formal recognition by (Ecology)…that an environmental laboratory is capable of producing accurate analytical data." [WAC 173-50-040] (Kammin, 2010)

**Accuracy:** The degree to which a measured value agrees with the true value of the measured property. USEPA recommends that this term not be used, and that the terms *precision* and *bias* be used to convey the information associated with the term *accuracy* (USGS, 1998).

**Analyte:** An element, ion, compound, or chemical moiety (pH, alkalinity) which is to be determined. The definition can be expanded to include organisms, e.g., fecal coliform, Klebsiella (Kammin, 2010).

**Bias:** The difference between the sample mean and the true value. Bias usually describes a systematic difference reproducible over time and is characteristic of both the measurement system and the analyte(s) being measured. Bias is a commonly used data quality indicator (DQI) (Kammin, 2010; Ecology, 2004).

**Blank:** A synthetic sample, free of the analyte(s) of interest. For example, in water analysis, pure water is used for the blank. In chemical analysis, a blank is used to estimate the analytical response to all factors other than the analyte in the sample. In general, blanks are used to assess possible contamination or inadvertent introduction of analyte during various stages of the sampling and analytical process (USGS, 1998).

**Calibration:** The process of establishing the relationship between the response of a measurement system and the concentration of the parameter being measured (Ecology, 2004).

**Check standard:** A substance or reference material obtained from a source independent from the source of the calibration standard; used to assess bias for an analytical method. This is an obsolete term, and its use is highly discouraged. See Calibration Verification Standards, Lab Control Samples (LCS), Certified Reference Materials (CRM), and/or spiked blanks. These are all check standards but should be referred to by their actual designator, e.g., CRM, LCS (Kammin, 2010; Ecology, 2004).

**Comparability:** The degree to which different methods, data sets and/or decisions agree or can be represented as similar; a data quality indicator (USEPA, 1997).

**Completeness:** The amount of valid data obtained from a project compared to the planned amount. Usually expressed as a percentage. A data quality indicator (USEPA, 1997).

**Continuing Calibration Verification Standard (CCV):** A quality control (QC) sample analyzed with samples to check for acceptable bias in the measurement system. The CCV is usually a midpoint calibration standard that is re-run at an established frequency during the course of an analytical run (Kammin, 2010).

**Control chart:** A graphical representation of quality control results demonstrating the performance of an aspect of a measurement system (Kammin, 2010; Ecology 2004).

**Control limits:** Statistical warning and action limits calculated based on control charts. Warning limits are generally set at +/- 2 standard deviations from the mean, action limits at +/- 3 standard deviations from the mean (Kammin, 2010).

**Data integrity:** A qualitative DQI that evaluates the extent to which a data set contains data that is misrepresented, falsified, or deliberately misleading (Kammin, 2010).

**Data quality indicators (DQI):** Commonly used measures of acceptability for environmental data. The principal DQIs are precision, bias, representativeness, comparability, completeness, sensitivity, and integrity (USEPA, 2006).

**Data quality objectives (DQO):** Qualitative and quantitative statements derived from systematic planning processes that clarify study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions (USEPA, 2006).

**Data set:** A grouping of samples organized by date, time, analyte, etc. (Kammin, 2010).

**Data validation:** An analyte-specific and sample-specific process that extends the evaluation of data beyond data verification to determine the usability of a specific data set. It involves a detailed examination of the data package, using both professional judgment and objective criteria, to determine whether the MQOs for precision, bias, and sensitivity have been met. It may also include an assessment of completeness, representativeness, comparability, and integrity, as these criteria relate to the usability of the data set. Ecology considers four key criteria to determine if data validation has actually occurred. These are:

- Use of raw or instrument data for evaluation.
- Use of third-party assessors.
- Data set is complex.
- Use of EPA Functional Guidelines or equivalent for review.

Examples of data types commonly validated would be:

- Gas Chromatography (GC).
- Gas Chromatography-Mass Spectrometry (GC-MS).
- Inductively Coupled Plasma (ICP).

The end result of a formal validation process is a determination of usability that assigns qualifiers to indicate usability status for every measurement result. These qualifiers include:

- No qualifier; data are usable for intended purposes.
- J (or a J variant); data are estimated, may be usable, may be biased high or low.
- REJ; data are rejected, cannot be used for intended purposes.
  (Kammin, 2010; Ecology, 2004).

**Data verification:** Examination of a data set for errors or omissions, and assessment of the Data Quality Indicators related to that data set for compliance with acceptance criteria (MQOs). Verification is a detailed quality review of a data set (Ecology, 2004).

**Detection limit** (limit of detection)**:** The concentration or amount of an analyte which can be determined to a specified level of certainty to be greater than zero (Ecology, 2004).

**Duplicate samples:** Two samples taken from and representative of the same population, and carried through and steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variability of all method activities including sampling and analysis (USEPA, 1997).

**Field blank:** A blank used to obtain information on contamination introduced during sample collection, storage, and transport (Ecology, 2004).

**Initial Calibration Verification Standard (ICV):** A QC sample prepared independently of calibration standards and analyzed along with the samples to check for acceptable bias in the measurement system. The ICV is analyzed prior to the analysis of any samples (Kammin, 2010).

**Laboratory Control Sample (LCS):** A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples (USEPA, 1997).

**Laboratory Control Sample (LCS)/LCS Duplicate:** A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples (USEPA, 1997). Monitors lab's process for bias and precision.

**Lower Limit of Quantitation (LLOQ)**: The LLOQ is the lowest concentration at which the laboratory has demonstrated target analytes can be reliably measured and reported with a certain degree of confidence. The LLOQ must be ≥ the lowest point in the calibration curve and is verified annually for organics.

**Matrix spike/Matrix Spike Duplicate:** A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias and precision errors due to interference or matrix effects (Ecology, 2004).

**Matrix spike:** A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects (Ecology, 2004).

**Measurement Quality Objectives** (MQOs)**:** Performance or acceptance criteria for individual data quality indicators, usually including precision, bias, sensitivity, completeness, comparability, and representativeness (USEPA, 2006).

**Measurement result:** A value obtained by performing the procedure described in a method (Ecology, 2004).

**Method:** A formalized group of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, data analysis), systematically presented in the order in which they are to be executed (EPA, 1997).

**Method blank:** A blank prepared to represent the sample matrix, prepared and analyzed with a batch of samples. A method blank will contain all reagents used in the preparation of a sample, and the same preparation process is used for the method blank and samples (Ecology, 2004; Kammin, 2010).

**Method Detection Limit (MDL):** This definition for detection was first formally advanced in 40CFR 136, October 26, 1984 edition. MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero (Federal Register, October 26, 1984).

**Method Detection Limit (MDL):** This definition for detection was first formally advanced in 40 CFR 136, October 26, 1984 edition. The MDL is defined there as the minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, and reported to be greater than zero (Federal Register, October 26, 1984). In 2017 per SW-846 MDLs were eliminated for all 8000 series organics methods.

**Percent Relative Standard Deviation (%RSD):** A statistic used to evaluate precision in environmental analysis. It is determined in the following manner:

$$\%RSD = (100 * s)/x$$

where s is the sample standard deviation and x is the mean of results from more than two replicate samples (Kammin, 2010).

**Parameter:** A specified characteristic of a population or sample. Also, an analyte or grouping of analytes. Benzene and nitrate + nitrite are all parameters (Kammin, 2010; Ecology, 2004).

**Population:** The hypothetical set of all possible observations of the type being investigated (Ecology, 2004).

**Precision:** The extent of random variability among replicate measurements of the same property; a data quality indicator (USGS, 1998).

**Quality assurance (QA):** A set of activities designed to establish and document the reliability and usability of measurement data (Kammin, 2010).

**Quality Assurance Project Plan (QAPP):** A document that describes the objectives of a project, and the processes and activities necessary to develop data that will support those objectives (Kammin, 2010; Ecology, 2004).

**Quality control (QC):** The routine application of measurement and statistical procedures to assess the accuracy of measurement data (Ecology, 2004).

**Relative Percent Difference (RPD):** RPD is commonly used to evaluate precision. The following formula is used:

$$[Abs(a-b)/((a + b)/2)] * 100$$

where "Abs()" is absolute value, and a and b are results for the two replicate samples. RPD can be used only with two values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than two replicate samples (Ecology, 2004).

**Replicate samples:** Two or more samples taken from the environment at the same time and place, using the same protocols. Replicates are used to estimate the random variability of the material sampled (USGS, 1998).

**Representativeness:** The degree to which a sample reflects the population from which it is taken; a data quality indicator (USGS, 1998).

**Sample (field):** A portion of a population (environmental entity) that is measured and assumed to represent the entire population (USGS, 1998).

**Sample (statistical):** A finite part or subset of a statistical population (USEPA, 1997).

**Sample Detection Limit (SDL):** The MDL adjusted to reflect sample-specific actions such as dilution or the use of smaller aliquot sizes, or to report results on a dry-weight basis.

**Sensitivity:** In general, denotes the rate at which the analytical response (e.g., absorbance, volume, meter reading) varies with the concentration of the parameter being determined. In a specialized sense, it has the same meaning as the detection limit (Ecology, 2004).

**Spiked blank:** A specified amount of reagent blank fortified with a known mass of the target analyte(s); usually used to assess the recovery efficiency of the method (USEPA, 1997).

**Spiked sample:** A sample prepared by adding a known mass of target analyte(s) to a specified amount of matrix sample for which an independent estimate of target analyte(s) concentration is available. Spiked samples can be used to determine the effect of the matrix on a method's recovery efficiency (USEPA, 1997).

**Split sample:** A discrete sample subdivided into portions, usually duplicates (Kammin, 2010).

**Standard Operating Procedure (SOP):** A document which describes in detail a reproducible and repeatable organized activity (Kammin, 2010).

**Surrogate:** For environmental chemistry, a surrogate is a substance with properties similar to those of the target analyte(s). Surrogates are unlikely to be native to environmental samples. They are added to environmental samples for quality control purposes, to track extraction efficiency and/or measure analyte recovery. Deuterated organic compounds are examples of surrogates commonly used in organic compound analysis (Kammin, 2010).

**Systematic planning:** A step-wise process which develops a clear description of the goals and objectives of a project, and produces decisions on the type, quantity, and quality of data that will be needed to meet those goals and objectives. The DQO process is a specialized type of systematic planning (USEPA, 2006).

### *References for QA Glossary*

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